Atomic physics: structure, interactions, and entanglement

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Chapter 1

Atomic energy levels and wavefunctions

1.1 Bohr Model

This lecture should be review for everyone, think of it as a warmup for a quantum mechanical analysis of atoms.

When discussing spectroscopic measurements and spectroscopy of atoms we will use frequencies, wavelengths, and wavenumbers. The wavelength and frequency are related by

\[ \lambda \nu = c \]

with \( c \) the speed of light. The wavenumber is

\[ \tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \]

We will mostly use SI units (m, kg, s). However wavenumbers are almost always discussed in cgs units cm\(^{-1}\) not m\(^{-1}\). We will follow this tradition. A good number to remember is 1 cm\(^{-1}\) \(\simeq\) 30 GHz\(^1\).

Spectroscopic experiments performed in the 1800s showed that different elements were associated with absorption and emission spectra consisting of discrete spectral lines. In 1885 Johann Balmer introduced an empirical equation describing the wavelengths of the observed spectral lines. In 1888 Johannes Rydberg realized that it was more useful to invert the Balmer formula to give an expression for the observed wavenumbers. In modern notation Rydberg’s formula is

\[ \tilde{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

It was found that a great deal of spectroscopic data could be described by this formula using integers \( n_1 \) and \( n_2 \) and different “Rydberg” constants \( R \) for different elements. It was a mystery where this formula came from.

\(^1\)The 3 in this relation is an approximation to 2.99792458 so the exact relation is 1 cm\(^{-1}\) = 29.9792458 GHz.

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The triumph of Bohr’s atomic model of 1913 was that it explained the Rydberg formula and gave a value of the Rydberg constant in terms of fundamental quantities. Bohr’s model goes as follows. Assume an electron with mass $m$ and charge $-e$ orbiting a fixed nucleus with charge $+e$. Let’s consider a circular orbit with angular momentum $L = n\hbar$ with $n$ an integer. This is an assumption. The idea of insisting on quantizing the angular momentum in units of $\hbar$ can be interpreted geometrically. The deBroglie wavelength is $\lambda_{\text{dB}} = h/p$ with $p$ the momentum. The circumference of an orbit of radius $r$ is $2\pi r = 2\pi L/p$. Thus the number of deBroglie wavelengths that fit in the orbit is

$$\frac{2\pi r}{\lambda_{\text{dB}}} = \frac{2\pi L}{p\hbar} = \frac{2\pi L}{h} = \frac{L}{\hbar} = n.$$  

We see that assuming that $L = n\hbar$ corresponds to assuming an integral number of deBroglie wavelengths fit into the orbit. So this is a kind of matching condition.

The energy of the orbiting electron is

$$E = \frac{1}{2}mv^2 - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} = \frac{1}{2}mv^2 - \frac{q^2}{r},$$

where $q = \frac{e}{\sqrt{4\pi\varepsilon_0}}$. Using $q$ we don’t need to carry around the SI factors of $4\pi\varepsilon_0$. For a stationary orbit we set the electrostatic force equal to the centripetal acceleration times the mass so

$$\frac{q^2}{r^2} = \frac{mv^2}{r}$$

which gives

$$r = \frac{q^2}{mv^2}.$$  

The angular momentum is $L = rmv = n\hbar$ so $v = \frac{n\hbar}{mr}$ and we can solve for $r$ as

$$r = n^2 \frac{\hbar^2}{mq^2}.$$
Note that $r \sim n^2$ and the scaling factor called the Bohr radius is

$$a_0 = \frac{\hbar^2}{mq^2}.$$  

Inserting the solutions for $r, v$ into the energy expression we find

$$E_n = -\frac{1}{n^2} \times \hbar c R$$

with $R$ which has units of inverse length or wavenumbers given by

$$R = \frac{mq^4}{4\pi c \hbar^3}.$$  

Alternatively we can write

$$E_n = -\frac{E_R}{n^2}$$

with $E_R = \hbar c R$ the Rydberg energy.

Thus Bohr related the Rydberg constant to the mass and charge of the electron, the speed of light and Planck’s constant $\hbar$. The Rydberg constant has the numerical value

$$R_\infty = 109737.31568508(65) \text{ (cm}^{-1}\text{)}.$$  

The Rydberg is one of the most precisely measured constants in physics. The value $R_\infty$ is the value for an infinitely heavy nucleus. In real atoms $R$ varies a little from element to element due to reduced mass effects. That is to say we should replace $m$ by $\mu = \frac{mM}{m+M}$ with $M$ the nuclear mass to get the Rydberg for different elements. Also if the nucleus has charge $Z$ it is easy to check that the energies are

$$E_n = -\frac{E_R}{n^2} \times Z^2.$$  

If we assume that the observed discrete spectral lines correspond to transitions between states with energies $E_{n_1}$ and $E_{n_2}$ then the energy difference is

$$\Delta E = E_{n_2} - E_{n_1} = \hbar c R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

and the wavenumber corresponding to this energy is

$$\tilde{\nu} = \frac{\Delta E}{\hbar c} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

which is the Rydberg formula.
1.1.1 Atomic units

Atomic units define all physical quantities in terms of

- $e$ — electronic charge
- $\hbar$ — Planck’s constant
- $c$ — speed of light
- $m$ — electron mass

Important quantities are

- fine structure constant: $\alpha = \frac{q^2}{\hbar c} \sim \frac{1}{137}$ ($q^2 \equiv \frac{e^2}{4\pi\varepsilon_0}$)
- length (Bohr radius): $a_0 = \frac{\hbar^2}{mq^2} \sim 0.0529$ nm
- Rydberg constant: $R = \frac{mq^4}{4\pi\hbar^3c} \sim 109737$ cm$^{-1}$
- energy (Hartree): $E_H = 2 \times \hbar cR = mc^2\alpha^2 = \frac{mq^4}{\hbar^2} = \frac{q^2}{a_0} = 27.2$ eV
- time: $\frac{\hbar}{E_H} = \frac{a_0}{\alpha c} = \frac{\hbar^3}{mq^2} \sim 2.4 \times 10^{-17}$ s
- velocity: $\frac{a_0E_H}{\hbar} = \alpha c = \frac{q^2}{\hbar} \sim 2.2 \times 10^6$ m/s
- electric field: $q \frac{\hbar}{a_0^2} \sim 5.1 \times 10^{11}$ V/m
- electric dipole: $ea_0 \sim 8.5 \times 10^{-30}$ Cm ($= 2.54$ D)
- magnetic moment: $2\mu_B = \frac{e\hbar}{m} \sim 1.85 \times 10^{-23}$ J/T
- magnetic field: $\frac{E_H}{2\mu_B} = \frac{\hbar}{ea_0} \sim 2.35 \times 10^5$ T.

It used to be common to define $E_R = E_H/2 = 13.6$ eV as the atomic unit of energy. This has the nice feature that the ionization energy of hydrogen is equal to $E_R$. Modern usage is based on the Hartree as the unit of energy. Beware when reading older papers as it may not be made explicit which definition is in use.

Physical quantities will be in either SI or cgs units. We will mostly use SI units which are convenient for calculating experimental parameters. A downside is that SI units clutter many formulae with factors of $4\pi\varepsilon_0$. We will mostly get rid of these by using $q \equiv e/\sqrt{4\pi\varepsilon_0}$ in electrostatic expressions.

1.2 Hydrogenic bound state wavefunctions

The Bohr model is ad-hoc and does not have a convincing theoretical basis. Quantum mechanics provides a theoretical framework for studying atomic systems. Nonrelativistic quantum mechanics verifies the predictions of the Bohr model for Hydrogen on the basis of
exact calculations. Using perturbation theory approximate results are obtained for He and heavier atoms. This quickly becomes very complicated as we will see later in the course.

Precision measurements show differences between the predictions of nonrelativistic quantum mechanics and experimental energy levels. The relativistic Dirac equation can be used to calculate energy levels in good agreement with experiment. This is so, despite the fact that already for the two-body problem of a proton and an electron the Dirac equation cannot be used and finite nuclear mass corrections must be put in by hand. This procedure is embodied in the Bethe-Salpeter equation.

The Schrödinger equation for bound eigenstates of the Hydrogen atom is

\[
\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{q^2}{r} - E\right) \psi(r) = 0.
\]

(1.1)

Here \( r \) refers to the position of the electron relative to the nucleus, \(-e\) is the charge of the electron, \(+e\) is the nuclear charge, \( q^2 = e^2/4\pi\epsilon_0 \), \( \mu = m_e m_p / (m_e + m_p) \) is the reduced mass, \( m_p \) is the proton mass, \( m_e \) is the electron mass, and \( E \) is the energy of the relative motion. This equation describes the relative motion of the electron and nucleus. It is derived starting from the two body problem and separating into center of mass and relative coordinates. Since \( m_p/m_e = 1846 \), the reduced mass of the hydrogen atom is \( \mu = m_e^{-1} \frac{1}{1+1846} \approx m_e \times 0.99946 \) which is only a small correction compared to the electron mass.

We can generalize to a nucleus of charge \( Ze \) by writing

\[
\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Zq^2}{r} - E\right) \psi(r) = 0.
\]

(1.2)

In spherical coordinates \( \nabla^2 = \frac{1}{r^2} \frac\partial{}\partial r \left(r^2 \frac\partial{}\partial r\right) - \frac{1}{r^2} \hat{L}^2(\theta, \phi) \). We seek a solution by separation of variables in the form \( \psi(r) = R(r)Y_{lm}(\theta, \phi) \). The spherical harmonics satisfy

\[
\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi),
\]

\[
\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi).
\]

We thus get the radial equation

\[
-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr}\right) R + \left[ -\frac{Zq^2}{r} + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} \right] R = ER.
\]

(1.3)

Normalization of the wavefunction implies that \( \int_0^\infty dr r^2 |R|^2 = 1 \) which shows that the units of \( R \) are \( [R] = 1/\text{m}^{3/2} \).

Before solving this equation we can develop some intuition about the solutions by looking at the effective potential given by the terms in the square brackets

\[
V_{\text{eff}}(r) = -\frac{Zq^2}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}
\]

which are illustrated in Fig. 1.2. The negative term proportional to \( 1/r \) comes from the attractive Coulomb interaction. The positive term proportional to \( 1/r^2 \) is an effective repulsive potential proportional to \( \langle \hat{L}^2 \rangle \). For a given value of the energy \( E \) there will be a maximum
value of $l$ for which the potential is attractive and $E$ is found to be negative. If $E$ were not negative the solution would correspond to an unbound scattering state. As $E$ increases, i.e. approaches 0 from below, larger and larger angular momenta $l$ are possible. As we will see $0 \leq l \leq n - 1$, with $n$ the principal quantum number which determines the energy.

The bound $l \leq n - 1$ can be understood quantitatively by analysis of the effective potential. For $l > 0 V_{\text{eff}}(r) \to +\infty$ at the origin and tends to 0 as $r \to \infty$. For a bound state to exist we need a minimum at some radius $r_0$ satisfying $V_{\text{eff}}(r_0) < 0$. Solving $dV_{\text{eff}}/dr = 0$ we find $r_0 = \frac{\hbar^2}{2\mu q^2}l(l+1)$ and $V_{\text{eff}}(r_0) = -E_H/[2l(l+1)]$. For a bound solution we need $E = K + V < 0$. Now

$$K(r_0) = E - V(r_0) = -\frac{E_H}{2n^2} + \frac{E_H}{2l(l+1)}$$

which must be positive. This gives the requirement $n^2 > l(l+1)$ or $l \leq n - 1$. We will see that this limit on $l$ also emerges from the direct solution of the radial equation.

To proceed we introduce a scaling factor $\kappa = \sqrt{-\frac{2\mu E}{\hbar^2}}$ which has dimensions of inverse length, and the dimensionless parameter $\gamma = (-Z^2\mu q^4/(2\hbar^2 E))^{1/2}$. Since bound states have energy $E < 0$ these parameters are positive. Putting $z = \kappa r$ and $\phi(z) = \frac{1}{\kappa\nu z}R(z/\kappa)$ gives the dimensionless radial equation

$$\frac{d^2\phi}{dz^2} - \frac{l(l+1)}{z^2}\phi + \frac{2\gamma}{z}\phi - \phi = 0. \tag{1.4}$$

For large $z$ we have $\phi'' - \phi = 0$ which implies $\phi \sim e^{\pm z}$. In order for $\phi$ to remain finite at infinity we must choose the minus sign. We therefore seek a solution of the form $\phi(z) = e^{-z}f(z)$. The equation for $f$ is

$$\frac{d^2 f}{dz^2} - 2\frac{df}{dz} - \frac{l(l+1)}{z^2}f + \frac{2\gamma}{z}f = 0. \tag{1.5}$$

We seek a power series solution of the form

$$f(z) = z^\nu \sum_{j=0}^{\infty} b_j z^j$$
1.2 Hydrogenic bound state wavefunctions

where $\nu$ is an unknown number, not necessarily integer. If we can find values for $\nu$ and $b_j$ such that the left hand side of (1.5) is identically zero for every power of $z$ then we will have found a solution. This is the basis of the power series solution method.

Substitution into the differential equation yields

$$\sum_{j=0}^{\infty} b_j \left\{ [(\nu + j)(\nu + j - 1) - l(l + 1)] z^{j-2} + [2\gamma - 2(\nu + j)] z^{j-1} \right\} = 0. \quad (1.6)$$

Putting the coefficient of the lowest power of $z$ to zero (the term $z^{-2}$) gives

$$\nu (\nu - 1) = l(l + 1),$$

which has solutions $\nu = l + 1$ or $\nu = -l$. We require that $f$ remains finite at $z = 0$ which forces us to choose $\nu = l + 1$. We then have

$$\sum_{j=0}^{\infty} b_j \left\{ [(l + j + 1)(l + j) - l(l + 1)] z^j + [2\gamma - 2(l + j + 1)] z^{j+1} \right\} = 0$$

or

$$\sum_{j=1}^{\infty} b_j (2l + j + 1) j z^j + \sum_{j=0}^{\infty} b_j [2\gamma - 2(l + j + 1)] z^{j+1} = 0$$

which can be written as

$$\sum_{j=0}^{\infty} \left\{ b_{j+1} (2l + j + 2)(j + 1) + b_j [2\gamma - 2(l + j + 1)] \right\} z^{j+1} = 0.$$

Setting the coefficient of $z^{j+1}$ to zero gives the recursion relation

$$b_{j+1} = \frac{2(l + j + 1) - 2\gamma}{(2l + j + 2)(j + 1)} b_j. \quad (1.7)$$

In order for the power series to terminate at say $j = j'$ we require that $\gamma = l + j' + 1$ which implies that $\gamma$ is an integer we will call $n$ and

$$-\frac{Z^2 \mu q^4}{2\hbar^2 E} = (l + j' + 1)^2 = n^2$$

or

$$E = -\frac{Z^2 \mu q^4}{2\hbar^2} \frac{1}{(l + j' + 1)^2} = -\frac{Z^2 \mu E_H}{2(l + j' + 1)^2} = -\frac{Z^2 \mu E_H}{2n^2}$$

where $E_H$ is the Hartree energy we found from the Bohr model, corrected for the reduced mass. Since $n = l + j' + 1$ and $j' \geq 0$ we have $n \geq l + 1$ or $l \leq n - 1$. The allowed energies can therefore be labeled as

$$E_n = -\frac{Z^2 \mu E_H}{2n^2}$$

with $n \geq 1$ since $l \geq 0$. With this result for the energy the scaling length $\kappa$ takes the value $\kappa = \frac{\mu Z}{m a_\mu}$ where $a_\mu$ is the Bohr radius. We will simplify the notation by introducing a reduced Bohr radius $a_\mu = \hbar^2/(\mu q^2)$ so that $\kappa = Z/n a_\mu$. 

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1 Atomic energy levels and wavefunctions

Note that if the power series did not terminate then for large values of \( j \) we would have 
\[ b_j \sim \frac{2^j}{j!} b_0. \]

Thus \( f \) would tend to \( e^{2z} \) times a polynomial in \( z \) and we would get \( \phi \sim e^{-z} e^{2z} = e^z \) which diverges. It is therefore necessary to terminate the recursion relation in order to obtain a normalizable solution.

To summarize the results so far we have found the energy eigenvalues
\[ E_n = -\frac{Z^2 \mu E_H}{2n^2} \]
and the corresponding radial functions
\[ \phi_{n,l}(z) = e^{-z} z^{l+1} \sum_{j=0}^{n-l-1} b_j z^j \]
\[ b_j = -2 \frac{n-l-j}{(2l+j+1)j} b_{j-1}, \quad \text{for } j \geq 1. \] (1.8)

The first coefficient \( b_0 \) will be fixed by a normalization condition.

This result can be written in terms of associated Laguerre polynomials \(^2\)
\[ L^\alpha_n(z) = \sum_{j=0}^{n} \binom{n+\alpha}{n-j} \left( -\frac{z}{\alpha} \right)^j \frac{(-z)^j}{j!} \] (1.9)
where the binomial coefficient is
\[ \binom{n}{m} = \frac{n!}{m!(n-m)!}. \]

It can be seen by comparing the ratio of successive terms in Eq. (1.9) with Eq. (1.8) that
\[ \phi_{n,l}(z) = b_0 e^{-z} L_{n-l-1}^{2l+1}(2z). \] (1.10)

Thus
\[ R_{n,l}(r) = \frac{\phi_{n,l}(z)}{z} = b_0 e^{-z} L_{n-l-1}^{2l+1}(2z) \] (1.11)

\(^2\)Unfortunately several different definitions of these functions have been used. The most common definition which we use here is that given in e.g. Abramowitz & Stegun, Handbook of Mathematical Functions, or http://mathworld.wolfram.com/LaguerrePolynomial.html. The older definition is (Bethe, Landau & Lifshitz, Schiff) \( L^\alpha_n(z) = (-1)^n n! \sum_{j=0}^{n-a} \binom{n}{\alpha+j} \left( -\frac{z}{j} \right)^j \). Also the convention used in Griffiths Introduction to Quantum Mechanics is different than the one we are using.
1.2 Hydrogenic bound state wavefunctions

where \( z = \kappa r \). To fix the coefficient \( b_0 \) we require that

\[
1 = \int d^3r \left| \psi_{nlm}(r) \right|^2 = \int_0^\infty dr \, r^2 |R_{n,l}(r)|^2 \int d\Omega |Y_{l,m}|^2 = \frac{b_0^2}{\kappa^3} \int_0^\infty dz \, z^{2l+2} e^{-2z} \left[ L_{n-l-1}^{2l+1}(2z) \right]^2 = \frac{b_0^2}{2^{2l+3} \kappa^3} \int_0^\infty dz \, z^{2l+2} e^{-z} \left[ L_{n-l-1}^{2l+1}(z) \right]^2.
\]

To evaluate this integral we use the result

\[
\int_0^\infty dz \, \left[ L_k^n(z) \right]^2 e^{-z} z^{k+1} = \frac{(n+k)!}{n!} (2n+k+1)
\]

which leads to

\[
b_0 = \left( \kappa^3 2^{2l+2} (n-l-1)! \right)^{1/2} \frac{1}{n(n+l)!}.
\]

Finally combining all the pieces we arrive at the normalized hydrogenic wave functions

\[
\psi_{nlm}(r,\theta,\phi) = R_{n,l}(r) Y_{l,m}(	heta,\phi)
\]

where the radial functions are

\[
R_{n,l}(r) = \left( \frac{4Z^3(n-l-1)!}{a_\mu^3 n^4 (n+l)!} \right)^{1/2} e^{-\frac{Zr}{a_\mu}} \left( \frac{2Zr}{na_\mu} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2Zr}{na_\mu} \right).
\]

It should be emphasized that multiplying the radial functions by an arbitrary complex constant with unit magnitude would preserve the normalization condition and still give valid solutions since the Schrödinger equation for the hydrogen atom is a linear homogeneous differential equation. It is conventional to take the constant to be +1. An equivalent statement is that the overall phase of the wavefunction has no physical significance. However, the relative phase of two different solutions \( n,l \) and \( n',l' \) is important since it determines the phase of matrix elements between different atomic states. The relative phase is fixed by the definition (1.13).

The wavefunctions have the inner product

\[
\int d^3r \, \psi_{n',l',m'}^* \psi_{n,l,m} = \int_0^\infty dr \, r^2 R_{n',l'} R_{n,l} \int d\Omega Y_{l',m'}^* Y_{l,m} = \left( \int_0^\infty dr \, r^2 R_{n',l'} R_{n,l} \right) \delta_{l,l'} \delta_{m,m'}.
\]

The radial overlap integral inside the parentheses does not in general vanish for \( n, l \) different from \( n', l' \). When \( n = n', l = l' \) the radial integral is unity and \( \int d^3r \left| \psi_{n,l,m} \right|^2 = 1 \). When \( n \neq n' \) and \( l = l' \) the integral is zero. However for \( n \neq n' \) and \( l \neq l' \) the integral is in general nonzero.
For convenience we list some of the lowest order wavefunctions. The first five radial functions are

\[
R_{1,0}(r) = \left( \frac{Z}{a_\mu} \right)^{3/2} 2 e^{-Zr/a_\mu} \\
R_{2,0}(r) = \left( \frac{Z}{2a_\mu} \right)^{3/2} 2 \left( 1 - \frac{Zr}{2a_\mu} \right) e^{-Zr/a_\mu} \\
R_{2,1}(r) = \left( \frac{Z}{2a_\mu} \right)^{3/2} \frac{2}{\sqrt{3}} \left( \frac{Zr}{2a_\mu} \right) e^{-Zr/a_\mu} \\
R_{3,0}(r) = \left( \frac{Z}{3a_\mu} \right)^{3/2} 2 \left[ 1 - 2 \left( \frac{Zr}{3a_\mu} \right) + \frac{2}{3} \left( \frac{Zr}{3a_\mu} \right)^2 \right] e^{-Zr/a_\mu} \\
R_{3,1}(r) = \left( \frac{Z}{3a_\mu} \right)^{3/2} \frac{4\sqrt{2}}{3} \left( \frac{Zr}{3a_\mu} \right) \left[ 1 - \frac{1}{2} \left( \frac{Zr}{3a_\mu} \right) \right] e^{-Zr/a_\mu} \\
R_{3,2}(r) = \left( \frac{Z}{3a_\mu} \right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \left( \frac{Zr}{3a_\mu} \right)^2 e^{-Zr/a_\mu}. 
\]
The first few angular functions are

\[
Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, \quad Y_{1,0}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_{1,\pm1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi},
\]

\[
Y_{2,0}(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), \quad Y_{2,\pm1}(\theta, \phi) = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi},
\]

\[
Y_{2,\pm2}(\theta, \phi) = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}.
\]

Plots of some radial functions \(R_{n,l}^2\) and \((r/a)^2 R_{n,l}^2\) the probability of finding the electron in a spherical shell of radius \(r\) are given in Fig. 1.3. Note that the wavefunction has \(n - l - 1\) nodes at finite \(r\). When \(l = n - 1\) the wavefunction has a single maximum giving a well localized, classical like state with the probability distribution being in the form of a torus as can be seen in Fig. 1.4. These are referred to as circular states.
1.2.1 Expectation values of $r^k$

With wavefunctions in hand we can calculate expectation values of powers of $r$. This is straightforward but tedious. A recursion relation due to Kramers\(^3\) provides a more compact solution.

Using the transformations that took us from the radial equation (1.3) to the dimensionless (1.4) with $\kappa = 1/(na_\mu)$ we can write expectation values as dimensionless integrals using

$$\langle r^k \rangle_{nl} = \int_0^\infty dr r^2 R_{nl} r^k R_{nl} = (na_\mu)^k \int_0^\infty dz \tilde{\phi}^2(z) z^k$$

where we have simply written $\tilde{\phi}(z) = \phi_{nl}(z)$ and

$$\tilde{\phi}'' - \frac{l(l+1)}{z^2} \tilde{\phi} + \frac{2n}{z} \tilde{\phi} - \tilde{\phi} = 0.$$ 

Making the change of variables $y = nz$ and $\phi(y) = \tilde{\phi}(z)$ gives the expectation value

$$\langle r^k \rangle_{nl} = \frac{a_k}{n} \int_0^\infty dy \phi^2(y)y^k \equiv \frac{a_k}{n} \langle y^k \rangle$$

and the radial equation

$$\phi'' - \frac{l(l+1)}{y^2} \phi + \frac{2}{y} \phi = \frac{\phi}{n^2}$$

(1.16)

where now $' \equiv d/dy$. Note that $\phi(0) = \phi(\infty) = 0$ for all $n, l$ which will be useful when integrating by parts.

Now multiply (1.16) by $y^k\phi$ to get

$$\int dy \phi''y^k\phi = l(l+1)\langle y^{k-2} \rangle - 2\langle y^{k-1} \rangle + \frac{1}{n^2} \langle y^k \rangle.$$ 

On the other hand

$$\int dy \phi''y^k\phi = \int dy (\phi'y^k\phi)' - k \int dy \phi'y^{k-1}\phi - \int dy (\phi')^2y^k$$

$$= (\phi'y^k\phi)|_0^\infty - k \int dy \phi'y^{k-1}\phi - \int dy (\phi')^2y^k$$

$$= -k \int dy \phi'y^{k-1}\phi - \int dy (\phi')^2y^k.$$

In addition

$$\int dy \phi'y^k\phi = \frac{\phi^2}{2}y^k|_0^\infty - \frac{k}{2} \int dy \phi'y^{k-1}\phi = -\frac{k}{2} \langle y^{k-1} \rangle$$

and

$$\int dy (\phi')^2y^k = \frac{1}{k+1}(\phi')^2y^{k+1}|_0^\infty - \frac{2}{k+1} \int dy \phi'\phi''y^{k+1}$$

$$= -\frac{2}{k+1} \int dy \phi'\phi''y^{k+1}.$$ 

Then multiply (1.16) by $y^{k+1}\phi'$ to get

$$\int dy \phi''y^{k+1}\phi' = l(l+1) \int dy \phi\phi'y^{k-1} - 2 \int dy \phi\phi'y^k + \frac{1}{n^2} \int dy \phi\phi'y^{k+1}$$

$$= -\frac{l(l+1)(k-1)}{2} \langle y^{k-2} \rangle + k \langle y^{k-1} \rangle - \frac{k+1}{2n^2} \langle y^k \rangle$$

so

$$\int dy (\phi')^2y^k = \frac{l(l+1)(k-1)}{k+1} \langle y^{k-2} \rangle - \frac{2k}{k+1} \langle y^{k-1} \rangle + \frac{1}{n^2} \langle y^k \rangle.$$ 

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Combining the above equalities we get
\[ \frac{k + 1}{n^2} \langle y^k \rangle - (2k + 1) \langle y^{k-1} \rangle + \frac{k[(2l + 1)^2 - k^2]}{4} \langle y^{k-2} \rangle = 0. \]

Reverting to quantities with dimensions we get Kramers’ recursion relation
\[ \frac{k + 1}{n^2} \langle r^k \rangle_{nl} - (2k + 1)a_\mu \langle r^{k-1} \rangle_{nl} + \frac{k[(2l + 1)^2 - k^2]}{4}a_\mu^2 \langle r^{k-2} \rangle_{nl} = 0. \]  
(1.17)

To use the recursion relation we need two starting values. Clearly \( \langle r^0 \rangle_{nl} = < 1 >_{nl} = 1. \) In addition we can use
\[ \langle \frac{1}{r} \rangle_{nl} = \int_0^\infty dr rR^2_{nl} = \frac{1}{n^2 a_\mu}. \]
This result can be found from integration of radial wavefunctions or more simply using the Virial theorem \( 2\langle \hat{K} \rangle = n\langle \hat{V} \rangle \) where \( \hat{K}, \hat{V} \) are the operators of kinetic and potential energy and \( \hat{V} \sim r^n. \) With these starting values in hand we find
\[ \langle r \rangle_{nl} = \frac{a_\mu}{2} [3n^2 - l(l + 1)]. \]  
(1.18)

The recursion to negative powers can be found using
\[ \langle \frac{1}{r^2} \rangle_{nl} = \frac{2}{n^3(2l + 1)a_\mu^2} \]  
(1.19)
which can be derived by integration of the radial wavefunction. An explicit expression for the expectation value for all integer powers can be found in Bethe & Salpeter.

The absolute value squared of the wavefunction \( |\psi_{nlm}(r, \theta, \phi)|^2 \) is interpreted as the probability distribution of the electron in space. Normalization of the wavefunction ensures that the integrated probability to find the electron somewhere is unity. The probability to find the electron between \( r \) and \( r + dr \) is \( dP = P(r)dr = |\psi|^2 4\pi r^2 dr. \) The average value of \( r \) is
\[ \langle r \rangle = \int_0^\infty dr P(r)r = \frac{a_\mu}{2} [3n^2 - l(l + 1)] \] from Eq. (1.18). It is not hard to show that for a nucleus of charge \( Z \) this is modified to \( \langle r \rangle_Z = \langle r \rangle / Z. \) The stronger nuclear charge pulls the electron in closer to the nucleus.

For the ground state of hydrogen \( n = 1, l = 0 \) we have \( \langle r \rangle = 3a_\mu/2 \) which is larger than \( a_\mu. \) Alternatively we might ask what is the most likely value of \( r \) to measure. That is given by the radius for which the probability \( P(r) \) is maximum. Solving \( dP/dr = 0 \) for the hydrogen ground state gives
\[ \frac{4}{dr}r^2e^{-2r/a_\mu} = (2r - 2r^2/a_\mu)e^{-r/a_\mu} = 0 \] which is solved by \( r = a_\mu. \) The most likely position to observe the electron at is just the Bohr radius.

### 1.3 Large \( n \) wavefunctions

As the principal quantum number \( n \) tends to infinity the wavefunctions approach a universal form that depends on \( l \) but is independent of \( n. \) We can determine this limiting form from the radial equation
\[ -\frac{\hbar^2}{2\mu} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R + \left[ -\frac{Zq^2}{r} + \frac{\hbar^2}{2\mu} \frac{l(l + 1)}{r^2} \right] R = ER. \]  
(1.3)
1.3 Large $n$ wavefunctions

\[ n=20, \, b=0.0225 \]

\[ n=100, \, b=0.0021 \]

Figure 1.6: Comparison of the asymptotic wavefunctions of Eq. (1.22) (yellow) with the exact expressions from Eq. (1.13) (blue) for $Z = 1$, $n = 20, 100$, and $l = 0, 1, 2$.

Using $E_n = -Z^2E_H/2n^2$ we see that for $r/a_0 \ll 2n^2/Z$ we can neglect the term proportional to $E$ so that

$$
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R + \left[ \frac{2\mu Zq^2}{\hbar^2 r} - \frac{l(l+1)}{r^2} \right] R = 0.
$$

(1.20)

Putting $r = \hbar^2/(\mu q^2)z = a_\mu z$ and $R(r) = \phi(z)/a_\mu^{3/2}$ this becomes

$$
\frac{d^2\phi}{dz^2} + \frac{2}{z} \frac{d\phi}{dz} + \frac{2Z}{z} \phi - \frac{l(l+1)}{z^2} \phi = 0.
$$

(1.21)

This has the solution

$$
\phi(z) = \frac{b}{\sqrt{2Zz}} J_{2l+1} \left( \sqrt{8Zz} \right)
$$

with $J$ a Bessel function and $b$ a constant. Using the asymptotic form of the Bessel function

$$
J_{2l+1}(\sqrt{8Zz}) \simeq \frac{2^{1/2}}{\pi^{1/2}(8Zz)^{1/4}} \cos \left( \sqrt{8Zz} - l\pi - \frac{3\pi}{4} \right)
$$

we can write the wavefunction as

$$
\phi_{\infty,l}(z) \simeq \frac{b}{\pi^{1/2}(2Zz)^{3/4}} \cos \left( \sqrt{8Zz} - l\pi - \frac{3\pi}{4} \right).
$$

(1.22)
This is valid for \(1/(8Z) \ll z \ll 2n^2/Z\). The wavefunction is a decaying sinusoid with an increasing in \(z\) frequency and phase shift proportional to \(\pi l\). We can get a visual impression of the accuracy of the large \(n\) approximation by comparing with the exact wavefunctions from Eq. (1.13). As can be seen in Fig. 1.6 the approximation (1.22) is quite accurate as regards the amplitude variation with \(r\), for intermediate values of \(r\), but less so as regards the phase. This is a typical situation that it is relatively simple to give an accurate estimate for the amplitude of the wavefunction, while the phase is a more sensitive function of parameters. It is also the case that for \(r \sim 2n^2/Z\) even the amplitude becomes inaccurate.

### 1.4 Parabolic states

The Schrödinger equation can be solved exactly in the presence of a static electric field by using parabolic coordinates. With a field \(E = E_z e_z\) we need to solve

\[
\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Zq^2}{r} - eE_z r \cos \theta - E\right) \psi(r) = 0. \tag{1.23}
\]

This can be solved by separation of variables in parabolic coordinates. After separation of variables the solutions are labeled by four quantum numbers \(|n, n_1, n_2, m⟩\) where \(n\) and \(m\) have the same meaning as for the spherical solutions, \(n_{1,2} \geq 0\) and

\[
n = n_1 + n_2 + |m| + 1.
\]

The parabolic wavefunctions are related to the spherical solutions \(|n, l, m⟩\) by [1]

\[
|n, n_1, n_2, m⟩ = \sum_{l=0}^{n-1} (-1)^{(-1+n-m+n_1-n_2)/2} \times C_{a_1-a_2-n_1-n_2-m}^{l-m} |n, l, m⟩. \tag{1.24}
\]

The inverse relation is

\[
|n, l, m⟩ = \sum_{n_2=0}^{n-|m|} \sum_{n_1=0}^{n-n_2-|m|} (-1)^{(-1+n-m+n_1-n_2)/2} \times C_{a_{n_1}-a_{n_2}-n_2-n_1-m}^{l-m} |n, n_1, n_2, m⟩. \tag{1.25}
\]

### 1.5 Spectroscopic notation

A set of quantum numbers \(n, l, m\) define the atomic orbital of an electron. The standard spectroscopic notation for the orbitals is

\[
l = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \ 11 \ 12 \ 13 \ 14 \ 15 \ ...
\]

\[
s \ p \ d \ f \ g \ h \ i \ k \ l \ m \ n \ o \ q \ r \ t \ u \ ...
\]

The first letters stand for sharp, principal, diffuse, fundamental, and the rest follow the alphabet skipping \(j\) which is reserved for the total angular momentum. The set of atomic
orbits in a multielectron atom is referred to as a configuration. As we consider atoms with more and more electrons successive orbitals fill up. All the electrons do not simply occupy the lowest energy orbital due to quantum statistics.

Quantum mechanics distinguishes between two fundamentally different types of particles: bosons with integer spin and fermions with half integer spin. Bosons satisfy Bose-Einstein statistics and more than one boson can have the same quantum numbers. The most common example is the photon which has spin one. Fermions satisfy Fermi-Dirac statistics and we cannot have more than one fermion in the same quantum state. Electrons have spin $\frac{1}{2}$ and are therefore fermions. The quantum numbers describing the state of an electron in an atomic orbital in an uncoupled representation are $n, l, m_l, s, m_s$ with $l = 0, 1, 2, \ldots n - 1$, $-l \leq m_l \leq l$, $s = 1/2$, and $m_s = \pm 1/2$. Since two electrons cannot have the same quantum numbers a given value of $l$ can only accommodate $(2l + 1) \times 2$ electrons corresponding to $2l + 1$ values of the $e_z$ projection of angular momentum $m_l$ and 2 values of the electron spin projection $m_s$. Specific values of $n, l$ denote a shell and the number of electrons in filled $l = 0, 1, 2, 3, \ldots$ shells is $2, 6, 10, 14, \ldots$.

The ground state configurations for the first elements in the periodic table are

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1s</td>
</tr>
<tr>
<td>He</td>
<td>1s$^2$</td>
</tr>
<tr>
<td>Li</td>
<td>1s$^2$2s</td>
</tr>
<tr>
<td>Be</td>
<td>1s$^2$2s$^2$</td>
</tr>
<tr>
<td>B</td>
<td>1s$^2$2s$^2$2p</td>
</tr>
<tr>
<td>C</td>
<td>1s$^2$2s$^2$2p$^2$</td>
</tr>
<tr>
<td>N</td>
<td>1s$^2$2s$^2$2p$^3$</td>
</tr>
<tr>
<td>O</td>
<td>1s$^2$2s$^2$2p$^4$</td>
</tr>
<tr>
<td>F</td>
<td>1s$^2$2s$^2$2p$^5$</td>
</tr>
<tr>
<td>Ne</td>
<td>1s$^2$2s$^2$2p$^6$</td>
</tr>
<tr>
<td>Na</td>
<td>1s$^2$2s$^2$2p$^6$3s</td>
</tr>
<tr>
<td>Mg</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$</td>
</tr>
<tr>
<td>Al</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p</td>
</tr>
<tr>
<td>Si</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^2$</td>
</tr>
<tr>
<td>P</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^3$</td>
</tr>
<tr>
<td>S</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^4$</td>
</tr>
<tr>
<td>Cl</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^5$</td>
</tr>
<tr>
<td>Ar</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$</td>
</tr>
<tr>
<td>K</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$(3d)$^4$s</td>
</tr>
<tr>
<td>Ca</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$(3d$^2$)$^4$s$^2$</td>
</tr>
</tbody>
</table>

and so on. The notation for each component of the configuration is $nl^q$ with $q$ the number
of electrons with the same \( n, l \) values. For \( l = s, p, d, f, \ldots \), \( q \) is at most 2, 6, 10, 14, \ldots. We see that the shells fill up sequentially until we reach \( K \) which skips 3\( d \) and puts the outermost electron in 4\( s \). This is denoted in the table by writing \((3d)\). The reason for this has to do with interactions between the electrons. An empirical rule which does not explain, but helps to remember this, is that the orbitals tend to fill up with increasing \( n + l \).

Atoms with filled shells are relatively stable and react only weakly with other elements. These are the noble gases He, Ne, Ar, Kr, Xe, Rn in the last column of the periodic table shown in Fig. 1.7. Atoms with a single electron outside a closed shell are very reactive. These are the alkali atoms, H, Li, Na, K, Rb, Cs, Fr in the first column. In between the first and last columns the elements have intermediate behaviors. We will discuss more of the general features later on.

The energy levels of the alkali atoms are analogous to those of H because the closed inner shells provide an effectively spherical charge distribution. To see this let’s calculate the charge distribution of a filled shell. The effective charge distribution of an electron in state \(|nlm\rangle\) is

\[
\rho(r) = -e|\psi_{nlm}(r)|^2
\]

corresponding to a total charge of

\[
\int d^3 r \rho(r) = -e.
\]

The density separates into radial and angular parts as \( \rho(r) = |R_{nl}(r)Y_{lm}(\theta, \phi)|^2 \). For a filled
shell with quantum numbers \( n, l \) the charge density is

\[
\rho(r) = \sum_{j=1}^{2(2l+1)} \rho_j = -2e \sum_{m=-l}^{l} |R_{nl}(r)Y_{lm}(\theta, \phi)|^2 = -2eR_{nl}^2(r) \sum_{m=-l}^{l} |Y_{lm}(\theta, \phi)|^2 = -2eR_{nl}^2(r) \frac{2l + 1}{4\pi}.
\]

We see that the charge distribution of a filled shell has radial symmetry. The Coulomb interaction between a valence electron at position \( r_0 \) and the filled shell is

\[
V(r_0) = \frac{-e}{4\pi\epsilon_0} \int d^3r \frac{\rho(r)}{|r - r_0|} = q^2 \frac{2(2l + 1)}{4\pi} \int d^3r \frac{R_{nl}^2(r)}{|r - r_0|},
\]

By Gauss’s law the integral is

\[
4\pi \int_0^{r_0} dr \frac{r^2 R_{nl}^2(r)}{r} \int_0^{r_0} dr \frac{r^2 R_{nl}^2(r)}{r}
\]

so

\[
V(r_0) = V(r_0) = q^2 \frac{2(2l + 1)}{4\pi} \int_0^{r_0} dr \frac{r^2 R_{nl}^2(r)}{r}.
\]

Thus we get a hydrogen like interaction with radial symmetry and modifications to the precise form of the radial potential depending on \( R_{nl} \). The dependence on \( l \) breaks the degeneracy of the single electron Coulomb problem as we will see in the next section.

Also magnetic interactions due to the spin and orbital magnetic moments of the electrons affect the atomic energy levels. A similar calculation for the magnetic interactions shows that they vanish for a single electron outside a filled shell. Thus we get hydrogen like structure for the alkali atoms. The situation for atoms with unfilled shells is more complicated, since nonradial Coulomb interactions, and magnetic interactions, must all be taken into account.

1.6 Quantum defects

The Schrödinger equation can only be solved exactly for hydrogen. However atoms with a single electron outside a closed shell are “hydrogen like”. These are the alkali atoms H, Li, Na, K, Rb, Cs, Fr seen in the first column of Fig. 1.7. Their energy level structure resembles that of hydrogen except that the degeneracy between levels with the same \( n \) but different \( l \) is broken. The reason for this can be seen from a qualitative argument.

Consider the Cs atom. It has one stable isotope \(^{133}\text{Cs}\) and atomic number \( Z = 55 \). The electronic configuration is [Xe]6s with the outermost electron in the 6s orbital. The Xe core
is stable and interacts only weakly with external fields. The electronic properties of the Cs atom are largely determined by the outer electron. When the electron is far from the core it sees an effective nuclear charge of $Z - (Z - 1) = 1$, just like in the hydrogen atom. However, when the electron is close to the nucleus the screening of the nuclear charge is reduced and the electron eventually sees a charge of $Z - 0 = Z$ and a potential of $-Zq^2/r$. This is described by Eq. (1.26) and is shown qualitatively in Fig. 1.8. We could write the potential as

$$V_{\text{eff}}(r) = -\frac{q^2}{r} - f_{sc}(r) \frac{(Z - 1)q^2}{r} = -Z_{\text{eff}}(r) \frac{q^2}{r}$$

where $f_{sc}$ is a function describing the partial screening and $Z_{\text{eff}}$ is a smooth function which tends to $Z$ as $r \to 0$ and tends to 1 as $r \to \infty$. The deeper potential binds the electron more strongly and lowers the Cs energy levels compared to what they are in hydrogen for the same quantum numbers.

Excited states of the Cs atom correspond to the outer electron having different values of $n, l$. Increasing $n$ does not change the screening behavior very much, since the partial screening only occurs when the electron is close to the origin, and the majority of the probability density is outside the electron core. However, the partial screening does depend strongly on $l$. Orbitals with $l = 0$ (s orbitals) have more of the electron density closer to the origin and therefore experience less screening. Orbitals with $l > 0$ have the electron density further from the origin and therefore the nucleus is more effectively screened. As $l$ increases the screening by the core becomes more and more effective until eventually there is perfect screening and the energy levels become hydrogenic.

This behavior with the partial screening dependent on $l$, but only weakly varying with $n$ is described by the quantum defect. We modify the Rydberg formula to

$$E_n = -\frac{E_H}{2(n^*)^2} = -\frac{E_H}{2(n - \mu_l)^2}$$

where $n^* = n - \mu_l$ is an effective quantum number and $\mu_l$ is the quantum defect. According to the argument given above the defects are positive since $E_n$ is lower than in hydrogen.

For Cs the defects are $\mu_0 = 4.05, \mu_1 = 3.58, \mu_2 = 2.47, \mu_3 = 0.03$ and $\mu_l \simeq 0$ for $l > 3$. The weak dependence on $n$ results in corrections proportional to $1/n^2$. Many more details
can be found in the book by Gallagher\textsuperscript{4}.

1.7 Bound and continuum Coulomb wave functions

The question arises as to how we can find the wavefunction for an atomic state with nonzero quantum defect. One approach is to devise an expression for $V_{\text{eff}}(r)$ and solve the Schrödinger equation with this effective potential. As an example we might take the effective potential due to the nucleus and the core to be

$$V_{\text{eff}}(r) = \frac{1}{4\pi\epsilon_0} e \frac{1}{r} + \frac{1}{4\pi\epsilon_0} (Z - 1)e \frac{1}{2r^2} r_n.$$ \hfill (1.27)

Here $r_n$ is an effective core size containing a spherically symmetric charge of $Ze$. This model can be solved exactly leading to

$$\mu_l = l + \frac{1}{2} - \sqrt{(l + 1/2)^2 - A}$$ \hfill (1.28)

with

$$A = \frac{2\mu(Z - 1)q^2 r_n}{\hbar^2}.$$ \hfill (1.29)

This predicts $\mu_l \to 0$ as $l \to \infty$ which is the correct trend, but the detailed predictions do not agree well with experiment.

For more refined screening models it is typically only possible to solve the Schrödinger equation numerically. An example of a model potential that has been used to accurately reproduce alkali atom energy levels is\textsuperscript{[2]}

$$V_l(r) = -\frac{Z_l(r)}{r} - \frac{\alpha_c}{2r^4} \left[ 1 - e^{-(r/r_c)\sigma} \right]$$

$$Z_l(r) = 1 + (Z - 1)e^{-a_1 r} - r(a_3 + a_4 r)e^{-a_2 r}.$$ \hfill (1.30)

Here $Z$ is the nuclear charge of the atom, and $\alpha_c$ is the static polarizability of the positive ion core. These two parameters are known. In addition there are five fitting parameters: $r_c$ which is a short range cut-off, and $a_1 - a_4$. For each value of $l$ the Schrödinger equation is solved numerically with the model potential and the parameters are adjusted to reproduce experimentally measured energy levels with different values of $n$. The results are accurate to one part in $10^5$ and the numerically calculated wavefunctions can then be used to predict other quantities of interest. This is a widely used method that works well for alkali atoms.

An alternative approach is to solve the Schrödinger equation analytically with a pure Coulomb potential but no longer insist that the quantum number $n$ is an integer. This is called the Coulomb approximation resulting in Coulomb, or quantum defect, wavefunctions $R_{\gamma,l}$ with energy $E_\gamma = -E_m/2\gamma^2$. We then set $\gamma = n^* = n - \mu_l$ to match the experimentally observed energy levels. This approach has the advantage that we obtain an analytical expression for the wavefunction that can be used to calculate other properties of interest. The drawback is that the wavefunction is divergent, since $\gamma$ is not integer. Nevertheless such wavefunctions can be very useful.

Let us see how this works. The Schrödinger equation for stationary states of an atom with nuclear charge $Z$ is
\[
\left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{r} - E \right) \psi(r) = 0
\] (1.29)
where $q^2 = e^2/4\pi\varepsilon_0$, $-e$ is the charge on an electron, and $\mu = m_eM/(m_e + M)$ is the reduced mass with $m_e$ the electron mass and $M$ the nuclear mass. Separating variables with $\psi(r) = R(r)Y_{lm}(\theta, \phi)$ we get the radial equation
\[
\frac{1}{r^2 \partial_r} \left( r^2 \partial_r \right) R + \left[ \frac{2\mu E}{\hbar^2} + \frac{2Z\mu q^2}{\hbar^2} \right] - \frac{l(l+1)}{r^2} R = 0.
\]

**Bound states**

Putting $z = \kappa r$ with $\kappa = \sqrt{-2\mu E/\hbar^2}$ and $\phi(z) = zR(z/\kappa)$ gives
\[
\frac{d^2\phi}{dz^2} - \frac{l(l+1)}{z^2} \phi + \frac{2\gamma}{z} \phi - \phi = 0
\] (1.30)
with the dimensionless parameter $\gamma = (-\mu Z^2q^4/(2\hbar^2E))^{1/2} = Z(-E_H/2E)^{1/2}$. We previously solved this equation using a series expansion and arrived at normalizable bound state solutions when $\gamma = n$ is a non-negative integer and $E_n = -E_H/2n^2$, $E_H$ being the Hartree energy.

Let us now solve the equation in a more general form. The solutions of Eq. (1.30) are the Whittaker functions\(^5\) $M_{\gamma,l+1/2}(2z), W_{\gamma,l+1/2}(2z)$. (Whittaker & Watson §16.1). The function $M_{\gamma,l+1/2}(2z)$ does not exist when $2l + 1$ is integer which is the case here. We therefore use the $W$ functions to write a first solution as
\[
\phi_+(z) = W_{\gamma,l+1/2}(2z).
\]
Since (1.30) is a 2nd order differential equation a fundamental solution requires two linearly independent solutions. The second solution is (Whittaker & Watson §16.31) $\phi_- = W_{-\gamma,l+1/2}(-2z)$. These solutions can be written in terms of confluent hypergeometric functions of the second kind $U$, as\(^6\)
\[
\phi_+(z) = W_{\gamma,l+1/2}(2z) = e^{-z}(2z)^{l+1}U(1 + l - \gamma, 2 + 2l, 2z),
\]
\[
\phi_-(z) = W_{-\gamma,l+1/2}(-2z) = e^z(-2z)^{l+1}U(1 + l + \gamma, 2 + 2l, -2z).
\]

The radial solution that decays exponentially as $z \to \infty$ is $\phi_+$ and since $\kappa = 1/(a_0\gamma)$ with $a_0$ the Bohr radius we can write
\[
P_{\gamma,l}(r) = r R_{\gamma,l}(r) = \frac{a_0}{\gamma^2[\Gamma(\gamma + l + 1)\Gamma(\gamma - l)]^{1/2}} \times \gamma e^{-r/(a_0\gamma)}(2r/(a_0\gamma)^{l+1})^{1/2}U(1 + l - \gamma, 2 + 2l, 2r/(a_0\gamma)).
\] (1.31)

\(^5\)These satisfy the differential equation $\frac{d^2W_{\gamma,l}(z)}{dz^2} + \left[ -\frac{1}{4} + \frac{\gamma}{z} + \frac{\gamma^2 - \mu^2}{z^2} \right] W_{\gamma,l}(z) = 0$.

\(^6\)The function $U$ can be expressed in terms of the confluent hypergeometric function $\Gamma(1)_F$ through the identity
\[
U(a, b, z) = \frac{\Gamma(b-1)}{\Gamma(a)} z^{1-b} 1_F(a - b + 1, 2 - b, z) + \frac{\Gamma(1-b)}{\Gamma(a-b + 1)} 1_F(a, b, z)
\]
which is valid for $b$ not an integer. In our case $b$ is an integer and $U(a, b, z) = \lim_{\beta \to b} U(a, \beta, z)$. 
The prefactor involving $\Gamma$ functions has been added to satisfy the normalization condition for the wavefunctions
\[
\int d^3r \, |\psi_{\ell m}(r)|^2 = \int_0^\infty dr \, r^2 R^2_{\gamma l}(r) \int d\Omega \, |Y_{lm}|^2 = \int_0^\infty dr \, r^2 \frac{R^2_{\gamma l}(r)}{a_0} = 1.
\]
In atomic units $r = a_0 z$ so
\[
\int_0^\infty dr \, r^2 R^2_{\gamma l}(r) = a_0^3 \int_0^\infty dz \, z^2 R^2_{\gamma l}(a_0 z).
\]
To satisfy the normalization condition we rescale (1.31) by $1/a_0^{3/2}$ so that the normalized and scaled wavefunctions are
\[
P_{\gamma l}(r) = r R_{\gamma l}(r) = \frac{1}{\sqrt{a_0}} \frac{1}{\gamma} \frac{1}{[\Gamma(\gamma + l + 1)\Gamma(\gamma - l)]^{1/2}} \times e^{-r/(a_0 \gamma)}(2r/(a_0 \gamma))^{l+1} U(1 + l - \gamma, 2 + 2l, 2r/(a_0 \gamma)).
\]
For integer values of $\gamma = n$, $\Gamma(n) = (n - 1)!$ and we can use $U(1 + l - n, 2 + 2l, z) = (-1)^{n-l-1}(n - l - 1)!L^{2l+1}_{n-l-1}(z)$ so that (1.32) reduces to
\[
R_{\gamma-n,l}(r) = (-1)^{n-l-1} \left( \frac{4(n - l - 1)!}{a_0^3 n^4(n + l)!} \right)^{1/2} e^{-r/(a_0 n)}(2r/(a_0 n))^{l} L^{2l+1}_{n-l-1}(2r/(a_0 n)).
\]
This agrees with (1.13) apart from the phase factor $(-1)^{n-l-1}$. In order to get the correct signs for matrix elements between different states we compensate this phase to arrive at the Coulomb wavefunctions which connect smoothly with the hydrogenic solutions in the form
\[
P_{\gamma l}(r) = r R_{\gamma l}(r) = (-1)^{l+1-l-<\gamma>} \frac{1}{\sqrt{a_0}} \frac{1}{\gamma} \frac{1}{[\Gamma(\gamma + l + 1)\Gamma(\gamma - l)]^{1/2}} \times e^{-r/(a_0 \gamma)}(2r/(a_0 \gamma))^{l+1} U(1 + l - \gamma, 2 + 2l, 2r/(a_0 \gamma))
\]
where $<\gamma>$ is the nearest integer to $\gamma$.

For non-integer values of $\gamma$ these functions generalize the bound state wavefunctions, but they may diverge at the origin. For $l \geq 0$ the limiting form of $R_{\gamma l}(r)$ near the origin is
\[
R_{\gamma l}(r) \sim \frac{1}{2^{l+1}} \frac{\Gamma(2l + 1)}{\Gamma(l + 1 - \gamma)\sqrt{\Gamma(\gamma - l)\Gamma(\gamma + l + 1)}} r^{l+1}
\]
which diverges at the origin. Nevertheless $\lim_{r \to 0} r^2 R^2_{\gamma l}(r) \sim r^{-2l}$ which is finite for $l = 0$. Therefore wavefunctions with $l = 0$ are normalizable even though $\gamma$ is not an integer. For higher $l$ it is necessary to choose an inner cutoff radius when calculating matrix elements. Some guidance for selection of the cutoff can be found in papers on quantum defect theory [3]. For $l > 0$ it is recommended to use $r_{\min} = a_0(l + 1)/2$.

Figure 1.9 shows the H and Cs 6s wavefunctions. The expectation value $<r> = 3/2 n^2 a_0$ is seen to agree well with the H plot. For Cs the 6s electron is shielded from the nuclear charge by the core electrons so the estimate $3/2 n^2 a_0/Z$, which would apply for an unshielded nucleus, is a few times smaller than the actual size of the Cs 6s wavefunction. Nevertheless there is a large difference between H 6s and Cs 6s, as evidenced by the large value of the quantum defect. A plausible value for the radius of the core electron charge distribution in Cs might be the radius which contains only 0.001 of the valence electron probability. From numerical integration I find this to be $0.11 \times a_0 = 5.8$ pm which is only a factor of 3 bigger than the above estimate for $r_n$. 

December 15, 2015 M. Saffman
Continuum states

We now consider positive energy solutions corresponding to unbound states. Equation (1.30) then takes the form

$$\frac{d^2 \phi}{dz^2} - \frac{l(l + 1)}{z^2} \phi - \frac{2\eta}{z} \phi + \phi = 0$$  \hspace{1cm} (1.35)

where for \( E > 0 \) we have used \( \eta = -(E_H/2E)^{1/2} \), \( r = -\eta a_0 z = |\eta| a_0 z \), and \( R(r) = R(|\eta| a_0 z) = \phi(z)/z \). Note that the energy is

$$E = \frac{E_H}{2\eta^2}.$$  

The energy eigenvalue \( \eta \) is negative, and the continuum state energy is positive.

The solutions of (1.35) are the regular Coulomb function \( F_l(\eta, z) \) and the irregular coulomb function \( G_l(\eta, z) \). A good reference for these is Abramowitz & Stegun, Ch. 14.

The solution that vanishes at the origin is

$$F_l(\eta, z) = \frac{2^l e^{-\pi \eta/2} |\Gamma(l + 1 + i\eta)|}{\Gamma(2l + 2)} z^{l+1} e^{-iz} _1 F_1(l + 1 - i\eta, 2l + 2, 2iz).$$

Here \(_1 F_1\) is Kummer’s confluent hypergeometric function \(_1 F_1(a, b, z) = \sum_{k=0}^\infty \frac{(a)_k}{(b)_k} \frac{z^k}{k!}\) where the Pochhammer symbol is \((a)_k = \Gamma(a + k)/\Gamma(a)\).

It is often convenient to work with \( P_{\eta,l}(r) = r R_{\eta,l}(r) \) which takes the form

$$P_{\eta,l}(r) = (|\eta| a_0) F_l(\eta, r/|\eta| a_0)$$

$$= (|\eta| a_0) \frac{2^l e^{-\pi \eta/2} |\Gamma(l + 1 + i\eta)|}{\Gamma(2l + 2)}$$

$$\times \left( \frac{r}{|\eta| a_0} \right)^{l+1} e^{-ir/|\eta| a_0} _1 F_1(l + 1 - i\eta, 2l + 2, 2ir/|\eta| a_0).$$ \hspace{1cm} (1.36)

For large \( r \) the wave function has the asymptotic form

$$P_{\eta,l}(r) \rightarrow \infty \left( |\eta| a_0 \right) \sin \left( r/|\eta| a_0 - \eta \ln 2r/|\eta| a_0 - l\pi/2 + \sigma_l \right)$$ \hspace{1cm} (1.37)
where \( \sigma_l = \arg[\Gamma(l + 1 + i\eta)] \) is the Coulomb phase. The inner product of the Coulomb wave functions is

\[
\int_0^\infty dr \, P_{\eta,l} P_{\eta',l} \sim \eta\eta' a_0^2 \int_0^\infty dr \, \sin(r/|\eta|a_0 - \eta \ln 2r/|\eta|a_0 - l\pi/2 + \sigma_l) \\
\times \sin(r/|\eta'|a_0 - \eta' \ln 2r/|\eta'|a_0 - l\pi/2 + \sigma_l)
\]

\[
\simeq \eta\eta' a_0^2 \int_0^\infty dr \, \sin(r/|\eta|a_0) \sin(r/|\eta'|a_0)
\]

\[
= \frac{\pi}{2} \eta^2 a_0^3 \delta(1/|\eta| - 1/|\eta'|).
\]

The continuum states are delta function normalized. We define energy normalized wave functions \( P_{\eta,l}^{(E)} \) that satisfy \( \langle P_{\eta',l}^{(E')} | P_{\eta,l}^{(E)} \rangle = \delta(E - E') \) using

\[
\delta(1/|\eta| - 1/|\eta'|) = \left| \frac{dE}{d(1/|\eta|)} \right| \delta(E - E') = \frac{\mu e^4}{\hbar^2|\eta|} \delta(E - E').
\]

Thus the energy normalized continuum wave functions are

\[
P_{\eta,l}^{(E)}(r) = \left( \frac{2\mu^2 e^4}{\pi|\eta|\hbar^4} \right)^{1/2} P_{\eta,l}(r)
\]

\[
= \left( \frac{|\eta|}{e^2} \right)^{1/2} \sqrt{\frac{2}{\pi}} \frac{2^l e^{-\eta\eta/2} |\Gamma(l + 1 + i\eta)|}{\Gamma(2l + 2)} \left( \frac{r}{|\eta|a_0} \right)^{l+1} e^{-ir/|\eta|a_0}
\]

\[
\times {}_1F_1(l + 1 - i\eta, 2l + 2, 2i\gamma/|\eta|a_0).
\]

Note the energy normalized functions have units of \((\text{length} \times \text{energy})^{-1/2}\) so that \( \int dr (P_{\eta,l}^{(E)})^2 \) has units of inverse energy. Finally we rescale such that \( \langle P_{\eta',l}^{(E')} | P_{\eta,l}^{(E)} \rangle = \delta(E - E') \) has units of inverse energy measured in Hartrees, in other words \( \langle P_{\eta',l}^{(E')} | P_{\eta,l}^{(E)} \rangle \) is now a pure number. Since a Hartree is \( E_H = m_e q^4/h^2 \) we put

\[
P_{\eta,l}^{(E)}(r) = \sqrt{E_H / e^2} \sqrt{|\eta|} \left( \frac{2}{\pi} \frac{2^l e^{-\eta\eta/2} |\Gamma(l + 1 + i\eta)|}{\Gamma(2l + 2)} \right) \left( \frac{r}{|\eta|a_0} \right)^{l+1} e^{-ir/|\eta|a_0} {}_1F_1(l + 1 - i\eta, 2l + 2, 2i\gamma/|\eta|a_0).
\]

The irregular Coulomb functions \( G_l \) are nonzero but finite at the origin for \( l = 0 \) and diverge at the origin for \( l > 0 \). They are nonetheless of use when treating problems involving non-hydrogenic atoms. They are defined by (Abramowitz & Stegun 14.1.14)

\[
G_l(\eta, z) = \frac{1}{2} \left[ H_l^+(\eta, z) + H_l^-(\eta, z) \right]
\]

with

\[
H_l^\pm(\eta, z) = (\mp i)^l e^{(\pi\eta/2)} e^{\pm i\sigma_l(n)} e^{\pm iz} (\mp 2iz)^{l+1} U(1 + l \pm i\eta, 2 + 2l, \mp 2iz).
\]
The asymptotic behavior at large $z$ of the Coulomb functions is

$$F_l(\eta, z) \sim \frac{l(l+1) + \eta^2}{2z} \cos \theta_l + \sin \theta_l \rightarrow \sin \theta_l$$

$$G_l(\eta, z) \sim \cos \theta_l - \frac{l(l+1) + \eta^2}{2z} \sin \theta_l \rightarrow \cos \theta_l$$

with $\theta_l = z - \eta \ln(2z) - \pi l/2 + \sigma_l$, $\sigma_l = \arg[\Gamma(l+1+i\eta)]$. Some plots of $F_l, G_l$ are shown in Fig. 1.10.

### 1.7.1 Choice of wavefunctions

When solving bound state problems we could unambiguously find the physically relevant solution by requiring that the wavefunction be normalized. Since continuum wavefunctions are not normalized in the usual sense of being square integrable we need a different method. We note that as regards the bound state wavefunctions as $n \to \infty$ the solution $P_{\gamma, l}(r)$ tends to zero near the origin as $\gamma \to \infty$. We will require that $P_{\gamma, l}$ and $P_{\eta, l}$ match at $r = 0$ as $\gamma \to \infty$ from below and $\eta \to -\infty$ from above. This implies that we pick the regular Coulomb function $F_l$ which vanishes at the origin. The asymptotic form of the wavefunction is thus given by (1.37). The continuum wave functions are of particular utility for calculating photoionization cross sections. For hydrogen we use the regular Coulomb functions which give accurate results. Photoionization will be treated in detail in a later chapter.

The positive energy states in a non-Coulomb potential are no longer given by $F_l(\eta, z)$ since the modified potential results in a phase shift of the continuum waves. Instead the asymptotic wave functions are given by

$$\phi(r) \sim \sin \left( \frac{r}{|\eta|a_0 - \eta \ln 2r/|\eta|a_0 - l\pi/2} + \sigma_l + \delta_l \right)$$

$$= \cos(\delta_l) \sin \left( \frac{r}{|\eta|a_0 - \eta \ln 2r/|\eta|a_0 - l\pi/2} + \sigma_l \right)$$

$$+ \sin(\delta_l) \cos \left( \frac{r}{|\eta|a_0 - \eta \ln 2r/|\eta|a_0 - l\pi/2} + \sigma_l \right)$$

(1.42)

where the additional phase $\delta_l$ is due to the modified potential. This can equivalently be written as a linear combination of regular and irregular Coulomb functions

$$\phi(r) = \cos(\delta_l) F_l(r) + \sin(\delta_l) G_l(r).$$

The value of $\delta_l$ at threshold was shown by Seaton to be [4]

$$\delta_l = \lim_{n \to \infty} \pi \mu_{n,l}.$$
The factor of $\pi$ accounts for the fact that a $\pi$ phase shift (half a wavelength) in the wavefunction corresponds to a unit change of the effective radial quantum number.

### 1.8 Matrix elements

The importance of calculating wavefunctions is that they can then be used to evaluate matrix elements of operators between atomic states. The matrix elements in turn are needed to determine perturbative corrections to energies, mixing coefficients, and transition rates between states. The bound-bound radial matrix elements for electric dipole transitions are

$$ R_{n,l}^{n',l+1} = \int_0^\infty dr \ r^2 R_{n',l+1} r R_{n,l}. $$

(1.43)

Since the wavefunctions have units of $m^{-3/2}$ the matrix element has units of length. As the radial wavefunctions are real the matrix element is symmetrical, $R_{n,l}^{n',l+1} = R_{n',l+1}^{n,l}$. We will in turn treat matrix elements of hydrogenic and quantum defect wavefunctions.

#### 1.8.1 Hydrogenic wavefunctions

For the hydrogenic states closed form expressions exist for matrix elements of bound-bound, bound-continuum, and continuum-continuum states. For hydrogenic states the dipole matrix element is[5]

$$ R_{n,l}^{n',l+1} = a_0 (-1)^{n-l-1} \frac{\sqrt{(n' + l + 1)!(n + l)!}}{4(2l + 1)!} \frac{(4n'n')^{l+2}(n' - n)n' + n - 2l - 4}{(n' + n)n'} \times \left[ 2F_1(-n' - l - 2), -(n - l - 1), 2l + 2, -4n'n/(n' - n)^2 \right] $$

$$ - \left( \frac{n' - n}{n' + n} \right)^2 2F_1(-(n' - l), -(n - l - 1), 2l + 2, -4n'n/(n' - n)^2) \right] \ (1.44)$$

Using this expression we find, for example, that for the Hydrogen Lyman $\alpha$ transition

$$ R_{1,0}^{2,1} = \frac{128\sqrt{2}}{81\sqrt{3}} a_0. $$

This result can be readily checked by integration of the wavefunctions of Eqs. (1.15). Equation (1.44) fails when $n' = n$. In this case we can use the simpler expression

$$ R_{n,l}^{n,l+1} = -a_0 \frac{3}{2} n \sqrt{n^2 - (l + 1)^2}. $$

(1.45)

Another useful result is the matrix element for transitions between circular states

$$ R_{n,n-1}^{n+1,n} = \frac{2^{1/2} 4^{n+1}(n + 1)^{n+2} n^{n+5/2}}{(2n + 1)^{2n+5/2}}. $$

(1.46)

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1.8.2 Quantum defect wavefunctions

For the quantum defect wavefunctions there are no closed form analytical results available and matrix elements must be calculated numerically. This is straightforward for small \( n \), but subject to numerical instabilities for large \( n \). We see from Eq. (1.33) that the wavefunction \( R_{\gamma l} \) involves the confluent hypergeometric function of the second kind

\[
U(1 + l - \gamma, 2 + 2l, 2r/(a_{0}\gamma)).
\]

Although \( U \) can be defined in terms of a convergent infinite power series, summation of the series involves adding large terms of alternating sign leading to numerical instabilities when \( r \) and \( \gamma \) are both large.

One solution is to use recurrence relations to stably generate high order hypergeometric functions. For example (Abramowitz & Stegun 13.4.15) give the expression

\[
U(a-1,b,z) = -(b-2a-z)U(a,b,z) - a(1+a-b)U(a+1,b,z).
\]

Starting with a small value of \( a \) and evaluating \( U(a,b,z), U(a+1,b,z) \) this can be used to generate \( U(a-1,b,z) \). Iterating the recursion relation we can generate \( U \) for large positive values of \( \gamma \). Once the wavefunctions have been found, numerical integration to calculate matrix elements \( R_{\gamma l'}^{l} \) is straightforward.

An alternative that is more efficient than numerical integration is to use approximate analytical expressions based on a WKB approach. There are many similar, but slightly different, expressions in the literature\(^7\). A formula that agrees to within one percent or better with numerical integration of quantum defect wavefunctions is\(^7\)

\[
R_{\gamma l}^{l',l'=\pm 1} = (-1)^{n'-n} \frac{\gamma_{c}^{5}}{\gamma' \gamma^{3/2}(\gamma' - \gamma)} \times \left[ \frac{1-y}{\pi} \sin[\pi(\gamma' - \gamma)] + J'_{\gamma - \gamma'}[y(\gamma' - \gamma)] \right]
\]

where \( y = [1 - ((l + l' + 1)/(2\gamma_{c}))^{2}]^{1/2} \), \( \gamma_{c}^{3} = 2(\gamma\gamma')^{2}/(\gamma + \gamma') \), and \( \gamma = n - \mu, \gamma' = n' - \mu' \) with \( \mu, \mu' \) the quantum defects. The functions on the right hand side are the Anger functions

\[
J_{\gamma}(z) = \frac{1}{\pi} \int_{0}^{\pi} d\theta \cos(\gamma\theta - z \sin(\theta)),
\]

\[
J'_{\gamma}(z) = \frac{1}{\pi} \int_{0}^{\pi} d\theta \sin(\gamma\theta - z \sin(\theta)) \sin(\theta).
\]

The preceding discussion covers the case of bound-bound matrix elements. We will return later on to calculating bound-continuum and continuum-continuum matrix elements.

\(^7\)For a recent survey see [6]
Chapter 2

Fine and hyperfine structure

In this chapter we explore corrections to atomic energy levels due to relativistic effects and electron nucleus interactions. These result in fine structure and hyperfine structure. These corrections depend on the fine structure constant

$$\alpha = \frac{2}{4\pi\epsilon_0} \frac{e^2}{\hbar c} = \frac{q^2}{\hbar c}$$

with a numerical value $\alpha \simeq 1/137$. As we will see fine structure corrections to the energy of a level with principal quantum number $n$ scale as $E_n\alpha^2$ so the fractional corrections are $O(10^{-4})$.

There are several ways in which the appearance of $\alpha^2$ can be understood. In our calculations of atomic energy levels in Ch. 1 we assumed the electron was a point particle, in accordance with our current understanding. Nevertheless we may define a classical electron radius $r_e$ as the radius of a sphere containing a uniformly distributed charge $e$ that has an electromagnetic potential equal to the electron rest energy $mc^2$. The potential energy is $U = \frac{3}{2}q^2/r_e$ so

$$r_e = \frac{3}{5}q^2/mc^2.$$ 

The characteristic length scale of atomic structure is the Bohr radius $a_0 = \frac{\hbar^2}{me}$ so

$$\frac{r_e}{a_0} = \frac{3}{5}\frac{q^4}{\hbar^2c^2} = \frac{3}{5}\alpha^2.$$ 

We see that $r_e/a_0 \simeq \alpha^2$. From this perspective fine structure corrections can be thought of as accounting for the effective “electromagnetic” size of the electron.

Despite this qualitative motivation we will see that the fine structure energies depend on a quantum characteristic of the electron, the orientation of the electron spin. If the orbital and spin degrees of freedom of the electron were independent then we could label the eigenstates with the quantum numbers $n, l, m_l, s, m_s$. As we will see the operators $\hat{L}_z$ and $\hat{S}_z$ do not commute with the Hamiltonian when we account for fine structure. A complete set of commuting observables will consist of $\hat{H}, \hat{J}, \hat{J}_z, \hat{L}, \hat{S}$ where $\hat{J} = \hat{L} + \hat{S}$ is the total angular momentum of the electron. The spectroscopic notation for fine structure levels in this $LS$ coupling description is

$$n^{2S+1}L_J$$

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where \( n \) is the principal quantum number, \( 2S + 1 \) is the multiplicity of the level, \( L \) is the orbital angular momentum quantum number, and \( J \) is the value of the total angular momentum. A specific fine structure state is specified by 5 quantum numbers \( n, L, S, J, m_J \).

A word about notation. Capital letters \( J, L, S, J_m \), etc. refer to the angular momentum quantum numbers of an atomic state. Lowercase letters \( j, l, s, j_m \), etc. refer to the quantum numbers of a single electron orbital. For hydrogen, and the alkali atoms, the atomic state and the single electron orbital coincide and we will most often use lower case letters to specify the quantum state.

### 2.1 Fine structure

Selection rules for electric dipole transitions restrict spectroscopic lines to transitions between states with \( l \) differing by \pm 1. We will discuss these rules later on. On the other hand careful measurements of the hydrogen spectrum reveal additional spectral components, and slightly different frequencies compared to what is predicted by the Schrödinger equation. These differences are due to the fine structure of hydrogen which arises as a result of relativistic effects. Fine structure effects are also readily seen in other alkali atoms. Observations of the fine structure of the Na 3s-3p transition revealed a splitting into two components: 589.8 nm (D1 line) and 589.2 nm (D2 line). The splitting suggested an additional quantum number which turned out to be the electron spin.
The energies of the first few states of Hydrogen, including fine structure are shown in Fig. 2.1. The Dirac equation provides a relativistically consistent framework for describing the fine structure of hydrogen, including the electron spin. Although the Dirac equation can be solved exactly for hydrogen (apart from finite mass effects which must be added to the solutions ex post facto), we will follow a simpler approach and account for the fine structure by adding physically motivated relativistic terms to the Schrödinger equation, and finding the energy corrections from perturbation theory.

We can anticipate the fine structure corrections using the energy eigenvalues found from solving the Dirac equation

\[ E_{nj} = mc^2 \left\{ \frac{1}{1 + \frac{Z^2\alpha^2}{[n-(j+\frac{1}{2})+\sqrt{(j+\frac{1}{2})^2-Z^2\alpha^2}]^{1/2}}} - 1 \right\}. \]  \hspace{1cm} (2.1)

Here \( j = l \pm 1/2 \) is the total angular momentum of the electron due to coupling of the orbital angular momentum (integer \( l \times \hbar \)) and the electron’s spin angular momentum of \( \hbar/2 \). If we expand (2.1) in powers of \( \alpha \) we get

\[ E_{nj} \simeq E_n \left[ 1 - \frac{Z^2\alpha^2}{n^2} \left( \frac{3}{4} - \frac{n}{j + 1/2} \right) + \mathcal{O}(Z^4\alpha^4) \right]. \]  \hspace{1cm} (2.2)

The leading term recovers the Bohr energy levels \( E_n = -Z^2E_H/2n^2 \) and the next term gives the first relativistic corrections proportional to \( E_n\alpha^2 \), hence the name fine structure constant for \( \alpha \). Equation (2.1) is an exact result from the solution of the Dirac equation for the Coulomb potential. This was first done by Gordon and by Darwin in 1928[8, 9]. Remarkably Eq. (2.1) was derived by Sommerfeld already in 1916 on the basis of a relativistic generalization of the Bohr model[10] without accounting for electron spin. However the procedure he used can be questioned[11] and the interpretation of the quantum numbers was not correct.

In the case of hydrogen the degeneracy with respect to \( l \) is partially lifted so that states with different \( l \) and different \( j \) no longer have the same energy. However states with different \( l \) and the same \( j \) are still degenerate. This degeneracy is lifted in alkali atoms with small \( l \) due to the nonzero quantum defects. Notice that the correction scales as \( Z^2E_n \sim Z^4 \) so the fine structure effects increase rapidly with atomic number \( Z \).

### 2.1.1 Derivation of fine structure

Instead of solving the Dirac equation we will calculate the fine structure splitting by accounting perturbatively for three effects: relativistic kinetic energy, spin-orbit coupling, and the so-called Darwin term. These result in the energy corrections

\[ \text{December 15, 2015 M. Saffman} \]
\[
\Delta E_{n,\text{kin}} = - \left( \frac{Z^2 \alpha^2 E_n}{n^2} \right) \left( 3 - \frac{n}{l + \frac{1}{2}} \right) \text{ for all } l
\]
\[
\Delta E_{n,\text{so}} = - \left( \frac{Z^2 \alpha^2 E_n}{n^2} \right) \frac{n}{l(l+\frac{1}{2})(l+1)} \frac{\langle \hat{S} \cdot \hat{L} \rangle}{\hbar^2}, \text{ for } l \neq 0
\]
\[
\Delta E_{n,D} = - \left( \frac{Z^2 \alpha^2 E_n}{n^2} \right) n, \text{ for } l = 0,
\]
When these corrections are combined we recover Eq. (2.2). Note that the order \( \alpha^2 \) energy correction in Eq. (2.2) is always negative due to the dominance of the kinetic energy correction. The spin-orbit term can have either sign, and the Darwin term is positive. It will be apparent in the following derivations that the simplified approach sometimes leads to slightly wrong numerical prefactors. The point of this exercise is to understand the physical phenomena resulting in fine structure shifts. Quantitatively accurate results are found by solving the Dirac equation.

**Relativistic kinetic energy**

The relativistic expression for the kinetic energy of the electron is

\[
T = \sqrt{c^2 p^2 + m^2 c^4} - mc^2
\]
\[
\approx \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}
\]
\[
= \frac{p^2}{2m} - \frac{1}{2mc^2} \left( \frac{p^2}{2m} \right)^2.
\]

The nonrelativistic kinetic energy is \( T_0 = p^2 / 2m \) so the correction is

\[
T - T_0 = - \frac{1}{2mc^2} T_0^2
\]
and the expectation value of the correction is

\[
\langle T - T_0 \rangle = - \frac{1}{2mc^2} \langle T_0^2 \rangle
\]
\[
= - \frac{1}{2mc^2} \langle (E - V)^2 \rangle
\]
\[
= - \frac{1}{2mc^2} \langle (E_n - V)^2 \rangle
\]

where \( E, V \) are the energy and potential without correcting for relativistic effects. Expanding the square we find

\[
\Delta E = \langle T - T_0 \rangle
\]
\[
= - \frac{1}{2mc^2} \left[ E_n^2 - 2E_n \langle V \rangle + \langle V^2 \rangle \right].
\]
The potential is $V = -Zq^2/r$ and

$$\langle V \rangle = -\frac{Z^2q^2}{a_0n^2}, \quad \langle V^2 \rangle = \frac{2Z^4q^4}{a_0^2n^3(2l + 1)}.$$ 

Using these expressions we find

$$\Delta E = - \left( \frac{Z^2\alpha^2E_n}{n^2} \right) \left( \frac{3}{4} - \frac{n}{l + \frac{3}{2}} \right).$$

### Spin-Orbit interaction

The angular momentum of the electron has contributions from the orbital motion and from the intrinsic spin. The intrinsic spin couples to the magnetic field via the Zeeman effect giving an energy shift $-\mu \cdot B$ where $\mu$ is the electron moment and $B$ is the magnetic field. Since the magnetic field at the electron depends on its motion in the electric field of the nucleus there is a coupling between the spin and the orbital motion.

In the rest frame of the nucleus the field at the electron at position $r$ is $E = \frac{Ze}{4\pi\epsilon_0} \frac{\hat{r}}{r^2}$. In the rest frame of the electron there is a magnetic field

$$B' = -\frac{\gamma}{c} \beta \times E$$

with $\beta = v/c$, $\gamma = 1/\sqrt{1 - \beta^2}$. To order $v^2/c^2$ we have $B' = \frac{v}{c} E \hat{e}_z$.

The orbital motion has angular momentum $l = rp = rmv$ so $v = l/mr$ and

$$B' = \frac{l}{mc^2} \frac{Ze}{4\pi\epsilon_0} \frac{\hat{e}_z}{r^3} = \frac{1}{mc^2} \frac{Ze}{4\pi\epsilon_0} \frac{\hat{1}}{r^3}.$$

The electron magnetic moment can be written as $\mu_s = -g_s\frac{\mu_B}{h}\hat{s}$ with $g_s \simeq 2$ and $\mu_B = e\hbar/2m$. The spin-orbit contribution to the Hamiltonian is therefore

$$-\mu_s \cdot B' = \frac{g_s\mu_B}{h} \frac{Ze}{mc^2} \frac{\hat{1} \cdot \hat{s}}{4\pi\epsilon_0} \frac{r^3}{r^3} = \frac{Zq^2}{m^2c^2} \frac{\hat{1} \cdot \hat{s}}{r^3}.$$

It turns out that this expression is twice larger than it should be. The reason is due to a subtlety of relativistic transformation of the fields. The rest frame of the electron is not an inertial frame, and we have to account for this when transforming the fields. Doing so gives an extra factor of $1/2$ (this is known as the Thomas precession) resulting in

$$H_{so} = \frac{Zq^2}{2m^2c^2} \frac{\hat{1} \cdot \hat{s}}{r^3}.$$ 

The energy shift is

$$\Delta E = \langle H_{so} \rangle = \frac{Zq^2}{2m^2c^2} \langle \frac{1}{r^3} \hat{s} \rangle.$$ 

We then use

$$\langle \frac{1}{r^3} \rangle = \frac{Z^3}{a_0^3} \frac{1}{n^3l(l + 1)(l + 1/2)}.$$
This expression diverges if \( l = 0 \) but in that case \( B' = 0 \) and there is no spin-orbit interaction.

We then need to find the expectation value of the numerator in the state \(|nmls_{lm_s}\rangle\). This is a problem because the operator \( \hat{l} \cdot \hat{s} \) is not diagonal in this basis - it couples states with different \( m_l, m_s \). The solution is to evaluate expectation values in the coupled basis which has eigenstates specified by the quantum numbers \( n, l, s, j, m_j \). We can use \( \hat{j} = \hat{l} + \hat{s} \) to get

\[
\hat{j}^2 = (\hat{l} + \hat{s})^2 = \hat{l}^2 + \hat{s}^2 + 2\hat{l} \cdot \hat{s}
\]

and taking expectation values in the state \(|nlsjm_j\rangle\) we get

\[
\langle \hat{l} \cdot \hat{s} \rangle = \frac{1}{2} \langle \hat{j}^2 - \hat{l}^2 - \hat{s}^2 \rangle = \frac{\hbar^2}{2} \left[ j(j+1) - l(l+1) - s(s+1) \right].
\]

It should be emphasized that the operator equation \( \hat{j} = \hat{l} + \hat{s} \) is always true however \( j = l + s \) may or may not be true since \( |l - s| \leq j \leq l + s \). For \( s = 1/2 \) we have \( j = l - 1/2 \) or \( j = l + 1/2 \). We see that the interaction \( \hat{l} \cdot \hat{s} \) is diagonal in the coupled basis.

Combining the above results we arrive at

\[
\Delta E = - \left( \frac{Z^2 \alpha^2 E_n}{n^2} \right) \frac{n}{l(l+\frac{1}{2})(l+1)} \frac{1}{2} \left[ j(j+1) - l(l+1) - s(s+1) \right] \tag{2.3}
\]

for \( l \neq 0 \).

This calculation applies to hydrogen or a hydrogenic atom with nuclear charge \( Z \). In multielectron atoms the potential is not Coulombic and it is desirable to have a generalization of this formula to account for an arbitrary \( V_{\text{eff}}(r) \). To do so we note that the force on the electron is \(-eE = -\nabla V_{\text{eff}} \) so the radial electric field is \( E = \frac{1}{e} \nabla V_{\text{eff}} = \frac{1}{e} \frac{dV_{\text{eff}}}{dr} \hat{e}_r \). If we replace \( E \) by this expression in the preceding derivation we arrive at

\[
H_{\text{so}} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV_{\text{eff}}}{dr} \hat{l} \cdot \hat{s}. \tag{2.4}
\]

**Darwin term**

The so-called Darwin term is a purely quantum mechanical effect related to the wavelike nature of the electron. This is also referred to as zitterbewegung (trembling motion). The electron has rest energy \( mc^2 \). Setting this equal to a frequency we get

\[
mc^2 = \hbar \omega = \hbar ck = \hbar c \frac{2\pi}{\lambda}.
\]

Inverting this expression we can define a wavelength

\[
\lambda = \frac{2\pi \hbar c}{mc^2} = \frac{2\pi \hbar}{mc}.
\]

It is convention to divide this quantity by \( 2\pi \) which defines the Compton wavelength of the electron

\[
\lambda_C = \frac{\hbar}{mc} = 3.86 \times 10^{-13} \text{ m}.
\]
From a quantum mechanical perspective, the position of the electron is not well defined at scales shorter than the Compton wavelength. This results in an effective smearing of the potential seen by the electron over a region $\Delta x \sim \lambda_C$.

We will account for this by replacing $V(\mathbf{r})$ with $V(\mathbf{r} + \mathbf{q})$ where $\mathbf{q}$ is a vector which samples the volume around $\mathbf{r}$ and has expectation value of $\langle q^2 \rangle \sim \lambda_C^2$. Expanding about $\mathbf{r}$ the potential is

$$V(\mathbf{r} + \mathbf{q}) = V(\mathbf{r}) + \nabla V \cdot \mathbf{q} + \frac{1}{2} \sum_{ij} q_i q_j \frac{\partial^2 V}{\partial x_i \partial x_j} + \ldots$$

Assuming $\langle \mathbf{q} \rangle = 0$ we find a correction to the potential $\Delta V = V(\mathbf{r} + \mathbf{q}) - V(\mathbf{r})$ with expectation value

$$\langle \Delta V \rangle = \left\langle \frac{1}{2} \sum_{ij} q_i q_j \frac{\partial^2 V}{\partial x_i \partial x_j} \right\rangle = \frac{1}{2} \sum_{ij} \left\langle \frac{\partial^2 V}{\partial x_i \partial x_j} \right\rangle \langle q_i q_j \rangle .$$

We assume the displacements in different directions are uncorrelated so $\langle q_i q_j \rangle = \langle q_i^2 \rangle \delta_{ij}$ and

$$\langle \Delta V \rangle = \frac{1}{2} \sum_i \left\langle \frac{\partial^2 V}{\partial x_i^2} \right\rangle \langle q_i^2 \rangle = \frac{\lambda_C^2}{6} \langle \nabla^2 V \rangle .$$ (2.5)

For the last equality we used $\langle q_i^2 \rangle = \langle q_y^2 \rangle = \langle q_z^2 \rangle = \langle q^2 \rangle / 3 = \lambda_C^2 / 3$. We then use $V = -Zq^2/r$ and $\nabla^2 (1/r) = -4\pi\delta(r)$ to get

$$\frac{4\pi Zq^2 \lambda_C^2}{6} \langle \delta(r) \rangle .$$

Comparison with solutions of the Dirac equation show that this is almost correct except that the coefficient $1/6$ should be $1/8$. Making this correction we have

$$\Delta E = \frac{\pi Zq^2 \lambda_C^2}{2} \langle \delta(r) \rangle .$$

The expectation value $\langle \delta(r) \rangle = \int d^3 r |\psi_{n0}|^2 \delta(r)$ vanishes when $l > 0$ since the wavefunction is zero at the origin. When $l = 0$ we find $\langle \delta(r) \rangle = |\psi_{n00}(0)|^2 = \frac{Z^3}{\pi n^3 a_0}$. This last expression comes from the definition of the radial functions (1.12) and the expression for the associated Laguerre polynomial at the origin $L_n^k(0) = \left( \frac{n+k}{n} \right)$. We therefore arrive at

$$\Delta E = \frac{Z^4 q^2 \lambda_C^2}{2n^3 a_0^3} = - \left( \frac{Z^2 \alpha^2 E_n}{n^2} \right) n ,$$

for $l = 0$ only.

It may be surprising that this correction is positive. If we consider an electron at distance $r_0$ from the nucleus then the effect of averaging the Coulomb potential which is proportional to $-1/r$ in a small region about $r_0$ leads to a lowering, not raising, of the potential energy. The explanation is that the dominant contribution to the Coulomb potential comes from the part of the wavefunction where $r \to 0$. Since $r$ cannot be negative the averaging over a finite range of $r$ effectively raises the potential energy.

Combining the three contributions we arrive at the correction given by Eq. (2.2). A level $E_n$ is split into two levels $E_{n,j}$ with $j = l \pm 1/2$. The term in parentheses $3/4 - n/(j + 1/2) \leq 3/4 - n/n = -1/4$ so this term is always negative and the fine structure correction lowers the energy of the state.

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Table 2.1: Fine structure splitting of the first resonance lines in alkali atoms. Wavelengths are vacuum values. Theory values are based on Eq. (2.2) with the substitutions $n \rightarrow n^* = n - \mu_p$ and $Z \rightarrow Z^{1/2}$. The theory value for H has been corrected for finite mass effects.

2.1.2 Comparison with experiment

The alkali atoms range from light (H and Li) to relatively heavy (Cs and Fr). This gives a wide range of fine structure splittings which are listed in Table 2.1. The fine structure corrections to $n = 2, 3$ are in Fig. 2.1. As shown in Table 2.1 the $n = 2$ hydrogen fine structure is predicted very well by the theory of the preceding section. Differences between experiment and theory can be attributed to spin-other orbital shifts, hyperfine shifts, and QED effects.

The hydrogenic theory cannot be directly used to predict the fine structure splittings of the alkalis heavier than hydrogen due to electron correlation and screening effects. Although all three contributions to the hydrogen fine structure are in principle present in the alkali series the relativistic momentum and Darwin terms do not provide useful information. That is because the small relativistic corrections are swamped by the large quantum defects. Furthermore they are independent of $j$ and do not contribute to the fine structure splitting. Only the spin orbit term is $j$ dependent and gives a finite contribution to the fine structure splitting. In principle we should include spin orbit effects for all of the atomic electrons, including those in the filled inner shells. However, the spatial average of $\hat{l} \cdot \hat{s}$ for a filled shell is zero, provided there are no spin-radial position correlation effects. To a first approximation we include only the valence electron in the spin orbit calculation.

We can develop a very simple approximate expression by using the hydrogenic results and making the replacements $n \rightarrow n^* = n - \mu_l$ and $Z \rightarrow Z^{1/2}$. The smaller effective value of $Z$ accounts for the fact that the nuclear charge is screened for a large part of the electron wavefunction. We see from the table that this adjusted theory works quite well for the heavy alkalis and disagrees by about a factor of 2 with experiment for Na. The fine structure splitting is anomalously small in Li and the theory greatly overpredicts the actual value in this case. While the substitution $Z \rightarrow Z^{1/2}$ appears ad hoc it is well motivated by a model of an inner region with zero screening and an outer fully screened region, with the two regions weighted by the amount of time the valence electron spends in each one.

Considering only the spin orbit term in Eq. (2.3) we see that the component with $j_+ = l + 1/2$ is shifted up in energy while the component with $j_- = l - 1/2$ is shifted down. It is easily checked that the magnitude of the shift of $j_+$ is a factor of $\frac{2j_+-1}{2j_++1}$ smaller than
the magnitude of the $j_-$ shift. This scaling preserves the position of the “center of mass” of
the level since $j_+$ has $2j_+ + 1$ and $j_-$ has $2j_- + 1$ Zeeman components. Summed over the
Zeeman states the total shift is $\sim (2j_+ + 1)\frac{2j_+ - 1}{2j_+ + 1} - (2j_- + 1) = 0$. We will see later that also
for multielectron atoms there is no center of mass shift. This is to be expected since the spin
orbit interaction is internal to the atomic constituents and cannot raise or lower the total
energy. However, it is possible for the ordering of the energy of the fine structure components
with $j$ to be inverted. This is seen in some alkali atom states and in multielectron atoms
with less than half filled shells. The inversion arises because the expectation value of $V_{\text{eff}}$ in
the expression (2.4) changes sign due to strong electron correlation effects.

2.1.3 Fine structure wavefunctions

The fine structure states specified by $n, l, s, j, m_j$ are linear superpositions of states with
definite values of the orbital and spin angular momentum. For one electron atoms we have

$$|nljm_j\rangle = |nl\rangle \left(C_{lm_j}^{jm_j, l, m_j - 1/2, l, m_j - 1/2}\uparrow + C_{lm_j}^{jm_j, l, m_j + 1/2, l, m_j + 1/2}\downarrow\right)$$

where $|\chi\rangle$ is the spin state and $|\uparrow\rangle = |1/2, 1/2\rangle$, $|\downarrow\rangle = |1/2, -1/2\rangle$. The electron wavefunction is

$$\psi(r)|\chi\rangle = (r|nljm_j\rangle|\chi\rangle = R_{nl}(r) \left(C_{lm_j}^{jm_j, l, m_j - 1/2, 1/2, 1/2}\uparrow + C_{lm_j}^{jm_j, l, m_j + 1/2, 1/2, -1/2}\downarrow\right)$$

Here $R_{nl}(r)$ is given by (1.13) for Hydrogen and approximated by (1.31) for the other alkali
atoms.

2.2 Hyperfine structure

Additional atomic energy levels appear due to the interaction of the nucleus with the electro-
magnetic fields of the electrons. This has an even smaller energy scale than the fine structure
and is called hyperfine structure. The hyperfine structure of the ground state of hydrogen is
responsible for the 21 cm line (1420.4058 MHz) seen in astrophysics and for the 9192631770
Hz splitting of the Cs atom ground state which is used to define the second. Hyperfine states
are also of great importance in quantum computing for encoding qubits.

The general form of the hyperfine interaction is

$$\hat{H}_{\text{hf}} = \sum_k \hat{T}_k \cdot \hat{N}_k$$

where $\hat{T}_k$ is a rank $k$ spherical tensor operator acting on the electronic degrees of freedom
and $\hat{N}_k$ acts on the nuclear degrees of freedom. Even $k$ are electric interactions and odd $k$
are magnetic interactions. The $k = 0$ interaction is just the Coulomb part of the Hamiltonian
and has no dependence on magnetic quantum numbers. The $k = 1$ interaction is magnetic
dipole and $k = 2$ is electric quadrupole. These are the dominant hyperfine interaction terms.

Before proceeding to detailed calculations let us estimate the expected magnitude of
the hyperfine interaction. Part of the relativistic physics is due to the magnetic dipole
interaction between the magnetic moment $\mu_p$ of the proton and the magnetic moment $\mu_B$ of the electron. The magnetic moment of the proton depends on its internal (quark) structure. We can estimate it as

$$\mu_p \sim \mu_B \frac{m}{m_p} = \frac{e\hbar}{2m_p}$$

where $m_p$ is the proton mass. If we think of the electron as being localized in a ring with radius $a_0$ the magnetic field at the nucleus due to the orbital motion is

$$B_{el} \sim \mu_0 \frac{e\alpha c}{4\pi a_0^2} = \mu_0 \mu_B \frac{m^3q^6}{2\pi \hbar^5} = \mu_0 \mu_B \frac{2\pi a_0^3}{m^3}.$$  

The Zeeman interaction energy is

$$B_{el}\mu_p = \left( \frac{\mu_0 \mu_B}{2\pi a_0^3} \right) \left( \mu_B \frac{m}{m_p} \right) = \frac{1}{2} \frac{m}{m_p} \alpha^2 E_H.$$  

with $\alpha = q^2/\hbar c$ the fine structure constant. We see that the energy scale is a factor $\frac{m}{m_p} \sim 0.001$ smaller than the scale of the fine structure corrections. The predicted frequency is

$$\frac{B_{el}\mu_p}{\hbar} \sim 95 \text{ MHz}.$$  

As we will see the actual energy scale for hydrogen is about 15 times larger due to a larger magnetic moment of the proton and some angular factors.

### 2.2.1 The Zeeman effect

All quantum mechanical spins have associated with them a magnetic moment $\hat{\mu}$ which leads to a magnetic interaction Hamiltonian $\hat{H}_m = -\hat{\mu} \cdot \mathbf{B}$ where $\mathbf{B}$ is the magnetic field. The field exerts a torque on the magnetic moment which tends to align it with the external field. Thus the energy is lowest when the moment $\hat{\mu}$ is parallel to the field. This interaction can be derived as a nonrelativistic limit of the Dirac equation which describes the interaction of a particle carrying charge and spin with the electromagnetic field. A more heuristic approach assumes the existence of $\hat{H}_m$ by analogy with the classical interaction of a magnetic moment and a magnetic field.

Consider first a charged particle moving in the $x-y$ plane with orbital angular momentum $\hat{\mathbf{L}}$. The angular momentum is $\mathbf{L} = \hat{\mathbf{r}} \times \mathbf{p}$ and $\langle \hat{L}_z \rangle = m_L \hbar$ where $-l \leq m_L \leq l$. There is a classical magnetic moment associated with the motion of the particle with mass $m$ and charge $q$ given by the product of the current and the area enclosed by the orbit. For a circular motion we have classically $\mathbf{L} = mrv \hat{e}_z$ and $\mathbf{\mu} = I \mathbf{Ae}_z = \left( \frac{m}{2\pi r} \right) (\pi r^2) \mathbf{e}_z = \left( \frac{q}{2m} \right) mrv \mathbf{e}_z$. It can be shown that the same relationship holds for any motion in the $x-y$ plane. Thus $\mathbf{\mu} = \gamma \mathbf{L}$ where the gyromagnetic ratio is $\gamma = \frac{q}{2m}$.

For the specific case of an electron with charge $-e$ and mass $m_e$ we get a gyromagnetic ratio $\gamma_0 = -\frac{e}{2m_e}$ which is negative because the electron charge is negative. Thus the magnetic moment is directed opposite to the angular momentum. This classical relation between magnetic moment and angular momentum has been shown experimentally to also be true when we describe the particle with quantum mechanics. We thus have $\hat{\mathbf{\mu}}^{(e)} = \gamma_0 \hat{\mathbf{L}}$. It is
customary to introduce a characteristic unit of magnetic moment called the Bohr magneton defined as \( \mu_B = \hbar |\gamma_0| = \frac{e \hbar}{2m_e} > 0 \). Thus \( \gamma_0 = -\frac{\mu_B}{\hbar} \) and the relation between magnetic moment and orbital angular momentum can be written as

\[
\hat{\mu}^{(e)} = -\frac{\mu_B}{\hbar} \hat{L}.
\] (2.7)

In the presence of a field \( \mathbf{B} = B_z \mathbf{e}_z \) the energy shift is determined by the \( z \) component of \( \hat{\mu} \) which takes on the values \( \langle \hat{\mu}^{(e)}_z \rangle = -\mu_B \frac{\langle \hat{L}_z \rangle}{\hbar} = -\mu_B m_L. \) Thus the energy shift is \( \Delta E = \langle \hat{H}_m \rangle = +\mu_B m_L B. \)

There is a similar relation between angular momentum and magnetic moment for intrinsic spin \( \hat{S} \) as well as a composite angular momentum \( \hat{J} \). The only difference is that the value of the gyromagnetic ratio depends on the type of spin and also on the particular particle being considered. It is common usage to quantify the change in gyromagnetic ratio with a dimensionless coefficient \( g \), called the Landé \( g \)-factor.

Consider first an electron. The relations between the magnetic moment and the angular momentum are written as

\[
\hat{\mu}^{(e)}_L = g_L \gamma_0 \hat{L} = -g_L \frac{\mu_B}{\hbar} \hat{L} \] (2.8a)
\[
\hat{\mu}^{(e)}_S = g_S \gamma_0 \hat{S} = -g_S \frac{\mu_B}{\hbar} \hat{S} \] (2.8b)
\[
\hat{\mu}^{(e)}_{Jz} = g_J \gamma_0 \hat{I}_z = -g_J \frac{\mu_B}{\hbar} \hat{I}_z. \] (2.8c)

For an electron \( g_L = 1, \) \( g_S \approx 2, \) and \( g_J \) depends on \( j \) in a way which we will see later. Thus \( g \) depends on the type of angular momentum under consideration.

For other particles the value of \( g \) is different and depends both on the type of particle and type of angular momentum. Since nuclear particles are much heavier than electrons magnetic effects are much smaller and it is convenient to introduce a nuclear magneton defined as \( \mu_N = \frac{e \hbar}{2m_p} \) where \( m_p \) is the mass of the proton. The nuclear gyromagnetic ratio is \( \gamma_N = \mu_N / \hbar = \frac{e}{2m_p} \) which is positive. The relations for the proton analogous to Eqs. (2.8) for the electron are

\[
\hat{\mu}^{(p)}_L = g_L^{(p)} \gamma_N \hat{L} = g_L^{(p)} \frac{\mu_N}{\hbar} \hat{L} \] (2.9a)
\[
\hat{\mu}^{(p)}_S = g_S^{(p)} \gamma_N \hat{S} = g_S^{(p)} \frac{\mu_N}{\hbar} \hat{S} \] (2.9b)
\[
\hat{\mu}^{(p)}_{Iz} = g_I^{(p)} \gamma_N \hat{I}_z = g_I^{(p)} \frac{\mu_N}{\hbar} \hat{I}_z. \] (2.9c)

Note we have used the letter \( I \) which is customary to denote a composite nuclear spin instead of \( J \). The proton \( g \) factors are \( g_L^{(p)} = 1, \) and \( g_S^{(p)} = 5.586. \)

Similarly for neutrons we have

\[
\hat{\mu}^{(n)}_L = g_L^{(n)} \gamma_N \hat{L} = g_L^{(n)} \frac{\mu_N}{\hbar} \hat{L} \] (2.10a)
\[
\hat{\mu}^{(n)}_S = g_S^{(n)} \gamma_N \hat{S} = g_S^{(n)} \frac{\mu_N}{\hbar} \hat{S} \] (2.10b)
\[
\hat{\mu}^{(n)}_{Iz} = g_I^{(n)} \gamma_N \hat{I}_z = g_I^{(n)} \frac{\mu_N}{\hbar} \hat{I}_z \] (2.10c)
Table 2.2: Landé $g$ factors for the spin of elementary particles and some nuclei. The left and right columns give the $g$ factors for use with nuclear or Bohr magnetons. The electron and nuclear magnetons are $\mu_B = 9.2740 \times 10^{-24} \text{ J/T}$ and $\mu_N = 5.0508 \times 10^{-27} \text{ J/T}$.

<table>
<thead>
<tr>
<th>particle</th>
<th>$g(\mu_N)$</th>
<th>$g(\mu_B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron</td>
<td>-</td>
<td>2.0023</td>
</tr>
<tr>
<td>proton</td>
<td>5.5857</td>
<td>0.003042</td>
</tr>
<tr>
<td>neutron</td>
<td>-3.8261</td>
<td>-0.002084</td>
</tr>
<tr>
<td>$^{85}$Rb nucleus</td>
<td>-0.539829</td>
<td>-0.000294</td>
</tr>
<tr>
<td>$^{87}$Rb nucleus</td>
<td>-1.82697</td>
<td>-0.000995</td>
</tr>
<tr>
<td>$^{133}$Cs nucleus</td>
<td>-0.732625</td>
<td>-0.000399</td>
</tr>
<tr>
<td>$^{165}$Ho nucleus</td>
<td>-1.192</td>
<td>-0.000649</td>
</tr>
</tbody>
</table>

with $g_L^{(n)} = 0$, and $g_S^{(n)} = -3.826$.

The values of the $g$ factor for the basic constituents of atoms and for a few nuclei are summarized in Table 2.2.

**Alternative derivation of the Zeeman interaction**

We can also derive this interaction more directly without resorting to the full machinery of the Dirac equation by introducing the Hamiltonian of a particle with charge $q$ and mass $m$ interacting with an electromagnetic vector potential $\mathbf{A}$ which reads

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cm}} - \frac{q}{2m}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{\hat{p}}) + \frac{q^2}{2m} \mathbf{A}^2.$$  

We then choose a transverse gauge $\nabla \cdot \mathbf{A} = 0$. In this gauge

$$\langle \psi | \mathbf{\hat{p}} \cdot \mathbf{A} | \psi \rangle = \langle \psi | -i \nabla \cdot \mathbf{A} | \psi \rangle = \langle \psi | [-i(\nabla \cdot \mathbf{A}) | \psi \rangle - i \mathbf{A} \cdot (\nabla | \psi \rangle) \rangle,$$

so $\mathbf{A}$ and $\mathbf{\hat{p}}$ commute and we can write

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cm}} - \frac{q}{m} \mathbf{A} \cdot \mathbf{\hat{p}} + \frac{q^2}{2m} \mathbf{A}^2.$$  

When the field is not too strong we can neglect the $\mathbf{A}^2$ term which leaves the magnetic interaction $\hat{\mathcal{H}}_m = -\frac{2}{m} \mathbf{A} \cdot \mathbf{\hat{p}}$. We now introduce a constant magnetic field by putting $\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{\hat{r}}$.

We can check the gauge condition is satisfied since

$$\nabla \cdot \mathbf{A} = \nabla \cdot \left( \frac{1}{2} \mathbf{B} \times \mathbf{\hat{r}} \right) = \frac{1}{2} (\nabla \times \mathbf{B}) \cdot \mathbf{\hat{r}} - \frac{1}{2} \mathbf{B} \cdot (\nabla \times \mathbf{\hat{r}}) = \frac{1}{2} (\nabla \times \mathbf{B}) \cdot \mathbf{\hat{r}}.$$

Provided the magnetic field is constant in time $\nabla \times \mathbf{B} = 0$ and we get $\nabla \cdot \mathbf{A} = 0$, which is the transverse gauge condition. We then use the triple product rule to write

$$\mathbf{A} \cdot \mathbf{\hat{p}} = \frac{1}{2} (\mathbf{B} \times \mathbf{\hat{r}}) \cdot \mathbf{\hat{p}} = \frac{1}{2} \mathbf{B} \cdot (\mathbf{\hat{r}} \times \mathbf{\hat{p}}) = \frac{1}{2} \mathbf{B} \cdot \mathbf{\hat{L}} = \frac{1}{2} \mathbf{\hat{L}} \cdot \mathbf{B},$$
where the last equality follows provided $B$ is constant in space, at least over the extent of the wavefunction. We thus find
\[ \hat{H}_m = -\frac{q}{2m} \hat{L} \cdot B. \]
Specializing to the case of an electron with charge $-e$ and mass $m_e$ we have
\[ \hat{H}^{(e)}_m = \frac{e}{2m_e} \hat{L} \cdot B = \frac{\mu_B}{\hbar} \hat{L} \cdot B \]
where $\mu_B = q\hbar/(2m_e)$ is a positive quantity. Finally, we can write this as $\hat{H}^{(e)}_m = -\hat{\mu}^{(e)} \cdot B$
where
\[ \hat{\mu}^{(e)} = -\frac{\mu_B}{\hbar} \hat{L} \]
which agrees with Eq. (2.7).

### 2.2.2 Magnetic dipole interaction

The hyperfine interaction in the ground state of hydrogen couples the states $|j = 1/2, m_j = \pm 1/2\rangle$ with the nuclear states $|I = 1/2, m_I = \pm 1/2\rangle$ to form coupled states $|j, I; f, m_f\rangle$. We abbreviate these as $|f, m_f\rangle$ with the four possibilities $|1, 1\rangle, |1, 0\rangle, |1, -1\rangle$, and $|0, 0\rangle$. The hyperfine interaction results in an energy splitting of the $f = 1$ and $f = 0$ states.

Let’s solve this problem for the general case of an arbitrary Hydrogenic state. There is an interaction between the proton magnetic moment at the origin and the magnetic field due to the electron. The magnetic field is due to the orbital motion and the intrinsic spin. We can write
\[ B(0) = B_l(0) + B_s(0) \]
where the field due to the orbital motion is
\[ B_l(0) = \frac{\mu_0 I}{2r} e_z = \frac{\mu_0}{2r} \left( -\frac{eV}{2\pi r} \right) e_z = -\frac{\mu_0 e^2}{4\pi mr^3} \hat{\rho} \]
and the field due to the intrinsic spin moment is
\[ B_s(0) = -\frac{\mu_0}{4\pi r^3} [\hat{\mu}_s - 3(\hat{\mu}_s \cdot e_r)e_r] + \frac{2\mu_0}{3} \hat{\mu}_s \delta(r) \]
where $e_r$ is a unit vector pointing from the electron to the origin and $r$ is the electron coordinate. The last term is the singular contribution due to the point like nature of the electron which only contributes to the field at the origin when the electron is also at the origin.

The interaction of the proton moment with this field gives a magnetic dipole Hamiltonian
\[
\hat{H}_{\text{md}} = -\hat{\mu}_p \cdot [B_l(0) + B_s(0)] \\
= -\frac{\mu_0 e^2}{4\pi m r^3} \hat{\rho} + \frac{\mu_0}{4\pi r^3} \hat{\mu}_p \cdot [\hat{\mu}_s - 3(\hat{\mu}_s \cdot e_r)e_r] - \frac{2\mu_0}{3} \hat{\mu}_p \cdot \hat{\mu}_s \delta(r) \\
= \frac{\mu_0 \mu_B}{2\pi\hbar} \hat{\mu}_p \cdot \hat{\rho} + \frac{1}{3} \hat{\rho} \cdot \delta(r) + \frac{4\mu_0 \mu_B}{3\hbar} \hat{\mu}_p \cdot \hat{\rho} \delta(r).
\]
We now express the proton moment in terms of the nuclear spin operator $\hat{\mathbf{I}}$ and the nuclear magneton $\mu_N$ as $\hat{\mu}_p = g_p \mu_N \frac{\hat{I}}{\hbar}$ which results in
\[
\hat{H}_{\text{md}} = \frac{\mu_0 \mu_B g_p}{2\pi\hbar^2} \left( \hat{\mathbf{I}} \cdot \hat{\rho} + \frac{8\pi}{3} \hat{\mathbf{I}} \cdot \delta(r) \right). \tag{2.12}
\]
The first term in parentheses can be simplified by introducing \( \mathbf{G} = \hat{\mathbf{r}} - \hat{s} + 3\frac{(\hat{s} \cdot \mathbf{r})}{r^2} \). We wish to evaluate \( \frac{\hat{\mathbf{r}}}{r^2} \) in states of definite \( j \). We can do so using the Landé projection theorem to write
\[
\langle \hat{\mathbf{I}} \cdot \hat{\mathbf{G}} \rangle = \left\langle \frac{\hat{\mathbf{I}} \cdot \hat{j} (\hat{\mathbf{G}} \cdot \hat{j})}{r^2 \hat{j}^2} \right\rangle = \left\langle \frac{\hat{\mathbf{I}} \cdot \hat{j} (\hat{\mathbf{G}} \cdot \hat{j})}{j(j+1)\hbar^2 r^2} \right\rangle.
\]
We then use
\[
\hat{\mathbf{I}} \cdot \hat{j} = \frac{\hat{f}^2 - \hat{I}^2 - \hat{j}^2}{2}
\]
and
\[
\hat{\mathbf{G}} \cdot \hat{j} = \left( \hat{\mathbf{r}} - \hat{s} + 3\frac{(\hat{s} \cdot \mathbf{r})}{r^2} \right) \cdot (\hat{\mathbf{r}} + \hat{s}) = \hat{I}^2 - 3\left( \hat{s}^2 - \frac{(\hat{s} \cdot \mathbf{r})^2}{r^2} \right).
\]
The term in parentheses can be shown to vanish for \( s = 1/2 \). Thus \( \hat{\mathbf{G}} \cdot \hat{j} = \hat{I}^2 \) and
\[
\left\langle \frac{\hat{\mathbf{I}} \cdot \hat{\mathbf{G}}}{r^2} \right\rangle = \left\langle \frac{\hat{f}^2 - \hat{I}^2 - \hat{j}^2}{2} \frac{\hat{I}^2}{j(j+1)\hbar^2 r^2} \right\rangle
= \frac{\hbar^2 l(l+1)f(f+1) - I(I+1) - j(j+1)}{2j(j+1)} \left\langle \frac{1}{r^2} \right\rangle
= \frac{\hbar^2 l(l+1)f(f+1) - I(I+1) - j(j+1)}{2j(j+1)} \frac{1}{a_0^3 n^3 \ell(\ell+1/2)(\ell+1)}
= \frac{\hbar^2}{a_0^3 n^3} \frac{f(f+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)}.
\]
The second term in parentheses proportional to \( \hat{\mathbf{I}} \cdot \hat{s} \) has a nonzero expectation value only for states with \( l = 0 \). When \( l = 0 \) then \( j = s \) and \( \hat{f} = \hat{\mathbf{I}} + \hat{j} = \hat{\mathbf{r}} + \hat{s} \) so that \( \langle \hat{\mathbf{I}} \cdot \hat{s} \rangle = \frac{1}{2} \left\langle \hat{f}^2 - \hat{I}^2 - \hat{s}^2 \right\rangle \). The expectation value of the delta function is
\[
\langle \delta(r) \rangle = \frac{1}{\pi a_0^3 n^3}.
\]
Thus
\[
\frac{8\pi}{3} \langle \hat{\mathbf{I}} \cdot \hat{s} \delta(r) \rangle = \frac{8\pi}{3} \frac{[f(f+1) - I(I+1) - s(s+1)]}{2} \frac{\hbar^2}{\pi a_0^3 n^3}
= \frac{4\hbar^2}{3a_0^3 n^3} [f(f+1) - I(I+1) - s(s+1)]
\]
Combining the two terms in Eq. (2.12) gives the result
\[
\Delta E = \left\langle \mathcal{H}_{m\ell} \right\rangle
= \frac{\mu_0 \mu_B \mu_N g_p}{2\pi a_0^3 n^3} \left\{ \frac{f(f+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)} (1 - \delta_0) \right. \\
+ \left. \frac{4}{3} [f(f+1) - I(I+1) - s(s+1)] \delta_0 \right\}
= \frac{\mu_0 \mu_B \mu_N g_p}{2\pi a_0^3 n^3 j(j+1)(2l+1)} [f(f+1) - I(I+1) - j(j+1)]
= \frac{\hbar A}{2} [f(f+1) - I(I+1) - j(j+1)]
\]
2.2 Hyperfine structure

where the hyperfine constant is

\[ A = \frac{g_p}{\hbar n^3 j(j + 1)(2l + 1)} E_H \alpha^2 \frac{m}{m_p} \text{ (Hz)}, \]

with \( \alpha \) the fine structure constant. With the factors grouped in this way we see that

\[ \Delta E = \hbar A (\hat{I} \cdot \hat{J}). \]

Using \( g_p = 5.586 \) and replacing \( m \) by \( \mu = mm_p/(m + m_p) \) the numerical value of the hyperfine constant in the hydrogen ground state \((l = 0, j = 1/2)\) is \( A = 1.4205 \times 10^9 \text{ Hz} \). For the 1s ground state the energy shifts are

\[ f = 1 : \quad \Delta E = + \frac{A}{4}, \]
\[ f = 0 : \quad \Delta E = - \frac{3A}{4}. \]

As with the fine structure splitting we see that the center of mass of the level is not changed. The hyperfine splittings of the lowest states in H are

\[ 1s_{1/2}, A = 1420.5 \text{ MHz}, \quad f = 1 \leftrightarrow f = 0 : \quad 1420.5 \text{ MHz} \]
\[ 2s_{1/2}, A = 177.56 \text{ MHz}, \quad f = 1 \leftrightarrow f = 0 : \quad 177.56 \text{ MHz} \]
\[ 2p_{1/2}, A = 59.186 \text{ MHz}, \quad f = 1 \leftrightarrow f = 0 : \quad 59.186 \text{ MHz} \]
\[ 2p_{3/2}, A = 11.837 \text{ MHz}, \quad f = 2 \leftrightarrow f = 1 : \quad 23.674 \text{ MHz}. \]

The ground state hyperfine energies for alkali atoms are given in Table 2.3.

<table>
<thead>
<tr>
<th>atom</th>
<th>I</th>
<th>f</th>
<th>( U_-/hA )</th>
<th>( U_+/hA )</th>
<th>( (U_+ - U_-)/hA )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>1/2</td>
<td>0, 1</td>
<td>-3/4</td>
<td>1/4</td>
<td>1</td>
</tr>
<tr>
<td>(^2\text{H}, \text{^6Li})</td>
<td>1/2</td>
<td>1/2, 3/2</td>
<td>-1</td>
<td>1/2</td>
<td>3/2</td>
</tr>
<tr>
<td>(^7\text{Li}, \text{^23Na}, \text{^39K}, \text{^41K}, \text{^87Rb})</td>
<td>3/2</td>
<td>1, 2</td>
<td>-5/4</td>
<td>3/4</td>
<td>2</td>
</tr>
<tr>
<td>(^8\text{Rb})</td>
<td>5/2</td>
<td>2, 3</td>
<td>-7/4</td>
<td>5/4</td>
<td>3</td>
</tr>
<tr>
<td>(^{133}\text{Cs})</td>
<td>7/2</td>
<td>3, 4</td>
<td>-9/4</td>
<td>7/4</td>
<td>4</td>
</tr>
<tr>
<td>(^{40}\text{K})</td>
<td>4</td>
<td>7/2, 9/2</td>
<td>-5/2</td>
<td>2</td>
<td>9/2</td>
</tr>
</tbody>
</table>

Table 2.3: Hyperfine energies of the stable alkali atom isotopes, all having \( j = 1/2 \). \(^{87}\text{Rb}\) is not stable but has a half life of \( 4.9 \times 10^{10} \text{ years} \) and \(^{40}\text{K}\) has a half life of \( 1.2 \times 10^9 \text{ years} \).

2.2.3 Electric quadrupole interaction

States with \( j > 1/2 \) also have an electric quadrupole interaction. This couples the quadrupole charge moment of the nucleus to the derivatives of the electric field at the origin. The derivation of this interaction is more complicated. The result is

\[ \Delta E(F) = B \frac{3K(K + 1) - 2I(I + 1)J(J + 1)}{4I(2I - 1)J(2J - 1)}. \]
where $K = F(F + 1) - I(I + 1) - J(J + 1)$ and $B$ is the electric quadrupole hyperfine constant.

States with $j > 1$ also have a magnetic octopole constant. This is usually a very small correction to the energy splittings.

2.2.4 Hyperfine interaction in spherical tensor form

It is sometimes convenient to work with the spherical tensor form of the hyperfine interaction. Generally as was written in Eq. (2.6) the hyperfine interaction Hamiltonian is

$$\hat{H}_{\text{hf}} = \sum_k \hat{T}_k \cdot \hat{N}_k = \hat{T}_0 \cdot \hat{N}_0 + \hat{T}_1 \cdot \hat{N}_1 + \hat{T}_2 \cdot \hat{N}_2 + ...$$

where $\hat{T}_k$ is a rank $k$ spherical tensor operator acting on the electronic degrees of freedom and $\hat{N}_k$ acts on the nuclear degrees of freedom. Even $k$ are electric interactions and odd $k$ are magnetic interactions. The $k = 0$ interaction is just the Coulomb part of the Hamiltonian and has no dependence on magnetic quantum numbers. The $k = 1$ interaction is magnetic dipole and $k = 2$ is electric quadrupole. These are the dominant hyperfine interaction terms.


Coupled hyperfine states are $|IJFM⟩ = \sum M_{I,I,M} C^{FM}_{IM_1,JM_1} |IM_1⟩|JM_1⟩$. The expectation value of $\hat{H}_{\text{hf}}$ in a coupled state is

$$U_{\text{hf}} = ⟨FM|\hat{H}_{\text{hf}}|FM⟩ = U_{\text{hf},0} + U_{\text{hf},1} + U_{\text{hf},2} + ...$$

The magnetic dipole interaction is

$$U_{\text{hf},1} = ⟨IJFM|\hat{T}_1 \cdot \hat{N}_1 |IJFM⟩.$$
### Table 2.4: Hyperfine constants of $^{87}$Rb for the $s, p, d$ states. Values for states with $n \leq 10$ are taken from [13]. Values for $n = 20, 24$ are from Spreeuw arxiv. Values in parentheses are estimates using the assigned value of $a$. The total hyperfine splitting of the $ns$ states is $2A$, of the $nd_{3/2}$ states $6A$ and of the $nd_{5/2}$ states $9A$.

<table>
<thead>
<tr>
<th>state $\nu$</th>
<th>$A$ (MHz)</th>
<th>$a = A(n - \nu)^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>$\nu_{A}$</td>
<td>$a = A(n - \nu)^3$</td>
</tr>
<tr>
<td>$p$</td>
<td>$\nu_{A}$</td>
<td>$a = A(n - \nu)^3$</td>
</tr>
<tr>
<td>$d$</td>
<td>$\nu_{A}$</td>
<td>$a = A(n - \nu)^3$</td>
</tr>
</tbody>
</table>

### Table 2.5: Hyperfine constants of Cs for the $s, p, d$ states. Values for states with $n \leq 10$ are taken from Arimondo RMP. Values for $n = 20, 24$ are from Spreeuw arxiv. Values in parentheses are estimates using the assigned value of $a$. The total hyperfine splitting of the $ns$ states is $4A$, of the $nd_{3/2}$ states $12A$ and of the $nd_{5/2}$ states $20A$.

<table>
<thead>
<tr>
<th>state $\nu$</th>
<th>$A$ (MHz)</th>
<th>$a = A(n - \nu)^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>$\nu_{A}$</td>
<td>$a = A(n - \nu)^3$</td>
</tr>
<tr>
<td>$p$</td>
<td>$\nu_{A}$</td>
<td>$a = A(n - \nu)^3$</td>
</tr>
<tr>
<td>$d$</td>
<td>$\nu_{A}$</td>
<td>$a = A(n - \nu)^3$</td>
</tr>
</tbody>
</table>

Combining (2.15), (2.16) we deduce that

$$
\langle I|\hat{N}_1|I\rangle \langle J|\hat{T}_1|J\rangle = A\sqrt{I(I+1)(2I+1)}\sqrt{J(J+1)(2J+1)}
$$

so the diagonal hyperfine shifts are

$$
U_{hf,1} = A(-1)^{F+I+J}S_{JF}^{II} \sqrt{(2I+1)(I+1)}\sqrt{(2J+1)(J+1)} = A \frac{K}{2}
$$

with $K = F(F + 1) - I(I + 1) - J(J + 1)$ in agreement with Eq. (2.14).

In the context of third order hyperfine-Stark perturbation theory we need off-diagonal matrix elements $\langle n'J'||\hat{T}_1||nJ\rangle$. When $J, J'$ are both $S$ states we can use the expression

$$
\langle n'J'||\hat{T}_1||nJ\rangle \approx \left( \langle n'J'||\hat{T}_1||n'J'\rangle \langle nJ||\hat{T}_1||nJ\rangle \right)^{1/2}.
$$

This approximation works well due to the fact that the hyperfine interaction for $s$ states is dominated by the Fermi contact interaction which depends on the value of the wavefunction at the origin.

#### 2.2.5 Scaling with $n$

The hyperfine interaction is rapidly diminished in states with higher radial and angular quantum numbers. The magnetic dipole interaction is proportional to $|\psi_{nl}(0)|^2 \sim \delta_{00}/n^3$ as is seen in Eq. (2.13) for hydrogenic wavefunctions. The scaling is thus strictly $1/n^3$ for hydrogen. Also higher multipole contributions to the hyperfine splitting tend to scale as $1/n^3$. In other elements wavefunctions for higher $l$ states need not vanish at the origin. Nonetheless the observed splittings are well described by a $1/n^3$ scaling. Some numerical values for Rb and Cs $ns$ states are given in Tables 2.4, 2.5.
2.3 Lamb shift

The final correction to atomic energy levels in hydrogenic atoms comes from quantum electrodynamic (QED) effects. This is known as the Lamb shift after Willis Lamb who made the first measurement of this effect. The Lamb shift removes the degeneracy of $2s_{1/2}$ and $2p_{1/2}$ predicted by Dirac theory, which played a key role in the development of the theory of QED in the 1940s.

The corrections to hydrogen are shown in Fig. 2.2. The $1s$ state is shifted up by 8173 MHz and the $2s_{1/2}$ state is shifted up by a smaller amount. The $2s_{1/2} - 2p_{1/2}$ states acquire a separation of about 1058 MHz. The original measurement by Lamb and Retherford[14] put the shift at about 1000 MHz. More recent experimental and theoretical values are in excellent agreement with each other which serves as a precision test of QED. A detailed calculation of the Lamb shift requires quantum field theory. Nevertheless it is instructive to estimate the shift using a simplified treatment[15].

The physical mechanism responsible for the Lamb shift is the interaction of the electron with zero point fluctuations of the electromagnetic field. The leading order processes are shown in Fig. 2.3. The electron self energy correction is due to emission and reabsorption of virtual photons. This leads to a delocalization of the electron over a region determined by the strength of the field fluctuations. As in the calculation of the Darwin contribution to fine structure in Sec. 2.1.1 this delocalization implies an averaging of the Coulomb interaction with the nucleus over a finite volume which results in an increase of energy. This effect only occurs for $s$ states and raises their energy.

The next order effect is due to the second diagram in Fig. 2.3. This is called vacuum polarization and leads to the creation of a certain density of electron-positron pairs surrounding the electron. The electron-positron pair get polarized by the Coulomb field from the nucleus which binds the $s$ electron more tightly. The electron-positron pairs are confined...
2.3 Lamb shift

Figure 2.3: Leading contributions to the Lamb shift are the self energy (left) and vacuum polarization (right).

to a localized region around the electron of order the Compton wavelength and this gives a very small correction in hydrogen. However, if the Bohr radius were made smaller by using a heavy electron this effect becomes important. As we will see this occurs in muonic hydrogen (µH).

The following calculation is in cgs units. The number of electromagnetic field modes per unit volume per unit frequency interval is

$$\rho(\nu) d\nu = 8\pi \frac{\nu^2}{c^3} d\nu.$$  

Each mode is a harmonic oscillator with zero point energy $h\nu/2$ so the energy density is

$$W_\nu = \frac{h\nu}{2} \rho(\nu) = 4\pi \frac{h\nu^3}{c^3}.$$  

From classical electromagnetism the energy density is

$$W_\nu = \frac{1}{8\pi} (\langle E^2_\nu \rangle + \langle B^2_\nu \rangle) = \frac{1}{4\pi} \langle E^2_\nu \rangle = \frac{1}{8\pi} E^2_\nu$$

where the angle brackets denote time averaging. Thus

$$E^2_\nu = \frac{32\pi^2 h\nu^3}{c^3}.$$  

A free electron driven by this field amplitude at frequency $\nu$ will execute harmonic motion with a time averaged square amplitude

$$\langle q^2_\nu \rangle = \frac{e^2}{32\pi^4 m^2 \nu^4} E^2_\nu = \frac{h e^2}{\pi^2 c^3 m^2 \nu}.$$  

For each frequency the Coulomb potential of the electron is modified by

$$\Delta V = \langle V(r + q_\nu) \rangle - \langle V(r) \rangle$$

where the angle brackets now represent a quantum mechanical expectation value. Following
the same assumptions about isotropy of the fluctuations as led to (2.5) we arrive at

\[
\langle \Delta V \rangle = \frac{\langle q^2 \rangle}{6} \langle \nabla^2 V \rangle = \frac{2\hbar e^4}{3\pi c^3 m^2 \nu} \delta(r)
\]

\[
= \frac{2\hbar e^4}{3\pi^2 c^3 m^2 n^3 a_0^3 \nu} \delta_{l0}
\]

\[
= -\frac{4}{3\pi} \frac{E_H \alpha^3}{n^3 \nu}.
\]

(2.17)

To get the total energy shift we should then integrate over frequency which gives

\[
\Delta E = -\frac{4}{3\pi} \frac{E_H \alpha^3}{n^3} \ln(\nu_{\text{max}}/\nu_{\text{min}}).
\]

(2.18)

QED provides a framework with which the energy shift can be calculated precisely. Heuristically we can proceed by invoking physically reasonable limits for \(\nu\). We take

\[
h \nu_{\text{max}} = mc^2
\]

and \(\nu_{\text{min}}\) to be the orbital frequency of the electron. Using \(v = \alpha c / n\) and an orbital radius of \(n^2 a_0\) we find

\[
\nu_{\text{min}} = \frac{-E_H}{\hbar n^3}.
\]

Thus \(\nu_{\text{max}}/\nu_{\text{min}} = -mc^2 n^3 / E_H = n^3/\alpha^2\) and

\[
\Delta E = -\frac{4}{3\pi} \frac{E_H \alpha^3}{n^3} \ln(n^3/\alpha^2).
\]

(2.19)

Plugging in numbers we find \(\Delta E_{n=1}/h = 10.7\) GHz and \(\Delta E_{n=2}/h = 1620\) MHz. These numbers are about 50% too large which is not bad considering the approximate character of the calculation.

## 2.4 Radius of the proton

See handwritten notes.
Chapter 3

Interactions with static electromagnetic fields

In this chapter we will explore atomic interactions with magnetic and electric fields known as the Zeeman and Stark effects. These interactions give shifts to energy levels and can couple different states together. The Zeeman Hamiltonian has been derived in Sec. 2.2.1 and the Stark Hamiltonian will be derived in 3.4.

3.1 Zeeman effect in fine structure states

Consider a fine structure state $|ls; jm\rangle$ which is an eigenstate of $\hat{J}_z = \hat{L}_z + \hat{s}_z, \hat{J}^2, \hat{L}^2, \hat{s}^2$. In the presence of a magnetic field $B$ the Zeeman interaction with the electron has two contributions

$$\hat{H}_{ZL} = -\hat{\mu}_L \cdot B = \frac{\mu_B}{\hbar} g_L \hat{L} \cdot B,$$
$$\hat{H}_{ZS} = -\hat{\mu}_S \cdot B = \frac{\mu_B}{\hbar} g_S \hat{S} \cdot B.$$

The Zeeman Hamiltonian accounting for interaction with the orbital and spin moments is thus

$$\hat{H}_Z = \hat{H}_{ZL} + \hat{H}_{ZS} = -\hat{\mu}_J \cdot B$$

where

$$\hat{\mu}_J = -\frac{\mu_B}{\hbar} \left( g_L \hat{L} + g_S \hat{S} \right).$$

Since $g_L \neq g_S$ the magnetic moment $\hat{\mu}_J$ is not proportional to $\hat{J} = \hat{L} + \hat{S}$. This will be evident in what follows where we will find off-diagonal matrix elements between states of different $j\langle j'm'|\hat{\mu}_J|jm\rangle$, whereas $\langle j'm'|\hat{J}|jm\rangle \sim \delta_{jj'}$.

Let’s start by calculating diagonal matrix elements of $\hat{\mu}_J$ with a magnetic field $B = Be_z$ parallel to the quantization axis $e_z$. The Hamiltonian can then be written

$$\hat{H}_{Z,z} = -\hat{\mu}_{J,z} B = \frac{\mu_B}{\hbar} B \left( g_L \hat{L}_z + g_S \hat{S}_z \right).$$

Since $\hat{J}_z = \hat{L}_z + \hat{S}_z$ we can introduce an effective $g_J$ factor in the coupled basis defined by

$$\hat{H}_{Z,z} = \frac{\mu_B}{\hbar} B g_J \hat{J}_z.$$
from which it follows that
\[ g_J \hat{J}_z = g_L \hat{L}_z + g_S \hat{S}_z. \]  
(3.5)

We emphasize that (3.5) only applies to the \( z \) component not to the full operator since \( \hat{\mu}_J \) is not proportional to \( \hat{J} \) and therefore \( \hat{H}_z \neq \frac{\mu_B}{\hbar} g_J \hat{J} \cdot \mathbf{B} \).

To find the value of \( g_J \) we calculate the energy shift for a weak field
\[ \Delta E_{(jm)} = \langle jm | \hat{H}_{z,e} | jm \rangle = \mu_B g_J B m. \]  
(3.6)

Provided the magnetic field is small and does not mix states of different \( j \), then \( j \) is a good quantum number and we can use the Landé projection theorem to write
\[ \langle \mathbf{L} \cdot \mathbf{B} \rangle = \frac{\langle (\mathbf{L} \cdot \hat{J})(\mathbf{B} \cdot \hat{J}) \rangle}{J^2} = \frac{j(j+1) + l(l+1) - S(S+1)}{2j(j+1)} \langle \mathbf{B} \cdot \hat{J} \rangle \]  
(3.7)

and similarly
\[ \langle \mathbf{S} \cdot \mathbf{B} \rangle = \frac{j(j+1) - l(l+1) + S(S+1)}{2j(j+1)} \langle \mathbf{B} \cdot \hat{J} \rangle. \]  
(3.8)

Equations (3.7, 3.8) allow us to write the expectation value of the Zeeman Hamiltonian in terms of the operator \( \hat{J} \) in the alternative form
\[ \langle \hat{H}_z \rangle = \frac{\mu_B}{\hbar} \left[ g_L \frac{j(j+1) + l(l+1) - S(S+1)}{2j(j+1)} + g_S \frac{j(j+1) - l(l+1) + S(S+1)}{2j(j+1)} \right] \langle \mathbf{B} \cdot \hat{J} \rangle \]
or
\[ \langle \hat{H}_{z,e} \rangle = \frac{\mu_B}{\hbar} \left[ g_L \frac{j(j+1) + l(l+1) - S(S+1)}{2j(j+1)} + g_S \frac{j(j+1) - l(l+1) + S(S+1)}{2j(j+1)} \right] B m. \]

Comparison with (3.6) shows that
\[ g_J = g_L \frac{j(j+1) + l(l+1) - S(S+1)}{2j(j+1)} + g_S \frac{j(j+1) - l(l+1) + S(S+1)}{2j(j+1)} \]  
(3.9a)

\[ \cong \frac{3}{2} - \frac{l(l+1) - S(S+1)}{2j(j+1)}. \]  
(3.9b)

It’s always good to check a calculation in two different ways so let’s compute \( g_J \) without using the Landé projection theorem. The Zeeman Hamiltonian diagonal matrix element in the coupled basis with a field along \( e_z \) is
\[ \langle \alpha ls; jm | \hat{H}_{z,e} | \alpha ls; jm \rangle = \frac{\mu_B}{\hbar} \langle \alpha ls; jm | g_L \hat{L}_z + g_S \hat{S}_z | \alpha ls; jm \rangle \]
where \( \alpha \) denotes any additional quantum numbers. Using Wigner-Eckart we get
\[ \langle \alpha ls; jm | \hat{H}_{z,e} | \alpha ls; jm \rangle = \frac{\mu_B}{\hbar \sqrt{2j+1}} \left[ \left( g_L \langle \alpha ls; j || \hat{L}_z || \alpha ls; j \rangle + g_S \langle \alpha ls; j || \hat{S}_z || \alpha ls; j \rangle \right) C_{jm10}^{jm} \right. \]
\[ = \frac{\mu_B B m \sqrt{2j+1}}{\hbar \sqrt{j(j+1)}} (-1)^{ls+lt+j} \]
\[ \times \left( g_L S_{s1}^{jls} \sqrt{l(l+1)(2l+1)} + g_S S_{jls}^{s1} \sqrt{s(s+1)(2s+1)} \right). \]
3.1 Zeeman effect in fine structure states

Evaluating the 6j symbols we find again Eq. (3.9a).

The above results are valid for small fields giving a linear Zeeman shift. At field strengths for which $|\mu_B B| \approx E_{fs}$, with $E_{fs}$ the energy separation between states of different $j$ the Hamiltonian $\hat{H}_Z$ has significant off-diagonal matrix elements. The state $|jm\rangle$ in the coupled basis can be written as

$$|jm\rangle = \sum_{m_{1m_s}} C^{ jm}_{lm_{1m_s}} |m_{l}; m_s\rangle.$$  

We therefore have matrix elements

$$\langle j'm'|\hat{H}_Z|jm\rangle = \mu_B B \langle j'm'|g_L \hat{L}_z + g_S \hat{S}_z|jm\rangle$$

$$= \mu_B B \sum_{m_{1m_s}m_{1m'_s}} C^{jm'}_{lm_{1m}_s}(m_1 + 2m_s)C^{jm}_{lm_{1m_s}} \langle m{l}; m_s'|m_1m_s\rangle$$

$$= \mu_B B \sum_{m_{1m_s}m_{1m'_s}} C^{jm'}_{lm_{1m}_s}(m_1 + 2m_s)C^{jm}_{lm_{1m_s}} \delta_{l,l'} \delta_{m_1,m_1'} \delta_{s,s'} \delta_{m_1,m_1'}$$

$$= \mu_B B \sum_{m_{1m_s}} C^{jm'}_{lm_{1m}_s}(m_1 + 2m_s)C^{jm}_{lm_{1m_s}}. \quad (3.10)$$

When $j' = j, m' = m$ Eq. (3.10) should agree with (3.6) which implies the identity

$$\sum_{m_{1m_s}} (m_1 + 2m_s) (C^{jm}_{lm_{1m_s}})^2 = m \left[ 1 + \frac{j(j + 1) - l(l + 1) + s(s + 1)}{2j(j + 1)} \right].$$

**Selection rules**

To find the selection rules for the Zeeman interaction let us use the Wigner-Eckart theorem again. For a magnetic field $\mathbf{B}$ pointing in an arbitrary direction

$$\langle \alpha'j'm'|\hat{H}_Z|\alpha jm\rangle = \frac{\mu_B B}{\hbar} \sum_{q=-1,0,1} (-1)^q B_{-q} \langle j'm'|g_L \hat{L}_q + g_S \hat{S}_q|jm\rangle$$

$$= \frac{\mu_B B g_L \langle \alpha'j'\parallel \hat{L}\parallel \alpha j\rangle + g_S \langle \alpha'j'\parallel \hat{S}\parallel \alpha j\rangle}{\sqrt{2j' + 1}} \sum_{q=-1,0,1} (-1)^q B_{-q} C^{jm'}_{jm_{1q}}.$$

Here $\alpha = (n, l, s)$ plus any additional quantum numbers. The Clebsch-Gordan coefficient can be nonzero only if $m' = m + q$ so $|m' - m| \leq 1$ and $|j' - j| \leq 1$. The coefficient $C^{j0}_{j010} = 0$ so $|j, m = 0\rangle \rightarrow |j', m = 0\rangle$ is not allowed. In addition the orbital and spin angular momentum operators do not act on radial degrees of freedom. Therefore the matrix element can be nonzero only if $\alpha' = \alpha$. To summarize the selection rules are

$$|m' - m| \leq 1,$$

$$|j' - j| \leq 1, \quad |j, m = 0\rangle \rightarrow |j, m = 0\rangle \text{ forbidden,}$$

$$\alpha' = \alpha.$$
Zeeman effect in hydrogen $2p$

As an example consider the $2p_{1/2}, 2p_{3/2}$ states of Hydrogen. The $g_J$ factors are\(^1\) $g_{3/2} = 4/3$, $g_{1/2} = 2/3$. Working in the basis \{\(|3/2, 3/2\rangle, |3/2, 1/2\rangle, |3/2, -1/2\rangle, |3/2, -3/2\rangle, |1/2, 1/2\rangle, |1/2, -1/2\rangle\} the Zeeman eigenvalue problem becomes $\hat{H}|\psi\rangle = E|\psi\rangle$ with

$$\hat{H} = E_{fs} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} + \mu_B B \begin{pmatrix} 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2/3 & 0 & 0 & -\sqrt{2}/3 & 0 \\ 0 & 0 & -2/3 & 0 & 0 & -\sqrt{2}/3 \\ 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & -\sqrt{2}/3 & 0 & 0 & 1/3 & 0 \\ 0 & 0 & -\sqrt{2}/3 & 0 & 0 & -1/3 \end{pmatrix}$$

and $E_{fs}$ the fine structure splitting. We have taken the $2p_{1/2}$ level to define the zero of energy. The eigenvalues and eigenstates can be found analytically.

Without performing all the algebra we can understand the structure as follows. At small fields the Zeeman slopes $(\Delta E_{jm}/\mu_B B)$ are $2, 2/3, -2/3, -2, 1/3, -1/3$. At large fields the orbital and spin moments decouple. The energy shift of an uncoupled state $|m_l; m_s\rangle$ is

$$\Delta E_{|m_l; m_s\rangle} = \langle m_l; m_s|\hat{H}_Z|m_l; m_s\rangle = (\mu_B B)(g_L m_l + g_S m_s)$$

and we have Zeeman slopes $2, 1, 0, 0, -1, -2$. At zero magnetic field the coupled Zeeman

---

\(^1\)There is a trick for deducing the $g_{3/2}$ factor without using the explicit expression for $g_J$. The $|3/2, 3/2\rangle$ state has Zeeman slope corresponding to $m_l = 1$ and $m_s = 1/2$. Thus the slope (in units of $\mu_B B$) must be $m_l + 2m_s = g_J \times (m = j)$ so $g_J = 2/(3/2) = 4/3$. 
3.2 Zeeman effect in hyperfine states

states in terms of the uncoupled states are

\[
|\frac{3}{2}, \frac{3}{2}\rangle = |1; 1/2\rangle \\
|\frac{3}{2}, 1\rangle = \sqrt{\frac{2}{3}}|0; 1/2\rangle + \sqrt{\frac{1}{3}}|1; -1/2\rangle \\
|\frac{3}{2}, -1\rangle = \sqrt{\frac{2}{3}}|0; -1/2\rangle + \sqrt{\frac{1}{3}}|1; 1/2\rangle \\
|\frac{3}{2}, -3\rangle = |-1; -1/2\rangle \\
|1/2, 1\rangle = \sqrt{\frac{2}{3}}|1; -1/2\rangle - \sqrt{\frac{1}{3}}|0; 1/2\rangle \\
|1/2, -1\rangle = \sqrt{\frac{1}{3}}|0; -1/2\rangle - \sqrt{\frac{2}{3}}|1; 1/2\rangle.
\]

The states $|\frac{3}{2}, \pm 3/2\rangle$ only couple to a single uncoupled state so there is no field induced state mixing and we get a linear Zeeman shift with slope $E/\mu B = \pm g_{3/2}3/2 = \pm 2$ irrespective of the field strength. At small field there is negligible state mixing so the Zeeman slopes are just $g_{Jm}$. At large fields the Zeeman coupling overwhelms the fine structure coupling and the orbital and spin angular momenta decouple. In this limit (referred to as Paschen-Back) the total angular momentum $j$ is no longer a good quantum number and we add the orbital and intrinsic spin Zeeman shifts separately. The remaining four states have Zeeman slopes of $0(|1; -1/2\rangle, |-1; 1/2\rangle), 1(|0; 1/2\rangle, -1(|0; -1/2\rangle)$. These two sets of eigenvalues connect continuously as the field is changed between the small (linear Zeeman) and large (Paschen-Back) regimes. Smoothly connecting the states gives the behavior seen in Fig. 3.1.

### 3.1.1 $J J$ coupling

The Zeeman effect in multielectron atoms depends on the type of coupling scheme that occurs. In $J J$ coupling the orbital and spin momenta of each electron or group of electrons are coupled to form $J_1 = L_1 + S_1$ and $J_2 = L_2 + S_2$. The angular momenta of each group are then coupled to give the total angular momentum $J = J_1 + J_2$.

The $g$ factor in $J J$ coupling is

\[
g(J_1, J_2, J) = g(L_1 S_1 J_1) \frac{J(J + 1) + J_1(J_1 + 1) - J_2(J_2 + 1)}{2J(J + 1)} + g(L_2 S_2 J_2) \frac{J(J + 1) + J_2(J_2 + 1) - J_1(J_1 + 1)}{2J(J + 1)}. \tag{3.11}
\]

### 3.2 Zeeman effect in hyperfine states

Analogous results hold for the energy shifts and mixing of hyperfine states. In the coupled basis the total angular momentum is $\mathbf{F} = \mathbf{J} + \mathbf{I}$. The Zeeman Hamiltonian is

\[
\hat{H}_Z = -\hat{\mu}_F \cdot \mathbf{B} = \frac{\mu_B}{\hbar} (g_J \hat{\mathbf{J}} + g_I \hat{\mathbf{I}}) \cdot \mathbf{B}. \tag{3.12}
\]

The $g_J$ factor is defined in Eq. (3.9a) and $g_I$ depends on the nuclear structure. The Landé factors of nucleons (protons and neutrons) are proportional to $\mu_N$ the nuclear magneton.
The nucleon moments combine to give a $g_I$ which is isotope dependent. Since $\mu_N/\mu_B \sim .001$ and the nuclear Zeeman effect is defined as being proportional to $g_I\mu_B$ the nuclear Landé factor $g_I$ is proportional to $\mu_N/\mu_B$ and is typically $\ll 1$. Nevertheless the nuclear moment plays an important role in some situations as we will see.

Since $\hat{F} = \hat{J} + \hat{I}$ is the same equation as $\hat{J} = \hat{L} + \hat{S}$ with the substitutions $\hat{J} \to \hat{F}$, $\hat{L} \to \hat{J}$, and $\hat{S} \to \hat{I}$ all of the results of the previous section for the fine structure Zeeman effect apply also to hyperfine structure with an appropriate relabeling. For convenience the relevant formulae are

$$|FM\rangle = \sum_{M_JM_I} C_{JMJ,M_I}^{FM}|M_J; M_I\rangle,$$

$$g_F = g_J \frac{F(F + 1) + J(J + 1) - I(I + 1)}{2F(F + 1)} + g_I \frac{F(F + 1) - J(J + 1) + I(I + 1)}{2F(F + 1)},$$

$$\langle \alpha JJ; FM | \hat{J} z | \alpha JJ; FM \rangle = \mu_B B_z g_F M,$$

$$\langle \alpha JJ; F'M' | \hat{J} z | \alpha JJ; FM \rangle = \mu_B B_z \sum_{M_JM_I} C_{JMJ'M_I}^{F'M}(g_J M_J + g_I M_I) C_{JMJ,M_I}^{FM}(3.13d)$$

We can write (3.13d) in a different form using the Wigner-Eckart theorem

$$\langle \alpha JJ; F'M'|\hat{J}Z|\alpha JJ; FM \rangle = \frac{\mu_B}{\hbar} \sum_q (-1)^q B_{-q} \langle \alpha JJ; F'M'|g_J \hat{J}_q + g_I \hat{I}_q | \alpha JJ; FM \rangle$$

$$= \frac{\mu_B}{\hbar \sqrt{2F' + 1}} \sum_q (-1)^q B_{-q} C_{FM1q}^{F'M} \times \left( g_J \langle \alpha JJ; F'|\hat{J}|\alpha JJ; F \rangle + g_I \langle \alpha JJ; F'|\hat{I}|\alpha JJ; F \rangle \right).$$

The reduced matrix elements are

$$\langle \alpha JJ; F'|\hat{J}|\alpha JJ; F \rangle = \hbar (-1)^{1+J+I} \sqrt{(2F + 1)(2F' + 1)J(J + 1)(2J + 1)} S_{IJF}^{F'F}$$

$$\langle \alpha JJ; F'|\hat{I}|\alpha JJ; F \rangle = \hbar (-1)^{1+J+I} \sqrt{(2F + 1)(2F' + 1)I(I + 1)(2I + 1)} S_{IJF}^{F'F}$$

so the off-diagonal Zeeman matrix element is

$$\langle \alpha JJ; F'M'|\hat{J}Z|\alpha JJ; FM \rangle = \mu_B \sum_q (-1)^q B_{-q} C_{FM1q}^{F'M} \sqrt{2F + 1} (-1)^{1+J+I}$$

$$\times \left( g_J (-1)^F \sqrt{J(J + 1)(2J + 1)} S_{IJF}^{F'F} + g_I (-1)^{F'} \sqrt{I(I + 1)(2I + 1)} S_{IJF}^{F'F} \right).$$

For a field polarized along $e_z$ we have the selection rule $M' = M$ and this reduces to

$$\langle \alpha JJ; F'M'|\hat{J}Z|\alpha JJ; FM \rangle = \mu_B B_z C_{FM10}^{F'M} \sqrt{2F + 1} (-1)^{1+J+I}$$

$$\times \left( g_J (-1)^F \sqrt{J(J + 1)(2J + 1)} S_{IJF}^{F'F} + g_I (-1)^{F'} \sqrt{I(I + 1)(2I + 1)} S_{IJF}^{F'F} \right).$$

This expression is equivalent to (3.13d). The diagonal matrix element is thus

$$\langle \alpha JJ; FM | \hat{J}Z|\alpha JJ; FM \rangle = \mu_B B_z C_{FM10}^{F'M} \sqrt{2F + 1} (-1)^{1+F+J+I}$$

$$\times \left( g_J \sqrt{J(J + 1)(2J + 1)} S_{IJF}^{F'F} + g_I \sqrt{I(I + 1)(2I + 1)} S_{IJF}^{F'F} \right).$$

Evaluating the angular factors we recover (3.13c).
3.2 Zeeman effect in hyperfine states

3.2.1 Alkali atom with \( I = 3/2 \)

As an example consider the ground state of an alkali atom with \( I = 3/2 \) and \( J = 1/2 \). We write the coupled hyperfine states \(|JIFm_F\rangle\) as \(|F,m_F\rangle_{hf}\), and the uncoupled states as \(|m_J,m_I\rangle\). The hyperfine states are

\[
\begin{align*}
|2,2\rangle_{hf} &= |1/2,3/2\rangle \\
|2,1\rangle_{hf} &= \frac{\sqrt{3}}{2}|1/2,1/2\rangle + \frac{1}{2}|1/2,3/2\rangle \\
|2,0\rangle_{hf} &= \frac{1}{\sqrt{2}}|1/2,-1/2\rangle + \frac{1}{\sqrt{2}}|1/2,1/2\rangle \\
|2,-1\rangle_{hf} &= \frac{1}{2}|1/2,-3/2\rangle + \frac{\sqrt{3}}{2}|1/2,-1/2\rangle \\
|2,-2\rangle_{hf} &= |1/2,-3/2\rangle \\
|1,1\rangle_{hf} &= \frac{1}{2}|1/2,1/2\rangle - \frac{\sqrt{3}}{2}|1/2,3/2\rangle \\
|1,0\rangle_{hf} &= \frac{1}{\sqrt{2}}|1/2,-1/2\rangle - \frac{1}{\sqrt{2}}|1/2,1/2\rangle \\
|1,-1\rangle_{hf} &= \frac{\sqrt{3}}{2}|1/2,-3/2\rangle - \frac{1}{2}|1/2,-1/2\rangle. 
\end{align*}
\]

Let us consider \( s \) states, for which the hyperfine energies are given by the eigenvalues of the Hamiltonian

\[
\hat{H}_{hf} = \hbar \mathbf{A} \cdot \hat{\mathbf{S}} = \frac{\hbar A}{2} \left( \hat{F}^2 - \hat{I}^2 - \hat{S}^2 \right)
\]

where \( A \) is the hyperfine constant. We previously wrote the hyperfine magnetic dipole interaction as proportional to \( \mathbf{1} \cdot \mathbf{J} \). When considering \( s \) states that have \( \hat{\mathbf{L}} = 0 \) we can use \( \mathbf{J} = \hat{\mathbf{S}} \). This accounts for the magnetic dipole interaction, the next term due to electric quadrupole vanishes for \( s \) states with \( J = 1/2 \). The energies of the states with \( F = I+1/2 = 2 \) are \( U_+ = 3\hbar A/4 \) and for \( F = I-1/2 = 1 \) they are \( U_- = -5\hbar A/4 \). The hyperfine splitting is thus \( U_{hf} = U_+ - U_- = 2A \).

Now consider the effect of a magnetic field taking the quantization axis along the field direction so the Zeeman Hamiltonian is

\[
\hat{H}_{Z,z} = -\mu_F \cdot \mathbf{B} = \frac{\mu_B}{\hbar} \left( g_S \hat{S}_z + g_L \hat{L}_z + g_I \hat{I}_z \right) B_z.
\]

The \( g \) factors are \( g_S \simeq 2.0023 \), \( g_L = 1 \), and for \(^{87}\text{Rb} \) \( g_I \simeq -0.000995 \). The magnetic field shifts the energies of the coupled states, and mixes them. Again we consider \( s \) states and neglect the contribution from the small nuclear moment. The diagonal matrix elements are

\[
\begin{align*}
\langle 2,\pm 2|\hat{H}'|2,\pm 2\rangle_{hf} &= \pm 2U_B \\
\langle 2,\pm 1|\hat{H}'|2,\pm 1\rangle_{hf} &= \pm U_B \\
\langle 2,0|\hat{H}'|2,0\rangle_{hf} &= 0 \\
\langle 1,\pm 1|\hat{H}'|1,\pm 1\rangle_{hf} &= \mp U_B \\
\langle 1,0|\hat{H}'|1,0\rangle_{hf} &= 0
\end{align*}
\]
where $U_B = g_S \mu_B B_z / 4$. The nonzero off-diagonal matrix elements are

$$
\begin{align*}
\langle 2, \pm 1 \mid \hat{H}' \mid 1, \pm 1 \rangle_{\text{hf}} &= \sqrt{3} U_B \\
\langle 2, 0 \mid \hat{H}' \mid 1, 0 \rangle_{\text{hf}} &= 2U_B
\end{align*}
$$

The perturbed states in the presence of a magnetic field are

$$
\begin{align*}
|2, 2\rangle_{\text{hf}}' &= |2, 2\rangle_{\text{hf}} \\
|2, 1\rangle_{\text{hf}}' &= |2, 1\rangle_{\text{hf}} + \frac{\sqrt{3} U_B}{2a} |1, 1\rangle_{\text{hf}} \\
|2, 0\rangle_{\text{hf}}' &= |2, 0\rangle_{\text{hf}} + \frac{U_B}{a} |1, 0\rangle_{\text{hf}} \\
|2, -1\rangle_{\text{hf}}' &= |2, -1\rangle_{\text{hf}} + \frac{\sqrt{3} U_B}{2a} |1, -1\rangle_{\text{hf}} \\
|2, -2\rangle_{\text{hf}}' &= |2, -2\rangle_{\text{hf}} \\
|1, 1\rangle_{\text{hf}}' &= |1, 1\rangle_{\text{hf}} - \frac{\sqrt{3} U_B}{2a} |2, 1\rangle_{\text{hf}} \\
|1, 0\rangle_{\text{hf}}' &= |1, 0\rangle_{\text{hf}} - \frac{U_B}{a} |2, 0\rangle_{\text{hf}} \\
|1, -1\rangle_{\text{hf}}' &= |1, -1\rangle_{\text{hf}} - \frac{\sqrt{3} U_B}{2a} |2, -1\rangle_{\text{hf}}
\end{align*}
$$

Labeling the basis states as $|1\rangle = |2, 2\rangle_{\text{hf}}$, $|2\rangle = |2, 1\rangle_{\text{hf}}$, $|3\rangle = |2, 0\rangle_{\text{hf}}$, $|4\rangle = |2, -1\rangle_{\text{hf}}$, $|5\rangle = |2, -2\rangle_{\text{hf}}$, $|6\rangle = |1, 1\rangle_{\text{hf}}$, $|7\rangle = |1, 0\rangle_{\text{hf}}$, and $|8\rangle = |1, -1\rangle_{\text{hf}}$, the energies are found from the equation

$$
\text{det}
\begin{bmatrix}
\frac{3\hbar^2}{4} + 2U_B - E & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{3\hbar^2}{4} + U_B - E & 0 & 0 & 0 & \sqrt{\hbar^2} & 0 & 0 \\
0 & 0 & \frac{3\hbar^2}{4} + U_B - E & 0 & 0 & 0 & \sqrt{\hbar^2} & 0 \\
0 & 0 & 0 & \frac{3\hbar^2}{4} + 2U_B - E & 0 & 0 & 0 & \sqrt{\hbar^2} \\
0 & 0 & 0 & 0 & \frac{3\hbar^2}{4} + U_B - E & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{3\hbar^2}{4} + U_B - E & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{3\hbar^2}{4} + 2U_B - E & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3\hbar^2}{4} + U_B - E
\end{bmatrix} = 0
$$

(3.16)

The energy eigenvalues are
Zeeman effect in hyperfine states

Figure 3.2: Zeeman effect in $^{87}$Rb ground hyperfine states. The states are labelled with $f,m_f$ at low fields and $m_j,m_I$ at high fields. The right hand panel shows the high field magic magnetic field values.

The energies as a function of magnetic field are shown in Fig. 3.2. This was first worked out by Breit and Rabi[16].

\[
\begin{align*}
E_1 &= \frac{3hA}{4} + 2UB, \\
E_2 &= -\frac{hA}{4} + \sqrt{(hA)^2 + 2hAU_B + 4U_B^2}, \\
E_3 &= -\frac{hA}{4} + \sqrt{(hA)^2 + 4U_B^2}, \\
E_4 &= -\frac{hA}{4} + \sqrt{(hA)^2 - 2hAU_B + 4U_B^2}, \\
E_5 &= \frac{3hA}{4} - 2UB, \\
E_6 &= -\frac{hA}{4} - \sqrt{(hA)^2 - 2hAU_B + 4U_B^2}, \\
E_7 &= -\frac{hA}{4} - \sqrt{(hA)^2 + 4U_B^2}, \\
E_8 &= -\frac{hA}{4} - \sqrt{(hA)^2 + 2hAU_B + 4U_B^2}.
\end{align*}
\]

The energies as a function of magnetic field are shown in Fig. 3.2. This was first worked out by Breit and Rabi[16].

### 3.2.2 High-field level crossing

It appears from Fig. 3.2 that the $^{87}$Rb levels do not cross as the field is increased. A similar Zeeman hyperfine structure is seen for any of the alkali atoms. In fact this is not the case. At high fields the states with $m_j = +1/2$ cross[17]. To see this it is simplest to consider the combined hyperfine and Zeeman Hamiltonian in the uncoupled $m_I,m_J$ basis[18]. The Hamiltonian reads

\[
\hat{H} = hA\frac{\hat{I} \cdot \hat{J}}{\hbar^2} + \frac{g_J \mu_B}{\hbar} \hat{J} \cdot \mathbf{B} + \frac{g_I \mu_B}{\hbar} \hat{I} \cdot \mathbf{B}.
\]
Putting $B = Be_z$, the diagonal matrix elements are

$$\langle m_J m_I | \hat{H} | m_J m_I \rangle = \hbar A m_J m_I + \mu_B B (g_J m_J + g_I m_I).$$

Consider hydrogen with $m_J = 1/2$ and $m_I = \pm 1/2$. The levels cross when

$$\hbar A (1/2)(1/2) + \mu_B B (g_J (1/2) + g_I (1/2)) = \hbar A (1/2)(-1/2) + \mu_B B (g_J (1/2) + g_I (-1/2))$$

so

$$B_{\text{cross}} = - \frac{\hbar A}{2 \mu_B g_I}.$$  

Using $g_I = 0.003042$ and $A = 1.4204$ GHz gives $B_{\text{cross}} = -16.68$ T. Analogous crossings also occur in atoms with larger nuclear spin.

### 3.3 “Magic” magnetic fields

Hyperfine states play an important role in time keeping since they are used in atomic clocks. The transition between the $^{133}\text{Cs}$ states $|3, 0\rangle$ and $|4, 0\rangle$ at zero magnetic and electric field is defined to have a frequency of

$$\nu_0 = 9192631770 \text{ Hz}.$$  

Accurate measurements of the Cs clock transition frequency are used to correct drift in microwave oscillators to form a stable time reference known as an atomic clock.

In order to make sure the clock frequency is accurate it is necessary to minimize magnetic and electric field noise. To understand what level of noise can be tolerated we need to know the sensitivity of the clock frequency to external fields. For weak magnetic fields $\nu_0$ is independent of $B$ since the involved atomic states have $m_F = 0$.

It is difficult to operate a clock in an environment with $B = 0$ since any small transverse field perturbation will cause transitions to states with $m_F \neq 0$. To stabilize against such transitions it is desirable to apply a small longitudinal bias field $B_z e_z$. This shifts the energy of states with $m_F = \pm 1$ relative to the $m_F = 0$ states and suppresses transitions.

In such a situation small fluctuations of $B_z$ will cause a shift in the clock frequency. We can see this as follows. The Cs $6s_{1/2}$ ground state has $I = 7/2, F = 3, 4$ and $(2 \times 3 + 1) + (2 \times 4 + 1) = 16$ Zeeman states. The hyperfine shifts are $\Delta E_{F=3} = - \frac{9A}{4}, \Delta E_{F=4} = + \frac{7A}{4}$, with the hyperfine constant $A = 2.2981579425$ GHz. The Landé $g$ factors are $g_J = g_s = 2.0025$ and $g_I = -0.0003989$. The energy eigenvalues are found using the same approach as in the $^{87}\text{Rb}$ example of Eq. (3.16).

The energy eigenvalues of $|0\rangle \equiv |3, 0\rangle$ and $|1\rangle \equiv |4, 0\rangle$ are found to be

$$U_0 = \frac{\hbar \omega_0}{16} \left( -1 - 8 \sqrt{1 + \left( \frac{\mu_B B_z}{\hbar \omega_0} \right)^2 (g_J - g_I)^2} \right)$$

$$U_1 = \frac{\hbar \omega_0}{16} \left( -1 + 8 \sqrt{1 + \left( \frac{\mu_B B_z}{\hbar \omega_0} \right)^2 (g_J - g_I)^2} \right)$$
3.3 “Magic” magnetic fields

with $\omega_0 = 2\pi \nu_0$. The field dependent transition frequency is thus

$$\omega(B) = \omega_0 \sqrt{1 + \left(\frac{\mu_B B_z}{\hbar \omega_0}\right)^2 (g_J - g_I)^2}$$

and putting $B_z = B_0 + \delta B$ we find

$$\frac{d\omega(B)}{d\delta B} = \frac{\mu_B B_0 (g_J - g_I) \mu_B (g_J - g_I)}{\hbar \omega_0} \frac{\mu_B B_z}{\hbar}.$$  

This corresponds to a frequency shift

$$\delta \nu(\delta B) = \nu(B_0 + \delta B) - \nu(B_0) = 8.55 \times 10^{10} B_0 \delta B \text{ Hz/T}.$$  

Taking $B_0 = 0.1 \text{ G} = 10^{-5} \text{ T}$ and $\delta B = 1 \mu \text{ G} = 10^{-10} \text{ T}$ we get $\delta \nu = 8.6 \times 10^{-5} \text{ Hz}$. State of the art Cs clocks (NIST-F1 atomic fountain) operate with a relative frequency uncertainty of $\sim 1 \times 10^{-15} \nu_0 = 9 \times 10^{-6} \text{ Hz}$. We see that extremely good magnetic field shielding and stabilization are necessary to reach this level of performance.

There is an alternative approach which greatly reduces the sensitivity to magnetic noise. Suppose we use the states $|0\rangle \equiv |3, -1\rangle$ and $|1\rangle \equiv |4, 1\rangle$. The $g_F$ factors are $-1/4$ and $+1/4$ respectively, so the linear Zeeman shift cancels for this pair of states. The nonlinear dependence on $B$ found from diagonalization is

$$U_0 = \frac{\hbar \omega_0}{16} \left[ -1 - 16 \frac{\mu_B B_z g_I}{\hbar \omega_0} - 8 \sqrt{1 + \left(\frac{\mu_B B_z}{\hbar \omega_0}\right)^2 (g_J - g_I)^2} - \frac{1}{2} \frac{\mu_B B_z}{\hbar} (g_J - g_I) \right],$$

$$U_1 = \frac{\hbar \omega_0}{16} \left[ -1 + 16 \frac{\mu_B B_z g_I}{\hbar \omega_0} + 8 \sqrt{1 + \left(\frac{\mu_B B_z}{\hbar \omega_0}\right)^2 (g_J - g_I)^2} + \frac{1}{2} \frac{\mu_B B_z}{\hbar} (g_J - g_I) \right].$$

The field dependent transition frequency is

$$\omega(B) = \omega_0 \left[ 2 \frac{\mu_B B_z g_I}{\hbar \omega_0} + \frac{1}{2} \sqrt{1 + \left(\frac{\mu_B B_z}{\hbar \omega_0}\right)^2 (g_J - g_I)^2} + \frac{1}{2} \frac{\mu_B B_z}{\hbar} (g_J - g_I) \right].$$  

(3.17)
When $\mu_B B_z (g_J - g_I) \ll \hbar \omega_0$ we can approximate this by

$$\omega(B) \approx \omega_0 \left[ 1 + 2 \frac{\mu_B B_z g_I}{\hbar \omega_0} + \frac{1}{2} \left( \frac{\mu_B B_z}{\hbar \omega_0} \right)^2 (g_J - g_I)^2 \right].$$

Examination of this last expression shows that for small $B_z$ the derivative $d\omega(B)/dB_z < 0$ and for large $B_z$ the derivative $d\omega(B)/dB_z > 0$. There must therefore be a point inbetween where the derivative vanishes and the transition frequency is insensitive to the value of the magnetic field. This is referred to as a “magic” field value $B_{\text{magic}}$. We find

$$B_{\text{magic}} \approx -\frac{2 \hbar \omega_0}{\mu_B (g_J - g_I)^2}. \quad (3.18)$$

Putting in numerical values the magic condition from (3.18) is $B_{\text{magic}} \approx 0.000131$ T = 1.31 G. Numerical solution of (3.17) without approximating the squareroots gives a more accurate value $B_{\text{magic}} = 0.000139$ T = 1.39 G. Although this operating point is not used in atomic clocks it is used in quantum information experiments where long coherence times for qubits encoded in hyperfine states are desired. The NIST F1 Cs fountain clock\[19\] uses the $|3, 0\rangle \leftrightarrow |4, 0\rangle$ clock transition with a small bias field of $B_0 \approx 0.98 \pm 0.001$ mG. This implies a frequency uncertainty of $8 \times 10^{-7}$ Hz and a fractional uncertainty of $9 \times 10^{-17}$. There are additional factors contributing to the total clock uncertainty.

### 3.4 Stark effect

Electric fields also result in shifts and mixing of atomic levels. This is known as the Stark effect. We will start by establishing the form of the Hamiltonian.

#### 3.4.1 Light-atom Hamiltonian

To describe the interaction of a charged particle with an electromagnetic we choose the Hamiltonian such that the Lorentz force law is obtained. The fields can be described in terms of vector and scalar potentials $A(\hat{r}, t), \phi(\hat{r}, t)$ as $E = -\frac{\partial A}{\partial t} - \nabla \phi, B = \nabla \times A$. Assume the Hamiltonian

$$\hat{\mathcal{H}} = \frac{1}{2m} [\hat{p} - qA(\hat{r}, t)]^2 + q\phi(\hat{r}, t) \quad (3.19)$$

for a particle of mass $m$ and charge $q$ interacting with the field. The total momentum is now $\hat{p}_{\text{tot}} = \hat{p} - qA(\hat{r}, t)$ and has a mechanical and a field dependent part with $\hat{p} = -i\hbar \nabla$. The velocity operator can be defined by

$$\hat{v} = \frac{\hat{p}_{\text{tot}}}{m} = \frac{\hat{p} - qA(\hat{r}, t)}{m}.$$ 

We then use Ehrenfest’s theorem to find the equations of motion for the expectation values $\langle \hat{r} \rangle$ and $\langle \hat{v} \rangle$. After some algebra one finds$^2$

$$\frac{d}{dt} \langle \hat{r} \rangle = \frac{\langle \hat{p} - qA(\hat{r}, t) \rangle}{m} = \langle \hat{v} \rangle$$

$^2$There are some subtleties in the derivation which requires the assumption of quasiclassical particle motion.
and
\[
\frac{d}{dt} \mathbf{p}_{\text{tot}} \equiv \mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})
\]
which is the Lorentz force law. This justifies the choice of the Hamiltonian (3.19).

Now consider an atomic electron, with charge \(-e\) interacting with an external field. The Hamiltonian is
\[
\hat{\mathcal{H}} = \frac{1}{2m} \left[ \hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}}, t) \right]^2 - e\phi(\hat{\mathbf{r}}, t) + V(\hat{\mathbf{r}})
\]
where \(V\) represents the Coulomb interaction between the electron and the nucleus. We will work in the Coulomb gauge where \(\nabla \cdot \mathbf{A} = 0\) which can always be chosen with a suitable gauge transformation. With no additional free charges \(\phi = 0\) and
\[
\hat{\mathcal{H}} = \frac{1}{2m} \left[ \hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}}, t) \right]^2 + V(\hat{\mathbf{r}})
\]
\[
= \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) + \frac{e}{m} \hat{\mathbf{p}} \cdot \mathbf{A} + \frac{e^2}{2m} A^2.
\]
To get the last line we used the Coulomb gauge condition which guarantees that \(\hat{\mathbf{p}} \cdot \mathbf{A} = \mathbf{A} \cdot \hat{\mathbf{p}}\).

We then write this as
\[
\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}'
\]
with
\[
\hat{\mathcal{H}}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}})
\]
the Hamiltonian of the unperturbed atomic electron and
\[
\hat{\mathcal{H}}' = \frac{e}{m} \hat{\mathbf{p}} \cdot \mathbf{A} + \frac{e^2}{2m} A^2
\]
a perturbation due to coupling to the field. For field strengths that are not too large we can neglect the \(A^2\) term giving an effective interaction Hamiltonian of
\[
\hat{\mathcal{H}}' = \frac{e}{m} \hat{\mathbf{p}} \cdot \mathbf{A}.
\]
This is referred to as the velocity form of the interaction.

We can also write the perturbation in a so-called length form. The Heisenberg equation of motion \(\frac{d\hat{\mathbf{r}}}{dt} = \frac{i}{\hbar} [\hat{\mathcal{H}}, \hat{\mathbf{r}}]\) can be approximated by
\[
\frac{d\hat{\mathbf{r}}}{dt} \approx \frac{i}{\hbar} [\hat{\mathcal{H}}_0, \hat{\mathbf{r}}]
\]
\[
= \frac{i}{\hbar} (\hat{\mathcal{H}}_0 \hat{\mathbf{r}} - \hat{\mathbf{r}} \hat{\mathcal{H}}_0)
\]
so
\[
\langle j | \hat{\mathbf{p}} | i \rangle = m \langle j | \frac{d\hat{\mathbf{r}}}{dt} | i \rangle + q \mathbf{A} \langle j | i \rangle
\]
\[
= \frac{im}{\hbar} \langle j | \hat{\mathcal{H}}_0 \hat{\mathbf{r}} - \hat{\mathbf{r}} \hat{\mathcal{H}}_0 | i \rangle + q \mathbf{A} \delta_{ji}
\]
\[
= \frac{im}{\hbar} (E_j - E_i) \langle j | \hat{\mathbf{r}} | i \rangle + q \mathbf{A} \delta_{ji}
\]
\[
= im \omega_{ji} \langle j | \hat{\mathbf{r}} | i \rangle + q \mathbf{A} \delta_{ji}.
\]
We will be interested in situations where the field mediates coupling between two different states so $\delta_{ji} = 0$ and
\[
\langle j | \hat{p} | i \rangle = i m \omega_{ji} \langle j | \hat{r} | i \rangle.
\]
This is valid for all states $|i\rangle, |j\rangle$ so we can write the perturbation Hamiltonian as
\[
\hat{H}' = \frac{e}{m} \hat{p} \cdot \mathbf{A} = i e \omega_{ji} \hat{r} \cdot \mathbf{A}.
\]
For a vector potential oscillating at frequency $\omega_{ji}$, $\mathbf{A} = A_0(r) e^{-i \omega_{ji} t}$ we get $E = -\frac{\partial \mathbf{A}}{\partial t} = i \omega_{ji} \mathbf{A}$ so
\[
\hat{H}' = i e \omega_{ji} \hat{r} \cdot \left( -\frac{i E}{\omega_{ji}} \right) = e \hat{r} \cdot E = -(e \hat{r}) \cdot E = -\hat{d} \cdot E
\]
with $\hat{d} = -e \hat{r}$ the dipole moment of the electron. This is referred to as the length form of the interaction. Although approximations were made in going from the velocity to length forms, for the great majority of problems they give identical answers. We will mostly use the length form.

**Selection rules**

Transitions between atomic states driven by the perturbation $\hat{H}' = -\hat{d} \cdot E$ are referred to as electric dipole transitions. Writing the position operator as $\hat{r} = \sum_q \hat{r}_q e_q^*\rangle$ the matrix element between fine structure states $|nls; jm\rangle$ is
\[
\langle n'ls'; j'm' | \hat{r} | nls; jm \rangle = e E \cdot \sum_q e_q^* \langle n'ls'; j'm' | \hat{r}_q | nls; jm \rangle
\]
\[
= e E \cdot \sum_q e_q^* \langle n'ls'; j'm' | \hat{r} | nls\rangle \frac{C_{j'm'}}{\sqrt{2j'+1}} C_{j1m}^*.
\]
The position operator $\hat{r}$ does not act on spin degrees of freedom so the reduced matrix element is, using Eq. (A-50),
\[
\langle n'ls'; j'm' | \hat{r} | nls\rangle = \delta_{ss'}(-1)^{j+l'+j'+1} \sqrt{(2j+1)(2j'+1)} S_{j1l'}^{lsj} \langle n'l' | \hat{r} | nl \rangle. \tag{3.21}
\]
The $6j$ symbol $S_{j1l'}^{lsj}$ can be nonzero only if $l, 1, l'$ and $j', 1, j$ both satisfy a triangle condition which says that $|l' - l| \leq 1$ and $|j' - j| \leq 1$. In addition the operator $\hat{r}$ has odd parity so the matrix element can only be nonzero if the initial and final states have opposite parity. This, combined with the requirement that $|l' - l| \leq 1$, says that $l' = l \pm 1$. To summarize the selection rules are
\[
|m' - m| \leq 1,
|j' - j| \leq 1, \quad j, m = 0 \to j, m = 0 \text{ forbidden},
l' = l \pm 1,

s' = s.
\]
These rules are valid for one electron atoms, i.e. hydrogen and atoms with a single valence electron outside a closed shell. We will consider the more general case of multielectron states later.
3.4 Stark effect

3.4.2 Quadratic Stark effect

We now wish to calculate the response of an atomic state to the perturbation $\hat{H} = -\hat{d} \cdot \mathbf{E}$ when $\mathbf{E}$ is a constant field. We will return to the more complicated case of an oscillating in time field in a later chapter.

It is convenient to describe the energy shift in terms of the polarizability of the atom. The energy of a fixed dipole $d$ in a field $E$ is given by the classical expression $-Ed$. When the dipole is induced we write $d(E) = \alpha E$, with $\alpha$ the polarizability. The energy of the dipole must then be modified to account for the energy expended by the field in creating the dipole. The Stark energy in this case is

$$U = -E \int_0^E dE' d(E') = -\frac{1}{2} \alpha E^2. \quad (3.22)$$

As we will see the angular momentum structure of atoms complicates this picture since the energy shift depends on both the magnitude and the direction of the applied field. We will account for this by introducing a tensor polarizability.

From 2nd order perturbation theory we have for the change in energy of state $|a\rangle = |n_a l_a j_a m_a\rangle$ (we suppress $s$ in the state labeling since it will be spectator in the Stark interaction)

$$\Delta U_a = U_a(E) - U_a(0) = \langle a| \hat{H}|a\rangle + \sum_{b \neq a} \frac{|\langle b| \hat{H}|a\rangle|^2}{U_a - U_b}. \quad (3.23)$$

Since $|jm\rangle$ has definite parity the first order matrix element is $\langle j_a m_a| \hat{H}|j_a m_a\rangle = 0$. The exception is when there are degenerate states with opposite parity, in which case there is a linear Stark effect. We will take this up in the next section and first proceed with the quadratic Stark effect

$$\Delta U_a = \sum_{b \neq a} \frac{|\langle b| \hat{H}|a\rangle|^2}{U_a - U_b}. \quad (3.24)$$

Note that if $|a\rangle$ is the ground state then $U_b > U_a$ and the energy shift is always negative. In principle the sum extends over all discrete and continuum states. Let us take a closer look at the sum over states and rewrite it as

$$\sum_{b \neq a} \frac{\langle a| \hat{H}^\dagger|b\rangle \langle b| \hat{H}|a\rangle}{U_a - U_b} = \sum_{b \neq a} \frac{\langle a| (E \cdot \hat{d})^\dagger|b\rangle \langle b| E \cdot \hat{d}|a\rangle}{U_a - U_b}$$

$$= \sum_{b \neq a} \frac{\langle a| (E \cdot \hat{d})^\dagger|b\rangle \langle b| E \cdot \hat{d}|a\rangle}{U_a - \hat{H}_0}$$

$$= \sum_b \frac{\langle a| (E \cdot \hat{d})^\dagger|b\rangle \langle b| E \cdot \hat{d}|a\rangle}{U_a - \hat{H}_0}$$

$$= \langle a| \hat{H}_{E1}|a\rangle. \quad (3.24)$$

In passing from the first to the second lines we used the identity $f(\hat{H}_0)|b\rangle = f(U_b)|b\rangle$ where $f$ is an arbitrary function and $\hat{H}_0|b\rangle = U_b|b\rangle$. In passing from the 2nd to the 3rd lines in (3.24) we used the fact that $\langle n_a l_a j_a m_a| \hat{d} \cdot \mathbf{E}|n_a l_a j_a m_a\rangle = 0$ so the sum can be extended over
all $b$, and then used $\sum_b |n_b l_b j_b m_b\rangle\langle n_b l_b j_b m_b| = \mathbb{I}$ to arrive at the effective electric dipole ($E_1$) operator

$$\hat{H}_{E_1} = (\mathbf{E} \cdot \hat{d})^\dagger \frac{1}{U_a - \hat{\mathcal{H}}_0} (\mathbf{E} \cdot \hat{d}) = (\mathbf{E}^* \cdot \hat{d}) \left( \mathbf{E} \cdot \frac{1}{U_a - \hat{\mathcal{H}}_0} \hat{d} \right).$$

(3.25)

We then use the identity (A-60)

$$(\hat{S}_{k_1} \cdot \hat{T}_{k_1})(\hat{U}_{k_2} \cdot \hat{V}_{k_2}) = \sum_k (-1)^{k-k_1-k_2} \left\{ \hat{S}_{k_1} \otimes \hat{U}_{k_2} \right\}_k \cdot \left\{ \hat{T}_{k_1} \otimes \hat{V}_{k_2} \right\}_k$$

which is valid provided all components of $\hat{T}_{k_1}$ and $\hat{U}_{k_2}$ commute. Applying this identity to (3.25) we find

$$\hat{H}_{E_1} = \sum_{k=0}^2 (-1)^k \{ \mathbf{E}^* \otimes \mathbf{E} \}_k \cdot \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{\mathcal{H}}_0} \hat{d} \right\}_k.$$  

(3.26)

This recoupling of the operators isolates the field dependent term from the dipole operators which act on the atomic degrees of freedom. The Hamiltonian is seen to be the sum of three terms with $k = 0, 1, 2$. The field dependent parts with $q = 0$ are

$$\{ \mathbf{E}^* \otimes \mathbf{E} \}_0 = -\frac{1}{\sqrt{3}} \mathbf{E}^* \cdot \mathbf{E} = -\frac{E^2}{\sqrt{3}},$$

$$\{ \mathbf{E}^* \otimes \mathbf{E} \}_1 = \frac{i}{\sqrt{2}} (\mathbf{E} \times \mathbf{E}^*) \cdot \mathbf{e}_z = 0,$$

$$\{ \mathbf{E}^* \otimes \mathbf{E} \}_2 = -\frac{1}{\sqrt{6}} [E^2 - 3(E \cdot \mathbf{e}_z)(E^* \cdot \mathbf{e}_z)] = -\frac{1}{\sqrt{6}} (E^2 - 3E_z^2).$$

When $\mathbf{E}$ is an oscillating field it is possible to have $\mathbf{E}$ and $\mathbf{E}^*$ not parallel to each other so that the $k = 1$ term is not zero. For the static case we are considering here the field is real and $\mathbf{E} \times \mathbf{E}^* = 0$. There are also components $k = 2, q = \pm 1, \pm 2$ which we will not need for perturbative calculation of energy shifts.

Using the definition of the scalar product we find from (3.26)

$$\hat{H}_{E_1} = -\frac{E^2}{\sqrt{3}} \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{\mathcal{H}}_0} \hat{d} \right\}_0 - \frac{1}{\sqrt{6}} (E^2 - 3E_z^2) \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{\mathcal{H}}_0} \hat{d} \right\}_2.$$  

(3.27)
The atomic dipole operator terms simplify as follows. We have

\[
\langle n_{a,j_a,m_a} \left| \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{H}_0} \hat{d} \right\} \right| n_{a,j_a,m_a} \rangle = \sum_{qr} C_{1q1r}^{00} \langle n_{a,j_a,m_a} | \hat{d}_{1q} \frac{1}{U_a - \hat{H}_0} \hat{d}_{1r} | n_{a,j_a,m_a} \rangle \\
= \sum_{qrn'} C_{1q1r}^{00} \langle n_{a,j_a,m_a} | \hat{d}_{1q} | n'' j'' m'' \rangle \langle n'' j'' m'' | \frac{1}{U_a - \hat{H}_0} | n' j' m' \rangle \langle n' j' m' | \hat{d}_{1r} | n_{a,j_a,m_a} \rangle \\
= \sum_{qrn'} C_{1q1r}^{00} \langle n_{a,j_a,m_a} | \hat{d}_{1q} | n' j' m' \rangle \frac{1}{U_a - U'} \langle n' j' m' | \hat{d}_{1r} | n_{a,j_a,m_a} \rangle \\
= \sum_{qrn'} C_{1q1r}^{00} \frac{\langle n_{a,j_a} | \hat{d} | n' j' \rangle \langle n' j' | \hat{d} | n_{a,j_a} \rangle}{U_a - U'} C_{j' m' 1q}^{j a m a 1r} C_{j' m' 1q}^{j a m a 1r} \sqrt{(2j_a + 1)(2j' + 1)} \\
= \frac{1}{\sqrt{3}(2j_a + 1)} \sum_{n',j'} (-1)^{j_a - j'} \frac{|\langle n' j' | \hat{d} | n_{a,j_a} \rangle|^2}{\sqrt{2j' + 1}(U_a - U')} \times \left( -C_{j' m' a 10}^{j a m a 10} C_{j' m' a 10}^{j a m a 10} + C_{j' m' a 11}^{j a m a 11} C_{j' m' a 11}^{j a m a 11} C_{j' m' a 11}^{j a m a 11} - (-1)^{j_a - j'} \frac{\sqrt{2j' + 1}}{\sqrt{2j_a + 1}} \right)
\]

It can be shown that

\[-C_{j' m' a 10}^{j a m a 10} C_{j' m' a 10}^{j a m a 10} + C_{j' m' a 11}^{j a m a 11} C_{j' m' a 11}^{j a m a 11} C_{j' m' a 11}^{j a m a 11} = (-1)^{j_a - j'} \frac{\sqrt{2j' + 1}}{\sqrt{2j_a + 1}}\]

for \(j' = j_a, j_a \pm 1\). Thus

\[
\langle n_{a,j_a,m_a} \left| \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{H}_0} \hat{d} \right\} \right| n_{a,j_a,m_a} \rangle = \frac{1}{\sqrt{3}(2j_a + 1)} \sum_{n',j'} \frac{|\langle n' j' | \hat{d} | n_{a,j_a} \rangle|^2}{U' - U_a}
\]

and we define the scalar polarizability by

\[
\alpha_0 = \frac{2}{\sqrt{3}} \langle n_{a,j_a,m_a} \left| \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{H}_0} \hat{d} \right\} \right| n_{a,j_a,m_a} \rangle = \frac{2}{3(2j_a + 1)} \sum_{n',j'} \frac{|\langle n' j' | \hat{d} | n_{a,j_a} \rangle|^2}{U' - U_a}.
\]

Following a similar procedure we find

\[
\langle j_{m_a} | \left\{ \hat{d} \otimes \frac{1}{U_a - \hat{H}_0} \hat{d} \right\} | j_{m_a} \rangle = \sum_{q r n' j'' m''} C_{1q1r}^{20} \frac{\langle n' j' | \hat{d} | n_{a,j_a} \rangle^2}{\sqrt{(2j_a + 1)(2j' + 1)(U_a - U')} C_{j' m' 1q}^{j a m a 1r} C_{j' m' 1q}^{j a m a 1r}} \\
= \frac{\sqrt{6}}{4} m_a^2 - j_a(j_a + 1) \frac{\alpha_2}{j_a(2j_a - 1)}.
\]
with the tensor polarizability

\[ \alpha_2 = \left[ \frac{40(2j_a - 1)j_a}{3(2j_a + 3)(2j_a + 1)(j_a + 1)} \right]^{1/2} \sum_b (-1)^{j_a + j_b} S_{j_a j_b}^{j_a 1} \frac{\langle n_b j_b | \hat{d} | n_a j_a \rangle^2}{U_b - U_a}. \] (3.30)

The scalar polarizability \( \alpha_0 \) exists for all \( j_a \) while the tensor polarizability \( \alpha_2 \) is nonzero only when \( j_a \geq 1 \).

With the above definitions of \( \alpha_0, \alpha_2 \) the energy shift of the atomic state is

\[ \Delta U = -\frac{E_z^2}{2} \alpha_0 + \frac{E_z^2 - 3E_z^2}{4} \frac{3m_a^2 - j_a(j_a + 1)}{j_a(2j_a - 1)} \alpha_2. \] (3.31)

The introduction of the polarizabilities \( \alpha_0, \alpha_2 \) provides an analogy with the classical expression for the energy of an induced dipole in an electric field. The tensor polarizability has been defined such that when \( E = E_z \) and \( m_a = j_a \) the energy shift is

\[ \Delta U = -\frac{E_z^2}{2} (\alpha_0 + \alpha_2). \]

The above expressions for polarizability are in cgs units for which \( \alpha \) has dimensions of a volume. Notice that \( \sum m_a [3m_a^2 - j_a(j_a + 1)] = 0 \) so the tensor term introduces differential shifts depending on \( m_a^2 \) but does not change the average energy. Equation (3.31) looks the same in SI units but with \( \alpha_{SI} = 4\pi \epsilon_0 \alpha_{cgs} \).

**Polarizability of hydrogen**

As an example let us calculate the polarizability of the hydrogen ground state. The ground state has \( j = 1/2 \) so \( \alpha_2 = 0 \) and we only need

\[ \alpha_0 = \frac{1}{3} \sum_b \frac{\langle n_b j_b | \hat{d} | 1, 1/2 \rangle^2}{U_b - U_g}. \]

Since the hydrogenic integrals can be calculated analytically there is a closed form expression for the sum (see Bethe & Salpeter) and the result is \( \alpha_0 = \frac{9}{2} a_0^3 \), which is roughly the “volume” of the atom. This can be compared with the classical result for a conducting sphere of radius \( a_0 \) which has \( \alpha = a_0^3 \).

Instead of doing the exact calculation let’s see how we can get a pretty good estimate with little work. It is convenient to use the definition (3.23)

\[ \Delta U = e^2 E_z^2 \sum_{n=2}^{\infty} \frac{|\langle nlm | z | 100 \rangle|^2}{U_g - U_n}. \]

For simplicity we neglect fine structure and assume a \( e_z \) polarized field (since \( \alpha_2 = 0 \) the direction of the field does not matter). With these approximations the polarizability is

\[ \alpha_0 = -2e^2 \sum_{n=2}^{\infty} \frac{|\langle nlm | z | 100 \rangle|^2}{U_g - U_n} = 2e^2 \sum_{n=2}^{\infty} \frac{|\langle n10 | z | 100 \rangle|^2}{U_n - U_g}. \]
3.5 Linear Stark effect

We can estimate the infinite sum as follows. We have

\[
\frac{1}{U_n - U_g} = -\frac{2}{E_H} \left( \frac{1}{n^2} - 1 \right) = \frac{2}{E_H} \frac{n^2}{n^2 - 1} \leq \frac{8}{3E_H}
\]

so

\[
\alpha_0 \leq \frac{16}{3} \frac{e^2}{E_H} \sum_{n=2}^{\infty} |\langle n10|z|100 \rangle|^2.
\]

The sum is

\[
\sum_{n=2}^{\infty} |\langle n10|z|100 \rangle|^2 = \sum_{n=2}^{\infty} \langle 100|z|n10 \rangle \langle n10|z|100 \rangle
\]

\[
= \sum_{n=1}^{\infty} \sum_{lm} \langle 100|z|nlm \rangle \langle nlm|z|100 \rangle
\]

\[
= \langle 100|z^2|100 \rangle
\]

\[
= a_0^2.
\]

Thus

\[
\alpha_0 \leq \frac{16}{3} \frac{e^2}{E_H} a_0^2 = \frac{16}{3} a_0^3 \simeq 5.3 a_0^3.
\]

This is fairly close to the exact value \(\alpha_0 = 4.5 a_0^3\).

We might expect to calculate the exact value by summing the series

\[
\alpha_0 = 2e^2 \sum_{n=2}^{\infty} \frac{|\langle n10|z|100 \rangle|^2}{U_n - U_g}.
\]

Numerical evaluation of the sum through \(n = 10\) gives

\[
\alpha_0 \simeq 3.63.
\]

This is indeed an accurate estimate for the sum. Using the Gordon formula for radial matrix elements\(^5\) we find

\[
\alpha_0 = \frac{1024}{3} \sum_{n=2}^{\infty} \frac{n^9(n - 1)^{2n-6}}{(n + 1)^{2n+6}} = 3.6633
\]

which is only 81.3% of the exact value. The discrepancy lies in the fact that we are neglecting coupling to continuum states. This cannot be ignored since the field perturbation gives a finite probability for the electron to tunnel out of the Coulomb potential at large negative \(z\). Including coupling to the continuum states gives the exact result.

3.5 Linear Stark effect

The quadratic Stark effect is dominant because atomic eigenstates have definite parity and no permanent dipole moment. The dipole moment is therefore induced, and we get an energy shift which is quadratic in the field strength. The situation is different if there are
interactions with static electromagnetic fields. This occurs in excited fine structure levels. Consider the hydrogen \( n = 2 \) level which is split into \( 2s_{1/2}, 2p_{1/2}, 2p_{3/2} \), as shown in Fig. 3.4. Let’s consider first the interaction of \( 2s_{1/2}, 2p_{1/2} \) and label the states \( |1\rangle = |2p_{1/2}, m = 1/2\rangle, |2\rangle = |2p_{1/2}, m = -1/2\rangle, |3\rangle = |2s_{1/2}, m = 1/2\rangle, |4\rangle = |2s_{1/2}, m = -1/2\rangle \). In this basis the Hamiltonian is

\[
\hat{H} = \hbar \begin{pmatrix}
-L & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & -L & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix} + eE \begin{pmatrix}
0 & r_{13} & r_{14} & 0 \\
0 & 0 & r_{23} & r_{24} \\
r_{13} & r_{23} & 0 & 0 \\
r_{14} & r_{24} & 0 & 0
\end{pmatrix}.
\] (3.32)

The transition matrix elements are only nonzero between opposite parity \( s \) and \( p \) states. If we assume a \( z \) polarized field the selection rule on \( m \) is \( \Delta m = 0 \) so \( r_{14} = r_{23} = 0 \). We are left with

\[
\begin{align*}
    r_{13} &= \langle 3 | z | 1 \rangle = \frac{\langle 2s_{1/2}|| 2p_{1/2} \rangle}{\sqrt{2}} C_{1/2,1/2,0}^{1/2,1/2,1/2} = \frac{\langle 2s_{1/2}|| 2p_{1/2} \rangle}{\sqrt{6}}, \\
    r_{24} &= \langle 4 | z | 2 \rangle = \frac{\langle 2s_{1/2}|| 2p_{1/2} \rangle}{\sqrt{2}} C_{1/2,-1/2,0}^{1/2,-1/2,1/2} = -\frac{\langle 2s_{1/2}|| 2p_{1/2} \rangle}{\sqrt{6}}.
\end{align*}
\]

The reduced matrix element is

\[
\langle 2s_{1/2}|| 2p_{1/2} \rangle = -2S_{1/2,1/2}^{1/2,1/2,1/2} \int_0^\infty dr r^3 R_{20} R_{21} = -\frac{2}{\sqrt{6}} \int_0^\infty dr r^3 R_{20} R_{21}.
\]

The radial wavefunctions are

\[
R_{20} = \frac{1}{a_0^{3/2}} \frac{1 - (2a_0)}{2^{1/2}} e^{-r/(2a_0)},
\]

\[
R_{21} = \frac{1}{a_0^{3/2}} \frac{r / (2a_0)}{6^{1/2}} e^{-r/(2a_0)}.
\]

\[
\begin{array}{cccccc}
2p_{3/2} & 8 & 7 & 6 & 5 \\
-3/2 & 1/2 & 1/2 & 3/2 \\
9910 MHz
\end{array}
\]

\[
\begin{array}{cccc}
2s_{1/2} & 4 & 3 \\
L=1058 MHz
\end{array}
\]

\[
\begin{array}{cccc}
2p_{1/2} & 2 & 1 & 1/2 \\
-1/2 & 1/2 \\
m
\end{array}
\]

Figure 3.4: Stark effect in H \( 2s_{1/2}, 2p_{1/2}, 2p_{3/2} \) fine structure states.
3.5 Linear Stark effect

Figure 3.5: Stark effect in H 2s_{1/2}, 2p_{1/2} fine structure states.

and the radial integral evaluates to $-3^{3/2}a_0$. The reduced matrix element is therefore $3^{1/2}a_0$ and the matrix elements are $\pm\sqrt{3}a_0$. The Stark Hamiltonian including the Lamb shift is then

$$\hat{\mathcal{H}} = h \begin{pmatrix} -\mathcal{L} & 0 & 0 & 0 \\ 0 & -\mathcal{L} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} + \sqrt{3}e a_0 E \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}.$$ (3.33)

The eigenvalues are

$$U_1 = U_2 = \frac{-h\mathcal{L} - \sqrt{h^2\mathcal{L}^2 + 4U_s^2}}{2} \approx -h\mathcal{L} - U_s,$$

$$U_3 = U_4 = \frac{-h\mathcal{L} + \sqrt{h^2\mathcal{L}^2 + 4U_s^2}}{2} \approx +U_s.$$

Here we have introduced the Stark energy $U_s = \sqrt{3}e a_0 E$. When $U_s \gg h\mathcal{L}$ we get a linear Stark shift as can be seen in Fig. 3.5. The characteristic field strength for which a linear shift emerges is

$$E_0 = \frac{h\mathcal{L}}{\sqrt{3}e a_0} = 58.5 \text{ kV/m} = 585 \text{ V/cm}.$$

This is a modest field that can be applied without ionizing the atom.

The reason for the linear Stark effect is that the field mixes the odd parity states creating superpositions which have an effective permanent dipole moment. When $U_s \gg h\mathcal{L}$ the eigenvectors are

$$|u_\pm\rangle = \frac{|1\rangle \pm |3\rangle}{\sqrt{2}},$$

$$|v_\pm\rangle = \frac{|2\rangle \pm |4\rangle}{\sqrt{2}}.$$
These states have a nonzero dipole moment since
\[ \langle u_+|z|u_+ \rangle = \frac{\langle 1|z|1 \rangle + \langle 3|z|1 \rangle + \langle 1|z|3 \rangle + \langle 3|z|3 \rangle}{2} = \frac{\langle 3|z|1 \rangle + \langle 1|z|3 \rangle}{2} = \sqrt{3}a_0 \]
(3.34)

and
\[ \langle u_-|z|u_- \rangle = \frac{\langle 1|z|1 \rangle - \langle 3|z|1 \rangle - \langle 1|z|3 \rangle + \langle 3|z|3 \rangle}{2} = -\sqrt{3}a_0. \]
(3.35)

In other words these superpositions correspond to the electron being displaced to either positive or negative \( z \). The effective permanent dipole couples to the external field to give a linear shift.

Of course when \( U_s \ll \hbar \mathcal{L} \) the Stark effect gives a quadratic shift as in the previous section. The reader may wonder why there was no crossover to a linear shift in the previous discussion. The quadratic Stark effect becomes linear when the Stark shifts are large enough to create substantial admixtures of opposite parity states. For states separated by optical frequencies the required fields are huge, large enough to ionize the atom. The difference here is that the fine structure and QED splittings are small so the field needed to go from a quadratic to a linear shift is relatively small.

The above calculation neglects the \( 2p_{3/2} \) states. Including them we have a total of 8 states and we get a larger effect. For very detailed comparison of theory and experiment it would also be necessary to include the hyperfine structure in the calculations which would give a total of 16 states in the \( n = 2 \) level.

### 3.6 Stark effect in hyperfine structure

In order to calculate the Stark shift of individual hyperfine levels we need to evaluate \( \alpha_0, \alpha_2 \) in the coupled hyperfine basis. For the scalar polarizability we start with (3.28) and replace the sum over fine structure states with a sum over hyperfine states so
\[ \alpha_0^{(F)} = \frac{2}{3(2f_a + 1)} \sum_{n_j \neq f} \frac{|\langle n'j'|I f' || d || n_a j a I f_a \rangle|^2}{U' - U_a}. \]

After angular decoupling it can be shown that \( \alpha_0^{(F)} = \alpha_0^{(J)} \) with \( \alpha_0^{(J)} \) given by (3.28). For the tensor polarizability we find
\[ \alpha_2^{(F)} = \alpha_2^{(J)} \frac{3K(K - 1) - 4F(F + 1)J(J + 1)}{(2F + 3)(2F + 2)F(2F - 1)J(2J - 1)}. \]
where \( K = F(F + 1) + J(J + 1) - I(I + 1) \) and \( \alpha^{(J)}_2 \) is defined by (3.30). The energy shift of a hyperfine Zeeman state is
\[
\Delta U(F, M_F) = -\frac{E^2}{2} \alpha^{(F)}_0 + \frac{E^2 - 3E_2^2 M_F^2 - F(F + 1)}{F(2F - 1)} \alpha^{(F)}_2.
\]

### 3.7 Blackbody radiation induced level shifts

Atomic energy levels are shifted not only by applied external fields but also due to background blackbody radiation. This effect turns out to be important for atomic clocks\[20\]. If the two levels used to define a clock transition have different polarizabilities there will be a temperature dependent shift of the clock frequency. This is commonly referred to as a BBR shift and it represents one of the leading limitations to the accuracy of modern atomic clocks. For microwave frequency clocks such as the hydrogen 21 cm transition or the Cs microwave clock the participating hyperfine levels are connected with a \( j = 1/2 \) state so the tensor polarizability vanishes. This implies that all \( |F, M_F\rangle \) states have the same Stark shift, which would not appear to disturb the clock frequency. However, there are small tensor effects which arise at third order in perturbation theory accounting for a 2nd order interaction with the electric field and a first order hyperfine interaction.

In principle this effect should be calculated using the dynamic polarizability. However the Stark effect in atomic ground states is dominated by transitions to excited states with energies corresponding to an optical wavelength transition. The spectrum of blackbody radiation is at much lower frequencies and we can approximate the atomic response using the static polarizability. Detailed calculations\[21\] predict that in Cs the \( F = 3 \) and \( F = 4 \) static polarizabilities differ by
\[
k_s = -\frac{1}{2} [\alpha_0(F = 4) - \alpha_0(F = 3)] = -2.27 \times 10^{-10} \text{ Hz/(V/m)}^2.
\]
This implies a differential clock shift
\[
\frac{\delta \nu_{\text{BBR}}}{\nu_0} = \frac{1}{2} \frac{\alpha_0(F = 4) - \alpha_0(F = 3)}{\hbar \nu_0} \langle E^2 \rangle = \beta \left( \frac{T \ [K]}{300} \right)^4
\]
where \( \beta \) is a sensitivity coefficient which can be used to compare different clocks.

Let us see how well we can estimate \( k_s \) using a simplified approach. The main contribution to the polarizability of the Cs \( 6s_{1/2} \) ground state comes from the resonance lines \( 6s - 6p_{3/2} \) at 852 nm and \( 6s - 6p_{1/2} \) at 894 nm. Adding the contributions from these transitions we get
\[
\alpha_0 = \frac{1}{3} \left( \frac{|\langle 6p_{1/2} | d | 6s_{1/2} \rangle|^2}{U_{6p_{1/2}}} + \frac{|\langle 6p_{3/2} | d | 6s_{1/2} \rangle|^2}{U_{6p_{3/2}}} \right).
\]
We can approximate the differential hyperfine response by making the substitutions \( U_{6p_{1/2,3/2}} \rightarrow U_{6p_{1/2,3/2}} - \Delta U_{\text{hf}}(3, 4) \). We thus get
\[
\alpha_0(F = 3) \approx \frac{1}{3} \left( \frac{|\langle 6p_{1/2} | d | 6s_{1/2} \rangle|^2}{U_{6p_{1/2}} - \Delta U_{\text{hf}}(3)} + \frac{|\langle 6p_{3/2} | d | 6s_{1/2} \rangle|^2}{U_{6p_{3/2}} - \Delta U_{\text{hf}}(3)} \right),
\]
\[
\alpha_0(F = 4) \approx \frac{1}{3} \left( \frac{|\langle 6p_{1/2} | d | 6s_{1/2} \rangle|^2}{U_{6p_{1/2}} - \Delta U_{\text{hf}}(4)} + \frac{|\langle 6p_{3/2} | d | 6s_{1/2} \rangle|^2}{U_{6p_{3/2}} - \Delta U_{\text{hf}}(4)} \right).
\]
For Cs $\Delta U_{hf}(3) = -5.171$ GHz, $\Delta U_{hf}(4) = 4.022$ GHz, $U_{6p_{1/2}} = 335.12$ THz, $U_{6p_{3/2}} = 351.73$ THz. The reduced matrix elements are $\langle 6p_{1/2} | d | 6s_{1/2} \rangle = 3.19 e a_0$, $\langle 6p_{3/2} | d | 6s_{1/2} \rangle = 4.48 e a_0$. These can be calculated using Coulomb wave functions or extracted from measured lifetimes. Putting in the numbers we find

$$\alpha_0(F = 3) = 28.4138 \times 10^{-24} \text{ cm}^3$$

$$\alpha_0(F = 4) = 28.4145 \times 10^{-24} \text{ cm}^3$$

and

$$k_s = -0.63 \times 10^{-10} \text{ Hz/(V/m)}^2.$$  

This is a factor of 3.6 too small, but gives the correct order of magnitude of the effect. There are several reasons why our result is inaccurate. First we have only included the $6p$ levels. Accounting also for $np$ with $n > 6$ will give a little larger effect. More importantly we are accounting for the energy shifts due to the hyperfine interaction but are not including the state mixing. From perturbation theory

$$|a\rangle = |a^{(0)}\rangle + \sum_{b \neq a} \frac{\langle b^{(0)} | \hat{H}_{hf} | a^{(0)} \rangle}{U_{a}^{(0)} - U_{b}^{(0)}} |b^{(0)}\rangle.$$  

The state mixing due to the hyperfine interaction defined in Eq. (2.6) has not been accounted for in this simple approach.

The strength of the blackbody field can be found from the Planck distribution. In engineering units it is

$$\langle E \rangle^2 = (831.9 \text{ V/m})^2 \left( \frac{T \text{ [K]}}{300} \right)^4.$$  

At 300 K the shift of the $6s_{1/2}$ level is

$$\Delta U_{6s}/h = 690 \text{ kHz}$$

while the differential shift is

$$\left( \Delta U_{6s,F=4} - \Delta U_{6s,F=3} \right)/h = 4.4 \times 10^{-5} \text{ Hz}.$$  

This implies $\beta = 4.8 \times 10^{-15}$. The best known clock candidate, as regards BBR shifts, is the Al$^+$ clock which has $\beta$ three orders of magnitude smaller. The sensitivity to BBR shifts has motivated work towards putting atomic clocks inside cryostats since $\frac{d}{dt} \frac{\delta \nu_{BBR}}{\nu_0} \sim \beta T^3$. Reducing $T$ from 300 K to 4 K in a He cryostat reduces the sensitivity to temperature fluctuations by a factor of $(4/300)^3 = 2.4 \times 10^{-6}$. 


Chapter 4

Interactions with oscillating fields

4.1 Einstein’s 1917 theory

Einstein’s 1917 paper, written four years after Bohr’s theory of the atom and eight years before the invention of modern quantum mechanics, established a theoretical framework that is still valuable today. The theory predates quantum mechanics, yet it uses essentially quantum mechanical notions of transitions between stationary states, and is fully consistent with later results of quantum theory. Einstein considered a two-level atom with lower level 1 and upper level 2 interacting with a radiation field with energy density \( \rho \omega \) per unit frequency interval. Einstein assumed the density of atoms in the two levels was \( N_1 \) and \( N_2 \) and postulated the following rate equations

\[
\frac{dN_1}{dt} = AN_2 - B_{2\rightarrow 1} \rho \omega N_1 + B_{1\rightarrow 2} \rho \omega N_2, \tag{4.1a}
\]

\[
\frac{dN_2}{dt} = -AN_2 + B_{2\rightarrow 1} \rho \omega N_1 - B_{1\rightarrow 2} \rho \omega N_2. \tag{4.1b}
\]

As shown in Fig. 4.1 \( A \) is the rate for spontaneous decay from level 2 \( \rightarrow \) 1, \( B_{2\rightarrow 1} \) is the coefficient for induced absorption of a photon resulting in a transition from 1 \( \rightarrow \) 2, and \( B_{1\rightarrow 2} \) is the coefficient for induced emission of a photon resulting in a transition from 2 \( \rightarrow \) 1. Note that the total atomic density is conserved since \( \dot{N}_1 + \dot{N}_2 = 0 \). The units of the quantities appearing in the above equations are \( [N_1] = [N_2] = m^{-3}, [A] = s^{-1}, [B] = m^3 J^{-1} s^{-2}, \) and \( [\rho \omega] = J s m^{-3} \).

![Figure 4.1: Two level atom and transitions due to Einstein A, B coefficients.](image)

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In thermal equilibrium the populations are governed by Boltzmann factors,

\[ N_1 = \frac{e^{-U_1/k_BT}}{Z}, \quad N_2 = \frac{e^{-U_2/k_BT}}{Z}, \]

with \( Z = e^{-U_1/k_BT} + e^{-U_2/k_BT} \). Since the populations are stationary (\( \dot{N}_i = 0 \)) we can also write

\[ A = \left( B_{2\rightarrow1} \frac{N_1}{N_2} - B_{1\rightarrow2} \right) \rho_\omega = \left( B_{2\rightarrow1} e^{U_{21}/k_BT} - B_{1\rightarrow2} \right) \rho_\omega \]

where \( U_{21} = U_2 - U_1 \) is the energy difference between the two states.

The equilibrium radiation density is also a function of temperature. It can be written as \( \rho_\omega = \hbar \omega n_\omega f(T) \) where \( \hbar \omega \) is the energy of a photon with frequency \( \omega \), \( n_\omega \) is the density of states in frequency space, and \( f(T) \) gives the excitation number of each state at temperature \( T \). From a classical counting of modes, including a factor of two for two orthogonal polarization states, \( n_\omega = \omega^2/\pi^2 c^3 \). Since photons are spin 1 bosonic particles they satisfy Bose-Einstein statistics and \( f(T) = \frac{1}{e^{\hbar \omega/k_BT} - 1} \) which corresponds to the temperature dependence of Planck’s blackbody spectrum.

Einstein used the assumption of thermal equilibrium between radiation and matter to give a very simple derivation of \( f(T) \) and the Planck spectrum. We note that the A coefficient satisfies

\[ A = \frac{\hbar \omega^3}{\pi^2 c^3} (B_{2\rightarrow1} e^{U_{21}/k_BT} - B_{1\rightarrow2}) f(T). \]

We now require that all three unknowns \( A, B_{2\rightarrow1}, \) and \( B_{1\rightarrow2} \) are constants that do not depend on temperature. These constants depend on the microscopic details of the radiation - matter interaction and quantum mechanics is needed to calculate them. With the additional assumption that the stimulated rates are the same for absorption and emission, \( B_{2\rightarrow1} = B_{1\rightarrow2} \), we get

\[ A = \frac{\hbar \omega^3}{\pi^2 c^3} B_{2\rightarrow1} \left( e^{U_{21}/k_BT} - 1 \right) f(T). \]

In order for \( A \) and \( B_{2\rightarrow1} \) to be independent of \( T \) we require

\[ f(T) = \frac{1}{e^{U_{21}/k_BT} - 1} \]

so that\(^1\)

\[ A = \frac{\hbar \omega^3}{\pi^2 c^3} B_{2\rightarrow1}. \quad (4.2) \]

It follows that the radiation energy density per unit angular frequency is

\[ \rho_\omega = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{U_{21}/k_BT} - 1} = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{\hbar \omega/k_BT - 1}, \]

which is indeed the Planck spectrum. Note that if we had assumed the Planck spectrum instead of deriving it, the requirement that \( A \) be constant would also have led to the equality of \( B_{1\rightarrow2} \) and \( B_{2\rightarrow1} \).

\(^1\)Equation (4.2) will contain different numerical factors if \( B \) is defined per unit Hz instead of per unit angular frequency as we have done. In that case using \( \rho_\nu = \rho_\omega \frac{\omega}{\nu} = 2\pi \rho_\omega \) we would have found \( A = 2\pi \frac{\hbar \omega^3}{\pi^2 c^3} B_{2\rightarrow1} = \frac{8\pi \hbar \omega^3}{c^3} B_{2\rightarrow1}. \)
Thus Einstein provided a simple derivation of the Planck law based on a few reasonable assumptions: 1) thermal equilibrium between matter and radiation, 2) the rates of atomic excitation and de-excitation are due to elementary processes of spontaneous emission, stimulated emission, and stimulated absorption, 3) the coefficients governing these rates are constants independent of temperature, and 4) the coefficients for stimulated emission and absorption are the same.

Degeneracy

When level 1 has degeneracy factor $g_1$ and level 2 has degeneracy $g_2$ Eq. (4.2) is modified to

$$g_2 A = \frac{\hbar \omega^3}{\pi^2 c^3} g_1 B_{2\rightarrow 1}$$

$$A = \frac{\hbar \omega^3}{\pi^2 c^3} g_1 B_{2\rightarrow 1} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{1\rightarrow 2}.$$

There are no degeneracy factors in the second equality since both sides refer to a transition from $2 \rightarrow 1$ and the factors cancel. We therefore see that

$$B_{2\rightarrow 1} = \frac{g_2}{g_1} B_{1\rightarrow 2}.$$

The $A$ and $B$ coefficients, as well as the relations between them, have been derived from an empirical model of the radiation-matter interaction and by appealing to concepts of classical statistical mechanics. In the following sections we will establish quantum expressions for these coefficients, and for the spectral dependence of the radiation-matter coupling strength. The main theoretical tools will be time dependent perturbation theory using an electric dipole approximation to the interaction Hamiltonian.

4.1.1 Absorption area law

A useful result for the absorption cross section of a weak optical beam can be derived as follows. In (4.1) we assume the radiation field is weak so $N_2 \ll N_1$. We then make the

$$I_\omega(\omega)$$

$$\sigma(\omega)$$

$$\delta\omega$$

$$\omega_{21}$$

Figure 4.2: Broad band light spectrum interacting with a narrowband resonance.
replacement $\rho_\omega \to I_\omega / c$, where $I_\omega$ is the optical intensity per unit frequency, with units of $[I_\omega] = J/m^2$. The rate at which atoms are excited by photon absorption is then

$$R_{2\rightarrow 1} = B_{2\rightarrow 1} \frac{I_\omega(\omega)}{c} N_1 = N_1 \frac{\pi^2 c^2}{\hbar^3} AI_\omega(\omega).$$

Let us now assume that the intensity has a finite width frequency spectrum. In other words the radiation is not monochromatic and the spectrum may be broad compared to the width of the absorption cross section, as seen in Fig. 4.2. The atomic absorption cross section $\sigma(\omega)$ is typically a strongly peaked function of frequency, with the peak absorption occurring when $\omega = \omega_{21}$ the frequency of the atomic transition. The units of the cross section are $[\sigma] = m^2$. The rate at which photons are absorbed per unit volume is found by integrating the product of the photon flux times the absorption cross section times the density of atoms to give

$$R_{\text{abs}} = \int d\omega \frac{I_\omega(\omega)}{\hbar \omega} \sigma(\omega) N_1.$$

Setting $R_{2\rightarrow 1} = R_{\text{abs}}$ gives

$$\int d\omega \frac{I_\omega(\omega)}{\hbar \omega} \sigma(\omega) = \frac{\pi^2 c^2}{\hbar \omega^3} AI_\omega(\omega). \quad (4.3)$$

Let us now assume that $\sigma(\omega)$ is strongly peaked at the transition frequency $\omega_{21} = U_{21}/\hbar$, such that the spectral width of the absorption cross section $\delta\omega$ satisfies $\delta\omega \ll \omega_{21}$. We also assume that the intensity spectrum can be approximated as a constant with value $I_\omega(\omega) = I_\omega(\omega_{21})$. Then

$$\int d\omega \frac{I_\omega(\omega)}{\hbar \omega} \sigma(\omega) \simeq \frac{I_\omega(\omega_{21})}{\hbar \omega_{21}} \int d\omega \sigma(\omega) \quad (4.4)$$

and comparison with (4.3) gives

$$\int d\omega \sigma(\omega) = \frac{\pi^2 c^2}{\omega_{21}^2} A. \quad (4.5)$$

We thus arrive at the area law relating the scattering cross section to the Einstein $A$ coefficient

$$\int d\omega \sigma(\omega) = \frac{\lambda_{21}^2}{4} A.$$

This is known as the absorption area theorem which can be used to estimate $A$ based on absorption measurements. It is particularly useful since it is independent of the type of transition involved and is valid not only for electric dipole allowed transitions, but also higher multipoles. We will show in what follows that $\delta\omega \sim A$ so that $\int d\omega \sigma(\omega) \sim \delta\omega \sigma(\omega_{21}) \sim A\sigma(\omega_{21})$ and $\sigma(\omega_{21}) \sim \lambda_{21}^2$. The resonant photon absorption cross section of an atom is order $\lambda^2$ which can be orders of magnitude larger than the geometrical size of the atom.

4.2 Resonant absorption due to narrowband radiation

In experiments with lasers the radiation often has a frequency spectrum that is narrow compared to the width of the atomic resonance. Let’s calculate the absorption rate per atom in this case.
4.2 Resonant absorption due to narrowband radiation

The situation is shown in Fig. 4.3. Radiation with field amplitude \( E(\omega) \) is absorbed by an atom in lower level \(|1\rangle\). After excitation to the upper level \(|2\rangle\) the atom decays and emits a photon. The lifetime of the upper level is \( \tau = 1/\alpha = 1/\gamma \), where we will use the symbol \( \gamma = \alpha \) to denote the linewidth of the transition. The energy-time uncertainty condition \( \Delta U \Delta t \sim \hbar \) then implies \( \Delta U \sim \hbar / \tau \sim \hbar \gamma \).

In order to make the expression for the energy uncertainty of the excited state precise we proceed as follows. When the atom is in the upper level it decays at rate \( \gamma \). Another way of saying this is that the rate of energy loss satisfies \( \frac{dU_2}{dt} = -\gamma U_2 \) which has the solution \( U_2(t) = U_2(0)e^{-\gamma t} \). From a quantum mechanical perspective the state of the atom is \( |\psi(t)\rangle = c_1(t)|1\rangle + c_2(t)e^{-i\omega_21t}|2\rangle \) with \( \omega_{21} = (U_2-U_1)/\hbar \). The energy in the excited state is proportional to the probability of occupying the state which is proportional to \( |c_2(t)|^2 \). The relation \( U_2(t) = U_2(0)e^{-\gamma t} \) then implies that

\[
c_2(t)e^{-i\omega_{21}t} = c_2(0)e^{-\gamma t/2}e^{-i\omega_{21}t}.
\]

We can Fourier decompose \( c_2(t) \) as

\[
c_2(\omega) \sim \int_0^\infty dt \, c_2(0)e^{-\gamma t/2}e^{-i\omega_{21}t}e^{i\omega t} = \frac{1}{\frac{\gamma}{2} - i(\omega - \omega_{21})}.
\]

The integral starts at \( t = 0 \) since we assume there is no population in the excited level at negative times. The magnitude squared of the coefficient is \( |c_2(\omega)|^2 = C \frac{1}{\Delta^2 + \Delta^2} \) with \( \Delta = \omega - \omega_{21} \) and \( C \) an as yet unknown normalization coefficient. To fix \( C \) we require that

\[
1 = \int_{-\infty}^{\infty} d\omega |c_2(\omega)|^2 = C \int_{-\infty}^{\infty} d\omega \frac{1}{\frac{\gamma^2}{4} + \Delta^2} = C \frac{2\pi}{\gamma}.
\]

Thus we get the normalized lineshape function

\[
L(\Delta) = |c_2(\omega)|^2 = \frac{\gamma}{2\pi} \frac{1}{\frac{\gamma^2}{4} + \Delta^2} = \frac{2}{\pi \gamma} \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}}.
\]

The calculation was formulated in terms of a decay process but we can equally well interpret the probability \( P_2 = |c_2(\omega)|^2 \) as the likelihood of a photon being absorbed, and the atom
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thereby excited, as a function of the frequency \( \omega \) of the radiation. We see that the absorption lineshape \( L(\Delta) \) is Lorentzian and falls off as \( 1/\Delta^2 \). The full width at half maximum (FWHM) of the lineshape is \( \delta \omega_{\text{FWHM}} = \gamma \) so when the radiation is detuned from resonance by \( \pm \gamma/2 \) the probability of absorption falls to 1/2 of the peak value.

When the radiation is detuned from the atomic transition frequency, \( \Delta = \omega - \omega_{21} \neq 0 \). For small detunings \( |\Delta| < \sim \gamma \) we may visualize the interaction as a photon of frequency \( \omega \) being absorbed and the atom excited to state \( |2\rangle \). When the atom subsequently decays a photon of energy \( \hbar \omega_{\text{sp}} \simeq \hbar \omega_{21} \) is spontaneously emitted. The absorbed and emitted photons need not have exactly the same energy. The difference in energy \( \hbar(\omega_{\text{sp}} - \omega) \) is taken up by a change in the center of mass energy of the atom after the absorption-emission event. This effect can be used for laser cooling as we will discuss later.

When the incident radiation is very far detuned this picture breaks down and we may think of the interaction as a scattering process where the incident and scattered photons have the same frequency. In the two-level approximation the atom ends up in the same internal state after the interaction so this is referred to as Rayleigh scattering, as opposed to Raman scattering which leaves the atom in a different internal state. Note that even in the case of Rayleigh scattering the center of mass atomic energy may change due to the different momenta \( \hbar k \) and \( \hbar k_{\text{sp}} \) of the incident and scattered photons.

The lineshape function implies that the frequency dependence of the scattering cross section is given by

\[
\sigma(\Delta) = \sigma(0) \frac{L(\Delta)}{L(0)} = \sigma(0) \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}}
\]

where \( \sigma(0) \) is the resonant cross section. We can interpret the effective width of the scattering cross section as the inverse of the resonant lineshape function or \( \delta \omega = 1/L(0) = \pi \gamma/2 \). This justifies the statement made in the previous section that \( \delta \omega \sim A \).

The derivations used above are heuristic so it is fair to wonder whether or not the resulting lineshape expression (4.7) for the detuning dependent transition rate and cross section is accurate. The justification for this expression comes from solving the problem rigorously using density matrix theory. We will learn how to do this in a later section.

### 4.2.1 Saturation effects

When the light intensity is sufficiently strong population is redistributed between ground and excited states. This changes the number of atoms that can absorb an incident photon and therefore the attenuation of a weak beam is larger than that of a strong beam. This effect is known as saturated absorption.

We can readily find the steady-state ground and excited state populations using the rate Eqs. (4.1). In steady state

\[
N_2 = \frac{B_{2\rightarrow 1}^{\text{abs}} \rho_\omega}{A + B_{1\rightarrow 2}^{\text{ems}} \rho_\omega} N_1.
\]

Assuming \( g_1 = g_2 \) so \( B_{1\rightarrow 2}^{\text{ems}} = B_{2\rightarrow 1}^{\text{abs}} \) we find

\[
\frac{N_2}{N} = \frac{N_2}{N_1 + N_2} = \frac{1}{2} \frac{2B_{2\rightarrow 1}^{\text{abs}} \rho_\omega}{A}.
\]
Define a saturation parameter $s = 2B_{2-1}^{\text{abs}} \rho_\omega / A$ so that

$$\frac{N_2}{N} = \frac{s/2}{1 + s}$$

and

$$\frac{N_1}{N} = \frac{1 + s/2}{1 + s}.$$  

We see that for $s = 0$ there is no excited state population ($N_2 = 0$) and as $s \to \infty$ then $N_2 \to 1/2$.

A useful quantity is the difference in population of excited and ground states defined by $\Delta N = N_2 - N_1$. This is found to be

$$\Delta N = -N \frac{1}{1 + s}.$$  

At unit saturation ($s = 1$) we have $N_2/N = 1/4$, $N_1/N = 3/4$ and $\Delta N/N = -1/2$. So unit saturation corresponds to half of the maximum possible excited state population.

The dimensionless saturation parameter $s$ can be written as $s = I/I_s$ where $s$ is the optical intensity and $I_s\Delta$ is the saturation intensity at detuning $\Delta$. Since the light-matter interaction gets weaker at finite detuning according to the lineshape function $L(\Delta)$, the saturation intensity must increase inversely proportional to $L(\Delta)$. We can write this as

$$I_s\Delta = I_s \frac{L(0)}{L(\Delta)} = I_s \left(1 + \frac{4\Delta^2}{\gamma^2}\right)$$

where $I_s$ is the resonant saturation intensity. The intensity dependence of the populations is thus

$$N_1 = N \frac{1 + \frac{I}{2I_s\Delta}}{1 + \frac{I}{I_s\Delta}}$$

$$N_2 = N \frac{\frac{I}{2I_s\Delta}}{1 + \frac{I}{I_s\Delta}}$$

$$\Delta N = -N \frac{1}{1 + \frac{I}{I_s\Delta}}.$$  

We can express $I_s$ in terms of the linewidth $\gamma = A$ as follows. The intensity per unit frequency $I_\omega$ is related to the energy density by $c\rho_\omega = I_{\omega x} + I_{\omega y} + I_{\omega z} = 3I_\omega$ with the intensity along a single direction equal to $I_\omega = c\rho_\omega / 3$. We can therefore write $\rho_\omega = 3I_\omega / c$ so that

$$s_0 = \frac{I}{I_s} = \frac{2B_{2-1}^{\text{abs}} \rho_\omega}{A} = \frac{6\pi^2 c^2}{\hbar \omega_{21}^3} I_\omega.$$  

The effective intensity per unit frequency at resonance is $I_\omega = IL(0) = 2I/\pi\gamma$. We therefore arrive at $s_0 = \frac{12\pi c^2}{\hbar \gamma \omega_{21}} I$ and using $I_s = I/s_0$ the resonant saturation intensity is

$$I_s = \frac{\hbar \gamma \omega_{21}^3}{12\pi c^2}.$$  

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It is not hard to show that with degeneracy factors $g_1, g_2$ this becomes

$$I_s = \frac{g_1 \hbar \gamma \omega_{21}^3}{g_2 12\pi c^2}$$  \hspace{1cm} (4.8)$$

and the frequency dependent saturation parameter is

$$s = \frac{g_2 12\pi c^2}{g_1 \hbar \gamma \omega_{21}^3} \frac{I}{1 + 4\Delta^2/\gamma^2}.$$  

It is convenient to introduce the parameter $\sigma_0 \equiv \sigma(0) = \frac{g_2 3\lambda_2^3}{g_1 2\pi}$ which we will show below to be the resonant absorption cross section. The saturation parameter can then be expressed as

$$s = \frac{2\sigma_0 I}{\gamma 1 + 4\Delta^2/\gamma^2}.$$  

### 4.2.2 Scattering cross section and absorption

The atomic transition rate can be written in terms of a scattering cross section which describes the effective “scattering” area of a single atom. The scattering rate is equal to the rate of spontaneous decay from the excited state. This is given by

$$r = \gamma N_2 = \gamma N \frac{I_{2s\Delta}}{1 + \frac{I}{I_{s\Delta}}}.$$  

The scattering rate per atom is thus

$$\frac{r}{N} = \gamma \frac{I_{2s\Delta}}{1 + \frac{I}{I_{s\Delta}}} = \gamma \frac{I_{2s\Delta}}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{I}{I_s}}.$$  

Writing this as $r/N = \frac{I}{\hbar \omega} \sigma$ with $\sigma$ the scattering cross section we find

$$\sigma = \sigma_0 \frac{\omega/\omega_{21}}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{I}{I_s}}.$$  

with the low intensity resonant cross section given by

$$\sigma_0 = \frac{\hbar \gamma \omega_{21}}{2I_s}.$$  

Using the expression for the saturation intensity from Eq. (4.8), we find

$$\sigma_0 = \frac{g_2 3}{g_1 2\pi \lambda_{21}^2}.$$  

We see again that the resonant cross section $\sim \lambda^2$ with the proportionality coefficient now explicit.

The rate of scattering is equal to the rate at which energy is lost by a propagating optical beam since the spontaneous scattering occurs in random directions. Note that as $I \to \infty$ the
4.2 Resonant absorption due to narrowband radiation

spontaneous scattering rate tends to a limit of \((r/N)_{\text{max}} = \gamma/2\). The stimulated transitions do not deplete the propagating beam, and do not contribute to the scattering loss.

If the scattering rate is \(I/\hbar\omega\sigma\) per atom then in a unit volume we have a scattering rate of \(I/\hbar\omega\sigma N dz\). The differential change in intensity due to propagation over a distance \(dz\) is thus

\[
\frac{dI}{dz} = -\sigma N I = -\alpha I
\]

where the absorption coefficient is

\[
\alpha = \sigma N = \sigma_0 N \frac{\omega/\omega_{21}}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{r^2}{\gamma s}}.
\]  

(4.9)

The intensity decreases exponentially with \(z\) as

\[
I(z) = I(0)e^{-\alpha z}
\]

which is often referred to as Beer’s law. We see from (4.9) that for all intensities \(\alpha > 0\). The light always experiences loss. For this reason two-level atoms are not suitable for achieving optical gain and laser action.

4.2.3 Three levels

For calculations with real atoms we often wish to know the ground and excited state populations when the upper level can decay to a third level as shown in Fig. 4.4. The additional decay channel further broadens the excited state which effectively reduces the scattering cross section for light driving the \(|1\rangle \rightarrow |2\rangle\) transition. We will return to a full calculation of the dynamics and light-atom interaction using density matrix methods in Chapter ♠.

A simplified rate equation treatment is based on the set

\[
\begin{align*}
\frac{dN_1}{dt} &= \gamma_1 N_2 - B_{2-1}\rho_2 N_1 + B_{1-2}\rho_1 N_2 \\
\frac{dN_2}{dt} &= -\gamma N_2 + B_{2-1}\rho_2 N_1 - B_{1-2}\rho_1 N_2 \\
\frac{dN_3}{dt} &= \gamma_3 N_2,
\end{align*}
\]

(4.10a)

(4.10b)

(4.10c)

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where $\gamma = \gamma_1 + \gamma_3$. The long time steady state solution is $N_1 = N_2 = 0$ and $N_3 = N$. At short time we can put $dN_2/dt \approx 0$ and find a quasi-steady, excited state population

$$\frac{N_2}{N} \approx \frac{1}{2} \frac{2B_{2-1}^{abs} \rho_\omega / \gamma}{1 + 2B_{2-1}^{abs} \rho_\omega / \gamma} \left( 1 - \frac{N_3}{N} \right).$$

Define a saturation parameter $s = 2B_{2-1}^{abs} \rho_\omega / \gamma = I/I_{s\Delta}$ so

$$\frac{N_2}{N} \approx \frac{1}{2} \frac{I/I_{s\Delta}}{1 + I/I_{s\Delta}} \left( 1 - \frac{N_3}{N} \right).$$

The width of the upper level is $\hbar \gamma$ (not $\hbar \gamma_1$) so $I_{s\Delta} = I_s(1 + 4\Delta^2/\gamma^2)$ with $I_s = h\gamma \omega_{21}^3/(12\pi c^2)$. Thus

$$\frac{N_2}{N} \approx \frac{1}{2} \frac{I/I_{s\Delta}}{1 + I/I_{s\Delta}} \left( 1 - \frac{N_3}{N} \right).$$

The scattering rate per atom is $r/N = \gamma N_2/N = I/I_{s\omega} \sigma$ so the scattering cross section is

$$\sigma = \frac{\hbar \omega \gamma}{I} \frac{N_2}{N} \approx \frac{\hbar \omega \gamma}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{I}{I_s}} \left( 1 - \frac{N_3}{N} \right)$$

and for $N_3 \ll N$ we get

$$\sigma = \frac{\hbar \omega \gamma}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{I}{I_s}} = \sigma_0 \frac{\omega/\omega_{21}}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{I}{I_s}},$$

where $\sigma_0 = 3\lambda_{21}^2/2\pi$. This expression is valid only at short times for which $N_3 \ll N$. In addition we need to add a correction for the branching ratio of the scattered photons which end up in $|1\rangle$ with probability $\gamma_1/\gamma < 1$ while a fraction $\gamma_3/\gamma$ result in atom transfer to state $|3\rangle$ where the atom becomes dark to the incident light and no longer scatters any photons. We therefore write the short term effective cross section as

$$\sigma = \sigma_0 \frac{\gamma_1}{\gamma} \frac{\omega/\omega_{21}}{1 + \frac{4\Delta^2}{\gamma^2} + \frac{I}{I_s}}.$$ (4.11)

With degeneracy factors $g_1, g_2$ Eq. (4.11) stays the same except $\sigma_0 \rightarrow \sigma_0 g_2 g_1$ and $I_s \rightarrow I_s g_1 g_2$.

### 4.3 Refractive index

The refractive index of a gas of two-level atoms can be calculated in analogy to the calculation of the scattering rate in Sec. 4.2. Recall from Eq. (4.6) that the amplitude of the upper level is

$$c_2 \sim \frac{1}{\gamma/2 - i\Delta} = \frac{\gamma/2 + i\Delta}{\gamma^2/4 + \Delta^2}.$$

Note that $\text{Im}(c_2) = \frac{2\Delta}{\gamma} \text{Re}(c_2)$. Keeping only the real part of $c_2$ we arrived at $\frac{dI}{dz} = -\sigma NI$. Since $I \sim |\mathcal{E}|^2$ with $\mathcal{E}$ the complex field amplitude this is equivalent to

$$\text{Re} \left[ \frac{d\mathcal{E}}{dz} \right] = \text{Re} \left[ -\frac{\sigma N}{2} \mathcal{E} \right].$$
4.4 Electric dipole transitions

Since $\sigma N$ is real we can as well write this as

$$\frac{d\mathcal{E}}{dz} = \frac{-\sigma N}{2} \mathcal{E}$$
$$= \frac{-\sigma_0 N}{2} \omega \frac{1}{\omega_2 1 + \frac{4\Delta^2}{\gamma^2} + \frac{I_s}{L}} \mathcal{E}.$$  \hspace{1cm} (4.12)

If we were to repeat the derivation leading to (4.12), but include the imaginary part of $c_2$ we would arrive at

$$\frac{d\mathcal{E}}{dz} = \frac{-\sigma_0 N}{2} \omega \frac{1 + i\frac{2\Delta}{\gamma}}{\omega_2 1 + \frac{4\Delta^2}{\gamma^2} + \frac{I_s}{L}} \mathcal{E}.$$  \hspace{1cm} (4.13)

Writing the complex field amplitude in terms of two real variables $F, \phi$ as $\mathcal{E} = Fe^{i\phi}$ we get

$$\frac{dF}{dz} = \frac{-\sigma_0 N}{2} \omega \frac{1}{\omega_2 1 + \frac{4\Delta^2}{\gamma^2} + \frac{I_s}{L}} F,$$
$$\frac{d\phi}{dz} = \frac{-\sigma_0 N}{2} \omega \frac{\Delta}{\gamma} \frac{1}{\omega_2 1 + \frac{4\Delta^2}{\gamma^2} + \frac{I_s}{L}}.$$  

Since the phase change per unit length is $d\phi/dz$ which we can set equal to $k\delta n$ the refractive index change due to the atoms is

$$\delta n = \frac{1}{k} \frac{d\phi}{dz} = \frac{-\sigma_0 N}{k} \omega \frac{\Delta}{\gamma} \frac{1}{\omega_2 1 + \frac{4\Delta^2}{\gamma^2} + \frac{I_s}{L}}.$$ \hspace{1cm} (4.14)

4.4 Electric dipole transitions

The semiclassical interaction Hamiltonian describing electric dipole coupling of an atomic electron to an optical field is $H_{E1} = -\mathbf{d} \cdot \mathbf{E}$ with $\mathbf{d} = -e\mathbf{r}$, $-e$ is the charge of an electron, $\mathbf{r}$ is the position operator, and $\mathbf{E}$ is the classical electric field. As was discussed in Sec. 3.4.1 this form of the interaction Hamiltonian is valid for not too large field strengths where we may neglect interaction terms proportional to $A^2$, with $A$ the vector potential.

Consider an optically induced transition $|\alpha\rangle \rightarrow |\alpha'\rangle$, where $\alpha, \alpha'$ stand for the set of quantum numbers specifying the states. The real valued optical field expressed in a spherical basis is

$$\mathbf{E} = \sum_q \frac{\mathcal{E}_q^*}{2} e^{i(kr-\omega t)} \mathbf{e}_q + \sum_q \frac{\mathcal{E}_q}{2} e^{-i(kr-\omega t)} \mathbf{e}_q^*$$ \hspace{1cm} (4.15)

where $q = 0, \pm 1$ and $\mathbf{e}_0 = \mathbf{e}_z$, $\mathbf{e}_\pm = \mp(\mathbf{e}_x \pm i\mathbf{e}_y)/\sqrt{2}$. Note that the amplitude and unit vector coefficients $\sim \mathcal{E}_q^* \mathbf{e}_q^*$ (plus $(\mathcal{E}_q^* \mathbf{e}_q^*)^*$ to ensure the field is real). This is in accordance with the usual rule for writing a vector in a spherical basis, $\mathbf{A} = \sum_q A_q \mathbf{e}_q^*$, as in (A-24).
component of the field is nonzero we get more complicated elliptically polarized states. When more than one field will see the polarization direction rotate in a clockwise direction. This is right hand circular polarization. These relations are summarized in Table 4.1. An observer looking from the source towards +\( \hat{r} \) along the direction of propagation of the field will see the polarization direction rotate in a counterclockwise direction. This is left hand circular polarization.

If the only nonzero amplitude is \( \mathcal{E}_+ \) the field is

\[
\mathbf{E} = \frac{\mathcal{E}_+^*}{2} e^{i(k\cdot r - \omega t)} \mathbf{e}_+ + \frac{\mathcal{E}_+}{2} e^{-i(k\cdot r - \omega t)} \mathbf{e}_+^*
\]

\[
= -\frac{|\mathcal{E}_+|}{23/2} e^{i(k\cdot r - \omega t - \phi_+)} (\mathbf{e}_x + i\mathbf{e}_y) - \frac{|\mathcal{E}_+|}{23/2} e^{-i(k\cdot r - \omega t - \phi_+)} (\mathbf{e}_x - i\mathbf{e}_y)
\]

\[
= -\frac{|\mathcal{E}_+|}{21/2} \left[ \cos(k \cdot r - \omega t - \phi_+) \mathbf{e}_x - \sin(k \cdot r - \omega t - \phi_+) \mathbf{e}_y \right].
\]

An observer looking from the source towards +\( \hat{r} \) along the direction of propagation of the field will see the polarization direction rotate in a clockwise direction. This is right hand circular polarization. These relations are summarized in Table 4.1. When more than one component of the field is nonzero we get more complicated elliptically polarized states.

Circularly polarized light carries spin angular momentum of \( \pm \hbar \) per photon. We would like to establish the connection between the sign of the spin and the handedness of circular polarization. The electric dipole transition matrix element is

\[
\langle \alpha' | H_{\text{E1}} | \alpha \rangle = \langle \alpha' | e \mathbf{E} \cdot \hat{r} | \alpha \rangle
\]

\[
= e \sum_\alpha' \frac{\mathcal{E}_q^*}{2} e^{-i\omega t} \langle \alpha' | e^{ikr} \mathbf{e}_q \cdot \hat{r} | \alpha \rangle + e \sum_\alpha' \frac{\mathcal{E}_q}{2} e^{i\omega t} \langle \alpha' | e^{-ikr} \mathbf{e}_q^* \cdot \hat{r} | \alpha \rangle.
\]
If the atomic wavefunction is localized to a region much less than the wavelength of the radiation \( \lambda \gg n^2a_0 \), we can make the dipole approximation \( e^{ikr} = 1 \) and simplify the matrix element to

\[
\langle \alpha' \mid H_{E1} \mid \alpha \rangle = e \sum_q \frac{\mathcal{E}_q^*}{2} e^{-i\omega t} \langle \alpha' \mid \mathbf{e}_q \cdot \mathbf{r} \mid \alpha \rangle + e \sum_q \frac{\mathcal{E}_q}{2} e^{i\omega t} \langle \alpha' \mid \mathbf{e}_q^* \cdot \mathbf{r} \mid \alpha \rangle. \tag{4.17}
\]

In the case of absorption we annihilate a photon with amplitude \( \sim e^{-i\omega t} \) (positive energy) so the first term applies

\[
\langle \alpha' \mid H_{E1} \mid \alpha \rangle_{\text{abs}} = e \sum_q \frac{\mathcal{E}_q^*}{2} \langle \alpha' \mid \mathbf{e}_q \cdot \mathbf{r} \mid \alpha \rangle e^{-i\omega t}.
\]

The position operator is

\[
\hat{\mathbf{r}} = \sum_p r_p \mathbf{e}_p^*
\]

and

\[
\mathbf{e}_q \cdot \hat{\mathbf{r}} = \hat{r}_q
\]

so

\[
\langle \alpha' \mid H_{E1} \mid \alpha \rangle_{\text{abs}} = e \sum_q \frac{\mathcal{E}_q^*}{2} \langle \alpha' \mid \hat{r}_q \mid \alpha \rangle e^{-i\omega t}. \tag{4.18}
\]

For emission we use the second term in (4.17) so the matrix element is

\[
\langle \alpha' \mid H_{E1} \mid \alpha \rangle_{\text{ems}} = e \sum_q \frac{\mathcal{E}_q}{2} \langle \alpha' \mid \mathbf{e}_q^* \cdot \hat{\mathbf{r}} \mid \alpha \rangle e^{i\omega t}
\]

\[
= e \sum_q (-1)^q \frac{\mathcal{E}_q}{2} \langle \alpha' \mid \hat{r}_{-q} \mid \alpha \rangle e^{i\omega t}. \tag{4.19}
\]

Consider for example a transition from a state \( |\alpha\rangle = |njm\rangle \) with total angular momentum \( j \), and \( z \) component of angular momentum \( m \) to a state \( |\alpha'\rangle = |n'j'm'\rangle \). The absorption matrix element is \( \langle n'j'm'\mid \hat{r}_q \mid njm\rangle \). The selection rules that express conservation of angular momentum are \( j - 1 \leq j' \leq j + 1, m' = m + q \). The angular momentum projection of the final state is increased by \( q \), the angular momentum of the absorbed photon. If these conditions are not met the matrix element is identically zero. For emission the matrix element is \( \langle j'm'\mid \hat{r}_{-q} \mid jm\rangle \) which may be nonzero provided \( j - 1 \leq j' \leq j + 1, m' = m - q \). The angular momentum of the final state is decreased by \( q \), the angular momentum of the emitted photon. Thus light for which \( \mathcal{E}_+ (\mathcal{E}_-) \) is nonzero carries \( +h (-h) \) angular momentum per photon and has left(right) hand circular polarization. These relations are listed in Table 4.1. It is common to refer to light carrying \( \pm h \) of angular momentum as \( \sigma_+ (\sigma_-) \) polarization.

For states \( |nlm\rangle \) we can give more explicit relations for the matrix elements. As an example the matrix element for an absorption process taking the atom from \( |n_al_a\rangle \rightarrow |n_bl_b\rangle \) is

\[
\langle n_bl_b \mid H_{E1} \mid n_al_a \rangle = e \sum_q \frac{\mathcal{E}_q^*}{2} \langle n_bl_b \mid \mathbf{e}_q \cdot \hat{\mathbf{r}} \mid n_al_a \rangle e^{-i\omega t}
\]

\[
= e \frac{\mathcal{E}_1^*}{2} \langle n_bl_b \mid \hat{r}_1 \mid n_al_a \rangle e^{-i\omega t}
\]
Interactions with oscillating fields

Figure 4.5: Feynman diagrams corresponding to co- and counter-rotating absorption and emission of a photon.

where the 2nd line is for absorption of $\sigma_+$ light. Using $r_1 = r \sqrt{4\pi/3}Y_{11}$ the matrix element is

$$
\langle n_{b}l_{b}m_{b}|\hat{a}_{1}|n_{a}l_{a}m_{a}\rangle = \int dr r^2 R_{n_{b}l_{b}}(r)R_{n_{a}l_{a}}(r) \int d\Omega Y_{l_{b}m_{b}}^* \sqrt{4\pi/3}Y_{11}Y_{l_{a}m_{a}}
$$

$$
= \left(\frac{2l_{1} + 1}{2l_{b} + 1}\right)^{1/2} C_{l_{a}010}^{l_{b}0} C_{l_{a}m_{a}11}^{l_{b}m_{b}} \int dr r^3 R_{n_{b}l_{b}}(r)R_{n_{a}l_{a}}(r).
$$

The absorption and emission matrix elements identified in (4.18,4.19) are resonant processes. When the light frequency is tuned close to the transition frequency these are the dominant terms. However, also the nonresonant processes where a photon is emitted while the atom makes a transition to a higher energy state, or a photon is absorbed while the atom makes a transition to a lower energy state must be accounted for in some cases. Feynman diagrams corresponding to these processes are shown in Fig. 4.5. The resonant processes are often called “co-rotating” while the non-resonant processes are called “counter-rotating”. Although counter-rotating processes do not conserve energy at each time step, and are therefore suppressed, they must be accounted for to obtain accurate results when the detuning is large. We will see this when we treat the dynamic Stark effect.

4.5 Fermi’s golden rule

Using time dependent perturbation theory we can calculate the rate at which the radiation field induces transitions between atomic states. The Hamiltonian $\hat{H}_0$ has a complete set of stationary eigenstates $|j\rangle$ satisfying $\hat{H}_0|j\rangle = E_j|j\rangle$. The perturbation $\hat{H}'$ induces transitions between the stationary states. We write a general state $|\psi\rangle = \sum_j c_j|j\rangle$ and solving $i\hbar \frac{d|\psi\rangle}{dt} = \hat{H}'|\psi\rangle$ with the initial condition $c_i(0) = 1$, $c_{j\neq i}(0) = 0$ we find

$$
c_j(t) \approx \frac{-i}{\hbar} \int_0^t dt' e^{(E_j - E_i)t/\hbar} \langle j|\hat{H}'|i\rangle.
$$
The transition probability is therefore
\[
P_{j \rightarrow i} = |c_j(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t dt' e^{i(E_j-E_i)t/\hbar} \langle j | \hat{H}' | i \rangle \right|^2.
\]

Let us first consider the case where \( \hat{H}' \) is constant in time. Then
\[
P_{j \rightarrow i} = \frac{|\langle j | \hat{H}' | i \rangle|^2}{\hbar^2} y(\omega_{ji}, t)
\]
where
\[
y(\omega, t) = \frac{\sin^2(\omega t/2)}{(\omega/2)^2}.
\]
The function \( y \) has the following properties
\[
\int_{-\infty}^{\infty} d\omega y(\omega, t) = 2\pi t
\]
and
\[
\lim_{t \to \infty} \frac{y(\omega, t)}{2\pi t} = \delta(\omega).
\]
The behavior of \( y(\omega, t) \) for increasing \( t \) is shown in Fig. 4.6. The characteristic width of \( y(\omega, t) \) is \( 1/t \) and the peak value at \( \omega = 0 \) is \( t^2 \). As \( t \) tends to \( \infty \) we get a \( \delta \) function.

Now consider interaction with an oscillating field \( E = \frac{\xi}{2} e^{-i\omega t} \hat{\epsilon} + c.c. \) so
\[
\hat{H}' = \hat{H}_0 e^{-i\omega t} + c.c.
\] (4.20)
with \( \hat{H}_0 = \frac{\xi}{2} \hat{\epsilon} \cdot \hat{r} \). We find the same result for the transition probability as in the case of a constant \( \hat{H}' \) except the argument of the \( y \) function becomes \( \omega - \omega_{ji} = \Delta \). The quantity \( \Delta \) is the detuning of the external field from the atomic transition. Positive detuning \( \omega > \omega_{ji} \) is called “blue” detuning and \( \omega < \omega_{ji} \) is called “red” detuning. The transition probability with the oscillating field is thus
\[
P_{j \rightarrow i} = \frac{|\langle j | \hat{H}_0' | i \rangle|^2}{\hbar^2} y(\Delta, t).
\]

Figure 4.6: Lineshape function from time dependent perturbation theory.
We now want to take the limit as $t \to \infty$. Note that $\Delta = \omega - \omega_{ji} = (\omega + \omega_i) - \omega_j = \frac{E_i}{\hbar} - \frac{E_f}{\hbar}$ where $E_i, E_f$ now refer to the total energy of the atom plus the field. Then use
\[
\lim_{t \to \infty} \frac{y(\Delta, t)}{2\pi t} = \delta(\Delta) = \hbar \delta(E_i - E_f) = \hbar \delta(E_f - E_i).
\]
So in the long interaction time limit we get
\[
P_{j-i} \to \frac{|\langle j| H'_0 |i\rangle|^2}{\hbar^2} (2\pi t) \hbar \delta(E_f - E_i) = \frac{2\pi}{\hbar} |\langle j| H'_0 |i\rangle|^2 \delta(E_f - E_i) t.
\]
The transition rate is the rate of increase of probability per unit time or
\[
R_{j-i} = \frac{P_{j-i}}{t} = \frac{2\pi}{\hbar} |\langle j| H'_0 |i\rangle|^2 \delta(E_f - E_i). \tag{4.21}
\]
Equation (4.21) was first derived by Dirac and is known as Fermi’s golden rule (FGR). When there is a density of final states per unit energy interval $\Xi(E_f)$ we must integrate over the final energy to get
\[
R_{j-i} = \int dE_f \frac{2\pi}{\hbar} |\langle j| H'_0 |i\rangle|^2 \Xi(E_f) \delta(E_f - E_i)
\]
\[
= \frac{2\pi}{\hbar} |\langle j, E_f = E_i| H'_0 |i\rangle|^2 \Xi(E_f = E_i). \tag{4.22}
\]

The derivation of FGR appears suspicious. We start with perturbation theory which is valid for short times, and then assume $t \to \infty$. Nonetheless for atomic problems (4.21,4.22) are usually very accurate. The time $t$ at which we use FGR must satisfy $t_{\text{min}} < t < t_{\text{max}}$. The long time $t_{\text{max}}$ must be small enough so that $P_{j-i} \ll 1$ for all $j$ or $\sum_j R_{j-i} t_{\text{max}} \ll 1$. This ensures that perturbation theory is valid. We also require that $t_{\text{min}}$ is large enough so that the width of $y(\Delta, t)$ is small compared to the scale of variations of $\langle j| H'_0 |i\rangle$ and $\Xi(E_f)$. If this is the case then the $\delta$ function approximation is accurate. It can be shown that for atomic problems this requirement corresponds to $\omega_{ji} \gg A$ which is generally true. When in doubt it is necessary to check if the FGR result can be applied.

We can now use FGR to find the Einstein $B$ coefficient. For a weak radiation field the transition rate from $1 \to 2$ per atom is
\[
R_{2-1} = B_{2-1} \rho \omega.
\]
This should be equal to $R_{j-i}$ from Eq. (4.21). We can integrate over frequency to get
\[
\int d\omega R_{2-1} = \int d\omega B_{2-1} \rho \omega(\omega)
\]
\[
= B_{2-1} \rho
\]
\[
= B_{2-1} \frac{\epsilon_0}{2} |\mathcal{E}|^2 \tag{4.23}
\]
where we have used the expression $\rho = \frac{\epsilon_0}{2} |\mathcal{E}|^2$ for the total energy density in the field.
Integrating (4.21) over frequency gives
\[
\int d\omega R_{j\leftarrow i} = \frac{2\pi}{\hbar} |\langle j|\hat{H}_0'|i\rangle|^2 \int d\omega \delta(E_f - E_i) = \frac{2\pi}{\hbar^2} |\langle j|\hat{H}_0'|i\rangle|^2 \int d\omega \delta(\omega_j - (\omega + \omega_i)) = \frac{2\pi}{\hbar^2} |\langle j|\hat{H}_0'|i\rangle|^2.
\] (4.24)

Then set Eqs. (4.23, 4.24) equal to each other and use \( \hat{H}_0' = \frac{e^2}{2} \hat{e}^* \cdot \hat{r} \) to get
\[
B_{2\leftarrow 1} = \frac{\pi e^2}{\epsilon_0 \hbar^2} |\hat{e}^* \cdot \langle 2|\hat{r}|1\rangle|^2.
\] (4.25)

If the radiation is unpolarized then we can replace the matrix element by a reduced matrix element according to
\[
|\hat{e}^* \cdot \langle 2|\hat{r}|1\rangle|^2 \rightarrow |\langle 2||\hat{r}||1\rangle|^2 / 3
\] to get
\[
B_{2\leftarrow 1} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle 2||\hat{r}||1\rangle|^2. \quad \text{(unpolarized light)}
\] (4.26)

Using the Einstein relation between \( A \) and \( B \) we find
\[
A = \frac{\omega^3 e^2}{3\pi \epsilon_0 \hbar c^3} |\langle 2||\hat{r}||1\rangle|^2.
\] (4.27)

We will see later that the same result is found from directly calculating \( A \) with a quantum treatment of the radiation field.

When the lower and upper levels are degenerate with factors \( g_1, g_2 \) Eqs. (4.26, 4.27) get modified to
\[
A_{1\leftarrow 2} = \frac{\omega^3 e^2}{3\pi \epsilon_0 \hbar c^3} g_2 |\langle 1||\hat{r}||2\rangle|^2
\] (4.28a)
\[
B_{2\leftarrow 1}^{\text{abs}} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} g_1 |\langle 2||\hat{r}||1\rangle|^2,
\] (4.28b)
\[
B_{1\leftarrow 2}^{\text{em}} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} g_2 |\langle 2||\hat{r}||1\rangle|^2.
\] (4.28c)

We have added the superscripts “abs” and “em” to emphasize whether absorption or emission is being described.

We can use the lineshape function (4.7) to find the effective density of states in the FGR result Eq. (4.22)
\[
R_{j\leftarrow i} = \frac{2\pi}{\hbar} \int dE_f |\langle j, E_f = E_i|\hat{H}_0'|i\rangle|^2 \Xi(E_f) \delta(E_f - E_i).
\]

The density of states is normalized so that \( \int d\omega \Xi(\omega) = \text{number of states} \). In the case of absorption there is only one final state with the atom excited and one less photon in the radiation field. Thus the number of final states is one, and we have simply \( \Xi(\omega) = L(\omega) \), i.e. the single state is distributed over the region of support of \( L(\omega) \).
Then use $\Xi(E_f) dE_f = \Xi(\omega_f) d\omega_f$ so

$$\Xi(E_f) = \frac{\Xi(\omega_f)}{\hbar} = \frac{2}{\pi \hbar \gamma} \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}}$$

and

$$R_{2-1} = \frac{2\pi}{\hbar} \int d\omega_f \ h |\langle 2 | \hat{H}_0' | 1 \rangle|^2 \frac{2}{\pi \hbar \gamma} \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}} \frac{\delta(\omega_f - \omega_i)}{\hbar}$$

$$= \frac{4}{\hbar^2 \gamma} |\langle 2 | \hat{H}_0' | 1 \rangle|^2 \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}}.$$  (4.29)

Here we have used the initial energy $E_i = \hbar(\omega_1 + \omega)$ and the final energy $E_f = E_i$ which implies $\omega_1 + \omega = \omega_2 + \Delta$ or $\Delta = \omega - (\omega_2 - \omega_1) = \omega - \omega_2$.

Assuming light polarized along $e_q$ we have $|\langle 2 | \hat{H}_0' | 1 \rangle|^2 = \frac{e^2 |\mathcal{E}_q|^2}{4} |\langle 2 | \hat{r}_q | 1 \rangle|^2$ and

$$R_{2-1} = \frac{e^2 |\mathcal{E}_q|^2}{\hbar^2 \gamma} |\langle 2 | \hat{r}_q | 1 \rangle|^2 \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}}.$$  (4.30)

Equation (4.30) gives the transition rate due to monochromatic radiation when the excited state has decay rate $\gamma$. Let’s verify consistency with our previous results. Using (4.25) the transition rate can be written as

$$B_{2-1} = \frac{\pi e^2}{\epsilon_0 \hbar^2} |\langle 2 | \hat{r}_q | 1 \rangle|^2 \rho_\omega.$$  (4.26)

Replacing $\rho_\omega$ by $\frac{\rho}{\delta \omega_{\text{eff}}} = \frac{\epsilon_0 |\mathcal{E}_q|^2}{2 \delta \omega_{\text{eff}}} \frac{1}{\delta \omega_{\text{eff}}}$, with $\delta \omega_{\text{eff}}$ the effective linewidth we get a transition rate

$$\frac{\pi e^2 |\mathcal{E}_q|^2}{2 \hbar^2 \delta \omega_{\text{eff}}} |\langle 2 | \hat{r}_q | 1 \rangle|^2$$

which agrees with (4.30) on resonance provided we put $\delta \omega_{\text{eff}} = \pi \gamma/2$. Noting that $L(0) = 2/\pi \gamma = 1/\delta \omega_{\text{eff}}$ we again verify the value of the effective resonant linewidth.

Before continuing let’s verify that the use of FGR was justified. We found in Eq. (4.28) the spontaneous decay rate

$$A_{1-2} = \frac{\omega^2 e^2}{3 \pi \epsilon_0 \hbar c^3} 1_g |\langle 1 | \hat{r} | 2 \rangle|^2.$$  (4.28)

The matrix element is proportional to the atomic length scale or $a_0$. So

$$A_{1-2} \sim \frac{\omega^2 e^2 a_0^2}{3 \pi \epsilon_0 \hbar c^3}.$$  (4.28)

To apply FGR we need $t_{\text{min}} < t < t_{\text{max}}$ where

$$t_{\text{min}} \sim 1/\omega.$$  (4.28)
4.6 Calculation of the spontaneous emission rate

which is the frequency scale over which the rate varies, and

\[ t_{\text{max}} \sim 1/A \]

which is the characteristic time for a transition to occur. So we need \( 1/\omega < t < 1/A \) or \( \omega \gg A \). This can be written as

\[ 1 \gg \frac{A}{\omega} = \frac{16\pi}{3} \frac{\epsilon_0 \hbar^3 \omega^2}{m^2 c^3 e^2}. \]

Putting \( \omega \sim E_H/\hbar \) gives

\[ 1 \gg 4 \frac{\alpha^3}{3} \]

with \( \alpha \) the fine structure constant. Since \( \alpha^3 < 10^{-6} \) this relation is well satisfied and the use of FGR is justified.

4.6 Calculation of the spontaneous emission rate

Let’s summarize the results obtained so far. Starting with the Einstein rate equations, and drawing on the concept of thermal equilibrium, we related the phenomenological \( A, B \) coefficients to each other. Accounting for saturation effects at finite intensity and spontaneous emission we found expressions for the absorption cross section and line shape. We then used time dependent perturbation theory to relate the \( B \) coefficient to a quantum mechanical radial matrix element. With the Einstein relation between \( A \) and \( B \), Eq. (4.2), we can then express all coefficients in terms of fundamental constants and atomic matrix elements. In this section we verify the consistency of these results by calculating the \( A \) coefficient directly from quantum mechanics. In order to do this we first need to quantize the electromagnetic field.

4.6.1 Quantization of the electromagnetic field

Field quantization is based on recognizing that the electromagnetic field is equivalent to an infinite set of harmonic oscillators. Each harmonic oscillator is quantized using the canonical procedure. The result is a representation of the field as a sum over modes at frequencies \( \omega_j \), each with a definite number \( n_j \) of excitations, or quanta. Each excitation contributes an energy \( \hbar \omega_j \). So that the energy of the electromagnetic field can be written as

\[ E = \hbar \sum_j \omega_j \left( n_j + \frac{1}{2} \right). \tag{4.31} \]

The factor \( 1/2 \) accounts for the zero point energy, or vacuum fluctuations of the field.

4.6.2 Quantization of the harmonic oscillator

To start with let’s see how to quantize a harmonic oscillator with coordinate \( q \), mass \( m \), and conjugate momentum \( p = m \dot{q} \). The classical energy of the oscillator is

\[ E = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}. \tag{4.32} \]

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where $\omega$ is the natural frequency of the oscillator. For example a mass on a spring with force constant $k$ has $\omega^2 = k/m$, or a LC circuit has $\omega^2 = 1/(LC)$.

The Hamiltonian is usually, but not always, given by the energy. Here we can use

$$H = \frac{p^2}{2m} + \frac{m\omega^2q^2}{2}.$$  \hspace{1cm} (4.33)

We can check that this is the correct Hamiltonian by noting that the canonical equations of motion,

$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m},$$
$$\dot{p} = -\frac{\partial H}{\partial q} = -m\omega^2q,$$  \hspace{1cm} (4.34)

are the correct equations that would be found from Newton’s laws.

In the quantum theory $p,q,$ and $H$ become operators

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{q}^2}{2},$$  \hspace{1cm} (4.35)

and $\hat{q}, \hat{p}$ satisfy the commutation relation

$$[\hat{q}, \hat{p}] = \hat{q}\hat{p} - \hat{p}\hat{q} = i\hbar.$$  \hspace{1cm} (4.36)

The operators $\hat{p}, \hat{q}, \hat{\mathcal{H}}$ are observables represented by hermitian operators (e.g. $\hat{p} = \hat{p}^\dagger$).

It is convenient to make a change of basis to the non-hermitian operators $\hat{a}, \hat{a}^\dagger$ defined by

$$\hat{a} = \frac{1}{\sqrt{2m\hbar\omega}} (m\omega\hat{q} + i\hat{p}),$$  \hspace{1cm} (4.37)
$$\hat{a}^\dagger = \frac{1}{\sqrt{2m\hbar\omega}} (m\omega\hat{q} - i\hat{p}).$$  \hspace{1cm} (4.38)

Note that $\hat{a}$ is dimensionless. The position and momentum operators are then expressible as

$$\hat{q} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger),$$  \hspace{1cm} (4.39)
$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}} (\hat{a}^\dagger - \hat{a}).$$  \hspace{1cm} (4.40)

Using (4.36) we get

$$[\hat{a}, \hat{a}^\dagger] = 1,$$  \hspace{1cm} (4.41)

while $[\hat{a}, \hat{a}] = [\hat{a}^\dagger, \hat{a}^\dagger] = 0$. Using (4.35) we find

$$\hat{\mathcal{H}} = \frac{\hbar\omega}{2} (\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}) = \hbar\omega \left( \hat{a}^\dagger\hat{a} + \frac{1}{2} \right).$$  \hspace{1cm} (4.42)
4.6 Calculation of the spontaneous emission rate

Eigenstates of the Hamiltonian are states of definite energy satisfying

$$\hat{H}|n\rangle = \hbar \omega \left( \hat{a}^{\dagger} \hat{a} + \frac{1}{2} \right) |n\rangle = E_n |n\rangle,$$  (4.43)

where $E_n$ is the energy of state $|n\rangle$. It is convenient to define the number operator $\hat{N} = \hat{a}^{\dagger} \hat{a}$ so that

$$\hat{H} = \hbar \omega \left( \hat{N} + \frac{1}{2} \right).$$  (4.44)

Thus

$$\hat{N} |n\rangle = \left( \frac{E_n}{\hbar \omega} - \frac{1}{2} \right) |n\rangle = n |n\rangle,$$  (4.45)

so that the eigenvalue of the number operator is $n = E_n / \hbar \omega - 1/2$. The states $|n\rangle$ are known as Fock or number states.

We want to now show that the eigenvalue $n$ is a nonnegative integer. First note that

$$\hat{N} \hat{a} = \hat{a}^{\dagger} \hat{a} \hat{a} = (\hat{a} \hat{a}^{\dagger} - 1) \hat{a} = \hat{a} \hat{N} - \hat{a} = \hat{a} (\hat{N} - 1),$$  (4.46)

$$\hat{N} \hat{a}^{\dagger} = \hat{a}^{\dagger} \hat{a} \hat{a}^{\dagger} = \hat{a}^{\dagger} (\hat{a}^{\dagger} \hat{a} + 1) = \hat{a}^{\dagger} \hat{N} + \hat{a}^{\dagger} = \hat{a}^{\dagger} (\hat{N} + 1).$$  (4.47)

Using these results we find that

$$\hat{N} (\hat{a} |n'\rangle) = (n' - 1) (\hat{a} |n'\rangle),$$  (4.48)

$$\hat{N} (\hat{a}^{\dagger} |n'\rangle) = (n' + 1) (\hat{a}^{\dagger} |n'\rangle).$$  (4.49)

Hence $\hat{a} |n'\rangle$, $\hat{a}^{\dagger} |n'\rangle$ are eigenkets of the number operator with eigenvalues $n' - 1$ and $n' + 1$ respectively. This is the reason why $\hat{a}$ and $\hat{a}^{\dagger}$ are referred to as annihilation and creation operators, since they annihilate and create one unit of excitation.

Applying this process repeatedly we generate a series of kets and their eigenvalues

$$|n'\rangle \quad \hat{a} |n'\rangle \quad \hat{a}^{2} |n'\rangle \quad \ldots \quad (4.50)$$

$$n' \quad n' - 1 \quad n' - 2 \quad \ldots \quad (4.51)$$

Now since $\hat{N}$ is hermitian we know that the eigenvalue $n'$ must be real and furthermore the norm of any vector is greater than or equal to zero. If the norm is zero the vector itself is zero. If $|n'\rangle$ is a nontrivial eigenket the norm is positive, or

$$\langle n'|n'\rangle > 0.$$  (4.52)

Now

$$\langle n'|\hat{N}|n'\rangle = \langle n'|\hat{a}^{\dagger} \hat{a}|n'\rangle = n' \langle n'|n'\rangle.$$  (4.53)

This is the norm of the vector $\hat{a} |n'\rangle$ which must be greater than or equal to zero, hence

$$n' \langle n'|n'\rangle \geq 0.$$  (4.54)

Comparing (4.52) and (4.54) we see that $n' \geq 0$. Thus the eigenvalues of $\hat{N}$ are nonnegative. If $n' = 0$ then from (4.53)

$$\hat{a}|0\rangle = 0.$$  (4.55)
and repeated application of the annihilation operator yields only zero. We can now see, by looking at the sequence of kets in Eq. (4.51), that if \( n' \) were not an integer we could repeatedly apply \( \hat{a} \) and eventually generate a ket with a negative eigenvalue, which is not allowed. The only way to prevent this is for the eigenvalues of \( \hat{N} \) to be positive integers or zero, which is the desired result.

We now want to normalize the kets. Since \( \hat{a}|n\rangle \) is an eigenket of \( \hat{N} \) with eigenvalue \( n - 1 \) we see that \( \hat{a}|n\rangle \) can differ from \( |n - 1\rangle \) by a constant. Write

\[
|n - 1\rangle = \frac{1}{\alpha_n} \hat{a}|n\rangle, \tag{4.56}
\]

with the constant \( \alpha_n \) to be determined. From (4.53) the norm of \( \hat{a}|n\rangle \) is

\[
\langle n|\hat{a}^\dagger\hat{a}|n\rangle = n\langle n|n\rangle = |\alpha_n|^2\langle n - 1|n - 1\rangle. \tag{4.57}
\]

In order to have both \( \langle n|n\rangle \) and \( \langle n - 1|n - 1\rangle \) normalized to unity we choose \( |\alpha_n| = \sqrt{n} \). The phase is arbitrary, and we take \( \alpha_n \) to be real so that

\[
\hat{a}|n\rangle = \sqrt{n}|n - 1\rangle \quad \text{for} \quad n > 0, \tag{4.58}
\]

and \( \hat{a}|0\rangle = 0 \).

For the creation operator we use

\[
\langle n|\hat{a}\hat{a}^\dagger|n\rangle = \langle n|\hat{a}^\dagger\hat{a} + 1|n\rangle = (n + 1)\langle n|n\rangle = n + 1, \tag{4.59}
\]

so that

\[
\hat{a}^\dagger|n\rangle = \sqrt{n + 1}|n + 1\rangle. \tag{4.60}
\]

Applying (4.60) \( n \) times to the ground state \( |0\rangle \) we find the useful result

\[
|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle. \tag{4.61}
\]

For completeness let’s collect the following useful results:

\[
\begin{align*}
\hat{N}|n\rangle &= n|n\rangle \\
\hat{a}|0\rangle &= 0 \\
\hat{a}|n\rangle &= \sqrt{n}|n - 1\rangle \\
\hat{a}^\dagger|n\rangle &= \sqrt{n + 1}|n + 1\rangle \\
|n\rangle &= \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle \\
\langle n|m\rangle &= \delta_{nm} \\
\sum_{n=0}^{\infty} |n\rangle\langle n| &= I, \tag{4.62}
\end{align*}
\]

where the last two equalities follow from the general theory of hermitian operators.

Returning now to the energy eigenvalues we see that the energy of state \( |n\rangle \) is \( E_n = \hbar\omega(n + 1/2) \).
4.6.3 Expansion of the field in plane waves

In source free space the Maxwell equations are

\[ \nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}, \]  
\[ \nabla \times \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}, \]  
\[ \nabla \cdot \mathbf{E} = 0, \]  
\[ \nabla \cdot \mathbf{H} = 0. \]  

We will work with a plane wave expansion of the fields in terms of basis functions \( e^{i(k \cdot r - \omega t)} \).

Write

\[ \mathbf{E} = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k \omega_k \mathcal{E}_k e^{i(k \cdot r - \omega t)} e_k + c.c. \]  
\[ \mathbf{H} = \sqrt{\frac{1}{\epsilon_0 V}} \sum_k \omega_k \mathcal{H}_k e^{i(k \cdot r - \omega t)} e'_k + c.c., \]

where \( \omega_k = c|\mathbf{k}| \) and \( e_k \) is a unit polarization vector. In this calculation the \( e_k \) are not in a spherical basis. The amplitudes \( \mathcal{E}_k, \mathcal{H}_k \) depend on \( \mathbf{k} \) and \( \omega_k \) but have no explicit dependence on \( \mathbf{r} \) and \( t \). We have pulled out a factor \( \sqrt{1/\epsilon_0 V} \) with \( V \) a volume for later convenience. The quantization volume is taken to be a cube with sides of length \( L \), so \( V = L^3 \). The allowable wavenumbers are then given by the discrete set \( \mathbf{L}k = 2\pi(n_x \hat{x} + n_y \hat{y} + n_z \hat{z}) \) where the integers \( n_x, n_y, n_z \) take on all possible positive and negative values, including zero.

Since the Maxwell equations must be satisfied for all \( \mathbf{r} \) and \( t \) each Fourier mode of the fields must individually satisfy the reciprocal space Maxwell equations

\[ (\mathbf{k} \times e_k) \mathcal{E}_k = e'_k \mu_0 \omega_k \mathcal{H}_k, \]  
\[ (\mathbf{k} \times e'_k) \mathcal{H}_k = -e_k \epsilon_0 \omega_k \mathcal{E}_k, \]  
\[ \mathbf{k} \cdot e_k = 0, \]  
\[ \mathbf{k} \cdot e'_k = 0. \]

The last two equalities say that \( e_k \) and \( e'_k \) are perpendicular to \( \mathbf{k} \). The first two equalities can be solved by putting,

\[ \mathcal{H}_k = \frac{\mathcal{E}_k}{c \mu_0} \]  
\[ e'_k = \frac{k}{k} \times e_k = \hat{k} \times e_k, \]

where we have used \( \mathbf{k} \times (\mathbf{k} \times e_k) = -k^2 e_k \), since \( e_k \) and \( \mathbf{k} \) are perpendicular, and \( \hat{k} \) is a unit vector. Using these solutions the expansions for the fields become

\[ \mathbf{E} = \sqrt{\frac{1}{\epsilon_0 V}} \sum_{k} e_{ks} \omega_k \mathcal{E}_{ks}(t)e^{ik \cdot r} + c.c. \]  
\[ \mathbf{H} = \sqrt{\frac{1}{\epsilon_0 V}} \sum_{k} (\mathbf{k} \times e_{ks}) \omega_k \mathcal{E}_{ks}(t)e^{ik \cdot r} + c.c., \]
and we have defined the time dependent amplitudes as $\mathcal{E}_{ks}(t) = \mathcal{E}_{ks}e^{-i\omega_k t}$. We have also introduced an index $s = 1, 2$ that labels the two orthogonal transverse polarization directions ($e_{ks} \cdot e_{k's} = \delta_{ss'}$).

### 4.6.4 Energy of the field

We are now ready to calculate the energy of the field in the volume $V$ using the classical formula

$$u = \frac{1}{2} \int d^3r (\epsilon_0 E \cdot E + \mu_0 H \cdot H).$$

(4.76)

To do the integral we will need the formulas

$$\int d^3r e^{i (k-k') \cdot r} = V \delta_{kk'},$$

$$(\hat{k} \times e_{ks}) \cdot (\hat{k} \times e_{k's}) = \delta_{ss'}.$$

Adding the contributions from the electric and magnetic fields we get

$$u = 2 \sum_{ks} \omega_k^2 |\mathcal{E}_{ks}(t)|^2.$$  

(4.77)

To make the relationship to a harmonic oscillator explicit define the real variables

$$q_{ks}(t) = \mathcal{E}_{ks}(t) + \mathcal{E}_{ks}^*(t),$$

(4.78)

$$p_{ks}(t) = -i\omega_k [\mathcal{E}_{ks}(t) - \mathcal{E}_{ks}^*(t)].$$

(4.79)

Recalling the time dependence of $\mathcal{E}_{ks}(t)$ we see that $q$ and $p$ satisfy

$$\frac{\partial q_{ks}(t)}{\partial t} = p_{ks}(t),$$

(4.80a)

$$\frac{\partial p_{ks}(t)}{\partial t} = -\omega_k^2 q_{ks}(t).$$

(4.80b)

When we identify the Hamiltonian with the energy $u$ it can be written as

$$H = u = 2 \sum_{ks} \omega_k |\mathcal{E}_{ks}(t)|^2$$

$$= \frac{1}{2} \sum_{ks} \left(p_{ks}^2(t) + \omega_k^2 q_{ks}^2(t)\right).$$

(4.81)

The canonical equations of motion are then

$$\frac{\partial q_{ks}(t)}{\partial t} = \frac{\partial H}{\partial p_{ks}(t)} = p_{ks}(t),$$

(4.82a)

$$\frac{\partial p_{ks}(t)}{\partial t} = -\frac{\partial H}{\partial q_{ks}(t)} = -\omega_k^2 q_{ks}(t).$$

(4.82b)

We note that Eqs. (4.80) and (4.82) are identical which validates the description of the field as an infinite set of independent harmonic oscillators.
4.6.5 Quantization of the field

Quantization of the field is now straightforward. We simply use the same procedure as in Eqs. (4.35-4.42) for the harmonic oscillator.

The annihilation and creation operators are given by
\[
\hat{a}_{ks}(t) = \frac{1}{\sqrt{2\hbar \omega}} (\omega q_{ks}(t) + i \hat{p}_{ks}(t)) = \sqrt{\frac{2\omega_k}{h}} \hat{E}_{ks}(t), \quad (4.83)
\]
\[
\hat{a}^\dagger_{ks}(t) = \frac{1}{\sqrt{2\hbar \omega}} (\omega q_{ks}(t) - i \hat{p}_{ks}(t)) = \sqrt{\frac{2\omega_k}{h}} \hat{E}^\dagger_{ks}(t). \quad (4.84)
\]

They satisfy the commutation relations
\[
\left[ \hat{a}_{ks}, \hat{a}^\dagger_{k's'} \right] = \delta_{kk'} \delta_{ss'}. \quad (4.85)
\]

In terms of them we can write the Hamiltonian as
\[
\hat{H} = \sum_{ks} \hbar \omega_k \left( \hat{a}^\dagger_{ks} \hat{a}_{ks} + \frac{1}{2} \right). \quad (4.86)
\]

This multimode Hamiltonian is a superposition of Hamiltonians for each mode of the field. We can thus write
\[
\hat{H} = \sum_{ks} \hat{H}_{ks}
\]
where
\[
\hat{H}_{ks} = \hbar \omega_k \left( \hat{a}^\dagger_{ks} \hat{a}_{ks} + \frac{1}{2} \right). \quad (4.88)
\]

Each single-mode component of the Hamiltonian has energy eigenstates that satisfy
\[
\hat{H}_{ks} | n_{ks} \rangle = \hbar \omega_k \left( n_{ks} + \frac{1}{2} \right) | n_{ks} \rangle. \quad (4.89)
\]

The general multimode energy eigenstate is the direct product of the singlemode states
\[
| \{ n_{ks} \} \rangle = | n_{k_1 s_1}, n_{k_1 s_2}, n_{k_2 s_1}, \ldots \rangle. \quad (4.90)
\]

4.6.6 Electric and magnetic field operators

The electric and magnetic field operators are given by
\[
\hat{E} = \sqrt{\frac{\hbar}{2\epsilon_0 V}} \sum_{k,s} \sqrt{\omega_k} \hat{a}_{ks} e^{i(k \cdot r - \omega_k t)} e_{ks} + H.c. \quad (4.91)
\]
\[
\hat{H} = \sqrt{\frac{\hbar}{2\epsilon_0 V c \mu_0}} \sum_{k,s} \sqrt{\omega_k} \hat{a}_{ks} e^{i(k \cdot r - \omega_k t)} (\hat{k} \times e_{ks}) + H.c. \quad (4.92)
\]

The fields are represented by hermitian operators so they are observables. All components do not, however, commute, so all field components are not simultaneously observable.
4.7 Atomic spontaneous decay rate

Using the quantized electromagnetic field we can rigorously calculate the radiative decay rate of an atom in vacuum. This provides a first principles calculation of the Einstein $A$ coefficient. As we will see the answer depends on the local density of states of the electromagnetic field. It is possible using resonant cavities to either increase or decrease the density of states, and thereby modify the spontaneous decay rate. This possibility was first pointed out by E. Purcell in the 1940s and was demonstrated using atoms in resonant cavities in the 1980s. At the current time there is a large amount of research activity related to the so-called Purcell effect.

The dipole interaction Hamiltonian between an atom and the field is $\hat{H}_1 = -\hat{\mathbf{E}} \cdot \hat{\mathbf{d}} = e\hat{\mathbf{E}} \cdot \hat{\mathbf{r}}$ for an electron of charge $-e$. Thus for each field mode we get

$$\hat{H}_1 = H_{10} (\sqrt{\omega_k a_{k,s} e_{k,s} \cdot \hat{\mathbf{r}} e^{i\phi} + H.c.})$$

with $H_{10} = e\sqrt{\hbar/(2\epsilon_0 V)}$ and $\phi = k \cdot \mathbf{r} - \omega_k t$. Now assume the atom and field are in initial state $|i\rangle = |e,n\rangle$ representing the atom in the excited state $|e\rangle$ and $n$ photons in field mode $(k, s)$. Using Fermi’s golden rule the transition rate to final state $|f\rangle = |g,n+1\rangle$ which represents the atom in the ground state and $n+1$ photons in the field is

$$\gamma_{k,s} = \frac{2\pi}{\hbar} |\langle f|\hat{H}_1|i\rangle|^2 \delta(E_f - E_i).$$

Using the dipole approximation $e^{i\mathbf{k} \cdot \mathbf{r}} \simeq 1$, $E_i = E_e$, $E_f = E_g + \hbar \omega_k$, and $\langle n+1|\hat{a}^\dagger|n\rangle = \sqrt{n+1}$ we find

$$\gamma_{k,s} = \gamma_{k,s}^{sp} + \gamma_{k,s}^{stim}$$

where

$$\gamma_{k,s}^{sp} = \frac{\pi e^2 \omega_k}{\epsilon_0 V} |\langle g|e_{k,s}^\ast \cdot \hat{\mathbf{r}} |e\rangle|^2 \delta(E_e - E_g - \hbar \omega_k),$$

$$\gamma_{k,s}^{stim} = n_{k,s} \gamma_{k,s}^{sp}.$$ (4.96b)

The stimulated rate is $n_{k,s}$ times larger than the spontaneous rate. If we repeat the above calculation for a transition $|i\rangle = |g,n\rangle \rightarrow |f\rangle = |e,n-1\rangle$ we find $\gamma_{k,s}^{abs} = \gamma_{k,s}^{stim} (e_{k,s}^\ast \rightarrow e_{k,s})$. There is no spontaneous absorption when $n_{k,s} = 0$.

To find the total spontaneous emission rate when the field is initially in the vacuum state we must sum the rate calculated for a single mode over all field modes. That is

$$\gamma^{sp} = \sum_{k,s} \gamma_{k,s}^{sp} = \frac{\pi e^2}{\epsilon_0 V} \sum_k \omega_k |e_{k,s}^\ast \cdot \mathbf{r}_{ge}|^2 \delta(E_e - E_g - \hbar \omega_k)$$

where $\mathbf{r}_{ge} = \langle g|\hat{\mathbf{r}}|e\rangle$. We then approximate the sum as an integral

$$\sum_{k,s} \rightarrow \int d^3 k \rho(k) \ldots$$
with the density of states\(^2\) \(\rho(k) = \frac{V}{8\pi^2}d^3k\). Note this is the density of states for each polarization state. The total density of states including polarization is twice this. The delta function can be written as \(\delta(E_e - E_g - \hbar\omega_k) = \delta[h(\omega_0 - \omega_k)] = \frac{1}{\hbar}\delta(\omega_0 - \omega_k)\) where \(\omega_0 = (E_e - E_g)/\hbar\) is the atomic transition frequency.

Using the above we find

\[
\gamma^{sp} = \frac{e^2}{8\pi^2\epsilon_0\hbar} \sum_s \int_0^\infty dk \, ck^3 \delta(\omega_0 - \omega_k) \int d\theta_k \, d\phi_k \sin \theta_k |e_{k,s}^* \cdot r_{ge}|^2.
\]

Note the volume has dropped out since the \(1/V\) factor that came from the field mode squared cancelled the factor of \(V\) in the density of states. Using \(\delta(\omega_0 - \omega_k) = \frac{1}{c}\delta(k - k_0)\) the integral over \(k\) gives

\[
\int_0^\infty dk \, ck^3 \frac{1}{c}\delta(k - k_0) = k_0^3 = \frac{\omega_0^3}{c^3}.
\]

The integral over angles can be simplified by choosing a coordinate system with \(k_z\) along \(r_{ge}\) and \(e_{k,1}^*\) in the plane of \(r_{ge}\) and \(k\). With these choices \(|r_{ge} \cdot e_{k,1}^*|^2 = |r_{ge}|^2 \sin^2 \theta_k\) and \(|r_{ge} \cdot e_{k,2}^*|^2 = 0\). Thus

\[
\gamma^{sp} = \frac{e^2 \omega_0^3 |r_{ge}|^2}{8\pi^2\epsilon_0\hbar c^3} \int_0^\pi d\theta_k \int_0^{2\pi} d\phi_k \sin^3 \theta_k.
\]

The angular integrals give \(8\pi/3\) and we arrive at the final result

\[
\gamma^{sp} = \frac{\omega_0^3 |d_{ge}|^2}{3\pi\epsilon_0\hbar c^3}.
\]  \((4.97)\)

This is in agreement with (4.27) provided we replace the matrix element in (4.97) with a reduced matrix element. For real atoms the reduced matrix element must be augmented with factors depending on the total angular momentum as we discuss in the next chapter.

This quantum calculation of the spontaneous decay rate of an excited atom was first done by Weisskopf and Wigner in 1930\[22\]. The result agrees with what is found from equating the decay rate to the energy loss rate due to Larmor radiation from a classical electron oscillator model provided we put \(\varepsilon x_0 = 2|d_{ge}|\) where the electron is assumed to have a motion \(x = x_0 \cos \omega_0 t\) and \(\omega_0\) is the atomic transition frequency.

\[\text{December 15, 2015 M. Saffman}\]
Chapter 5

Lifetimes of excited states

5.1 Radiative lifetime of fine structure states - electric dipole transitions

We can use the result for the $A$ coefficient, or equivalently the radiative decay rate $\gamma$, to calculate the lifetime of fine structure states. The radiative lifetime $\tau$ of an excited state is defined as the inverse of the rate of spontaneous emission $\gamma$. The spontaneous emission rate from an excited fine structure state $|n_e J_e L_e m_e\rangle$ to the ground state is

$$\gamma = \frac{\omega_{eg}^3 e^2}{3\pi\epsilon_0 hc^3} \sum_{m_g=-J_g}^{J_g} \sum_{q=0,\pm1} |\langle n_g L_g s J_g m_g | r_{-q} | n_e L_e s J_e m_e \rangle|^2$$

where we have summed over the ground state levels $-J_g \leq m_g \leq J_g$ and all possible polarizations $q = 0, \pm1$ of the emitted radiation.

Using the Wigner-Eckart theorem the square of the matrix element can be written as

$$|\langle n_g L_g s J_g m_g | r_{-q} | n_e L_e s J_e m_e \rangle|^2 = \frac{|\langle n_g L_g s J_g | r | n_e L_e s J_e \rangle|^2}{2J_g + 1} \left( C_{J_g m_g}^{J_e m_e -1-q} \right)^2.$$  \hspace{1cm} (5.2)

The sum over $m_g, q$ can be evaluated with the identity

$$\sum_{m_g=-J_g}^{J_g} \sum_{q} \left( C_{J_g m_g}^{J_e m_e -1-q} \right)^2 = \frac{2J_g + 1}{2J_e + 1}$$

giving

$$\gamma = \frac{\omega_{eg}^3 e^2}{3\pi\epsilon_0 hc^3} \frac{1}{2J_e + 1} |\langle n_g L_g s J_g | r | n_e L_e s J_e \rangle|^2$$

$$= \frac{4ck^3\alpha}{3} \frac{1}{2J_e + 1} |\langle n_g L_g s J_g | r | n_e L_e s J_e \rangle|^2$$  \hspace{1cm} (5.3)

with $k$ the transition wavenumber and $\alpha$ the fine structure constant. The decay rate is thus the same for all Zeeman levels of the excited state. This must be so due to rotational invariance. Since $\langle r \rangle \sim a_0$ and $a_0/\lambda \sim \alpha$ we see that $\gamma \sim k\alpha^3$.
We can further reduce the expression for $\gamma$ using (see (A-50,A-53))

$$\langle n_g L_g s_J g | r | n_e L_e s_J e \rangle^2 = \max(L_g, L_e)(2J_g + 1)(2J_e + 1) \left( S^{L_e} s_J e \right)^2 \left( R_{n_e L_e n_g L_g} \right)^2$$

with $s = 1/2$ the electron spin. Thus

$$\gamma = \frac{e^2 \omega^3_{eg}}{3\pi \epsilon_0 \hbar c^3} \max(L_g, L_e)(2J_g + 1)(2J_e + 1) \left( S^{L_e} s_J e \right)^2 \left( R_{n_e L_e n_g L_g} \right)^2. \quad (5.4)$$

As an example the Rb $5P_{3/2}$ state decays to the $5S_{1/2}$ ground state. The radial matrix element is $R_{5P_{3/2},5S_{1/2}} \approx 5.14a_0$, with $a_0$ the Bohr radius. This is calculated using the Coulomb wave functions of Ch. 1. We find for the decay rate $\gamma/2\pi = 5.98 \times 10^6$ s$^{-1}$. The experimentally measured value agrees with this to a few percent.

It is interesting to examine the lifetime Eq. (5.4) in more detail for a cycling transition $|J_e, m_e = J_e \rangle \rightarrow |J_g = J_e - 1, m_g = J_g \rangle$. For a one electron atom $s = 1/2$, $J_e = L_e + 1/2$, $L_g = L_e - 1$, which results in

$$\gamma_{D2} = \frac{e^2 \omega^3_{eg}}{3\pi \epsilon_0 \hbar c^3} \frac{J_e - 1/2}{2J_e} \left( R_{n_e L_e n_g L_g} \right)^2.$$

We have added the subscript D2 since when $n_g, n_e$ are the ground and first resonance levels and $l_g = 0, l_e = 1$ this corresponds to the alkali D2 transition. The result for the D1 type transition $|J_e \rangle \rightarrow |J_g = J_e \rangle$, $S = 1/2$, $J_e = L_e - 1/2$, $L_g = L_e - 1$, is

$$\gamma_{D1} = \frac{e^2 \omega^3_{eg}}{12\pi \epsilon_0 \hbar c^3} \frac{1}{J_e(1 + J_e)} \left( R_{n_e L_e n_g L_g} \right)^2.$$

We see that for $L_e = 1$ and $J_e = 3/2$ (D2 line) or $J_e = 1/2$ (D1 line) the radiative decay rate is the same

$$\gamma_{(D1 \text{ or } D2)} = \frac{e^2 \omega^3_{eg}}{9\pi \epsilon_0 \hbar c^3} \left( R_{n_e L_e n_g L_g} \right)^2.$$

In alkali atoms with nonzero quantum defects that differ slightly for the two fine structure levels the radial matrix elements are not equal for the two cases and there is a small difference in the decay rates. In Cs, the heaviest of the alkalis, the difference is relatively large $\gamma_{D1} = 2\pi \times 4.561 \times 10^6$ s$^{-1}$ and $\gamma_{D2} = 2\pi \times 5.223 \times 10^6$ s$^{-1}$.

### 5.1.1 Radiative lifetime due to electric quadrupole transitions

The radiative decay rate for a quadrupole transition can be found using a Wigner-Weisskopf type calculation as is usually applied to dipole allowed transitions. For an electric dipole transition

$$\gamma_{E1} = \left( \frac{\alpha e^3 c}{2\pi} \right) \left[ \frac{8\pi}{3} \right] \sum_{j_g} \sum_{m_g} \langle n_g j_g l_g m_g | \hat{r} \hat{C}_1 | n_e j_e l_e m_e \rangle^2.$$

Here $C_{kq} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}$ and the factor in square brackets of $8\pi/3$ appears from the angular integration of $\mathbf{r} \cdot \mathbf{e}$ in the calculation of the decay rate. Application of the Wigner-Eckart
5.1 Radiative lifetime of fine structure states - electric dipole transitions

\[ \gamma_{E1} = \left( \frac{\alpha e k_e^3}{2\pi} \right) \left[ \frac{8\pi}{3} \right] \left| \langle n_g j_g l_g m_g | \hat{n} \hat{C}_1 | n_e j_e l_e m_e \rangle \right|^2 / (2j_e + 1). \]

The analogous expression for electric quadrupole (E2) transitions is

\[ \gamma_{E2} = \left( \frac{\alpha e k_e^3}{2\pi} \right) \left[ 2\pi \right] \sum_{m_g = -j_g}^{j_g} \sum_q |a_q| \langle n_g j_g l_g m_g | r^2 \hat{C}_2 | n_e j_e l_e m_e \rangle |^2 \]

with \( a_q = (-1)^q \sqrt{10} \sum_{\mu \nu} C_{\mu \nu}^{j_g} k_{\mu \nu} \). The factor in square brackets of \( 2\pi \) again appears from an angular integration. The Wigner-Eckart theorem gives

\[ \gamma_{E2} = \left( \frac{\alpha e k_e^5}{2\pi} \right) \left[ 2\pi \right] \sum_{m_g = -j_g}^{j_g} \sum_{q = -2}^{2} |a_q C_{j_g m_g}^{j_e m_e 2q}|^2. \]

Recalling that \( \sum_{m_g = -j_g}^{j_g} \sum_{q = -2}^{2} |C_{j_g m_g}^{j_e m_e 2q}|^2 = \frac{2j_g + 1}{2j_e + 1} \), it can be verified that

\[ \sum_{m_g = -j_g}^{j_g} \sum_{q = -2}^{2} |a_q C_{j_g m_g}^{j_e m_e 2q}|^2 = \frac{2j_g + 1}{2j_e + 1}. \]

Thus, the quadrupole radiative decay rate is

\[ \gamma_{E2} = \frac{\alpha e k_e^5}{15(2j_e + 1)} \langle n_g j_g l_g | r^2 \hat{C}_2 | n_e j_e l_e \rangle |^2. \]  \]  \]  \]  \]  \]  \]  \]  \]  \]

Since \( \langle r^2 \rangle \sim a_0^2 \) and \( a_0/\lambda \sim \alpha \), we see that \( \gamma \sim k e^5 \), which is a factor of \( e^2 \) smaller than E1 allowed decay.

This can be further simplified for a one electron atom \( (s = 1/2) \) using

\[ \langle n_g j_g l_g | r^2 \hat{C}_2 | n_e j_e l_e \rangle |^2 = (2j_e + 1)(2j_g + 1) \left( \frac{\ell_g}{j_g} \frac{j_g}{\ell_e} \frac{1}{2} \right)^2 \left( C_{\ell_g \ell_e 020}^{\ell_e 0} \right)^2 \left( \int dr r^4 R_{\ell_g l_g} R_{\ell_e l_e} \right)^2 \]

to arrive at

\[ \gamma = \frac{\alpha e k_e^5}{15} (2j_g + 1)(2j_e + 1) \left( \frac{\ell_g}{j_e} \frac{j_g}{\ell_e} \frac{1}{2} \right)^2 \left( C_{\ell_g \ell_e 020}^{\ell_e 0} \right)^2 \left( R_{n_G l_G}^{n_e l_e} \right)^2. \]

where \( R_{n_G l_G}^{n_e l_e} = \int dr r^4 R_{n_G l_G} R_{n_e l_e} \). For quadrupole decay from \( d \to s \) we have \( \ell_e = 2, \ell_g = 0, j_g = 1/2 \) which gives

\[ \gamma_{d_{3/2}, d_{5/2}} = \frac{1}{15} \alpha e k_e^5 \left( R_{n_G l_G}^{n_e l_e} \right)^2. \]

Using \( R_{n_G l_G}^{n_e l_e} = 37.5a_0^2 \) for Cs6s–5d we get \( \gamma = 20.9 \) s\(^{-1}\).
5.2 Radiative lifetime due to magnetic dipole allowed decay

Some atomic states do not have electric dipole allowed transitions to lower lying levels. Such states have long lifetimes and are referred to as metastable. Higher order multipoles contribute to radiative decay in this case, the leading effect being magnetic dipole transitions. To calculate the rate of magnetic dipole decay we may repeat the Wigner-Weisskopf calculation leading to Eq. (5.1), but for the case of a magnetic interaction. Alternatively we can arrive at the correct result without much work by noting the following. The radiative decay rate comes about from considering the transition rate as calculated from Fermi’s golden rule which is proportional to the square of the interaction Hamiltonian. The electric dipole Hamiltonian is $\mathcal{H}_{E1} = -\mathbf{d} \cdot \mathbf{E}$ and the magnetic dipole interaction Hamiltonian of an electron in a fine structure state $|J, m_J\rangle$ is $\mathcal{H} = -\hat{\mu} \cdot \mathbf{B}$. In free space $|\mathbf{B}| = |\mathbf{E}|/c$ (SI units) so the rate for magnetic dipole transitions is just that given in (5.1) multiplied by $1/c^2$ and with $\mathbf{d}$ replaced by $\hat{\mu}$.

We find for fine structure states $|nLS; Jm_J\rangle$

$$\gamma_M = \frac{\omega_{eg}^3}{3\pi\epsilon_0\hbar c^5} \sum_{m_g=-J_g}^{J_g} \sum_{q=0, \pm 1} \langle n LS Jg | \mu \rangle | n LS Jg \rangle^2.$$

Using the Wigner-Eckart theorem this reduces to

$$\gamma_M = \frac{\omega_{eg}^3}{3\pi\epsilon_0\hbar c^5} \frac{1}{2J_e + 1} | \langle n LS Jg | \hat{\mu} \rangle | n LS Jg \rangle|^2. \quad (5.10)$$

Since the magnetic moment operator does not couple to the radial state of the atom the rate is only nonzero for $n_g = n_e$. Using $\hat{\mu} = -g_J \mu_B \hat{J}/\hbar = -g_L \mu_B \hat{L}/\hbar - g_S \mu_B \hat{S}/\hbar$ we arrive at

$$\gamma_M = \frac{\mu_B^2 \omega_{eg}^3}{3\pi\epsilon_0\hbar c^5} \frac{1}{2J_e + 1} | \langle n LS Jg | g_L \hat{L} + g_S \hat{S} \rangle | n LS Jg \rangle|^2. \quad (5.11)$$

### 5.2.1 Radiative lifetime of the H hyperfine transition

Let us apply this formula to the spontaneous decay of the Hydrogen hyperfine state $1s_{1/2} F_e = 1 \rightarrow 1s_{1/2} F_g = 0$. Since $L = 0$ we have

$$\gamma_M = \frac{g_s^2 \mu_B^2 \omega_{eg}^3}{3\pi\epsilon_0\hbar c^5} \frac{1}{2F_e + 1} | \langle ISF_g | ISF_e \rangle |^2 \quad (5.12)$$

with $I = s = 1/2$ and $\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{s}}$. The reduced matrix element is

$$\langle ISF_g | ISF_e \rangle = \sqrt{(2F_e + 1)(2F_g + 1)} \begin{pmatrix} s & I & F_e \end{pmatrix} \begin{pmatrix} F_g & 1 & s \end{pmatrix} \langle s || \hat{s} || s \rangle = \sqrt{3} \begin{pmatrix} 1/2 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} 0 & 1/2 & 1/2 \end{pmatrix} \langle s || \hat{s} || s \rangle = \frac{\sqrt{3}}{2} \hbar$$

where we have used the formula for the reduced matrix element of the angular momentum operator (Sobelman 4.148) $\langle J || J || J' \rangle = \sqrt{J(J + 1)(2J + 1)} \delta_{JJ'}$. Thus, with $g_s = 2$,

$$\gamma_M = \frac{\mu_B^2 \omega_{eg}^3}{3\pi\epsilon_0\hbar c^5} = 2.87 \times 10^{-15} \text{ s}^{-1} \quad (5.13)$$

The $1/e$ lifetime is $\tau = 1.1 \times 10^7$ years.
5.2.2 Lifetimes of Ho metastable states

Let us now consider a more complex case, the metastable ground states of Ho. The groundstates are \(^4I_J\) with \(J = 15/2, 13/2, 11/2, 9/2\), \(L = 6\), and \(S = 3/2\). The ground state has \(J = 15/2\) and the energies of the metastable components are 5419.7 cm\(^{-1}\)(\(J = 13/2\)), 8605.16 cm\(^{-1}\)(\(J = 11/2\)), and 10695.75 cm\(^{-1}\)(\(J = 9/2\)).

The reduced matrix element in Eq. (5.12) is

\[
|\langle n_g S_g J_g | g_L \hat{L} + g_S \hat{S} | n_e L_e S_e J_e \rangle | = g_L (-1)^{L_e + L + S} \sqrt{(2J_e + 1)(2J_g + 1)} \begin{pmatrix} L & S & J_e \\ J_g & 1 & J_e \end{pmatrix} \langle L | \hat{L} | L \rangle + g_S (-1)^{L_e + S + L + 1} \sqrt{(2J_e + 1)(2J_g + 1)} \begin{pmatrix} S & L & J_e \\ J_g & 1 & S \end{pmatrix} \langle S | \hat{S} | S \rangle \]

\times \left[ g_L \begin{pmatrix} L & S & J_e \\ J_g & 1 & L \end{pmatrix} \langle L | \hat{L} | L \rangle + g_S \begin{pmatrix} S & L & J_e \\ J_g & 1 & S \end{pmatrix} \langle S | \hat{S} | S \rangle \right].

(5.15)

We find

\[
\begin{align*}
\gamma_{13/2 \rightarrow 15/2}^{M1} &= 53.0 \text{ s}^{-1} \\
\gamma_{11/2 \rightarrow 13/2}^{M1} &= 16.6 \text{ s}^{-1} \\
\gamma_{9/2 \rightarrow 11/2}^{M1} &= 4.23 \text{ s}^{-1}.
\end{align*}
\]

5.3 Lifetime of highly excited states

As the principal quantum number \(n\) increases the radiative lifetime \(\tau\) grows as a power law, \(\tau \sim n^q\). Using simple estimates we can determine the exponent \(q\).

From the preceding discussion we know that \(\gamma \sim \omega_{eg}^3 |\langle g | r | e \rangle|^2\). The matrix element is largest when \(|g\rangle, |e\rangle\) have similar \(n\) so the wavefunctions overlap strongly. Let us assume \(n_e = n\) and \(n_g = n - 1\). Then

\[
\hbar \omega_{eg} = \frac{E_H}{2} \left( -\frac{1}{n^2} + \frac{1}{(n-1)^2} \right) \\
\sim \frac{E_H}{n} \\
\sim \frac{1}{n^3}.
\]

The matrix element can be estimated as

\[
|\langle n - 1 | r | n \rangle|^2 = \left| \int d^3 r \psi_g^* r \psi_e \right|^2 \\
\sim \left( \sqrt{a_0(n - 1)^2} \sqrt{a_0n^2} \right)^2 \\
\sim a_0^2 n^4.
\]
Thus
\[\gamma_{n-1\rightarrow n} \sim \left( \frac{1}{n^3} \right)^3 n^4 \sim \frac{1}{n^5}\]
and
\[\tau \sim n^5.\]

This is not a good estimate for the lifetime since there is a faster decay route. The excited atom could also decay directly to the ground state. For \(n \gg 1\) the frequency is \(\hbar \omega \sim E_n/2n_g^2\) which is independent of \(n\). The matrix element is determined by the value of the excited state wavefunction near the origin. For hydrogen we have \(\psi_{nl}(r \rightarrow 0) \sim r^l/n^{3/2}\) so
\[|\langle g \mid r \mid n \rangle|^2 \sim \frac{1}{n^3}.\]

Thus
\[\gamma_{g\rightarrow n} \sim \frac{1}{n^3}\]
and
\[\tau \sim n^3.\]

We see that the decay is primarily to the ground state. Even though the matrix element is small the \(\omega^3\) factor favors this decay mode.

This scaling applies at zero temperature. At finite temperature the lifetime is \(\tau_T = \tau/N(\omega_{eg})\) where \(N(\omega_{eg})\) is the blackbody occupation number at temperature \(T\) and frequency \(\omega_{eg}\). We have
\[N(\omega) = \frac{1}{e^{\hbar \omega/k_B T} - 1}.\]

At room temperature \(k_B T \sim 0.01\ eV\) and the correction to the excited state to ground state decay is negligible. However for the transition \(n \rightarrow n-1\) the frequency is small and
\[N \sim \frac{k_B T}{\hbar \omega} \sim n^3.\]

Thus at finite \(T\) the lifetime due to decay to the neighboring \(n\) state scales as
\[\tau_T \sim n^5/n^3 \sim n^2.\]

Detailed calculations which account for all decay channels give finite temperature lifetimes in the range
\[\tau_T \sim n^{2.5} - n^3.\]

### 5.3.1 Lifetime of circular Rydberg states

Circular Rydberg states with \(|m| = l = n - 1\) have lifetimes that scale as \(\tau \sim n^5\) instead of the \(\tau \sim n^3\) scaling of low angular momentum states. The reason for this is that E1 selection rules only allow decay from \(|n, n-1, n-1\rangle\) to \(|n-1, n-2, n-2\rangle\). The principal quantum number can only change by one and we find \(\tau \sim n^5\). The lifetimes for low angular momentum and circular states are summarized in Table 5.1.
The long lifetimes of these states enable interesting quantum measurements which have been the subject of study in the group of S. Haroche in Paris. Let’s calculate the numerical value of the lifetime for decay from $|e\rangle \equiv |n, l = n - 1, m = n - 1\rangle$ to $|g\rangle \equiv |n - 1, l = n - 2, m = n - 2\rangle$ is

$$\tau = \frac{3\pi\epsilon_0\hbar c^3}{\omega_{eg}^3e^2|r_{eg}|^2}.$$  

The transition frequency is $\omega_{eg} = \frac{E_n}{2\hbar} \left[ \frac{1}{(n-1)^2} - \frac{1}{n^2} \right]$ and the matrix element is

$$r_{g\rightarrow e} = \langle n - 1, n - 2|\hat{r}|n, n - 1\rangle \frac{C_{n-1,n-1,1,-1}^{n-2,n-2}}{\sqrt{2n - 3}}.$$  

The Clebsch-Gordan coefficient evaluates to $C_{n-1,n-1,1,-1}^{n-2,n-2} = \sqrt{(2n - 3)/(2n - 1)}$ and the reduced matrix element is

$$\langle n - 1, n - 2|\hat{r}|n, n - 1\rangle = -\sqrt{n - 1} \int_0^\infty dr r^3 R_{n-1,n-2}R_{n,n-1}$$  

with $R_{n,l}$ hydrogenic wavefunctions. The radial integral can be evaluated using the Gordon formula, and has the value

$$\int_0^\infty dr r^3 R_{n-1,n-2}R_{n,n-1} = \frac{4^n(n^2 - n)^{n+1}}{(2n - 1)^{2n+1}\sqrt{(2n - 3)!}}a_0.$$  

The transition dipole moment is therefore

$$e^2|r_{g\rightarrow e}|^2 = 216^n\frac{n^{2n+2}(n - 1)^{2n+4}}{(2n - 1)^{4n+2}}e^2a_0^2$$  

and the lifetime is

$$\tau = \frac{3\pi\epsilon_0\hbar c^3}{E_n^3a_0^2e^2} \frac{(2n - 1)^{4n-1}}{2^{4n+1}n^{2n-4}(n - 1)^{2n-2}}.$$  

For $n = 50$ we find $\omega_{eg} = 2\pi \times 51.1$ GHz, $|r_{eg}|^2 = 2.91 \times 10^6a_0^2$, and $\tau = 34.2$ ms. The variation of lifetimes up to $n = 150$ is shown in Fig. 5.1. A 1 s lifetime is reached at $n = 100$. Note that if we had used the hydrogenic result $\langle r\rangle_{nl} = \frac{a_n}{2}[3n^2 - l(l + 1)]$ and estimated the matrix element by $|r_{eg}|^2 \approx \langle r\rangle_{50.49}\langle r\rangle_{51.50} = 6.12 \times 10^6a_0^2$ we would have been about a factor of 2.1 too large.

\footnote{It can be shown that $\langle n, n - 1||r||n - 1, n - 2\rangle = -\langle n - 1, n - 2||r||n, n - 1\rangle$.}

The transition frequency is $\omega_{eg} = \frac{E_n}{2\hbar} \left[ \frac{1}{(n-1)^2} - \frac{1}{n^2} \right]$ and the matrix element is

$$r_{g\rightarrow e} = \langle n - 1, n - 2|\hat{r}|n, n - 1\rangle \frac{C_{n-1,n-1,1,-1}^{n-2,n-2}}{\sqrt{2n - 3}}.$$  

The Clebsch-Gordan coefficient evaluates to $C_{n-1,n-1,1,-1}^{n-2,n-2} = \sqrt{(2n - 3)/(2n - 1)}$ and the reduced matrix element is

$$\langle n - 1, n - 2|\hat{r}|n, n - 1\rangle = -\sqrt{n - 1} \int_0^\infty dr r^3 R_{n-1,n-2}R_{n,n-1}$$  

with $R_{n,l}$ hydrogenic wavefunctions. The radial integral can be evaluated using the Gordon formula, and has the value

$$\int_0^\infty dr r^3 R_{n-1,n-2}R_{n,n-1} = \frac{4^n(n^2 - n)^{n+1}}{(2n - 1)^{2n+1}\sqrt{(2n - 3)!}}a_0.$$  

The transition dipole moment is therefore

$$e^2|r_{g\rightarrow e}|^2 = 216^n\frac{n^{2n+2}(n - 1)^{2n+4}}{(2n - 1)^{4n+2}}e^2a_0^2$$  

and the lifetime is

$$\tau = \frac{3\pi\epsilon_0\hbar c^3}{E_n^3a_0^2e^2} \frac{(2n - 1)^{4n-1}}{2^{4n+1}n^{2n-4}(n - 1)^{2n-2}}.$$  

For $n = 50$ we find $\omega_{eg} = 2\pi \times 51.1$ GHz, $|r_{eg}|^2 = 2.91 \times 10^6a_0^2$, and $\tau = 34.2$ ms. The variation of lifetimes up to $n = 150$ is shown in Fig. 5.1. A 1 s lifetime is reached at $n = 100$. Note that if we had used the hydrogenic result $\langle r\rangle_{nl} = \frac{a_n}{2}[3n^2 - l(l + 1)]$ and estimated the matrix element by $|r_{eg}|^2 \approx \langle r\rangle_{50.49}\langle r\rangle_{51.50} = 6.12 \times 10^6a_0^2$ we would have been about a factor of 2.1 too large.

\footnote{It can be shown that $\langle n, n - 1||r||n - 1, n - 2\rangle = -\langle n - 1, n - 2||r||n, n - 1\rangle$.}
For later reference we give some values of reduced matrix elements useful for calculating Rydberg coupling strengths

\[
\langle n-1, n-2| r | n, n-1 \rangle = -\frac{4^n n^{n+1} (n-1)^{n+3/2} \sqrt{4n^2 - 6n + 2}}{(2n-1)^{2n+1}} a_0,
\]

\[
\langle n+1, n| r | n, n-1 \rangle = \frac{2^{1/2} 4^{n+1} (n+1)^{n+2} n^{n+3}}{(2n+1)^{2n+5/2}} a_0.
\]

This exceptionally long $n^5$ lifetime only applies at zero temperature or in a cryostat close to zero temperature. At room temperature we recover $n^2$ scaling.
Chapter 6

Line broadening and line shapes

Several different physical mechanisms lead to line broadening which changes a narrow atomic transition into a spectrally broadened absorption or emission profile. We have already seen how the finite lifetime of an optically excited state leads to a Lorentzian line profile. The normalized form of this which was given in (4.7) is

\[ L(\omega) = \frac{2}{\pi\gamma} \frac{1}{1 + \frac{4\Delta^2}{\gamma^2}}, \]

(6.1)

where \( \gamma = 1/\tau \) is the radiative decay rate and \( \Delta = \omega - \omega_0 \) is the detuning of the optical frequency \( \omega \) from the atomic transition frequency \( \omega_0 \). The line profile is normalized so that \( \int_{-\infty}^{\infty} d\omega L(\omega) = 1 \).

This type of broadening is referred to as “homogeneous” broadening since it affects all atoms in a sample in the same way. In general line broadening mechanisms may be homogeneous or inhomogeneous if the amount of broadening is different for each atom in a sample. The most important line broadening mechanisms, and their type, are:

- radiative (natural) broadening (homogeneous)
- Doppler broadening (inhomogeneous)
- pressure (collisional) broadening (homogeneous)

### 6.1 Doppler broadening

Consider an atom that is moving with velocity \( \mathbf{v} \) in the laboratory frame. The atom is illuminated by radiation emitted by a stationary source (such as a laser or a lamp) of frequency \( \omega \) and wavevector \( \mathbf{k} \). In the reference frame of the moving atom the frequency appears to be \( \omega' = \omega - \mathbf{k} \cdot \mathbf{v} \). In other words when the atom is moving towards the source (\( \mathbf{k} \cdot \mathbf{v} < 0 \)) the light appears to be “blue” shifted to higher frequency and when the atom is moving away from the source (\( \mathbf{k} \cdot \mathbf{v} > 0 \)) the light appears to be “red” shifted to lower frequency. This is the Doppler effect which is present whenever there is a relative motion of the source.
and observer (in this case the atom). If the light is propagating along \( \mathbf{e}_z \) then we can write \( \mathbf{k} = k \mathbf{e}_z \) and \( \mathbf{k} \cdot \mathbf{v} = kv_z \) so the Doppler shifted frequency is \( \omega' = \omega - kv_z = \omega(1 - v_z/c) \). We recognize the usual Doppler effect giving a frequency shift of \( -\omega v_z/c \). Note that this is the “first order” Doppler effect. Even when \( \mathbf{k} \cdot \mathbf{v} = 0 \) there is a “second order” relativistic Doppler effect. For most atomic physics problems related to the center of mass motion of an atom \( |v/c| \ll 1 \) and the first order Doppler effect is all we need to take into account. The line shape is shown in Fig. 6.1.

The Doppler effect turns out to be important in connection with “optical molasses” which can be used to cool atomic motion. We will take this up later.

In a gas of atoms in thermal equilibrium at temperature \( T \) the atomic velocity is described by the Maxwell-Boltzmann distribution. According to Boltzmann statistics the probability of occurrence of velocity \( v \) is proportional to \( e^{-mv^2/2k_B T} \) with \( m \) the atomic mass, and \( k_B \) the Boltzmann constant. The probability of an atom having speed \( v \) is

\[
 f(v) = a e^{-mv^2/2k_B T} = a e^{-mv^2_z/2k_B T} e^{-mv^2_x/2k_B T} e^{-mv^2_y/2k_B T} 
\]

with \( a \) a normalization constant. Requiring \( \int d^3v f(v) = 1 \) gives \( a = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \). There are some characteristic quantities associated with \( f(v) \). The rms velocity is

\[
 v_{\text{rms}} = \langle v^2 \rangle^{1/2} = \left( \frac{3k_B T}{m} \right)^{1/2}.
\]

The most probable velocity \( v_p \) is that for which the isotropic probability distribution is maximum. This is found from the condition \( \frac{d}{dv} \langle v^2 f(v) \rangle = 0 \) which occurs for \( v = v_p = \left( \frac{2k_B T}{m} \right)^{1/2} \). We see that \( v_p < v_{\text{rms}} \).

Using \( f(v) \) we can find the one-dimensional velocity distribution function. This is

\[
 f(v_z) = \int dv_x dv_y f(v) = \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-mv_z^2/2k_B T}.
\]

It is convenient to rewrite this in terms of \( v_p \) as

\[
 f(v_z) = \frac{1}{\pi^{1/2} v_p} e^{-v_z^2/v_p^2}.
\]
The density of atoms with $v_z$ between $v_z$ and $v_z + dv_z$ is

$$n(v_z) = \frac{N}{\pi^{1/2}v_p} e^{-v_z^2/v_p^2}$$

where $N = \int_{-\infty}^{\infty} dv_z n(v_z)$ is the total number of atoms in the sample.

We are now ready to determine the lineshape function due to Doppler broadening. Defining the $z$ axis to be along the direction of light propagation we found above that the Doppler shifted frequency seen by an atom is $\omega' = \omega(1 - v_z/c)$. Solving for the velocity gives $v_z = \frac{c}{\omega}(\omega - \omega')$ and using $n(v_z)|dv_z| = n(\omega')|d\omega'|$ we find

$$n(\omega') = n(v_z) \left| \frac{dv_z}{d\omega'} \right| = \frac{c}{\omega} n(v_z) = \frac{cN}{\pi^{1/2}\omega v_p} e^{-c^2(\omega - \omega')^2/\omega'^2 v_p^2}.$$

A stationary atom absorbs most strongly when the source frequency coincides with the atomic transition frequency, i.e. $\omega = \omega_a$ so the Doppler broadened absorption line profile is

$$D(\omega) = 1 - n(\omega') = \frac{c}{\omega} \frac{\omega_a v_p}{\pi^{1/2}\omega v_p} e^{-c^2(\omega - \omega_a)^2/\omega^2 v_p^2}.$$

This is normalized so that $\int_{-\infty}^{\infty} d\omega D(\omega) = 1$.

We see that Doppler broadening gives a Gaussian profile. The full width at half maximum (FWHM) can be written as $\delta \omega_D$ and satisfies

$$e^{-c^2(\delta \omega_D/2)^2/\omega_a^2 v_p^2} = 1/2.$$

Solving gives the Doppler width

$$\delta \omega_D = \frac{\omega_a}{c} \left( \frac{8 \ln 2}{m} \right)^{1/2} = 2 (\ln 2)^{1/2} \frac{\omega_a}{c} v_p.$$

In terms of the Doppler width the line profile is

$$D(\omega) = \frac{2 (\ln 2)^{1/2}}{\pi^{1/2}\delta \omega_D} e^{-4 \ln 2(\omega - \omega_a)^2/(\delta \omega_D)^2}.$$

For most atomic transitions at room temperature the Doppler broadening dominates the radiative broadening. As an example consider the H Lyman $\alpha$ line from $1s \rightarrow 2p$ at $\lambda = 121.6$ nm. The radiative lifetime of the $2p$ state is $\tau = 1.6$ ns which gives a Lorentzian linewidth of $\Delta \nu_{\text{FWHM}} = 99.5$ MHz. In a hydrogen discharge at $T = 1000$ K the Doppler linewidth would be $\delta \nu_D = \delta \omega_D/2\pi = 56$ GHz. In order to reduce the Doppler linewidth to be the same as the radiative linewidth we would have to cool the hydrogen gas to $T = 3.2$ mK. Thus very cold atoms are required to directly observe the radiative (natural) linewidth.

However if we are very far detuned then $L(\omega) \sim \gamma^2/\Delta^2$ and $D(\omega) \sim e^{-\Delta^2/\delta \omega_D^2}$. Thus for $\Delta \gg \gamma$ and $\Delta \gg \delta \omega_D$ absorption due to Doppler broadening becomes negligible compared to absorption due to the natural width and it may be possible to see the effect of the natural linewidth in the absorption spectrum.

December 15, 2015 M. Saffman
6.2 Absorption due to combined Radiative and Doppler broadening

Consider an optical beam propagating through a cell of length \( L \) containing a hot atomic vapor. The ratio of the output to the input intensity is given by \( T = I_{\text{out}}/I_{\text{in}} = e^{-\alpha L} \). The absorption coefficient is \( \alpha = \sigma n_a \), with \( \sigma \) the scattering cross section of a single atom, and \( n_a \) the density of atoms. Using for simplicity a two-level atomic model we can write the scattering cross section as

\[
\sigma = \frac{3\lambda^2}{2\pi} \frac{1}{1 + 4\frac{\Delta^2}{\gamma^2} + \frac{I}{I_s}},
\]

where \( \lambda \) is the transition wavelength, \( \gamma \) is the FWHM of the transition (natural linewidth), and \( \Delta = \omega - \omega_a \) is the detuning in radians between the optical frequency \( \omega \) and the atomic transition frequency \( \omega_a = 2\pi c/\lambda_a \). In this section we will assume weak saturation and neglect the intensity dependence. Note that the above formula should be used with caution when calculating the absorption of a real multilevel atom. It is approximately valid if we use for example a \( \sigma_+ \) polarized beam with a background axial magnetic field to define the quantization axis. Depolarizing Raman transitions as well as collisions between atoms, and with the walls will nonetheless lead to optical pumping, and loss of alignment.

Simple application of the above formula for a hot gas grossly overestimates the absorption. This is because the atoms have a temperature dependent velocity distribution that results in large Doppler broadening of the resonance as discussed in the previous section. To calculate the transmission of a probe beam in this situation we need to average over the thermal line profile.

The effective detuning including the Doppler shift for an atom with velocity \( \mathbf{v} \) and a probe beam propagating along \( \mathbf{e}_z \) is \( \Delta = \Delta_0 - kv_z \), where \( \Delta_0 = \omega - \omega_a \) is the detuning for a stationary atom and \( k = 2\pi/\lambda \). The Doppler broadened absorption profile, neglecting saturation effects, is thus

\[
\alpha = n_a \frac{3\lambda^2}{2\pi} \int dv_z \frac{f(v_z)}{1 + 4\left(\frac{\Delta_0 - kv_z}{\gamma}\right)^2},
\]

with \( n_a \) the atomic density. Using the expression for \( f(v_z) \) from above

\[
\alpha = n_a \frac{3\lambda^2}{2\pi} \left( \frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^\infty dv_z \frac{e^{-mv_z^2/2k_B T}}{1 + 4\left(\frac{\Delta_0 - kv_z}{\gamma}\right)^2}.
\]

For \( \Delta_0 = 0 \) we can use the result \( \int_{-\infty}^\infty dx \frac{e^{-ax^2}}{1 + b} = \frac{\pi^{1/2}}{\sqrt{b}} \left[ 1 - \text{Erf}(\sqrt{a/b}) \right] \), where \( \text{Erf}(x) = (2/\sqrt{\pi}) \int_0^x dt e^{-t^2} \) is the error function. A little algebra gives

\[
\alpha = n_a \frac{3\gamma^3}{8\pi^{3/2}} \left( \frac{m}{2k_B T} \right)^{1/2} e^{\frac{mv_z^2}{8k_B T}} \left[ 1 - \text{Erf} \left( \sqrt{\frac{m\gamma^2}{8k_B T}} \right) \right] \left( \frac{m\gamma^2}{8k_B^2 T} \right).
\]

For \( \Delta_0 \neq 0 \) we can express the integral in (6.4) in terms of the plasma dispersion function \( Z(z = a + ib) \) which has the integral definition

\[
Z(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty d\zeta \frac{e^{-\zeta^2}}{\zeta - z} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty d\zeta \left( \frac{\zeta-a}{b^2 + (\zeta-a)^2} \right) + \frac{i}{\sqrt{\pi}} \int_{-\infty}^\infty d\zeta \frac{be^{-\zeta^2}}{b^2 + (\zeta-a)^2}.
\]
The plasma dispersion function is also related to the error function through

\[ Z(z) = i\sqrt{\pi}e^{-z^2}\text{Erfc}(-iz) \] (6.6)

where \( \text{Erfc}(z) = 1 - (2/\sqrt{\pi})\int_0^z dt e^{-t^2} \) is the complementary error function. We then note

\[
\int_{-\infty}^{\infty} dv_z e^{-mv_z^2/2k_BT} = \frac{\gamma}{2k} \int_{-\infty}^{\infty} d\zeta \frac{be^{-\zeta^2}}{b^2 + (\zeta - a)^2} = \frac{\gamma}{2k} \sqrt{\pi} \text{Im}[Z(a + ib)]
\]

where \( a = \sqrt{m/(2k_BT)}\Delta_0/k \) and \( b = \sqrt{m/(8k_BT)\gamma/k} \). Using the expression for the full width at half maximum of the Doppler profile, \( \delta\omega_D = k\sqrt{8\ln 2k_BT/m} \) we have \( a = 2\sqrt{\ln 2}\Delta_0/\delta\omega_D \) and \( b = \sqrt{2\gamma/\delta\omega_D} \). In a hot vapor cell with a detuning larger than the Doppler width we will generally have \( |a| > 1 \) and \( b \ll 1 \). The absorption coefficient can be written as

\[
\alpha = n_a \frac{6\pi \sqrt{\ln 2} c^2}{\omega^2} \frac{\gamma}{\delta\omega_D} \text{Im}[Z(a + ib)].
\] (6.7)

For small arguments the Taylor expansion of the plasma dispersion function is

\[ Z(z) = i\pi^{1/2} - 2z - i\pi^{1/2}z^2 + \mathcal{O}(z^3). \]

Therefore for \( |\Delta_0| \ll \delta\omega_D \) and \( \gamma \ll \delta\omega_D \) we get

\[
\alpha \simeq n_a \frac{3\lambda^2}{2\pi} (\pi \ln 2)^{1/2} \frac{\gamma}{\delta\omega_D} + \mathcal{O}(\gamma/\delta\omega_D)^2.
\] (6.8)

We can calculate some characteristic numbers for a Rb cell by using the following approximate expression for the Rb vapor pressure as a function of temperature

\[
\log_{10} P_V = 15.88253 - \frac{4529.635}{T} + 0.00058663 T - 2.99138 \log_{10} T,
\]

where \( P_V \) is the vapor pressure in torr, and \( T \) is the temperature in K. This expression gives the vapor pressure of the liquid phase which is what we want since Rb melts at 39.31° C.
We can then calculate the density using the ideal gas law. Doing so gives the density curve shown in Fig. 6.2. Since the density rises much more steeply with temperature than the Doppler width does it is advantageous to heat the cell. Figure 6.2 also gives the FWHM of the Doppler profile $\delta\omega_D$.

The calculated absorption and transmission curves are shown in Fig. 6.3 for a 7 cm long cell. Note that the resonant absorption can be exceptionally large: at $T = 100$ C, $\alpha = 213$ cm$^{-1}$.

**Saturated absorption**

We can include saturation effects by keeping the factor of $I/I_s$ in the denominator of (6.2) and following the same procedure as above we arrive at

$$\alpha(I) = n_a \frac{6\pi\sqrt{\ln 2} c^2}{\omega^2} \frac{\gamma}{\delta\omega_D} \frac{1}{\sqrt{1 + I/I_s}} \text{Im}[Z(a + ib_I)].$$  \hspace{1cm} (6.9)

Here $a$ is the same as before and $b_I = b\sqrt{1 + I/I_s}$. The saturated transmission is calculated by solving

$$\frac{dI}{dz} = -\alpha(I)I.$$  \hspace{1cm} (6.10)

This equation has to be solved numerically. Representative results showing the influence of saturation at fixed temperature are shown in Fig. 6.4. Note that the unsaturated on resonance scattering cross section found from Eq. (6.9) is

$$\sigma = \frac{3}{2\pi} \lambda^2 \left( \sqrt{\pi \ln 2} \frac{\gamma}{\delta\omega_D} \right)$$

which agrees with Eq. (6.8). The effect of Doppler broadening is to reduce the maximal cross section that would be obtained for a homeogeneously broadened transition by the factor in parentheses which is numerically equal to 0.016 for Rb at 100 C. In the hot vapor saturation only becomes significant at large intensities of about $10^5$ times the saturation intensity. For

---

$^1$The conversion from torr to the SI unit of pressure is 1 torr = 133.32 Pascals.
Figure 6.4: Absorption coefficient and transmission for a 7 cm long Rb cell at T=125 C and $I/I_s = 1$ (red), $10^5$ (green), $5 \times 10^5$ (blue), and $10^6$ (yellow).

$^{87}$Rb the $^5S_{1/2}/F = 2, m_F = 2 \rightarrow ^2S_{1/2}/F = 3, m_F = 3$ cycling transition has a saturation intensity of $I_s = 16.7 \text{ W/m}^2$. Thus for a 1 mm diameter beam saturation effects will only be important for powers above about 1.3 W.

6.3 Saturated absorption spectroscopy - qualitative discussion

It is also possible to use nonlinear spectroscopy techniques to observe the radiative linewidth in the presence of much larger Doppler broadening. A useful and widely used method is saturated absorption spectroscopy. From Eq. (6.9) the absorption coefficient is

$$
\alpha(I) = n_a \frac{6\sqrt{\ln 2} c^2}{\omega^2} \frac{\gamma}{\delta \omega_D} \frac{1}{\sqrt{1 + I/I_s}} \text{Im}[Z(a + ibI)].
$$

with $a = 2\sqrt{\ln 2} \Delta_0/\delta \omega_D$, $b = \sqrt{\ln 2} \gamma/\delta \omega_D$, $bI = b\sqrt{1 + I/I_s}$.

Now suppose the light consists of two beams, a strong pump beam with intensity $I_c$ propagating along $e_z$ and a weak probe beam with intensity $I_p \ll I_s$ propagating along $-e_z$. When the probe and pump beams are both resonant with the transition the saturation effect is governed by the pump beam and the probe has an absorption coefficient of

$$
\alpha_p \simeq \alpha_0 \text{Im}[Z(ib\sqrt{1 + I_c/I_s})] \frac{1}{\sqrt{1 + I_c/I_s}}
$$

with

$$
\alpha_0 = n_a \frac{6\pi \sqrt{\ln 2} c^2}{\omega^2} \frac{\gamma}{\delta \omega_D}.
$$

If the pump beam were turned off then the absorption coefficient would be

$$
\alpha'_p = \alpha_0 \text{Im}[Z(ib)].
$$
The reduction in absorption due to saturation of the transition by the pump beam is therefore
\[
\delta \alpha = \alpha_p - \alpha'_p = \alpha_0 \left( \text{Im}[Z(ib \sqrt{1+I_c/I_s})] / \sqrt{1+I_c/I_s} - \text{Im}[Z(ib)] \right)
\]
Using \( b \ll 1 \) and \( Z(z) = i\pi^{1/2} - 2z + O(z^2) \) we find
\[
\delta \alpha = \alpha_0 \left( \frac{\pi^{1/2} I_c}{I_s} + O(I_c^2/I_s^2) \right) \\
\simeq -\alpha_0 \frac{\pi^{1/2} I_c}{2I_s}.
\]
The probe absorption without a pump beam for \( b \ll 1 \) is \( \alpha'_p \simeq \alpha_0 \pi^{1/2} \) and the fractional change in absorption is therefore
\[
\frac{\delta \alpha}{\alpha'_p} = -\frac{I_c}{2I_s}.
\]
We see that a 10 % fractional decrease in probe absorption is obtained when \( I_c/I_s = 1/5 \).

The above discussion applies when both pump and probe are resonant. Since the two beams are counterpropagating this only occurs for atoms that are moving in the \( x-y \) plane giving no Doppler shift. For atoms that do have a \( z \) component of velocity there is no simultaneous resonance for pump and probe and the effect vanishes so we just see the normal (unsaturated) probe absorption. A fairly quantitative picture of the lineshape can be obtained by plotting \( \delta \alpha \) using the full expressions for \( \alpha(I, \Delta) \) as discussed below. This approach neglects any coherent interference between the two beams (there is actually a standing wave along \( z \)). A full treatment requires solving the density matrix equations which is beyond the scope of this discussion.

When there is more than one excited state additional absorption dips occur at what are called “crossover” resonances. Call the ground state 0 and the excited states 1, 2 with a separation \( \omega_{21} \). If the laser is tuned in between the two resonances then atoms for which \( kv_z = \pm \omega_{21}/2 \) will result in simultaneous resonance of both pump and probe, and we again get a saturated absorption signal.

### 6.4 Saturated absorption spectroscopy - quantitative treatment

A beam propagating through an atomic vapor with absorption coefficient \( \alpha \) has an intensity dependence \( dI/dz = -\alpha I \). The number of photons scattered per unit time in a differential volume \( dV = Adz \) is \( r_s = \gamma n_e dV \) where \( \gamma \) is the radiative decay rate of the upper level, \( n_e \) is the density of excited atoms, and \( A \) is the cross sectional beam area. The number of photons absorbed in volume \( dV \) per unit time is \( r_a = (I/\hbar \omega)\alpha Adz = (I/\hbar \omega)\alpha dV \). Equating \( r_s \) to \( r_a \) gives
\[
n_e = \frac{I}{\hbar \omega \gamma} \alpha
\]
or
\[ \alpha = \frac{\hbar \omega \gamma}{I} n_e. \]

For a stationary atom
\[ n_e = n \frac{I/2I_s}{1 + 4\Delta^2/\gamma^2 + I/I_s} \]
with \( n \) the total density. When the atoms are in thermal equilibrium this generalizes to
\[ n = n_0 f(v_z) \]
with the normalized Maxwell-Boltzmann distribution
\[ f(v_z) = \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-mv_z^2/2k_B T}. \]

Thus
\[ n_e(v_z) = n_0 f(v_z) \frac{I/2I_s}{1 + 4\Delta^2/\gamma^2 + I/I_s} = n_0 f(v_z) \frac{I/2I_s\Delta_v}{1 + I/I_s\Delta_v} \]
with \( I_s\Delta_v = I_s (1 + 4\Delta^2/\gamma^2) \) and \( \Delta_v = \Delta_0 - kv_z \). It will be useful to write this last expression as
\[ n_e(v_z) = n_0 f(v_z) \left( \frac{I_{2I_s\Delta_v}}{1 + 4\Delta^2/\gamma^2} \right) \left( \frac{1}{1 + I/I_s\Delta_v} \right). \]

The expression in the first parentheses gives the unsaturated dependence of the excited state population on intensity and detuning, while the second parentheses describes saturation.

The total absorption coefficient is given by \( \alpha = \int dv_z \alpha(v_z) \) where
\[ \alpha(v_z) = \frac{\hbar \omega \gamma}{I} n_e(v_z) \]
\[ = \frac{\hbar \omega \gamma}{I} n_0 f(v_z) \left( \frac{I_s}{1 + 4\Delta^2/\gamma^2} \right) \left( \frac{1}{1 + I/I_s\Delta_v} \right) \]
\[ = \frac{3\lambda^2}{2\pi} n_0 f(v_z) \frac{1}{1 + 4\Delta^2/\gamma^2} \left( \frac{1}{1 + I_s/I_s\Delta_v} \right). \]

Let us now assume the population redistribution between ground and excited states is mainly due to a strong pump beam with intensity \( I_c \) propagating along \(-z\). The saturation effect is associated with the term in parentheses, where we replace \( I_s\Delta_v \) by \( I_s\Delta_{-v} \) since the pump is propagating opposite to the weak probe beam with intensity \( I_p \). The probe absorption is then
\[ \alpha_p(v_z) = \frac{3\lambda^2}{2\pi} n_0 f(v_z) \frac{1}{1 + 4\Delta^2/\gamma^2} \left( \frac{1}{1 + I_c/I_s\Delta_{-v}} \right) \]
\[ = \frac{3\lambda^2}{2\pi} n_0 f(v_z) \frac{1}{1 + 4\Delta^2/\gamma^2} \left( \frac{1 + 4\Delta^2/\gamma^2}{1 + 4\Delta^2/\gamma^2 + I_c} \right). \]

The absorption as given by Eq. (6.14) can be integrated in terms of plasma dispersion functions, the result is not compact. Alternatively we can easily integrate numerically to determine line shapes and the amount of power broadening in the saturated spectrum. As an
example consider a Cs vapor with $L = .01$ m, $T = 300$ K, $n_0 = 6.1 \times 10^{16}$ m$^{-3}$, $\lambda = 0.852$ µm and $\gamma = 2\pi \times 5.2 \times 10^6$ s$^{-1}$. The saturation intensity is $I_s \simeq 17$. W/m$^2$. Lineshapes for several saturating intensities are shown in Fig. 6.5. As the pump intensity is increased the dip gets deeper but also broader.

In alkali atoms with hyperfine structure there are multiple saturation dips as well as crossover dips. Optical pumping also leads to redistribution of population which complicates the atomic response. A detailed treatment can be found in many papers. See for example M. Himsworth and T. Freegarde, Phys. Rev. A 81, 023423 (2010).

### 6.5 Pressure broadening

Atomic collisions can result in decay of population from an excited state as well as elastic phase shifts. The increased decay rate leads to broadening of the transition. Since the rate of collisions is proportional to the density and therefore also proportional to pressure in an ideal gas this is called pressure broadening. Elastic collisions can lead to broadening and shifts of the line center. We will treat the cases of inelastic and elastic collisions separately.

#### 6.5.1 Inelastic collisions

Assume a density of excited state atoms $N_e$ that satisfies

$$\frac{dN_e}{dt} = -(\gamma + R)N_e.$$  

Here $\gamma$ is the radiative decay rate and $R$ is the additional decay rate due to inelastic collisions. The solution for $N_e$ is

$$N_e(t) = N_e(0)e^{-(\gamma + R)t}.$$  

We therefore have an effective lifetime of

$$\tau_{\text{eff}} = \frac{1}{\gamma + R}.$$  

Inelastic collisions between different atomic species can lead to this kind of collision induced decay. We can write the collision rate for species $A$ due to collisions with a background species $B$ as $R = n_B \langle v_{AB} \rangle \sigma_{\text{inel}}$ where the mean rate of collisions is

$$\langle v_{AB} \rangle = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2}$$

![Figure 6.5: Saturated absorption lineshape for Cs vapor with $I_c/I_s = 1, 3, 10$.](image)
with the reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$. Then the effective lifetime can be written as

$$\frac{1}{\tau} = \gamma + n_B \langle v_{AB} \rangle \sigma_{\text{inel}}.$$

Thus the slope of $1/\tau$ vs. $n_B \langle v_{AB} \rangle$ is proportional to $\sigma_{\text{inel}}$ and the intercept at zero density of $n_B$ gives the radiative rate $\gamma$.

In an ideal gas $pV = Nk_B T$ and $n_B = N_B / V = p / k_B T$ so

$$\frac{1}{\tau} = \gamma + \kappa p$$

with $\kappa = \sigma_{\text{inel}} \sqrt{8/\pi \mu k_B T}$. The coefficient of pressure broadening is $\kappa$ and at large pressure $\tau \sim 1/p$. This is homogeneous pressure broadening.

### 6.5.2 Elastic collisions

Elastic collisions can lead to both broadening and shift of transitions. In some applications it is of interest to minimize line shifts since they lead to uncertainty in the actual transition frequency. This is of particular importance in atomic clock research. We can think of an elastic collision as perturbing the energy of an atomic level by an amount $\delta U$ which corresponds to a frequency shift of $\delta \omega = \delta U / \hbar$. The integrated frequency shift over the duration of a collision gives a phase shift

$$\delta \phi = \int dt \ \delta \omega(t).$$

This phase shift can broaden and shift the transition lineshape.

Let’s proceed with a quantitative calculation. We will first relate phase shifts to a field correlation function and then use the Wiener-Khinchine theorem to relate the field correlation to the intensity lineshape. Finally we will show how the phase shift can be related to an
integral of the elastic scattering cross section over the two-body collision impact parameter and thereby establish a link between the scattering cross section and the lineshape.

To start consider the two-time field correlation

\[ B(\tau) = \langle \mathcal{E}(t)\mathcal{E}^*(t+\tau) \rangle_t. \]

This is the time averaged correlation of the field and the field delayed by time \( \tau \). We can evaluate the correlation function as an integral

\[
B(\tau) &= \lim_{T \to \infty} \int_{-T/2}^{T/2} dt \, \mathcal{E}(t)\mathcal{E}^*(t+\tau) \\
&= \frac{1}{2\pi} \lim_{T \to \infty} \int_{-T/2}^{T/2} dt \int d\omega \, \mathcal{E}(\omega)e^{-i\omega t} \int d\omega' \, \mathcal{E}^*(\omega')e^{i\omega'(t+\tau)} \\
&= \int d\omega d\omega' \mathcal{E}(\omega)\mathcal{E}^*(\omega')e^{i\omega'\tau} \lim_{T \to \infty} \int_{-T/2}^{T/2} dt \frac{1}{2\pi} e^{i(\omega'-\omega)t} \\
&= \frac{1}{\sqrt{2\pi}} \int d\omega \sqrt{2\pi} |\mathcal{E}(\omega)|^2 e^{i\omega\tau}. 
\]

The spectral intensity distribution and the field correlation function are thus related by

\[ I(\omega) \sim |\mathcal{E}(\omega)|^2 = \frac{1}{2\pi} \int d\tau B(\tau)e^{-i\omega\tau} \]

and

\[ B(\tau) = \int d\omega |\mathcal{E}(\omega)|^2 e^{i\omega\tau} \]

which is known as the Wiener-Khinchine theorem.

Now consider the field \( \mathcal{E}_j \) due to atom number \( j \). If we have \( N \) atoms the total field is \( \mathcal{E} = \sum_j \mathcal{E}_j \). An unperturbed atom generates a field \( \mathcal{E}_j = \mathcal{E}_0 e^{-i\omega_0 t} \) with \( \omega_0 \) the unperturbed atomic transition frequency. Due to a collisional perturbation

\[ \mathcal{E}_j(t) = \mathcal{E}_0 e^{-i\omega_0 t} e^{-i\phi_j(t)} \]

with \( \phi_j(t) \) the perturbation phase shift. The field correlation function is

\[
B(\tau) = \langle \mathcal{E}(t)\mathcal{E}^*(t+\tau) \rangle_t \\
= \langle \sum_j \mathcal{E}_j(t) \sum_k \mathcal{E}_k^*(t+\tau) \rangle_t \\
= \langle \sum_j \mathcal{E}_j(t)\mathcal{E}_j^*(t+\tau) \rangle_t + \langle \sum_{j \neq k} \mathcal{E}_j(t)\mathcal{E}_k^*(t+\tau) \rangle_t.
\]

We assume the last term vanishes since the atoms are uncorrelated and that the ensemble of atoms is statistically homogeneous so the first term can be written as

\[
B(\tau) = \langle \sum_j \mathcal{E}_j(t)\mathcal{E}_j^*(t+\tau) \rangle_t \\
= N\langle \mathcal{E}_j(t)\mathcal{E}_j^*(t+\tau) \rangle_t \\
= NB_1(\tau).
\]
The spectral intensity becomes

\[ I(\omega) = NI_1(\omega) = \frac{N}{2\pi} \int d\tau B_1(\tau)e^{-i\omega \tau}. \]

To find the lineshape \( I(\omega) \) we just need \( B_1(\tau) \). Dropping the subscript \( j \) the collision perturbed field of one atom is \( E(t) = E_0 e^{-i\omega_0 t} e^{-i\phi(t)} \) and

\[
B_1(\tau) = |E_0|^2 e^{i\omega_0 \tau} \langle e^{-i\phi(t)} e^{i\phi(t+\tau)} \rangle = |E_0|^2 e^{i\omega_0 \tau} \langle e^{i\Delta\phi(t,\tau)} \rangle
\]

where we have introduced the differential collisional phase

\[ \Delta\phi(t,\tau) = \phi(t + \tau) - \phi(t). \]

We assume the differential phase is statistically stationary in time so that

\[ \langle e^{i\Delta\phi(t,\tau)} \rangle = b(\tau) \tag{6.15} \]

only depends on \( \tau \) and \( B_1(\tau) = |E_0|^2 e^{i\omega_0 \tau} b(\tau) \). Then note that

\[
db(\tau) = \langle e^{i\Delta\phi(t,\tau+d\tau)} \rangle - \langle e^{i\Delta\phi(t,\tau)} \rangle = \langle e^{i\Delta\phi(t,\tau)} \langle e^{i[\Delta\phi(t,\tau+d\tau)-\Delta\phi(t,\tau)]} \rangle - 1 \rangle.
\]

The quantity in square brackets \( \Delta\phi(t,\tau+d\tau) - \Delta\phi(t,\tau) \) is the differential collisional phase in time \( d\tau \). We assume this is not correlated with \( \Delta\phi(t,\tau) \) and make the approximation

\[ db(\tau) \simeq \langle e^{i\Delta\phi(t,\tau)} \rangle \langle e^{i[\Delta\phi(t,\tau+d\tau)-\Delta\phi(t,\tau)]} - 1 \rangle = b(\tau) \langle e^{i[\Delta\phi(t,\tau+d\tau)-\Delta\phi(t,\tau)]} - 1 \rangle. \tag{6.16} \]

We now relate the differential collisional phase to the rate of atomic collisions. The number of collisions in time \( d\tau \) is

\[ dn = \frac{N}{V} \bar{v}(2\pi \rho \, d\rho) d\tau \]

with \( N/V \) the density of atoms, \( \bar{v} \) the average relative velocity, and \( \rho \) the impact parameter. If \( \phi(\rho) \) is the phase shift due to a collision with impact parameter \( \rho \) then we can express the time average in (6.16) as an ensemble average over impact parameters as

\[ \langle e^{i[\Delta\phi(t,\tau+d\tau)-\Delta\phi(t,\tau)]} \rangle = 2\pi \frac{N}{V} \bar{v} d\tau \int_0^\infty d\rho \rho e^{i\phi(\rho)} \]

and

\[ \langle e^{i[\Delta\phi(t,\tau+d\tau)-\Delta\phi(t,\tau)]} - 1 \rangle = 2\pi \frac{N}{V} \bar{v} d\tau \int_0^\infty d\rho \rho \left( e^{i\phi(\rho)} - 1 \right) = -\left( \frac{N}{V} \bar{v} d\tau \right) \int_0^\infty d\rho \, 2\pi \rho \left( (1 - \cos(\phi(\rho)) - i \sin(\phi(\rho))) \right). \]
The integral has units of area and gives the collisional cross sections. Define

$$\sigma_b = 2\pi \int_0^\infty d\rho \, 2\pi \rho (1 - \cos(\phi(\rho)))$$

$$\sigma_s = 2\pi \int_0^\infty d\rho \, 2\pi \rho \sin(\phi(\rho))$$

then from (6.16)

$$db = -b(\tau) \frac{N}{\bar{v}} \bar{v} d\tau (\sigma_b - i\sigma_s)$$

which can be integrated to give

$$b(\tau) = e^{-\frac{N}{\bar{v}} (\sigma_b - i\sigma_s) \tau}$$

with $b(0) = 1$ which follows from the definition (6.15).

The intensity spectrum is found from the Fourier transform of $B(\tau)$ as

$$I(\omega) = N \frac{1}{2\pi} \int d\tau \, B_1(\tau) e^{-i\omega \tau}$$

$$\sim \frac{\left(\frac{N}{\bar{v}} \bar{v} \sigma_b\right)^2}{(\omega - \omega_0 - \frac{N}{\bar{v}} \bar{v} \sigma_s)^2 + \left(\frac{N}{\bar{v}} \bar{v} \sigma_b\right)^2}$$

$$= \frac{1}{1 + 4 \left(\omega - \omega_0 - \frac{N}{\bar{v}} \bar{v} \sigma_s\right)^2 / \left(2\frac{N}{\bar{v}} \bar{v} \sigma_b\right)^2}$$

(6.17)

We see that the FWHM lineshape is broadened by an amount $2\frac{N}{\bar{v}} \bar{v} \sigma_b$ and the line center is shifted by an amount $\frac{N}{\bar{v}} \bar{v} \sigma_s$. To actually calculate the changes to the lineshape we need to find $\phi(\rho)$ which can be done if we know the dependence of the atomic interaction on distance.
Chapter 7

Light scattering and Photoionization

Interactions of radiation fields and atoms lead to many different phenomena including two-level dynamics, as described by the Einstein $A, B$ coefficients, and coherent Rabi oscillations. In contrast to coherent oscillations due to stimulated transitions radiation can also couple two or more atomic levels by spontaneous processes which we group under the description “light scattering”. We will distinguish several different processes involving scattering of radiation. Also charged particles can be scattered by atoms. These processes were first known as Rutherford scattering and can for example result in electron impact excitation of atomic states. In this chapter we will only consider interaction of atoms with electromagnetic radiation.

7.1 Light Scattering

Let’s start by comparing several types of light scattering.

7.1.1 Rayleigh and Raman scattering

An incident photon is absorbed and reradiated in a spontaneous process. The initial state of the photon is $|\nu\rangle = |\omega, k\rangle$ with $\omega$ the frequency and $k$ the three dimensional wave vector. The initial state of the atom is $|\psi\rangle = |i, K\rangle$ where $i$ labels an internal state and $\hbar K$ is the center of mass momentum. The scattering process can be described as

$$|\nu\rangle|\psi\rangle \rightarrow |\nu'\rangle|\psi'\rangle.$$  

The final states are

$$|\nu'\rangle = |\omega', k'\rangle$$
$$|\psi'\rangle = |f, K'\rangle.$$ 

When the internal atomic state is not changed, $|f\rangle = |i\rangle$, we speak of Rayleigh scattering. In this case the change in energy and momentum are

$$\Delta U = U_f - U_i = \frac{\hbar^2 K'^2}{2M} + \hbar \omega' - \frac{\hbar^2 K^2}{2M} - \hbar \omega$$
$$\Delta p = p_f - p_i = \hbar (K' + k') - \hbar (K + k).$$

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Keeping track of both the atom and field energy and momentum we require that \( \Delta U = \Delta p = 0 \).

We see that if \( k' = k \), i.e. the photon is scattered into the same spatial mode as the incident photon then \( K' = K \) and \( \omega' = \omega \) so the atomic and photon states are unchanged

\[
| \nu' \rangle = | \nu \rangle \\
| \psi' \rangle = | \psi \rangle.
\]

This is spontaneous Rayleigh scattering.

On the other hand if \( k' \neq k \) the atomic momentum changes to

\[
K' = K + (k - k')
\]

while the scattered photon has frequency

\[
\omega' = \omega + \frac{\hbar}{2M} \left( K^2 - K'^2 \right)
\]

\[
= \omega + \frac{\hbar}{2M} \left( -2K \cdot (k - k') - |k - k'|^2 \right).\]

In this case the atomic internal state is unchanged but the center of mass motion does change. This is generally still referred to as Rayleigh scattering. Note that the change in atomic momentum can be used to cool atoms. We will return to this topic in a later chapter.

A different situation arises when the internal state of the atom changes from \( |i \rangle \rightarrow |f \rangle \). This is called Raman scattering. The energy change \( U_f - U_i \) associated with the internal state must now be included when determining the change in the center of mass momentum which leads to so-called Raman cooling techniques.

For a sufficiently high energy photon the final atomic state will have positive energy corresponding to a “free” electron. This is a generalization of Raman scattering involving a transition from a bound to a continuum state of the atom. Strictly speaking this is photon absorption not scattering since there is no photon present in the final state.

The continuum electron with positive energy may move arbitrarily far away from the atomic nucleus. When the electron is close to the nucleus its motion is affected by the Coulomb field and may emit a photon leading to the electron transitioning back to a bound state. This process is known as recombination.

### 7.1.2 Compton and Thomson scattering

A different type of spontaneous scattering process involves the interaction of radiation with free electrons. This gives Compton scattering, or Thomson scattering in the low intensity, nonrelativistic limit. This type of scattering is often encountered in plasma physics. Although photons can be scattered by electrons it is not possible for a free electron to absorb a photon. Such a process does not simultaneously conserve energy and momentum.

To see this we write the initial energy as

\[
U_i = \hbar \omega_i + \sqrt{(mc^2)^2 + p_i^2 c^2}
\]
where $\omega_i$ is the initial photon frequency, $m$ is the electron mass, and $p_i$ is the initial electron momentum. The final energy is

$$U_f = \hbar \omega_f + \sqrt{(mc^2)^2 + p_f^2 c^2}.$$  

Conservation of momentum says

$$P_i = \hbar k_i + p_i = P_f = \hbar k_f + p_f.$$  

If the photon is absorbed then we need to satisfy

$$\sqrt{(mc^2)^2 + p_f^2 c^2} = \hbar \omega_i + \sqrt{(mc^2)^2 + p_i^2 c^2}$$

$$p_f = \hbar k_i + p_i.$$  

The second equation says $p_i^2 = p_f^2 + \hbar^2 k_i^2 - 2 \hbar p_f \cdot k_i$ and inserting into the first equation gives

$$[(mc^2)^2 + p_f^2 c^2]^{1/2} = \hbar \omega_i + [(mc^2)^2 + c^2 p_f^2 + \hbar^2 k_i^2 - 2 \hbar p_f \cdot k_i]^{1/2}.$$  

Squaring this equation gives

$$\omega_i [(mc^2)^2 + p_f^2 c^2]^{1/2} = c^2 p_f \cdot k_i,$$

and squaring again gives

$$\omega_i^2 [(mc^2)^2 + p_f^2 c^2] = c^4 p_f^2 k_i^2 \cos^2(\theta) = c^2 \omega_i^2 p_f^2 \cos^2(\theta)$$

with $\theta$ the angle between $p_f$ and $k_i$. We thus require

$$c^2 \omega_i^2 p_f^2 [1 - \cos^2(\theta)] + \omega_i^2 m^2 c^4 = 0.$$  

Each of the two terms is nonnegative so this cannot be satisfied. Absorption of photons only occurs for bound electrons, and results in the change of the internal atomic state. This in turn implies that when we consider highly excited atoms in Rydberg states photon absorption and emission is largely determined by the atomic wavefunctions near the origin.

### 7.2 Photoionization

Photoionization is important for several reasons.

1) This is the basic process by which photons are detected. An incident photon is converted to an electron in an external circuit which can then be counted. This is also important for energy generation from sunlight and there is a great deal of current effort involved in optimizing the efficiency of this process.

2) Photoionization spectroscopy is important for measurements of atomic properties. The current of photogenerated electrons will turn on/off when $\hbar \omega + U_i = 0$. Thus if we
Table 7.1: ISM properties.

<table>
<thead>
<tr>
<th>ISM</th>
<th>H</th>
<th>volume %</th>
<th>$T$ (K)</th>
<th>density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular clouds</td>
<td>H$_2$</td>
<td>&lt; 1%</td>
<td>10-20</td>
<td>$10^2 - 10^6$</td>
</tr>
<tr>
<td>cold neutrals</td>
<td>atomic H</td>
<td>1 - 5%</td>
<td>50-100</td>
<td>20 - 50</td>
</tr>
<tr>
<td>warm neutrals</td>
<td>atomic H</td>
<td>10 - 20%</td>
<td>6,000-10,000</td>
<td>0.2 - 0.5</td>
</tr>
<tr>
<td>warm ionized</td>
<td>ionized H II</td>
<td>20 - 50%</td>
<td>8,000</td>
<td>0.2 - 0.5</td>
</tr>
<tr>
<td>fully ionized H II</td>
<td>ionized H II</td>
<td>&lt; 1%</td>
<td>8,000</td>
<td>100 - 10,000</td>
</tr>
</tbody>
</table>

know $\omega$ we can determine the energy of the atomic state.

3) Photoionization is a basic process in astrophysics. Much of the interstellar medium (ISM) is ionized and the density of ionized matter is influenced by the cross sections for photoionization and recombination. Thus understanding these processes is important for interpreting astrophysical observations of the different regions listed in Table 7.1.

Different observation methods are used for studying these regions:

- molecular clouds - radio, infrared lines
- Cold neutral medium (CNM) - 21 cm line $F = 0 \leftrightarrow 1$.
- Warm neutral medium (WNM) - 21 cm line $F = 0 \leftrightarrow 1$.
- Warm ionized medium (WIM) - H$_\alpha$ emission, pulsar dispersion
- H II - H$_\alpha$ emission, pulsar dispersion

The H$_\alpha$ emission is the transition from $n = 3p-2s$ in H at 656 nm. This gives a strong red emission line. This type of emission results from recombination. The process $e^- + p \rightarrow H^*$ gives excited H$^*$ which then decays to $n = 3$ followed by H$_\alpha$ emission. Measuring the strength of H$_\alpha$ radiation can be used to probe the recombination rate.

### 7.2.1 Photoionization Cross section

According to Fermi’s golden rule the transition probability per unit time from an initial state $|i\rangle$ to a final state $|f\rangle$ is

$$P_{i\rightarrow f} = \frac{2\pi}{\hbar} |H_{fi}|^2 \delta(E_f - E_i),$$

where $H_{fi}$ is the matrix element of the perturbation causing the transition. When the final state is part of a continuum we have

$$P_{i\rightarrow f} = \lim_{\epsilon \rightarrow 0} \int_{E_i-\epsilon}^{E_i+\epsilon} dE_f \frac{2\pi}{\hbar} |H_{fi}|^2 \delta(E_f - E_i) \Xi(E_f) = \frac{2\pi}{\hbar} |H_{fi}|^2 \Xi(E_f = E_i),$$
with \( \Xi(E_f) \) the density of final states. If we evaluate the matrix element using energy normalized wave functions the density of states is \( \Xi(E) = 1 \). The transition rate is therefore

\[
P_{1\rightarrow f} = \frac{2\pi}{\hbar}|\langle f(E)|H|i \rangle|^2,
\]

where \( f(E) \) is an energy normalized continuum state. We can also write the transition rate as the photon flux/unit area/unit time multiplied by the cross section for photoionization or \( (I/\hbar\omega)\sigma \) with \( I \) the optical intensity, and \( \sigma \) the cross section. We therefore have

\[
\sigma = \frac{2\pi\omega}{I}|\langle f(E)|H|i \rangle|^2.
\]

We define the optical field as

\[
E = \sum_q \frac{\mathcal{E}_q}{2} e^{i(k\cdot r - \omega t)} \hat{e}_q + \frac{\mathcal{E}^*_q}{2} e^{-i(k\cdot r - \omega t)} \hat{e}^*_q.
\]

This is the same as in Sec. 4.4 where we discussed bound-bound transitions. The matrix element for absorption is

\[
\langle f(E)|H_{E1}|i \rangle = \epsilon \sum_q \frac{\mathcal{E}_q}{2} \langle f(E)|\hat{r}_q|i \rangle e^{-i\omega t}.
\]

When the radiation has a single polarization component this reduces to

\[
\langle f(E)|H_{E1}|i \rangle = \frac{\mathcal{E}_q}{2} \langle f(E)|\hat{r}_q|i \rangle e^{-i\omega t}
\]

so the absorption cross section is

\[
\sigma = \frac{\pi\omega e^2|\mathcal{E}_q|^2}{2I}|\langle f(E)|r_q|i \rangle|^2.
\]

In SI units the intensity is \( I = \frac{\omega c}{2}|\mathcal{E}_q|^2 \) and in cgs units \( I = (c/8\pi)|\mathcal{E}_q|^2 \). The absorption cross section is thus

\[
\sigma_{\text{SI}} = \frac{\pi\omega e^2}{\epsilon_0 c}|\langle f(E)|r_q|i \rangle|^2, \quad (7.1a)
\]

\[
\sigma_{\text{cgs}} = \frac{4\pi^2\omega e^2}{c}|\langle f(E)|r_q|i \rangle|^2. \quad (7.1b)
\]

### 7.2.2 Numerical calculation

The cross section can be calculated using the Coulomb wave functions from Sec. 1.5. We write the bound wavefunction and the unbound energy normalized wave functions as

\[
\psi_{\gamma lm} = \frac{P_{\gamma l}(r)}{r} Y_{lm}(\theta, \phi),
\]

\[
\psi_{\eta l'm'}^{(E)} = \frac{P_{\eta l'}^{(E)}(r)}{r} Y_{l'm'}(\theta, \phi).
\]
and assume the light beam has polarization \( \mathbf{e}_q \). The matrix element in (7.1) is then

$$\langle \eta l' m' | r_q | \gamma l m \rangle = (-1)^{l'+(1+l'+\gamma)/2} \frac{1}{\sqrt{2l'+1}} C^{l' m'}_{l m 1 q} \sqrt{I_{l'}} R_{\eta l'; \gamma l}.$$  

where \( l' = \text{max}(l, l') \) and \( R_{\eta l'; \gamma l} = \int_0^\infty dr r P^{(E)}_{\eta l'}(r) P_{\gamma l}(r) \). The cross section is therefore (cgs units)

$$\sigma_{m q} = 2\pi^2 \alpha_0^2 \left( \frac{1}{\gamma^2} + \frac{1}{\eta^2} \right) \sum_{l'=l\pm 1} K_{m q}^{l''} R_{\eta l'; \gamma l}^2,$$

(7.2)

where \( \alpha \) is the fine structure constant, \( 1/\eta^2 = 2\hbar \omega/E_H - 1/\gamma^2 \), \( E_H \) is a Hartree,

$$K_{m q}^{l''} = \frac{l_>^2}{2l'+1} \left( C^{l' m'}_{l m 1 q} \right)^2,$$

and

$$R_{\eta l'; \gamma l} = \left( \frac{1}{\Gamma(\gamma + l + 1) \Gamma(\gamma - l) \sqrt{2|\eta|}} \right) \left( \frac{2l' e^{-\pi \eta/2} |\Gamma(l' + 1 + i\eta)|}{\pi (2l' + 2)} \right) \times \int_0^\infty dz \frac{z^{l'+1}}{[\eta]} e^{i z/|\eta|} \, \, _1F_1^*(l' + 1 - i\eta, 2l' + 2, 2iz/|\eta|) \times e^{-z/\gamma} \left( \frac{2z}{\gamma} \right)^{l'+1} U(1 + l - \gamma, 2 + 2l, 2z/\gamma).$$

(7.3)

Here we have written the continuum wavefunction for the case of a hydrogenic atom with a pure Coulomb potential.

In some cases we will be interested in the cross section averaged over all possible orientations of the atoms and the ionizing radiation. This is given by

$$\bar{\sigma} = \frac{1}{2l + 1} \sum_{m, q} \sigma_{m q} = 2\pi^2 \alpha_0^2 \left( \frac{1}{\gamma^2} + \frac{1}{\eta^2} \right) \sum_{l'=l\pm 1} \bar{K}_{m q}^{l''} R_{\eta l'; \gamma l}^2,$$

with \( \bar{K}_{m q}^{l''} = \frac{l_>^2}{3(2l+1)} \) which follows from \( \sum_{m, q} \left( C^{l' m'}_{l m 1 q} \right)^2 = 2l' + 1 \). The factor of 1/3 in the definition of \( \bar{\sigma} \) accounts for the radiation being uniformly divided among all 3 possible polarizations. The \( m = 0, q = 0 \) factors and the averaged factors are given in Table 7.2 for the lowest few angular momentum states. We see that for \( l > 0 \) the cross section for \( m = 0, q = 0 \) is always larger than the orientation averaged cross section.

Quantitative values for the cross section can be found by evaluation of the matrix elements. In the case of hydrogen there is an exact expression for the matrix element (Gordon (1929)) and computed cross section tables are available[23]. For atoms with quantum defects we can use numerical integration of Coulomb wavefunctions.

### 7.2.3 Photoionization of fine structure states

The dependence of the photoionization rate on choice of fine structure states is captured by the expression (7.2)

$$\sigma = \frac{4\pi^2 \hbar \omega \alpha}{E_H} a_0^2 K_{l m 1 q}^{l' m'} R_{\eta l'; \gamma l}^2.$$  

(7.4)
7.2 Photoionization

<table>
<thead>
<tr>
<th>$l$</th>
<th>$l'$</th>
<th>$K_{l00}'$</th>
<th>$K_{l00}$</th>
<th>$K_{l00}' / K_{l00}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$1/3$</td>
<td>$1/3$</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$1/3$</td>
<td>$1/9$</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>$4/15$</td>
<td>$2/9$</td>
<td>$6/5$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$4/15$</td>
<td>$2/15$</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>$9/35$</td>
<td>$1/5$</td>
<td>$9/7$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$9/35$</td>
<td>$1/7$</td>
<td>$9/5$</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>$16/63$</td>
<td>$4/21$</td>
<td>$4/3$</td>
</tr>
</tbody>
</table>

Table 7.2: Angular factors for $m = 0$ and averaged photoionization cross sections.

Here the transition is $|nlsm\rangle \rightarrow |n'l'j'sm'\rangle$ due to light with polarization $e_q$ in a spherical basis,

$$K_{ljm'q}^{l'j'm'} = l'(2j + 1) \left\{ \frac{l'}{l} \right\}^2 \left( C_{ljm'q}^{j'm'} \right)^2,$$

where $s = 1/2$ is the electron spin and $l_\geq = \max(l,l')$.

As an example let us tabulate the angular factors for the $d_{5/2}$ level:

(e$z$ polarized light)

- $d_{5/2}, m = 1/2 \rightarrow p_{3/2}, m = 1/2$: $K = 6/25$
- $d_{5/2}, m = 1/2 \rightarrow f_{5/2}, m = 1/2$: $K = 1/1225$
- $d_{5/2}, m = 1/2 \rightarrow f_{7/2}, m = 1/2$: $K = 12/49$

(e$x$ polarized light)

- $d_{5/2}, m = 3/2 \rightarrow p_{3/2}, m = 1/2$: $K = 6/25$
- $d_{5/2}, m = 3/2 \rightarrow f_{5/2}, m = 1/2$: $K = 16/1225$
- $d_{5/2}, m = 3/2 \rightarrow f_{5/2}, m = 5/2$: $K = 2/245$
- $d_{5/2}, m = 3/2 \rightarrow f_{7/2}, m = 1/2$: $K = 3/49$
- $d_{5/2}, m = 3/2 \rightarrow f_{7/2}, m = 5/2$: $K = 15/49$

(e$x$ polarized light)

- $d_{5/2}, m = 5/2 \rightarrow p_{3/2}, m = 3/2$: $K = 2/5$
- $d_{5/2}, m = 5/2 \rightarrow f_{5/2}, m = 3/2$: $K = 2/245$
- $d_{5/2}, m = 5/2 \rightarrow f_{7/2}, m = 3/2$: $K = 1/49$
- $d_{5/2}, m = 5/2 \rightarrow f_{7/2}, m = 7/2$: $K = 3/7$

For given $l, l'$ the radial integrals are only weakly dependent on $j'$ so for the $m = 1/2$ initial state with $e_z$ polarized light we get a cross section of

$$\sigma \sim \frac{6}{25} R_{d-p}^2 + \frac{12}{49} R_{d-f}^2$$

$$\sim .24 R_{d-p}^2 + .24 R_{d-f}^2.$$
For the $m = 3/2$ initial state with $e_x$ polarized light we get
\[
\sigma \sim \frac{1}{2} \frac{6}{25} R_{d-p}^2 + \frac{1}{2} \frac{18}{49} R_{d-f}^2 \\
\sim .12 R_{d-p}^2 + .18 R_{d-f}^2.
\]
For the $m = 5/2$ initial state with $e_x$ polarized light we get
\[
\sigma \sim \frac{1}{2} \frac{12}{25} R_{d-p}^2 + \frac{1}{2} \frac{13}{27} R_{d-f}^2 \\
\sim .2 R_{d-p}^2 + .21 R_{d-f}^2.
\]

### 7.2.4 High energy approximation

We can gain some analytical insight by making a high energy approximation. When the energy of the free photoelectron is large compared to the energy of the atomic ground state the electron - nucleus interaction will be weak. In this limit we describe the free electron by a plane wave
\[
\psi_k(r) = \frac{1}{(2\pi)^{3/2}} e^{i k \cdot r}.
\]
These are not normalized wavefunctions since
\[
\int d^3r |\psi_k|^2 \to \infty.
\]
The wavefunctions are instead $\delta$ function normalized since
\[
\int d^3r \psi^*_{k'}(r) \psi_k(r) = \frac{1}{(2\pi)^3} \int d^3r e^{i (k-k') \cdot r} = \delta(k - k').
\]
Wavefunctions $\psi_E$ which are normalized with respect to energy satisfy
\[
\int d^3r \psi^*_{E'}(r) \psi_E(r) = \delta(E - E')
\]
so
\[
\int_{E-\delta E}^{E+\delta E} dE \int d^3r \psi^*_{E'}(r) \psi_E(r) = 1.
\]
The $k$ normalized wavefunctions satisfy
\[
\int_{k-\delta k}^{k+\delta k} d^3k \int d^3r \psi^*_{k'}(r) \psi_k(r) = 1
\]
and comparing the two expressions for unity we see that
\[
|\psi_E|^2 dE = |\psi_k|^2 d^3k = |\psi_k|^2 k^2 dk.
\]
The wavefunctions with different normalizations are thus related by
\[
\psi_E = k \left( \frac{dE}{dk} \right)^{1/2} \psi_k.
\]
The free electron has kinetic energy \( E = \frac{\hbar^2 k^2}{2m} \) so \( \frac{dE}{dk} = \frac{\hbar^2}{m} \) and \( (\frac{dE}{d^2})^{1/2} = \left(\frac{m}{\hbar^2} \right)^{1/2} \). The energy normalized wavefunctions are thus

\[
\psi_E(r) = \left(\frac{mk}{\hbar^2}\right)^{1/2} \frac{1}{(2\pi)^{3/2}} e^{ikr}.
\]

The cross section from Eq. (7.1) is (SI units)

\[
\sigma = \frac{\pi \omega_0 \epsilon^2}{\epsilon_0 c} |\langle f_E | \mathbf{e} \cdot \mathbf{r} | i \rangle|^2. \tag{7.5}
\]

From here on we will use \( k_0, \omega_0 \) for the photon and \( k \) for the electron.

At this point we are going to backtrack. The above expression for the cross section is based on the dipole approximation where we approximate \( \mathbf{E} \cdot \mathbf{r} \sim \mathbf{r} e^{i k_0 \cdot \mathbf{r}} \) by simply \( \mathbf{r} \). Since free electrons do not absorb photons the absorption must occur near the core where the electronic wavefunction is strongly modified. However, we are here basing our calculation on a free electron wavefunction which is not localized. We should therefore keep the exponential factor in the field and write

\[
\sigma = \frac{\pi \omega_0 \epsilon^2}{\epsilon_0 c} |\langle f_E | \mathbf{e} \cdot \mathbf{r} e^{i k_0 \cdot \mathbf{r}} | i \rangle|^2 \tag{7.6}
\]

where \( k_0 \) is the wavevector of the light. This expression gives the cross section for photoemission of an electron along \( k \). This is a differential cross section which we should write as

\[
\frac{d\sigma}{d\Omega} = \frac{\pi \omega_0 \epsilon^2}{\epsilon_0 c} |\langle f_E | \mathbf{e} \cdot \mathbf{r} e^{i k_0 \cdot \mathbf{r}} | i \rangle|^2. \tag{7.7}
\]

The total absorption cross section is then \( \sigma = \int d\Omega \frac{d\sigma}{d\Omega} \).

Using the expression for the energy normalized wavefunction and assuming a bound state \( \psi_{nl} \) we arrive at

\[
\frac{d\sigma}{d\Omega} = \frac{1}{(2\pi)^3} \frac{\pi e^2 m \omega_0 k}{\epsilon_0 c \hbar^2} \left| \int d^3 r e^{-i \mathbf{K} \cdot \mathbf{r}} \mathbf{e}_q \cdot \mathbf{r} \psi_{nl}(\mathbf{r}) \right|^2 \tag{7.8}
\]

where \( \mathbf{K} = k - k_0 \).

The integral looks like a Fourier transform of the initial wavefunction with respect to the momentum difference \( \mathbf{K} \), except for the additional factor of \( \mathbf{e}_q \cdot \mathbf{r} \) which accounts for the light polarization direction. Now the above expression comes from the length form of the interaction \( \hat{H}_r = e \mathbf{r} \cdot \mathbf{E} \). We can simplify this expression using the velocity form of the interaction, \( \hat{H}_v = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} = -i \frac{\hbar}{m} \mathbf{A} \cdot \nabla \). The electric field is \( \mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t} \). When there are no free charges so \( \phi = 0 \) we can write

\[
|\mathbf{E}| = \left| \frac{\partial \mathbf{A}}{\partial t} \right| = \omega_0 |\mathbf{A}|
\]

with \( \omega_0 \) the frequency of the light. Therefore we can convert the differential cross section from the length form of the interaction to the velocity form by multiplying with \( \left(\frac{\hbar}{m \omega_0}\right)^2 \) and

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making the replacement $r \rightarrow \nabla$. In this way we obtain

$$\frac{d\sigma}{d\Omega} = \frac{1}{(2\pi)^3\epsilon_0 cm\omega_0} \int d^3r e^{-ik_0r} e_q \cdot \nabla \psi_{nl}(r) \left| \psi_{nl}(K) \right|^2.$$

Integrating by parts gives

$$\int d^3r e^{-iKr} e_q \cdot \nabla \psi_{nl}(r) = \frac{1}{(2\pi)^3} \int d^3r e^{-iKr} \psi_{nl}(r) |\tilde{\psi}_{nl}(K)|^2.$$

We assumed the bound state wavefunction vanishes at infinity and introduced the Fourier transform of the wavefunction $\tilde{\psi}_{nl}$. The differential cross section is thus

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2h\alpha k^{3/2}}{m\omega_0} (K \cdot e_q)^2 |\tilde{\psi}_{nl}(K)|^2.$$

This expression is familiar from the quantum theory of scattering. In the first Born approximation, corresponding to weak scattering, the differential cross section is proportional to the Fourier transform of the scattering potential evaluated at the wavenumber $K = k - k_0$ corresponding to the change in direction of the incident flux due to the scattering process.

Let the incident radiation field propagate along $e_z$ and be polarized along $e_x$ as seen in Fig. 7.1. Then $k_0 \cdot e_q = 0$ and $K \cdot e_q = k \cdot e_q = k \sin(\theta) \cos(\phi)$ with $\theta$ the scattering angle. Thus

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2h\alpha k^{3/2}}{m\omega_0} \sin^2(\theta) \cos^2(\phi) |\tilde{\psi}_{nl}(K)|^2.$$

Calculation of the cross section is now reduced to finding the Fourier transform of the bound state wavefunction. It should be no surprise that this can be done analytically for
Hydrogen. The results are expressed in terms of Gegenbauer polynomials. Let’s work this out for the 1s state of Hydrogen. The wavefunction is

$$\psi_{10} = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0}.$$ 

The Fourier transform is

$$\tilde{\psi}_{10}(K) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} \frac{1}{(2\pi)^{3/2}} \int d^3r e^{-iK \cdot r} e^{-r/a_0}.$$ 

Let us choose a coordinate system with $e_z$ along $K$ so the integral is

$$\int d^3r e^{-iK \cdot r} e^{-r/a_0} = \int d^3r e^{-iK r \cos(\theta)} e^{-r/a_0}$$

$$= \int_0^\infty dr r^2 e^{-r/a_0} \int_0^\pi d\theta \sin(\theta) e^{-iKr \cos(\theta)} \times 2\pi$$

$$= 2\pi \int_0^\infty dr r^2 e^{-r/a_0} 2 \sin(Kr)$$

$$= 8\pi a_0^3 \left(\frac{1}{1 + K^2 a_0^2}\right)^2.$$ 

Combining with the prefactor we find

$$\tilde{\psi}_{10}(K) = \frac{2^{3/2}}{\pi} \frac{a_0^{3/2}}{(1 + K^2 a_0^2)^2}$$

and

$$\frac{d\sigma}{d\Omega} = \frac{32\hbar k^3 \sin^2(\theta) \cos^2(\phi)}{m\omega_0} \frac{a_0^3}{(1 + K^2 a_0^2)^4}.$$ 

To get the total scattering cross section we need to integrate over the full $4\pi$ solid angle. Now

$$K^2 = K \cdot K = k^2 + k_0^2 - 2kk_0 \cos \theta.$$ 

The use of a plane wave for the continuum state assumes

$$\frac{\hbar^2 k^2}{2m} \gg \frac{E_H}{2n^2}$$

so

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega_0 - \frac{E_H}{2} \simeq \hbar\omega_0$$

or

$$\frac{\hbar^2 k^2}{2m} \simeq \hbarck.$$ 

Thus

$$\frac{k_0}{k} = \frac{\hbar k}{2mc} = \frac{v}{2c}.$$
where \( v \) is the velocity of the emitted electron. We will assume nonrelativistic motion so \( v/c \ll 1 \). Then

\[
K^2 = k^2 \left( 1 + \frac{k_0^2}{k^2} - \frac{2k_0 \cos \theta}{k} \right) \simeq k^2 \left( 1 - \frac{v}{c} \cos \theta \right) \simeq k^2
\]

and

\[
1 + K^2 a_0^2 \simeq 1 + k^2 a_0^2 \simeq k^2 a_0^2.
\]

With these approximations

\[
\frac{d\sigma}{d\Omega} = \frac{32 \hbar \alpha \sin^2(\theta) \cos^2(\phi)}{m \omega_0 k a_0^5}.
\]

Integrating over the solid angle gives a factor of \( 4\pi/3 \) and the total scattering cross section is

\[
\sigma \simeq \frac{128\pi \hbar \alpha}{3m \omega_0} \frac{1}{k^3 a_0^5}.
\]

We see that the cross section scales as

\[
\frac{1}{\omega_0 k^5} \sim \frac{1}{\omega_0 \omega_0^{5/2}} = \frac{1}{\omega_0^{7/2}}.
\]

The cross section decreases very rapidly as the photon energy increases.
Chapter 8
Dynamic polarizability

The Stark effect describes the energy shifts of atomic states due to electrical fields. When the field is static and longitudinally polarized we refer to the energy shift as being due to the DC Stark effect. Energy shifts due to high frequency electric fields depend on the frequency of the field and on its polarization structure. The resulting shifts are referred to as the AC Stark effect. The polarizability of an atomic state provides a compact way of calculating the DC and AC Stark shifts. The polarizability is defined on the basis of the lowest multipole interaction between an atom and an external field which is the electric dipole (E1), calculated at second order in the field strength. This gives energy shifts proportional to the optical intensity. Higher powers of the field can also be important in some cases. These are referred to as hyperpolarizability shifts.

The energy of a fixed dipole \(d\) in a field \(E\) is given by the classical expression \(-Ed\). When the dipole is induced we write \(d(E) = \alpha E\), with \(\alpha\) the polarizability. The energy of the dipole must then be modified to account for the energy expended by the field in creating the dipole. The Stark energy in this case is

\[
U = -E \int_0^E dE' d(E') = -\frac{1}{2} \alpha E^2. \quad (8.1)
\]

When the field is oscillating we write \(E = |\mathcal{E}| \cos(\omega t) = \frac{\mathcal{E}}{2} e^{-i\omega t} + \frac{\mathcal{E}^*}{2} e^{i\omega t}\). The time averaged energy of the dipole is

\[
U_{ac} = \langle U \rangle = -\frac{1}{2} \langle \alpha E^2 \rangle = -\frac{1}{4} \alpha |\mathcal{E}|^2. \quad (8.2)
\]

We will interpret the quantum version of this expression as the energy shift of an atom in an oscillating field. As we will see in the general case the field has a vector structure and \(\alpha\) is a tensor which embodies the angular momentum structure of the atomic state.

8.1 Polarizability and oscillator strengths

8.1.1 Polarizability of an electron

In highly excited atoms the Coulomb interaction between the outer electron and the nucleus is weak. In this situation the atomic polarizability, as deduced from the polarizability of the bound electron, approaches that of a free electron. It is therefore instructive to start by
calculating the polarizability of an electron. This can be done with a classical model. We will calculate using cgs units. An electron in the field \( E = |\mathcal{E}| \cos(\omega t) \mathbf{e}_x \) has an equation of motion
\[
m_e \frac{d^2 x}{dt^2} + m_e \omega_0^2 x = -e \mathbf{E} \cdot \mathbf{e}_x = -e |\mathcal{E}| \cos(\omega t).
\]
Here \( \omega_0 \) is the unforced natural oscillation frequency of a bound electron and for a free electron we will put \( \omega_0 = 0 \). The solution is
\[
x(t) = e \frac{|\mathcal{E}|}{m_e \omega^2 - \omega_0^2} \cos(\omega t).
\]
The dipole moment is therefore
\[
d = -e x e_x = \frac{-e^2 |\mathcal{E}|}{m_e (\omega^2 - \omega_0^2)} \cos(\omega t) \mathbf{e}_x.
\]
We introduce the polarizability through the definition \( d = \alpha E \) giving
\[
\alpha = -\frac{e^2}{m_e} \frac{1}{\omega^2 - \omega_0^2}.
\]
(8.3)
A free electron has
\[
\alpha_{\text{cgs}} = -\frac{e^2}{m_e \omega^2}
\]
and a so-called ponderomotive energy shift
\[
U = -\frac{1}{4} \alpha_{\text{cgs}} |\mathcal{E}|^2 = \frac{e^2 |\mathcal{E}|^2}{4m_e \omega^2}.
\]
We have added the subscript cgs to emphasize that this is the cgs result. The corresponding expression in SI units is (see Eq. 8.20)
\[
\alpha_{\text{SI}} = -\frac{4\pi e_0 e^2}{m_e \omega^2}.
\]

8.1.2 Polarizability of an atomic state

The electron polarizability can be generalized to describe the polarizability due to interaction of a bound electron in a real atom with an external driving field. The field couples an initial atomic state \( |\psi_a\rangle \) to a state \( |\psi_b\rangle \). The energy shift from 2nd order perturbation theory is
\[
U = \frac{\langle \psi_a | \hat{\mathcal{H}} | \psi_b \rangle \langle \psi_b | \hat{\mathcal{H}} | \psi_a \rangle}{U_a + \hbar \omega - U_b} + \frac{\langle \psi_a | \hat{\mathcal{H}} | \psi_b \rangle \langle \psi_b | \hat{\mathcal{H}} | \psi_a \rangle}{U_a - (U_b + \hbar \omega)}
\]
\[
= -\frac{2}{\hbar} \frac{\langle \psi_a | \hat{\mathcal{H}} | \psi_b \rangle \langle \psi_b | \hat{\mathcal{H}} | \psi_a \rangle}{\omega_{ba}} \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2}.
\]
(8.4)
The two terms in this expression are referred to as co- and counter-rotating contributions corresponding to the diagrams shown in Fig. 8.1. They correspond to Feynman diagrams where a photon is either absorbed or emitted with the transition $|\psi_a\rangle \rightarrow |\psi_b\rangle$. When $\omega_{ba} = (U_b - U_a)/\hbar \approx \omega$ the first term is resonant and strongly dominates; however both terms should be included to obtain accurate results.

The Hamiltonian for an electric dipole interaction is $\langle \psi_b | \hat{H} | \psi_a \rangle = e \langle \psi_b | x | \psi_a \rangle \mathcal{E}/2$ where we have taken the light to be $e_x$ polarized. The energy shift is thus

$$U = -\frac{e^2}{2\hbar} \frac{\omega_{ba}}{\omega^2} |\langle \psi_b | x | \psi_a \rangle|^2 |\mathcal{E}|^2.$$

Equating this expression with $\frac{1}{\hbar} \alpha |\mathcal{E}|^2$ we arrive at

$$\alpha = \frac{2e^2}{\hbar} \frac{\omega_{ba}}{\omega^2} |\langle \psi_b | x | \psi_a \rangle|^2.$$

This can be written as

$$\alpha = \frac{e^2}{m_e} \frac{1}{\omega_{ba} - \omega^2 f_{b-a}} \tag{8.5}$$

with

$$f_{b-a} = \frac{2m_e \omega_{ba}}{\hbar} |\langle \psi_b | x | \psi_a \rangle|^2. \tag{8.6}$$

The expression for $\alpha$ corresponds to (8.3) with the replacement $\omega_0 \rightarrow \omega_{ba}$. The additional dimensionless factor $f_{b-a}$ is called the absorption oscillator strength for the quantum transition $|\psi_a\rangle \rightarrow |\psi_b\rangle$. We can interpret the oscillator strength as the relative strength of the quantum transition compared to a classical electron oscillator. This concept is widely used in spectroscopy and astrophysics and is particularly useful because the oscillator strength satisfies constraint relations known as sum rules. As we will see later the sum rule for a single electron is $\sum_b f_{b-a} = 1$, which implies that the absorption oscillator strength for a transition $|\psi_a\rangle \rightarrow |\psi_b\rangle$ where the initial state is the atomic ground state is at most unity. Thus an atomic transition out of the ground state can at most have a strength corresponding to that of a classical electron oscillator. The oscillator strength, which is a dimensionless number, thus provides a convenient way of assessing the relative strength of an atomic transition.

It is convenient to work with an averaged oscillator strength which is independent of the polarization and atomic orientation. Let the initial and final states be specified by $n, J, M$ quantum numbers as $|\psi_a\rangle = |n_a, j_a, m_a\rangle, |\psi_b\rangle = |n_b, j_b, m_b\rangle$. We divide by the number of polarization components (3) and the initial state degeneracy $g_a = 2j_a + 1$ and sum over polarization, and initial and final states to get

$$\bar{f}_{b-a} = \frac{2m_e \omega_{ba}}{\hbar} \frac{1}{3(2j_a + 1)} \sum_{m_a, m_b, q} |\langle n_b, j_b, m_b | r_q | n_a, j_a, m_a \rangle|^2$$

$$= \frac{2m_e \omega_{ba}}{3\hbar(2j_a + 1)} |\langle n_b, j_b | r | n_a, j_a \rangle|^2 \sum_{m_a, m_b, q} \frac{(C_{j_a m_a 1 q}^{m_b j_b})^2}{2j_b + 1}.$$
It can be shown that the sum is unity which results in
\[ \bar{f}_{b \leftarrow a} = \frac{2m_e \omega_{ba}}{3h(2j_a + 1)} |\langle n_b j_b | r | n_a j_a \rangle|^2. \]  \hfill (8.7)
In this expression \( \bar{f}_{b \leftarrow a} \) is an absorption oscillator strength, \( \omega_{ba} > 0 \) and \( a \) labels the ground state. This rotationally averaged oscillator strength is the quantity which is commonly reported in spectroscopic tables and we will henceforth drop the overbar. Absorption and emission oscillator strengths are related by
\[ (2j_a + 1)f_{b \leftarrow a} = -(2j_b + 1)f_{a \leftarrow b}. \]
Note that when \( U_b > U_a \) corresponding to an absorption process the oscillator strength is positive, while for emission the oscillator strength is negative. The rotationally averaged polarizability is therefore
\[ \alpha(\omega) = \frac{2e^2}{3h(2j_a + 1)} \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} |\langle n_b j_b | r | n_a j_a \rangle|^2. \]  \hfill (8.8)
We will refer to this quantity later as the scalar polarizability of an atomic state.

Comparing (8.7) with Eq. (5.3) we get an expression for the radiative lifetime of an excited state in terms of the absorption oscillator strength in the form
\[ \gamma_{a \leftarrow b} = \frac{1}{4\pi \varepsilon_0} \frac{2e^2 \omega_{ba}^2 (2j_a + 1)}{2j_b + 1} \bar{f}_{b \leftarrow a}. \]  \hfill (8.9)
This way of expressing the radiative lifetime is particularly useful because spectroscopic tables of transitions in complex atoms often list the \( A \) coefficient of the upper state and \( \log_{10}(gf) \) where \( g = 2j_a + 1 \) is the degeneracy factor of the lower level and \( f = \bar{f}_{b \leftarrow a} \) is the absorption oscillator strength. The effective radiative decay rate of the transition can then be easily found from Eq. (8.9) and information in spectroscopy tables. The Stark shift of a level \( a \) due to coupling to levels \( b \) in a field with intensity \( I \) is then
\[ U_{ac} = \frac{1}{4 \varepsilon_0 c m_e} \sum_u \frac{1}{\omega_{ba}^2 - \omega^2} \bar{f}_{b \leftarrow a} = -\frac{e^2 I}{2 \varepsilon_0 c m_e (2j_a + 1)} \sum_u 10^{\log_{10}(gf)} \frac{\omega_{ba}^2}{\omega_{ba}^2 - \omega^2}. \]  \hfill (8.10)

### 8.2 Polarizability tensor

We may calculate the polarizability tensor as a sum over electric dipole matrix elements. As in the case of the static polarizability we will find an irreducible representation of the polarizability tensor in a spherical basis. Let us recall the expressions for the static scalar and tensor polarizabilities of the fine structure state \( n_a j_a \)
\[ \alpha_0 = \frac{2e^2}{3h(2j_a + 1)} \sum_{n_b j_b} \frac{|\langle n_b j_b | r | n_a j_a \rangle|^2}{\omega_{ba}}, \quad \text{from 3.28} \]
\[ \alpha_2 = \frac{e^2}{\hbar} \left[ \frac{(2j_a - 1) j_a}{3(2j_a + 3)(2j_a + 1)(j_a + 1)} \right]^{1/2} \sum_{n_b j_b} (-1)^{j_a + j_b} S^{j_a j_b}_{1j_a 2} \frac{|\langle n_b j_b | d | n_a j_a \rangle|^2}{\omega_{ba}}, \quad \text{from 3.30} \]
with  $\hbar \omega_{ba} = U_b - U_a$.

To find the corresponding expressions for the dynamic polarizability we could repeat the procedure followed in Chapter 3. Alternatively we can take a shortcut by noting that the frequency dependence in Eq. (8.8) is of the form $\frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2}$ and the same frequency dependence should also apply to the tensor component. The scalar and tensor dynamic polarizabilities are thus

$$\alpha_0 = \frac{2e^2}{3\hbar(2j_a + 1)} \sum_{n_b,j_b} \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \langle n_b, j_b | \hat{r} | n_a, j_a \rangle^2,$$

(8.11a)

$$\alpha_2 = \frac{e^2}{\hbar} \left[ \frac{40(2j_a - 1)j_a}{3(2j_a + 3)(2j_a + 1)(j_a + 1)} \right]^{1/2} \sum_{n_b,j_b} (-1)^{j_a+j_b} S_{1j_a}^{1j_b} \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \langle n_b, j_b | \hat{r} | n_a, j_a \rangle^2.$$

(8.11b)

Using these expressions we find in analogy with Eq. (3.31) for the dynamic Stark effect due to the scalar and tensor polarizabilities

$$\Delta U = -\frac{|\mathbf{E}|^2}{4} \alpha_0 + \frac{|\mathbf{E}|^2 - 3|\mathbf{E}_z|^2}{8} \frac{3m_a^2 - j_a(j_a + 1)}{j_a(2j_a - 1)} \alpha_2.$$

(8.12)

There is in general also a vector polarizability corresponding to a first rank tensor. We found that the vector response was proportional to $\mathbf{E} \times \mathbf{E}^*$ which vanishes for static fields that are of necessity linearly polarized. For oscillating fields this is no longer the case. It can be shown that the vector polarizability is

$$\alpha_1 = -\frac{e^2}{\hbar} \left[ \frac{6}{(2j_a + 1)(j_a + 1)j_a} \right]^{1/2} \sum_{n_b,j_b} (-1)^{j_a+j_b} S_{1j_a}^{1j_b} \frac{\omega}{\omega_{ba}^2 - \omega^2} \langle n_b, j_b | \hat{r} | n_a, j_a \rangle^2.$$

We see that $\alpha_1 = 0$ when $j_a = 0$ and in the static limit of $\omega = 0$. The Stark shift due to the vector polarizability for light with polarization $\mathbf{e}_q$ is

$$\Delta U = -\frac{1}{4} m_q \beta^2 |\mathbf{e}_q|^2.$$

(8.13)

We see that there is no vector shift for linearly polarized light ($q = 0$) and that the effect of the vector polarizability is analogous to a linear Zeeman shift.

### 8.2.1 Polarizability in Cartesian coordinates

For an arbitrary optical polarization and atomic state the AC Stark shift can be written in the form

$$U_{ac} = -\frac{1}{4} |\mathbf{E}|^2 (\mathbf{e}^*)^T \cdot \mathbf{\alpha} \cdot \mathbf{e}$$

(8.14)

where the optical field is $\mathbf{E} = (\mathbf{E}/2)e^{-i\omega t} \mathbf{e} + (\mathbf{E}^*/2)e^{i\omega t} \mathbf{e}^*$, and $\mathbf{\alpha} = \alpha_0 + \alpha_1 + \alpha_2$ is the polarizability tensor. In order to evaluate (8.14) for a field with arbitrary polarization we need the components $\alpha_{\kappa q}$ for $\kappa = 0, 1, 2$ and $-\kappa \leq q \leq \kappa$ in a spherical basis or the
components $\alpha_{ij}$ in a Cartesian basis $(i,j) = (x,y,z)$. In some cases it is simpler to work in a Cartesian basis for which the polarizability of state $|a\rangle$ is $\alpha_{ij} = \alpha^s \delta_{ij} + \alpha_{ij}^v + \alpha_{ij}^t$ where

$$\alpha^s = \frac{2e^2}{3\hbar} \sum_{b \neq a} \sum_i \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} \langle a|r_i|b\rangle \langle b|r_i|a\rangle$$

$$\alpha_{ij}^v = \frac{e^2}{\hbar} \sum_{b \neq a} \frac{\omega}{\omega_{ba}^2 - \omega^2} [(\langle a|r_i|b\rangle \langle b|r_j|a\rangle) - \langle a|r_j|b\rangle \langle b|r_i|a\rangle]$$

$$\alpha_{ij}^t = \frac{e^2}{\hbar} \sum_{b \neq a} \frac{\omega_{ba}}{\omega_{ba}^2 - \omega^2} [(\langle a|r_i|b\rangle \langle b|r_j|a\rangle) + \langle a|r_j|b\rangle \langle b|r_i|a\rangle] - \alpha^s \delta_{ij}.$$

Here $i,j$ label Cartesian components. The components $\alpha^s, \alpha^v, \alpha^t$ are the scalar, vector, and tensor components of the polarizability. It is readily verified that the vector polarizability is antisymmetric, and the tensor part has zero trace.

The most general polarization of the optical field is $\epsilon = a_x e_x + a_y e_y + a_z e_z$ with the normalization $\sum_i |a_i|^2 = 1$. The energy shift is therefore

$$U_{ac} = -\frac{1}{4} |\epsilon|^2 \left( \sum_i |a_i|^2 \alpha_{ii} + \sum_{i \neq j} a_i^* a_j \alpha_{ij} \right).$$

It can be verified that for linearly polarized light the Stark shift found from Eqs. (8.14,8.15) agrees with Eq. (8.12).

### 8.2.2 Comparison with two level atom

It is instructive to compare the result for the energy shift with that obtained from a two-level atom with transition frequency $\omega_a$. For the two-level case the light induced pseudo-potential can be written as

$$U = \frac{\hbar \Delta}{2} \ln \left( 1 + \frac{I/I_s}{1 + 4\Delta^2/\gamma^2} \right).$$

Here $\Delta = \omega - \omega_a$ is the detuning, $I_s$ is the saturation intensity and $\gamma$ is the natural linewidth. We will derive this expression later on.

For small intensity and $\Delta \gg 0$ we have

$$U \simeq \frac{\hbar \Delta}{2} \frac{I/I_s}{1 + 4\Delta^2/\gamma^2} \simeq \frac{\hbar \gamma^2 I}{8\Delta I_s}.$$ 

The saturation intensity can be written as $I_s = \hbar \gamma \omega_a^3/(12\pi c^2)$ and $I = \frac{\omega c}{2} |\epsilon|^2$. We thus have

$$U = \frac{3\pi \epsilon_0 c^3}{4\omega_a^3} \frac{\gamma}{\Delta} |\epsilon|^2$$

and the effective two-level polarizability is

$$\alpha_{\text{two-level}} = -\frac{3\pi \epsilon_0 c^3 \gamma}{\omega_a^3 \Delta}.$$
To compare with the polarizability of a real atom we might consider a model based on a $J = 0 \rightarrow J' = 0$ transition, except that this is forbidden by angular momentum selection rules. We therefore assume a $J = 0$ ground state coupling to a $J = 1$ excited state. There is no vector or tensor polarizability in the ground state and we find

$$U_{ac} = -\frac{12e^2}{4\hbar} \frac{\omega_a}{2\omega_a(-\Delta)} \langle n'J'||r||nJ \rangle^2 |E|^2 = \frac{1}{4\hbar \Delta} \frac{1}{3} \langle n'J'||d||nJ \rangle^2 |E|^2. \quad (8.17)$$

Using Eq. (5.3)

$$\gamma_{J \rightarrow J'} = \frac{\omega_a^3}{3\pi\varepsilon_0 \hbar c^3} \frac{1}{2J' + 1} \langle n'J'||d||nJ \rangle^2$$

the effective polarizability can be written as

$$\alpha = -\frac{\langle n'J'||d||nJ \rangle^2}{3\hbar \Delta} = -\frac{3\pi\varepsilon_0 c^3}{\omega_a^3} \frac{\gamma}{\Delta} = \alpha_{\text{two-level}}.$$

### 8.2.3 Stark shift induced by a Gaussian laser beam

A linearly polarized field acting on a $J = 1/2$ atomic state gives an AC Stark shift

$$\Delta U = -\frac{1}{4} \alpha |E|^2.$$

Here $\alpha$ is the scalar polarizability. This expression is valid in both cgs and SI units, either of which can be used for calculating numerical values. It is common to report values of the polarizability in cgs units for which the polarizability has units of volume, whereas it is more convenient to work with the field in SI units.

A mixed calculation can be done as follows. In cgs units

$$\Delta U_{\text{cgs}} = -\frac{1}{4} \alpha_{\text{cgs}} |E_{\text{cgs}}|^2.$$

The conversion factor for the field between the two sets of units is $E_{\text{cgs}} = (10^4/c_{\text{SI}})E_{\text{SI}}$. The subscripts cgs or SI refer to quantities in the respective units, e.g. $c_{\text{SI}} = 299792458$.

A Gaussian beam with $1/e^2$ intensity radius $w$ has a peak field strength of

$$E_{\text{SI}} = \left(\frac{2I_{\text{SI}}}{\varepsilon_0 c_{\text{SI}}} \right)^{1/2} = \left(\frac{4P_{\text{SI}}}{\pi \varepsilon_0 c_{\text{SI}} w_{\text{SI}}^2} \right)^{1/2}.$$  

Thus the peak Stark shift is

$$\Delta U_{\text{cgs}} = -\left(\frac{10^8}{\pi \varepsilon_0 c_{\text{SI}}^3} \right) \left(\frac{\alpha_{\text{cgs}} P_{\text{SI}}}{w_{\text{SI}}^2} \right)$$

or, using $1 \text{ J} = 10^7 \text{ ergs}$,

$$\Delta U_{\text{SI}} = -\left(\frac{10}{\pi \varepsilon_0 c_{\text{SI}}^3} \right) \left(\frac{\alpha_{\text{cgs}} P_{\text{SI}}}{w_{\text{SI}}^2} \right). \quad (8.18)$$
Alternatively we can do the calculation by first converting \( \alpha \) to SI units. To find the conversion factor we note

\[
\Delta U_{\text{SI}} = -\frac{1}{4} \alpha_{\text{SI}} |\mathcal{E}_{\text{SI}}|^2 = -\left( \frac{1}{\pi \epsilon_0 c_{\text{SI}}} \right) \left( \frac{\alpha_{\text{SI}} P_{\text{SI}}}{w_{\text{SI}}^2} \right).
\]

Comparing Eqs. (8.18,8.19) we have

\[
\alpha_{\text{SI}} = 4\pi \epsilon_0 \alpha_{\text{cgs}}
\]

\[
[\alpha_{\text{SI}}] = 4\pi \epsilon_0 \times 10^{-6} [\alpha_{\text{cgs}}] \text{ (Cm}^2/\text{V})
\]

where [...] means the numerical value of the quantity in brackets. As indicated the units of \( \alpha_{\text{SI}} \) are Cm\(^2\)/V. As an example, for \( \alpha_{\text{cgs}} = 200 \times 10^{-24} \) cm\(^3\), a beam with \( w = 600 \mu\text{m} \) and \( P = 5588 \) W gives a well depth of 3 mK.

For reference some values of polarizability of the heavy alkalis at common wavelengths are:

Rb:

\[
\begin{align*}
\lambda &= 532 \text{ nm} \quad & \alpha_{\text{cgs}} &= -33.7 \times 10^{-24} \text{ cm}^3 \\
\lambda &= 770 \text{ nm} \quad & \alpha_{\text{cgs}} &= -1310. \times 10^{-24} \text{ cm}^3 \\
\lambda &= 1064 \text{ nm} \quad & \alpha_{\text{cgs}} &= 97. \times 10^{-24} \text{ cm}^3
\end{align*}
\]

Cs:

\[
\begin{align*}
\lambda &= 532 \text{ nm} \quad & \alpha_{\text{cgs}} &= -31.9 \times 10^{-24} \text{ cm}^3 \\
\lambda &= 780 \text{ nm} \quad & \alpha_{\text{cgs}} &= -247. \times 10^{-24} \text{ cm}^3 \\
\lambda &= 1064 \text{ nm} \quad & \alpha_{\text{cgs}} &= 168. \times 10^{-24} \text{ cm}^3
\end{align*}
\]

As an example let’s calculate the energy shift induced by a laser beam on a Cs atom. A Gaussian beam of power \( P = 0.01 \) W, and wavelength 1064 nm is focused to a spot with waist \((1/e^2\) intensity radius) of \( w = 1 \mu\text{m} \) generates an electric field

\[
\mathcal{E} = \left( \frac{4P}{\pi \epsilon_0 cw^2} \right)^{1/2} = 2.2 \times 10^6 \text{ V/m}.
\]

It is worth noting that the oscillating electric field amplitude is remarkably large using a very small power of 1 mW. This field is close to the breakdown voltage in air which is approximately \( 3 \times 10^6 \) V/m. The AC Stark shift is

\[
\Delta U = -\frac{1}{4} 4\pi \epsilon_0 \alpha_{\text{cgs}} |\mathcal{E}|^2 = 2.2 \times 10^{-26} \text{ J}.
\]

It is useful to express the AC Stark shift in temperature units

\[
\Delta U = k_B \times 1.6 \text{ mK},
\]

with \( k_B \) the Boltzmann constant. We see that the focused 10 mW laser beam provides a potential shift of 1.6 mK. Particles with less kinetic energy than this will be trapped in
the focused beam. This forms the basis of optical tweezers which are widely used in atomic physics and biological experiments.

If we were to use a shorter wavelength laser the polarizability may be negative and the potential is raised in regions of nonzero intensity. It is still possible to trap particles in such a case using a light beam which is arranged to have an intensity minimum surrounded by higher intensity regions. Such optical traps are referred to as blue detuned, since the negative polarizability occurs for wavelengths shorter than (on the blue side of) a transition.

### 8.3 Polarizability of Cs

As an example of the general theory let’s calculate the polarizability of some states in Cs. In order to calculate the polarizability of any particular state we need to calculate the reduced matrix elements from the state of interest to all other states connected by E1 allowed transitions. Forbidden transitions due to magnetic dipole, electric quadrupole, or higher multipoles are only important when near resonant with the transition and we will ignore these contributions.

There are several approaches to calculating the matrix elements. For closed transitions where the Einstein $A$ coefficient is known from experiments we can extract the matrix element from the expression for $\gamma$. For other transitions we can numerically calculate the matrix elements using Coulomb wavefunctions, model potentials, or WKB methods. In the last 20 years there has been great progress in ab-initio calculations of matrix elements for the alkalis, and other heavy atoms. These methods require detailed knowledge of specialized techniques. It is possible to check for self-consistency of results using oscillator strength sum rules. For alkali atom valence electrons the sum rules give only a partial check since the oscillator strength sum for a single valence state is not equal to unity, and differences as high as 5-10% occur in the heavy alkalis because of core polarization effects.

We will use the Coulomb wavefunction method, where the wavefunctions are defined using known quantum defect values. In order to capture the most important resonances we sum over several low lying transitions. There is an uncertainty in this method when determining matrix elements between states of nonzero orbital angular momentum since the integrand diverges at small $r$. To avoid the divergence we choose a cutoff length, but the value of the matrix element depends on the cutoff. We will fix the cutoff for transitions $njl \rightarrow n'j'l'$ such that the calculated matrix element agrees with known values, either from experiment for cycling transitions, or from more sophisticated calculations. We then use the same cutoff for different $n'$ but the same $l',j'$. Comparison with other results suggests that we can expect absolute accuracies of a few percent using this approach.

The AC Stark shift of the hyperfine states due to scalar and tensor polarizabilities is

$$\Delta U = -\frac{1}{2}|E|^2 \left[ \alpha_0 + \alpha_2 C(F,m_F) \right]$$

where

$$C(F,m_F) = \frac{[3m_F^2 - F(F + 1)][3X(X - 1) - 4F(F + 1)J(J + 1)]}{F(2F - 1)(2F + 2)(2F + 3)J(2J - 1)}$$

with $X = F(F + 1) + J(J + 1) - I(I + 1)$. The effective excited state polarizabilities are

$$\alpha_{\text{eff}} = \alpha_0 + C\alpha_2.$$
\[ \alpha_0 = \frac{2e^2}{3h(2J + 1)} \sum_{\gamma \neq \gamma'} \frac{\omega_{\gamma'\gamma}}{\omega_{\gamma'\gamma}^2 - \omega^2} |\langle \gamma' || \hat{r} || \gamma \rangle|^2 \]
\[ \alpha_2 = \frac{e^2}{\hbar} \left[ \frac{40(2J - 1)J}{3(2J + 3)(2J + 1)(J + 1)} \right]^{1/2} \sum_{\gamma \neq \gamma'} \frac{\omega_{\gamma'\gamma}}{\omega_{\gamma'\gamma}^2 - \omega^2} \left( -1 \right)^{J + J'} S^{|J| J'}_{1 J 2} |\langle \gamma' || \hat{r} || \gamma \rangle|^2. \]

For the purposes of numerical calculations we need values for the radial matrix elements. Accurate values for these using all-order methods and calculated directly between fine structure states are available[24]. Alternatively we can calculate the matrix elements in terms of uncoupled states \(|nLS\rangle\) using the relation
\[
|\langle n' L' S J' || r || n L S J \rangle|^2 = (2J + 1)(2J' + 1) \left( S^{|LSJ|}_{J'1L} \right)^2 \max(L, L') \left( R_{nL(J)}^{n'L'(J')} \right)^2
\]
with \( R_{nL(J)}^{n'L'(J')} = \int_0^\infty dr r^3 R_{n'L'(J')} R_{nL(J)} \) the radial matrix element. The notation \( L(J) \) is to remind us that the wavefunctions of the fine structure states \( L_J, L_{J'} \) are slightly different, and have different quantum defects. Therefore the radial integrals between uncoupled states \( nL, n'L' \) implicitly depend on \( J, J' \). We calculate these radial matrix elements using quantum defect wavefunctions or a WKB approximation. Some matrix elements between low lying states are given in Table 8.1.

### 8.3.1 Cs \( 6s_{1/2}, 6p_{1/2}, 6p_{3/2} \) states

A partial Grotrian diagram of Cs is shown in Fig. 8.2. The transitions between low lying states lead to resonances in the polarizability that are shown in Figs. 8.3, 8.4, 8.5, 8.6.
<table>
<thead>
<tr>
<th>final state</th>
<th>transition theory</th>
<th>theory</th>
<th>Cwf</th>
<th>WKB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6s_{1/2}$</td>
<td>-0.8523</td>
<td>6.324</td>
<td>5.477</td>
<td>0.</td>
</tr>
<tr>
<td>$7s_{1/2}$</td>
<td>1.470</td>
<td>6.473</td>
<td>-5.606</td>
<td>0.</td>
</tr>
<tr>
<td>$8s_{1/2}$</td>
<td>0.7946</td>
<td></td>
<td></td>
<td>0.</td>
</tr>
<tr>
<td>$9s_{1/2}$</td>
<td>0.6588</td>
<td></td>
<td></td>
<td>0.</td>
</tr>
<tr>
<td>$10s_{1/2}$</td>
<td>0.6036</td>
<td></td>
<td></td>
<td>0.</td>
</tr>
<tr>
<td>$5d_{3/2}$</td>
<td>3.614</td>
<td>3.19</td>
<td>6.18</td>
<td>0.7</td>
</tr>
<tr>
<td>$5d_{5/2}$</td>
<td>3.491</td>
<td>9.66</td>
<td>-6.24</td>
<td>0.7</td>
</tr>
<tr>
<td>$6d_{3/2}$</td>
<td>0.9211</td>
<td>2.05</td>
<td>3.97</td>
<td>0.7</td>
</tr>
<tr>
<td>$6d_{5/2}$</td>
<td>0.9175</td>
<td>6.01</td>
<td>-3.88</td>
<td>0.7</td>
</tr>
<tr>
<td>$7d_{3/2}$</td>
<td>0.6985</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>$7d_{5/2}$</td>
<td>0.6975</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>$8d_{3/2}$</td>
<td>0.6220</td>
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<td>0.7</td>
</tr>
<tr>
<td>$8d_{5/2}$</td>
<td>0.6215</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 8.1: Reduced matrix elements in the $j$ basis $\langle n'j'l's||r||njls\rangle$ and radial matrix elements $R_{6p_{3/2}}^{nlj}$, in the $nl$ basis for the Cs $6p_{3/2}$ state. The reduced and radial matrix elements are related by $|\langle n'j'l's||r||njls\rangle| = \sqrt{(2j+1)(2j'+1)\max(l,l')} S_{j1}^{l'j's} R_{nlj}^{n'l'jr}$. Cwf are values calculated using Coulomb wavefunctions with experimental values for quantum defects, and $r_{\text{min}}$ a small $r$ cutoff to avoid divergence. WKB are values calculated using Kaulakys WKB theory with experimental values for quantum defects. Matrix elements are given in atomic units.
Figure 8.2: Grotrian diagram for Cs. Transition wavelengths are given in nm.

Figure 8.3: Scalar and tensor polarizabilities for the Cs $6s_{1/2}$ and $6p_{3/2}$ states.
As an example of a more complex atom let's calculate the polarizability of Ho. There is one stable isotope $^{165}$Ho with nuclear spin $I = 7/2$. The ground state has $J = 15/2$, $S = 15/2$, and $F = 17/2$. The ground state is a member of the $^3H_g$ multiplet with $M_J = 15/2$. The excited states are members of the $^5H_u$ multiplet.
$g_J = 2J + 1$ and we therefore need to consider the scalar and tensor polarizabilities. The Grotrian diagram of Ho is shown in Fig. 8.7. There is a very complex forest of levels. To name one particular feature the four lowest energy odd-parity levels all have the same valence configuration $4f^{11}6s^2$ but have $J = 9/2, 11/2, 13/2, 15/2$. These are fine structure levels of the ground configuration with magnetic dipole transitions at energies of more than 5000 cm$^{-1}$. As these levels decay via magnetic dipole transitions they are long lived. Also the lowest energy even parity levels with $J = 19/2, 21/2$ are metastable and decay via electric quadrupole and octupole transitions.

Calculating radial matrix elements is challenging and we will therefore rely on oscillator strengths given in the literature [25]. With linearly polarized light there is no vector contribution and the light shift of a hyperfine Zeeman state $|F, M\rangle$ is

$$U_{ac} = -\frac{1}{4} |\mathcal{E}|^2 [\alpha_0 + C(F, M)\alpha_2]$$

with

$$C(F, M) = \frac{[3M_F^2 - F(F+1)] [3X(X-1) - 4F(F+1)J(J+1)]}{F(2F-1)(2F+2)(2F+3)J(2J-1)}$$

where $X = F(F+1) + J(J+1) - I(I+1)$. The scalar and tensor polarizabilities expressed in terms of absorption oscillator strengths $f_{u\rightarrow g}$ are (in SI units)

$$\alpha_0 = 4\pi \epsilon_0 \frac{e^2}{m_e (2J+1)} \sum_u 10^{\log_{10}^{\text{g}}(g_j f_{u\rightarrow g})} \frac{\omega^2_{ug} - \omega^2}{\omega^2_{ug} - \omega^2},$$

$$\alpha_2 = 4\pi \epsilon_0 \frac{e^2}{m_e} \left[ \frac{30(2J-1)J}{(2J+3)(2J+1)^3(J+1)} \right]^{1/2} \sum_u \frac{\omega^2_{ug} - \omega^2}{\omega^2_{ug} - \omega^2} (-1)^J S_{1J2}^{f_1 f_2} 10^{\log_{10}^{\text{g}}(g_j f_{u\rightarrow g})}.$$
Figure 8.8: Scalar and tensor polarizability of the Ho ground state.
Chapter 9

Coherent interaction of atoms and light

Interaction of radiation with multilevel atomic systems is of importance to many physical phenomena. A widely used approach is a semi-classical description where the atomic system with its discrete levels is treated quantum mechanically and the radiation field is treated classically. Within the semiclassical approximation there are several possible approaches. The most straightforward is to solve the Schrödinger equation for the levels coupled by the optical field. This approach is useful for many situations, but does not allow spontaneous emission to be treated consistently. The effects of spontaneous emission can be included using a non-Hermitian Hamiltonian and Monte Carlo wave function methods. Alternatively a density matrix formalism leading to a master equation allows for a full description of spontaneous emission. This approach will allow us to identify and characterize decay times for the population and the coherence, commonly referred to as $T_1$ and $T_2$ times.

9.1 Rabi Oscillations

We will start with the simpler Schrödinger equation approach and afterwards show that the results obtained are in agreement with those found from a density matrix treatment. Interaction of a two level atom with a monochromatic field results in deterministic rotation of the atomic state within the basis of the optically coupled levels. Here we assume a single atom interacting with the field and solve the Schrödinger equation directly. Writing $|\psi\rangle = c_g(t)e^{-i\omega t}|g\rangle + c_e(t)e^{-i\omega t}|e\rangle$ the Hamiltonian can be written as $\hat{H} = \hat{H}_0 + \hat{V}_d$, with the unperturbed Hamiltonian $\hat{H}_0 = \hbar\omega_g|g\rangle\langle g| + \hbar\omega_e|e\rangle\langle e|$. The atom-field electric dipole interaction is described by $\hat{V}_d = -\hat{d}E$ with $\hat{d} = -e\hat{r}$ (the charge on an electron is $-e$) and the electric field is $E = (\mathcal{E}/2)e^{-i\omega t} + c.c$. Using

\[
\hat{r} = \hat{I} \hat{r} \hat{I}
\]

\[
= (|g\rangle\langle g| + |e\rangle\langle e|)\hat{r}(|g\rangle\langle g| + |e\rangle\langle e|)
\]

\[
= |e\rangle\hat{r}|g\rangle\langle g| + |g\rangle\hat{r}|e\rangle\langle e| + r_{eg}|e\rangle\langle g| + r_{ge}|g\rangle\langle e|
\]

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the interaction Hamiltonian is written \( \hat{V}_d = -E_d|e\rangle\langle g| + H.c. \) and the Schrödinger equation then gives

\[
\begin{align*}
\hbar \dot{c}_g + \hbar \omega_c c_g &= \hbar \omega_c c_g - E_d e^g_c e^{-i(\omega_c - \omega_g)t}, \\
\hbar \dot{c}_e + \hbar \omega_c c_e &= \hbar \omega_c c_e - E_d e^g_c e^{i(\omega_c - \omega_g)t}.
\end{align*}
\]

We are interested in the near resonant situation where the detuning \( \Delta = \omega - \omega_{eg} \ll \omega_{eg} = \omega_e - \omega_g \). Dropping therefore the counterrotating terms on the r.h.s. of Eqs. (9.1) we get

\[
\begin{align*}
\frac{dc_g}{dt} &= i \frac{\Omega^*}{2} c_e e^{i\Delta t}, \\
\frac{dc_e}{dt} &= i \frac{\Omega}{2} c_g e^{-i\Delta t}
\end{align*}
\]

(9.1a) (9.1b)

with the complex Rabi frequency \( \Omega = d_{eg} \mathcal{E}/\hbar \).

To solve Eqs. (9.2) it is convenient to use the variables \( \bar{c}_g = e^{-i\Delta t/2} c_g \), \( \bar{c}_e = e^{i\Delta t/2} c_e \), which satisfy the set

\[
\begin{align*}
\frac{d\bar{c}_g}{dt} &= -i \frac{\Delta}{2} \bar{c}_g + i \frac{\Omega^*}{2} \bar{c}_e, \\
\frac{d\bar{c}_e}{dt} &= i \frac{\Delta}{2} \bar{c}_e + i \frac{\Omega}{2} \bar{c}_g
\end{align*}
\]

(9.3a) (9.3b)

The solutions with initial amplitudes \( \bar{c}_g(0) = \bar{c}_{g0}, \bar{c}_e(0) = \bar{c}_{e0} \) are

\[
\begin{align*}
\bar{c}_g(t) &= \left[ \cos \left( \frac{\Omega' t}{2} \right) - i \frac{\Delta}{\Omega'} \sin \left( \frac{\Omega' t}{2} \right) \right] \bar{c}_{g0} + \left[ \frac{\Omega^*}{\Omega} \right] e^{-i\frac{\Delta t}{2}} \sin \left( \frac{\Omega' t}{2} \right) \bar{c}_{e0}, \\
\bar{c}_e(t) &= i \frac{\Omega}{\Omega'} e^{-i\frac{\Delta t}{2}} \sin \left( \frac{\Omega' t}{2} \right) \bar{c}_{g0} + \left[ \cos \left( \frac{\Omega' t}{2} \right) + i \frac{\Delta}{\Omega'} \sin \left( \frac{\Omega' t}{2} \right) \right] \bar{c}_{e0}
\end{align*}
\]

(9.4a) (9.4b)

with \( \Omega' = \sqrt{\Omega^2 + \Delta^2} \) the effective off-resonance Rabi frequency. We can write the solution as a rotation matrix \( \hat{U}(t, t_0) \bar{c}(t_0) \) with

\[
\hat{U}(t, t_0) = \begin{pmatrix}
\cos \left( \frac{\Omega'(t-t_0)}{2} \right) - i \frac{\Delta}{\Omega'} \sin \left( \frac{\Omega'(t-t_0)}{2} \right) & i \frac{\Omega^*}{\Omega'} \sin \left( \frac{\Omega'(t-t_0)}{2} \right) \\
\frac{\Omega}{\Omega'} \sin \left( \frac{\Omega'(t-t_0)}{2} \right) & \cos \left( \frac{\Omega'(t-t_0)}{2} \right) + i \frac{\Delta}{\Omega'} \sin \left( \frac{\Omega'(t-t_0)}{2} \right)
\end{pmatrix}.
\]

(9.5)

Transforming back to the variables without tildes we have \( \bar{c}(t) = \hat{U}(t, t_0) \bar{c}(t_0) \) with

\[
\begin{align*}
U(t, t_0) &= \begin{pmatrix} e^{i\Delta t/2} & 0 \\
0 & e^{-i\Delta t/2} \end{pmatrix} \hat{U}(t, t_0) \begin{pmatrix} e^{-i\Delta t_0/2} & 0 \\
0 & e^{i\Delta t_0/2} \end{pmatrix} \\
&= \begin{pmatrix} e^{i\Delta(t-t_0)/2} & \cos \left( \frac{\Omega'(t-t_0)}{2} \right) - i \frac{\Delta}{\Omega'} \sin \left( \frac{\Omega'(t-t_0)}{2} \right) \\
\frac{ie^{-i\Delta(t+t_0)/2}}{\Omega} \sin \left( \frac{\Omega'(t-t_0)}{2} \right) & e^{-i\Delta(t-t_0)/2} \cos \left( \frac{\Omega'(t-t_0)}{2} \right) + i \frac{\Delta}{\Omega'} \sin \left( \frac{\Omega'(t-t_0)}{2} \right) \end{pmatrix}.
\end{align*}
\]

(9.6)

Although the phase factors in (9.6) look odd as they depend on both \( t-t_0 \) and \( t+t_0 \) they are needed to track the full phase dependence of the wavefunction. We can easily verify that for
9.1 Rabi Oscillations

\[ |g\rangle \quad \Delta = \omega - \omega_{eg} \]

\[ \begin{align*}
|e\rangle &\quad \text{\Omega}_1 \\
\end{align*} \]

Figure 9.1: Rabi oscillations of a two-level system with \((\Omega = 2\pi, \Delta = 0)\) and \((\Omega = 2\pi, \Delta = 4\pi)\).

\[ t_2 > t_1 > t_0, \ U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0) \] which must be true for a unitary transformation. If we are only interested in final probabilities, and not the amplitudes, it is sufficient to propagate the state with the simpler \(\tilde{U}(t, t_0)\).

When the driving field is resonant so \(\Delta = 0\) and the field amplitude is constant the interaction Hamiltonian has no explicit time dependence and \(U(t, t_0) = U(t - t_0)\), so the matrix takes on the simple form

\[
U(t - t_0) = \begin{pmatrix}
\cos \left(\frac{\Omega(t-t_0)}{2}\right) & ie^{-i\phi} \sin \left(\frac{\Omega(t-t_0)}{2}\right) \\
-ie^{i\phi} \sin \left(\frac{\Omega(t-t_0)}{2}\right) & \cos \left(\frac{\Omega(t-t_0)}{2}\right)
\end{pmatrix}
\] (9.7)

where \(\Omega = |\Omega|e^{i\phi}\).

If the atom is initially in the ground state the time dependent probabilities to be in the ground and excited states are

\[
|c_g(t)|^2 = \cos^2 \left(\frac{\Omega t}{2}\right) + \frac{\Delta^2}{\Omega^2 + \Delta^2} \sin^2 \left(\frac{\Omega t}{2}\right),
\]

\[
|c_e(t)|^2 = \frac{|\Omega|^2}{|\Omega|^2 + \Delta^2} \sin^2 \left(\frac{\Omega t}{2}\right). \] (9.8)

The population oscillations are shown in Fig. 9.1. If the driving field is resonant, \(\Delta = 0, \Omega' = \Omega\) and the amplitude to be in the excited state will reach unity at time \(\Omega t/2 = \pi/2\) or \(t = \pi/\Omega\). This defines a so-called \(\pi\) pulse of duration \(t_\pi = \pi/\Omega\) which inverts the population between the two states.

It is also interesting to examine the phase evolution of a quantum state under Rabi oscillations. Suppose we start with the state \(|\psi\rangle = c_g|g\rangle + c_e|e\rangle\). A resonant \(2\pi\) pulse, \(\Omega t = 2\pi\), has the evolution matrix

\[
U(t - t_0) = \begin{pmatrix}
-1 & 0 \\
0 & -1
\end{pmatrix}
\] (9.9)

which results in the transformation

\[ |\psi\rangle \rightarrow -|\psi\rangle = e^{i\pi}|\psi\rangle. \]
Recall that rotation of a spin 1/2 object about the $z$ axis by $2\pi$ results in the same transformation

$$|\psi\rangle \rightarrow e^{-iJ_z\theta/\hbar}|\psi\rangle = e^{-i(\pm1/2)(2\pi)}|\psi\rangle = e^{i\pi/2}|\psi\rangle = e^{i\pi}|\psi\rangle.$$ 

A $2\pi$ pulse applied to a two-level system is analogous to rotation of a spin 1/2 through an angle of $2\pi$. In both cases we are rotating between the two quantum states of the object. Classically a $2\pi$ rotation has no observable effect. In quantum mechanics the phase of the wave function can change. The quantum phase can be observed using an interference experiment, and this phase is an essential ingredient in many protocols that are used to create entanglement between different spins.

### 9.1.1 Radiatively broadened excited state

Applications of Rabi dynamics may involve excited states that are radiatively broadened. When radiative decay takes place to additional levels that are not coupled to the ground and excited states that participate in the coherent dynamics the time dependence of the populations may be altered significantly.

Consider the level scheme of Fig. 9.2 where the population in $|e\rangle$ decays with rate $\gamma_p$ to a state $|p\rangle$ that does not participate in the Rabi dynamics. In this situation Eqs. (9.2) take the form

$$\dot{c}_g = \frac{i\Omega^*}{2}c_e e^{i\Delta t},$$

$$\dot{c}_e = -\frac{\gamma_p}{2}c_e + \frac{i\Omega}{2}c_g e^{-i\Delta t}. \tag{9.11}$$

The decay term $(-\gamma_p/2)c_e$ comes from a non-Hermitian contribution to the Hamiltonian. We again introduce the variables $\tilde{c}_g = e^{-i\Delta t/2}c_g$, $\tilde{c}_e = e^{i\Delta t/2}c_e$, which satisfy the set

$$\frac{d\tilde{c}_g}{dt} = -\frac{i}{2}c_g + \frac{i\Omega^*}{2}c_e$$

$$\frac{d\tilde{c}_e}{dt} = \frac{i\Delta}{2}c_e + \frac{i\gamma_p}{2}c_g, \tag{9.13}$$

Analytical solutions for $c_g, c_e$ can be readily written down, but are cumbersome.
Relative phase of ground and excited state evolution

Consider the following sequence of operations. We start with an atom in the ground state \(|\psi\rangle = |g\rangle\), excite it to \(|e\rangle\) with a \(\pi\) pulse, wait a time \(T\), then rotate it back to the ground state with a second \(\pi\) pulse. What will be the phase of the wavefunction relative to its initial phase?

The initial state at \(t = 0\) is \(|\psi\rangle = |g\rangle\). Assume a perfect \(\pi\) pulse that is on resonance and has duration \(t_\pi = \pi/|\Omega|\). From Eqs. (9.4) using \(c_g(0) = 1\), \(c_e(0) = 0\) we get \(c_g(t_\pi) = 0\) and \(c_e(t_\pi) = i\) so that

\[ |\psi(t_\pi)\rangle = ie^{i\omega_e t_\pi}|e\rangle. \]

We then wait a time \(T\) so that the state becomes

\[ |\psi(t_\pi + T)\rangle = ie^{-i\omega_e(t_\pi+T)}|e\rangle = c_e(t_\pi + T)e^{-i\omega_e(t_\pi+T)}|e\rangle \]

with \(c_e(t_\pi + T) = i\). Then apply a \(\pi\) pulse to give

\[ |\psi(2t_\pi + T)\rangle = -e^{-i\omega_g(2t_\pi+T)}|g\rangle. \]

If we had simply kept the atom in the ground state for a time \(2t_\pi + T\) the wavefunction would have been

\[ |\psi'(2t_\pi + T)\rangle = e^{-i\omega_g(2t_\pi+T)}|g\rangle. \]

The difference between the two cases is a multiplicative factor of

\[-1.\]

The atom does not pick up a phase that depends on the time in the excited state.

9.2 Time dependent Rabi frequency

Exact solutions of the two-level Rabi problem are only known for constant \(\Omega\) and for some specific time dependent pulse shapes. The case of a Gaussian pulse amplitude \(\Omega(t) = \frac{\theta_0}{\sqrt{2\pi}\sigma^2}e^{-t^2/2\sigma^2}\) and constant detuning \(\Delta(t) = \Delta_0\) is not analytically solvable. An asymptotic solution was given by Berman et al.[26], valid for integration limits of \(-\infty < t < \infty\), \(c_g(-\infty) = 1\) and \(\Delta_0 \gg \Omega_0\).

Making the rotating wave approximation the equations of motion are

\[
\frac{dc_g}{dt} = i\frac{\theta_0}{\sqrt{8\pi}\sigma^2}e^{-t^2/2\sigma^2}e^{i\Delta_0 t}c_e, \tag{9.14a}
\]

\[
\frac{dc_e}{dt} = i\frac{\theta_0}{\sqrt{8\pi}\sigma^2}e^{-t^2/2\sigma^2}e^{-i\Delta_0 t}c_g. \tag{9.14b}
\]

We are interested in the case where the pulse is applied symmetrically about the maximum so we will integrate from \(-\tau_p/2\) to \(\tau_p/2\) with \(\tau_p\) the pulse length. At zero detuning the problem can be solved exactly giving \(\begin{pmatrix} c_g(t) \\ c_e(t) \end{pmatrix} = U \begin{pmatrix} c_g(-\tau_p/2) \\ c_e(-\tau_p/2) \end{pmatrix}\) with

\[
U = \begin{pmatrix} \cos(\theta(t)/2) & i e^{-i\phi_0} \sin(\theta(t)/2) \\ i e^{i\phi_0} \sin(\theta(t)/2) & \cos(\theta(t)/2) \end{pmatrix}
\]

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Thus to obtain a pulse area $\tau$ corrections to this expression are (Berman) so that, putting $z$ to evaluate the last integral use $\theta = 0 = \bar{\theta}$ $\tau_p$ we should use a peak amplitude $\theta_0 = \bar{\theta} / f(\tau_p/2)$. When $\tau_p = 5(10) \sigma$ then $f(\tau_p/2) = 0.988(0.999999)$. At large detuning the excited state amplitude is small so to first order, $c_g \simeq 1$ and

$$c_e(t) \simeq i \frac{\theta_0}{\sqrt{8\pi \sigma^2}} \int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'}$$

$$= i \frac{\theta_0}{4} e^{-\Delta_0^2 \sigma^2/2} \left[ \text{erf} \left( \frac{t + i \Delta_0 \sigma^2}{2\sqrt{\sigma}} \right) - \text{erf} \left( \frac{-\tau_p/2 + i \Delta_0 \sigma^2}{2\sqrt{\sigma}} \right) \right]. \quad (9.15)$$

Corrections to this expression are ($\theta_0^2 / (\Delta_0 \sigma)^2$). At the end of the pulse, $t = \tau_p/2$, we find

$$c_e(t) = i \frac{\theta_0}{2} e^{-\Delta_0^2 \sigma^2/2} \text{Re} \left[ \text{erf} \left( \frac{\tau_p + i \Delta_0 \sigma^2}{2\sqrt{\sigma}} \right) \right]. \quad (9.16)$$

The next approximation to $c_g$ is

$$c_g(t) \simeq i \frac{\theta}{\sqrt{8\pi \sigma^2}} \int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'} c_e(t')$$

$$= \frac{\theta^2}{\sqrt{128 \pi \sigma^2}} e^{-\sigma^2 \Delta_0^2/2} \text{erf} \left( \frac{-\tau_p/2 + i \Delta_0 \sigma^2}{2\sqrt{\sigma}} \right) \int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'}$$

$$- \frac{\theta^2}{\sqrt{128 \pi \sigma^2}} e^{-\sigma^2 \Delta_0^2/2} \int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'} \text{erf} \left( \frac{t' + i \Delta_0 \sigma^2}{2\sqrt{\sigma}} \right). \quad (9.15)$$

To evaluate the last integral use

$$\text{erf}(z) = 1 + \frac{ie^{-z^2}}{\pi} \int_{-\infty}^{\infty} d\zeta \frac{e^{-\zeta^2}}{\zeta - iz}$$

so that, putting $z = \frac{t' + i \Delta_0 \sigma^2}{2\sqrt{\sigma}}$,

$$\int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'} \text{erf} \left( \frac{t' + i \Delta_0 \sigma^2}{2\sqrt{\sigma}} \right) = \int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'}$$

$$+ \frac{i}{\pi} \int_{-\tau_p/2}^{\tau_p/2} dt' e^{-t'^2/2\sigma^2} e^{i\Delta_0 t'} e^{-z^2} \int_{-\infty}^{\infty} d\zeta \frac{e^{-\zeta^2}}{\zeta - iz}.$$
9.3 Rabi oscillations with more than one excited state

If there is more than one excited state the equations of motion generalize to

\[
\frac{dc_g}{dt} = \frac{i}{2} \sum_{j=1}^{K} \Omega_j^* e^{i\Delta_j t} c_j, \quad (9.17a)
\]

\[
\frac{dc_j}{dt} = \frac{i}{2} \Omega_j e^{-i\Delta_j t} c_g, \quad j = 1, \ldots K \quad (9.17b)
\]

with \( K \) the number of distinct excited states. It is readily checked that these equations conserve the total population since \( \frac{d}{dt} \left( |c_g|^2 + \sum_j |c_j|^2 \right) = 0 \). If we start with the atom in the ground state then the excited state population will be bounded at all times by \( \sum_j |c_j(t)|^2 \leq |c_g(0)|^2 = 1 \).

A variant on this model describes \( N \) two-level atoms with strong interactions \( V_{ij} \) between excited atoms. If \( |V_{ij}| \gg |\Omega_j| \) it is only possible to excite a single atom at a time. Decomposing the \( N \) atom state as \( |\psi\rangle = c_g |g...g\rangle + c_1 |e...g\rangle + \ldots + c_N |g.....e\rangle \) the equations of motion are

\[
\frac{dc_g}{dt} = \frac{i}{2} \sum_{j=1}^{N} \Omega_j^* e^{i\Delta_j t} c_j, \quad (9.18a)
\]

\[
\frac{dc_j}{dt} = \frac{i}{2} \Omega_j e^{-i\Delta_j t} c_g, \quad j = 1, \ldots N. \quad (9.18b)
\]

These equations are mathematically identical to (9.17), and therefore the total excited state population is bounded by \( \sum_j |c_j|^2 \leq |c_g(0)|^2 = 1 \) if all atoms start in the ground state.

When all the field couplings and detunings are equal \( \Omega_j = \Omega, \Delta_j = \Delta \), it is useful to introduce the symmetric state \( |s\rangle = \frac{1}{\sqrt{N}} \sum_j (|g...e\rangle + |g...eg\rangle + \ldots + |e....g\rangle) \) and the state decomposition \( |\psi\rangle = c_g |g\rangle + c_s |s\rangle \). We can then write the dynamical equations as

\[
\frac{dc_g}{dt} = \frac{i}{2} \Omega_N^* e^{i\Delta t} c_s, \quad (9.19a)
\]

\[
\frac{dc_s}{dt} = \frac{i}{2} \Omega_N e^{-i\Delta t} c_g, \quad (9.19b)
\]

These are equivalent to the equations for a single two-level atom but with the Rabi frequency replaced by the collectively enhanced frequency \( \Omega_N = \sqrt{N}\Omega \). This symmetric description is strictly valid when all \( \Omega_j \) and \( \Delta_j \) are equal. We can check the range of validity by comparing solutions of (9.18) and (9.19).

We can further generalize the model (9.18) to account for dephasing that arises due to the interaction of ground state and excited atoms. We add an interaction potential \( V_{ij} = V(r_i^{(g)}, r_j^{(e)}) \) for atom \( i \) at position \( r_i^{(g)} \) in the ground state and atom \( j \) at position \( r_j^{(e)} \) in the excited state. The Schrödinger equations generalize to

\[
\frac{dc_g}{dt} = \frac{i}{2} \sum_{j=1}^{N} \Omega_j^* e^{i\Delta_j t} c_j + \frac{i}{2} \sum_{j=1}^{N} V_j c_j, \quad (9.20a)
\]

\[
\frac{dc_j}{dt} = \frac{i}{2} \Omega_j e^{-i\Delta_j t} c_g + iV_j c_g, \quad j = 1, \ldots N \quad (9.20b)
\]
where we have defined an interaction potential for each excited atom \( V_j = \sum_{i \neq j} V_{ij} \). It is easily verified that Eqs. (9.20) also conserve the total population and therefore we still have \( \sum_j |c_j|^2 \leq |c_g(0)|^2 = 1 \) if all atoms start in the ground state.

Numerical solutions of Eqs. (9.20) for moderate numbers of atoms indicate evolution towards a state with \( \sum_j |c_j|^2 \sim 1/2 \). The question arises as to why the excited state population limit is not saturated. We can extract some insight from considering a two atom problem. Taking a real Rabi frequency \( \Omega_1 = \Omega_2 = \Omega \) and \( \Delta_1 = \Delta_2 = 0 \) the eigenmodes are

\[
\begin{align*}
    u_1 & = \cos \left[ (V_1^2 + V_2^2 + (V_1 + V_2)\Omega + \Omega^2/2) t \right], \\
    u_2 & = \sin \left[ (V_1^2 + V_2^2 + (V_1 + V_2)\Omega + \Omega^2/2) t \right].
\end{align*}
\]

The solution satisfying the initial condition \( c_g(0) = 1, c_1(0) = c_2(0) = 0 \) is \( c_g(t) = u_1 \) and \( c_1(t) = a_1 u_2, c_2(t) = a_2 u_2 \) with \( a_1, a_2 \) constants. Conservation of population requires that \( |a_1|^2 + |a_2|^2 \leq 1 \) and therefore the time averaged excited state population is bounded by 1/2. This is true no matter how large the dephasing caused by \( V_1, V_2 \). The same situation holds for three atoms with the arguments of \( u_1, u_2 \) extended to depend on \( V_1, V_2, V_3 \). This is also true when the \( \Omega_j \) are not all equal.

When \( \Delta_j = 0 \) the \( N+1 \) equations for \( N \) atoms admit \( N-1 \) zero eigenvalues and a pair of complex conjugate eigenvalues \( \pm i\lambda \). It follows that the ground state evolves as \( c_g = \cos(\lambda t) \) and the singly excited states evolve as \( c_j = a_j \sin(\lambda t) \) with \( \sum_j |a_j|^2 \leq 1 \). This implies that the time averaged excited state population is bounded by 1/2 and for Rabi frequency large compared to the detunings it will approach 1/2. Numerical solutions suggest that this is also the case for arbitrary \( \Delta_j \).

### 9.3.1 Dephasing

Other forms of dephasing couple the excited state population to dark excited states which are decoupled from the light. This results in the excited state population approaching the blockade limit of 1. A situation giving this type of dephasing is the presence of an excited state AC Stark shift that depends on the position of each atom. This could for example be introduced by a random spatial field such as a laser speckle field. A set of model equations for this behavior which includes an atom specific dephasing term \( \delta_j \) is

\[
\begin{align*}
    \frac{dc_g}{dt} & = \frac{i}{2} \sum_{j=1}^{N} \Omega_j^* e^{i\Delta_j t} c_j + i \sum_{j=1}^{N} V_j c_j, \quad (9.21a) \\
    \frac{dc_j}{dt} & = i\delta_j c_j + \frac{i}{2} \Omega_j e^{-i\Delta_j t} c_g + iV_j c_j, \quad j = 1, \ldots, N. \quad (9.21b)
\end{align*}
\]

Numerical solutions verify that the excited state population exceeds 1/2 for some parameters.

### 9.4 Density matrix description of two-level atom and field

To calculate the interaction of a two-level atom with a radiation field we can solve the Schrödinger equation directly as in the solution for Rabi flopping. That solution neglected
the finite lifetime of the excited state. For weak decay we can add terms like $-i(\gamma/2)|e\rangle\langle e|$ into the Hamiltonian. However, the resulting Hamiltonian is non-Hermitian and does not strictly conserve probability. A consistent approach that does not rely on Monte-Carlo techniques uses the density matrix.

The Hamiltonian can be written as

$$\hat{H} = \hat{H}_a + \hat{H}_1. \quad (9.22)$$

Here $\hat{H}_a$ describes the unperturbed atom and $\hat{H}_1$ is the field-atom interaction potential. Consider a two-level atom with lower level $|g\rangle$ and upper level $|e\rangle$. All atoms which spontaneously decay from the upper level populate the lower level, and there is no spontaneous decay out of the lower level. Then $(\hat{H}_a)_{ij} = \delta_{ij}U_i$ with $U_i$ the unperturbed energy of level $|i\rangle$ ($i = e, g$). The interaction potential should account for shifts of the unperturbed levels due to the ac Stark effect and dipole induced coupling between levels due to the interaction $\hat{H}_1 = -\hat{d} \cdot \mathbf{E}$, with $\hat{d}$ the dipole moment operator and $\mathbf{E}$ the classical electric field. Since the energy eigenstates have definite parity the diagonal elements of $\hat{d}$ vanish at first order in the field. Neglecting for the moment $2^{nd}$ order AC Stark shifts we find

$$\hat{H}_1 = \begin{bmatrix} 0 & -\mathbf{E} \cdot \hat{d}_{eg} \\ -\mathbf{E} \cdot \hat{d}_{ge} & 0 \end{bmatrix} \quad (9.23)$$

where $\hat{d}_{eg} = \langle e|\hat{d}|g\rangle$. We can simplify the notation by writing $\mathbf{E} \cdot \hat{d}_{eg} = E\hat{d}$ so

$$\hat{H}_1 = -E \begin{bmatrix} 0 & \hat{d}^* \\ \hat{d} & 0 \end{bmatrix}. \quad (9.24)$$

Using $\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar} \left[ \hat{\rho}, \hat{H} \right]$ we get the density matrix equations of motion

$$\frac{d\rho_{gg}}{dt} = -\frac{i}{\hbar} E (d\rho_{ge} - d^*\rho_{eg}) \quad (9.25a)$$
$$\frac{d\rho_{ee}}{dt} = -\frac{i}{\hbar} E (d^*\rho_{eg} - d\rho_{ge}) \quad (9.25b)$$
$$\frac{d\rho_{eg}}{dt} = -i\omega_a\rho_{eg} - \frac{i}{\hbar} Ed\rho_{eg} - \frac{i}{\hbar} Ed^*(\rho_{ee} - \rho_{gg}) \quad (9.25c)$$
$$\frac{d\rho_{ge}}{dt} = i\omega_a\rho_{ge} + \frac{i}{\hbar} Ed^*(\rho_{ee} - \rho_{gg}) \quad (9.25d)$$

where $\hbar\omega_a = U_e - U_g$ is the separation of the atomic levels. We see that $\frac{d\rho_{gg}}{dt} + \frac{d\rho_{ee}}{dt} = 0$ (which follows from $\rho_{gg} + \rho_{ee} = 1$) and $\frac{d\rho_{eg}}{dt} = (\frac{d\rho_{ge}}{dt})^*$ (which follows from the fact that $\hat{\rho}$ is Hermitian). It is therefore sufficient to keep only one of the off-diagonal elements, say $\rho_{eg} = \rho_{ge}^*$. We can account for decay processes phenomenologically. The upper level population is assumed to have a radiative lifetime $T_1$. In a closed system all the population that leaves the upper level enters the lower level which grows at a rate $\rho_{ee}/T_1$. The atomic coherence is assumed dephased with a characteristic time $T_2$. With these definitions the density matrix
equations become
\[
\frac{d\rho_{gg}}{dt} = \frac{\rho_{ee}}{T_1} - \frac{i}{\hbar} E (d\rho_{eg}^* - d^* \rho_{eg}) \tag{9.26a}
\]
\[
\frac{d\rho_{ee}}{dt} = -\frac{\rho_{ee}}{T_1} + \frac{i}{\hbar} E (d^* \rho_{eg} - d\rho_{eg}^*) \tag{9.26b}
\]
\[
\frac{d\rho_{eg}}{dt} = -(\frac{1}{T_2} + i\omega_a)\rho_{eg} - \frac{i}{\hbar} Ed(\rho_{ee} - \rho_{gg}) . \tag{9.26c}
\]

We wish to solve for the atomic dynamics in the presence of a monochromatic driving field \( E = |E| \cos(\omega t + \theta) = \frac{\xi}{2} e^{-i\omega t} + c.c. \), where \( E = |E| e^{-i\theta} \). Putting \( \rho_{eg} = \tilde{\rho}_{eg} e^{-i\omega t} \) gives
\[
\frac{d\rho_{gg}}{dt} = \rho_{ee} T_1 - \frac{i}{2\hbar} (E d\tilde{\rho}_{eg}^* - E^* d^* \tilde{\rho}_{eg} + E^* d^* \tilde{\rho}_{eg} - E d\tilde{\rho}_{eg}^*) \tag{9.27a}
\]
\[
\frac{d\rho_{ee}}{dt} = -\rho_{ee} T_1 + \frac{i}{2\hbar} (E d\tilde{\rho}_{eg}^* - E^* d^* \tilde{\rho}_{eg} + E^* d^* \tilde{\rho}_{eg} - E d\tilde{\rho}_{eg}^*) \tag{9.27b}
\]
\[
\frac{d\tilde{\rho}_{eg}}{dt} = (i\Delta - \frac{1}{T_2})\tilde{\rho}_{eg} - \frac{i d}{2\hbar} (E + E^* e^{2i\omega t}) (\rho_{ee} - \rho_{gg}) . \tag{9.27c}
\]

We have introduced the detuning \( \Delta = \omega - \omega_a \).

Exact solutions to these equations are difficult to come by. When the driving field is near resonant with the atomic transition \( |\Delta| \ll \omega, \omega_a \) and it is a good approximation to neglect all the rapidly oscillating terms on the right hand side of Eqs. (9.27). This is known as the rotating wave approximation (RWA) which takes the form
\[
\frac{d\rho_{gg}}{dt} = \frac{\rho_{ee}}{T_1} - \frac{i}{2} (\Omega \tilde{\rho}_{eg}^* - \Omega^* \tilde{\rho}_{eg}) \tag{9.28a}
\]
\[
\frac{d\rho_{ee}}{dt} = -\frac{\rho_{ee}}{T_1} + \frac{i}{2} (\Omega \tilde{\rho}_{eg}^* - \Omega^* \tilde{\rho}_{eg}) \tag{9.28b}
\]
\[
\frac{d\tilde{\rho}_{eg}}{dt} = (i\Delta - \frac{1}{T_2})\tilde{\rho}_{eg} - \frac{i \Omega}{2} (\rho_{ee} - \rho_{gg}) . \tag{9.28c}
\]

Here we have introduced the complex Rabi frequency \( \Omega = dE/\hbar \). These density matrix equations are often referred to as optical Bloch equations since they have the same form as in Bloch’s description of nuclear magnetic resonance[27].

Defining the inversion by \( w = \rho_{ee} - \rho_{gg} \) we can reduce the two level problem in the RWA to two equations
\[
\frac{dw}{dt} = -\frac{1+w}{T_1} + i \left( \Omega \tilde{\rho}_{eg}^* - \Omega^* \tilde{\rho}_{eg} \right) \tag{9.29a}
\]
\[
\frac{d\tilde{\rho}_{eg}}{dt} = (i\Delta - \frac{1}{T_2})\tilde{\rho}_{eg} - \frac{i \Omega}{2} w . \tag{9.29b}
\]

When there is no driving field \( \Omega = 0 \) and the steady state solutions are \( w = -1 \) and \( \tilde{\rho}_{eg} = 0 \). Although we are working with a model of a closed transition it is often desirable to allow for
an incoherent pumping mechanism that creates a net inversion in the absence of a driving field. To do so we generalize Eqs.(9.29) to

\[
\frac{d w}{dt} = -w - w(0) T_1 + i \left( \Omega \rho_{eg}^* - \Omega^* \rho_{eg} \right),
\]

(9.30a)

\[
\frac{d \rho_{eg}}{dt} = \left( i \Delta - \frac{1}{T_2} \right) \rho_{eg} - i \frac{\Omega}{2} w.
\]

(9.30b)

where \(w(0)\) is the zero field inversion. We see that the population inversion \(w\) acts as a source term for the coherence and that the coherence acts as a source term for changes in the population inversion. The coherent dynamics evolves on the frequency scale set by \(\Omega\).

The steady state solutions are a balance between the coherent dynamics and decay processes governed by the time constants \(T_1, T_2\). Setting the time derivatives to zero we find the stationary solutions

\[
w = w^{(0)} \frac{1 + \Delta^2 T_2^2}{1 + \Delta^2 T_2^2 + T_1 T_2 |\Omega|^2},
\]

\[
\tilde{\rho}_{eg} = -i \frac{\Omega T_2}{2} \left( 1 - i \Delta T_2 \right) \frac{1}{1 + \Delta^2 T_2^2}.
\]

(9.31)

Before proceeding let us specialize the notation. In the limit of very small incident field \((\Omega \to 0)\) the FWHM absorption linewidth (imaginary part of the polarization) is given by \(\gamma = 2/T_2\). Also we have quite generally

\[
\frac{1}{T_2} = \frac{1}{2 T_1} + \gamma_c
\]

where \(\gamma_c\) is the dipole dephasing rate due to collisions. This equation says that in the absence of collisions the decay rate of the coherence is one half the decay rate of the population. We can understand this qualitatively since the coherence \(\sim c_e\) and the population \(\sim |c_e|^2\). Neglecting collisions we have \(T_1 = 1/\gamma\) and \(T_2 = 2/\gamma\). The ground and excited state populations for an initially unexcited atom \((w^{(0)} = -1)\) are

\[
\rho_{gg} = \frac{1 - w}{2} = \frac{1 + 4 \Delta^2 / \gamma^2 + |\Omega|^2 / \gamma^2}{1 + 4 \Delta^2 / \gamma^2 + 2 |\Omega|^2 / \gamma^2},
\]

\[
\rho_{ee} = \frac{1 + w}{2} = \frac{1 + 2 |\Omega|^2 / \gamma^2}{1 + 4 \Delta^2 / \gamma^2 + 2 |\Omega|^2 / \gamma^2}.
\]

For the purpose of practical calculations the following definitions are useful. The inversion is given by

\[
w = \frac{w^{(0)}}{1 + \frac{2 \Omega^2}{\gamma^2 + 4 \Delta^2}}.
\]

(9.32)

On resonance this can be written in the form \(w = w^{(0)}/(1 + I/I_{sat})\) where \(I_{sat} = \epsilon_0 n c h^2 \gamma^2/(4d^2)\) and \(n\) is the refractive index. Using the result \(d^2 = 3\pi \epsilon_0 c^3 h \gamma / \omega_a^3\), which is true for electric dipole transitions, we can write the saturation intensity as

\[
I_{sat} = \frac{n h \gamma \omega_a^3}{12 \pi c^2}.
\]

(9.33)
Apart from the factor of \( n \) we have included here this is the same result found from our earlier treatment based on the rate equations with \( A, B \) coefficients.

The classical macroscopic polarization density is the sum of the individual atomic polarizations. Introducing the atomic density \( n_a \) we get for the polarization density

\[
P(t) = n_a \langle \hat{d} \rangle = n_a \text{Tr}[\hat{\rho} \hat{d}] = n_a d(\rho_{eg} + \rho_{ge})
\]

\[
= n_a w(0) \frac{d^2}{2\hbar} \left( \frac{1 + \Delta^2 T_2^2}{1 + \Delta^2 T_2^2 + \Omega^2 T_1^2} \right) \left( \frac{\Delta - i/T_2}{\Delta^2 + \left( \frac{i}{T_2} \right)^2} \mathcal{E} e^{-i\omega t} + \text{c.c.} \right)
\]

\[
= n_a w(0) \frac{d^2}{\hbar \gamma} \frac{1}{1 + 2|\Omega|^2/\gamma^2} \left( \frac{2\Delta/\gamma - i}{1 + 4\Delta^2/\gamma^2} \mathcal{E} e^{-i\omega t} + \text{c.c.} \right). \tag{9.34}
\]

It is apparent from Eq. (9.34) that \( P(t) \) includes terms at frequencies \( \omega \) and \( -\omega \) proportional to all odd powers of \( E \).

Finally let’s make a connection with the Lindblad form of the master equation. In the Born-Markov approximation the density operator evolves according to the Lindblad equation

\[
\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}] + \sum_j \hat{L}_j \hat{\rho} \hat{L}_j^\dagger - \frac{1}{2} \hat{L}_j^\dagger \hat{L}_j \hat{\rho} - \frac{1}{2} \hat{\rho} \hat{L}_j^\dagger \hat{L}_j.
\]

This is derived in the QM primer notes. It is not hard to show that with the substitutions

\[
\hat{H} = U_g |g\rangle \langle g| + U_e |e\rangle \langle e| - E \hat{d}
\]

\[
\hat{L}_j = \sqrt{\gamma} \sigma = \sqrt{\gamma} |g\rangle \langle e|
\]

and the substitutions \( T_1 = 1/\gamma, T_2 = 2/\gamma \), we recover the Bloch equations (9.26).

### 9.4.1 Comparison with Schrödinger equation solution

We can compare the dynamics found from the density matrix equations with the Schrödinger equation Rabi oscillation solutions. When \( T_1, T_2 \to \infty \) the two descriptions give the same results. With finite decay times significant differences are seen as shown in Fig. 9.3. The Schrödinger equation solution for the average excited state population at large detuning is

\[
\langle P_e \rangle = \frac{|\Omega|^2}{|\Omega|^2 + \Delta^2} \approx \frac{|\Omega|^2}{2\Delta^2}.
\]

The factor of 1/2 comes from taking the time average of \( \sin^2(\Omega t/2) \). The stationary solution of the density matrix equations at large detuning is

\[
\rho_{ee} \approx \frac{|\Omega|^2}{4\Delta^2},
\]

which is twice smaller. We see that at short times the average of \( \rho_{ee} \) is indeed close to \( \langle P_e \rangle \). However, at long times, there is a loss of coherence, and the population oscillations decay towards a stationary solution of \( \rho_{ee} = \langle P_e \rangle / 2 \). Accurate prediction of the excited state population requires solving the density matrix equations, even at time scales several times shorter than \( T_1 \).
9.5 Rate equations

Using $T_1 = 1/\gamma, T_2 = 2/\gamma$ the density matrix equations (9.29) take the form

\[
\frac{d\rho_{eg}}{dt} = \left(i\Delta - \frac{\gamma}{2}\right)\rho_{eg} - i\frac{\Omega}{2}w.
\]

(9.35b)

When $|\Delta| \gg \gamma, |\Omega|$ the coherence $\tilde{\rho}_{eg}$ is slaved to the inversion and we can adiabatically eliminate the coherence by setting $\frac{d\tilde{\rho}_{eg}}{dt} = 0$ which gives a closed equation for the inversion

\[
\frac{dw}{dt} = -\gamma(1 + w) - \frac{2|\Omega|^2}{1 + \frac{4\Delta^2}{\gamma^2}}w.
\]

(9.36a)

Even when the detuning is not large this effective rate equation for $w$ provides an efficient method for finding asymptotic solutions of the dynamics. Rewriting in terms of populations $P_e = \rho_{ee}, P_g = \rho_{gg}$ we find

\[
\frac{dP_e}{dt} = -\gamma P_e - \frac{|\Omega|^2}{1 + \frac{4\Delta^2}{\gamma^2}}(P_e - P_g),
\]

(9.36a)

\[
\frac{dP_g}{dt} = \gamma P_e + \frac{|\Omega|^2}{1 + \frac{4\Delta^2}{\gamma^2}}(P_e - P_g).
\]

(9.36b)

We see that when $|\Delta|$ is large the coherent redistribution of population proceeds at a rate proportional to $\gamma|\Omega|^2/\Delta^2 = |\Omega| \times (\gamma|\Omega|/\Delta^2)$. For large detuning this is slower than the resonant rate of $\Omega$. 

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The rate equations (9.36) which were derived from the optical Bloch equations reproduce the Einstein description in terms of A,B coefficients. Putting \( N_g = P_g, N_e = P_e, \gamma = A, \) and \( \frac{|\Omega|^2}{1 + \frac{4\Delta^2}{\gamma^2}} = B \rho_\omega \) we get

\[
\begin{align*}
\frac{dN_e}{dt} &= -AN_e - B \rho_\omega N_e + B \rho_\omega N_g, \\
\frac{dN_g}{dt} &= AN_e + B \rho_\omega N_e - B \rho_\omega N_g,
\end{align*}
\]

which are just the Einstein rate equations (4.1).

### 9.5.1 Multilevel rate equations

Let’s generalize the rate equations to more than two levels. Assume there are \( N_g \) lower states, all radiatively stable, and \( N_e \) excited states which can decay to the lower states with decay rate \( \gamma \). The total number of states is \( N = N_g + N_e \). The multilevel rate equations are

\[
\begin{align*}
\frac{dP_{e,k}}{dt} &= -\gamma P_{e,k} - \sum_{j=1}^{N_g} \frac{|\Omega_{jk}|^2}{1 + \frac{4\Delta^2}{\gamma^2}} (P_{e,k} - P_{g,j}), \\
&= -\gamma P_{e,k} - \sum_{j=1}^{N_g} \frac{|\Omega_{jk}|^2}{1 + \frac{4\Delta^2}{\gamma^2}} (P_{e,k} - P_{g,j}), \\
&= -\gamma \sum_{k=1}^{N_e} b_{jk} P_{e,k} + \sum_{k=1}^{N_e} \frac{|\Omega_{jk}|^2}{1 + \frac{4\Delta^2}{\gamma^2}} (P_{e,k} - P_{g,j}), \\
&= -\gamma \sum_{k=1}^{N_e} b_{jk} P_{e,k} + \sum_{k=1}^{N_e} \frac{|\Omega_{jk}|^2}{1 + \frac{4\Delta^2}{\gamma^2}} (P_{e,k} - P_{g,j}).
\end{align*}
\]

The fractional branching coefficients are

\[
b_{jk} = \frac{|\langle g, j | r_{m_j - m_k} | e, k \rangle|^2}{\sum_j |\langle g, j | r_{m_j - m_k} | e, k \rangle|^2}
\]

where \( q = -1, 0, 1 \). These are normalized so that \( \sum_j b_{jk} = 1 \).

We can also go one step further and eliminate the excited state populations. If the excited state excitation and decay occur on fast time scales relevant to the ground state dynamics the excited state populations are slaved and we can put \( dP_{e,k} dt \approx 0 \) to get

\[
P_{e,k} = -\sum_{j=1}^{N_g} \frac{|\Omega_{jk}|^2}{1 + \frac{4\Delta^2}{\gamma^2}} (P_{e,k} - P_{g,j}),
\]

which can be written as

\[
P_{e,k} = \frac{\sum_{j=1}^{N_g} \frac{|\Omega_{jk}|^2}{\gamma^2} P_{g,j}}{1 + \frac{4\Delta^2}{\gamma^2} + \sum_{j=1}^{N_g} \frac{|\Omega_{jk}|^2}{\gamma^2}}.
\]

This is then inserted into (9.38b) to give a closed set of equations for the ground state populations.
Chapter 10

Multiphoton coherent transitions

When more than two atomic levels are coupled together with a multi-frequency optical field interesting interference effects can arise. These coherent interference effects have spectacular consequences including, but not limited to, lasing without inversion, electromagnetically induced transparency (EIT), slow light, dark state population transfer, and enhanced nonlinear optical susceptibilities.

10.1 Two-photon Rabi Oscillations

Rabi oscillations can be driven by multi-photon processes. In general the rate of an \( n \) photon process scales with the \( n \)th power of the field, and is typically much less than the rate of single photon transitions. Nonetheless we can achieve fast multi-photon transitions when there is an intermediate level in resonance or near to resonance with the single photon transition. Consider the coupling scheme shown in Fig. 10.1. The Hamiltonian is \( \hat{H} = \hat{H}_0 + \hat{V}_d \), with the unperturbed Hamiltonian \( \hat{H}_0 = \hbar \omega_g |g\rangle\langle g| + \hbar \omega_e |e\rangle\langle e| + \hbar \omega_r |r\rangle\langle r| \). The interaction Hamiltonian, keeping only quasiresonant terms, is \( \hat{V}_d = -E_1 d_{eg}|e\rangle\langle g| - E_2 d_{re}|r\rangle\langle e| + H.c. \). Writing the atomic wavefunction as \( |\psi\rangle = c_g(t)e^{-i\omega_g t}|g\rangle + c_e(t)e^{-i\omega_e t}|e\rangle + c_r(t)e^{-i\omega_r t}|r\rangle \) the Schrödinger equation gives

\[
\begin{align*}
\hbar \dot{c}_g &= -E_1 d_{ge}c_e e^{-i(\omega_e - \omega_g)t}, \quad (10.1a) \\
\hbar \dot{c}_e &= -E_1 d_{eg}c_g e^{i(\omega_e - \omega_g)t} - E_2 d_{re}c_r e^{-i(\omega_r - \omega_e)t}, \quad (10.1b) \\
\hbar \dot{c}_r &= -E_2 d_{re}c_e e^{i(\omega_r - \omega_e)t}. \quad (10.1c)
\end{align*}
\]

Note these equations neglect spontaneous emission.

We assume small single photon detunings \( \Delta_1 = \omega_1 - \omega_{eg} \)

Figure 10.1: Coupling scheme for two-photon Rabi oscillations in a ladder configuration.
and $\Delta_2 = \omega_2 - \omega_{re}$ and drop counterrotating terms to get

\[
\frac{dc_g}{dt} = i \frac{\Omega_1}{2} c_e e^{i \Delta_1 t}, \quad (10.2a)
\]

\[
\frac{dc_e}{dt} = i \frac{\Omega_1}{2} c_g e^{-i \Delta_1 t} + i \frac{\Omega_2^*}{2} c_r e^{i \Delta_2 t}, \quad (10.2b)
\]

\[
\frac{dc_r}{dt} = i \frac{\Omega_2}{2} c_e e^{-i \Delta_2 t}. \quad (10.2c)
\]

Define the two-photon detuning $\Delta = \Delta_1 + \Delta_2 = \omega_1 + \omega_2 - \omega_{rg}$, the difference of detunings $\delta = \Delta_1 - \Delta_2$, $c_g = \tilde{c}_g e^{i \Delta t/2}$, $c_e = \tilde{c}_e e^{-i \delta t/2}$, and $c_r = \tilde{c}_r e^{-i \Delta t/2}$ to get

\[
\frac{d\tilde{c}_g}{dt} = -i \frac{\Delta}{2} \tilde{c}_g + i \frac{\Omega_1}{2} \tilde{c}_e \quad (10.3a)
\]

\[
\frac{d\tilde{c}_e}{dt} = i \frac{\delta}{2} \tilde{c}_e + i \frac{\Omega_1}{2} \tilde{c}_g + i \frac{\Omega_2^*}{2} \tilde{c}_r \quad (10.3b)
\]

\[
\frac{d\tilde{c}_r}{dt} = i \frac{\Delta}{2} \tilde{c}_r + i \frac{\Omega_2}{2} \tilde{c}_e. \quad (10.3c)
\]

The general solution requires finding the roots of a cubic equation. This can be written down in closed form when all coefficients on the right hand side of (10.3) are piecewise continuous in time. A useful approximate solution can be found when $\delta \gg |\Omega_1|, |\Omega_2|$ so that we can use the slaved solution for the intermediate level amplitude $\tilde{c}_e \simeq -\frac{\Omega_1}{\delta} \tilde{c}_g - \frac{\Omega_2}{\delta} \tilde{c}_r$ to get

\[
\frac{d\tilde{c}_g}{dt} = -i \frac{\Delta_1'}{2} \tilde{c}_g - i \frac{\Omega_1^*}{2} \tilde{c}_r \quad (10.4a)
\]

\[
\frac{d\tilde{c}_r}{dt} = i \frac{\Delta_2'}{2} \tilde{c}_r - i \frac{\Omega_2^*}{2} \tilde{c}_g \quad (10.4b)
\]

where $\Delta_1' = \Delta + \frac{|\Omega_1|^2}{\delta}$, $\Delta_2' = \Delta - \frac{|\Omega_2|^2}{\delta}$ are the effective detunings including a.c. Stark shifts of the ground and excited states and $\Omega_R = \Omega_1 \Omega_2/\delta = \Omega_1 \Omega_2/(2\Delta_1 - \Delta)$ is the two-photon Rabi frequency.

A short calculation gives the solutions

\[
c_g(t) = e^{(\Delta - \Delta_-) t/2} \left[ \cos \left( \frac{\Omega t}{2} \right) - i \frac{\Delta_+}{\Omega'} \sin \left( \frac{\Omega t}{2} \right) \right] c_{g0} - i \frac{\Omega_1^*}{\Omega'} e^{i(\Delta - \Delta_-) t/2} \sin \left( \frac{\Omega t}{2} \right) c_{r0} \quad (10.5a)
\]

\[
c_r(t) = -i \frac{\Omega_R}{\Omega'} e^{-i(\Delta + \Delta_-) t/2} \sin \left( \frac{\Omega t}{2} \right) c_{g0} + e^{-i(\Delta + \Delta_-) t/2} \left[ \cos \left( \frac{\Omega t}{2} \right) + i \frac{\Delta_+}{\Omega'} \sin \left( \frac{\Omega t}{2} \right) \right] c_{r0} \quad (10.5b)
\]

with $\Omega' = \sqrt{|\Omega_R|^2 + \Delta_+^2}$ the effective off-resonance Rabi frequency and $\Delta_\pm = (\Delta_1' \pm \Delta_2')/2$.

### 10.1.1 Phase shifts

Let’s look in more detail at the phase shifts accumulated during a $2\pi$ Rabi pulse. In the case of a two-level system driven by a single field the ground state accumulates a phase of
\( e^{i\pi} = -1 \) due to a resonant \( 2\pi \) pulse. This can be understood as being analogous to the quantum mechanical effect of rotation of a spin \( 1/2 \) particle (which has two levels) by \( 2\pi \).

The situation is more complicated for the three level problem driven by two fields. Even for a resonant \( 2\pi \) rotation there is an additional phase accumulation due to AC Stark shifts. We will define resonant in an operational manner as the field detunings which lead to full population transfer from the ground to excited state. This occurs when \( \Delta_+ = \Delta + \frac{|\Omega_1|^2 - |\Omega_2|^2}{\Delta} = 0 \). Using \( \delta = \Delta_1 - \Delta_2 = 2\Delta_1 - \Delta \) we can write the resonance condition as

\[
\Delta (2\Delta_1 - \Delta) + \frac{|\Omega_1|^2}{2} - \frac{|\Omega_2|^2}{2} = 0.
\]

Solving for \( \Delta \) we find

\[
\Delta = \Delta_1 \left( 1 \pm \sqrt{1 + \frac{|\Omega_1|^2 - |\Omega_2|^2}{2\Delta_1^2}} \right).
\]

We are interested in situations where there is two-photon resonance or near resonance while \( \Delta_1 \) is large to eliminate scattering from the intermediate level. We therefore take the minus sign to get

\[
\Delta = \Delta_1 \left( 1 - \sqrt{1 + \frac{|\Omega_1|^2 - |\Omega_2|^2}{2\Delta_1^2}} \right)
\]

\[
\simeq \frac{|\Omega_2|^2 - |\Omega_1|^2}{4\Delta_1} \equiv \Delta_{ac}.
\] (10.6)

We see that \( \Delta \) should be set to \( \Delta_{ac} \) in order to cancel the quadratic Stark shift of the transition due to the two fields. It should also be emphasized that the process of adiabatically eliminating the intermediate level automatically accounts for the second order AC Stark terms. These do not need to be added separately.

Using \( \Delta = \Delta_{ac} \) the phase shift accumulated by the ground state during a \( 2\pi \) ground-excited state pulse is

\[
\phi_{2\pi} = \pi + \frac{\Delta - \Delta_{ac}}{2} - 2t_{\pi}
\]

\[
= \pi + \left( \Delta_{ac} - \frac{|\Omega_1|^2}{2\delta} - \frac{|\Omega_2|^2}{2\delta} \right) \frac{\pi}{|\Omega_R|}
\]

\[
\simeq \pi - \frac{|\Omega_1|^2}{2\Delta_1 |\Omega_R|}
\]

\[
\simeq \pi \left[ 1 - \frac{|\Omega_1|}{|\Omega_2|} \text{sign}(\Delta_1) \right].
\] (10.7)

In the last lines we have made the approximation \( |\Delta_1| \gg |\Delta| \) so \( \delta \simeq 2\Delta_1 \). Note that in the balanced situation where \( \Omega_1 = \Omega_2 \) the phase shift is zero. This is in contrast to the case of a resonant single photon transition which will always give a \( \pi \) phase shift. The analytical expression (10.7) can be verified by numerical integration of the three coupled equations (10.2) in the limit of large \( \Delta_1 \). This phase shift is important in understanding entanglement creation with Rydberg state interactions[28].
10.1.2 Doppler broadened two-photon Rabi transitions

Consider a two-photon Rabi oscillation from a ground state $|g\rangle$ via an intermediate state $|p\rangle$ to an excited state $|r\rangle$. The laser parameters (intensity and detunings) are chosen such that we have a $\pi$ pulse when on resonance. For nonzero detuning the excited state population depends on detuning as

$$P_r = \frac{1}{1 + (\Delta_0/\Omega)^2} \sin^2 \left(\frac{\pi}{2} \sqrt{1 + (\Delta_0/\Omega)^2}\right),$$

where $\Delta_0$ is the detuning and $\Omega$ is the two-photon Rabi frequency.

This formula applies to stationary atoms. When the laser excitation is due to copropagating beams with wavevectors $k_1, k_2$ we must make the substitution

$$\Delta_0 \rightarrow \Delta(v) = \Delta_0 - (k_1 + k_2)v$$

where $v$ is the component of the atomic velocity parallel to $k_1, k_2$. For an atom cloud thermalized at temperature $T_a$ the normalized velocity distribution along any axis is

$$f(v) = \sqrt{\frac{m}{2\pi k_B T_a}} e^{-mv^2/2k_B T_a}.$$

The population of the excited state due to a $\pi$ pulse, averaged over the Doppler broadening, is thus

$$P_r = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dz \frac{e^{-z^2}}{1 + (\Delta_0 - \beta z)^2/\Omega^2} \sin^2 \left(\frac{\pi}{2} \sqrt{1 + (\Delta_0 - \beta z)/\Omega^2}\right)$$

where $\beta = (k_1 + k_2) \sqrt{2k_B T_a/m} = \omega_D/(2\sqrt{\ln 2})$. The last equality shows $\omega_D = 1.67\beta$ where $\omega_D$ is the full width at half maximum of the absorption profile for a weak excitation beam.
For $^{87}$Rb with $\lambda_1 = 780$ nm, $\lambda_2 = 480$ nm, $T_a = 50$ $\mu$K gives $\beta/(2\pi) = 0.328 \times 10^6$ Hz, and $T_a = 500$ $\mu$K gives $\beta/(2\pi) = 1.04 \times 10^6$ Hz. Some numerical examples are given in Fig. 10.2. For $T_a = 500$ $\mu$K the excitation profile has a FWHM of 1.85 and 2.31 MHz for $\Omega/2\pi = 0.1$ and 1.0 MHz. Note that when the Rabi frequency is comparable to $\beta$ the presence of power broadening means that little reduction in line width will be observed by reducing the temperature.

In the context of coherent manipulation of atomic states the relevant figure of merit is the excitation probability for a $\pi$ pulse for zero detuning ($\Delta_0 = 0$). The excitation probability as a function of $\beta$ for several values of $\Omega$ is shown in Fig. 10.3. Although we need $\Omega \gg \beta$ for high excitation probability, the condition $\Omega \approx \beta$ is sufficient for $P_r \approx 0.7$.

### 10.1.3 Decohering spontaneous emission

The two-photon Rabi analysis was performed assuming $\delta \gg |\Omega_1|, |\Omega_2|$ so that the population of the intermediate level $|p\rangle$ could be assumed small. Within this approximation two-photon Rabi cycles between $|g\rangle$ and $|e\rangle$ can be driven with small errors of $O(|\Omega_1|^2/\delta, |\Omega_2|^2/\delta)$. As an example design parameters for a two-photon Rydberg gate involve $|\Omega_R|/2\pi \sim 1$ MHz, $|\Omega_{1,2}|/2\pi \sim 200$ MHz, and $\delta/2\pi \sim 36$ GHz, which gives intermediate state amplitudes of order $5 \times 10^{-3}$. Fractional Rabi cycle errors are of order $|\Omega_{1,2}|^2/\delta \Omega_R \sim 0.01$.

The main contribution to decoherence during a Rabi cycle is the possibility of a spontaneous emission from the intermediate state. The population of $|p\rangle$ is

$$
|c_p|^2 \simeq \left| \frac{\Omega_1}{\delta} \tilde{c}_g + \frac{\Omega_2}{\delta} \tilde{c}_e \right|^2 \\
= \frac{|\Omega_1|^2}{\delta^2} \left( |c_g|^2 + |c_e|^2 + e^{i(2\phi+\chi)} \tilde{c}_g^* \tilde{c}_e + e^{-i(2\phi+\chi)} \tilde{c}_g \tilde{c}_e^{*} \right)
$$

(10.9)

where we have defined the phase angles through $\Omega_1 = |\Omega_1|e^{i\phi}$, $\Omega_2 = \Omega_1 e^{i\chi}$. The expression in parentheses is $1 - O(|\Omega_1|^2/\delta^2)$ so to lowest order in $|\Omega_1/\delta|$ the probability of a sponta-
neous emission is \( p = |\Omega_1|^2 t_{\text{pulse}}/\delta^2 \tau = |\Omega_R|^2 t_{\text{pulse}}/\delta \tau \) where \( \tau \) is the radiative lifetime of the intermediate state and \( t_{\text{pulse}} \) is the pulse time.

### 10.2 Two-photon Raman transitions with selection rules

The results of the previous section can be readily generalized to the \( \Lambda \) type coupling scheme shown in Fig. 10.4. This is equivalent to Fig. 10.1 except that \(|p\rangle\) is now the highest energy state. We can therefore use Eqs. (10.2) rewritten as

\[
\begin{align*}
\dot{c}_g &= i \frac{\Omega_1^*}{2} c_p e^{i \Delta_1 t}, \\
\dot{c}_p &= i \frac{\Omega_1}{2} c_g e^{-i \Delta_1 t} + i \frac{\Omega_2}{2} c_e e^{-i \Delta_2 t}, \\
\dot{c}_e &= i \frac{\Omega_2^*}{2} c_p e^{i \Delta_2 t},
\end{align*}
\]

(10.10)

with the definitions \( \Delta_1 = \omega_1 - \omega_{pg}, \Delta_2 = \omega_2 - \omega_{pe} \) and the two-photon detuning \( \Delta = \omega_1 - \omega_2 - \omega_{eg} = \Delta_1 - \Delta_2 \). We assume that only field 1 couples to the \(|g\rangle \leftrightarrow |p\rangle\) transition and only field 2 couples to the \(|e\rangle \leftrightarrow |p\rangle\) transition. For example this would be the case if the lower level were \( J = 1 \) and the upper level \( J = 0 \), state \(|g\rangle = |1, M = -1\rangle\), state \(|e\rangle = |1, M = 1\rangle\), and fields 1,2 are \( \sigma_\pm \) polarized.

It is convenient to transform to new variables to remove the exponential factors in Eqs. (10.10). Defining \( \tilde{c}_g = \tilde{\tilde{c}}_g e^{i \delta_g t}, \tilde{c}_c = \tilde{\tilde{c}}_c e^{i \delta_c t}, \) and \( \tilde{c}_p = \tilde{\tilde{c}}_p e^{-i \delta_p t} \) gives the set

\[
\begin{align*}
\frac{d}{dt} \tilde{\tilde{c}}_g &= -i \delta_g \tilde{\tilde{c}}_g + i \frac{\Omega_1^*}{2} \tilde{\tilde{c}}_p e^{i (\Delta_1 - \delta_p - \delta_g) t}, \\
\frac{d}{dt} \tilde{\tilde{c}}_p &= i \delta_p \tilde{\tilde{c}}_p + i \frac{\Omega_1}{2} \tilde{\tilde{c}}_g e^{i (-\Delta_1 + \delta_g + \delta_p) t} + i \frac{\Omega_2}{2} \tilde{\tilde{c}}_e e^{i (-\Delta_2 + \delta_g + \delta_p) t}, \\
\frac{d}{dt} \tilde{\tilde{c}}_e &= -i \delta_c \tilde{\tilde{c}}_e + i \frac{\Omega_2^*}{2} \tilde{\tilde{c}}_p e^{i (\Delta_2 - \delta_p - \delta_c) t}.
\end{align*}
\]

(10.11)

Figure 10.4: Coupling scheme for two-photon Rabi oscillations in a \( \Lambda \) configuration.
We now choose \( \delta_p = \Delta_1 - \delta_g = \Delta_2 - \delta_e \) to remove the time varying exponentials from the equations for the state amplitudes. Taking into account that for large detunings the excited state population is small we can use the slaved solution

\[
\tilde{c}_p = \frac{\Omega_1}{2\delta_p} \tilde{c}_g + \frac{\Omega_2}{2\delta_p} \tilde{c}_e.
\]

Reinserting into Eqs. (10.11) we get

\[
\begin{align*}
\frac{d}{dt} \tilde{c}_g &= -i\delta_g \tilde{c}_g + i \frac{|\Omega_1|^2}{4\delta_p} \tilde{c}_g + i \frac{\Omega_1^* \Omega_2}{4\delta_p} \tilde{c}_e, \\
\frac{d}{dt} \tilde{c}_e &= -i\delta_e \tilde{c}_e + i \frac{|\Omega_2|^2}{4\delta_p} \tilde{c}_e + i \frac{\Omega_1 \Omega_2^*}{4\delta_p} \tilde{c}_g.
\end{align*}
\] (10.12a, 10.12b)

The parameters \( \delta_g, \delta_e \) are constrained by the requirement \( \delta_e - \delta_g = \Delta_2 - \Delta_1 \). It is convenient to introduce the two-photon detuning \( \Delta = \Delta_1 - \Delta_2 \) and put \( \delta_g = -\delta_e \) which gives \( \delta_e = -\Delta/2, \delta_g = \Delta/2, \) and \( \delta_p = (\Delta_1 + \Delta_2)/2 \). The effective two-level equations of motion are therefore

\[
\begin{align*}
\frac{d}{dt} \tilde{c}_g &= -i\frac{\Delta}{2} \tilde{c}_g + i \frac{|\Omega_1|^2}{2(\Delta_1 + \Delta_2)} \tilde{c}_g + i \frac{\Omega_1^* \Omega_2}{2(\Delta_1 + \Delta_2)} \tilde{c}_e, \\
\frac{d}{dt} \tilde{c}_e &= i\frac{\Delta}{2} \tilde{c}_e + i \frac{|\Omega_2|^2}{2(\Delta_1 + \Delta_2)} \tilde{c}_e + i \frac{\Omega_1 \Omega_2^*}{2(\Delta_1 + \Delta_2)} \tilde{c}_g.
\end{align*}
\] (10.13a, 10.13b)

We can rewrite these in a more compact form by defining \( \Delta'_1 = \Delta - |\Omega_1|^2/(\Delta_1 + \Delta_2), \Delta'_2 = \Delta + |\Omega_2|^2/(\Delta_1 + \Delta_2) \), and the effective Rabi frequency \( \Omega' = \Omega_1 \Omega_2^*/(\Delta_1 + \Delta_2) \) to get

\[
\begin{align*}
\frac{d}{dt} \tilde{c}_g &= -i\frac{\Delta'_1}{2} \tilde{c}_g + i \frac{\Omega'_R}{2} \tilde{c}_e, \\
\frac{d}{dt} \tilde{c}_e &= i\frac{\Delta'_2}{2} \tilde{c}_e + i \frac{\Omega'_R}{2} \tilde{c}_g.
\end{align*}
\] (10.14a, 10.14b)

These are the same equations as (10.4) with a flip in the sign of \( \Omega_R \). We can therefore immediately write down the solutions from Eqs. (10.5) as

\[
\begin{align*}
\tilde{c}_g(t) &= e^{i\frac{(\Delta_1 - \Delta'_2)}{2}} \left[ \cos \left( \frac{\Omega'_R t}{2} \right) - i \frac{\Delta_+}{\Omega'} \sin \left( \frac{\Omega'_R t}{2} \right) \right] c_{g0} + i \frac{\Omega'_R}{\Omega'} e^{-i\frac{(\Delta_1 + \Delta'_2)}{2}} \left[ \cos \left( \frac{\Omega'_R t}{2} \right) + i \frac{\Delta_+}{\Omega'} \sin \left( \frac{\Omega'_R t}{2} \right) \right] c_{e0}, \\
\tilde{c}_e(t) &= i \frac{\Omega'_R}{\Omega'} e^{-i\frac{(\Delta_1 + \Delta'_2)}{2}} \sin \left( \frac{\Omega'_R t}{2} \right) c_{g0} + e^{-i\frac{(\Delta_1 + \Delta'_2)}{2}} \left[ \cos \left( \frac{\Omega'_R t}{2} \right) + i \frac{\Delta_+}{\Omega'} \sin \left( \frac{\Omega'_R t}{2} \right) \right] c_{e0}
\end{align*}
\] (10.15a, 10.15b)

with \( \Omega' = \sqrt{|\Omega_R|^2 + \Delta_+^2} \) the effective off-resonance Rabi frequency and \( \Delta_+ = (\Delta'_1 \pm \Delta'_2)/2 \). Note that when the two-photon detuning (including ac Stark shifts) given by \( \Delta_+ \) is zero the magnitude of the effective Rabi frequency is \( |\Omega_R| = |\Omega_1||\Omega_2|/(\Delta_1 + \Delta_2) \). Neglecting the
Stark shifts two-photon resonance implies $\Delta = 0$ so that $\Delta_1 + \Delta_2 = 2\Delta_1$ and we get the oft quoted result $|\Omega_R| = |\Omega_1||\Omega_2|/2\Delta_1$.

This type of Raman transition has many uses. As an example suppose we wish to create superpositions of two different hyperfine ground states separated by a microwave frequency. These can be coupled directly by Rabi oscillations driven by a microwave field. However the coupling is slow since the transition is an M1 magnetic dipole transition, and the matrix element is small. Much faster coupling, with negligible spontaneous emission, can be achieved using two optical photons.

### 10.3 Dark state dynamics

Three level atomic dynamics lead to some remarkable effects. One of these is the existence of dark states that allow for transferring population between two levels, via a third level, without ever populating the third level. Referring again to Fig. 10.4 for the $\Lambda$ configuration, the case of two-photon resonance is $\Delta_1 = \Delta_2$. In this case Eqs. (10.11) reduce to

\[
\frac{d}{dt} \tilde{c}_g = i\frac{\Omega^*_1}{2} \tilde{c}_p, \quad (10.16a)
\]

\[
\frac{d}{dt} \tilde{c}_p = i\delta_p \tilde{c}_p + i\frac{\Omega_1}{2} \tilde{c}_g + i\frac{\Omega_2}{2} \tilde{c}_e, \quad (10.16b)
\]

\[
\frac{d}{dt} \tilde{c}_e = i\frac{\Omega^*_2}{2} \tilde{c}_p. \quad (10.16c)
\]

Here we have dropped the tildes on the amplitudes. Let’s write these in vector matrix form as $\frac{d}{dt} \mathbf{c} = M \mathbf{c}$ with

\[
\mathbf{c} = \begin{pmatrix} c_g(t) \\ c_p(t) \\ c_e(t) \end{pmatrix}, \quad M = i \begin{pmatrix} 0 & \Omega^*_1/2 & 0 \\ \Omega_1/2 & \delta_p & \Omega_2/2 \\ 0 & \Omega^*_2/2 & 0 \end{pmatrix}.
\]

The matrix $M$ has three eigenvalues and eigenvectors. One of them is a “dark state” eigenvector

\[
\mathbf{u}_1 = \begin{pmatrix} \frac{\Omega_2}{\sqrt{|\Omega_1|^2 + |\Omega_2|^2}} \\ 0 \\ \frac{\Omega_1}{\sqrt{|\Omega_1|^2 + |\Omega_2|^2}} \end{pmatrix} \quad (10.17)
\]

with eigenvalue $\lambda_1 = 0$. This is a stationary state that is completely decoupled from the light fields. If we prepare the atom in state $\mathbf{u}_1$ at time $t = 0$ it will stay there for all subsequent times.

Now suppose we start out with $|\Omega_1| \gg |\Omega_2|$ then $\mathbf{u}_{1,i} \simeq (0, 0, 1)$ which corresponds to all population in $|e\rangle$. If the fields are changed adiabatically to $|\Omega_1| \ll |\Omega_2|$ the eigenvector changes to $\mathbf{u}_{1,f} \simeq (-1, 0, 0)$ which corresponds to all population in $|g\rangle$. Provided that the change is adiabatic there will be no coupling to the other eigenvectors $\mathbf{u}_2, \mathbf{u}_3$. Since $\mathbf{u}_1$ has zero overlap with the optically excited state $|p\rangle$ there will never be any population in $|p\rangle$ and hence no spontaneous emission. Thus we can transfer population from $|e\rangle$ to $|g\rangle$ without
ever populating the intermediate state! This type of adiabatic transfer is often performed with a so-called counterintuitive pulse sequence where the popultaiton starts in $|e\rangle$ with $\Omega_2$ the large field followed by $\Omega_1$ being turned on when the population is mostly in $|g\rangle$. This is known as STIRAP for Stimulated Raman Adiabatic Passage\cite{29}.

The condition for this to be true is that the change is adiabatic. This will be so if the transfer frequency $\Omega = \pi/T$, with $T$ the $\pi$ pulse transfer time, is small compared to the gap to $\lambda_2$ or $\lambda_3$. The other eigenvalues are

$$\lambda_{2,3} = i\frac{\delta_p \pm \sqrt{\delta_p^2 + |\Omega_1|^2 + |\Omega_2|^2}}{2}.$$ 

When the excited state detuning $\delta_p = 0$ the adiabatic condition is

$$|\Omega| \ll \frac{\sqrt{|\Omega_1|^2 + |\Omega_2|^2}}{2}.$$ 

This says that the rate must be small compared to the root mean square of the one-photon Rabi frequencies.

In the limit of large excited state detuning the adiabatic condition is

$$|\Omega| \ll \frac{|\Omega_1|^2 + |\Omega_2|^2}{4|\delta_p|}.$$ 

This says that the rate must be small compared to the average ground state AC Stark shift. Note that if $\Omega_1 = \Omega_2$ the adiabatic condition becomes

$$|\Omega| \ll \frac{|\Omega_1|^2}{2|\delta_p|} = |\Omega_R|$$

with $\Omega_R$ the two-photon Raman rate. The conclusion is that while dark state transfer is possible, it must not be too fast. If the goal is to rapidly transfer population with no spontaneous emission from the intermediate state resonant or near-resonant STIRAP has the potential for being faster than a far detuned two-photon transition driven by both fields simultaneously.

Another attractive feature of STIRAP is that near perfect transfer of atomic population from initial to final states can be achieved despite variations in the pulse area. As long as the initial and final dark states $u_1$ correspond to all population in the initial and final atomic states, and the transition is performed adiabatically, very high fidelity population transfer can be achieved.
Chapter 11

Laser Cooling and Magnetic Trapping of Atoms

11.1 Energy and momentum conservation

Interaction of an atom with a photon must conserve energy and momentum. It is instructive to evaluate the consequences of energy and momentum conservation using a particle like picture of the interaction. Initially the atom is in the ground state with energy $U_{ai} = U_i + \frac{1}{2}mv_i^2$ and momentum $p_i = mv_i$. The photon has energy $U_{\nu} = h\omega$ and momentum $p_{\nu} = \hbar k$. After absorption there is no photon but the atom has $U_a = h\omega_a + \frac{1}{2}mv_a^2$ and $p_a = mv_a$ where $h\omega_a$ is the energy separation of the atomic levels, and $v_a$ is the atomic center of mass velocity. A photon is then spontaneously emitted in a random direction with energy $U_{sp} = h\omega_{sp}$ and momentum $p_{sp} = \hbar k_{sp}$. After spontaneous emission the atom is in a ground state and has energy $U_{af} = U_f + \frac{1}{2}mv_f^2$ and momentum $p_f = mv_f$. We allow for a change of atomic state with $U_i$ and $U_f$ possibly different.

Energy and momentum conservation between the initial and final states implies

\begin{align}
U_i + \frac{1}{2}mv_i^2 + h\omega &= U_f + \frac{1}{2}mv_f^2 + h\omega_{sp} \\
mv_i + \hbar k &= mv_f + \hbar k_{sp}.
\end{align}

(11.1)  \hspace{2cm} (11.2)

The parameters of the atomic motion after the interaction are

\begin{align}
\frac{1}{2}mv_f^2 &= (U_i - U_f) + \frac{1}{2}mv_i^2 + \hbar(\omega - \omega_{sp}) \\
mv_f &= mv_i + \hbar(k - k_{sp}).
\end{align}

(11.3)  \hspace{2cm} (11.4)

We will consider the implications of these relations for several different geometries. In the remainder of this section we exclude Raman transitions and use $U_f = U_i$.

11.1.1 One beam in 1D

In a one-dimensional geometry there are two possibilities. If the emitted photon propagates parallel to the incident photon the atomic kinetic energy is unchanged. When the emitted
Table 11.1: Light scattering parameters for several atoms.

<table>
<thead>
<tr>
<th>parameter</th>
<th>units</th>
<th>$^{87}\text{Rb}$</th>
<th>$^{133}\text{Cs}$</th>
<th>$^{165}\text{Ho}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{cooling}$</td>
<td>(µm)</td>
<td>0.7802</td>
<td>0.8523</td>
<td>0.4105</td>
</tr>
<tr>
<td>$\gamma/2\pi$</td>
<td>(MHz)</td>
<td>6.07</td>
<td>5.23</td>
<td>32.5</td>
</tr>
<tr>
<td>$r_{s,max} = \gamma/2$</td>
<td>(10^6 s^{-1})</td>
<td>19.1</td>
<td>16.4</td>
<td>100.2</td>
</tr>
<tr>
<td>$t_{\min}$ (for $N_s = 100$)</td>
<td>(µs)</td>
<td>5.2</td>
<td>6.1</td>
<td>0.98</td>
</tr>
<tr>
<td>$T_r = 2U_r/k_B$</td>
<td>(µK)</td>
<td>0.3620</td>
<td>0.1983</td>
<td>0.6831</td>
</tr>
</tbody>
</table>

photon propagates antiparallel to the incident photon we have $mv_f = mv_i + \hbar(k + k_{sp})$ or

$$v_f = v_i + \frac{\hbar(k + k_{sp})}{m}. \quad (11.5)$$

We can write $k + k_{sp} = 2k - (k - k_{sp}) = 2k[1 - (k - k_{sp})/2k]$ and use $|k - k_{sp}|/k \approx \gamma/\omega$ which is negligible. Thus for a one-dimensional scattering process

$$v_f \approx v_i + 2v_r \quad (11.6)$$

where the recoil velocity is $v_r = \hbar k/m$. The factor of 2 comes from a kick of $v_r$ for both absorption and emission in the opposite direction.

The momentum changing events happen half the time so on average the momentum changes by $\hbar k$ for each scattering event, and $d\bar{p}/dt = \hbar kr_s$ with $r_s$ the scattering rate. Assuming an atom initially at rest we find $\bar{p} = \hbar kr_st$ and

$$\bar{K} = \frac{\bar{p}^2}{2m} = U_r(r_st)^2 = U_rN_s^2.$$ 

with $U_r = (\hbar k)^2/(2m)$ the recoil energy and $N_s = r_st$ the number of scattering events. The quantity $\bar{K}$ is the average kinetic energy acquired by an atom. It increases proportional to the square of the number of scattering events $N_s^2$.

If we take the average over many atoms we would expect to observe $\bar{K}$ of kinetic energy per atom. There are also fluctuations in the kinetic energy associated with the stochastic nature of the emission process. For each scattered photon $\delta p = \delta p_+ = 0$ or $\delta p = \delta p_- = 2\hbar k$ with equal probability. In a random walk with steps $\delta p$ we have $\langle \delta p_N^2 \rangle = N\langle \delta p^2 \rangle$ where $N$ is the number of events. Since there are two types of events

$$\langle \delta p_N^2 \rangle = N_+\delta p_+^2 + N_-\delta p_-^2 = \frac{N_s}{2}[0 + (2\hbar k)^2] = 2(\hbar k)^2N_s. \quad (11.7)$$

The variance of the momentum after one scattering event is

$$\text{Var}(\delta p) = \langle (\delta p - \langle \delta p \rangle)^2 \rangle = \langle (\delta p)^2 \rangle - \langle \delta p \rangle^2 = 2(\hbar k)^2 - (\hbar k)^2 = (\hbar k)^2.$$ 

After $N$ scattering events $\text{Var}(\delta p_N) = N(\hbar k)^2$. We can define a temperature in terms of the momentum variance by

$$T = \frac{\text{Var}(\delta p_N)}{2m(k_B/2)} = \frac{N_s(\hbar k)^2}{mk_B} = \frac{2U_r}{k_Br_st}.$$
The temperature increases proportional to the interaction time, whereas the mean kinetic energy increases as the square of the time.

For reference some characteristic scattering parameters for different atoms are given in Table 11.1.

11.1.2 One beam in 3D

The preceding example is not realistic since a real atom emits photons into 3D. The momentum transfer on absorption is directed along the beam axis \( e_z \): \( \delta p_a = \hbar k e_z \). The momentum transfer on emission in the direction specified by polar angles \( \theta, \phi \) is \( \delta p_p = -\hbar k e(\theta, \phi) \) with 
\[
e(\theta, \phi) = \cos \theta e_z + \sin \theta \cos \phi e_x + \sin \theta \sin \phi e_y.
\]
The momentum change in one absorption - emission cycle is thus
\[
\delta p = [(1 - \cos \theta) e_z - \sin \theta \cos \phi e_x - \sin \theta \sin \phi e_y] \hbar k.
\]

The average momentum change per cycle is 
\[
\bar{\delta p} = \frac{1}{4\pi} \int d\Omega \, \delta p = \hbar k e_z.
\]
The average of the square of the momentum change per cycle is
\[
\langle (\delta p)^2 \rangle = \frac{1}{4\pi} \int d\Omega \, (\delta p)^2 = \frac{4}{3} (\hbar k)^2.
\]

The sum of the components is \( 2(\hbar k)^2 \) which is the same as in the 1D emission model.

The transverse kinetic energy after \( N = r_s t \) cycles is
\[
K_x = K_y = \frac{1}{3} U_r r_s t
\]
so the transverse temperature is
\[
T_x = T_y = K_x/(k_B/2) = \frac{2U_r}{3k_B} N_s.
\]

The axial kinetic energy is on average
\[
\bar{K}_z = U_r (r_s t)^2.
\]
For each cycle \( \delta p_z = \hbar k \) and \( \langle (\delta p_z)^2 \rangle = (4/3)(\hbar k)^2 \). Thus for each cycle
\[
\langle (\delta p_z^2) \rangle = \langle (\delta p_z)^2 \rangle - (\bar{\delta p}_z)^2 = \left( \frac{4}{3} - 1 \right) (\hbar k)^2 = \frac{1}{3} (\hbar k)^2.
\]
The momentum variance after \( N \) cycles is \( N \times \frac{1}{3}(\hbar k)^2 \) and the axial temperature is
\[
T_z = \frac{2U_r}{3k_B} N_s,
\]
which is the same as the transverse temperature. We see that in the 3D model the total fluctuations summed over Cartesian axes are the same as in the 1D emission model.

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11.2 Light forces

The concept of force is classical. In quantum mechanics we can define a quantity whose expectation value corresponds to force in the classical limit. By analogy with Newton’s definition $F = \frac{d\mathbf{p}}{dt}$ we define a quantum mechanical force operator as

$$\hat{F} = \frac{d\hat{\mathbf{p}}}{dt}.$$ 

Using Ehrenfest’s theorem the expectation value of the force is

$$\langle \hat{F} \rangle = -\frac{i}{\hbar} \langle [\hat{p}, \hat{H}] \rangle = -\langle \nabla_r \hat{H} \rangle,$$

where $r$ is the center of mass atomic coordinate.

We consider a two-level atom with states $|g\rangle, |e\rangle$, and transition frequency $\hbar \omega_a = U_e - U_g$ which interacts with a scalar optical field $E = \frac{\mathbf{E}(r,t)}{2} e^{-i\omega t} + c.c.$ We assume a dipole interaction Hamiltonian $\hat{H}_1 = -E \hat{d} \hat{d}$. The total Hamiltonian can be written as $\hat{H} = \hat{H}_0 + \hat{H}_a + \hat{H}_1$ where

$$\begin{align*}
\hat{H}_0 &= \frac{\hat{p}^2}{2m} \\
\hat{H}_a &= U_g |g\rangle\langle g| + U_e |e\rangle\langle e| = \frac{U_g + U_e}{2} \hat{I} + \frac{U_e - U_g}{2} (|e\rangle\langle e| - |g\rangle\langle g|) \\
\hat{H}_1 &= -E \hat{d} \hat{d}.
\end{align*}$$

It is convenient to introduce the following operators

$$\begin{align*}
\hat{s}_+ &= |e\rangle\langle g| \\
\hat{s}_- &= \hat{s}_+^\dagger = |g\rangle\langle e| \\
\hat{s}_z &= |e\rangle\langle e| - |g\rangle\langle g|.
\end{align*}$$

The matrix representation of these operators in the basis $\{|g\rangle, |e\rangle\}$ is

$$\begin{align*}
\hat{s}_+ &= \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, & \hat{s}_- &= \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, & \hat{s}_z &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}
\end{align*}$$

We assume states of definite parity so the matrix elements of $\hat{d}$ are $\langle g|\hat{d}|g\rangle = \langle e|\hat{d}|e\rangle = 0$ and $\langle e|\hat{d}|g\rangle = \langle g|\hat{d}|e\rangle^* = d_0$. We can therefore write the dipole operator as $\hat{d} = d_0 \hat{s}_+ + d_0^* \hat{s}_-$. Using the $\hat{s}$ operators we can write the Hamiltonian as

$$\begin{align*}
\hat{H} &= \hat{H}_0 + \frac{\hbar \omega_a}{2} \hat{s}_z - \left( \frac{\mathbf{E}(r,t)}{2} e^{-i\omega t} + \frac{\mathbf{E}^*(r,t)}{2} e^{i\omega t} \right) (d_0 \hat{s}_+ + d_0^* \hat{s}_-) \\
&= \hat{H}_0 + \frac{\hbar \omega_a}{2} \hat{s}_z - \left( \frac{\mathbf{E}(r,t)d_0}{2} e^{-i\omega t} \hat{s}_+ + \frac{\mathbf{E}^*(r,t)d_0^*}{2} e^{i\omega t} \hat{s}_- \right) \\
&\quad - \left( \frac{\mathbf{E}(r,t)d_0^*}{2} e^{-i\omega t} \hat{s}_- + \frac{\mathbf{E}(r,t)^*d_0}{2} e^{i\omega t} \hat{s}_+ \right).
\end{align*}$$

We have dropped the constant term $\frac{U_g + U_e}{2} \hat{I}$ since it has no influence on the dynamics.
The state vector can be written as
\[ |\psi\rangle = |\phi(r)\rangle \left( c_g(t)e^{-i\omega_g t}|g\rangle + c_e(t)e^{-i\omega_e t}|e\rangle \right). \]

Here we assume the center of mass state described by $|\phi(r)\rangle$ is the same for both internal energy levels. This is only an assumption, and will not be true when there are correlations or entanglement between the internal and external degrees of freedom.

The expectation value of the Hamiltonian is
\[ \langle \psi | \hat{\mathcal{H}} | \psi \rangle = \langle \psi | \hat{\mathcal{H}}_0 | \psi \rangle + \frac{\hbar \omega_0}{2} (|c_e|^2 - |c_g|^2) \]
\[ - \frac{\mathcal{E}(r,t)}{2} d_0 e^{-i\omega t} c_g c_e^* e^{i\omega t} - \frac{\mathcal{E}^*(r,t)}{2} d_0^* e^{i\omega t} c_g^* c_e e^{-i\omega t} \]
\[ - \frac{\mathcal{E}^*(r,t)}{2} d_0 e^{-i\omega t} c_g^* c_e e^{i\omega t} - \frac{\mathcal{E}(r,t)}{2} d_0^* e^{i\omega t} c_g c_e e^{-i\omega t}. \]

The last two terms correspond to exciting the atom while emitting a photon or deexciting the atom while absorbing a photon. These counterrotating terms are rapidly oscillating compared to the near resonant terms and can be neglected when the light is near resonant with the atomic transition frequency. This is the rotating wave approximation in which case the Hamiltonian can be written as
\[ \hat{\mathcal{H}}^{(rwa)} = \hat{\mathcal{H}}_0 + \frac{\hbar \omega_0}{2} \hat{s}_z - \frac{\hbar}{2} \left( \Omega(r,t)e^{-i\omega t} \hat{s}_+ + \Omega^*(r,t)e^{i\omega t} \hat{s}_- \right) \]
where $\Omega(r,t) = \mathcal{E}(r,t)d_0/\hbar$ is the Rabi frequency.

We can now evaluate the force operator as
\[ \hat{F} = -\nabla_r \hat{\mathcal{H}} \]
\[ = \frac{\hbar}{2} \left( \nabla_r \Omega(r,t)e^{-i\omega t} \hat{s}_+ + \nabla_r \Omega^*(r,t)e^{i\omega t} \hat{s}_- \right). \] (11.9)

The expected value of the force is
\[ \langle \hat{F} \rangle = \frac{\hbar}{2} \left( \langle \psi | \nabla_r \Omega(r,t) \hat{s}_+ | \psi \rangle e^{-i\omega t} + \langle \psi | \nabla_r \Omega^*(r,t) \hat{s}_- | \psi \rangle e^{i\omega t} \right). \]

We now invoke a semiclassical description of the center of mass motion and assume the atomic wavefunction $|\phi(r,t)\rangle$ has an extent that is small compared to the wavelength of the light. We assume that $|\phi(r,t)\rangle$ describes the time dependent atomic position and approximate the matrix elements appearing in the expression for the force as e.g.
\[ \langle \psi | \nabla_r \Omega(r,t) \hat{s}_+ | \psi \rangle \approx \nabla_r \Omega(r,t) \langle \psi | \hat{s}_+ | \psi \rangle. \]

The position $r$ in the above equation is assumed to be the time dependent position of the atomic center of mass. With this approximation
\[ \langle \hat{F} \rangle = \frac{\hbar}{2} \left( \nabla_r \Omega(r,t) \langle \psi | \hat{s}_+ | \psi \rangle e^{-i\omega t} + \nabla_r \Omega^*(r,t) \langle \psi | \hat{s}_- | \psi \rangle e^{i\omega t} \right). \] (11.10)

Equation (11.10) provides an accurate description of optically induced forces on atoms. To evaluate it we need to specify the space and time dependence of the optical field and then
solve the atomic dynamics to find the expectation values of the atomic raising and lowering operators \( \hat{s}_+, \hat{s}_- \).

The stationary solutions for the atomic variables are from (9.31)

\[
\begin{align*}
  w &= w^{(0)} \frac{1 + 4\Delta^2/\gamma^2}{1 + 4\Delta^2/\gamma^2 + I/I_s} \\
  \tilde{\rho}_{eg} &= -i w \frac{\Omega}{\gamma} \frac{1 - i2\Delta/\gamma}{1 + 4\Delta^2/\gamma^2}.
\end{align*}
\]

Here we have assumed a two-level atom subject to radiative decay so \( \gamma = 1/T_1 = 2/T_2 \) and combined the expressions \( \gamma = \omega_0^2/\gamma \), \( I_s = \hbar\omega_0^2/4\pi\epsilon_0 c \), \( \Omega = d\mathcal{E}/\hbar \), and \( I = \epsilon_0|\mathcal{E}|^2/2 \) to obtain the useful relation

\[
\Omega = \gamma \left( \frac{I}{2I_s} \right)^{1/2}.
\]

This shows that at unit saturation, \( I = I_s \), the Rabi frequency is \( \Omega = \gamma/\sqrt{2} \).

### 11.3 Radiation pressure and dipole force

The solution for \( \tilde{\rho}_{eg} \) given by Eqs. (11.11) can be combined with the force expression Eq. (11.10) to determine the dependence of the optical force on intensity and detuning. The expectation values of the atomic raising and lowering operators evaluate to

\[
\begin{align*}
  \langle \hat{s}_+ \rangle &= \text{Tr}[\hat{\rho}\hat{s}_+] = \rho_{ge} \\
  \langle \hat{s}_- \rangle &= \text{Tr}[\hat{\rho}\hat{s}_-] = \rho_{eg}.
\end{align*}
\]

We find for the force

\[
F = \left\langle \hat{F} \rightangle = -\frac{\hbar}{\gamma^2} \frac{\left( \Delta - i\gamma/2 \right) \Omega \nabla \Omega^* + \left( \Delta + i\gamma/2 \right) \Omega^* \nabla \Omega}{1 + 4\Delta^2/\gamma^2 + I/I_s}.
\]

The detuning appearing in the expression for the force should now be modified to account for the Doppler shift seen by a moving atom. Thus we use \( \Delta = \Delta_0 - \mathbf{k} \cdot \mathbf{v} \) where \( \Delta_0 = \omega - \omega_a \) is the detuning for a stationary atom, and \( \mathbf{v} \) is the atomic velocity.

The force can be separated into two parts as

\[
F = -\frac{\hbar\Delta}{2} \frac{\nabla I/I_s}{1 + 4\Delta^2/\gamma^2 + I/I_s} + i \frac{\epsilon_0 c \hbar \gamma}{2I_s} \frac{\mathcal{E} \nabla \mathcal{E}^* - \mathcal{E}^* \nabla \mathcal{E}}{4 \left( 1 + 4\Delta^2/\gamma^2 + I/I_s \right)} \]

where we have reintroduced the field amplitude using \( \Omega = \sqrt{\epsilon_0 c/I_s(\gamma/2)|\mathcal{E}|} \).

The first part of \( F \) is a conservative force, referred to as the gradient or dipole force \( F_d \). It arises from absorption and stimulated emission processes that result in coherent exchange of momentum between the atom and the field. Integrating the dipole force we see that it can be written as \( F_d = -\nabla U \) where \( U \) is the pseudo potential

\[
U = \frac{\hbar\Delta}{2} \ln \left( 1 + \frac{I}{I_s} \frac{\gamma}{1 + 4\Delta^2/\gamma^2} \right).
\]
The second part of $\mathbf{F}$ is referred to as the light pressure or radiation force, $\mathbf{F}_r$. It is due to absorption and spontaneous emission which in the simplest case of a propagating optical wave leads to heating of the atomic motion due to the random direction of the spontaneously emitted photon. The radiation force is directed along the gradient of the optical phase. To see this put $\mathbf{E} = |\mathbf{E}| e^{i\phi}$ and use $\mathbf{E} \nabla \mathbf{E}^* - \mathbf{E}^* \nabla \mathbf{E} = -2i|\mathbf{E}|^2 \nabla \phi$ to get

$$\mathbf{F}_r = \frac{\hbar \gamma}{2 \left( 1 + \frac{4\Delta^2}{\gamma^2} + \frac{I_s}{I_s} \right)} \nabla \phi. \quad (11.13)$$

**Several plane waves**

For future reference let's calculate the forces for a field consisting of the sum of several plane waves

$$\mathbf{E} = \sum_j \mathbf{E}_j e^{i(k_j \cdot r - \omega_j t)}.$$  

In the ideal plane wave limit the amplitudes $\mathbf{E}_j$ are strictly constant. The total intensity is

$$I = \frac{\varepsilon_0 c}{2} |\mathbf{E}|^2 = \frac{\varepsilon_0 c}{2} \left\{ \sum_j |\mathbf{E}_j|^2 + \sum_{j,k \neq j} \mathbf{E}_j^* \mathbf{E}_k e^{i[(k_j - k_k) \cdot r - (\omega_j - \omega_k) t]} \right\} = \sum_j I_j + \frac{\varepsilon_0 c}{2} \sum_{j,k \neq j} \mathbf{E}_j^* \mathbf{E}_k e^{i[(k_j - k_k) \cdot r - (\omega_j - \omega_k) t]} \quad (11.14)$$

Note that the above definition implies $I = \sum_j I_j$ because of interference terms. When the $\omega_j$ are all different and we average over a sufficiently long time for which the beats average out then $\mathbf{F} = \sum_j I_j$. Using Eq. (11.12) the dipole force is

$$\mathbf{F}_d = -i \frac{\hbar \Delta}{2} \left\{ \sum_j \frac{1}{I_s} \sum_{j,k \neq j} \mathbf{E}_j^* \mathbf{E}_k e^{i(\mathbf{q}_{jk} \cdot r - \delta_{jk} t)} \mathbf{q}_{jk} \right\} \quad (11.15)$$

where we have introduced the difference wavenumbers $\mathbf{q}_{jk} = k_j - k_k$ and frequencies $\delta_{jk} = \omega_j - \omega_k$. Using Eq. (11.13) we find for the radiation force

$$\mathbf{F}_r = \frac{\hbar \gamma}{2} \left\{ \sum_j \frac{1}{I_s} \sum_{j,k \neq j} \mathbf{E}_j^* \mathbf{E}_k e^{i(\mathbf{q}_{jk} \cdot r - \delta_{jk} t)} (k_j + k_k) \right\}. \quad (11.16)$$

This formula reduces to that given by Grynberg and Robilliard[30] for low intensities.

### 11.4 Slowing atoms

The classical equations for atom slowing in one dimension are simply

$$m \frac{dv}{dt} = \mathbf{F}. \quad (11.17)$$
The atomic velocity satisfies \( \frac{dv}{dt} = \frac{dv}{dx} \frac{dx}{dt} = v \frac{dv}{dx} \), so
\[
\frac{dv}{dx} = \frac{F}{mv}. \tag{11.17}
\]

Consider an atom moving along \( e_x \) with initial velocity \( v_0 \). The force from a slowing beam propagating along \(-e_x\) is
\[
F = -\frac{\hbar k\gamma s}{2} \frac{1}{1 + 4 \frac{(\Delta_0 + kv)^2}{\gamma^2} + s}.
\]

Here \( s = I/I_{\text{sat}} \) is the saturation parameter, \( \Delta_0 \) is the laser detuning, and \( k = 2\pi/\lambda \). Integrating (11.17) gives
\[
-\frac{\hbar k\gamma s}{2m} x = \int_{v_0}^{v(x)} dv' \left[ 1 + 4 \frac{(\Delta_0 + kv')^2}{\gamma^2} + s \right]
\]
\[
= \frac{k^2}{\gamma^2} \left[ v^4(x) - v_0^4 \right] + \frac{8k\Delta_0}{3\gamma^2} \left[ v^3(x) - v_0^3 \right]
\]
\[
+ \frac{1}{2} \left[ 1 + s + 4\Delta_0^2/\gamma^2 \right] \left[ v^2(x) - v_0^2 \right]. \tag{11.18}
\]

This is a quartic equation for \( v(x) \) which can be solved for the velocity profile. It is useful to know the value of \( x \) at which the atom is brought to rest. Putting \( v(x) = 0 \) we find
\[
x_{\text{stop}} = \frac{mv_0^2}{3\hbar k\gamma^3 s} \left[ 6k^2 v_0^2 + 3\gamma^2(1 + s) + 16kv_0\Delta_0 + 12\Delta_0^2 \right].
\]

In order to stop the atoms in the shortest possible distance we should choose \( \Delta_0 = -\frac{2}{3}kv_0 \) which gives
\[
x_{\text{stop, min}} = \frac{mv_0^2}{9\hbar k\gamma^3 s} \left[ 2k^2 v_0^2 + 9(1 + s)\gamma^2 \right].
\]

Putting in numbers for Cs atoms on the D2 transition \((6s_{1/2} - 6p_{3/2} \, \lambda = 852 \, \text{nm with} \, \gamma = 2\pi \times 5.23 \times 10^6 \, \text{s}^{-1})\) we find with \( s = 1 \) and \( v_0 = 100 \, \text{m/s} \)
\[
x_{\text{stop, min}} = 9.8 \, \text{m}.
\]

This is much larger than the typical size of a laser beam in a MOT. Thus only atoms in the low velocity tail of the thermal distribution can be stopped. Putting \( x_{\text{stop}} = 0.01 \, \text{m} \) we find
\[
v_0 = 15.6 \, \text{m/s}.
\]

The Maxwell-Boltzmann distribution for the magnitude \( v \) of the velocity is
\[
f(v) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}. \tag{11.19}
\]

This is normalized so that \( \int_0^\infty dv \, 4\pi v^2 f(v) = 1 \). Using Cs numbers we find that at \( T = 300 \, \text{K} \) the velocity \( v_0 = 15.6 \, \text{m/s} \) contains about \( 4 \times 10^{-4} \) of the atoms. Thus a MOT with cm sized beams is only capturing a very small fraction of the available atoms.

Rapid stopping is possible due to the very large acceleration induced by light. The maximum acceleration is \( a_{\text{max}} = \frac{1}{2m} \hbar k = 57900 \, \text{m/s}^2 \). This is approximately 5900 times larger than the gravitational acceleration.
11.5 Optical Molasses

Atoms can be not just slowed but their velocity fluctuations cooled using optical molasses. Consider two counterpropagating beams, both red detuned from the atomic transition by an amount $\Delta$. The average force on an atom is then the difference of the forces from the two beams. Using expressions from the previous section it is straightforward to show that for small velocities the force on an atom is $F = -\beta v$ with the damping constant

$$\beta = 8\hbar k^2 \frac{(-\Delta/\gamma)}{(1 + 4\Delta^2/\gamma^2)^2 I_s}.$$ 

Since $\Delta < 0$ for molasses the coefficient $\beta$ is positive. The time rate of change of the momentum is

$$\frac{dp}{dt} = F = -\frac{\beta}{m} p$$

with the solution

$$p(t) = p(0)e^{-t/\tau_m}$$

where the molasses time constant is $\tau_m = m/\beta$. The kinetic energy is therefore damped according to

$$\frac{1}{2m}p^2(t) = \frac{1}{2m}p^2(0)e^{-2t/\tau_m}.$$ 

This energy damping rate is balanced by the heating rate from spontaneous emission in random directions. At a finite temperature the cooling and heating rates balance leading to equilibrium. As was shown in the slides in class the minimum equilibrium temperature which is called the Doppler temperature is reached for a detuning $\Delta = -\gamma/2$ giving

$$k_B T_D = \frac{\hbar \gamma}{2}.$$ 

This corresponds to about 126 $\mu$K for Cs.

11.6 Loading a MOT

Consider a vapor at room temperature containing atoms of density $n_a$, plus background atoms of density $n_b$. A MOT is loaded from the vapor and contains $N$ atoms. The rate equation describing the loading process is

$$\frac{dN(t)}{dt} = R - \Gamma N(t) - \beta N^2(t).$$ \hspace{1cm} (11.20)

Here $N(t)$ is the number of trapped atoms, $R$ is the rate at which atoms are loaded from the background vapor, $\Gamma = \Gamma_c + \Gamma_{op}$ is the total linear loss rate due to background collisions with a rate constant $\Gamma_c$ and optical pumping processes to untrapped atomic states with rate constant $\Gamma_{op}$. The constant $\beta$ accounts for losses due to collisions between trapped atoms.

The steady state number of atoms in the MOT is

$$N_0 = \frac{\Gamma}{2\beta} \left( -1 + \sqrt{1 + \frac{4R\beta}{\Gamma^2}} \right) = \frac{R}{\Gamma} - \beta \frac{R^2}{\Gamma^3}.$$
We see that when two-body losses can be neglected the steady state number of atoms is given by \( R/\Gamma \), the ratio of the loading rate to loss rate. Solving (11.20) we get the loading curve

\[
N(t) = \frac{R}{\Gamma} \frac{\Gamma - \Gamma \cosh[(\Gamma + 2\beta N_0)t] + (\Gamma + 2\beta N_0) \sinh[(\Gamma + 2\beta N_0)t]}{\Gamma^2 + 2\beta R + 2\Gamma \beta \cosh[(\Gamma + 2\beta N_0)t]}. 
\]

For small \( \beta \) this simplifies to

\[
N(t) \approx \frac{R}{\Gamma} \left( 1 - e^{-\Gamma t} \right).
\]

At short times the number of atoms grows linearly as \( N(t) \approx Rt \). When two body losses can be neglected, which is the case for low density, or small atom number MOTs, measurement of the steady state atom number and the loading time constant are sufficient to determine \( \Gamma \) and \( R \).

The decay dynamics starting from \( N_0 \) but with the loading turned off are found from solving \( \frac{dN(t)}{dt} = -\Gamma N(t) - \beta N^2(t) \) which gives the loss curve

\[
N(t) = N_0 e^{\Gamma t} \left( 1 + \frac{\beta N_0}{\Gamma} \right) - \frac{\beta N_0}{\Gamma}.
\]

If \( \beta N_0 \ll \Gamma \) we get simple exponential decay \( N \sim e^{-\Gamma t} \). When this is not the case the initial decay is more rapid than the long time behavior as can be seen in Fig. 11.1.

To directly measure a loss curve the most obvious approach is to turn off the quadrupole magnetic field, and then measure the number of atoms remaining at later times. However, this procedure would lead to loss even if \( \Gamma \) and \( \beta \) were zero since finite temperature atoms will spatially diffuse out of the 3D optical molasses [31]. If the magnetic gradient field is strong enough atoms in low field seeking Zeeman states can be magnetically trapped so that the loss rate due to background and two-body collisions can be measured.

If we extract the loss rate \( \Gamma \) from a loss curve measurement the ratio \( R/\Gamma \) can extracted from a loading curve measurement, and \( R \) can then be determined. It is also possible to
measure \( R \) directly by varying the ratio of \( n \) and \( n_b \). Say we load a MOT with \( N \) atoms. In the absence of two-body losses the rate equation (11.20) can be expanded to

\[
\frac{dN(t)}{dt} = R' n_a \sigma_a \bar{v}_a - N(t) \left( n_a \sigma_a \bar{v}_a + n_b \sigma_b \bar{v}_b \right).
\]

We have introduced cross sections \( \sigma_{a,b} \), average thermal velocities \( \bar{v}_{a,b} \), and loading rate constant \( R' \) for the atoms being trapped. Note the rate constant \( R' \) is a dimensionless number that only depends on the optical, magnetic, and geometrical parameters of the MOT.

Defining the collisional rates for trapped and background atoms as \( r_a = n_a \sigma_a \bar{v}_a \), \( r_b = n_b \sigma_b \bar{v}_b \) we have

\[
\frac{dN(t)}{dt} = R' r_a - N(t) (r_a + r_b).
\]

The solution is

\[
N(t) = N_{eq} \left( 1 - e^{-t/\tau} \right)
\]

where \( N_{eq} = R' / (1 + r_b / r_a) \) and \( \tau = 1 / (r_a + r_b) \).

If we measure \( N_{eq} \) and \( \tau \) for different values of \( n_a \) and assume \( n_b \) is constant we can fit the data to extract the three unknown parameters: \( R', r_a, \) and \( r_b \). Alternatively we can keep \( n_a \) constant and vary \( n_b \) by changing vacuum conditions. While it is difficult to control these parameters careful measurements have shown that MOT loading data can be used to measure vacuum conditions with good accuracy[32].

It is also possible using photon scattering measurements to determine \( s_a = \alpha n_a \) where \( \alpha \) is a calibration factor that is not known accurately, but is assumed to be constant as we vary \( n_a \). We can therefore write

\[
N_{eq} = \frac{R'}{1 + \frac{r_b}{r_a s_a}} \quad (11.21)
\]

\[
\tau = \frac{1}{r_b + r'_a s_a} \quad (11.22)
\]

where \( r'_a = \sigma_a \bar{v}_a / \alpha \). So that measuring \( N_{eq} \) and \( \tau \) for different values of \( s_a \) we can extract the three unknown parameters: \( R', r_b, \) and \( r'_a \). We then have \( r_a = r'_a s_a \).

### 11.7 Trapping forces

Many different beam configurations can be used to create a MOT. The standard and most widely used is the 6 beam \( \sigma_+ - \sigma_- \) configuration with each \( \sigma_+ - \sigma_- \) beam pair counterpropagating along orthogonal axes. However smaller numbers of beams can be used. Four beam MOTs in a tetrahedral configuration have been demonstrated and two beam MOTs using tightly focused beams to give transverse trapping have been shown. We will first derive a general expression for the MOT force and then use it to check the stability of some different configurations.

The radiation pressure force on a stationary atom from a single beam propagating along \( \hat{k} \) is from (11.13)

\[
F = \frac{\hbar k \gamma}{2} \frac{L}{1 + \frac{4 \Delta^2}{\gamma^2} + \frac{L}{\tau} \hat{k}}.
\]
Generalizing to a $J_g = 0 \rightarrow J_e = 1$ transition in the presence of a magnetic field $\mathbf{B}(\mathbf{r})$ the force is

$$F = \frac{\hbar k \gamma}{2} \sum_{q=-1,0,1} \frac{I_q}{T_q} \hat{k}$$

where $\delta_q = \frac{q \mu_B g_e B}{\hbar}$ with $\mu_B$ the Bohr magneton, $g_e$ the excited state Landé factor, and the quantization axis chosen parallel with $\mathbf{B}(\mathbf{r})$ the magnetic field at position $\mathbf{r}$. The intensity of spherical component $q$ is $I_q = |\mathbf{e}^* \cdot \mathbf{e}_{Bq}|^2$, $\mathbf{e}$ is the polarization state of the light, and $\mathbf{e}_{Bq}$ is the basis vector of spherical component $q$ relative to the local quantization axis. The total intensity is $I = \sum_q I_q$.

If there are $N$ beams the total force is

$$F = \frac{\hbar k \gamma}{2} \sum_{j=1}^{N} \sum_{q=-1,0,1} \frac{I_{jq}}{T_q} \hat{k}_j$$

with $I_{jq} = I_j |\mathbf{e}_j^* \cdot \mathbf{e}_{Bq}|^2$ and $I = \sum_j I_j = \sum_j \sum_q I_{jq}$. This expression neglects interference between different beams and is only expected to be accurate for intensities small compared to the saturation intensity.

Evaluation of the force expression requires specifying the vectors $\hat{k}_j$, $\mathbf{e}_j$, $\mathbf{e}_B$. Using spherical polar coordinates we parameterize $\hat{k}_j$ with the polar and azimuthal angles $(\theta_j, \phi_j)$. The spherical components of the light can be taken to be

$$\begin{align*}
\mathbf{e}_{j0} &= \hat{k}_j = (\theta_j, \phi_j) \\
\mathbf{e}_{ja} &= (\theta_j + \pi/2, \phi_j) \\
\mathbf{e}_{jb} &= \mathbf{e}_{j0} \times \mathbf{e}_{ja} \\
\mathbf{e}_{j1} &= -\frac{1}{\sqrt{2}}(\mathbf{e}_{ja} + i\mathbf{e}_{jb}) \\
\mathbf{e}_{j,-1} &= \frac{1}{\sqrt{2}}(\mathbf{e}_{ja} - i\mathbf{e}_{jb})
\end{align*}$$

These choices guarantee $\mathbf{e}_{jq}^* \cdot \mathbf{e}_{jp} = \delta_{qp}$ and $\mathbf{e}_{j1} \times \mathbf{e}_{j,-1} = \mathbf{e}_{j0}$. The spherical components of the basis defined by the local magnetic field direction are similarly

$$\begin{align*}
\mathbf{e}_{B,0} &= \frac{\mathbf{B}}{B} = (\theta_B, \phi_B) \\
\mathbf{e}_{B,a} &= (\theta_B + \pi/2, \phi_B) \\
\mathbf{e}_{B,b} &= \mathbf{e}_{B,0} \times \mathbf{e}_{B,a} \\
\mathbf{e}_{B,1} &= -\frac{1}{\sqrt{2}}(\mathbf{e}_{B,a} + i\mathbf{e}_{B,b}) \\
\mathbf{e}_{B,-1} &= \frac{1}{\sqrt{2}}(\mathbf{e}_{B,a} - i\mathbf{e}_{B,b})
\end{align*}$$

With these definitions we can evaluate $F$. As an example suppose beam 1 is right hand circular polarized and propagates along $\mathbf{e}_z$. The circular polarization basis vectors are

$$\begin{align*}
\mathbf{e}_{rhc} &= \frac{\mathbf{e}_x - i\mathbf{e}_y}{\sqrt{2}}, \\
\mathbf{e}_{lhc} &= \frac{\mathbf{e}_x + i\mathbf{e}_y}{\sqrt{2}}.
\end{align*}$$
The polarization amplitudes in a spherical basis are therefore
\[
\begin{align*}
\epsilon_{1,1}^* \cdot \epsilon_{\text{rhc}} &= 0, \\
\epsilon_{1,0}^* \cdot \epsilon_{\text{rhc}} &= 0, \\
\epsilon_{1,-1}^* \cdot \epsilon_{\text{rhc}} &= -1
\end{align*}
\]
so the polarization state is \(\epsilon_1 = -\epsilon_{1,-1}\).

The condition for a three dimensional trap is that all force components are everywhere directed towards the origin. We can express this condition as
\[
x F_x(r) < 0, \quad y F_y(r) < 0, \quad z F_z(r) < 0
\]
for all \(r\).

**Six beam MOT**

For the standard six beam \(\sigma_+ - \sigma_-\) MOT with a quadrupole magnetic field as in Fig. 11.2 we take
\[
\begin{align*}
\hat{k}_1 &= (0, 0), & \text{propagating towards } +z \\
\hat{k}_2 &= (\pi, 0), & \text{propagating towards } -z \\
\hat{k}_3 &= (\pi/2, 0), & \text{propagating towards } +x \\
\hat{k}_4 &= (\pi/2, \pi), & \text{propagating towards } -x \\
\hat{k}_5 &= (\pi/2, \pi/2), & \text{propagating towards } +y \\
\hat{k}_6 &= (\pi/2, 3\pi/2), & \text{propagating towards } -y.
\end{align*}
\]

We orient the quadrupole field to have symmetry axis along \(e_z\) giving Cartesian components \(B = b(-x/2, -y/2, z)\). The amplitude has been defined so that \(\frac{\partial B}{\partial z} = be_z\). In a spherical coordinate system \(\theta_B = \tan^{-1}(\sqrt{x^2 + y^2}/2z), \phi_B = \tan^{-1}(y/x)\).
Trapping forces directed towards the origin are obtained with the polarization settings
\[ \epsilon_1 = \epsilon_2 = \epsilon_{\text{lh}} \]
\[ \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = \epsilon_{\text{rh}}. \]

The polarization basis vectors \( \epsilon_j \) are to be understood to refer to the coordinate system of \( \hat{\mathbf{k}}_j \). The explicit values expressed in space fixed \( x,y,z \) components are
\[ \epsilon_1 = \frac{e_x + ie_y}{\sqrt{2}}, \quad \epsilon_2 = \frac{e_x - ie_y}{\sqrt{2}}, \]
\[ \epsilon_3 = \frac{e_y - ie_z}{\sqrt{2}}, \quad \epsilon_4 = \frac{e_y + ie_z}{\sqrt{2}}, \]
\[ \epsilon_5 = \frac{e_z - ie_x}{\sqrt{2}}, \quad \epsilon_6 = \frac{e_z + ie_x}{\sqrt{2}}. \]

It is common practice to specify the polarization states in terms of \( \sigma_+ , \sigma_- \) angular momentum states. This notation is ambiguous since the sign of the angular momentum depends on the direction of the quantization axis which in turn is related to the local magnetic field direction. With respect to quantization axes directed towards \( +z, +x, +y \) for \( z > 0, x > 0, y > 0 \) in the quadrupole magnetic field specified above the angular momentum states of the light are
\[ +z/ -z : \quad \epsilon_1/\epsilon_2 = \epsilon_{\text{lh}}/\epsilon_{\text{lh}} = \sigma_+/\sigma_- \]
\[ +x/ -x : \quad \epsilon_3/\epsilon_4 = \epsilon_{\text{rh}}/\epsilon_{\text{rh}} = \sigma_-/\sigma_+ \]
\[ +y/ -y : \quad \epsilon_5/\epsilon_6 = \epsilon_{\text{rh}}/\epsilon_{\text{rh}} = \sigma_-/\sigma_+. \]

The spatial extent of the MOT cloud can be estimated assuming a Gaussian distribution. The potential energy along say \( x \) is
\[ U(x) = \int_0^x dx' \frac{\partial U}{\partial x} = -\int_0^x dx' F_x(x'). \]
Near the origin the force has a nearly linear slope so \( F_x \simeq f_xx \) and
\[ U(x) \simeq -\frac{1}{2} f_xx^2. \]

The density distribution then scales as
\[ n(\mathbf{r}) = n_0e^{-U/k_BT} = n_0e^{-f_x x^2/2k_BT}e^{-f_y y^2/2k_BT}e^{-f_z z^2/2k_BT}. \]

The rms width of the distribution along each axis is
\[ \sigma_j = (k_BT/f_j)^{1/2}. \]

11.8 MOT number density measurements

This section gives the formulas for measuring the number density of a MOT using absorption and fluorescence imaging techniques. The geometry is shown in Fig. 11.3. A weak probe
beam propagates along the $x$ axis and its intensity is measured with and without the atoms present. This gives a transmission coefficient that can be written as

$$T = \frac{P_{\text{out}}}{P_{\text{in}}},$$ (11.24)

where $P$ is the power in the probe beam. When the Rayleigh length of the probe beam is not long compared to the thickness of the atomic cloud the transmission must be calculated numerically, while in the thin cloud approximation we can derive an approximate analytical expression for the transmission. To do so we write the intensity in the large Rayleigh length limit as

$$I(x, y, z) = I_0(x) e^{-2(y^2+z^2)/w_0^2},$$ (11.25)

where $w_0$ is the beam waist and $P_{\text{in}} = \pi w_0^2 I_0(-\infty)/2$. The assumption of a weak probe beam implies that the absorption is independent of transverse position $(y, z)$ so that

$$T = e^{-\int dx \alpha(x)},$$ (11.26)

where $\alpha(x)$ is the absorption along $x$ for $y = z = 0$. The absorption coefficient can be written as $\alpha(x) = n(x, y = 0, z = 0)\sigma$ where $n$ is the atomic density and $\sigma$ is the absorption cross section. If we assume a gaussian density distribution of the form $n(x, y, z) = n_0 e^{-2x^2/w_x^2} e^{-2y^2/w_y^2} e^{-2z^2/w_z^2}$ and let the integration limits go to infinity we find

$$T = e^{-\sqrt{\frac{\pi}{2}} n_0 \sigma w_x}.$$ (11.27)

The fluorescence signal $F(x, z)$ recorded by the camera is an integral of the density along the $y$ axis. Thus

$$F(x, z) \sim \int dy \ n(x, y, z).$$ (11.28)

The peak fluorescence signal recorded at $x = z = 0$ is $F \sim \int dy \ n(0, y, 0)$, so the normalized signal can be written as

$$F(x, z) = \frac{\int dy \ n(x, y, z)}{\int dy \ n(0, y, 0)} = e^{-2x^2/w_x^2} e^{-2z^2/w_z^2}. $$ (11.29)
Fitting the normalized image $F$ to gaussians we can extract the values of $w_x$ and $w_z$.

The total number of atoms is

$$N = \int dx dy dz \ n(x, y, z) = \left(\frac{\pi}{2}\right)^{3/2} n_0 w_x w_y w_z. \quad (11.30)$$

Then using $n_0 w_x = -\ln T/(\sqrt{\pi}/2 \ \sigma)$ gives

$$N = -\frac{\pi \ln T}{2 \ \sigma} w_y w_z \quad (11.31)$$

with a peak density

$$n_0 = -\frac{2 \ln T}{\pi \ \sigma w_x}. \quad (11.32)$$

If we assume the atomic cloud is symmetric in the $x, y$ plane so that $w_y = w_x$ Eq. (11.31) can be expressed in terms of the measured values $T$, $w_x$, and $w_z$. To complete the calculation we will need the result that for a weak probe beam with laser-atom detuning $\Delta$ the absorption cross section is

$$\sigma = \frac{3\lambda^2}{2\pi} \frac{1}{1 + 4\Delta^2/\gamma^2}, \quad (11.33)$$

with $\gamma$ the natural linewidth of the atomic transition.

### 11.9 MOT temperature measurements

The temperature of a trapped atom cloud can be readily measured using time of flight methods. In one approach the atoms are released from the MOT and the delay time before they pass through a probe beam placed a small distance below the MOT is measured. The average delay time and the shape of the time of flight signal can be modeled assuming a Maxwell-Boltzmann distribution of atomic velocities, and the temperature determined by a curve fitting procedure.
A related approach is to turn off the MOT so that the atom cloud expands and collect images of the density distribution at different times after the release of the atoms. The initial distribution function of the atoms in the MOT can be written as

\[ f(r(0), p(0)) = N \left( \frac{2}{\pi w_r^2} \right)^{3/2} e^{-2r^2(0)/w_r^2} \frac{1}{(2\pi mk_BT)^{3/2}} e^{-p^2(0)/(2mk_BT)} \] (11.34)

where \( N \) is the number of atoms, \( w_r \) is the gaussian radius of the density distribution, \( m \) is the atomic mass, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The density is given by \( f_r(r) = \int dp \ f(r, p) \), and the total number of atoms is \( N = \int dr \ f_r(r) \).

Let us now turn off the trapping potential at \( t = 0 \) so that the atomic cloud expands. For a free expansion with no collisions the atoms move ballistically with constant velocity so that \( r(t) = r(0) + \frac{p(0)}{m} t \) and \( p(t) = p(0) \). The time dependent density is found by substituting the above expressions into \( f(r(t), p(t)) \). The integration is readily performed in Cartesian coordinates with the result

\[ f_r(r) = N \left( \frac{2}{\pi w_r^2(t)} \right)^{3/2} e^{-2r^2/w_r^2(t)}. \] (11.35)

The spherically symmetric form of the distribution is unchanged, but the size of the cloud is now time dependent and is given by

\[ w_r(t) = w_r \left[ 1 + 4k_B T t^2 / (mw_r^2) \right]^{1/2}. \] (11.36)

Thus a plot of the cloud radius at large times should be linearly proportional to \( t \).

It may be convenient to characterize the cloud experimentally by its full width at half maximum density, which we write as \( d_{1/2} \). We have \( d_{1/2} = \sqrt{2 \ln 2} \ w_r \) so that

\[ d_{1/2}(t) = d_{1/2} \left( 1 + \frac{8 \ln 2 \ k_B T t^2}{md_{1/2}^2} \right)^{1/2}. \]

In the presence of gravity the cloud expands asymmetrically. This can be calculated using \( r(t) = r(0) + \frac{p(0)}{m} (t/m) - \left( \frac{1}{2} \right) g t^2 \hat{y} \) and \( p(t) = p(0) - mg \hat{y} \) where \( g \) is the gravitational acceleration along \(-\hat{y}\). Performing the momentum integrations we find

\[ f_r(r) = N \left( \frac{2}{\pi w_r^2(t)} \right)^{3/2} e^{-2r^2/w_r^2(t)} e^{-gt^2(4y+gt^2)/(2w_r^2(t))} \]

The cloud width along the horizontal and vertical axes is of course unaffected by gravity and given by Eq. (11.36), while along the \( y \) axis the center of the cloud moves to \( y = -gt^2/2 \).

11.10 Lower temperatures

It was discovered in the late 1980s [33] that atoms in a magneto-optical trap had temperatures well under the Doppler temperature \( k_B T_D = h\gamma/2 \). These lower temperatures appear due...
to the multilevel structure of atoms used for laser cooling\cite{34, 35}. Common names for subDoppler cooling are Sisyphus cooling and polarization gradient cooling.

Sisyphus cooling can take atoms down to slightly under 1 µK. This is about a factor of ten higher than the recoil temperature \( k_B T_r = k_B \frac{(\hbar k)^2}{2m} = k_B \times 99 \text{ nK} \) for Cs. Sub-recoil temperatures can be reached using stimulated scattering processes. Common techniques include Raman cooling and velocity selective coherent population trapping (VSCPT). Accurate calculations of the lower limit of these cooling methods are involved due to the need to quantize the center of mass motion of the atom. We will only give a qualitative explanation of Raman cooling.

### 11.10.1 Sisyphus cooling

Consider a \( J = 1/2 \) ground state coupled to a \( J = 3/2 \) excited state. The E1 dipole allowed transitions are shown in Fig. 11.5. Using two counterpropagating beams with perpendicular linear polarization the polarization state varies along \( z \). Where the light is \( \sigma_+ \) polarized the \( m = 1/2 \) state has the largest light shift and since \( 1/2 \leftrightarrow 3/2 \) is a closed transition the atomic state is pumped from \( m = -1/2 \) to \( m = +1/2 \). Where the light is \( \sigma_- \) polarized the \( m = -1/2 \) state has the largest light shift and since \( -1/2 \leftrightarrow -3/2 \) is a closed transition the atomic state is pumped from \( m = 1/2 \) to \( m = -1/2 \).

Let’s make a rough estimate of the achievable temperature. The energy scale of the position dependent light shifts is \( U \sim \hbar \Omega^2/\Delta \). The excited state population is \( \rho_{ee} \sim \Omega^2/\Delta^2 \) and the photon scattering rate is \( r_s \sim \gamma \Omega^2/\Delta^2 \), with \( \gamma \) the excited state linewidth. The
cooling force is

\[ F \sim \frac{dU}{dx} \times \text{prob. repump at top of hill} \]

\[ \sim U \frac{\tau_s}{\hbar \tau_{\text{motion}}} \]

\[ \sim U \frac{\lambda}{r_s} \frac{\hbar}{\lambda/v} \]

\[ \sim \hbar k^2 \Delta v. \]

The friction coefficient is thus

\[ \beta = \frac{\hbar k^2 \Delta}{\gamma}. \]

There is also heating due to fluctuations of the force from pumping between the ground Zeeman states. The momentum diffusion coefficient is

\[ D_p = \frac{d}{dt} \langle p^2 \rangle \]

which can be estimated as

\[ D_p \sim \frac{(U/\lambda)^2}{r_s} \sim \frac{\hbar^2 k^2 \Omega^2}{r_s \gamma}. \]

The equilibrium temperature is

\[ T = \frac{D_p}{\beta} = \hbar \frac{\Omega^2}{\Delta}. \]

We see that the temperature is proportional to intensity divided by detuning. The light-atom interaction and the photon scattering rate also decrease so the cooling process gets slower, but very low temperatures can be reached. Early experiments with Cs atoms [36] reached under 3 µK which is about 40 times less than the Doppler temperature.

### 11.10.2 Raman cooling

One method of reaching subrecoil temperatures is Raman cooling. The basic arrangement is illustrated in Fig. 11.6. An atom moving along the \( e_z \) axis is irradiated by counterpropagating beams with frequencies \( \omega_1, \omega_2 \) and Rabi frequencies \( \Omega_1, \Omega_2 \). A stimulated Raman process involves stimulated absorption of one photon at \( \omega_1 \) and stimulated emission of one photon at \( \omega_2 \). The first photon gives a momentum transfer to the atom of \( \delta p = -\hbar k_1 \) so that

\[ v_1 = v_0 - \frac{\hbar k_1}{m_a} \]

with \( m_a \) the atomic mass. The second photon gives an additional transfer of \( \delta p = -\hbar k_2 \) so that

\[ v_2 = v_1 - \frac{\hbar k_2}{m_a} = v_0 - \frac{\hbar k_1}{m_a} - \frac{\hbar k_2}{m_a}. \]

This two-photon process occurs when a resonance condition between initial and final states is satisfied, i.e.

\[ \omega_1 + k_1 v_0 - (\omega_2 - k_2 v_1) = \omega_{21}. \]
We prepare the laser beams so that $\omega_1 - \omega_2 = \omega_{21} + \delta$ and the resonance condition becomes

$$\delta = -k_1 v_0 - k_2 v_1 = -(k_1 + k_2)v_0 + \frac{\hbar k_1 k_2}{m_a}.$$

Since $\omega_{21}$ is much less than an optical frequency we can put $k_1 \approx k_2 \approx k$ and

$$\delta = -2kv_0 + \frac{\hbar k^2}{m_a}.$$

Varying $\delta$ we select different velocity classes of atoms which participate in the stimulated transfer process, thereby removing $2\hbar k$ of momentum. The atom must then be moved back to state $|1\rangle$ to repeat the process. This is done by absorbing a photon in resonance with the $|2\rangle - |e\rangle$ transition followed by a spontaneous decay. If the absorbed photon is provided by beams propagating in both directions this imparts no net momentum on average, whereas the spontaneous decay gives $\hbar k$ in a random direction. Thus on average we can remove up to $\hbar k$ of momentum for each Raman cycle.

Resonance therefore occurs when

$$v_0 = \frac{\hbar k}{2m_a} - \frac{\delta}{2k}.$$

The recoil velocity from scattering of one photon is $v_r = \hbar k/m_a$ so we can write this as

$$v_0 = \frac{v_r}{2} - \frac{\delta}{2k}.$$

The implementation of this cooling scheme involves starting with a large value of $\delta$ to cool rapidly moving atoms and ramping $\delta$ down, close to $\delta_{\text{min}} = kv_r$ to cool close to zero velocity.
For cooling of an untrapped gas the directions of the two beams are swapped back and forth to cool positive and negative motion. For trapped atoms which are oscillating in space this is not necessary. The original demonstration of this technique gave temperatures below 100 nK with Na atoms[37].
Chapter 12

Optical traps and atomic coherence

12.1 Loading atoms in dipole traps

Consider loading of atoms from a MOT vapor into a dipole trap created by a tightly focused single beam. We can estimate the number of atoms that can be captured as follows. Assume the far-off resonance trap (FORT) is defined by a single beam with wavelength $\lambda_f$ focused to a waist $w_0$. The trap potential expressed as a temperature then has the spatial dependence

$$T_f(r, z) = T_m e^{-2r^2/w^2(z)} \frac{1 + z^2/z_r^2}{1 + z^2/z_r^2},$$

where $T_m$ is the maximum trap depth at the center of the trap at $z = r = 0$, $w^2(z) = w_0^2(1 + z^2/z_r^2)$, and the Rayleigh length is $z_r = \pi w_0^2/\lambda_f$. A first approximation of the capture volume assumes that all atoms in the region where $T_f > T_c$ are captured, while those outside this region are lost. We expect that the capture temperature $T_c$ will be similar to $T_a$, the kinetic temperature of the atoms in the MOT, provided $T_a$ is smaller than $T_m$. Define a factor

![Volume vs. Temperature](image.png)

Figure 12.1: Effective FORT capture volume as a function of the atomic kinetic temperature for $T_m = 250 \mu K$, $w_0 = 3 \mu m$, and $\lambda_f = 1.01 \mu m$. 

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\[ \chi = T_a / T_m, \] so that the capture volume vanishes for \( \chi = 1 \), and increases monotonically with decreasing \( \chi \). A simple calculation results in an expression for the capture volume as

\[ V = 2 \int_0^{z_m} dz \pi r_m^2(z) \]
\[ = \pi w_0^2 \int_0^{z_m} dz \left( 1 + \frac{z^2}{z_m^2} \right) \ln \left( \frac{z_m^2 + z^2}{z_m^2 + z_r^2} \right) \]
\[ = \frac{4\pi}{3} w_0^2 z_m + \frac{2\pi}{9} w_0^2 r_m^3 \left[ z_m^3 - 6z_m z_r^3 \tan^{-1} \left( \frac{z_m}{z_r} \right) \right] \quad (12.1) \]

with \( z_m = z_r \sqrt{1/\chi - 1} \). Let’s consider a numerical example. We have a maximum FOR T depth of \( T_m = 250 \mu K \), \( w_0 = 3 \mu m \), and \( \lambda_f = 1.01 \mu m \). The resulting effective capture volume is shown in Fig. 12.1 as a function of \( T_a \).

In some cases the effective length of the FOR T volume is limited by geometrical factors such as the size of the MOT that the FOR T is being loaded from, or the FOR T geometry itself when several beams are being overlapped to create the FOR T. In such a case we define the geometrical limiting length as \( 2z_{mg} \). When \( z_{mg} > z_m \) Eqs. (12.1) can be used. In the opposite limit when \( z_{mg} < z_m \) we find the expression

\[ V = \pi w_0^2 \int_0^{z_{mg}} dz \left( 1 + \frac{z^2}{z_m^2} \right) \ln \left( \frac{z_m^2 + z^2}{z_m^2 + z_r^2} \right) \]
\[ = \frac{4\pi}{3} w_0^2 z_{mg} + \frac{2\pi}{9} w_0^2 \left[ z_m^3 - 6z_m^3 \tan^{-1} \left( \frac{z_{mg}}{z_r} \right) \right] + \frac{\pi}{3} w_0^2 z_{mg} \left[ z_m^3 + 3z^3 \right] \ln \left( \frac{z_m^2 + z^2}{z_m^2 + z_r^2} \right) \quad (12.2) \]

A numerical example for this case is shown in Fig. 12.2. Assuming a MOT density of \( 10^{11} \text{ cm}^{-3} \) and \( T_a = 40 \mu K \) gives \( 1.6 \times 10^6 \) atoms captured into the FOR T.

Such a calculation of the number of captured atoms is only approximate since it neglects the distribution of atomic kinetic energy \( E \) at fixed atomic temperature \( T_a \). A more accurate
calculation of the number of trapped atoms results from
\[
N_T = n \int_{E_{\text{min}}}^{E_{\text{max}}} dE \, V(E) f(E)
\]  
(12.3)

where \( V(E) \) is given by Eq. (12.1) with \( \chi = E / k_B T_m \), \( n \) is the atomic density and
\[
f(E) = \frac{2}{\sqrt{\pi} (k_B T)^{3/2}} \sqrt{E} e^{-E / k_B T}.
\]

The maximum kinetic energy to be used in the integral is \( E_{\text{max}} = k_B T_m \). At first sight it would appear that we should use \( E_{\text{min}} = 0 \). This does not work since \( V(E) \) diverges as \( E \to 0 \). The reason is that the capture volume formally grows without limit as the kinetic energy decreases. In practice we should introduce a cutoff energy \( E_{\text{min}} \) for which the length of the capture volume approaches the thickness \( L_{\text{MOT}} \) of the cold MOT cloud from which the FOR T is being loaded. We then have
\[
E_{\text{min}} = \frac{k_B T_m}{1 + (L_{\text{MOT}} / 2\sigma)^2}.
\]

Equation (12.3) has to be integrated numerically. Using \( T_m = 250 \, \mu K \), \( w_0 = 3 \, \mu m \), \( \lambda_f = 1.01 \, \mu m \), \( L_{\text{MOT}} = 1. \, \text{mm} \), and \( n = 10^9 \, \text{cm}^{-3} \) gives \( N_T = 8.6 \) atoms whereas the result obtained from Eq. (12.1) without integrating over the energy distribution would have been about 2 atoms.

12.1.1 Density distribution in optical traps

Consider an attractive potential well created by the intensity distribution \( I = I_0 e^{-2x^2/w^2} \). In the far detuned limit the potential is \( U \sim I \) or \( U = U_0 e^{-2x^2/w^2} \) with \( U_0 < 0 \). The atomic density distribution in thermal equilibrium is \( n = n_0 e^{-(U-U_0)/k_B T} \approx n_0 e^{U_0 2x^2/w^2 k_B T} \). Comparing with a one-dimensional Gaussian distribution \( P(x, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-x^2/2\sigma^2} \) we see that the density distribution has standard deviation \( \sigma = \frac{w}{2} \sqrt{k_B T/|U_0|} \).

Two interfering plane waves with included angle \( 2\theta \) create an intensity pattern of the form \( I = I_0 \cos^2(\pi x/\Lambda) \), with \( \Lambda = \lambda / 2 \sin(\theta) \). The potential is \( U = U_0 \cos^2(\pi x/\Lambda) \) with \( U_0 < 0 \). The atomic density distribution near the potential minimum is \( n = n_0 e^{-(U-U_0)/k_B T} \approx n_0 e^{U_0 \pi^2 x^2 / \Lambda^2 k_B T} \). Comparing with a one-dimensional Gaussian distribution we find \( \sigma = \frac{\Lambda}{2^{1/2} \pi} \sqrt{k_B T/|U_0|} \).

12.1.2 Higher order potentials

Consider a one-dimensional trap with \( U = U_n z^n \). The virial theorem says that the time average of the kinetic energy \( \bar{K} \) and potential energy \( \bar{V} \) are related by \( 2 \langle K \rangle = n \langle V \rangle \). To prove this consider particles with position \( r_j \) and velocity \( v_j \). The kinetic energy is \( K = \)
\[ \sum_j \frac{1}{2} m v_j \cdot v_j \text{ and} \]
\[ \sum_j v_j \cdot \nabla v_j K = \sum_j v_j \cdot \nabla v_j \sum_j \frac{1}{2} m v_j' \cdot v_j' \]
\[ = \sum_j v_j \cdot \nabla v_j \frac{1}{2} m v_j \cdot v_j \]
\[ = \sum_j v_j \cdot m v_j \]
\[ = 2K. \quad (12.4) \]

Then use \( \nabla v_j K = p_j \) to write
\[ 2K = \sum_j p_j \cdot v_j = \frac{d}{dt} \left( \sum_j p_j \cdot r_j \right) - \sum_j r_j \cdot \frac{d}{dt} p_j. \]

We now average with respect to time. The time average of the derivative of a bounded function is zero. Thus
\[ 2\langle K \rangle = -\langle \sum_j r_j \cdot \frac{d}{dt} p_j \rangle \]
\[ = \langle \sum_j r_j \cdot \nabla r_j U \rangle. \quad (12.5) \]

The right hand side is called the virial of the mechanical system. If the potential \( U \) is a homogeneous function of coordinates of degree \( n \) then
\[ \nabla r_j U = \nabla r_j \sum_j U_n r_j^n = nU_n r_j^{n-1} \quad (12.6) \]
and
\[ \langle \sum_j r_j \cdot \nabla r_j U \rangle = \langle \sum_j r_j \cdot nU_n r_j^{n-1} \rangle = n\langle U \rangle \]
so
\[ 2\langle K \rangle = n\langle U \rangle \]
which is called the virial theorem. This proof follows L & L Mechanics.

Thermodynamics says that the average energy per degree of freedom is \( k_B T/2 \), thus
\[ \langle K \rangle + \langle U \rangle = (1 + n/2)\langle U \rangle = k_B T. \]

This implies that
\[ \langle U \rangle = U_n \langle z^n \rangle = \frac{k_B T}{1 + n/2} \]
so
\[ \langle z^n \rangle = \frac{k_B T}{(1 + n/2) U_n}. \]
For a quartic potential \( n = 4 \) and \( \langle z^4 \rangle = k_B T / 3U_4 \). To find the rms position spread we may assume Gaussian statistics for which \( \langle z^4 \rangle = 1/3 \langle z^2 \rangle^2 \). Thus

\[
z_{\text{rms}} = \langle z^2 \rangle^{1/2} = (3 \langle z^4 \rangle)^{1/4} = \left( \frac{k_B T}{U_4} \right)^{1/4}.
\]  

(12.7)

Suppose now that we have a potential that is axially symmetrical and quartic in the radial coordinate \( \rho^2 = x^2 + y^2 \). Then

\[
\rho_{\text{rms}} = \langle \rho^2 \rangle^{1/2} = \langle x^2 + y^2 \rangle^{1/2} = \sqrt{2} \langle x^2 \rangle^{1/2}.
\]  

(12.8)

Since the radial motion is two dimensional we have

\[
\langle K_\rho \rangle + \langle U_\rho \rangle = 3 \langle U_\rho \rangle = 2k_B T
\]

so

\[
\langle U_\rho \rangle = U_4 \langle \rho^4 \rangle = \frac{2k_B T}{3}
\]

and

\[
\langle \rho^4 \rangle = \frac{2k_B T}{3U_4}.
\]

We then use the Gaussian moment relation \( 3 \langle x^4 \rangle = \langle x^2 \rangle^2 \) to get

\[
\langle \rho^4 \rangle = \langle x^4 + y^4 + 2x^2y^2 \rangle = 2 \langle x^4 \rangle + 2 \langle x^2 \rangle^2 = \frac{8}{3} \langle x^2 \rangle^2
\]

which implies

\[
\langle x^2 \rangle = \left( \frac{k_B T}{4U_4} \right)^{1/2}.
\]

Using (12.8) we find

\[
\rho_{\text{rms}} = \sqrt{2} \left( \frac{k_B T}{4U_4} \right)^{1/4} = \left( \frac{k_B T}{U_4} \right)^{1/4}.
\]

12.2 Two-level coherence - Ramsey spectroscopy

Qubits can be encoded in any two-level quantum system. In this section we will use the terminology qubit and two-level system interchangeably. An arbitrary quantum state can be represented as a point on the Bloch sphere as shown in Fig. 12.3. The usefulness of the encoding depends on several different aspects of the qubits. On the one hand we want fast and accurate control of the qubit on the Bloch sphere. At the same time the decoherence rates as embodied in \( T_1 \) and \( T_2 \) should be as slow as possible. For high fidelity quantum
operations the ratio of $T_1$ or $T_2$ to the Rabi $\pi$ time should be 1000 or more. The frequency resolution of atomic clocks also depends on having long $T_1$ and $T_2$ times.

The $T_1$ time can be measured by preparing the qubit in $|0\rangle$ or $|1\rangle$ and measuring the rate at which population leaks over to the other state. The actual value of $T_1$ will depend on the qubit and the extent to which external perturbations drive unwanted transitions. An upper limit is set by the radiative decay time of the level which is higher in energy. This limit for microwave frequency qubits is typically irrelevant, although it may be a limiting timescale for optical frequency qubits with transition frequencies measured in hundreds of THz.

The $T_2$ time is most conveniently measured using Ramsey interferometry[38]. The pulse sequence is shown in Fig. 12.4. In an ideal setting the population measured at the end of the sequence will oscillate between $|0\rangle$ and $|1\rangle$. In a real experiment the oscillations decay due to decay of coherence. Let the energy separation between the levels be $\hbar(\omega_1 - \omega_0) = \hbar\omega_q$. We will refer to $\omega_q$ as the qubit frequency. At time $t = 0$ we apply a $\pi/2$ rotation using a resonant field with frequency $\omega = \omega_q$. According to Eq. (9.6) this gives the transformation

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} = \frac{I + iX}{\sqrt{2}},$$

where $X = \sigma_x$ is a Pauli operator. If the qubit is prepared in $|0\rangle$ then after the initial pulse
If so desired we could also account for a finite detuning during the rotations.

\[ \omega \]

seems inconsistent, but has been done to give the rotation operators a simpler mathematical form.

\[ \text{oscillates at frequency } \Delta. \]

If \( \phi \) decay. Conversely if \( \phi \) decay. The measured coherence time can only be as good as the reference pulses applied to the qubit are resonant, but allow for a frequency difference \( \omega_n \), making the substitution \( \omega_n T \rightarrow \omega_q T + \phi_n(T) \), where \( \phi_n \) is random variable which is meant to account for noise. so the state is

\[ |\psi(T)\rangle = e^{-i\omega_n T}|0\rangle + i e^{-i\omega_q T + \phi_n(T)}|1\rangle. \]

In the real world the qubit frequency will not be perfectly constant due to perturbations from external fields, or internal dynamics of composite particles. We will account for this by making the substitution \( \omega_q T \rightarrow \omega_q T + \phi_n(T) \), where \( \phi_n \) is random variable which is meant to account for noise. so the state is

\[ |\psi(T)\rangle = e^{-i\omega_n T}|0\rangle + i e^{-i\omega_q T + \phi_n(T)}|1\rangle. \]

We then apply another \( \pi/2 \) rotation with the external field which oscillates at frequency \( \omega \). However, the rotation will be about an axis which depends on the accumulated phase \( \phi = -\omega T - \phi_n(T) \). Here \( \phi_n \) is an additional random phase due to noise. From Eq. (9.6) the transformation is

\[ U_\phi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i e^{-i\phi} \\ i e^{i\phi} & 1 \end{pmatrix} = \frac{I + i \cos(\phi) X + i \sin(\phi) Y}{\sqrt{2}}. \]

After applying the second rotation the state is

\[ |\psi_2\rangle = U_\phi |\psi(T)\rangle = e^{-i\omega_n T} \left[ \frac{1 - e^{-i(\phi + \omega_q T + \phi_n)}}{2} |0\rangle + i \frac{e^{i\phi} + e^{i\omega_q T + \phi_n}}{2} |1\rangle \right]. \]

The probability of finding the qubit in state \( |0\rangle \) is

\[ P_0 = \frac{1 - \cos(\phi + \omega_q T + \phi_n)}{2} = \frac{1 - \cos[(\omega - \omega_q) T + \phi_n + \phi_n]}{2}. \]

This sinusoidal signal is referred to as a Ramsey oscillation.

There is a subtlety in Eq. (12.9) which needs clarification. We have assumed that the pulses applied to the qubit are resonant, but allow for a frequency difference \( \omega - \omega_q \). This seems inconsistent, but has been done to give the rotation operators a simpler mathematical form. We can always imagine a situation where \( \omega \) and \( \omega_q \) are different, but \( \omega \) is rapidly set to \( \omega_q \) during the short duration of the rotation pulses, and then allowed to be different again. If so desired we could also account for a finite detuning during the rotations.

Introducing the detuning \( \Delta = \omega - \omega_q \) we see that the probability of measuring \( |0\rangle \) oscillates at frequency \( \Delta \). If \( \phi_n \) and \( \phi_n \) are constant the oscillations will persist without decay. Conversely if \( \phi_n \) and \( \phi_n \) are stochastic variables the oscillation will have a decaying envelope. The time for the oscillations to decay to \( 1/e \) of the initial value is defined as the coherence, or \( T_2 \) time. Note that even if the qubit is perfect \( (\phi_n = 0) \) a nonzero \( \phi_n \) will mimic qubit decay. The measured coherence time can only be as good as the reference oscillator we use to measure it!
12.2.1 Decoherence of Ramsey fringes

Let’s look at an example. Suppose $\phi_{wn} = 0$ but $\phi_{qm}$ is a zero mean stochastic variable. The probability of observing $|0\rangle$ at time $t$ is

$$\frac{1 - \cos[\Delta t - \phi_{qn}(t)]}{2}$$

and the probability a half period later is

$$\frac{1 - \cos[\Delta(t + \pi/\Delta) - \phi_{qn}(t + \pi/\Delta)]}{2} = \frac{1 - \cos[\pi + \Delta t - \phi_{qn}(t + \pi/\Delta)]}{2} \approx \frac{1 - \cos[\pi + \Delta t - \phi_{qn}(t)]}{2}$$

In the last line we have assumed that the noise is approximately constant for one period of the Ramsey oscillation.

The peak to peak amplitude of the oscillations is therefore

$$a = \frac{1 - \cos[\Delta t - \phi_{qn}(t)]}{2} - \frac{1 - \cos[\pi + \Delta t - \phi_{qn}(t)]}{2}$$

$$= \frac{\cos[\pi + \Delta t - \phi_{qn}(t)]}{2} - \frac{\cos[\Delta t - \phi_{qn}(t)]}{2}$$

Choosing $\Delta t = 2n\pi$ we find $a = -\cos[\phi_{qn}(t)]$ so the oscillation amplitude has the maximum possible value of 1 when $\phi_{qn} = 0$.

Let’s assume $\phi_{qn}(t) = \beta t$ and $\beta$ has Gaussian statistics,

$$P(\beta) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\beta^2/2\sigma^2}$$

with $\sigma$ the standard deviation. This stochastic variation of the qubit frequency could for example be due to a fluctuating magnetic field so the accumulated phase is proportional to the fluctuation times time. We then find

$$\langle |a| \rangle = \langle \cos[\phi_{qn}(t)] \rangle$$

$$= \int_{-\infty}^{\infty} d\beta \cos(\beta t) \frac{1}{\sqrt{2\pi\sigma}} e^{-\beta^2/2\sigma^2}$$

$$= e^{-\sigma^2 t^2/2}. \quad (12.10)$$

The $T_2$ time is therefore

$$T_2 = \frac{2^{1/2}}{\sigma}.$$

The larger the phase fluctuations the faster the qubit coherence decays and the shorter the $T_2$ time. The observed Ramsey signal averaged over many measurements will have the functional form

$$\langle P_0 \rangle = \frac{1 - \cos(\Delta t)e^{-\sigma^2 t^2/2}}{2}.$$

This is shown in Fig. 12.5.
Figure 12.5: Decay of the Ramsey signal with Gaussian phase fluctuations and $\sigma = 0.05\Delta$.

12.2.2 Decoherence due to other degrees of freedom

In many cases decoherence occurs not due to variation in an external field but due to undesired entanglement between the qubit and other dynamical variables. An example of this is an atom in a harmonic trap. A qubit may be encoded in a spin degree of freedom, but the atom has additional quantum numbers associated with the center of mass motion. If the total energy is coupled to the spin state decoherence can arise.

Consider an atom in a harmonic trap with vibrational frequency $\omega$. The energies of the harmonic oscillator levels are $U(n) = \hbar \omega (1/2 + n)$. Assuming a Maxwell Boltzmann thermal distribution the probability of occupation of level $n$ is $P_n = a e^{-U(n)/k_B T}$, with $a$ a normalization constant. The total probability is unity so

$$1 = \sum_{n=0}^{\infty} P_n = a e^{-\hbar \omega / 2k_B T} \sum_{n=0}^{\infty} e^{-n \hbar \omega / k_B T} = a \frac{e^{\hbar \omega / 2k_B T}}{e^{\hbar \omega / k_B T} - 1}.$$

The occupation probability is thus

$$P_n = (1 - e^{-\hbar \omega / k_B T}) e^{-n \hbar \omega / k_B T}.$$

The expected value of $n$ is

$$\langle n \rangle = \sum_{n=0}^{\infty} n P_n = (1 - e^{-\hbar \omega / k_B T}) \sum_{n=0}^{\infty} n e^{-n \hbar \omega / k_B T} = \frac{1}{e^{\hbar \omega / k_B T} - 1}.$$

The temperature can therefore be expressed as

$$k_B T = \frac{\hbar \omega}{\ln(1 + 1/\langle n \rangle)}.$$ (12.11)

When $\langle n \rangle > 1$ we have quasiclassical motion and

$$k_B T \simeq \frac{\hbar \omega}{12 \langle n \rangle}.$$ (12.12)
Figure 12.6: Relation between $\langle n \rangle$ and temperature in a harmonic oscillator from (12.11) (solid blue line) and the approximation (12.12) (dashed red line). The inset shows the quantum behavior for small $\langle n \rangle$.

Figure 12.7: Spin qubit with GHz frequency encoded in an atom in a harmonic trap with vibrational levels $n$. Coupling between the spin and center of mass degrees of freedom results in a small spin dependent differential shift (DS) of the vibrational energies.

As can be seen in Fig. 12.6 the approximation (12.12) is quite accurate for $\langle n \rangle > 0.5$.

In three dimensions we specify the vibrational state by $n = (n_x, n_y, n_z)$ with the trap frequencies $\omega = (\omega_x, \omega_y, \omega_z)$. The occupation probability is

$$P_n = \left(1 - e^{-\beta \omega_x}\right) \left(1 - e^{-\beta \omega_y}\right) \left(1 - e^{-\beta \omega_z}\right) e^{-\beta n \cdot \omega}$$

with $\beta = \hbar / k_B T$. The expected value of $n$ is

$$\langle n \rangle = \left(\frac{1}{e^{\beta \omega_x} - 1}, \frac{1}{e^{\beta \omega_y} - 1}, \frac{1}{e^{\beta \omega_z} - 1}\right).$$

The coherence time $T_2$ of a qubit encoded in hyperfine ground states $|0\rangle, |1\rangle$ is affected by motional dephasing. Suppose we prepare the state

$$\rho(0) = |0\rangle \langle 0| \otimes \sum_n P_n |n\rangle \langle n|.$$ 

Here $n = (n_x, n_y, n_z)$ is a set of vibrational quantum numbers specifying the motional state and $P_n$ is given by (12.13). The $T_2$ time can be measured with Ramsey spectroscopy which involves the sequence $U = R_{\pi/2} U_n(t) R_{\pi/2}$. We will assume $R$ only acts on the electronic state and does not change $|n\rangle$. The free evolution operator for a time $t$ is

$$U_n(t) = e^{-i(\Delta_1(n) - \Delta)\sigma_z t/2}.$$
Here $\Delta = \omega - \omega_{10}$ is the detuning of the field driving $R$ from the atomic transition frequency $\omega_{10}$, 

$$\Delta_1(n) = \frac{1}{\hbar} [U_1(n) - U_0(n)] = (1/2 + n) \cdot (\omega_1 - \omega_0),$$

and $\omega_j$ are the trap frequencies when the atom is in electronic state $| j \rangle$. The trap frequencies depend on the electronic state due to the fractional differential light shift $\bar{\Delta}_{LS} = (U_1 - U_0) / (1/2 (U_0 + U_1))$. 

The situation is shown in Fig. 12.7.

With the assumption of $\bar{\Delta}_{LS} \ll 1$ which is generally the case we can write $\omega_1 \approx \omega_0 (1 + \bar{\Delta}_{LS} / 2)$ so $\Delta_1(n) = (1/2 + n) \cdot \omega_0 \bar{\Delta}_{LS} / 2$. If we renormalize $\omega_{10}$ by $\sum_{j=x,y,z} \omega_j (\omega_0 \bar{\Delta}_{LS} / 4)$ to account for the trap shift of the transition then 

$$\Delta_1(n) = \frac{\bar{\Delta}_{LS}}{2} n \cdot \omega_0.$$ 

The density matrix after a Ramsey sequence is therefore

$$\rho(t) = U \rho(0) U^\dagger = R_{\pi/2} U_n(t) R_{\pi/2} \left( |0\rangle \langle 0| \otimes \sum_n P_n |n\rangle \langle n| \right) R_{\pi/2}^\dagger U_n(t)^\dagger R_{\pi/2}^\dagger$$

$$= \sum_n P_n |n\rangle \langle n| R_{\pi/2} U_n(t) R_{\pi/2} |0\rangle \langle 0| R_{\pi/2}^\dagger U_n(t)^\dagger R_{\pi/2}^\dagger.$$ 

The probability of measuring the atom in $| 1 \rangle$ after time $t$ is

$$P_{|1\rangle}(t) = \text{Tr}_{\text{vib}} [\langle 1 | \rho(t) | 1 \rangle]$$

$$= \sum_{n'} \langle n' | \langle 1 | \rho(t) | 1 \rangle | n' \rangle$$

$$= \sum_n P_n | \langle 1 | R_{\pi/2} U_n(t) R_{\pi/2} | 0 \rangle |^2.$$ 

The operator product to be evaluated is

$$R_{\pi/2} U_n(t) R_{\pi/2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix} e^{-i \theta_n t/2} \begin{pmatrix} 1 & 0 \\ 0 & e^{i \theta_n t} \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix}$$

$$= \frac{1}{2} e^{-i \theta_n t/2} \begin{pmatrix} 1 - e^{i \theta_n t} & -i (1 + e^{i \theta_n t}) \\ -i (1 + e^{i \theta_n t}) & 1 + e^{i \theta_n t} \end{pmatrix}$$

with $\theta_n = \frac{\bar{\Delta}_{LS}}{2} n \cdot \omega_0 - \Delta$. Thus the measurement probability is

$$P_{|1\rangle}(t) = \frac{1}{2} \sum_n P_n [1 + \cos(\theta_n t)] = \frac{1}{2} + \frac{1}{2} \sum_n P_n \cos(\theta_n t). \quad (12.14)$$

When the atom is in the motional ground state $P_0 = 1$ and $P_{|1\rangle}(t) = \frac{1}{2} [1 + \cos(\Delta t)]$. 

December 15, 2015 M. Saffman
Semiclassical limit

At high temperatures a large number of vibrational states are occupied and evaluation of the sum in (12.14) becomes inefficient to evaluate. As $\hbar/T \to 0$ we can put

$$P_n \simeq \omega_x \omega_y \omega_z \beta^3 e^{-\beta n \omega_0}$$

and

$$P_{|1\rangle}(t) \simeq \frac{1}{2} + \frac{\beta^3 \omega_x \omega_y \omega_z}{2} \sum_n e^{-\beta n \omega_0} \cos \left[ \left( \frac{\bar{\Delta}_{LS}}{2} n \cdot \omega_0 - \Delta \right) t \right]$$

$$\simeq \frac{1}{2} + \frac{\beta^3 \omega_x \omega_y \omega_z}{2} \int \int \int_0^{\infty} dn_x dn_y dn_z e^{-\beta (n_x \omega_x + n_y \omega_y + n_z \omega_z)}$$

$$\times \cos \left[ \left( \frac{\bar{\Delta}_{LS}}{2} (n_x \omega_x + n_y \omega_y + n_z \omega_z) - \Delta \right) t \right]$$

$$= \frac{1}{2} + \frac{1}{2} \left( 1 + \frac{\bar{\Delta}_{LS}^2 t^2}{4 \beta^2} \right)^{3/2} \cos (\Delta t - \kappa)$$

with

$$\kappa = \tan^{-1} \left( \frac{12 \beta^2 \bar{\Delta}_{LS} t - 8 \beta^3}{8 \beta^3 - 6 \beta \bar{\Delta}_{LS}^2 t^2} \right).$$

The factor $\kappa$ gives a small correction to the Ramsey frequency. The peak to peak amplitude is thus $a = \left( 1 + \frac{\bar{\Delta}_{LS}^2 t^2}{4 \beta^2} \right)^{-3/2}$ and the time at which $a = 1/e$ is

$$T_2^* = \sqrt{e^{2/3} - 1} \frac{2 \hbar}{k_B T \bar{\Delta}_{LS}} = 1.947 \frac{\hbar}{\bar{\Delta}_{LS} k_B T}.$$

We can therefore write the detection probability as

$$P_{|1\rangle}(t) = \frac{1}{2} + \frac{1}{2} \left[ 1 + 0.948 (t/T_2^*) \right]^{3/2} \cos (\Delta t - \kappa)$$

with $\kappa \simeq \tan^{-1}(0.325 t/T_2^*)$. The amplitude agrees with the Kuhr, et al. solution[39] which was derived starting from a semiclassical model, while the factor $\kappa$ is somewhat different. Note that we have here used the notation $T_2^*$ instead of $T_2$. $T_2^*$ refers to the coherence time due to inhomogeneous dephasing, in this case, that due to atomic motion. This dephasing is “inhomogeneous”, it can be reversed using sequences of echo pulses, and the coherence time increased. The increased coherence time is ultimately limited by homogeneous dephasing corresponding to a limiting $T_2$. We will discuss such echo pulses later on.

A comparison of the quantum and semiclassical calculations is given in Fig. 12.8. We see close agreement for temperatures above 2 $\mu$K. When the radial and axial trap frequencies are commensurate revivals in the Ramsey amplitude occur, as seen in Fig. 12.9. The full revival time is given by $t = 2 \times 2\pi / (\omega_2 \bar{\Delta}_{LS}) = 0.8$ s, while partial revivals are seen at $t = 2 \times 2\pi / (\omega_x \bar{\Delta}_{LS}) = 0.16$ s. When the trap frequencies are not commensurate we still see partial revivals.
Figure 12.8: $T_2^*$ calculated with quantum and semiclassical models for $\omega_x = \omega_y = 2\pi \times 50$ kHz, $\omega_z = 2\pi \times 10$ kHz, and $\Delta_{LS} = 2.5 \times 10^{-4}$ which corresponds to Cs atoms with trap light at 780 nm.

Figure 12.9: Revivals in Ramsey amplitudes for $\Delta_{LS} = 2.5 \times 10^{-4}$ which corresponds to Cs atoms with trap light at 780 nm. The trap frequencies were a,b) $(\omega_x, \omega_y, \omega_z) = 2\pi \times (50, 50, 10)$ kHz, and c) $(\omega_x, \omega_y, \omega_z) = 2\pi \times (55, 40, 11.5)$ kHz. The solid lines in a) are curve fits to Eq. (12.15).
Chapter 13

Optical pumping and multilevel atomic dynamics

Many applications of atomic physics depend on preparation of specific atomic states. Examples include atomic clocks and magnetometers, precision measurements, studies of many-body spin dynamics, and quantum computation. Conversion of an arbitrary and unknown mixture of initial states to a desired target state reduces entropy. This cannot be achieved with unitary dynamics and instead requires some form of non-unitary evolution which transfers the atomic state entropy into increased entropy of a radiation field coupled to the atoms. This type of transformation is referred to as optical pumping. In its most basic form optical pumping is used to put all population in a single quantum state. In many cases the target state is a dark state that is decoupled from the optical field, although this is not a requirement. The concept can also be generalized to pump into superposition, or even entangled states. In this chapter we will study several examples of optical pumping dynamics in multilevel atoms.

13.1 Optical pumping - basic examples

A basic example of optical pumping is preparation of a single Zeeman substate of a \( J = 1/2 \) level. Consider the level diagram of Fig. 13.1 where a \( J = 1/2 \) ground state is coupled to a \( J = 1/2 \) excited state with \( \sigma_+ \) polarized light. Population in the state \( |J_g = 1/2, m_g = -1/2\rangle \) is excited to \( |J_e = 1/2, m_e = 1/2\rangle \) and can then decay to either \( m_g = -1/2 \) or \( m_g = 1/2 \). Population that decays to \( m_g = -1/2 \) will get excited again. Population that decays to \( m_g = +1/2 \) stays there since there is no state with \( m_e = +3/2 \). The state \( |J_g = 1/2, m_g = 1/2\rangle \) is a dark state for the \( \sigma_+ \) polarized light and population accumulates in this state in a characteristic time \( \tau \).

The optical pumping time constant depends on the photon scattering rate and the branching ratios from the excited to the ground states. Each time an atom is excited to \( |J_e = 1/2, m_e = 1/2\rangle \) it decays to \( m_g = -1/2 \) with probability \( b_- \) and to \( m_g = +1/2 \) with probability \( b_+ \). The ratio of the probabilities is given by

\[
\frac{b_+}{b_-} = \left( \frac{C_{1/2,1/2,1,0}^{1/2,1/2}}{C_{1/2,1/2,1,1}^{1/2,1/2,1,-1}} \right)^2 = \frac{1}{2}
\]
so \( b_+ = 1/3 \) and \( b_- = 2/3 \) and the rate of transfer of atoms from \( |J_g = 1/2, m_g = -1/2\rangle \) to \( |J_g = 1/2, m_g = 1/2\rangle \) is

\[
r = b_+ \gamma P_{|J_e=1/2, m_e=1/2\rangle} \leq \frac{1}{3} \frac{1}{2} = \frac{\gamma}{6}. \tag{13.1}
\]

Population accumulates in the dark state as \( P_{|J_g=1/2, m_g=1/2\rangle} = 1 - e^{-t/\tau} \) with \( \tau = 1/r \geq 6/\gamma \).

The next more complicated case is pumping of a \( J_g = 1/2 \) ground state by light scattering from a \( J_e = 3/2 \) excited state. This will also result in accumulation of population in the \( |J_g = 1/2, m_g = 1/2\rangle \) state even though this state is no longer a dark state. However, it is the lower state of a cycling transition so that subsequent excitation will only result in decay back to the same state. The drawback of this situation is that continuous excitation and decay of atoms from this state will cause heating, which is absent when the final state is a dark state.

Another interesting case is optical pumping between states with integer angular momentum. Consider a \( J_g = 1 \) ground state coupled to a \( J_e = 1 \) excited state, as shown in Fig. 13.2. Using \( \pi \) polarized light population in \( |J_g = 1, m_g = \pm 1\rangle \) will be excited and decay either to the original state, or to \( m_g = 0 \). Population in \( m_g = 0 \) will not be excited since \( C_{1010}^{10} = 0 \) so the matrix element connecting \( |J_g = 1, m_g = 0\rangle \) and \( |J_e = 1, m_1 = 0\rangle \) is zero.

The vanishing matrix element means that for \( \pi \) polarized light coupling a level \( J_g \) to a level \( J_e = J_g \) the state with \( m = 0 \) is a dark state which can be used as the target state for an optical pumping process. Let’s calculate the time constant for pumping into the \( m = 0 \) state when \( J_g = J_e = 1 \). Population initially in \( m_g = \pm 1 \) is excited to \( m_e = \pm 1 \) and will

Figure 13.2: Optical pumping of a \( J_g = 1 \) level with \( \pi \) polarized light via \( J_e = 1 \).
then decay back to the starting state or to the $m = 0$ state. The ratio of probabilities is

$$\frac{b_0}{b_1} = \left( \frac{C_{1,1,1,-1}^{1,0}}{C_{1,1,1,0}^{1,1}} \right)^2 = 1$$

and using $b_1 = b_{-1}$ with $b_0 + b_1 + b_{-1} = 1$ we find $b_0 = 1/3$. Thus the pumping rate into the dark state is the same as in Eq. (13.1) and is given by $r \leq \frac{2}{6}$. The time constant is again $\tau \geq \frac{6}{\gamma}$. Pumping into $m = 0$ when $J_g = J_e > 1$ works in the same way but is slower since some of the initial population will have to make multiple transitions to arrive at the dark state.

Vanishing of the matrix element can be understood from an angular momentum argument\(^1\). The initial and final states with unit angular momentum are vector objects as is the electric field. The initial state and the electric field combine to create a unit angular momentum object which is a vector. The only way to combine two vectors to create a vector is with the cross product so

$$\mathbf{v}_e \sim \mathbf{v}_g \times \mathbf{v}_E$$

where $e, g, E$ label the excited state, ground state, and electric field respectively. The transition matrix element $a$ is a scalar that should be linear in all three constituents and to form a scalar from the vector $\mathbf{v}_e$ we must use the dot product so

$$a \sim \mathbf{v}_e \cdot \mathbf{v}_e \sim \mathbf{v}_e \cdot (\mathbf{v}_j \times \mathbf{v}_E).$$

The $m = 0$ states and the $\pi$ polarized field are all aligned along $z$ so the triple product must vanish. It can be shown that for any $|J_g, m_g = 0\rangle$ to $|J_e = J_g, m = 0\rangle$ transition the matrix element also vanishes, i.e. $C_{J_00}^{J_00} = 0$ for any integer $J$.

We see that it is straightforward to optically pump an initially unknown population distribution into a definite final state in two cases. When the final state is a stretched state with $m = \pm J$ or when $m = 0$. When the final state is a dark state the light scattering will shut down and the atoms will not suffer any additional heating. The more general task of pumping into an intermediate value of $m$ is not straightforward and can not always be achieved with high success probability, although techniques have been demonstrated for this more general case\[^{40}\]. Alternatively, once the population is in $m = \pm J$ or $m = 0$ it can be transferred to a different state using coherent control techniques as have been discussed in the preceding chapters and have been demonstrated in the full 16 dimensional ground hyperfine manifold of Cs atoms\[^{41}\].

In addition to the $m = \pm J$ or $m = 0$ dark states there can also be superpositions of atomic states that are dark. We have already seen an example of this for the STIRAP dark state in Sec. 10.3. In general we are interested in optical pumping of a level with angular momentum $J_g$ via scattering from an excited level with angular momentum $J_e$. The levels are coupled by a matrix of coefficients $\mathbf{M}$ with dimensions $(2J_e + 1) \times (2J_g + 1)$. The condition for existence of a dark state in the lower level is that there exists a null vector $\mathbf{v}$ of dimension $2J_g + 1$ satisfying

$$\mathbf{Mv} = 0.$$ 

In general such a null vector will exist provided $J_e \leq J_g$.

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\(^1\)This argument is from the book by D. Budker, D. F. Kimball and D. P. DeMille, Atomic Physics.

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The actual fidelity of the optical pumping process will be less than perfect in a real situation. This is due to technical imperfections such as imperfect polarization of the light field, or background field fluctuations that cause additional transfers between levels. There are also limits imposed by off-resonant coupling to additional atomic levels so that even with perfect optical polarization the target states are not completely dark. We will explore some of these limits in the next section.

13.2 Optical pumping of Cesium

Suppose we have the goal of preparing a Cs atom in the hyperfine clock state $|4, 0\rangle$. We can use $\pi$ polarized light resonant with $f = 4 \rightarrow f' = 4$ and repump light resonant with $f = 3 \rightarrow f' = 4$. We will use D1 light at 894 nm for the pump and D2 light at 852 nm for the repump. It is advantageous to use the D1 transition for the pump light since the hyperfine splitting of the $6p_{1/2}$ level is several times larger than the hyperfine splittings of the $6p_{3/2}$ level which reduces off-resonant transitions out of the dark state. Since population can decay to the other hyperfine ground level $f = 3$ we also include a repumper. The repumper could be on either the D1 or D2 transition without making a significant difference to the final results.

The saturation intensities are shown in Fig. 13.3. Note that the saturation intensity for $|6s_{1/2}, 4, 1\rangle \rightarrow |6p_{1/2}, 4, 1\rangle$ is very high, $I_{s, 41 - 41} = 404 \text{ W/m}^2$. This value should be compared with the cycling transition $|6s_{1/2}, 4, 4\rangle \rightarrow |6p_{3/2}, 5, 5\rangle$ which has $I_{s, 44 - 55} = 11.1 \text{ W/m}^2$. To get at least unit saturation on all pump transitions with a $w = 100 \mu\text{m}$ waist beam we need $P = \frac{\pi}{2} w^2 I_s$ giving $P_{\text{pump,894}} = 6.4 \mu\text{W}$ and $P_{\text{repump,852}} = 1.7 \mu\text{W}$.

Let us first calculate the depumping rate of an atom in $|4, 0\rangle$ due to the pump light. If the pump light has perfect $\pi$ polarization the depumping is due to Raman transitions via...
\[ |3',0\rangle. \] A short calculation shows that the population in \( |3',0\rangle \) is
\[
\rho_{3'0,3'0} = \frac{\gamma^2 I}{8\Delta \nu_3^2 I_{s,3'0-40}}
\]
where \( \Delta = 2\pi \times 1167.7 \) MHz and the saturation intensity is
\[
I_{s,3'0-40} = \frac{\epsilon_0 \hbar^2 \gamma^2}{4d_{3'0,40}^2}.
\]
The scattering rate is thus
\[
r = \gamma \rho_{3'0,3'0},
\]
and the Raman rate of scattering out of \( |4,0\rangle \) is \( r_{R,\text{out}} = br \) where \( b \) is the Raman branching ratio. This unavoidable rate sets the upper limit for the pumping fidelity in the most basic approach.

We need the following quantities. The matrix element is
\[
d_{3'0,40} = -\frac{C_{3010}^{30}}{\sqrt{2 \times 3 + 1}} \sqrt{(2 \times 3 + 1)(2 \times 4 + 1)} S_{3,1,1/2}^{1/2,7/2,4}(6p_{1/2}||r||6s_{1/2})
\]
\[
= \frac{1}{\sqrt{6}} \times 4.489e a_0 = 1.833e a_0.
\]
The linewidth is \( \gamma = 1/(34.79 \) ns) and the saturation intensity is
\[
I_{s,3'0-40} = 25.3 \text{ W/m}^2 = 2.53 \text{ mW/cm}^2.
\]
A little thought shows that the branching ratio is \( b = b_{\text{out}}/b_{\text{total}} \) where
\[
b_{\text{out}} = 2 \left( C_{3011}^{41} S_{4,1,1/2}^{1/2,7/2,3} \right)^2 + 2 \left( C_{3011}^{41} S_{3,1,1/2}^{1/2,7/2,3} \right)^2
\]
and
\[
b_{\text{total}} = b_{\text{out}} + \left( C_{3010}^{40} S_{4,1,1/2}^{1/2,7/2,3} \right)^2.
\]
We find \( b_{\text{out}} = 1/21, b_{\text{total}} = 1/14, \) and \( b = 2/3. \) The depumping rate is therefore
\[
r_{R,\text{out}} = \frac{\gamma^3}{12\Delta \nu_3^2 I_{s,3'0-40}} I
\]

In order to understand how good the polarization should be to achieve this depumping rate let us assume that the electric field of the pump beam is
\[
\mathcal{E} = \mathcal{E}_0 e_0 + \mathcal{E}_1 e_1
\]
with \( |\mathcal{E}_1| \ll |\mathcal{E}_0|. \) The circularly polarized component drives the transition \( |4,0\rangle \rightarrow |4,1\rangle \) leading to an excited state population
\[
\rho_{4'1,4'1} \approx \frac{I_1}{2I_{s,1}}
\]

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with $I_{s,1}$ the saturation intensity for the $|4,0\rangle \rightarrow |4,1\rangle$ transition which is

$$I_{s,4'1-40} = \frac{c_0 \hbar^2 \gamma^2}{4d_{4'1,40}^2}.$$

The matrix element is

$$d_{4'1,40} = -\frac{C_{4111}^{41}}{\sqrt{2 \times 4 + 1}} \sqrt{(2 \times 4 + 1)(2 \times 4 + 1)} S_{41,1,1,1/2}^{1/2,7/2,4} (6p_{1/2}||r||6s_{1/2})$$

and the saturation intensity is

$$I_{s,4'1-40} = 40.4 \text{ W/m}^2 = 4.04 \text{ mW/cm}^2.$$

The Raman branching ratio is $b = b_{\text{out}}/b_{\text{total}}$ where

$$b_{\text{out}} = \left[ (C_{4110}^{41})^2 + (C_{4111}^{42})^2 \right] \left( S_{4,1,1,1/2}^{1/2,7/2,4} \right)^2 + \left[ (C_{4110}^{30})^2 + (C_{4110}^{31})^2 + (C_{4111}^{32})^2 \right] \left( S_{3,1,1,1/2}^{1/2,7/2,4} \right)^2$$

and

$$b_{\text{total}} = b_{\text{out}} + \left( C_{4111-1}^{41} C_{4111}^{1/2,7/2,4} \right)^2.$$

We find $b_{\text{out}} = 19/432$, $b_{\text{total}} = 1/18$, and $b = 19/24$. The depumping rate due to polarization errors is

$$r_{\text{pol, out}} = b_{\text{out}} \rho_{4'1,41} = \frac{19}{48} \frac{I_1}{I_{s,4'1-40}}.$$

Setting $r_{\text{pol, out}} = r_{\text{R, out}}$ gives

$$\frac{I_1}{I} = \frac{4 \gamma^2 I_{s,4'1-40}}{19 \Delta^2 I_{s,3'0-40}^{4'0-40}} = 5.2 \times 10^{-6}.$$

It is very difficult to reach this level of polarization purity so in practice the optical depumping rate will be set by residual polarization errors.

**Depumping rate with a magnetic bias field**

This number can be relaxed when we pump with a magnetic bias field since the Zeeman shift of $|4,1\rangle$ relative to $|4,0\rangle$ will suppress the unwanted depumping. There is a tradeoff since the Zeeman field also mixes $|4,0\rangle$ and $|3,0\rangle$ which increases the Raman rate from the $\pi$ polarized light. The modified polarization depumping rate is

$$r_{\text{pol, out}}(B) = \frac{r_{\text{pol, out}}(0)}{1 + 4 \frac{\Delta(B)^2}{\gamma^2}}$$

with $B$ the bias magnetic field. The Zeeman shift of $|6p_{1/2},4,1\rangle$ is $\hbar \Delta(B) = \mu_B g_F 6p_{1/2} B$ with the Landé factor $g_F 6p_{1/2} = 1/12$. The modified Raman depumping rate due to excited state mixing is

$$r_{\text{R, out}}(B) = r_{\text{R, out}}(0) + \gamma \rho_{4'0,40}(B)$$
where the population in \(|4',0\rangle\) due to Zeeman mixing is

\[
\rho_{4'0,4'0}(B) = \frac{I}{2I_s(B)}
\]

and

\[
I_s(B) = I_{s,3'0-40} \frac{\hbar^2 \Delta_{4'3'}^2}{|\langle 3',0|\mathcal{H}_Z|4',0\rangle|^2}.
\]

The Zeeman matrix element is \(\mu_BB/3\) and

\[
r_{R,\text{out}}(B) = r_{R,\text{out}}(0) \left( 1 + \frac{2\mu_B^2B^2}{3\hbar^2\gamma^2} \right).
\]

The total depumping rate at finite magnetic field is thus

\[
r_{\text{out}}(B) = r_{R,\text{out}}(0) \left( 1 + \frac{2\mu_B^2B^2}{3\hbar^2\gamma^2} \right) + r_{\text{pol,\text{out}}}(0) \frac{1}{1 + \frac{\mu_B^2B^2}{3\hbar^2\gamma^2}}.
\]

We see that the coefficient of the Raman rate is larger than of the polarization rate. Thus if we have good polarization purity the optimum is to work at very small \(B\). If the polarization rate is too large then the optimum will be at finite \(B\). Typical depumping time constants observed in the Saffman lab are about 10 ms. If we set \(I = I_{s,44-55}\) then we get a total depumping rate of \(r_{\text{out}}(0) = 10^3\) with \(I_1 \sim 0.0003I_{s,44-55}\), so the 10 ms implies good polarization purity.

For pump intensities of \(40 \times I_{s,44-55}\) to get unit saturation of the pumping rate, and the same polarization purity, the depumping is dominated by the polarization rate and we get \(r_{\text{out}}(0) \sim 38000\). This can be improved only slightly at finite magnetic field. Thus one should not use such high intensities.

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Pumping fidelity estimate

Without solving the full set of multilevel density matrix equations we can estimate the pumping purity by starting with a mixed state which has probability $P_{\text{in}}$ to be in $|4, 0\rangle$ and $P_{\text{out}}$ to be in $|4, 1\rangle, |4, -1\rangle, |3, 1\rangle, |3, 0\rangle, |3, -1\rangle$. We then equate the rates into and out of $|4, 0\rangle$ after one photon scattering event to find the equilibrium ratio $P_{\text{out}}/P_{\text{in}}$. Let’s assume $I_1/I_{894} = 0.0003$ as estimated above and take $B = 0$ for simplicity. The depumping rate is

$$r_{dp} = P_{\text{in}}(r_{R, out} + r_{\text{pol, out}}) = P_{\text{in}}\left(\frac{\gamma_{6p_{1/2}}^3 I_{894}}{12\Delta^2_{4'3'}} I_{s,6p_{1/2},3'0-40} + \gamma_{6p_{1/2}}^3 \frac{19}{48} I_{s,6p_{1/2},4'1-40}\right) = P_{\text{in}} r_{\text{out}}. \quad (13.2)$$

The pumping rate into the target state is $P_{\text{out}}$ times the average pumping rate from each of the 5 states. This assumes the population is evenly distributed among those 5 states which is not correct - this is just an estimate. We can neglect $|3, 0\rangle$ since with $\pi$ polarized repumping we couple to $|4', 0\rangle$ which does not decay back to $|4, 0\rangle$. Thus it takes at least two cycles to repump these atoms so using $\pi$ polarized repump light may not be optimal.

The states $|3, \pm 1\rangle$ are excited to $|6p_{3/2}, 4, \pm 1\rangle$. These states decay into the target state with branching ratio $b = 7/24$. The states $|4, \pm 1\rangle$ are excited to $|6p_{1/2}, 4, \pm 1\rangle$. These states decay into the target state with branching ratio $b = 5/24$. The pumping rate into the target state is thus

$$r_p = P_{\text{out}}\left(\frac{1}{2} \frac{\gamma_{6p_{3/2}}^3 I_{852}}{48 I_{s,6p_{3/2},4'1-31}} + \frac{1}{2} \frac{\gamma_{6p_{1/2}}^3 I_{894}}{48 I_{s,6p_{1/2},4'1-41}}\right) = P_{\text{out}} r_{\text{in}}. \quad (13.3)$$

We include saturation in the pump rate, but not in the depump rate where it is negligible for relevant intensities.

Equating the two rates gives

$$\frac{P_{\text{out}}}{P_{\text{in}}} = \frac{r_{\text{out}}}{r_{\text{in}}}. \quad \text{Equation}$$

The various saturation intensities are

- $I_{s,6p_{1/2},3'0-40} = 25.3$,
- $I_{s,6p_{1/2},4'1-40} = 40.4$,
- $I_{s,6p_{1/2},4'1-31} = 49.8$,
- $I_{s,6p_{1/2},4'1-41} = 404$.

all in units of W/m². Representative fidelity estimates are in Fig. 13.4.

Rate equation model

A more accurate calculation is based on a rate equation treatment. This calculates the rate of pumping out of and into each ground state, but neglects coherences. This is much more
13.3 Multilevel density matrix equations

A complete description of optical pumping when multiple atomic states are involved requires a density matrix treatment. As we have seen a two-level atom interacting with a radiation bath is described by a master equation in Lindblad form

\[ \frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] - \frac{\gamma}{2} \left( \hat{\sigma}^{\dagger} \hat{\sigma} \hat{\rho} + \hat{\rho} \hat{\sigma}^{\dagger} \hat{\sigma} - 2 \hat{\sigma} \hat{\sigma}^{\dagger} \hat{\rho} - 2 \hat{\rho} \hat{\sigma}^{\dagger} \hat{\sigma} \right). \]  
(13.4)

The Lindblad operators are \( \hat{L} = \sqrt{\gamma} \hat{\sigma} \) with \( \hat{\sigma}^{\dagger} = |e\rangle \langle g| \) a raising operator from \( |g\rangle \rightarrow |e\rangle \), i.e. \( \hat{\sigma}^{\dagger} |g\rangle = |e\rangle \) and \( \gamma \) is the population decay rate from \( |e\rangle \rightarrow |g\rangle \). This form of the master equation is valid for a single atom. For a many atom ensemble collisions also cause population redistribution and coherence decay. To describe these effects additional terms need to be added to the right hand side.

We can generalize the two-level master equation to \( N \) atomic levels \( |i\rangle, i = 1, \ldots, N \) interacting with a set of \( M \) fields \( E_j, \ j = 1, \ldots, M \). The density matrix evolution satisfies

\[ \frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] - \frac{1}{2} \sum_{i,j=1}^{N} \sum_{k,l=1}^{M} \gamma_{k\leftarrow i}^{l\rightarrow j} \left( \hat{\sigma}^{\dagger}_{k\leftarrow i} \hat{\sigma}_{lj} \hat{\rho} + \hat{\rho} \hat{\sigma}_{kl}^{\dagger} \hat{\sigma}_{lj} - 2 \hat{\sigma}_{lj} \hat{\rho} \hat{\sigma}_{kl}^{\dagger} - 2 \hat{\rho} \hat{\sigma}_{kl}^{\dagger} \hat{\sigma}_{lj} \right). \]
(13.5)

Figure 13.5: Estimate of \( \frac{E_{\text{out}}}{E_{\text{in}}} \) for polarization error of 0.001 and 0.003 using a rate equation model and an integration time of 30 µs.
In this equation we divide the atomic state space into $N_g$ ground state levels and $N_e$ excited levels and assume that spontaneous emission only occurs from levels labeled with $i$ or $j$ to levels labeled with $k$ or $l$. Thus $\sigma_{ki} = \sigma_{ik} = |i\rangle\langle k|$ is a raising operator and $\sigma_{lj} = |l\rangle\langle j|$ is a lowering operator. The decay factor is $\gamma_{k-i} = \frac{\gamma_{k-i} \gamma_{k-j}}{\sqrt{\gamma_{k-i} \gamma_{k-j}}}$ where the population decay rate from $i \rightarrow k$ is $\gamma_{k-i}$ and the vectorial decay constant is $\gamma_{k-i} = \gamma_{k-i} e_{ki}$ with $e_{ki}$ a spherical unit vector connecting states $|i\rangle$ and $|k\rangle$. For example in a hyperfine basis $|i\rangle = |a_i, f_i, m_i\rangle$, $|k\rangle = |a_k, f_k, m_k\rangle$ with $a_i, a_k$ additional quantum numbers and $f_i, m_i, f_k, m_k$ the total coupled angular momenta and angular momentum projections. The decay unit vectors in a spherical basis are then $e_{ki} = e_{g=m-m_k}$, and $e_q \cdot e_{q'} = \delta_{qq'}$. This formulation of the multilevel Lindblad equation can be derived using standard methods\(^3\).

Equation (13.5) accounts for the decay of population and coherence from excited states as well as transfer of coherence from a pair of excited states to a pair of ground states. This process turns out to be important in sub-Doppler laser cooling. Coherence transfer by spontaneous emission was first described by Barrat and Cohen-Tannoudji in 1961\(^4\). Several recent books treat multilevel atomic dynamics and optical pumping in great detail\(^4\).

It is instructive to evaluate (13.5) for a specific density matrix element $\hat{\rho}_{mn}$. Let us first rewrite (13.5) in a more convenient form

$$
\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] - \frac{1}{2} \sum_{i,j=1}^{N_e} \sum_{k=1}^{N_g} \gamma_{ki}^* |i\rangle\langle j| \hat{\rho} + \hat{\rho}|i\rangle\langle j| + \frac{1}{2} \sum_{i,j=1}^{N_e} \sum_{k,l=1}^{N_g} \gamma_{ki} \rho_{ji} |l\rangle\langle k|.
$$

(13.6)

Consider now the three cases: $(m,n)$ excited states, $(m,n)$ one excited and one ground state, and $(m,n)$ ground states. When $(m,n)$ are excited states we find

$$
\frac{d\hat{\rho}_{mn}}{dt} = -\frac{i}{\hbar} \langle m| [\hat{H}, \hat{\rho}] |n\rangle - \frac{1}{2} \sum_{j=1}^{N_g} \sum_{k=1}^{N_e} \gamma_{km} \gamma_{jn}^* \hat{\rho}_{mn} - \frac{1}{2} \sum_{i,j=1}^{N_e} \sum_{k=1}^{N_g} \gamma_{ki} \rho_{ji} \hat{\rho}_{mn}.
$$

If we specialize to a single excited hyperfine level $f_m = f_j = f_i = f_n$ then $\gamma_{k-m} \cdot \gamma_{k-j} = \gamma_{k-m} \gamma_{k-j} \delta_{jm}$, $\gamma_{k-i} \gamma_{k-n} = \gamma_{k-i} \gamma_{k-n} \delta_{in}$, and

$$
\frac{d\hat{\rho}_{mn}}{dt} = -\frac{i}{\hbar} \langle m| [\hat{H}, \hat{\rho}] |n\rangle - \frac{1}{2} \sum_{k=1}^{N_g} (\gamma_{k-m} + \gamma_{k-n}) \hat{\rho}_{mn} \quad (m,n) \text{ excited states}.
$$

When $(m,n)$ are an excited and a ground state we find

$$
\frac{d\hat{\rho}_{mn}}{dt} = -\frac{i}{\hbar} \langle m| [\hat{H}, \hat{\rho}] |n\rangle - \frac{1}{2} \sum_{j=1}^{N_g} \sum_{k=1}^{N_e} \gamma_{km} \gamma_{jn}^* \hat{\rho}_{mn}.
$$

Specializing again to a single excited hyperfine level this reduces to

$$
\frac{d\hat{\rho}_{mn}}{dt} = -\frac{i}{\hbar} \langle m| [\hat{H}, \hat{\rho}] |n\rangle - \frac{1}{2} \sum_{k=1}^{N_g} \gamma_{k-m} \hat{\rho}_{mn} \quad (m,n) \text{ (excited, ground) states}.
$$

\(^2\)This can be generalized in a straightforward way to several groups of levels decaying to more than one group of lower levels.

\(^3\)see for example Z. Ficek and S. Swain, *Quantum interference and coherence*, Springer (2005).

Finally when \((m, n)\) are both ground states we find
\[
\frac{d\hat{\rho}_{mn}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}]|m, n\rangle + \sum_{i,j=1}^{N_e} \gamma^m_{ni} \hat{\rho}_{ji} \quad (m, n) \text{ ground states.} \tag{13.7}
\]
When \(m = n\) and there is a single excited hyperfine level \(\gamma^m_{ni} \rightarrow \gamma_{m-j}\delta_{ij}\) and we get for the ground state population
\[
\frac{d\hat{\rho}_{mm}}{dt} = -\frac{i}{\hbar} \langle m | [\hat{H}, \hat{\rho}] | m \rangle + \sum_{j=1}^{N_e} \gamma_{m-j}\hat{\rho}_{jj}.
\]
When \(m \neq n\) and there is a single excited hyperfine level \(\gamma^m_{ni} \rightarrow \sqrt{\gamma_{ni-i} \gamma_{m-j}\delta_{mi-mn, mj-mm}}\) and the second term in (13.7) reduces to three possible terms corresponding to emission of a \(\pi, \sigma_+, \text{ or } \sigma_-\) photon. These three cases are the transfer of coherence to the ground state by spontaneous emission introduced by Barrat and Cohen-Tannoudji.

Two-level example

Let’s verify that (13.4) reproduces known results for a two-level atom (levels \(|g\rangle, |e\rangle\)) interacting with a single field \(E\). We have
\[
\hat{H} = U_g |g\rangle\langle g| + U_e |e\rangle\langle e| - E\hat{d} \\
= U_g |g\rangle\langle g| + U_e |e\rangle\langle e| - E(|g\rangle\langle g| + |e\rangle\langle e|)\hat{d} (|g\rangle\langle g| + |e\rangle\langle e|) \\
= U_g |g\rangle\langle g| + U_e |e\rangle\langle e| - Ed_{eg}|e\rangle\langle g| - Ed_{ge}|g\rangle\langle e|
\]
where \(d_{eg} = \langle e|\hat{d}| g \rangle\) and we have assumed \(|g\rangle, |e\rangle\) are states of definite parity so \(|g|\hat{d}| g \rangle = |e|\hat{d}| e \rangle = 0\). Writing formally \(\hat{\rho} = \sum_{i,j} \rho_{ij} |j\rangle\langle i|\) \(|i\rangle = \rho_{gg}|g\rangle\langle g| + \rho_{ee}|e\rangle\langle e| + \rho_{ge}|g\rangle\langle e| + \rho_{eg}|e\rangle\langle g|\) the commutator in (13.4) evaluates to give
\[
\begin{align*}
\frac{i\hbar}{2} \frac{d\rho_{gg}}{dt} &= E(d_{eg}\rho_{ge} - d_{ge}\rho_{eg}) \\
\frac{i\hbar}{2} \frac{d\rho_{ee}}{dt} &= -E(d_{eg}\rho_{ge} - d_{ge}\rho_{eg}) \\
\frac{i\hbar}{2} \frac{d\rho_{eg}}{dt} &= \hbar \omega_a \rho_{eg} + Ed_{eg}(\rho_{ee} - \rho_{gg}) \\
\frac{i\hbar}{2} \frac{d\rho_{ge}}{dt} &= -\hbar \omega_a \rho_{ge} - Ed_{ge}(\rho_{ee} - \rho_{gg})
\end{align*}
\]
where we have inserted \(\hbar \omega_a = U_e - U_g\).

Using \(\gamma_{gg} = \gamma_{ee} = \gamma_{ge} = 0\) and \(\gamma_{eg} = \gamma\) the second term on the right hand side of (13.5) evaluates to
\[
-\frac{i\hbar}{2} \left(\hat{\sigma}_{eg} \hat{\sigma}_{ge} \hat{\rho} + \hat{\rho} \hat{\sigma}_{eg} \hat{\sigma}_{ge} - 2\hat{\sigma}_{ge} \hat{\sigma}_{eg} \hat{\rho}\right)
= -\frac{i\hbar}{2} \left(|e\rangle\langle e|\hat{\rho} + \hat{\rho} |e\rangle\langle e| - 2|g\rangle\langle e|\hat{\rho}|g\rangle\langle e|\right)
= -\frac{i\hbar}{2} \left[2\rho_{ee} \langle e|\langle e| - |g\rangle\langle g|\hat{\rho} + \rho_{eg} |e\rangle\langle g| + \rho_{ge} |g\rangle\langle e|\right].
\]
Combining with the previous equations we get

\[
\begin{align*}
    i\hbar \frac{d\rho_{gg}}{dt} &= E(d_{eg}\rho_{ge} - d_{ge}\rho_{eg}) + i\hbar \gamma \rho_{ee} \\
    i\hbar \frac{d\rho_{ee}}{dt} &= -E(d_{eg}\rho_{ge} - d_{ge}\rho_{eg}) - i\hbar \gamma \rho_{ee} \\
    i\hbar \frac{d\rho_{eg}}{dt} &= -i\frac{\hbar \gamma}{2} \rho_{eg} + \hbar \omega_a \rho_{eg} + Ed_{eg}(\rho_{ee} - \rho_{gg}) \\
    i\hbar \frac{d\rho_{ge}}{dt} &= -i\frac{\hbar \gamma}{2} \rho_{ge} - \hbar \omega_a \rho_{ge} - Ed_{ge}(\rho_{ee} - \rho_{gg}).
\end{align*}
\]

We can easily verify that these equations are the same as (9.26) with the identifications \(T_1 = 1/\gamma\) and \(T_2 = 2/\gamma\).

**Multiple levels with near resonant fields**

In the more general situation of \(N\) atomic levels interacting with \(M\) fields the equations of motion are cumbersome. Explicit expressions for multifrequency coupling between ground and excited electronic states, each with multiple Zeeman sublevels, can be found in many papers[43, 44, 45, 46]. A particular feature is that coherences can be generated between levels that are not directly coupled by driving fields. For example if levels 1, 2 are coupled by \(E_{21}\) and levels 2, 3 are coupled by \(E_{32}\) we will get nonzero \(\rho_{31}\) even though there is no field \(E_{31}\).

As an example consider the situation shown in figure 13.6. Neighboring atomic levels \(|i\rangle, |j\rangle\) are coupled by a field \(E_{ji}\) with frequency \(\omega_{ji}\) that is detuned by \(\Delta_{ji} = \omega_{ji} - \frac{U_j - U_i}{\hbar}\). We assume, in the spirit of the RWA, that \(E_{ji}\) does not couple levels \(|i'\rangle, |j'\rangle\) due to the larger detuning involved. Let us suppose first that the levels in Fig. 13.6 are all radiatively stable over time scales of interest. This could correspond to a set of hyperfine ground levels. Then all \(\gamma_{ij} = 0\) and we only have to account for the coherent evolution \(i\hbar \frac{d\rho}{dt} = [\hat{H}, \hat{\rho}]\) driven by the external fields. Let field \(E_i\) with frequency \(\omega_{i,i-1}\) couple levels \(|i\rangle, |i-1\rangle\) so the Hamiltonian
is
\[ \hat{H} = \sum_{j=1}^{N} U_j |j\rangle \langle j| - \sum_{j=2}^{N} (E_j d_j |j\rangle \langle j-1| + E_j^* d_j^* |j-1\rangle \langle j|) \] (13.8)

with \( d_j = \langle j| \hat{d} |j-1\rangle \). We find
\[ i\hbar \frac{d\rho}{dt} = \sum_{i,j=1}^{N} U_i (\rho_{ij} |i\rangle \langle j| - \rho_{ji} |j\rangle \langle i|) \]
\[ + \sum_{j=1}^{N} \sum_{i=2}^{N} (E_i d_i \rho_{ji} |j\rangle \langle i-1| - E_i^* d_i^* \rho_{ji} |i-1\rangle \langle j|) \]
\[ + \sum_{j=1}^{N} \sum_{i=2}^{N} (E_i^* d_i^* \rho_{ji-1} |j\rangle \langle i| - E_i d_i \rho_{i-1,j} |i\rangle \langle j|). \]

Taking matrix elements by operating with \( \langle i| \ldots |j\rangle \) we get for the populations
\[ i\hbar \frac{d\rho_{jj}}{dt} = E_{j+1} (d_{j+1} \rho_{j+1,j} - d_{j+1}^* \rho_{j+1,j}) + E_j (d_j^* \rho_{j-1,j} - d_j \rho_{j-1,j}), \]
and for the coherences
\[ i\hbar \frac{d\rho_{jk}}{dt} = (U_j - U_k) \rho_{jk} + E_k d_k^* \rho_{j,k-1} - E_j d_j \rho_{j-1,k} + E_{k+1} d_{k+1} \rho_{j,k+1} - E_{j+1} d_{j+1}^* \rho_{j+1,k}. \]

When evaluating these equations we must keep in mind that the indices of \( \rho_{ij} \) are bounded by \( 1 \leq i,j \leq N \) and the indices of \( E_i, d_i \) are bounded by \( 2 \leq i \leq N \). To proceed write \( E_j = \frac{E_j}{2} e^{-i\omega_{j,j-1} t} + \frac{E_j^*}{2} e^{i\omega_{j,j-1} t} \) and \( \rho_{jk} = \tilde{\rho}_{jk} e^{-i\eta_{jk} t} \). The coherences rotate with the near resonant applied fields. This suggests the choice \( q_{jk} = \sum_{l=2}^{j} \omega_{l,l-1} - \sum_{l=2}^{k} \omega_{l,l-1} = (-1)^{\text{sign}(k-j+1)} \sum_{l=\min(j,k)}^{j}\omega_{l,l-1}. \) Thus, for example, when \( k = j - 1 \) we get \( q_{jk} = \omega_{j,j-1} \) which is the frequency driving the coherence \( \rho_{j,j-1} \). With these definitions the density matrix equations for the populations become
\[ \frac{d\rho_{jj}}{dt} = -i \frac{1}{2\hbar} \left( E_{j+1} e^{-i\omega_{j,j+1} t} + E_{j+1}^* e^{i\omega_{j,j+1} t} \right) \left( d_{j+1} \tilde{\rho}_{j,j+1} e^{-i\eta_{j,j+1} t} - d_{j+1}^* \tilde{\rho}_{j,j+1}^* e^{i\eta_{j,j+1} t} \right) \]
\[ -i \frac{1}{2\hbar} \left( E_j e^{-i\omega_{j,j-1} t} + E_j^* e^{i\omega_{j,j-1} t} \right) \left( d_j^* \tilde{\rho}_{j-1,j} e^{-i\eta_{j,j-1} t} - d_j \tilde{\rho}_{j-1,j}^* e^{i\eta_{j,j-1} t} \right), \]
\[ \simeq \frac{i}{2} \left( \Omega_{j+1}^* \tilde{\rho}_{j+1,j} - \Omega_{j+1} \tilde{\rho}_{j+1,j}^* \right) + \frac{i}{2} \left( \Omega_j \tilde{\rho}_{j-1,j}^* - \Omega_j^* \tilde{\rho}_{j-1,j} \right). \] (13.9)

The last line is valid in the limit of the RWA and \( \Omega_j = d_j \epsilon_j/\hbar \). The equations for the
coherences are
\[
\frac{d \rho_{jk}}{dt} = \left[ i q_{jk} - \frac{i}{\hbar} (U_j - U_k) \right] \tilde{\rho}_{jk} \\
- \frac{i}{2\hbar} \left( \mathcal{E}_k e^{-i\omega_{k,k-1}t} + \mathcal{E}_k^* e^{i\omega_{k,k-1}t} \right) d_{k,k-1}^* \tilde{\rho}_{jk,k-1} e^{-i q_{j,k-1}t} e^{i q_{j,k-1}t} \\
+ \frac{i}{2\hbar} \left( \mathcal{E}_j e^{-i\omega_{j,j-1}t} + \mathcal{E}_j^* e^{i\omega_{j,j-1}t} \right) d_{j,j-1}^* \tilde{\rho}_{j,j-1,k} e^{-i q_{j,j-1}t} e^{i q_{j,j-1}t} \\
- \frac{i}{2\hbar} \left( \mathcal{E}_{j+1} e^{-i\omega_{j+1,k-1}t} + \mathcal{E}_{j+1}^* e^{i\omega_{j+1,k-1}t} \right) d_{j,j+1}^* \tilde{\rho}_{j+1,k} e^{-i q_{j+1,k-1}t} e^{i q_{j+1,k}t} \\
+ \frac{i}{2\hbar} \left( \mathcal{E}_{j+1} e^{-i\omega_{j+1,j}t} + \mathcal{E}_{j+1}^* e^{i\omega_{j+1,j}t} \right) d_{j,j+1}^* \tilde{\rho}_{j+1,j} e^{-i q_{j+1,j}t} e^{i q_{j+1,j}t}.
\]

With the detunings \( \Delta_{jk} = q_{jk} - \frac{U_j - U_k}{\hbar} \), using the RWA and assuming \( j > k \) we arrive at
\[
\frac{d \rho_{jk}}{dt} \approx i \Delta_{jk} \tilde{\rho}_{jk} + \frac{i}{2} \left( \Omega_j \tilde{\rho}_{j-1,k} - \Omega_k^* \tilde{\rho}_{j,k-1} - \Omega_{k+1} \tilde{\rho}_{j,k+1} + \Omega_{j+1}^* \tilde{\rho}_{j+1,k} \right). \quad (13.10)
\]

Equations (13.9,13.10) are the multilevel generalizations of the master equation with fields coupling neighboring levels in the RWA, and without spontaneous decay. It can be checked that when there are two levels and one field (13.9,13.10) agree with Eqs. (9.28).

Let’s write out these equations for a four level atom with states \( |1\rangle, |2\rangle, |3\rangle, |4\rangle \) and three Rabi couplings \( \Omega_2, \Omega_3, \Omega_4 \). We find

\[
\begin{align*}
\frac{d \rho_{11}}{dt} &= \frac{i}{2} (\Omega_2^* \tilde{\rho}_{21} - \Omega_2 \tilde{\rho}_{21}^*), \quad (13.11a) \\
\frac{d \rho_{22}}{dt} &= \frac{i}{2} (\Omega_3^* \tilde{\rho}_{32} - \Omega_3 \tilde{\rho}_{32}^*), \quad \frac{i}{2} (\Omega_2^* \tilde{\rho}_{21} - \Omega_2 \tilde{\rho}_{21}^*), \quad (13.11b) \\
\frac{d \rho_{33}}{dt} &= \frac{i}{2} (\Omega_4^* \tilde{\rho}_{43} - \Omega_4 \tilde{\rho}_{43}^*), \quad \frac{i}{2} (\Omega_3^* \tilde{\rho}_{32} - \Omega_3 \tilde{\rho}_{32}^*), \quad (13.11c) \\
\frac{d \rho_{44}}{dt} &= \frac{i}{2} (\Omega_4^* \tilde{\rho}_{43} - \Omega_4 \tilde{\rho}_{43}^*), \quad (13.11d) \\
\frac{d \tilde{\rho}_{21}}{dt} &= i \Delta_{21} \tilde{\rho}_{21} + \frac{i}{2} [\Omega_2 (\rho_{11} - \rho_{22}) + \Omega_3^* \tilde{\rho}_{31}], \quad (13.11e) \\
\frac{d \tilde{\rho}_{31}}{dt} &= i \Delta_{31} \tilde{\rho}_{31} + \frac{i}{2} [\Omega_3 \tilde{\rho}_{21} - \Omega_2 \tilde{\rho}_{32} + \Omega_4^* \tilde{\rho}_{41}], \quad (13.11f) \\
\frac{d \tilde{\rho}_{32}}{dt} &= i \Delta_{32} \tilde{\rho}_{32} + \frac{i}{2} [\Omega_3 (\rho_{22} - \rho_{33}) - \Omega_2^* \tilde{\rho}_{31} + \Omega_4^* \tilde{\rho}_{42}], \quad (13.11g) \\
\frac{d \tilde{\rho}_{41}}{dt} &= i \Delta_{41} \tilde{\rho}_{41} + \frac{i}{2} [\Omega_4 \tilde{\rho}_{31} - \Omega_2^* \tilde{\rho}_{42}], \quad (13.11h) \\
\frac{d \tilde{\rho}_{42}}{dt} &= i \Delta_{42} \tilde{\rho}_{42} + \frac{i}{2} [\Omega_4 \rho_{32} - \Omega_2^* \tilde{\rho}_{41} - \Omega_3 \tilde{\rho}_{43}], \quad (13.11i) \\
\frac{d \tilde{\rho}_{43}}{dt} &= i \Delta_{43} \tilde{\rho}_{43} + \frac{i}{2} [\Omega_4 (\rho_{33} - \rho_{44}) - \Omega_4^* \tilde{\rho}_{42}]. \quad (13.11j)
\end{align*}
\]

Numerical solution of these ten coupled equations describes the dynamics of the populations and coherences. Since we are considering a situation with no spontaneous emission the
Figure 13.7: Numerical solution for populations in a four level system using Schrödinger equations (13.12) (left) and density matrix equations (13.11) (right). Parameters $\Omega_2 = \Omega_3 = \Omega_4 = 2\pi$, $\Delta_2 = 0.5$, $\Delta_3 = 0.6$, $\Delta_4 = .1$ and all population starts in level 1. The detunings in the density matrix solutions are $\Delta_{21} = \Delta_2$, $\Delta_{31} = \Delta_2 + \Delta_3$, $\Delta_{32} = \Delta_3$, $\Delta_{41} = \Delta_2 + \Delta_3 + \Delta_4$, $\Delta_{42} = \Delta_3 + \Delta_4$, $\Delta_{43} = \Delta_4$. The horizontal lines show the calculated sums of all populations.

Dynamics can also be found by solving the following four coupled Schrödinger equations

\[
\begin{align*}
\frac{dc_1}{dt} &= \frac{i}{2} \left( \Omega_2^* c_2 e^{i\Delta_2 t} \right) \\
\frac{dc_2}{dt} &= \frac{i}{2} \left( \Omega_2 c_1 e^{-i\Delta_2 t} + \Omega_3^* c_3 e^{i\Delta_3 t} \right) \\
\frac{dc_3}{dt} &= \frac{i}{2} \left( \Omega_3 c_2 e^{-i\Delta_3 t} + \Omega_4^* c_4 e^{i\Delta_4 t} \right) \\
\frac{dc_4}{dt} &= \frac{i}{2} \left( \Omega_4 c_3 e^{-i\Delta_4 t} \right)
\end{align*}
\]

Comparison of the numerical solutions in Fig. 13.7 verifies the consistency of Eqs. (13.12,13.11).

Including spontaneous emission

Using the RWA approximation we have found the equations

\[
\begin{align*}
\frac{d\rho_{jj}}{dt} &= \frac{i}{2} \left( \Omega_{j+1}^* \rho_{j+1,j} - \Omega_{j+1}\rho_{j,j+1}^* \right) + \frac{i}{2} \left( \Omega_j\rho_{j,j-1}^* - \Omega_{j+1}\rho_{j,j-1}^* \right), \\
\frac{d\rho_{jk}}{dt} &= \frac{i}{2} \left( \Omega_j\rho_{j,j-1,k} - \Omega_k\rho_{j,j,k-1} - \Omega_{k+1}\rho_{j,k+1} + \Omega_{j+1}\rho_{j+1,k} \right)
\end{align*}
\]

with $j > k$ in the second equation, $\rho_{jk} = \rho_{jk} e^{-i\omega_{jk} t}$, $q_{jk} = (-1)^{\text{sign}(k+1-j)} \frac{\omega_{l,l-1}}{\min(j,k+1)} \sum_{l=\min(j,k+1)}^{\max(j,k+1)} \omega_{l,l-1}$, $\omega_{l,l-1}$ is the applied frequency coupling $|l-1\rangle \rightarrow |l\rangle$ and $\Delta_{jk} = q_{jk} - \frac{U_{j}-U_{k}}{\hbar}$.

When spontaneous emission is present we must also include the second term on the right hand side of (13.5). We can do so by simply calculating the term from its definition which
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\[
\frac{d\rho_{jj}}{dt} = -j\sum_{k=j+1}^{N} \gamma_{jk} \rho_{kk} + \frac{i}{2} \left( \Omega_{j+1}^{*} \tilde{\rho}_{j+1,j} - \Omega_{j+1} \tilde{\rho}_{j,j+1} \right) + \frac{i}{2} \left( \Omega_{j}^{*} \tilde{\rho}_{j,j-1} - \Omega_{j} \tilde{\rho}_{j,j-1} \right),
\]

\[
\frac{d\tilde{\rho}_{jk}}{dt} = -\frac{1}{2} \left( \sum_{l=j}^{k-1} \gamma_{l-j} + \sum_{l=k}^{N} \gamma_{l-k} \right) \tilde{\rho}_{jk} + \frac{1}{2} \sum_{l=k+1}^{N} \gamma_{k-l} \tilde{\rho}_{jl} + \frac{1}{2} \sum_{l=j+1}^{N} \gamma_{j-l} \tilde{\rho}_{lk} + i \Delta_{jk} \tilde{\rho}_{jk} + \frac{i}{2} \left( \Omega_{j}^{*} \tilde{\rho}_{j-j-1,k} - \Omega_{k}^{*} \tilde{\rho}_{j,j+1,k-1} - \Omega_{k+1}^{*} \tilde{\rho}_{j,j,k-1} + \Omega_{j+1} \tilde{\rho}_{j,j+1,k} \right).
\]

The coefficient \(\gamma_{kl}\) is the population decay rate for \(|k\rangle \rightarrow |l\rangle\) and the state labeling is assumed to be such that the indices increase monotonically with increasing energy so that spontaneous emission always reduces the state index. Thus the radiative lifetime of state \(|k\rangle\) is \(\tau_{k} = \frac{1}{\gamma_{k}} = \left( \sum_{l=1}^{k-1} \gamma_{kl} \right)^{-1}\). Equivalently the FWHM of the absorption profile for a weak beam coupling to the upper level \(|j\rangle\) is \(\gamma_{j}\). Equations (13.13) can be used to study many topics including optical pumping in multi-level atoms.

**Multiple levels with non-resonant fields**

The structure of Eqs. (13.13) is governed by our notation which assumes the levels are numbered towards increasing energy and level \(|j-1\rangle\) is coherently coupled to \(|j\rangle\) by the Rabi frequency \(\Omega_{j}\). These equations can be straightforwardly applied to the case of heterogeneous couplings driven by both microwave and optical fields provided we respect the sign and conjugation symmetries of the terms on the right hand side. Since we have assumed that for each pair of levels only a single applied field gives significant coupling it is possible to go into a rotating frame for each pair of levels and define coherences \(\tilde{\rho}_{jk}\) that have no off-resonant driving terms on the right hand side. Since the independent variable \(t\) does not appear on the right hand side of the equations there is a steady state solution with all coherences equal to zero and all the population in the ground state, or a state which is dark with respect to the applied fields. This corresponds to perfect optical pumping.

When the Rabi frequencies are not sufficiently small compared to the detunings the optical pumping is no longer perfect. In this case \(t\) does appear on the right hand side and in general optical pumping does not lead to all population in a desired state. In order to study the fidelity of an optical pumping process it is necessary to include such off-resonant terms. In many cases of interest it is impractical to include all off-resonant terms since the number of coupled equations becomes very large and the time dependent driving terms oscillate very rapidly which leads to a set of stiff equations. It is therefore necessary to make some physically motivated choices about which terms to keep and which to neglect. Examples of how to do this can be found in the cited book by Happer, Jau, and Walker.

To handle this more general case we need to first establish an efficient notation. Figure 13.8 shows the six detunings \(\Delta_{ijk}\) when two optical frequencies \(\omega_{i}, i = 1,2\) couple three atomic levels \(i, j, k\) with transition frequencies \(\omega_{ij} = (U_{i} - U_{j})/\hbar\). Generalizing to \(N\) atomic
levels and $M$ fields the Hamiltonian (13.8) becomes

$$\hat{H} = \sum_{j=1}^{N} U_{j}|j\rangle\langle j| - \sum_{p=1}^{M} E_{p} \sum_{j,k=1}^{N} d_{jk}|j\rangle\langle k|$$  \hspace{1cm} (13.14)$$

with $d_{jk} = \langle j|\hat{d}|k\rangle$. Taking matrix elements by operating with $\langle k|...|l\rangle$ the coherent evolution of the populations is described by

$$i\hbar \frac{d\rho_{kk}}{dt} = \sum_{p=1}^{M} E_{p} \sum_{j=1}^{N} (d_{jk}\rho_{kj} - d_{kj}\rho_{jk}),$$

and for the coherences

$$i\hbar \frac{d\rho_{kl}}{dt} = (U_{k} - U_{l})\rho_{kl} + \sum_{p=1}^{M} E_{p} \sum_{i} (\rho_{ki}d_{it} - d_{ki}\rho_{it}).$$

To proceed write $E_{p} = \frac{\epsilon_{p}}{2} e^{-i\omega_{p}t} + \frac{\epsilon_{p}^{*}}{2} e^{i\omega_{p}t}$ and $\rho_{jk} = \tilde{\rho}_{jk} e^{-i\omega_{jk}t}$. The relation $\rho_{jk} = \rho_{kj}^{*}$ implies that $\tilde{\rho}_{jk} = \tilde{\rho}_{kj}^{*}$ and $q_{jk} = -q_{kj}$.

The equations of motion for the populations become

$$\frac{d\rho_{kk}}{dt} = -\frac{i}{2\hbar} \sum_{p} \left( \mathcal{E}_{p} e^{-i\omega_{p}t} + \mathcal{E}_{p}^{*} e^{i\omega_{p}t} \right) \sum_{j} \left( d_{jk}\tilde{\rho}_{kj} e^{-i\omega_{jk}t} - d_{kj}\tilde{\rho}_{jk} e^{-i\omega_{jk}t} \right)$$

$$= -\frac{i}{2\hbar} \sum_{pj} \mathcal{E}_{p} (d_{jk}\tilde{\rho}_{kj} e^{-i(\omega_{p}+q_{jk})t} - d_{kj}\tilde{\rho}_{jk} e^{-i(\omega_{p}+q_{jk})t}) + \mathcal{E}_{p}^{*} (d_{jk}\tilde{\rho}_{kj} e^{-i(\omega_{p}-q_{jk})t} - d_{kj}\tilde{\rho}_{jk} e^{-i(\omega_{p}-q_{jk})t})$$

$$= -\frac{i}{2\hbar} \sum_{pj} \mathcal{E}_{p} (d_{jk}\tilde{\rho}_{kj} e^{-i(\omega_{p}+q_{jk})t} - d_{kj}\tilde{\rho}_{jk} e^{-i(\omega_{p}-q_{jk})t}) + \mathcal{E}_{p}^{*} (d_{jk}\tilde{\rho}_{kj} e^{-i(\omega_{p}+q_{jk})t} - d_{kj}\tilde{\rho}_{jk} e^{i(\omega_{p}+q_{jk})t}).$$

In order to separate out the nonresonant terms we divide the sums into $\sum'_{j} \equiv \sum_{j=1}^{k-1}$ and $\sum''_{j} \equiv \sum_{j=k+1}^{N}$. In addition we assume the states are numbered in terms of increasing energy and that $q_{kj} > 0$ when $k > j$. We then make a rotating wave approximation by dropping
driving terms that oscillate like $e^{\pm i(\omega_p + q_{kj})t}$ to get

\[
\frac{d\rho_{kk}}{dt} = -\frac{i}{2\hbar} \sum_p \left( \sum_{j=1}^{k-1} -\mathcal{E}_p d_{kj} \bar{\rho}_{kj} e^{-i(\omega_p - q_{kj})t} + \mathcal{E}_p^* d_{kj} \bar{\rho}_{kj} e^{i(\omega_p - q_{kj})t} \right) -\frac{i}{2\hbar} \sum_p \left( \sum_{j=k+1}^N \mathcal{E}_p d_{kj} \bar{\rho}_{kj} e^{-i(\omega_p - q_{jk})t} - \mathcal{E}_p^* d_{kj} \bar{\rho}_{kj} e^{i(\omega_p - q_{jk})t} \right).
\]

Note that the right hand side contains factors $q_{kj}$ when $k > j$ in the sum and $q_{jk}$ when $j > k$ in the sum. The $q$ factors which appear are therefore always positive numbers so we have only kept co-rotating terms. If there was only one driving field $p = 1$ we could take $q_{kj} = \omega_p$ for $k > j$ and eliminate the time dependent factors. When we have more than one driving frequency this is no longer possible. We can write the population equations in a slightly more compact form by putting $q_{kj} = \omega_p$ and express the time dependencies by the detunings $\Delta_{p;kl} = \omega_p - \omega_{kj}$ to get

\[
\frac{d\rho_{kk}}{dt} = -\frac{i}{2\hbar} \sum_p \left( \sum_{j=1}^{k-1} -\mathcal{E}_p d_{kj} \bar{\rho}_{kj} e^{-i\Delta_{p;kl}t} + \mathcal{E}_p^* d_{kj} \bar{\rho}_{kj} e^{i\Delta_{p;kl}t} \right) -\frac{i}{2\hbar} \sum_p \left( \sum_{j=k+1}^N \mathcal{E}_p d_{kj} \bar{\rho}_{kj} e^{-i\Delta_{p;kl}t} - \mathcal{E}_p^* d_{kj} \bar{\rho}_{kj} e^{i\Delta_{p;kl}t} \right). \tag{13.15}
\]

The magnitudes of the detunings will depend on the states and fields involved. For example when $j, k$ both correspond to a state in the same electronic level and $p$ refers to an optical frequency the detunings will be large. Likewise if $j, k$ correspond to states in different electronic levels and $p$ refers to a lower frequency microwave signal the detunings will also be large. In such cases where the detuning is many THz it is necessary to drop those driving terms since it is virtually impossible to numerically integrate them over timescales of interest which are $\mu s - ms$.

For the coherences we find

\[
\frac{d\rho_{kl}}{dt} = -\frac{i}{2\hbar} \sum_p (\mathcal{E}_p e^{-i\omega_{pt} + \mathcal{E}_p^* e^{i\omega_{pt}}}) \sum_i \left( d_{il} d_{kl} e^{-i(\omega_{ki} - \omega_{li})t} - d_{ki} d_{il} e^{-i(\omega_{il} - \omega_{ki})t} \right) \]

\[
= -\frac{i}{2\hbar} \sum_p \mathcal{E}_p [d_{il} d_{kl} e^{-i(\omega_{p} - \omega_{lt})t} - d_{ki} d_{il} e^{-i(\omega_{p} - \omega_{lt})t}] + \mathcal{E}_{p}^* [d_{il} \bar{d}_{kl} e^{i(\omega_{p} - \omega_{lt})t} - d_{ki} \bar{d}_{il} e^{i(\omega_{p} - \omega_{lt})t}].
\]

Assume $k > l$ and divide the sum over $i$ into three terms: $\sum_i' \equiv \sum_{i=1}^{l-1}$, $\sum_i^* \equiv \sum_{i=l}^{k-1}$ and $\sum_i'' \equiv \sum_{i=k}^{N}$. Making the rotating wave approximation in the same way as for the
populations we get

\[
\frac{d\tilde{\rho}_{kl}}{dt} = -\frac{i}{2\hbar} \sum_p \sum_{i} -\mathcal{E}_p d_{ki} \tilde{\rho}_{il} e^{-i\Delta_{p,ki}t} + \mathcal{E}_p^* d_{il} \tilde{\rho}_{ki} e^{i\Delta_{p,il}t} \\
-\frac{i}{2\hbar} \sum_p \sum_{i} \mathcal{E}_p [d_{il} \tilde{\rho}_{ki} e^{-i\Delta_{p,il}t} - d_{ki} \tilde{\rho}_{il} e^{-i\Delta_{p,ki}t}] \\
-\frac{i}{2\hbar} \sum_p \sum_{i} \mathcal{E}_p d_{il} \tilde{\rho}_{ki} e^{-i\Delta_{p,il}t} - \mathcal{E}_p^* d_{ki} \tilde{\rho}_{il} e^{i\Delta_{p,kl}t}.
\] (13.16)

Equations (13.15,13.16) give the coherent evolution of the density matrix elements. Adding in the spontaneous emission terms we arrive at the set

\[
\frac{d\rho_{kk}}{dt} = -\sum_{j=1}^{k-1} \gamma_{j-k} \rho_{kk} + \sum_{j=k+1}^{N} \gamma_{k-j} \rho_{jj} \\
-\frac{i}{2\hbar} \sum_p \sum_{j=1}^{k-1} (\mathcal{E}_p d_{kj} \tilde{\rho}_{kj} e^{-i\Delta_{p,kj}t} + \mathcal{E}_p^* d_{jk} \tilde{\rho}_{kj} e^{i\Delta_{p,kj}t}) \\
-\frac{i}{2\hbar} \sum_p \sum_{j=k+1}^{N} (\mathcal{E}_p d_{kj} \tilde{\rho}_{kj} e^{-i\Delta_{p,kj}t} - \mathcal{E}_p^* d_{jk} \tilde{\rho}_{kj} e^{i\Delta_{p,kj}t}) .
\]

(13.17a)

\[
\frac{d\tilde{\rho}_{kl}}{dt} = -\frac{1}{2} \left( \sum_{j=1}^{k-1} \gamma_{j-k} \rho_{kl} + \sum_{j=1}^{l-1} \gamma_{j-l} \rho_{kl} \right) \\
+ \frac{1}{2} \sum_{j=k+1}^{N} \gamma_{k-j} \rho_{jl} + \frac{1}{2} \sum_{j=l+1}^{N} \gamma_{l-j} \rho_{kj} \\
-\frac{i}{2\hbar} \sum_p \sum_{j=1}^{l-1} (\mathcal{E}_p d_{kj} \tilde{\rho}_{kj} e^{-i\Delta_{p,kj}t} + \mathcal{E}_p^* d_{jk} \tilde{\rho}_{kj} e^{i\Delta_{p,kj}t}) \\
-\frac{i}{2\hbar} \sum_p \sum_{j=l}^{k-1} (\mathcal{E}_p d_{kj} \tilde{\rho}_{kj} e^{-i\Delta_{p,kj}t} - \mathcal{E}_p^* d_{jk} \tilde{\rho}_{kj} e^{i\Delta_{p,kj}t}) \\
-\frac{i}{2\hbar} \sum_p \sum_{j=k}^{N} (\mathcal{E}_p d_{kj} \tilde{\rho}_{kj} e^{-i\Delta_{p,kj}t} - \mathcal{E}_p^* d_{jk} \tilde{\rho}_{kj} e^{i\Delta_{p,kj}t}) .
\]

(13.17b)

Equations (13.17) are general enough to describe coupling of multilevel atoms to multiple driving fields with different frequencies. When generating numerical code from these equations it is helpful to visualize the algebraic terms with diagrams as shown in Fig. 13.9.

### 13.4 Optical pumping of Holmium

As an example of the use of (13.17) let’s consider optical pumping of the Holmium ground state manifold. We will start with a portion of the ground state levels and only consider \( F = 10, 11 \) coupling to electronically excited states \( F' = 11, 12 \) with fields \( \mathcal{E}_1, \mathcal{E}_2 \) as shown in

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Figure 13.9: Diagrams for the coherent driving terms in Eqs. (13.17). For the populations $\rho_{kk}$ there are two distinct diagrams giving four algebraic terms (top row). For the coherences $\rho_{kl}$, $k > l$ there are six distinct diagrams giving six algebraic terms (bottom two rows).

Fig. 13.10. Label the 92 states $|g/e,F,m_F\rangle$ as follows:

\begin{align*}
|g,10,-10\rangle & \ldots \ldots |g,10,10\rangle : 1 \ldots 21 \\
|g,11,-11\rangle & \ldots \ldots |g,11,11\rangle : 22 \ldots 44 \\
|e,11,-11\rangle & \ldots \ldots |e,11,11\rangle : 45 \ldots 67 \\
|e,12,-12\rangle & \ldots \ldots |e,12,12\rangle : 68 \ldots 92
\end{align*}

We take $\omega_1$ to be resonant with $|g,10\rangle \rightarrow |e,11\rangle$ and $\omega_2$ to be resonant with $|g,11\rangle \rightarrow$
Both fields are $\sigma_+ \text{ polarized and couple } |g, F, m_F \rangle \rightarrow |e, F', m_F + 1 \rangle$. The hyperfine splittings are $\delta_{11,10} = \omega_{g,11} - \omega_{g,10} = 2\pi \times 8.28 \text{ GHz}$ and $\delta_{12,11} = \omega_{e,12} - \omega_{e,11} = 2\pi \times 7.69 \text{ GHz}$. Light that resonantly couples $|g, 10 \rangle \rightarrow |e, 11 \rangle$ is therefore detuned by $\delta_{11,10} - \delta_{12,11} = 0.60 \text{ G Hz}$ from the $|g, 11 \rangle \rightarrow |e, 12 \rangle$ transition. This is a large detuning that is about 20 times bigger than the roughly 30 MHz linewidth of the excited state. This implies that non-resonant transition rates are suppressed by a factor of $4 \times 20^2 \sim 1600$ compared to resonant transitions. For this reason we will only keep resonant ground to excited state couplings when calculating coherences.

To assist with indexing define $n_{g10} = 21, n_{g11} = 23, n_{e11} = 23, n_{e12} = 25, n_g = n_{g10} + n_{g11} = 44, n_e = n_{e11} + n_{e12} = 48$, and $N = n_g + n_e = 92$. The detuning $\Delta_{p,kl}$ are similar to optical frequencies if $k, l$ both correspond to a ground or excited state. In such cases we will drop the corresponding driving terms on the right hand side of (13.17) since they are rapidly oscillating. As discussed above to reduce the number of equations we will only keep coherences that have resonant driving terms. These are for example coherences $\tilde{\rho}_{11,47}, \tilde{\rho}_{21,48}, \ldots \text{ and } \tilde{\rho}_{22,70}, \tilde{\rho}_{23,71}$. To reduce the number of coherence equations by a factor of two we will only define coherences $\tilde{\rho}_{kl}$ with $k > l$.

With the above definitions and approximations there are $N + n_g = 136$ equations to be integrated. There are $N$ equations for the populations

$$
\frac{d\rho_{kk}}{dt} = \sum_{j=n_g+1}^{N} \gamma_{jk}\rho_{jj} - \frac{i}{2\hbar} \left( (\mathcal{E}_1 d_{k1+}, k\tilde{\rho}_{k1+}, k) - (\mathcal{E}_1^* d_{k1+}, k\tilde{\rho}_{k1+}, k) \right), \ k = 1, \ldots, n_{g10}
$$

$$
\frac{d\rho_{kk}}{dt} = \sum_{j=n_g+1}^{N} \gamma_{jk}\rho_{jj} - \frac{i}{2\hbar} \left( (\mathcal{E}_2 d_{k2+}, k\tilde{\rho}_{k2+}, k) - (\mathcal{E}_2^* d_{k2+}, k\tilde{\rho}_{k2+}, k) \right), \ k = n_{g10} + 1, \ldots, n_g
$$

$$
\frac{d\rho_{kk}}{dt} = - \sum_{j=1}^{n_g} \gamma_{kj}\rho_{kk} - \frac{i}{2\hbar} \left( (-\mathcal{E}_1) d_{k1-, k}\tilde{\rho}_{k1-, k} + (\mathcal{E}_1^*) d_{k1-, k}\tilde{\rho}_{k1-, k} \right), \ k = n_g + 1, \ldots, n_g + n_{e11}
$$

$$
\frac{d\rho_{kk}}{dt} = - \sum_{j=1}^{n_g} \gamma_{kj}\rho_{kk} - \frac{i}{2\hbar} \left( (-\mathcal{E}_2) d_{k2-, k}\tilde{\rho}_{k2-, k} + (\mathcal{E}_2^*) d_{k2-, k}\tilde{\rho}_{k2-, k} \right), \ k = n_g + n_{e11} + 1, \ldots, N.
$$

We have used the subscript definitions $k_{1+} = k+n_g+2, k_{1-} = k-n_g-2, k_{2+} = k+n_g+4, k_{2-} = k-n_g-4$.
In addition there are \( n_g \) equations for the coherences

\[
\frac{d\hat{\rho}_{k,k_1}}{dt} = -\frac{1}{2}\sum_{j=1}^{n_g} \gamma_{kj} \hat{\rho}_{k,k_1} - \frac{i}{2\hbar} \mathcal{E}_1 d_{k,k_2} \left( \rho_{kk} - \rho_{k_1,k_2} \right), \quad k = n_g + 3, ..n_g + n_{e11}
\]

\[
\frac{d\hat{\rho}_{k,k_2}}{dt} = -\frac{1}{2}\sum_{j=1}^{n_g} \gamma_{kj} \hat{\rho}_{k,k_2} - \frac{i}{2\hbar} \mathcal{E}_2 d_{k,k_2} \left( \rho_{kk} - \rho_{k_2,k_2} \right), \quad k = n_g + n_{e11} + 3, ..N.
\]

These equations are adequate to describe pumping into the stretched state \( |g, 11, 11\rangle \). This is a bright state since a pumped atom will continue to scatter photons on the cycling transition \( |g, 11, 11\rangle \leftrightarrow |e, 12, 12\rangle \).

To convert these equations into numerical form we need a few more definitions. We will work under the assumption that excited states with angular momentum \( J = J_e \) decay only to a single ground state manifold with \( J = J_g \). Interaction with the nuclear spin \( I \) splits the upper and lower manifolds into hyperfine levels with angular momentum \( F \) and spin projection \( M \). The nuclear spin as well as the intrinsic electron spin \( S \) are constants of the motion. In this situation the decay \( \gamma_{k \rightarrow j} \) from \( |k\rangle = |n_k, L_k, S, J_k, I, F_k, M_k\rangle \) to \( |j\rangle = |n_j, L_j, S, J_j, I, F_j, M_j\rangle \) is

\[
\gamma_{k \rightarrow j} = \gamma_{E1} \times r^2_{kj} = \gamma_{E1} \times \frac{2F_k + 1}{2F_+ + 3} \left( \frac{S^J_{F_k,j_k} I_{F_k,j_k}}{S^J_{F_k,j_{k+1}} I_{F_k,j_{k+1}}} \right)^2 \left( \frac{C^F_{M_k,j_k} J_{F_k,j_k} \leftrightarrow C^F_{M_k,j_{k+1}} J_{F_k,j_{k+1}}} {C^F_{M_k,j_k} J_{F_k,j_k} \leftrightarrow C^F_{M_k,j_{k+1}} J_{F_k,j_{k+1}}} \right)^2
\]

where the total dipole allowed decay rate out of \( |k\rangle \) is \( \gamma_{E1} = \sum_j \gamma_{k \rightarrow j} \), and \( F_+ = I + J_g \) is the hyperfine coupled angular momentum of the lower level of the cycling transition \( |F_+, F_+\rangle \leftrightarrow |F_+ + 1, F_+ + 1\rangle \). The dimensionless factor \( r_{kj} \) is real but can be either positive or negative. Including the sign we have

\[
r_{kj} = (-1)^{1+I_1+J_j+F_k} \left( \frac{2F_k + 1}{2F_+ + 3} \right)^{1/2} \left( \frac{S^J_{F_k,j_k} I_{F_k,j_k}}{S^J_{F_k,j_{k+1}} I_{F_k,j_{k+1}}} \right) \frac{C^F_{M_k,j_k} J_{F_k,j_k} \leftrightarrow C^F_{M_k,j_{k+1}} J_{F_k,j_{k+1}}} {C^F_{M_k,j_k} J_{F_k,j_k} \leftrightarrow C^F_{M_k,j_{k+1}} J_{F_k,j_{k+1}}}.
\]

With \( \sigma_+ \) polarized light the dipole matrix elements \( d_{kj} \) couple states \( |F_k, M_k\rangle \) and \( |F_j, M_j = M_k, -1\rangle \), and can be written as

\[
d_{jk} = d_+ \times r_{kj}.
\]

Here \( d_+ \) is the matrix element for the cycling transition. The cycling matrix element and radiative decay rate are related by \( \gamma_{E1} = \omega_{e0}^3 d_+^2 / (3\pi\epsilon_0 hc^3) \). We introduce Rabi frequencies \( \Omega_1 = \mathcal{E}_1 d_+ / h \), \( \Omega_2 = \mathcal{E}_2 d_+ / h \) and saturation parameters \( s_1 = 2\Omega_1^2 / \gamma_{E1}^2 \), \( s_2 = 2\Omega_2^2 / \gamma_{E1}^2 \) (taking the fields to be real). With these definitions we can rewrite the equations of motion with
13.4 Optical pumping of Holmium

Figure 13.11: Holmium optical pumping using Eqs. (13.18). Initial population uniformly distributed in ground states, \( s_1 = 1, \ s_2 = 0.05 \). Total time is \( 10000/\gamma_{E1} = 49. \mu s \).

dimensionless coefficients \( r_{kj}, s_p \) as

\[
\frac{d\rho_{kk}}{d\tau} = \sum_{j=n_g+1}^{n} r_{kj}^2 \rho_{jj} - \frac{i}{2} \left( \frac{s_1}{2} \right)^{1/2} (r_{k,k_{1+}} \tilde{\rho}_{k_{1+},k} - r_{k_{1+},k} \tilde{\rho}_{k_{1+},k}) , \ k = 1,..n_{g10} \tag{13.18a}
\]

\[
\frac{d\rho_{kk}}{d\tau} = \sum_{j=n_g+1}^{N} r_{kj}^2 \rho_{jj} - \frac{i}{2} \left( \frac{s_2}{2} \right)^{1/2} (r_{k,k_{2+}} \tilde{\rho}_{k_{2+},k} - r_{k_{2+},k} \tilde{\rho}_{k_{2+},k}) , \ k = n_{g10} + 1,..n_g \tag{13.18b}
\]

\[
\frac{d\rho_{kk}}{d\tau} = - \sum_{j=1}^{n} r_{kj}^2 \rho_{kk} - \frac{i}{2} \left( \frac{s_1}{2} \right)^{1/2} (-r_{k_{1-},k} \tilde{\rho}_{k_{1-},k} + r_{k,k_{1-}} \tilde{\rho}_{k,k_{1-}}) , \ k = n_g + 1,..n_g + n_{e11} \tag{13.18c}
\]

\[
\frac{d\rho_{kk}}{d\tau} = - \sum_{j=1}^{n} r_{kj}^2 \rho_{kk} - \frac{i}{2} \left( \frac{s_2}{2} \right)^{1/2} (-r_{k_{2-},k} \tilde{\rho}_{k_{2-},k} + r_{k,k_{2-}} \tilde{\rho}_{k,k_{2-}}) , \ k = n_g + n_{e11} + 1,..N . \tag{13.18d}
\]

\[
\frac{d\tilde{\rho}_{k,k_{1-}}}{d\tau} = - \frac{1}{2} \sum_{j=1}^{n} r_{kj}^2 \tilde{\rho}_{k_{1-},k_{1-}} - \frac{i}{2} \left( \frac{s_1}{2} \right)^{1/2} r_{k_{1-},k} (\rho_{kk} - \rho_{k_{1-},k_{1-}}) , \ k = n_g + 3,..n_g + n_{e11} \tag{13.18e}
\]

\[
\frac{d\tilde{\rho}_{k,k_{2-}}}{d\tau} = - \frac{1}{2} \sum_{j=1}^{n} r_{kj}^2 \tilde{\rho}_{k_{2-},k_{2-}} - \frac{i}{2} \left( \frac{s_2}{2} \right)^{1/2} r_{k_{2-},k} (\rho_{kk} - \rho_{k_{2-},k_{2-}}) , \ k = n_g + n_{e11} + 3,..N . \tag{13.18f}
\]

where \( \tau = t/\gamma_{E1} \) is a dimensionless time. Sample numerical results are shown in Fig. 13.11.

If we changed the polarization of \( E_2 \) from \( \sigma_+ \) to \( \pi \) and tuned \( \omega_2 \) into resonance with \( |g, 11 \rangle \rightarrow |e, 11 \rangle \) we would pump into the dark state \( |g, 11, 0 \rangle \). The above equations predict perfect fidelity for dark state pumping if we ignore the off-resonant couplings of \( |g, 11 \rangle \rightarrow |e, 12 \rangle \). To actually determine the pumping fidelity we would need to include the off-resonant terms, but considering the very large excited state hyperfine splitting we expect the pumping fidelity to be high.

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Figure 13.12: Holmium optical pumping. The repumper with Rabi frequency $\Omega_1$ drives $F = 10 \rightarrow 11'$ and the pump field $\Omega_2$ drives $F = 11 \rightarrow 12'$. The six microwave fields couple $F = 4 \rightarrow 5, 5 \rightarrow 6, 6 \rightarrow 7, 7 \rightarrow 8, 8 \rightarrow 9, 9 \rightarrow 10$ with Rabi frequencies $\Xi_{4M} (F = 4 \rightarrow 5), \Xi_{5M} (F = 5 \rightarrow 6)$, etc. The orange numbers show the state indexing used for numerical solutions.

Optical and microwave fields

In order to fully pump the entire ground state manifold we need to also remove population from the $F = 4 \rightarrow 9$ hyperfine levels. To do this we add $\pi$ polarized microwave fields as shown in Fig. 13.12. We keep only the coherences on transitions that are driven by optical or microwave fields. We thus ignore coherences between excited states, and between ground states with different $m$ but keep the coherences between states $|10, M\rangle \leftrightarrow |11', M + 1\rangle$ and $|11, M\rangle \leftrightarrow |12', M + 1\rangle$. This gives a total of $N = 176$ states and $N_c = 387$ coherences. The number of dynamical variables, which is the same as the number of equations that must be integrated is 563.

The magnetic dipole Rabi frequencies coupling $|FM\rangle \rightarrow |F + 1, M\rangle$ are

$$
\Xi_{FM} = \frac{\mathcal{E}_F \mu_{FM}}{\hbar c}
$$

and with a $\mathbf{e}_z$ polarized field

$$
\mu_{FM} = \mu_F C_{FM10}^{F+1M}.
$$

(13.19)

with

$$
\mu_F = (\mu_B g_J)(-1)^{F+I+J+1} \sqrt{(2F+1)J(J+1)(2J+1)} \left\{ J \atop F+1 \right\} I \left\{ I \atop J \right\} F.
$$

The values of $\mu_{FM}$ are shown in Fig. 13.13. The strongest transition is $|6, 0\rangle \leftrightarrow |7, 0\rangle$ for which $\mu_{60} = \sqrt{209/52} \simeq 2.005$. With a microwave field strength of 10 W/m$^2 = 1$ mW/cm$^2$. 

13.4 Optical pumping of Holmium

Figure 13.13: Magnetic dipole transition strengths from $|FM\rangle \leftrightarrow |F+1M\rangle$ in Holmium.

Figure 13.14: Simulation of optical pumping of holmium into a single ground hyperfine state using the fields from Fig. 13.12.

this gives a Rabi frequency of $\Xi_{60}/2\pi = 9.75$ kHz. For comparison the same field strength driving the Cs $|3,0\rangle \leftrightarrow |4,0\rangle$ clock transition would give $\Xi_{30}/2\pi = 4.05$ kHz. A numerical example showing pumping all population from an initial uniformly distributed state to $|11,11\rangle$ is given in Fig. 13.14.
Chapter 14

Atomic interactions

In earlier chapters we have studied the interaction of atoms with electromagnetic fields as well as internal interactions between constituents of a single atom. We also discussed collisional broadening of resonance lines. We turn now to a more detailed look at interactions between different atoms. Interactions can be organized into short and long range categories. Interactions also depend on the internal atomic state. At short range, $R \sim a_0$ the electronic clouds overlap leading to repulsion. At long range where there is negligible overlap of the electron distributions the dominant interactions are $1/R^3$ magnetic dipole-dipole interactions and $1/R^6$ van der Waals interactions between induced electric dipoles. Although the long range interaction between ground state atoms is generically weak, very strong interactions can be observed for atoms in highly excited internal states. Much recent work has addressed slow collisions between laser cooled atoms [47, 48].

The change in interaction strength when going from ground states to excited states is shown in Fig. 14.1. A change of 12 orders of magnitude is possible. This large level of control has been used to entangle pairs of atoms [50, 49].

Figure 14.1: Two-body interaction strength for ground-state Rb atoms, Rb atoms excited to the 100s level, and ions, from [49].
14.1 Short range interaction

The strength of the short range interaction depends on the spin states of the outer electrons. For hydrogen or alkali atoms with single valence electrons on each atom we can form spin singlet or triplet states. Two electrons with the same spin state cannot share the same orbital so the triplet state repulsion is stronger than that of the singlet state which participates in covalent bonding. We can parameterize the short range interaction by singlet and triplet potentials $U_s, U_t$. For spin 1/2 particles in singlet(triplet) states we have $\hat{s}_1 \cdot \hat{s}_2 / \hbar^2 = -3/4, (1/4)$. The short range spin dependent potential is therefore written as

$$U_{sr} = \left( \frac{1}{4} - \frac{\hat{s}_1 \cdot \hat{s}_2}{\hbar^2} \right) U_s + \left( \frac{3}{4} + \frac{\hat{s}_1 \cdot \hat{s}_2}{\hbar^2} \right) U_t = \frac{1}{4} (U_s + 3U_t) + \frac{\hat{s}_1 \cdot \hat{s}_2}{\hbar^2} (U_t - U_s).$$

We see that when the singlet and triplet interaction strengths are equal the short range potential is independent of the spin state and is isotropic. The values of $U_s, U_t$ depend on the details of the short range electronic wavefunctions and can only be calculated approximately for most atoms. For ultracold atoms the interaction is specified in terms of a scattering length $a$. The scattering length can be positive or negative corresponding to repulsive or attractive interactions. At sufficiently low temperatures only $s$-wave scattering is important and the scattering cross section is $\sigma_s = 8\pi a^2$ for identical bosons, but vanishes for identical fermions.

Cold atom collisions have cross sections which may be several orders of magnitude larger than the size of an atom. It is also possible to use external fields to tune internal energy levels to a so-called Feshbach resonance such that the scattering length becomes extremely large and either positive or negative.[51]

14.2 Van der Waals interaction

Atoms in their ground state always exhibit a $1/R^6$ attractive van der Waals interaction at long range. We will see later how to calculate this fairly accurately. A first estimate can be made using a model due to F. London[52]. Consider two pairs of positive and negative charges $\pm e$ as shown in Fig. 14.2. The positive charges are fixed at $z = 0, R$ and the negative charges oscillate about these points with relative coordinates $z_1, z_2$. We take $R \gg |z_1|, |z_2|$ corresponding to well separated atoms. The pairs of charges form dipoles which interact with each other.
The potential energy due to oscillation of the charges about their equilibrium positions is

\[ U = \frac{1}{2} \frac{q^2}{b} z_1^2 + \frac{1}{2} \frac{q^2}{b} z_2^2 \]

where \( b \) is a constant with dimensions of \( m^3 \) and \( q^2 = e^2/4\pi\epsilon_0 \). We can relate this constant to atomic parameters by setting \( \frac{q^2}{b} = m\omega_0^2 \) with \( m \) the electron mass and \( \omega_0 \) a characteristic atomic frequency. The Hamiltonian for the two dipoles is

\[ \hat{H}_0 = \hat{p}_1^2 + \hat{p}_2^2 + \frac{q^2}{2b} (z_1^2 + z_2^2) \]

and the interaction Hamiltonian is

\[ \hat{H}_1 = \frac{q^2}{R} + \frac{q^2}{R - z_1 + z_2} - \frac{q^2}{R - z_1} - \frac{q^2}{R + z_2} \]

\[ \approx -\frac{2q^2}{R^3} z_1 z_2. \]  

(14.1)

We can diagonalize the total Hamiltonian \( \hat{H} = \hat{H}_0 + \hat{H}_1 \) using symmetric and antisymmetric coordinates

\[ z_{s/a} = \frac{z_1 \pm z_2}{\sqrt{2}}, \quad p_{s/a} = \frac{p_1 \pm p_2}{\sqrt{2}}. \]

With these definitions the Hamiltonian is

\[ \hat{H} = \frac{p_{s/a}^2}{2m} + \frac{1}{2} m\omega_{s/a}^2 z_{s/a}^2 + \frac{p_{a/s}^2}{2m} + \frac{1}{2} m\omega_{a/s}^2 z_{a/s}^2 \]

with the frequencies

\[ \omega_{s/a} = \frac{q}{\sqrt{mb}} \left( 1 + \frac{2b}{R^3} \right)^{1/2} = \omega_0 \left( 1 + \frac{2b}{R^3} \right)^{1/2}. \]

We see that the Hamiltonian is two uncoupled oscillators so the quantized energy is

\[ U_{n_s,n_a} = \hbar \omega_s(n_s + 1/2) + \hbar \omega_a(n_a + 1/2). \]

The ground state energy is

\[ U_{00} = \frac{\hbar}{2} (\omega_s + \omega_a) \]

\[ \approx \hbar \omega_0 \left( 1 - \frac{b^2}{2R^6} \right). \]  

(14.2)

Writing the energy as \( U = C_6/R^6 \) the \( C_6 \) coefficient is \( C_6 = -\hbar \omega_0 b^2/2 \) and using \( b^2 = q^4/(m^2\omega_0^4) \) we get

\[ C_6 = -\frac{\hbar q^4}{2m^2\omega_0^3}. \]

The atomic unit of \( C_6 \) is \( C_6^{a.u.} = E_1 a_0^6 \). Replacing \( \omega_0 \) by the frequency of the first resonance line in Cs (\( \omega_0 = 2\pi c/(852 \text{ nm}) \)) we find

\[ C_6^{a.u.,\text{Cs}} = -3270. \]

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This is close to twice smaller than the accepted value of \( -6890\) which is remarkably good agreement considering how simple the model is.

Better agreement can be reached using a three dimensional model for the oscillation of the dipoles. With \( \mathbf{R} = R e_z \) the Hamiltonian for the dipoles is

\[
\hat{H}_0 = \frac{\hat{p}_1^2 + \hat{p}_2^2}{2m} + \frac{q^2}{2b}(r_1^2 + r_2^2)
\]

and the interaction at order \( 1/R^3 \) is

\[
\hat{H}_1 = \frac{q^2}{R^3} (x_1x_2 + y_1y_2 - 2z_1z_2).
\]

We introduce coordinates

\[
\mathbf{r}_{s/a} = \frac{\mathbf{r}_1 \pm \mathbf{r}_2}{\sqrt{2}}, \quad \mathbf{p}_{s/a} = \frac{\mathbf{p}_1 \pm \mathbf{p}_2}{\sqrt{2}}
\]

in terms of which the Hamiltonian is

\[
\hat{\mathcal{H}} = \frac{\hat{p}_s^2}{2m} + \frac{\hat{p}_a^2}{2m} + \frac{1}{2} m \omega_{\perp s}^2 z_s^2 + \frac{1}{2} m \omega_{\perp a}^2 z_a^2 + \frac{1}{2} m \omega_{\perp s}^2 (x_s^2 + y_s^2) + \frac{1}{2} m \omega_{\perp a}^2 (x_a^2 + y_a^2).
\]

with the frequencies

\[
\omega_{\perp s/a} = \frac{q}{\sqrt{mb}} \left( 1 \pm \frac{2b}{R^3} \right)^{1/2}, \quad \omega_{\perp s/a} = \frac{q}{\sqrt{mb}} \left( 1 \pm \frac{b}{R^3} \right)^{1/2}.
\]

We now have two uncoupled 3D harmonic oscillators with ground state energy

\[
U_g = \frac{\hbar}{2} (\omega_{zs} + \omega_{za} + 2\omega_{\perp s} + 2\omega_{\perp a}).
\]

Following the same steps as for the 1D calculation the van der Waals coefficient is

\[
C_6 = -\frac{3\hbar q^4}{4m^2\omega_0^3}.
\]

The estimate for Cs becomes \(-4900\) a.u., which is much closer to the known value. We can improve the estimate slightly by accounting for the resonance doublet with a weighting of \(2/3\) for the \(s_{1/2} - p_{3/2}\) D2 transition and \(1/3\) for the \(s_{1/2} - p_{1/2}\) D1 transition. Using the Cs wavelengths 852 nm for the D2 transition and 894 nm for the D1 transition we find \(C_6 = -5160\) a.u. which is only about 25% smaller than the more accurate value of \(-6890\).[53]

### 14.3 Magnetic dipole-dipole interaction

A longer range \(1/R^3\) potential is also present due to the magnetic interaction of atomic spins. The classical interaction energy \(U\) between two magnetic moments \(\mathbf{\mu}_1, \mathbf{\mu}_2\) separated by the vector \(\mathbf{R}\) is

\[
U_{\text{md}} = \frac{\mu_0}{4\pi R^3} \left[ \mathbf{\mu}_1 \cdot \mathbf{\mu}_2 - 3 \frac{(\mathbf{\mu}_1 \cdot \mathbf{R})(\mathbf{\mu}_2 \cdot \mathbf{R})}{R^2} \right].
\]
When the dipoles are parallel to the axis joining them the interaction is attractive and when they are perpendicular to this axis the interaction is repulsive. Define the $\mathbf{e}_z$ axis as lying along $\mathbf{R}$ and the direction of $\mathbf{\mu}_1, \mathbf{\mu}_2$ as the unit vector $\hat{\mathbf{n}}$ which makes an angle $\theta$ with the $\mathbf{e}_z$ axis. Then $\mathbf{R} = z\mathbf{e}_z$ and
\[
\mathbf{\mu}_1 \cdot \mathbf{\mu}_2 - 3\frac{(\mathbf{\mu}_1 \cdot \mathbf{R})(\mathbf{\mu}_2 \cdot \mathbf{R})}{R^2} = \mu_1\mu_2 \left[1 - 3(\hat{\mathbf{n}} \cdot \mathbf{e}_z)^2\right] = \mu_1\mu_2 \left[1 - 3\cos^2(\theta)\right].
\]
The interaction vanishes for
\[
\theta = \cos^{-1}(1/\sqrt{3}) = 54.7 \text{ deg}.
\]
The quantum mechanical expression for the magnetic dipole interaction Hamiltonian between two atomic electrons is
\[
\hat{H}_{\text{md}} = \frac{\mu_0}{4\pi R^3} \left(\hat{\mathbf{\mu}}_1 \cdot \hat{\mathbf{\mu}}_2 - 3\frac{(\hat{\mathbf{\mu}}_1 \cdot \mathbf{R})(\hat{\mathbf{\mu}}_2 \cdot \mathbf{R})}{R^2}\right)
\]
with $\hat{\mathbf{\mu}}_1 = -g_J\mu_B\hat{J}_1/\hbar, \hat{\mathbf{\mu}}_2 = -g_J\mu_B\hat{J}_2/\hbar$. Thus
\[
\hat{H}_{\text{md}} = \frac{g_J g_J' \mu_0 \mu_B^2}{4\pi \hbar^2 R^3} \left[\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 - 3\frac{(\hat{\mathbf{J}}_1 \cdot \mathbf{R})(\hat{\mathbf{J}}_2 \cdot \mathbf{R})}{R^2}\right].
\]
If we take $\mathbf{R}$ to be along the quantization axis then
\[
\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 - 3\frac{(\hat{\mathbf{J}}_1 \cdot \mathbf{R})(\hat{\mathbf{J}}_2 \cdot \mathbf{R})}{R^2} = -2\hat{J}_{10}\hat{J}_{20} - \hat{J}_{1,1}\hat{J}_{2,-1} - \hat{J}_{1,-1}\hat{J}_{2,1}
\]
\[
= -\sqrt{6}\sum_q C^{20}_{1q1-q}\hat{J}_{1,q}\hat{J}_{2,-q}
\]
and
\[
\hat{H}_{\text{md}} = -\sqrt{6}\frac{g_J g_J' \mu_0 \mu_B^2}{4\pi \hbar^2 R^3} \sum_q C^{20}_{1q1-q}\hat{J}_{1,q}\hat{J}_{2,-q}. \quad (14.4)
\]
In an uncoupled basis $J_1, M_1, J_2, M_2$ are good quantum numbers and expectation values of $\hat{J}_{1,\pm 1}, \hat{J}_{2,\pm 1}$ all vanish. The spherical components of the vector $\mathbf{R}$ are $R_0 = R\cos\theta = R\sqrt{4\pi/3}Y_{00}(\theta, \phi), R_{\pm 1} = R\sqrt{4\pi/3}Y_{1\pm 1}(\theta, \phi)$ and
\[
\langle J_1, M_1, J_2, M_2|\hat{H}_{\text{md}}|J_1, M_1, J_2, M_2\rangle = \frac{g_J g_J' \mu_0 \mu_B^2}{4\pi \hbar^2 R^3}\hat{J}_{10}\hat{J}_{20} \left[1 - 3\cos^2(\theta)\right]. \quad (14.5)
\]
This last equation is also valid for hyperfine states $|F_1, M_{F1}\rangle, |F_2, M_{F2}\rangle$ with the replacements $J \rightarrow F$ and $g_J \rightarrow g_F$.

### 14.4 Electric multipole interactions

The electrostatic interaction of charge distributions which are separated by a distance $R$ that is large compared to the extent of each distribution can be described by a multipole interaction.
expansion. The geometry is shown in Fig. 14.3. The Coulomb energy between charges $e_a, e_b$ at positions $\mathbf{r}_a, \mathbf{r}_b$ relative to the center of each distribution is

$$V = \tilde{q}^2 \frac{1}{|\mathbf{R} + \mathbf{r}_b - \mathbf{r}_a|}$$

with $\tilde{q}^2 = \text{sign}(e_a e_b) |e_a e_b| / 4\pi\epsilon_0$. Taylor expanding in powers of $1/R$ leads to the general form of the multipole interaction between charges $e, e'$ which can be written in a compact form using spherical tensors \cite{54,55}

$$\hat{V}(\mathbf{R}) = \tilde{q}^2 \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} \frac{\hat{v}_{kk'}(\mathbf{n})}{R^{k+k'+1}}. \quad (14.6)$$

Here $\mathbf{n} = \mathbf{R}/R$ is a unit vector pointing from atom $a$ to atom $b$ which are separated by the vector $\mathbf{R}$, and

$$\hat{v}_{kk'}(\mathbf{n}) = (-1)^{k'} \left[ \frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} C_K(\mathbf{n}) \cdot \{ Q_k(\mathbf{r}_a) \otimes Q_{k'}(\mathbf{r}_b) \}_K$$

$$= (-1)^{k'} \left[ \frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} \sum_{M} (-1)^M C_{KM}(\mathbf{n}) \{ Q_k(\mathbf{r}_a) \otimes Q_{k'}(\mathbf{r}_b) \}_{KM} \quad (14.7)$$

where $K = k + k'$ and $M = -M$. The last line follows from VMK 3.1.8 (30).

The atomic $k$-pole electric moment operators are $Q_k(\mathbf{r}) = r^k C_k(\mathbf{e}_r)$ with (VMK 5.1.4 (7)) $C_k(\mathbf{e}_r) = \sqrt{\frac{4\pi}{2k+1}} Y_k(\theta, \phi)$. The $Q_k$ should be summed over all discrete charges or integrated over a continuous charge distribution. When the quantization axis lies along $\mathbf{n}$ we have $\theta_n = 0$ and $C_{KM}(\mathbf{n}) = \delta_{M0}$. Equation (14.7) thus simplifies to

$$\hat{v}_{kk'}(\mathbf{n}) = (-1)^{k'} \left[ \frac{(2K)!}{(2k)!(2k')!} \right]^{1/2} \{ Q_k(\mathbf{r}_a) \otimes Q_{k'}(\mathbf{r}_b) \}_{K0}. \quad (14.8)$$

### 14.5 Dipole-dipole interaction

Let's evaluate the general formulae for the case of two atoms in angular momentum states $|a\rangle = |j_a m_a\rangle, |b\rangle = |j_b m_b\rangle$ with the molecular axis $\mathbf{n}$ rotated by $\theta, \phi$ with respect to the
quantization axis. The (classical) operators $Q_1(r_a), Q_1(r_b)$ are to be evaluated with respect to the quantum states $|a\rangle, |b\rangle$ and we denote them by $Q_1^{(a)}, Q_1^{(b)}$. For the dipole-dipole interaction we can use Eqs. (14.6,14.8) with $k = k' = 1$ to write (using VMK 3.1.7 (20))

$$V_{dd} = -\frac{q^2}{R^3} \sqrt{6} \sum_M (-1)^M C_{2M}(n) \left\{ Q_1^{(a)} \otimes Q_1^{(b)} \right\}_{2M}$$

$$= -\frac{q^2 r_a r_b \sqrt{6}}{R^3} \left( -\frac{4\pi}{3} \right)^{3/2} \left( \frac{4\pi}{3} \right) \sum_{M,q} (-1)^M C_{2M,q} Y_{2M} (n) Y_a^{(a)} Y_b^{(b)}$$

$$= -\frac{q^2 r_a r_b \sqrt{6}}{R^3} \left( \frac{4\pi}{3} \right)^{3/2} \sum_{M,q} (-1)^M C_{2M,q} Y_{2M} (n) Y_a^{(a)} Y_b^{(b)} Y_{1M-q}. \quad (14.9)$$

Taking the molecular axis to lie in the $\hat{x} - \hat{z}$ plane so $\phi = 0$ and expanding the components $Y_{2M}(n)$ we get the explicit expression

$$V_{dd} = \frac{q^2 r_a r_b 4\pi}{R^3} \left\{ 1 - 3 \cos^2 \theta \right\} \left[ 2Y_{10}^{(a)} Y_{10}^{(b)} + Y_{11}^{(a)} Y_{1-1}^{(b)} + Y_{1-1}^{(a)} Y_{11}^{(b)} \right]$$

$$+ \frac{3}{\sqrt{2}} \sin \theta \cos \theta \left[ (Y_{11}^{(a)} - Y_{1-1}^{(a)}) Y_{10}^{(b)} + Y_{10}^{(a)} (Y_{11}^{(b)} - Y_{1-1}^{(b)}) \right]$$

$$- \frac{3}{2} \sin^2 \theta \left[ Y_{11}^{(a)} Y_{11}^{(b)} + Y_{1-1}^{(a)} Y_{1-1}^{(b)} \right]. \quad (14.10)$$

The first, second, and third lines contain terms for which the selection rule is $|\Delta M| = 0, 1, 2$ respectively. The simplified cases of $\Delta M = 0$ and $\Delta M = 2, 0, -2$ occur for $\theta = 0$ and $\theta = \pi/2$.

This can be expressed in terms of spherical components of the position operators $r_a, r_b$ using $r_q = r \sqrt{\frac{2\pi}{3}} Y_{1q}$ with $q = 1, 0, -1$. We find

$$V_{dd} = \frac{q^2}{R^3} \left\{ 1 - 3 \cos^2 \theta \right\} \left[ 2 r_a 0 r_{b0} + r_a 1 r_{b-1} + r_a -1 r_{b1} \right]$$

$$+ \frac{3}{\sqrt{2}} \sin \theta \cos \theta \left[ (r_a 1 - r_a -1) r_{b0} + r_a 0 (r_{b1} - r_{b-1}) \right]$$

$$- \frac{3}{2} \sin^2 \theta \left[ r_a 1 r_{b1} + r_a -1 r_{b-1} \right]. \quad (14.11)$$

When $n$ is parallel to the quantization axis we can use Eqs. (14.6,14.8) with $k = k' = 1$ to write (using VMK 3.1.7 (20))

$$V_{dd} = -\frac{\sqrt{6} q^2}{R^3} \left\{ Q_1^{(a)} \otimes Q_1^{(b)} \right\}_{20}$$

$$= -\frac{4\pi \sqrt{6} q^2 r_a r_b}{3 R^3} \sum_q C_{1q1q}^{20} Y_{1q}^{(a)} Y_{1q}^{(b)}$$

$$= \frac{q^2}{R^3} (x_a x_b + y_a y_b - 2 z_a z_b). \quad (14.12)$$

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The last line shows that the tensor expression reduces to the usual form of the dipole-dipole interaction which follows from

\[
V_{dd} = \frac{\tilde{q}^2}{R^3} \left[ r_a \cdot r_b - 3(r_a \cdot \hat{R})(r_b \cdot \hat{R}) \right]
\]

\[
= \frac{\tilde{q}^2}{R^3} (r_{ax}r_{bx} + r_{ay}r_{by} + r_{az}r_{bz} - 3r_{az}r_{bz})
\]

\[
= \frac{\tilde{q}^2}{R^3} (x_ax_b + y_ay_b - 2z_az_b).
\] (14.13)

### 14.6 Quadrupole-quadrupole interaction

It follows from Eqs. (14.6, 14.8) with \( k = k' = 2 \) that this interaction can be written as a tensor product of the form (see for example[56])

\[
V_{qq} = \frac{\sqrt{10} e^2}{R^5} \left\{ Q_2^{(a)} \otimes Q_2^{(b)} \right\}_{40}
\]

where the rank two quadrupole operators for atoms \( a, b \) have components (Sobelman, 7.45)

\[
Q_{2q} = \sqrt{\frac{4\pi}{5}} r^2 Y_{2q}(\theta, \phi).
\]

The tensor product is given by (VMK 3.1.7 (20))

\[
\left\{ Q_2^{(a)} \otimes Q_2^{(b)} \right\}_{40} = \sum_q C_{2q2q}^{(a)} Q_{2q}^{(a)} Q_{2q}^{(b)}
\]

\[
\quad = \frac{4\pi r_a^2 r_b^2}{5\sqrt{70}} \left[ 6Y_{20}^{(a)} Y_{20}^{(b)} + 4(Y_{21}^{(a)} Y_{21}^{(b)} + Y_{12}^{(a)} Y_{12}^{(b)} + Y_{22}^{(a)} Y_{22}^{(b)} + Y_{22}^{(a)} Y_{22}^{(b)} \right].
\] (14.14)

The matrix element in two-atom fine structure states \( |n,l; m_a m_b \rangle \) can be evaluated directly using (VMK 13.1.4 (25))

\[
\langle n\ell; m'_a m'_b | \left\{ Q_2^{(a)} \otimes Q_2^{(b)} \right\}_{40} | n\ell; m_a m_b \rangle = \frac{\langle n\ell||Q_2^{(a)}||n\ell\rangle \langle n\ell||Q_2^{(b)}||n\ell\rangle}{2j + 1} 
\]

\[
\times \sum_q C_{j_m a 2m}^{m'_a} C_{j_m b 2m}^{m'_b} C_{j_m 2m}^{40}.
\] (14.15)

Defining the change in the angular momentum projection \( m = m'_a - m_a = m_b - m'_b \) this reduces to (VMK 13.2.8 (105))

\[
\langle n\ell; m'_a m'_b | \left\{ Q_2^{(a)} \otimes Q_2^{(b)} \right\}_{40} | n\ell; m_a m_b \rangle = \frac{\langle n\ell||Q_2^{(a)}||n\ell\rangle \langle n\ell||Q_2^{(b)}||n\ell\rangle}{2j + 1} C_{j_m 2m}^{jm'_a} C_{j_m 2m}^{jm'_b} C_{j_m 2m}^{40} 
\]

\[
\quad = (2j + 1) \left\{ \begin{array}{c} l \cr j \end{array} \right\} \left\{ \begin{array}{c} j \cr l \end{array} \right\}^{1/2} \langle n\ell||r^2 Y_{22}\rangle^{2j + 1} C_{j_m 2m}^{jm'_a} C_{j_m 2m}^{jm'_b} C_{j_m 2m}^{40} 
\]

\[
\quad = \frac{5}{4\pi} (2j + 1)(2l + 1) \left\{ \begin{array}{c} l \cr j \end{array} \right\} \left\{ \begin{array}{c} j \cr l \end{array} \right\}^{1/2} \langle n\ell||r^2||n\ell\rangle^{2j + 1} 
\]

\[
\times (C_{l0 20}^{(a)})^2 C_{j_m 2m}^{jm'_a} C_{j_m 2m}^{jm'_b} C_{j_m 2m}^{40}.
\] (14.16)
The quadrupole interaction strength is thus

\[
\langle nl; m_a m_b' | V_{qq} | nl; m_a m_b' \rangle = \frac{5\sqrt{70} e^2 \langle nl||r^2||nl \rangle^2}{4 \pi R^5} (2j + 1)(2l + 1) \left\{ \begin{array}{ccc} l & j & 1/2 \\ j & l & 1 \end{array} \right\}^2 \times \left(C_{\ell 20}^{m} \right)^2 C_{jm_{a}2m}^{jm_{b}'} C_{jm_{a}2m}^{jm_{b}'} C_{jm_{a}2m}^{jm_{b}'} 
\]

(14.17)

For the case of \( s_{1/2} \) states there is no quadrupole interaction \((j = 1/2)\), for \( p_{3/2} \) states and \( m_a = m_b = 1/2, m = 0 \) we find

\[
\langle V_{qq} \rangle = \frac{1}{2 \pi} \frac{e^2 \langle nl||r^2||nl \rangle^2}{R^5}.
\]

(14.18)

For \( d_{5/2} \) states and \( m_a = m_b = 1/2, m = 0 \) we find

\[
\langle V_{qq} \rangle = \frac{16}{35 \pi} \frac{e^2 \langle nl||r^2||nl \rangle^2}{R^5}.
\]

(14.19)

### 14.7 Rydberg - Rydberg interaction

Taking the quantization axis parallel to the interatomic axis

\[
\hat{V}_{dd} = \frac{-q^2 \sqrt{6} }{R^3} \sum_{p} C_{1p1-p}^{20} r_A r_{B-p}
\]

(14.20)

where \( A, B \) label the two dipoles. In general the atomic state \( |\psi\rangle \) is a superposition of states with different values of \( l \) and possibly \( m \). Let us write \( |\psi\rangle = \sum_{i=1}^{N} c_i |l_m\rangle \), with \( N \) the number of basis states. The matrix element of \( \hat{V}_{dd} \) is thus

\[
\langle \psi_A \psi_B | \hat{V}_{dd} | \psi_A \psi_B \rangle = \frac{-q^2 \sqrt{6} }{R^3} \times \sum_{p} C_{1p1-p}^{20} \sum_{i_A, i_A', i_B, i_B'} c_{i_A} c_{i_A'}^* c_{i_B} c_{i_B'}^* \langle l_{i_A} m_{i_A} | r_A | l_{i_A} m_{i_A} \rangle \langle l_{i_B} m_{i_B} | r_{B-p} | l_{i_B} m_{i_B} \rangle.
\]

(14.21)

Atomic states with definite parity do not have a permanent dipole moment. A physical picture of the interaction mechanism is given in Fig. 14.4 which shows that a resonant interaction is possible due to coupling of each atom to nearby atomic states. The figure shows the simplest possible case of two atoms in the same \( ns \) level coupling to \( np \) and \((n-1)p\) levels. The situation can be generalized to account for atoms initially in different Zeeman substates[57], different levels, or even atoms of different types[58].

A general two-atom state is \( |nlm\rangle_A |\tilde{nl}\tilde{m}\rangle_B \). The matrix element between this initial state and a final state \( |n'l'm'\rangle_A |\tilde{n'}\tilde{l'}\tilde{m'}\rangle_B \) is

\[
\langle \tilde{V}_{dd} \rangle = A |n'l'm'|_B \langle \tilde{n'}\tilde{l'}\tilde{m'} | \hat{V}_{dd} | nl m \rangle_A |\tilde{n}\tilde{l}\tilde{m}\rangle_B
\]

\[
= \frac{-q^2 \sqrt{6} }{R^3} \sum_{p} C_{1p1-p}^{20} \langle n'l'm' | r_A | nl m \rangle_A \langle \tilde{n}\tilde{l}\tilde{m'} | r_{B-p} | \tilde{n'}\tilde{l'}\tilde{m}\rangle_B.
\]

(14.22)
The matrix element of $\hat{m}$ more compact notation for symmetrized two-atom kets be exchange symmetric when the initial state is. It is therefore convenient to introduce a

$$\langle nlm; n'l'm' \rangle \equiv \frac{1}{\sqrt{2(1 + \delta_{nm'}\delta_{ll'}\delta_{mm'})}} (|nlm\rangle_A|n'l'm'\rangle_B + |n'l'm'\rangle_A|nlm\rangle_B).$$

The most general matrix element that appears in the evaluation of $\langle \hat{V}_{dd} \rangle$ is

$$\{n_3l_3m_3; n_4l_4m_4| r_{Ap}r_{B-p} | n_1l_1m_1; n_2l_2m_2 \}$$

$$= \frac{1}{\sqrt{2(1 + \delta_{n_1n_2}\delta_{l_1l_2}\delta_{m_1m_2})}} \frac{1}{\sqrt{2(1 + \delta_{n_3n_4}\delta_{l_3l_4}\delta_{m_3m_4})}} \frac{1}{\sqrt{(2l_3 + 1)(2l_4 + 1)}} \times \left[ (n_3l_3|r|n_1l_1) (n_4l_4|r|n_2l_2) (C^{l_3m_3}_{l_1m_11} C^{l_4m_4}_{l_2m_21-p} + C^{l_4m_4}_{l_2m_21} C^{l_3m_3}_{l_1m_11-p}) + (n_4l_4|r|n_1l_1) (n_3l_3|r|n_2l_2) (C^{l_4m_4}_{l_1m_11} C^{l_3m_3}_{l_2m_21-p} + C^{l_3m_3}_{l_2m_21} C^{l_4m_4}_{l_1m_11-p}) \right]. \quad (14.23)$$

The matrix element of $\hat{V}_{dd}$ is therefore

$$\{n_3l_3m_3; n_4l_4m_4| \hat{V}_{dd} | n_1l_1m_1; n_2l_2m_2 \}$$

$$= -\frac{q^2}{R^3} \frac{1}{\sqrt{2(1 + \delta_{n_1n_2}\delta_{l_1l_2}\delta_{m_1m_2})}} \frac{1}{\sqrt{2(1 + \delta_{n_3n_4}\delta_{l_3l_4}\delta_{m_3m_4})}} \frac{1}{\sqrt{(2l_3 + 1)(2l_4 + 1)}} \times \sum_p C^{l_3m_3}_{l_1m_11-p} \left[ (n_3l_3|r|n_1l_1) (n_4l_4|r|n_2l_2) (C^{l_4m_4}_{l_1m_11} C^{l_3m_3}_{l_2m_21-p} + C^{l_3m_3}_{l_2m_21} C^{l_4m_4}_{l_1m_11-p}) + (n_4l_4|r|n_1l_1) (n_3l_3|r|n_2l_2) (C^{l_4m_4}_{l_1m_11} C^{l_3m_3}_{l_2m_21-p} + C^{l_3m_3}_{l_2m_21} C^{l_4m_4}_{l_1m_11-p}) \right]. \quad (14.24)$$

Let’s analyze the specific case where the initial states are spherically symmetric s states.
We have \( n_1 = n_2 = 0, l_1 = l_2 = 0, m_1 = m_2 = 0 \) and \( l_3 = l_4 = 1 \) which leads to
\[
\begin{align*}
\{ n_3 l_3; n_4 l_4 | \hat{V}_{dd} | n_00; n_00 \} &= -\frac{q^2}{R^3} \frac{2}{\sqrt{6}} \frac{1}{\sqrt{2(1 + \delta_{n_3 n_4} \delta_{m_3 m_4})}} \langle n_3 1 || r || n_0 \rangle \langle n_4 1 || r || n_0 \rangle \\
&\times \sum_p C_{lp1-p}^{20} (C_{001}^{1m_3} C_{001-p}^{1m_4} + C_{001p}^{1m_4} C_{001-p}^{1m_3}).
\end{align*}
\] (14.25)

The three combinations of \( m_3, m_4 \) which give a nonzero matrix element are \( m_3 = m_4 = 0 \) for which
\[
\begin{align*}
\{ n_3 10; n_4 10 | \hat{V}_{dd} | n_00; n_00 \} &= -\frac{q^2}{R^3} \langle n_3 1 || r || n_0 \rangle \langle n_4 1 || r || n_0 \rangle \frac{2\sqrt{2}}{3} \frac{1}{\sqrt{1 + \delta_{n_3 n_4}}} 
\end{align*}
\] (14.26)
and \( m_3 = 1, m_4 = -1 \) or \( m_3 = -1, m_4 = 1 \) for which
\[
\begin{align*}
\{ n_3 1m_3; n_4 1m_4 | \hat{V}_{dd} | n_00; n_00 \} &= -\frac{q^2}{R^3} \langle n_3 1 || r || n_0 \rangle \langle n_4 1 || r || n_0 \rangle \frac{\sqrt{2}}{3}.
\end{align*}
\] (14.27)

We see that the magnitude of the coupling strength is different for different orientations of the coupled states. Defining
\[
U_3(r) = \frac{q^2}{R^3} \langle n_3 1 || r || n_0 \rangle \langle n_4 1 || r || n_0 \rangle
\]
we get an interaction energy of
\[
-3 \sqrt{2} \frac{1}{3} \frac{U_3}{\sqrt{1 + \delta_{n_3 n_4}}}
\]
for the spherically symmetric coupled state with \( m_3 = m_4 = 0 \) and
\[
-3 \sqrt{2} \frac{U_3}{3}
\]
for the coupled states with orientation.

Consider a Förster resonance where \( ns + ns \rightarrow np + (n - 1)p \) as illustrated in Fig. 14.4. For \( n = 50 \) \(^{87}\text{Rb} \) atoms the reduced matrix elements are \( \langle 50s || r || 50p \rangle = 2520a_0 \) and \( \langle 50s || r || 49p \rangle = 2330a_0 \). The resulting interaction energy is \( h \times 12.2 \text{ MHz} \) at \( r = 8 \ \mu \text{m} \) (86.8 MHz for \( r = 8 \ \mu \text{m} \) and \( n = 80 \)).

This estimate neglects the effects of energy mismatch between the interacting states. Including orientation of the coupled states there are four degenerate interchange symmetric states given by
\[
\begin{align*}
|1\rangle &= |n00; n00\rangle \\
|2\rangle &= |n_1 10; n_2 10\rangle \\
|3\rangle &= |n_1 11; n_2 1 - 1\rangle \\
|4\rangle &= |n_1 1 - 1; n_2 11\rangle.
\end{align*}
\] (14.28)
We have, for convenience, replaced \( n_3, n_4 \) with \( n_1, n_2 \) and we assume \( n_1 \neq n_2 \). In order to find the energies of the possible states we need to diagonalize the total Hamiltonian \( \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \) where the dipole-dipole coupling gives the interaction

\[
\mathcal{H}_1 = -\sqrt{\frac{2}{3}} U_3 \begin{pmatrix}
0 & 2 & 1 & 1 \\
2 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 \\
\end{pmatrix}.
\]

In the degenerate case \( \mathcal{H}_0 = U_0 I \) and we find the energy eigenvalues \( U_{\pm} = \pm (2/\sqrt{3}) U_3 \) and 0, 0. The zero eigenvalues correspond to combinations of the \( l = 1 \) states only, which are never excited.

In a more typical situation we have imperfect Förster degeneracy with an energy defect \( \hbar \delta = E(n_1 p) + E(n_2 p) - 2E(ns) \). Thus

\[
\mathcal{H}_0 = \hbar \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \delta & 0 & 0 \\
0 & 0 & \delta & 0 \\
0 & 0 & 0 & \delta \\
\end{pmatrix}
\]

and the eigenvalues of \( \mathcal{H} \) are\[59, 60, 61\]

\[
U_{\pm}(R) = \frac{\hbar \delta}{2} \pm \sqrt{\left(\frac{\hbar \delta}{2}\right)^2 + \frac{4U_3^2(R)}{3}}.
\] (14.29)

When \( \delta = 0 \) the \( R \) dependence is \( U = \pm \frac{2}{3 \sqrt{2}} U_3(R) \sim 1/R^3 \) which we expect for a resonant dipole-dipole interaction.

When the two terms inside the square root in Eq. (14.29) are equal the interaction is intermediate between short range resonant dipole-dipole and long range van der Waals. This condition defines a crossover length \( R_C \) for which

\[
U_3(R_C) = \frac{\sqrt{3} \hbar \delta}{4}.
\]

For \( R \gg R_c \) the eigenvalues are

\[
U_{\pm}(R) \sim \frac{\hbar \delta}{2} \pm \frac{4U_3^2(R)}{3\hbar \delta}.
\]

The \( R \) dependent term is proportional to \( 1/R^6 \) so we have recovered the Van derWaals interaction which has strength

\[
U_{vdW} = \frac{C_6}{R^6} = \frac{4U_3^2(R)}{3\hbar \delta}.
\]

The \( C_6 \) coefficient is

\[
C_6 = \frac{4q^4}{3\hbar \delta} |\langle n'1||r||n0\rangle \langle n''1||r||n0\rangle|^2
\] (14.30)
where \( n', n'' \) label the near resonant \( p \) levels and

\[
\hbar \delta = E(n'p) + E(n''p) - 2E(ns).
\]

Since dipole matrix elements between neighboring states scale as \( n^2 \) the resonant interaction has scaling \( U_3 \sim n^4 \). In the van der waals limit the scaling is \( C_s \sim U_3^2/\delta \sim n^8/(1/n^3) \sim n^{11} \). In the heavy alkali atoms the quantum defects are such that \( \delta \sim 1/n^4 \) and \( C_6 \sim n^{12} \). Note also that \( C_6 \) can be positive or negative, depending on the sign of \( \delta \). This is different than the situation for ground state atoms where \( C_6 \) is always negative.

### 14.7.1 Fine structure effects

In real atoms it is necessary to account for fine structure effects. The usefulness of the Förster resonance for implementing blockade depends on the angular momentum of the coupled states. The most general matrix element between fine structure states is

\[
\langle \tilde{V}_{dd} \rangle = \langle n'_a l'_a j'_a m'_a | n'_b l'_b j'_b m'_b | \tilde{V}_{dd} | n_a l_a j_a m_a \rangle | n_b l_b j_b m_b \rangle.
\]

\[
= -\frac{q^2}{R^3} \sqrt{6} \sum_p C_{ip1-p}^{20} \langle n'_a l'_a j'_a m'_a | r_{ap} | n_a l_a j_a m_a \rangle \langle n'_b l'_b j'_b m'_b | r_{bp} | n_b l_b j_b m_b \rangle.
\]

The interaction preserves the projection of angular momentum along the interatomic axis: \( M = m_a + m_b = m'_a + m'_b = M' \). The strength and angular dependence of the interaction depend crucially on the choices of \( l, j, l', j' \) and \( M \). A comprehensive study of all the possible interaction channels for states that can be reached by one or two photon excitation from the ground state of neutral alkali atoms has been performed[57].

An example of a more complicated interaction including fine structure and Zeeman sublevels is shown in Fig. 14.5. Two ^87^Rb 43d<sub>5/2</sub> atoms have a very small Förster defect of less than 10 MHz which gives rise to a strong van der Waals interaction. Nevertheless there are
almost non-interacting superpositions of Zeeman substates as can be seen in the nearly flat potentials in the figure. The situation is somewhat analogous to the dark states we discussed in the context of optical pumping in Ch. 13. When the number of final states is less than or equal to the number of initial states it is possible to have superpositions of the initial states that zero interaction eigenvalues.

14.7.2 Different initial states

It is possible to reduce the Förster energy defect and obtain a stronger interaction by starting with two different initial states. The initial states could be different states of the same type of atom, but could also be states of two different atomic elements. If we restrict ourselves to single electron alkali atoms initially in $ns_{1/2}$ states the interaction strength can be expressed in a compact form.

In the rest of this section we follow the notation of [58] for the dipole-dipole interaction between atoms $a$ and $b$. The notation mostly follows the theory of [57] with some modifications, and slightly generalized to allow for the initial Rydberg pair states to be distinguishable. We characterize the strength of the interaction for a particular angular momentum channel by the $C_3$ and van der Waals coefficients. The label $\gamma_a = (z_a, n_a, l_a, j_a)$ denotes the quantum numbers of a single Rydberg level $a$. The coupling $(ab) \leftrightarrow (\alpha\beta)$ specifies an interaction channel $k$ coupling a pair of atoms in fine structure levels $a, b$ to a pair of atoms in fine structure levels $\alpha, \beta$. Here $z$ specifies the atomic species, $n$ is the principal quantum number, $l$ is the orbital angular momentum, and $j$ is the total electronic angular momentum of a fine structure state. We assume single electron $s = 1/2$ atoms throughout.

We define the $C_{3,k}$ coefficient of channel $k$ as

$$C_{3,k}(a, b, \alpha, \beta) = \frac{q^2 \langle \gamma_\alpha || r_a || \gamma_a \rangle \langle \gamma_\beta || r_b || \gamma_b \rangle}{\sqrt{(2j_\alpha + 1)(2j_\beta + 1)}},$$

(14.32)

with $q^2 = e^2/4\pi\epsilon_0$, $e$ is the electronic charge, $\epsilon_0$ is the permittivity of free space, and $\langle \gamma_a || r_a || \gamma_a \rangle$ is a reduced matrix element in the fine structure basis. This differs from the notation of [57] where the $C_3$ coefficient was defined in terms of radial matrix elements in the $n, l$ basis. Note that $C_{3,k}$ depends on a total of 14 parameters: $z_a, z_b, n_a, l_a, j_a, n_b, l_b, j_b, n_\alpha, l_\alpha, j_\alpha, n_\beta, l_\beta, j_\beta$.

The energy defect for channel $k$ is $\hbar\delta_k = \hbar(\delta_{a\alpha} + \delta_{b\beta}) = [U(\gamma_\alpha) - U(\gamma_a)] + [U(\gamma_\beta) - U(\gamma_b)]$. In the approximation that a single channel dominates the interaction the energy shift of a Förster eigenstate $|u_{k\ell}\rangle$ depends on the interatomic separation $R$ as

$$U_{k\ell}(m_a, m_b) = \frac{\hbar\delta_k}{2} \left[ 1 - \left( 1 + \frac{4D_{k\ell}(m_a, m_b)C_{3,k}^2}{\hbar^2\delta_k^2 R^6} \right)^{1/2} \right].$$

(14.33)

The angular factor $D_{k\ell}$ is always positive so for $\delta_k > 0 (< 0)$ the interaction is attractive(repulsive). The long range van der Waals interaction for eigenstate $\ell$ in channel $k$ is

$$U_{k\ell,\text{vdW}} = -\frac{D_{k\ell}C_{3,k}^2}{\hbar\delta_k} \frac{1}{R^6}.$$
Table 14.1: Interaction channels $k$, eigenvalues $D_{kl}$, and eigenvectors $|u_{kl}\rangle$ for atoms in $ns_{1/2}$ states. Eigenvalues $D_{kl}$ are for atoms in identical initial states $\gamma_a \neq \gamma_b$ with allowed couplings $(ab) \leftrightarrow (\alpha\beta)$. Eigenvalues $D'_{kl}$ are for atoms in initial states $\gamma_a = \gamma_b$ with allowed couplings $(ab) \leftrightarrow (\alpha\beta)$ and $(ab) \leftrightarrow (\beta\alpha)$. The eigenvectors specified in terms of states $|m_a, m_b\rangle$ are the singlet and triplet states $|u_{s}\rangle = \frac{1}{\sqrt{2}}(|1/2, -1/2\rangle - |1/2, 1/2\rangle)$, $|u_{t0}\rangle = \frac{1}{\sqrt{2}}(|1/2, -1/2\rangle + |1/2, 1/2\rangle)$, $|u_{t\pm}\rangle = |\pm 1/2, \pm 1/2\rangle$. States $s, t, t\pm$ are labeled as $\ell = 1, 2, 3, 4$ respectively.

| channel $k$ | $j_\alpha$ | $j_\beta$ | $m = m_a + m_b$ | $|u_{kl}\rangle$ | $D_{kl}$ | $D'_{kl}$ |
|-------------|-------------|-------------|----------------|-----------------|--------|--------|
| 1           | 1/2         | 1/2         | 0              | $|u_{s}\rangle$  | 0      | 0      |
|             |             |             | 0              | $|u_{t0}\rangle$ | 16/9   | 32/9   |
|             |             |             | 1              | $|u_{t\pm}\rangle$ | 4/9    | 8/9    |
| 2           | 1/2         | 3/2         | 0              | $|u_{s}\rangle$  | 2      | 4      |
|             |             |             | 0              | $|u_{t0}\rangle$ | 2/9    | 4/9    |
|             |             |             | 1              | $|u_{t\pm}\rangle$ | 14/9   | 28/9   |
| 3           | 3/2         | 1/2         | 0              | $|u_{s}\rangle$  | 2      | 4      |
|             |             |             | 0              | $|u_{t0}\rangle$ | 2/9    | 4/9    |
|             |             |             | 1              | $|u_{t\pm}\rangle$ | 14/9   | 28/9   |
| 4           | 3/2         | 3/2         | 0              | $|u_{s}\rangle$  | 2      | 4      |
|             |             |             | 0              | $|u_{t0}\rangle$ | 34/9   | 68/9   |
|             |             |             | 1              | $|u_{t\pm}\rangle$ | 22/9   | 44/9   |

We define a crossover distance $R_c$ marking the boundary between a $1/R^3$ resonant interaction and a $1/R^6$ van der Waals interaction by

$$R_c = \left(\frac{D_{kl}C_3^2}{\hbar^2\delta_k^6}\right)^{1/6}.$$ 

The angular factor $D_k(m_a, m_b)$ depends on the quantum numbers of the interacting states and can be calculated with the methods described in [58].

When we consider the interaction of atoms of different types, either two different atomic elements, or two different isotopes of one element, we have $\gamma_a \neq \gamma_b$ and only include the coupling $(ab) \leftrightarrow (\alpha\beta)$. Also for atoms of the same type but with $\gamma_a \neq \gamma_b$ there will usually only be a single coupling $(ab) \leftrightarrow (\alpha\beta)$ which is dominant. The $D_{kl}$ values for channel $k$ and eigenvector $\ell$ for $ns_{1/2}$ states are given in Table 14.1. Interaction of atoms of the same type which are prepared in the same levels, $\gamma_a = \gamma_b$, will have two sets of couplings of the same strength: $(ab) \leftrightarrow (\alpha\beta)$ and $(ab) \leftrightarrow (\beta\alpha)$. This gives the twice larger $D'_{kl}$ values given in Table 14.1.

Starting with a specific molecular Rydberg state $|\psi\rangle = \sum_{ij} c_{ij} |m_{ai}, m_{bj}\rangle$ the interaction energy due to channel $k$ is found by decomposing into the Förster eigenstates $|u_{kl}\rangle$. Writing $|\psi\rangle = \sum_{\ell} c_{\ell k} |u_{kl}\rangle$ with $c_{\ell k} = \langle u_{kl}|\psi\rangle$ we have

$$U_{|\psi\rangle,k} = \sum_{\ell} |c_{\ell k}|^2 U_{k\ell}.$$ 

When there are multiple interaction channels $\{k\}$, corresponding to additional values of $\gamma_a, \gamma_\beta$, the situation is more complicated and in general has to be treated by numerical
solutions that account for multiple channels. When $R \gg R_c$ so the interaction energy is small compared to the Förster energy defect there is negligible amplitude of the target states $\alpha, \beta$ and in a first approximation we may assume the energy shifts are additive. In this van der Waals limit the interaction energy is

$$U_{|\psi\rangle, \text{vdW}} = \sum_{k,\ell} |c_{k\ell}|^2 U_{k\ell, \text{vdW}}.$$  \hspace{1cm} (14.34)

At small $R$ where the interaction is resonant and there is substantial state mixing we must account for coupling between channels, which is most conveniently done numerically. The interchannel coupling may lead to nonadditive behavior, as has been discussed previously[62, 63].

The description so far has considered only the situation where the atoms are quantized along $\hat{z}$ which coincides with the molecular axis $\hat{R}$ connecting atom $a$ to atom $b$. The more general case of $\hat{R}$ at an angle $\theta$ with respect to $\hat{z}$ is important for calculating interaction strengths in three dimensional ensembles. The near spherical symmetry of the interaction which is known for coupling of indistinguishable atomic $ns_{1/2}$ states is substantially modified when we consider distinguishable atomic states. Details of the angular dependence of the interaction can be found in [58].

14.7.3 Interaction of ground and Rydberg states

We can use the Förster mechanism to calculate the strength of the interaction between a ground state and a Rydberg excited atom. Roughly speaking $U_{g-\text{Ryd}} \sim \sqrt{U_{g-g} U_{\text{Ryd-Ryd}}}$. Consider an $s_{1/2}$ alkali ground state $|g\rangle = |n_g, 0, 1/2\rangle$. The ground state interacts with an excited atom in a Rydberg $ns_{1/2}$ state $|r\rangle = |n_r, 0, m_r\rangle$ where $m_r = \pm 1/2$. Although we can readily calculate the interaction including the fine structure let’s just get an estimate of the coupling between a ground state $l_g = 0$ and an excited state $l_r = 0$.

The van der Waals $1/R^6$ interaction can be calculated by considering the dipole-dipole interaction with energy defect. The levels that lead to the smallest possible defect are shown in Fig. 14.6 for the case of Rb. The smallest energy defect for interaction with the 55s level

![Figure 14.6: Dipole-dipole coupling of ground and Rydberg states in Rb.](image)
The value given has been calculated using a weighted sum of the $p_{1/2}$ and $p_{3/2}$ levels.

The matrix element of $\hat{V}_{dd}$ between symmetrized states is

$$
\langle n_3l_3m_3; n_4l_4m_4 | \hat{V}_{dd} | n_1l_1m_1; n_2l_2m_2 \rangle = \frac{1}{R^3} \frac{1}{\sqrt{2(1 + \delta_{n_1n_2} \delta_{l_1l_2} \delta_{m_1m_2})}} \sqrt{2(1 + \delta_{n_3n_4} \delta_{l_3l_4} \delta_{m_3m_4}) \sqrt{(2l_3 + 1)(2l_4 + 1)}}
$$

$$
\times \sum_p C^{20}_{l_{1-p}} \left[ \langle n_3l_3||r||n_1l_1 \rangle \langle n_4l_4||r||n_2l_2 \rangle \left( C^{d_{3m_3}}_{l_{1-m_1}1p} C^{d_{4m_4}}_{l_{2-m_2}1-p} + C^{d_{4m_4}}_{l_{2-m_2}1p} C^{d_{3m_3}}_{l_{1-m_1}1-p} \right) \\
+ \langle n_4l_4||r||n_1l_1 \rangle \langle n_3l_3||r||n_2l_2 \rangle \left( C^{d_{4m_4}}_{l_{1-m_1}1p} C^{d_{3m_3}}_{l_{2-m_2}1-p} + C^{d_{3m_3}}_{l_{2-m_2}1p} C^{d_{4m_4}}_{l_{1-m_1}1-p} \right) \right] (14.36)
$$

where subscripts 1, 2, 3, 4 label the participating levels. Using the method detailed in the previous section we find

$$
C_6(5s - 55s) = \frac{2q^4}{3h\delta} \langle 5p||r||5s \rangle \langle 6p||r||55s \rangle + \langle 6p||r||5s \rangle \langle 5p||r||55s \rangle \rangle)^2. (14.37)
$$

Using the matrix elements $\langle 5p||r||5s \rangle = 5.14a_0$, $\langle 6p||r||5s \rangle = -0.589a_0$, $\langle 5p||r||55s \rangle = -0.011a_0$, and $\langle 6p||r||55s \rangle = 0.020a_0$, we get

$$
C_6(5s - 55s) = 8.9 \times 10^{-11} \text{ (Hz \, \mu m}^6) .
$$

For example at a density of $10^{12}$ cm$^{-3}$ the average interatomic spacing is 1 $\mu$m and the energy shift is exceedingly small.

There is however a much stronger interaction possible at large energy defect which takes advantage of the $n^2$ scaling of the radial matrix elements. The reduced matrix elements $\langle n'p||r||ns \rangle$ are shown in Fig. 14.7 for $n = 55$. We see that almost all of the oscillator

Figure 14.7: Rb radial matrix elements $\langle n'p||r||ns \rangle$ for $n = 55$ calculated from a weighted average of transitions to the $p_{1/2}$ and $p_{3/2}$ levels.
strength is divided between the transitions \( ns \to np \) and \( ns \to (n+1)p \). The largest matrix element is \( \langle 5p\|r\|5s \rangle = 3069a_0 \). The corresponding energy defect is

\[
h\delta = E(5p) + E(55p) - E(5s) - E(55s)
\]

\[
\simeq 12817 \text{ cm}^{-1}.
\] (14.38)

This is about 4.5 times larger than the defect considered above. However we pick up a huge factor in the matrix element and find

\[
C_6(5s - 55s) = 1.6 \ (\text{Hz} \ \mu\text{m}^6).
\]

This is a much larger effect. Assuming a density of \( 10^{14} \text{ cm}^{-3} \) the interaction strength of a Rydberg and ground state atom at an average spacing amounts to 25 kHz.
Chapter A

Appendix: Quantum theory of angular momentum

Detailed understanding of the structure and interaction of atoms and other three dimensional objects relies on the quantum mechanical description of angular momentum. In this section we summarize some essential parts of the quantum theory of angular momentum. The description is brief and is not intended to be a substitute for a quantum mechanics textbook which should be consulted for proofs of the results given below\(^1\).

The quantum theory of angular momentum is more involved than the theory of linear momentum. The main reason for this is that while different components of the linear momentum commute \([\hat{p}_i, \hat{p}_j] = 0\), the same is not true for angular momentum. Rotations in three dimensional space are not commutative. Angular momentum operators are the generators of rotations and it is therefore not surprising that different components of the angular momentum do not commute. The lack of commutation means that only one component at a time of the angular momentum can be specified with certainty, and that the product of the uncertainties in two components satisfy a Heisenberg uncertainty relation. These facts aare important in understanding the phenomena encountered in three dimensional quantum dynamics.

A.1 Angular momentum operators and states

We denote the angular momentum operator by \(\hat{\mathbf{J}}\) which has Cartesian components\(^2\):

\[
\hat{\mathbf{J}} = \hat{J}_x \mathbf{e}_x + \hat{J}_y \mathbf{e}_y + \hat{J}_z \mathbf{e}_z.
\]

Any operator satisfying the commutation relations \([\hat{J}_i, \hat{J}_j] = i\epsilon_{ijk} \hbar \hat{J}_k\) is an angular momentum. Equivalently any operator satisfying \(\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}}\) is an angular momentum. A complete set of commuting observables (CSCO) for states carrying angular momentum is provided by the operators \(\hat{J}_x^2, \hat{J}_y^2, \hat{J}_z^2\). The eigenstates of these operators are labeled \(|j, m\rangle\) where \(j \geq 0\) is the angular momentum and \(m\) is the “magnetic” quantum number which

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\(^2\)Since hats denote quantum operators we use \(\mathbf{e}_x\) etc., instead of the more customary \(\hat{x}\) to denote unit vectors.

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apparent text
and on taking the square root we get
\[ |\hat{J}| = \hbar \sqrt{j(j + 1)}. \]

If \(|\hat{J}|\) were less than this amount we would violate the uncertainty principle. Note that although \((\Delta \hat{J}_x)(\Delta \hat{J}_y) \geq \frac{\hbar}{2}\langle \hat{J}_z \rangle\) it is possible to prepare states for which e.g. \((\Delta \hat{J}_x) < \left(\frac{\hbar}{2}(\langle \hat{J}_z \rangle)\right)^{1/2}\) and \((\Delta \hat{J}_y) > \left(\frac{\hbar}{2}(\langle \hat{J}_z \rangle)\right)^{1/2}\). Such states are called spin-squeezed states and they are of interest for metrology with reduced quantum uncertainties. For example it has been demonstrated that atomic clocks with reduced uncertainties are possible using such states.

Returning to the algebraic development it is convenient to introduce the raising and lowering operators
\[ \hat{J}_\pm = \mp \frac{1}{\sqrt{2}} (\hat{J}_x \pm i \hat{J}_y). \]

The square of the angular momentum can be written in terms of these operators as \(\hat{J}^2 = -\hat{J}_+ \hat{J}_- - \hat{J}_- \hat{J}_+ + \hat{J}_z^2\). These operators raise or lower the value of \(m\) according to
\[ \hat{J}_\pm |j, m\rangle = \mp \frac{1}{\sqrt{2}} \sqrt{j(j + 1) - m(m \pm 1)} \hbar |j, m \pm 1\rangle. \]

We also have the commutation relations \([\hat{J}_2, \hat{J}_\pm] = 0\), \([\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm\), and \([\hat{J}_+, \hat{J}_-] = -\hbar \hat{J}_z\).

Repeated application of (A-4) shows that
\[ \hat{J}_+ \hat{J}_- |j, m\rangle = -\frac{j(j + 1) - m(m - 1)}{2} \hbar^2 |j, m\rangle \]
\[ \hat{J}_- \hat{J}_+ |j, m\rangle = -\frac{j(j + 1) - m(m + 1)}{2} \hbar^2 |j, m\rangle \]

In the case of integer values of \(j = l\) the angular momentum states can be written in a coordinate representation in terms of the spherical harmonics \(Y_{l,m}(\theta, \phi) = \langle \theta, \phi|l, m\rangle\). The eigenvalue relations then take the form
\[ \hat{L}^2 Y_{l,m}(\theta, \phi) = l(l + 1) \hbar^2 Y_{l,m}(\theta, \phi) \]
\[ \hat{L}_z Y_{l,m}(\theta, \phi) = m \hbar Y_{l,m}(\theta, \phi) \]

where
\[ \hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \]
\[ \hat{L}_z = -i \hbar \frac{\partial}{\partial \phi}. \]

The three dimensional Laplacian is related to \(\hat{L}^2\) by
\[ \nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{1}{r^2 \hbar^2} \hat{L}^2. \]
A.1.1 Addition of angular momenta

In order to describe the states of composite systems which are combinations of subsystems with angular momenta $\hat{J}_1, \hat{J}_2, \ldots$ it is necessary to understand how the individual momenta combine to give a total angular momentum $\hat{J}$. For example we could have $\hat{J}_1 = \hat{L}$ and $\hat{J}_2 = \hat{s}$ corresponding to orbital and spin degrees of freedom of a particle. Alternatively we could have $\hat{J}_1 = \hat{s}_1$ and $\hat{J}_2 = \hat{s}_2$ corresponding to spin degrees of freedom of two different particles.

Two angular momenta $\hat{J}_1, \hat{J}_2$ acting in separate Hilbert spaces $\mathcal{E}_1, \mathcal{E}_2$ can be combined to give a coupled angular momentum

$$\hat{J} = \hat{J}_1 \otimes \hat{I}_2 + \hat{I}_1 \otimes \hat{J}_2 = \hat{J}_1 + \hat{J}_2$$

$$= (\hat{J}_{1x} + \hat{J}_{2x})\mathbf{e}_x + (\hat{J}_{1y} + \hat{J}_{2y})\mathbf{e}_y + (\hat{J}_{1z} + \hat{J}_{2z})\mathbf{e}_z$$

$$= \hat{J}_x\mathbf{e}_x + \hat{J}_y\mathbf{e}_y + \hat{J}_z\mathbf{e}_z. \quad (A-8)$$

We assume that the angular momenta $\hat{J}_1, \hat{J}_2$ act in different spaces and thus commute with each other. It is important to understand that Eq. (A-8) applies to operators and does not imply that the value of the coupled angular momentum $j$ is always equal to $j_1 + j_2$. As we will see one of the results of angular momentum coupling theory is that $j$ can take on a range of possible values for fixed $j_1, j_2$.

Some insight into states of coupled angular momenta can be obtained with the vector model of Fig. A.2. In an uncoupled basis $j_1, m_1$ and $j_2, m_2$ are “good” quantum numbers, i.e. they are constant in time and describe the states of the separate subsystems. The sum of the angular momentum projections $m = m_1 + m_2$ is also a good quantum number, although the vector sum $|\mathbf{J}_1 + \mathbf{J}_2|$ is not constant as the two vectors may precess about $\mathbf{e}_z$ at different rates. Interactions between $\mathbf{J}_1, \mathbf{J}_2$ cause them to be coupled and precess about the composite vector $\mathbf{J}$. In the coupled basis the magnitude of $\mathbf{J}$ and its’ projection along $\mathbf{e}_z$ are constant so $j, m$ are good quantum numbers. However, in the coupled basis, $m_1, m_2$ are time varying and are no longer good quantum numbers.
To understand rigorously the effect of angular momentum coupling consider first an uncoupled basis corresponding to the observables $\hat{J}_1, \hat{J}_2$. A CSCO is formed by the operators $\{\hat{J}_1^2, \hat{J}_{1z}, \hat{J}_2^2, \hat{J}_{2z}\}$. The states are labelled $|j_1, m_1; j_2, m_2\rangle$ and the eigenvalue relations are

\[
\begin{align*}
\hat{J}_1^2 |j_1, m_1; j_2, m_2\rangle &= j_1 (j_1 + 1) \hbar^2 |j_1, m_1; j_2, m_2\rangle \tag{A-9a} \\
\hat{J}_{1z} |j_1, m_1; j_2, m_2\rangle &= m_1 \hbar |j_1, m_1; j_2, m_2\rangle \tag{A-9b} \\
\hat{J}_2^2 |j_1, m_1; j_2, m_2\rangle &= j_2 (j_2 + 1) \hbar^2 |j_1, m_1; j_2, m_2\rangle \tag{A-9c} \\
\hat{J}_{2z} |j_1, m_1; j_2, m_2\rangle &= m_2 \hbar |j_1, m_1; j_2, m_2\rangle. \tag{A-9d}
\end{align*}
\]

There are $(2j_1 + 1)(2j_2 + 1)$ states in this uncoupled basis.

We can couple the eigenstates to form states $|j_1, j_2; j, m\rangle$. In the coupled basis a CSCO is given by the operators $\{\hat{J}_1^2, \hat{J}_2^2, \hat{J}^2, \hat{J}_z\}$. The eigenvalue relations in the coupled basis are

\[
\begin{align*}
\hat{J}^2 |j_1, j_2; j, m\rangle &= j(j + 1) \hbar^2 |j_1, j_2; j, m\rangle \tag{A-10a} \\
\hat{J}_z |j_1, j_2; j, m\rangle &= m \hbar |j_1, j_2; j, m\rangle \tag{A-10b} \\
\hat{J}_1^2 |j_1, j_2; j, m\rangle &= j_1 (j_1 + 1) \hbar^2 |j_1, j_2; j, m\rangle \tag{A-10c} \\
\hat{J}_2^2 |j_1, j_2; j, m\rangle &= j_2 (j_2 + 1) \hbar^2 |j_1, j_2; j, m\rangle. \tag{A-10d}
\end{align*}
\]

In the coupled basis $j$ takes on the possible values $|j_1 - j_2|, |j_1 - j_2| + 1, ... j_1 + j_2$ and $-j \leq m \leq j$. The total number of states is unchanged since $\sum_{j=|j_1-j_2|}^{j_1+j_2} 2j + 1 = (2j_1 + 1)(2j_2 + 1)$.

An intuitive explanation for the range of allowed values of $j$ follows from vector additions in the triangle construction shown in Fig. A.3. Since any two of the angular momenta can be combined to give the third we require that

\[
\begin{align*}
j &\leq j_1 + j_2 \tag{A-11a} \\
j_1 &\leq j + j_2 \tag{A-11b} \\
j_2 &\leq j_1 + j \tag{A-11c}
\end{align*}
\]

The last two conditions can be written as $j \geq j_1 - j_2$ and $j \geq j_2 - j_1$ which can be combined to give $j \geq |j_1 - j_2|$. This together with the first condition gives $|j_1 - j_2| \leq j \leq j_1 + j_2$. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{triangle.png}
\caption{Triangle condition for addition of angular momenta.}
\end{figure}
The transformation from the uncoupled to the coupled bases is expressed through the Clebsch-Gordan coefficients. They can be written as

$$|j_1, j_2; j, m\rangle = \hat{I}|j_1, j_2; j, m\rangle = \sum_{m_1, m_2} C^{jm}_{j_1 m_1 j_2 m_2} |j_1, m_1; j_2, m_2\rangle \langle j_1, m_1; j_2, m_2| |j_1, j_2; j, m\rangle \quad \text{(A-12)}$$

where

$$C^{jm}_{j_1 m_1 j_2 m_2} \equiv \langle j_1, m_1; j_2, m_2|j_1, j_2; j, m\rangle \quad \text{(A-13)}$$

are the Clebsch-Gordan coefficients. These coefficients vanish unless

$$|j_1 - j_2| \leq j \leq j_1 + j_2$$
$$m_1 + m_2 = m. \quad \text{(A-14a)}$$

The first of these conditions is the triangle condition, and the second condition expresses the conservation of the angular momentum projection along the quantization axis. The Clebsch-Gordan coefficients can be defined with different phase conventions. We will use the convention that

$$C^{j_1+j_2j_1+j_2}_{j_1 j_2 j_1 j_2} = \langle j_1, j_1; j_2, j_2|j_1, j_2; j_1 + j_2, j_1 + j_2\rangle = 1.$$

which results in all the Clebsch-Gordan coefficients being real. Some additional properties and particular values of Clebsch-Gordan coefficients are given in Sec. A.9.

There are many different notations in use for the Clebsch-Gordan coefficients. Some authors prefer to use the Wigner $3j$ symbols $\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}$ which have a higher symmetry. The $3j$ symbols are related to the Clebsch-Gordan coefficients by

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} = \frac{(-1)^{j+m+2j_1}}{\sqrt{2j+1}} C^{jm}_{j_1 m_1 j_2 m_2}. \quad \text{(A-15)}$$

### A.2 Scalar and vector operators

Quantum mechanical operators can be grouped according to their properties under rotation. The simplest case is that of a scalar operator which is invariant under rotations. This is expressed mathematically by the statement that a scalar operator $\hat{O}$ commutes with all components of the angular momentum $\hat{J}$, i.e. $[\hat{O}, \hat{J}] = 0$.

To see that this implies that expectation values are independent of rotation of the operator consider the matrix elements $\langle\alpha, j, m|\hat{O}|\beta, j', m'\rangle$. Here $\alpha, \beta$ are additional quantum numbers which do not depend on the orientation of the states. There are a total of $(2j + 1)(2j' + 1)$ matrix elements. We want to show that if $j \neq j'$ or $m \neq m'$ the matrix elements vanish, and when $j = j'$ and $m = m'$ all $2j + 1$ matrix elements are equal.
To prove this consider the commutator $[\hat{O}, \hat{J}_z] = 0$. Thus

$$0 = \langle \alpha, j, m | [\hat{O}, \hat{J}_z] | \beta, j', m' \rangle = (m' - m) \hbar \langle \alpha, j, m | \hat{O} | \beta, j', m' \rangle.$$

So if $m' \neq m$ the matrix element must vanish and if $m' = m$ we define the quantity $O_m = \langle \alpha, j, m | \hat{O} | \beta, j', m \rangle$.

We then consider the commutators $[\hat{J}_\pm, \hat{O}] = 0$. Evaluation of matrix elements of these commutators leads to the equalities

$$\sqrt{j(j + 1) - m(m + 1)} O_m = \sqrt{j'(j' + 1) - m(m + 1)} O_{m+1} \quad (A-16a)$$
$$\sqrt{j(j + 1) - m(m + 1)} O_{m+1} = \sqrt{j'(j' + 1) - m(m + 1)} O_m. \quad (A-16b)$$

If $j \neq j'$ there is a contradiction unless $O_m = 0$ for all $m$ and if $j = j'$ all the $O_m$ are equal. Thus for any scalar operator $\hat{O}$ we have that

$$\langle \alpha, j, m | \hat{O} | \beta, j', m' \rangle = O_m \delta_{jj'} \delta_{mm'}.$$

This is a convenient result since it is enough to calculate a single matrix element and the value of $m$ can be chosen to simplify the calculation as much as possible. Examples of scalar operators are $\hat{r}^2, \hat{p}^2, \hat{J}^2$.

One might think that any scalar quantity is a scalar operator, but this is not the case. Consider the Zeeman Hamiltonian $\hat{H} = -\hat{\mu} \cdot \hat{B}$. $\hat{H}$ is a scalar, but if it were a scalar operator levels with different values of $m$ would have the same Zeeman shift when a magnetic field is applied. This disagrees with experiment. The explanation is that a scalar operator is invariant under rotations of the operator with respect to the quantization axis. When the atom is rotated the direction of the dipole moment changes, but the magnetic field stays fixed which breaks the spherical symmetry.

The next type of operator to consider is a vector operator which we define by requiring that expectation values transform under rotation in the same way as classical vectors do. In classical physics a vector $\mathbf{V} = V_x e_x + V_y e_y + V_z e_z$ transforms to $\mathbf{V}' = R \mathbf{V} = V'_x e_x + V'_y e_y + V'_z e_z$ where $R$ is a $3 \times 3$ orthogonal rotation matrix. In terms of Cartesian components this can be written as $V'_i = \sum_j R_{ij} V_j$.

In quantum mechanics we require correspondingly that the expectation value of each component of $\mathbf{V}$ transforms as

$$\langle \psi | \hat{V}_i | \psi \rangle_i = \langle \psi | \hat{V}_i | \psi \rangle \rightarrow \langle \psi | \sum_j \hat{R}_{ij} \hat{V}_j | \psi \rangle = \sum_j \hat{R}_{ij} \langle \psi | \hat{V}_j | \psi \rangle. \quad (A-17)$$

A quantum mechanical state $|\psi\rangle$ transforms as

$$|\psi\rangle \rightarrow \hat{D}_R |\psi\rangle \quad \text{and} \quad \langle \psi | \rightarrow \langle \psi | \hat{D}_R^\dagger$$

where $\hat{D}_R$ is a rotation operator\(^3\). Thus

$$\langle \psi | \hat{V}_i | \psi \rangle \rightarrow \langle \psi | \hat{D}_R^\dagger \hat{V}_i \hat{D}_R | \psi \rangle \quad (A-18)$$

---

\(^3\)The operator for rotation of a state about axis $\mathbf{e}_j$ by an angle $\theta$ is $\hat{D}_R = e^{-i\theta \hat{J}_j / \hbar}$. This is readily shown for the case of orbital angular momentum $\hat{L}$ and can be generalized to an arbitrary angular momentum $\hat{J}$. An arbitrary rotation in three dimensions can be described by successive application of rotation operators about different axes.
and the requirement that the right hand sides of (A-17,A-18) are equal for arbitrary $|\psi\rangle$ results in

$$\hat{D}_R^\dagger \hat{V}_i \hat{D}_R = \sum_j \hat{R}_{ij} \hat{V}_j.$$ (A-19)

This must be true for an arbitrary rotation angle and thus must also apply to an infinitesimal rotation by an angle $\delta \theta$ about the $e_z$ axis. Then

$$\hat{D}_R = 1 - i \frac{\delta \theta \hat{J}_z}{\hbar}$$

and

$$R = \begin{pmatrix} 1 & -\delta \theta & 0 \\ \delta \theta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$ (A-19)

Keeping only linear terms in (A-19) leads to

$$[\hat{V}_x, \hat{J}_z] = -i \hbar \hat{V}_y, \quad [\hat{V}_y, \hat{J}_z] = i \hbar \hat{V}_x, \quad [\hat{V}_z, \hat{J}_z] = 0.$$ (A-20)

If we repeat the calculation for rotation about the other Cartesian axes we can write the results as a single commutation relation

$$[\hat{V}_i, \hat{J}_j] = i \epsilon_{ijk} \hbar \hat{V}_k.$$ (A-20)

Any operator which satisfies Eq. (A-20) thus has expectation values which transform under infinitesimal rotations in the same way as ordinary vectors do. Since finite rotations can be described as a succession of infinitesimal rotations the same relationship must hold. We therefore take Eq. (A-20) as the defining property of a vector operator. Examples of vector operators are the position $\hat{r}$, momentum $\hat{p}$, and orbital angular momentum $\hat{L}$ of a point particle.

### A.3 Rotation of states and operators

An angular momentum eigenket $|jm\rangle$ with respect to a quantization axis $e_z$ will in general be a superposition of eigenkets $|jm'\rangle$ with respect to a different quantization axis $e_{z'}$. The relation between the two sets of eigenkets is found by application of a rotation operator as in the previous section.

Rotations can be written in terms of Wigner $D$ functions $D^j_{mm'}$ which are defined as matrix elements of the rotation operator $\hat{D}$ between states $|jm\rangle, |j'm'\rangle$. These matrix elements are

$$\langle jm | \hat{D}(\alpha, \beta, \gamma) | j'm' \rangle = \delta_{jj'} D^j_{mm'}(\alpha, \beta, \gamma)$$

where $\alpha, \beta, \gamma$ are Euler angles. The transformation is defined by rotation of the coordinate system about $e_z$ by $\alpha$, followed by rotation about the new $e_{y'}$ by $\beta$, followed by rotation about the new $e_{z'}$ by $\gamma$. The rotation operators are unitary

$$\sum_{m=-j}^j D^j_{mm'}(\alpha, \beta, \gamma) D^{j'}_{mm''}(\alpha', \beta, \gamma) = \delta_{m'm''}.$$
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\[
\begin{array}{c|ccc}
 j = 1/2 & m' = 1/2 & -1/2 \\
 m = 1/2 & \cos(\beta/2) & \sin(\beta/2) \\
 -1/2 & -\sin(\beta/2) & \cos(\beta/2) \\
\end{array}
\]

Table A.1: Wigner $d_{mm'}^{j/2}(\beta)$ functions.

\[
\begin{array}{c|ccc}
 j = 1 & m' = 1 & 0 & -1 \\
 m = 1 & \cos^2(\beta/2) & \sin(\beta)/\sqrt{2} & \sin^2(\beta/2) \\
 0 & -\sin(\beta)/\sqrt{2} & \cos(\beta) & \sin(\beta)/\sqrt{2} \\
 -1 & \sin^2(\beta/2) & -\sin(\beta)/\sqrt{2} & \cos^2(\beta/2) \\
\end{array}
\]

Table A.2: Wigner $d_{mm'}^{j}(\beta)$ functions.

It is common to write the $D_{mm'}^{j}(\alpha, \beta, \gamma)$ in terms of a real function $d_{mm'}^{j}$ defined by

\[
D_{mm'}^{j}(\alpha, \beta, \gamma) = e^{-im\alpha}d_{mm'}^{j}(\beta)e^{-im'\gamma}.
\]

The $d_{mm'}^{j}$ have the explicit representation

\[
d_{mm'}^{j}(\beta) = (-1)^{j-m'}[(j + m)!(j \pm m)!(j + m')!(j - m')!]^{1/2} \times \sum_{k} (-1)^{k} \frac{(\cos \frac{\beta}{2})^{m+m'+2k}}{k!(j-m-k)!(j-m'-k)!(m+m'+k)!}.
\]

(A-21)

where the sum on $k$ runs over all integer values for which the factorial arguments are non-negative. Representative values for $j = 1/2, 1, 3/2$ are given in Tables A.1,A.2,A.3.

Note that for the special case of $j = 1/2$ the states rotate just like a classical vector, except with 1/2 of the actual rotation angle. For larger angular momenta this is no longer the case.

These functions have a number of symmetry properties including

\[
\begin{align*}
d_{mm'}^{j}(\beta) &= (-1)^{m-m'}d_{m-m'}^{j}(\beta) = d_{m'-m}^{j}(\beta) \\
d_{mm'}^{j}(-\beta) &= (-1)^{m-m'}d_{mm'}^{j}(-\beta) = d_{m'm}^{j}(\beta) \\
d_{mm'}^{j}(\beta \pm 2\pi n) &= (-1)^{2jn}d_{mm'}^{j}(\beta).
\end{align*}
\]

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Using the above we can find the action of the operator $\hat{J}_z$ on a rotated eigenket. We have

$$\langle jm'| \hat{J}_z \hat{D} | jm \rangle = \langle jm'| \hat{J}_z \sum_{m''} |jm''\rangle \langle jm''| \hat{D} | jm \rangle$$

$$= \langle jm'| \hat{J}_z \sum_{m''} |jm''\rangle D_{m''m}^j$$

$$= \hbar \langle jm'| \sum_{m''} jm''|jm''\rangle D_{m''m}^j$$

$$= \hbar D_{m'm}.\]$$

Thus rotation of a superposition state $|\psi\rangle = \sum_m c_m |jm\rangle$ changes $\langle \hat{J}_z \rangle = \hbar \sum_m |c_m|^2 m$ to

$$\langle \hat{J}_z \rangle' = \langle \psi| \hat{D}^\dagger \hat{J}_z \hat{D} | \psi \rangle$$

$$= \sum_{m'} c_{m'}^* \langle jm'| \hat{D}^\dagger \hat{J}_z \hat{D} \sum_m c_m |jm \rangle$$

$$= \sum_{mm'nn'} c_m c_{m'}^* \langle jm'| \hat{D}^\dagger |jn \rangle \langle jn| \hat{J}_z |jm \rangle$$

$$= \sum_{mm'nn'} c_m c_{m'}^* D_{nn'}^j D_{mm'}^j \langle jn| \hat{J}_z |jm \rangle$$

$$= \hbar \sum_{mm'nn'} c_m c_{m'}^* D_{nn'}^j D_{mm'}^j \delta_{nn'}$$

$$= \hbar \sum_{mm'n} c_m c_{m'}^* D_{nn'}^j D_{mm}^n$$

$$= \hbar \sum_{mm'n} c_m c_{m'}^* d_{nn'}^j d_{mm}^j.$$

For the special case of spin 1/2 and a rotation through an angle $\beta$ we get

$$\langle \hat{J}_z \rangle' = \frac{\hbar}{2} \left( |c_{1/2}|^2 - |c_{-1/2}|^2 \right) \cos^2(\beta/2) + \frac{\hbar}{2} \left( c_{1/2} c_{-1/2} + c_{1/2}^* c_{-1/2}^* \right) \cos(\beta/2) \sin(\beta/2).$$

When $c_{1/2} = 1$, $c_{-1/2} = 0$ we get $\langle \hat{J}_z \rangle' = \frac{\hbar}{2} \cos^2(\beta/2)$, i.e. the expectation value rotates at one half the geometrical rotation rate.

Let's consider a more complicated example. The Cs atom ground state has hyperfine levels with total angular momentum $f = 3$ or $f = 4$. An atom prepared in the clock state $|4, 0\rangle$ with $\langle \hat{F}_z \rangle = 0$ will have

$$\langle \hat{F}_z \rangle' = \hbar \sum_n d_{n0}^j d_{n0}^j$$

$$= \hbar \left\{ \frac{9}{64} + \frac{5}{32} [2 + (-2)] + \frac{35}{128} [4 + (-4)] \right\}$$

$$= 0. \quad (A-22)$$

We see from the intermediate stage of the calculation that there are probabilities of being in the rotated eigenkets of $9/64 = 0.14$ for $m' = 0$, $5/32 = 0.16$ for $m' = \pm 2$, and $35/128 = 0.27$ for $m' = \pm 4$. 
The same calculation, but with an initial stretched state $|4,4\rangle$ gives

\[
\langle \hat{F}_z \rangle' = \hbar \sum_n d_{n0}^i d_n^j \rho_n
\]

\[
= \hbar \left\{ \frac{9}{64} + \frac{5}{32} [2 + (-2)] + \frac{35}{128} [4 + (-4)] \right\}
\]

\[
= 0. \tag{A-23}
\]

### A.4 Spherical coordinates

Why do we care whether or not an operator is a vector operator? The usefulness of this identification appears when we wish to calculate matrix elements of vector operators, which are greatly simplified by use of the Wigner-Eckart theorem. However, in order to apply this theorem in a convenient form it is necessary to first work in a spherical basis instead of the Cartesian coordinate system we have been using so far.

An arbitrary vector $\mathbf{A}$ can be written in terms of Cartesian unit vectors as

\[
\mathbf{A} = A_x \mathbf{e}_x + A_y \mathbf{e}_y + A_z \mathbf{e}_z.
\]

Alternatively we can use spherical basis vectors \{\(\mathbf{e}_+, \mathbf{e}_0, \mathbf{e}_-\)\} which are defined by

\[
\mathbf{e}_0 = \mathbf{e}_z, \quad \mathbf{e}_1 = \mathbf{e}_+ = \frac{1}{\sqrt{2}}(\mathbf{e}_x + i\mathbf{e}_y), \quad \mathbf{e}_{-1} = \mathbf{e}_- = \frac{1}{\sqrt{2}}(\mathbf{e}_x - i\mathbf{e}_y)
\]

\[
\mathbf{e}_0^* = \mathbf{e}_z, \quad \mathbf{e}_1^* = \mathbf{e}_+ = \frac{1}{\sqrt{2}}(\mathbf{e}_x - i\mathbf{e}_y), \quad \mathbf{e}_{-1}^* = \mathbf{e}_- = \frac{1}{\sqrt{2}}(\mathbf{e}_x + i\mathbf{e}_y)
\]

We see that $\mathbf{e}_p^* = (-1)^p \mathbf{e}_{-p}$ and

\[
\mathbf{e}_p^* \mathbf{e}_q = (-1)^p \mathbf{e}_{-p} \mathbf{e}_q = \delta_{pq}.
\]

The inverse transformations are

\[
\mathbf{e}_x = \frac{1}{\sqrt{2}}(\mathbf{e}_1 - \mathbf{e}_{-1}), \quad \mathbf{e}_y = \frac{i}{\sqrt{2}}(\mathbf{e}_1 + \mathbf{e}_{-1}), \quad \mathbf{e}_z = \mathbf{e}_0.
\]

The $q^{th}$ component of a vector $\mathbf{A}$ is by definition $A_q = \mathbf{A} \cdot \mathbf{e}_q$. We wish to write $\mathbf{A}$ such that this definition holds in the spherical basis, and therefore write $\mathbf{A} = \sum_q A_q \tilde{\mathbf{e}}_q$, where the basis vectors $\tilde{\mathbf{e}}_q$ are to be determined. We therefore require

\[
\mathbf{A} \cdot \mathbf{e}_q = \sum_{q'} A_{q'} \tilde{\mathbf{e}}_{q'} \cdot \mathbf{e}_q = A_q.
\]

This is true provided $\tilde{\mathbf{e}}_{q'} \cdot \mathbf{e}_q = \delta_{q'q}$ which implies $\tilde{\mathbf{e}}_q = \mathbf{e}_q^*$. Thus in the spherical basis we have

\[
\mathbf{A} = \sum_{q=-1,0,1} A_q \mathbf{e}_q^* = \sum_{q=-1,0,1} (-1)^q A_{-q} \mathbf{e}_q, \tag{A-24}
\]

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where
\[ A_0 = A_z, \quad A_1 = A_+ = \frac{-1}{\sqrt{2}} (A_x + iA_y), \quad A_{-1} = A_- = \frac{1}{\sqrt{2}} (A_x - iA_y). \] (A-25)

The dot product of two vectors is
\[ \mathbf{A} \cdot \mathbf{B} = \sum_{j=x,y,z} A_j B_j \]
\[ = \left( \sum_{p=-1,0,1} A_p \mathbf{e}_p^* \right) \cdot \left( \sum_{q=-1,0,1} B_q \mathbf{e}_q^* \right) \]
\[ = \sum_{p,q=-1,0,1} A_p B_q \mathbf{e}_p^* \cdot \mathbf{e}_q^* \]
\[ = \sum_{p,q=-1,0,1} A_p B_q (-1)^q \mathbf{e}_{-q} \]
\[ = \sum_{p=-1,0,1} A_p B_{-p} (-1)^p. \] (A-26)

We can express any vector \( \mathbf{A} \) in terms of the spherical polar angles \( \theta, \phi \) as
\[ A_0(\theta, \phi) = |A| \cos \theta = |A| \sqrt{\frac{4\pi}{3}} Y_{10}(\theta, \phi) \]
\[ A_1(\theta, \phi) = -|A| \frac{e^{i\phi} \sin \theta}{\sqrt{2}} = |A| \sqrt{\frac{4\pi}{3}} Y_{11}(\theta, \phi) \]
\[ A_{-1}(\theta, \phi) = |A| \frac{e^{-i\phi} \sin \theta}{\sqrt{2}} = |A| \sqrt{\frac{4\pi}{3}} Y_{1-1}(\theta, \phi). \] (A-27)

Thus
\[ \mathbf{A}(\theta, \phi) = \sum_{q=-1,0,1} A_q(\theta, \phi) \mathbf{e}_q^* = |A| \sqrt{\frac{4\pi}{3}} \sum_q Y_{1q}(\theta, \phi) \mathbf{e}_q^*. \] (A-28)

For good measure let’s verify that equation (A-28) correctly reproduces \( \mathbf{A} \) in Cartesian coordinates. We have
\[ \mathbf{A} = |A| \sqrt{\frac{4\pi}{3}} (Y_{10} \mathbf{e}_0^* + Y_{11} \mathbf{e}_1^* + Y_{1-1} \mathbf{e}_{-1}^*) \]
\[ = |A| \sqrt{\frac{4\pi}{3}} \left[ \sqrt{\frac{3}{4\pi}} \cos \theta \mathbf{e}_z - \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \frac{(-1)}{\sqrt{2}} (\mathbf{e}_x - i\mathbf{e}_y) + \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \frac{1}{\sqrt{2}} (\mathbf{e}_x + i\mathbf{e}_y) \right] \]
\[ = |A| \left[ \cos \theta \mathbf{e}_z + \frac{1}{2} \left( \sin \theta e^{i\phi} + \sin \theta e^{-i\phi} \right) \mathbf{e}_x + \frac{i}{2} \left( \sin \theta e^{-i\phi} - \sin \theta e^{i\phi} \right) \mathbf{e}_y \right] \]
\[ = |A| \left[ \cos \theta \mathbf{e}_z + \sin \theta \cos \phi \mathbf{e}_x + \sin \theta \sin \phi \mathbf{e}_y \right] \]
\[ = A_z \mathbf{e}_z + A_x \mathbf{e}_x + A_y \mathbf{e}_y. \]
Note that the raising and lowering operators for the angular momentum defined in Eq. (A-3) are just the \( \pm \) components of the angular momentum in a spherical basis since

\[
\hat{J} = \hat{J}_x e_x + \hat{J}_y e_y + \hat{J}_z e_z \\
= -\hat{J}_x e_x - \hat{J}_y e_y + \hat{J}_0 e_0
\]

with \( \hat{J}_\pm = \pm \frac{1}{\sqrt{2}} \left( \hat{J}_x \pm i \hat{J}_y \right) \).

Finally we note that relation (A-20) which defines a vector operator can be written in a spherical basis as

\[
[\hat{J}_0, \hat{V}_q] = \hbar q \hat{V}_q, \\
[\hat{J}_\pm, \hat{V}_q] = \mp \frac{\hbar}{\sqrt{2}} \sqrt{2 - q(q + 1)} \hat{V}_{q \pm 1},
\]

where \( q = 1, 0, -1 \).

### A.5 Spherical tensors

Tensors can be thought of as higher dimensional generalizations of scalars and vectors. In classical physics tensors transform according to

\[
T_{ijk...} \to T'_{ijk...} = \sum_r \sum_s \sum_t ... R_{ir} R_{js} R_{kt} ... T_{rst...}.
\]

The number of indices of the tensor \( T \) defines its rank. A scalar is a rank 0 tensor, and a vector is a rank 1 tensor. In quantum mechanics we will mostly be only interested in tensors of rank 0, 1, or 2. A Cartesian tensor of rank 2 can be formed from two vectors \( \mathbf{U}, \mathbf{V} \) giving what is called a dyadic:

\[
T_{ij} = U_i V_j.
\]

This rank 2 tensor has \( 3 \times 3 = 9 \) components since \( i = x, y, z \) and \( j = x, y, z \) and it transforms according to Eq. (A-30) where two rotation matrices appear.

It turns out that it is not convenient to work with Cartesian tensors because they are reducible. That is to say a Cartesian tensor can be decomposed into objects which each transform like tensors of different ranks. Consider the rank 2 Cartesian tensor defined above. We can equivalently write it as

\[
T_{ij} = \left( \frac{\mathbf{U} \cdot \mathbf{V}}{3} \delta_{ij} \right) + \left( \frac{U_i V_j - U_j V_i}{2} \right) + \left( \frac{U_i V_j + U_j V_i}{2} - \frac{\mathbf{U} \cdot \mathbf{V}}{3} \delta_{ij} \right).
\]

It can be readily checked that the components \( T_{ij} \) defined by Eqs. (A-31) or (A-32) are the same. However the three terms in parentheses which appear in Eq. (A-32) have very different transformation properties. They are irreducible Cartesian tensors of ranks 0, 1, and 2. We can write

\[
T_{ij} = T_{ij}^{(0)} + T_{ij}^{(1)} + T_{ij}^{(2)}
\]
where

\[
T^{(0)}_{ij} = \frac{U \cdot V}{3} \delta_{ij} \tag{A-34a}
\]

\[
T^{(1)}_{ij} = \frac{U_i V_j - U_j V_i}{2} \tag{A-34b}
\]

\[
T^{(2)}_{ij} = \frac{U_i V_j + U_j V_i}{2} - \frac{U \cdot V}{3} \delta_{ij} \tag{A-34c}
\]

The first term \(T^{(0)}_{ij}\) is a scalar which is invariant under rotation. The second term \(T^{(1)}_{ij}\) is an antisymmetric tensor with zero trace (sum of the diagonal elements) which can be written as the vector product \(\epsilon_{ijk}(U \times V)_k/2\) and transforms as a vector. The last term \(T^{(2)}_{ij}\) is a symmetric rank 2 tensor with zero trace which transforms as a rank 2 tensor.

The number of independent components of these three terms is 1 (for the scalar), 3 (for the vector), and 5 (for the tensor). The total number of independent components is unchanged by the above decomposition since

\[3 \times 3 = 9 = 1 + 3 + 5\]

Note that the numbers on the right hand side of the above equality correspond to the number of possible states for objects with angular momenta 0, 1, and 2. Indeed by writing \(T_{ij}\) in the form of Eq. (A-33) we have decomposed it into irreducible tensors of rank 0, 1, 2, which are objects that transform like angular momentum states (or spherical harmonics) with \(l = 0, 1, 2\).

The decomposition (A-33) is the irreducible representation of the Cartesian tensor \(T_{ij}\). We write spherical tensors of rank 0, 1, 2 as \(T_0, T_1, T_2\). It can be shown that the elements \(T_{\kappa,q}\) of the spherical tensors of rank \(\kappa\) are related to the Cartesian components of the rank 2 tensor \(T_{ij}\) by

\[
T_{0,0} = \frac{1}{3} \sum_i T_{ii} \tag{A-35a}
\]

\[
T_{1,0} = T^{(1)}_{xy} \tag{A-35b}
\]

\[
T_{1,\pm 1} = \mp \frac{1}{\sqrt{2}} (T^{(1)}_{yz} \pm iT^{(1)}_{zx}) \tag{A-35c}
\]

\[
T_{2,0} = T^{(2)}_{zz} \tag{A-35d}
\]

\[
T_{2,\pm 1} = \mp \sqrt{\frac{3}{2}} (T^{(2)}_{zx} \pm iT^{(2)}_{zy}) \tag{A-35e}
\]

\[
T_{2,\pm 2} = \pm \sqrt{\frac{1}{6}} \left[ T^{(2)}_{xx} - T^{(2)}_{yy} \pm 2iT^{(2)}_{xy} \right] \tag{A-35f}
\]

These relations are specific to the decomposition of a rank 2 tensor. Higher rank Cartesian tensors are more complicated to work with since their irreducible representation is not unique. We define a spherical tensor of rank \(\kappa\) as an operator which satisfies the commutation relations

\[
\left[ \hat{J}_0, \hat{T}_{\kappa,q} \right] = \hbar q \hat{T}_{\kappa,q}, \tag{A-36a}
\]

\[
\left[ \hat{J}_\pm, \hat{T}_{\kappa,q} \right] = \mp \hbar \frac{1}{\sqrt{2}} \sqrt{\kappa(\kappa + 1) - q(q \pm 1)} \hat{T}_{\kappa,q,\pm 1}, \tag{A-36b}
\]
where $-\kappa \leq q \leq \kappa$. A vector is a first rank tensor and putting $\kappa = 1$ in this definition recovers the commutation relations for vector operators given in Eqs. (A-29).

### A.6 Matrix elements of spherical tensors and the Wigner-Eckart theorem

After these preliminaries we come to an important result which enables us to calculate matrix elements using the Wigner-Eckart theorem. Before stating the general form of this theorem let’s consider an example of calculating matrix elements of the position operator between angular momentum states. This task is important for example when calculating dipole matrix elements and Rabi frequencies for optically induced transitions between atomic states.

It follows from Eq. (A-28) that the position operator can be written in a spherical basis as

$$\hat{r}(\theta, \phi) = \sum_{q=-1,0,1} \hat{r}_q(\theta, \phi) e_q^* = |\hat{r}| \sqrt{\frac{4\pi}{3}} \sum_q Y_{1q}(\theta, \phi) e_q^* = \hat{r} \sqrt{\frac{4\pi}{3}} \sum_q Y_{1q}(\theta, \phi) e_q^*. \quad (A-37)$$

The matrix element of the position operator between angular momentum states is therefore

$$\langle n'l'm'|\hat{r}|nlm \rangle = \langle n'l'm'|\hat{r} \sqrt{\frac{4\pi}{3}} \sum_q Y_{1q} e_q^* |nlm \rangle$$

$$= \sqrt{\frac{4\pi}{3}} \sum_q e_q^* \langle n'l'm'|\hat{r}Y_{1q}|nlm \rangle$$

$$= \langle n'l'|\hat{r}|nl \rangle \sqrt{\frac{4\pi}{3}} \sum_q e_q^* \langle l'm'|Y_{1q}|lm \rangle.$$

Here $n, n'$ are radial or other quantum numbers specifying degrees of freedom which do not depend on the angular coordinates. To find the angular matrix element we use the identity

$$Y_{1m_1}(\theta, \phi)Y_{1m_2}(\theta, \phi) = \sum_{lm} \left[ \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)} \right]^{1/2} C^{l_10}_{l_20} C^{lm}_{lm_1l_2} Y_{lm}(\theta, \phi)$$

where $l$ runs over all values satisfying the triangle inequality ($|l_1 - l_2| \leq l \leq l_1 + l_2$) and for each value of $l$, $-l \leq m \leq l$. We then convert the matrix element into an integral over solid angle using $Y_{lm}(\theta, \phi) = \langle \theta, \phi|lm \rangle$ or, more compactly, $Y_{lm}(\Omega) = \langle \Omega|lm \rangle$. The spectral

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resolution of the identity is \( \hat{I} = \int d\Omega |\Omega\rangle \langle \Omega| \) from which it follows that
\[
\langle l' m'| Y_{\nu m'} | l m \rangle = \langle l' m'| \left( \int d\Omega |\Omega\rangle \langle \Omega| \right) Y_{\nu m'} \left( \int d\Omega' |\Omega'| \langle \Omega'| \right) | l m \rangle
\]
\[
= \int d\Omega \int d\Omega' Y_{\nu m'}^{*}(\Omega) |\Omega\rangle Y_{\nu m'} |\Omega'| Y_{lm}(\Omega')
\]
\[
= \int d\Omega Y_{\nu m'}^{*}(\Omega) \int d\Omega' Y_{\nu m'}^{*}(\Omega') \delta(\Omega - \Omega') Y_{lm}(\Omega')
\]
\[
= \int d\Omega Y_{\nu m'}^{*}(\Omega) Y_{\nu m'}(\Omega) Y_{lm}(\Omega).
\]

Thus
\[
\langle l' m'| Y_{1q} | l m \rangle = \int d\Omega Y_{\nu m'}^{*} Y_{1q} Y_{lm}
\]
\[
= \int d\Omega Y_{\nu m'}^{*} \sum_{l' m''} \left[ \frac{3(2l + 1)}{4\pi(2l'' + 1)} \right]^{1/2} C_{l010}^{\nu m''} C_{lm1q}^{l'' m''} Y_{\nu m''}
\]
\[
= \sum_{l' m''} \left[ \frac{3(2l + 1)}{4\pi(2l'' + 1)} \right]^{1/2} C_{l010}^{\nu m''} C_{lm1q}^{l'' m''} \int d\Omega Y_{\nu m'}^{*} Y_{\nu m''}
\]
\[
= \left[ \frac{3(2l + 1)}{4\pi(2l'' + 1)} \right]^{1/2} C_{l010}^{\nu m'} C_{lm1q}^{l'' m''}.
\]

and we get
\[
\langle n' l' m'| \hat{r} | n l m \rangle = \langle n' l' | r | n l \rangle \sqrt{\frac{2l + 1}{2l' + 1}} \sum_{q} C_{l010}^{\nu m'} C_{lm1q}^{l'' m''} e_{q}
\]

(A-38)

which is known as the Gaunt formula. The Clebsch-Gordan coefficient \( C_{l010}^{\nu m''} \) is zero when \( l' = l \) and \( C_{lm1q}^{l'' m''} \) is zero when \( |l' - l| > 1 \) thus the matrix element can only be nonzero when \( l' = l \pm 1 \). When this condition is satisfied we can use Eq. (A-64) to simplify the result to
\[
\langle n' l' m'| \hat{r} | n l m \rangle = (-1)^{l' - l - 1} \langle n' l' | r | n l \rangle \sqrt{\frac{\max(l, l')}{2l' + 1}} \sum_{q} C_{lm1q}^{l'' m''} e_{q}^{*}
\]

(A-40)

The matrix element of an individual component is nonzero only when \( l' = l \pm 1 \) and \( m'' = m + q \). We note that the matrix elements are the product of a factor \( \langle n' l' | r | n l \rangle \) which is independent of \( m, m', q \) and a geometrical factor which does depend on \( m, m', q \). Thus, the dependence on orientation of the matrix elements is always the same, for any radial dependence of the wavefunctions.

### A.6.1 Wigner-Eckart theorem

The Gaunt formula gives a complete description for the matrix elements of the position operator between angular momentum states \( |l m\rangle \). The result can be generalized to matrix
elements of arbitrary spherical tensors using the Wigner-Eckart theorem. It states that

$$\langle \beta j' m' | \hat{T}_{\kappa q} | \alpha j m \rangle = \frac{\langle \beta j' || \hat{T}_\kappa || \alpha j \rangle}{\sqrt{2j'+1}} (-1)^{2\kappa} C_{j' m' j m q}^{j m' \kappa}. \quad (A-41)$$

Here $\hat{T}_{\kappa q}$ is the $q^{th}$ component of a spherical tensor operator $\hat{T}_\kappa$ of rank $\kappa$ with $2\kappa + 1$ components $-\kappa \leq q \leq \kappa$. The tensor components satisfy the angular momentum commutation relations given in Eqs. (A-36). The symbol $\langle \beta j' || \hat{T}_\kappa || \alpha j \rangle$ is known as a reduced matrix element which is independent of $m, m'$.

Using the identity (VMK 8.7.2(4))

$$\sum_{m=-j}^{j} \sum_{q=-\kappa}^{\kappa} \left( C_{j' m' j m q}^{j m' \kappa} \right)^2 = 1$$

we have

$$\sum_{m=-j}^{j} \sum_{q=-\kappa}^{\kappa} \left( C_{j' m' j m q}^{j m' \kappa} \right)^2 = 2j' + 1 \quad \text{for} \quad |j - j'| \leq \kappa \quad \text{and} \quad j + j' \geq \kappa$$

so

$$\sum_{m=-j}^{j} \sum_{q=-\kappa}^{\kappa} \left| \langle \beta j', m + q | \hat{T}_{\kappa q} | \alpha j m \rangle \right|^2 = \left| \langle \beta j' || \hat{T}_\kappa || \alpha j \rangle \right|^2. \quad (A-42)$$

This shows that the sum of the squares of all nonzero matrix elements for all possible orientations of the initial state is equal to the reduced matrix element squared.

For completeness we note that the Wigner-Eckart theorem can also be written in terms of 3j symbols as

$$\langle \beta j' m' | \hat{T}_{\kappa q} | \alpha j m \rangle = (-1)^{j' - m'} \langle \beta j' || \hat{T}_\kappa || \alpha j \rangle \begin{pmatrix} j' & \kappa & j \\ -m' & q & m \end{pmatrix}. \quad (A-43)$$

Using Eq. (A-41) and the properties of the Clebsch-Gordan coefficients we can immediately write down selection rules for transition matrix elements of spherical tensor operators. For scalar operators ($\kappa = 0, q = 0$)

$$j' = j \quad (A-44a)$$
$$m' = m \quad (A-44b)$$

for vector operators ($\kappa = 1, q = -1, 0, 1$)

$$j' = j - 1, j, j + 1 \quad (A-45a)$$
$$j + j' \geq 1 (= \kappa) \quad (A-45b)$$
$$m' = m - 1, m, m + 1, \quad (A-45c)$$

and for rank 2 tensor operators

$$j' = j - 2, j - 1, j, j + 1, j + 2 \quad (A-46a)$$
$$j + j' \geq 2 (= \kappa) \quad (A-46b)$$
$$m' = m - 2, m - 1, m, m + 1, m + 2. \quad (A-46c)$$
The supplementary conditions (A-45b, A-46b) are due to the triangle inequalities Eqs. (A-11).

The selection rules for the matrix elements of spherical tensor operators have a very simple interpretation. The matrix element \( \langle \beta j' \left| \hat{T}_{\kappa q} \right| \alpha j m \rangle \) can only be nonzero if the angular momentum states \( |jm\rangle \) and \( |\kappa q\rangle \) can be combined to give a state \( |j'm'\rangle \). In other words the rules for matrix elements are just like the rules for combining angular momenta, i.e. the spherical tensor of rank \( \kappa \) is like an angular momentum of value \( \kappa \). This close analogy was pointed out above in connection with Eq. (A-33).

The Wigner-Eckart theorem states that matrix elements can be divided into the product of a reduced matrix element that has no orientation dependence and an angular term that is independent of the norm of the operator. The reduced matrix element can be calculated most easily by considering particular values of \( m, m', q \).

For example

\[
\langle n' j' \left| \hat{T}_{\kappa} \right| n j \rangle = (-1)^{2\kappa} \sqrt{2j' + 1} \frac{\langle n' j'0 \left| \hat{T}_{\kappa0} \right| n j0 \rangle}{C_{j'0 \kappa0}^{j0}},
\]

(A-47)

provided the denominator does not vanish.

Note that the reduced matrix element is not a usual Dirac brakket since in general \( \langle n' j' \left| \hat{T}_{\kappa} \right| n j \rangle \neq \langle n j \left| \hat{T}_{\kappa} \right| n' j' \rangle \). If \( \hat{T}_{\kappa0} \) is a real operator, which is often the case, then

\[
\langle n' j' \left| \hat{T}_{\kappa} \right| n j \rangle = (-1)^{2\kappa} \sqrt{2j' + 1} \frac{\langle n' j'0 \left| \hat{T}_{\kappa0} \right| n j0 \rangle}{C_{j'0 \kappa0}^{j0}}
\]

\[
= (-1)^{2\kappa} (-1)^{j-j'} \sqrt{2j + 1} \frac{\langle n j0 \left| \hat{T}_{\kappa0} \right| n' j'0 \rangle}{C_{j'0 \kappa0}^{j0}}
\]

\[
= (-1)^{j-j'} \langle n j \left| \hat{T}_{\kappa} \right| n' j' \rangle^* .
\]

Thus reversing the initial and final states introduces a phase factor of \( (-1)^{j-j'} \) in any real valued reduced matrix element.

To make these results more explicit let us consider an example. We wish to calculate the matrix element of a spherical harmonic \( Y_{1q} \) between orbital angular momentum states \( |l, m\rangle, |l', m'\rangle \). We need the reduced matrix element which from Eq. (A-47) is

\[
\langle l' \left| \hat{Y}_{10} \right| l \rangle = \sqrt{2l' + 1} \frac{\langle l'0 \left| \hat{Y}_{10} \right| l0 \rangle}{C_{l'0 l0}^{l0}}.
\]

We then use (A-38) to get

\[
\langle l'0 | \hat{Y}_{10} | l0 \rangle = \sqrt{\frac{3}{4\pi}} \sqrt{\frac{2l + 1}{2l' + 1}} \left( C_{l'0 l0}^{l0} \right)^2
\]

\[4\text{We suppress the quantum number } n \text{ in the brakket since it labels a radial dependence and } Y_{1q} \text{ has no dependence on } r. \]
so we can write
\[
\langle l' || \hat{Y}_1 || l \rangle = \sqrt{\frac{3}{4\pi}} \sqrt{2l' + 1} C_{l'010}^{l010}.
\]
Therefore
\[
\langle l'm' || \hat{Y}_q || lm \rangle = \left[ \frac{3(2l' + 1)}{4\pi (2l + 1)} \right]^{1/2} C_{l0j0}^{l'010} C_{lmq}^{j00}.
\]
which agrees with Eq. (A-39). This generalizes for a higher order spherical harmonic to (VMK 13.2.8(104))
\[
\langle l'm' || \hat{Y}_jq || lm \rangle = \left[ \frac{(2j + 1)(2l' + 1)}{4\pi (2l + 1)} \right]^{1/2} C_{l0j0}^{l'010} C_{lmq}^{j00}.
\]

An important result is that the tensor of a 2l-pole moment (with even \( l \)) is non-zero only when the total angular momentum is \( J \geq l/2 \) (L&L QM §75). Thus a quadrupole tensor operator \( (l = 2) \) requires \( J \geq 1 \).

### A.6.2 Landé projection theorem

An important special case of the Wigner-Eckart theorem can be used to calculate matrix elements of vector operators in terms of matrix elements of the angular momentum \( \hat{J} \). Consider a vector operator \( \hat{A} \). The Wigner-Eckart theorem implies that
\[
\langle \alpha jm_2 | \hat{A} | \alpha jm_1 \rangle = C \langle \alpha jm_2 | \hat{J} | \alpha jm_1 \rangle
\]
where \( C \) is a constant and \( \hat{J} \) is the angular momentum operator. To evaluate the constant use
\[
\langle \alpha jm_2 | \hat{A} \cdot \hat{J} | \alpha jm_2 \rangle = \sum_{m_1} \langle \alpha jm_2 | \hat{A} | \alpha jm_1 \rangle \cdot \langle \alpha jm_1 | \hat{J} | \alpha jm_2 \rangle
\]
\[
= C \sum_{m_1} \langle \alpha jm_2 | \hat{J} | \alpha jm_1 \rangle \cdot \langle \alpha jm_1 | \hat{J} | \alpha jm_2 \rangle
\]
\[
= C \langle \alpha jm_2 | \hat{J}^2 | \alpha jm_2 \rangle
\]
\[
= Cj(j+1)\hbar^2.
\]

Thus
\[
\langle \alpha jm_2 | \hat{A} | \alpha jm_1 \rangle = \frac{\langle \alpha jm_2 | \hat{A} \cdot \hat{J} | \alpha jm_2 \rangle}{j(j+1)\hbar^2} \langle \alpha jm_2 | \hat{J} | \alpha jm_1 \rangle.
\]  
(A-48)

The result (A-48) is often referred to as the Landé projection theorem. Since the matrix elements of vector operators in a given subspace corresponding to a particular value of \( j \) are all proportional to each other the matrix elements of an operator \( \hat{A} \) can be calculated by projecting \( \hat{A} \) onto \( \hat{J} \), multiplying by the matrix elements of \( \hat{J} \), and normalizing by the expectation value of \( \hat{J}^2 \) which is \( \langle \hat{J}^2 \rangle = j(j+1)\hbar^2 \).

This result can also be understood intuitively using the vector model of angular momentum coupling discussed above. Since \( j \) is a good quantum number, in the coupled basis the
expectation value of a vector $\mathbf{A}$ is given by the projection of $\mathbf{A}$ on $\mathbf{J}$ times the expectation value of $\mathbf{J}$, i.e. $\langle \mathbf{A} \rangle \sim \langle (\mathbf{A} \cdot \mathbf{J}) \mathbf{J} \rangle \sim \langle \mathbf{A} \cdot \mathbf{J} \rangle \langle \mathbf{J} \rangle$. We then have to normalize by $|\mathbf{J}|^2$, and since this is quantum mechanics we replace $|\mathbf{J}|^2$ by $j(j+1)\hbar^2$. Thus $\langle \mathbf{A} \rangle = \frac{\langle \mathbf{A} \mathbf{J} \rangle}{j(j+1)\hbar^2} \langle \mathbf{J} \rangle$ which is Eq. (A-48).

### A.6.3 Matrix elements of coupled angular momenta

In multielectron problems as well as when dealing with fine structure and hyperfine structure manifolds it is necessary to calculate matrix elements between states of coupled angular momenta.

When $\mathbf{J} = \mathbf{L} + \mathbf{s}$ coupled states $|nls; jm\rangle$ are linear combinations of states in the uncoupled basis $|nlm_l; sm_s\rangle$. Applying the Wigner-Eckart theorem we have

$$\langle n'l's'j'm'|\mathbf{T}_\kappa|nlsj\rangle = \frac{\langle n'l's'j'||\mathbf{T}_\kappa||nlsj\rangle}{\sqrt{2j'+1}} (-1)^{2\kappa} C_{j'mnkq} \tag{A-49}$$

When the tensor operator $\mathbf{T}_\kappa$ acts on the degrees of freedom of $\mathbf{L}$ and commutes with $\hat{s}$, the matrix element is only nonzero when $s = s'$ and is equal to (VMK 13.2.1(5))

$$\langle n'l's'j'||\mathbf{T}_\kappa||nlsj\rangle = \delta_{ss'}(-1)^{j+j'+s+\kappa} \sqrt{(2j+1)(2j'+1)} \left\{ \begin{array}{ccc} l & s & j \\ j' & \kappa & j' \end{array} \right\} \langle n'l'||\mathbf{T}_\kappa||nl\rangle. \tag{A-50}$$

When the tensor operator $\mathbf{T}_\kappa$ acts on the degrees of freedom of $\hat{s}$ and commutes with $\mathbf{L}$, the matrix element is only nonzero when $l = l'$ and is equal to (VMK 13.2.1(6))

$$\langle n'l's'j'||\mathbf{T}_\kappa||nlsj\rangle = \delta_{ll'}(-1)^{j+j'+s+\kappa} \sqrt{(2j+1)(2j'+1)} \left\{ \begin{array}{ccc} s & l & j \\ j' & \kappa & s' \end{array} \right\} \langle n'l'||\mathbf{T}_\kappa||ns\rangle. \tag{A-51}$$

These results are true for any uncoupled angular momenta, e.g. we can replace $\mathbf{L}$ by $\mathbf{J}_1$ and $\hat{s}$ by $\mathbf{J}_2$ in the above expressions. These results can be derived by expanding the coupled states in uncoupled states, using the Wigner-Eckart theorem, and then recombining the results with the expression below for the 6j symbols.

The 6j symbol in curly braces describes the coupling of three angular momenta. The large curly braces are standard notation, but they have the drawback of making equations clumsy to typeset. We introduce a more compact notation, in analogy to that for the Clebsch-Gordan coefficients, as

$$S_{abc}^{def} = \left\{ \begin{array}{ccc} a & b & c \\ d & e & f \end{array} \right\}. \tag{A-52}$$

We will use commas between the indices only when needed to avoid ambiguity. The 6j symbol can be written as a sum over Clebsch-Gordan coefficients (VMK 9.1(8))

$$S_{ijklmn}^{jklmn} = \frac{(-1)^{j_1+j_2+j_4+j_5}}{\sqrt{(2j_3+1)(2j_6+1)}} \sum C_{j_3m_4m_5} C_{j_3m_4m_5} C_{j_4m_4m_5} C_{j_4m_4m_5} C_{j_5m_5m_5} C_{j_5m_5m_5}. \tag{A-53}$$

The sum is to be taken over all possible values of $m_1, m_2, m_3, m_4, m_6$ while $m_5$ is held fixed. In practice it is most convenient to look up values needed in a table. The 6j symbols satisfy a number of symmetry relations. They are invariant under the permutation of any two columns or if the upper and lower arguments are interchanged in any two columns. The 6j symbols are zero unless triangle conditions are satisfied by $(a, e, f)$, $(d, b, f)$, and $(d, e, c)$. 


Angular reduction for transitions between hyperfine states

The reduction of reduced matrix elements is often needed when calculating matrix elements for atomic transitions. As an example consider electric dipole (E1) transitions between hyperfine states described by quantum numbers \( \{\gamma\} = n, L, S, J, I, F, m_F \). Here \( F = J + I \) and \( J = L + S \), and \( I, S \) which represent nuclear and electronic spin are unchanged by the dipole coupling to the optical field. We have

\[
\langle n' L'S'J'F' m_F' | r_q | n LSJF m_F \rangle = \frac{\langle n' L'S'J'F' || r || n LSJF \rangle}{\sqrt{2F' + 1}} C_{Fm_Flq}^{Fm_F'}.
\]

The reduced matrix element is decoupled using the relations

\[
\langle n' L'S; J'IF' || r || n LS; JIF \rangle = (-1)^{(1+I+J'+F)} \sqrt{(2F + 1)(2F' + 1)} S_{F1}^{JF} \langle n' L'S; J' || r || n LS; J \rangle
\]

\[
\langle n'; L'S'J' || r || n; LSJ \rangle = (-1)^{(1+S'L'+J)} \sqrt{(2J + 1)(2J' + 1)} S_{F1}^{SLJ} \langle n'; L' || r || n; L \rangle
\]

\[
\langle n' L' || r || nL \rangle = (-1)^{L' + (1 + L + L')/2} \sqrt{\max(L, L')} R_{n'L', nL}.
\]

In these relations the arguments in front of the semicolons in the reduced matrix elements indicate additional quantum numbers that are not involved in the decoupling relation. In addition it is important to maintain consistency in ordering of the arguments in kets and reduced matrix elements since for coupled kets \(|LSJ \neq |SLJ \rangle \). Inconsistency with argument ordering can lead to errors in calculations. In the final line the radial matrix element is defined as

\[
R_{n'L', nL} = \int_0^\infty dr \ r^3 R_{n'L'} R_{nL}
\]

with \( R_{nL} \) the spatial part of the atomic wavefunction. The wave function has units of \( m^{-3/2} \) so \( R_{n'L', nL} \) has units of length. Note that for alkali atoms with \( J \) dependent quantum defects the radial integral will be slightly different for the different fine structure states.

Combining the above terms we find for transitions between hyperfine states

\[
\langle n' L'S'J'F' m_F' | r_q | n LSJF m_F \rangle = (-1)^{1+I+J'+F+S+(1+L+L')/2} \times \sqrt{(2F + 1)(2J + 1)(2J' + 1)\max(L, L')} R_{n'L', nL} \times S_{J'1}^{LSJ} S_{F1}^{JF} C_{Fm_Flq}^{Fm_F'}.
\]

Alternatively, in terms of the reduced matrix element in the \( J \) basis we find

\[
\langle n' L'S'J'F' m_F' | r_q | n LSJF m_F \rangle = (-1)^{1+I+J'+F} \sqrt{(2F + 1)} S_{F1}^{JF} \times \langle n' L'S'J' || r || n LSJ \rangle C_{Fm_Flq}^{Fm_F'}. \]

We may also rewrite this expression as

\[
\langle n' L'S'J'F' m_F' | r_q | n LSJF m_F \rangle = C_{Fm_Flq}^{Fm_F'} c_{JIF}^{J'IF'} \langle n' L'S'J' || r || n LSJ \rangle
\]

with

\[
c_{JIF}^{J'IF'} = (-1)^{1+I+J'+F} \sqrt{2F + 1} S_{F1}^{JF}.
\]

We see that the transition matrix element is a product of three terms: a Clebsch-Gordon coefficient \( C_{Fm_Flq}^{Fm_F'} \) which contains the orientational dependence, a coefficient \( c_{JIF}^{J'IF'} \) which contains the remaining dependence on the initial and final angular momenta, and a reduced matrix element which depends on the radial overlap of the wavefunctions.

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A.7 Tensor products

We will sometimes wish to calculate tensors defined by the composition of two irreducible tensors $\hat{T}_\kappa, \hat{U}_\eta$. There are three different operations to consider, the tensor product, the direct product, and the scalar product. The tensor product defines a new irreducible tensor

$$\hat{V}_\upsilon = \left\{ \hat{T}_\kappa \otimes \hat{U}_\eta \right\}_\upsilon,$$

where $|\kappa - \eta| \leq \upsilon \leq \kappa + \eta$. The components of the tensor $\hat{V}_\upsilon$ are defined by

$$\hat{V}_{\upsilon \mu} = \left\{ \hat{T}_\kappa \otimes \hat{U}_\eta \right\}_{\upsilon \mu} = \sum_{q,r} C^{\upsilon \mu}_{\kappa \eta q r} \hat{T}_\kappa \hat{U}_\eta.$$

The direct product, being the sum of irreducible tensors, is in general reducible and can be written as

$$T_{\kappa \eta} \hat{U}_{\kappa} = \sum_{\upsilon = |\kappa - \eta|}^{\kappa + \eta} C_{\kappa \eta \upsilon q r} \hat{V}_{\upsilon \mu}.$$

The scalar product of two irreducible tensors of the same rank is defined by

$$\left( \hat{T}_\kappa \cdot \hat{U}_\kappa \right) = \sum_{q} (-1)^{-q} T_{\kappa q} \hat{U}_{\kappa, -q} \quad \text{(A-57)}$$

which gives a rank zero result. The irreducible tensor product of zero rank is

$$\left\{ \hat{T}_\kappa \otimes \hat{U}_\kappa \right\}_{00} = \sum_{q,r} C^{00}_{\kappa \eta q r} \hat{T}_\kappa \hat{U}_\eta = \frac{1}{\sqrt{2\kappa + 1}} \sum_{q} (-1)^{\kappa - q} T_{\kappa q} \hat{U}_{\kappa, -q} \quad \text{(A-58)}$$

Equations (A-57) and (A-58) are related by

$$\left( \hat{T}_\kappa \cdot \hat{U}_\kappa \right) = (-1)^{-\kappa} \sqrt{2\kappa + 1} \left\{ \hat{T}_\kappa \otimes \hat{U}_\kappa \right\}_{00}.$$

When two tensors $\hat{T}_{\kappa q}(1), \hat{U}_{\eta r}(2)$ act on independent systems 1, 2 characterized by quantum numbers $n_1, j_1, m_1$ and $n_2, j_2, m_2$ which couple to states $j, m$ the matrix element of the scalar product in the coupled representation is (VMK 13.1.4(29))

$$\langle n'_1 j'_1 n'_2 j'_2 n' m' | (\hat{T}_\kappa(1) \cdot \hat{U}_\kappa(2)) | n_1 j_1 n_2 j_2 m \rangle = \delta_{j j'} \delta_{m m'} (-1)^{j_1 + j_2}$$

$$\langle n'_1 j'_1 | \hat{T}_\kappa(1) | n_1 j_1 \rangle \langle n'_2 j'_2 | \hat{U}_\kappa(2) | n_2 j_2 \rangle S_{j_2 j_2}^{j_1 j_1} \quad \text{(A-59)}$$

Provided all components of $\hat{T}_{k_1}$ and $\hat{U}_{k_2}$ commute we can recouple the quadruple scalar product

$$\langle \hat{S}_{k_1} \cdot \hat{T}_{k_1} \rangle \langle \hat{U}_{k_2} \cdot \hat{V}_{k_2} \rangle = \sum_{k} (-1)^{k-k_1-k_2} \left\{ \hat{S}_{k_1} \otimes \hat{U}_{k_2} \right\}_{k} \cdot \left\{ \hat{T}_{k_1} \otimes \hat{V}_{k_2} \right\}_{k} \quad \text{(A-60)}$$
The reduced matrix element of the tensor product \( \hat{V}_\nu = \left\{ \hat{T}_{\kappa_1}(1) \otimes \hat{U}_{\kappa_2}(2) \right\}_\nu \) of operators acting on different subsystems is given by (Edmonds, (7.1.5))

\[
\langle \alpha' j'_1 j'_2 j' m' | \hat{V}_\nu | \alpha j_1 j_2 j m \rangle = \sqrt{(2j_1 + 1)(2j_2 + 1)(2\nu + 1)} \sum_{\alpha''} \langle \alpha' j'_1 | \hat{T}_{\kappa_1}(1) | \alpha'' j_1 \rangle \langle \alpha'' j'_2 | \hat{U}_{\kappa_2}(2) | \alpha j_2 \rangle.
\]

(A-61)

Here the parameters in curly braces specify a 9j symbol and \( \alpha, \alpha', \alpha'' \) are shorthand for additional quantum numbers specifying the states.

### A.8 Composite states of spin 1/2 particles

As an example of composition of angular momenta let us calculate the possible states that occur when we combine \( N \) spin 1/2 objects. This can be done by direct construction for not too large \( N \).

**Two spins**

It is convention to define the state \(| J, M \rangle\) with a +1 coefficient, i.e.

\[ |11\rangle = | \uparrow \uparrow \rangle. \]

In this notation a ket with numerals inside is a state \(| JM \rangle\) and a ket with arrows inside denotes \(| M_1 M_2 \rangle\). Using lowering operators we can generate the other two \( J = 1 \) states and requiring \( \langle 00|10\rangle = 0 \) we find the four states

\[
|1, 1\rangle = | \uparrow \uparrow \rangle, \\
|1, 0\rangle = \frac{1}{\sqrt{2}}(| \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle), \\
|1, -1\rangle = | \downarrow \downarrow \rangle, \\
|0, 0\rangle = \frac{1}{\sqrt{2}}(| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle).
\]

**Three spins**

For three spins we have \( 2^3 = 8 \) states. The total angular momentum is \( J = 3/2, 1/2 \) giving \( 4 + 2 = 6 \) states. Where are the two missing states? They reside in a second \( J = 1/2 \) multiplet. We can see that this must occur by considering the tensor product

\[
\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} = (1 \oplus 0) \otimes \frac{1}{2} = \frac{3}{2} \oplus \left( \frac{1}{2} \right)_A \oplus \left( \frac{1}{2} \right)_B.
\]

A state with \( J = 1/2, M \) is in general a linear combination of the states \(| 1/2, M \rangle_A, | 1/2, M \rangle_B \). Different multiplets with the same \( J \) are distinguished by different symmetry properties under particle exchange.

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We can construct the states starting with \(|\frac{3}{2}, \frac{3}{2}\rangle = |\uparrow\uparrow\uparrow\rangle\). Applying the lowering operator to both sides we find the four \(J = \frac{3}{2}\) states

\[
\begin{align*}
|\frac{3}{2}, \frac{3}{2}\rangle &= |\uparrow\uparrow\uparrow\rangle, \\
|\frac{3}{2}, 1/2\rangle &= \frac{1}{\sqrt{3}}(|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\uparrow\uparrow\downarrow\rangle), \\
|\frac{3}{2}, -1/2\rangle &= \frac{1}{\sqrt{3}}(|\uparrow\downarrow\downarrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\downarrow\downarrow\uparrow\rangle), \\
|\frac{3}{2}, -3/2\rangle &= |\downarrow\downarrow\downarrow\rangle.
\end{align*}
\]

We can write

\[
\begin{align*}
|\frac{1}{2}, \frac{1}{2}\rangle &= a|\uparrow\downarrow\rangle + b|\downarrow\uparrow\rangle + c|\downarrow\uparrow\rangle \quad (A-62a) \\
|\frac{1}{2}, -1/2\rangle &= (b + c)|\downarrow\downarrow\rangle + (a + c)|\downarrow\uparrow\rangle + (a + b)|\uparrow\downarrow\rangle \quad (A-62b)
\end{align*}
\]

with \(a, b, c\) unknown complex coefficients. Normalization and orthogonality give 6 real equations

\[
\begin{align*}
|a|^2 + |b|^2 + |c|^2 &= 1, \\
|a + b|^2 + |b + c|^2 + |a + c|^2 &= 1, \\
a + b + c &= 0, \\
a^*(b + c) + b^*(a + c) + c^*(a + b) &= 0.
\end{align*}
\]

A solution is \(a = 1/\sqrt{3}, b = -e^{i\pi/3}/\sqrt{3}, c = e^{i2\pi/3}/\sqrt{3}\), but this only gives us one state \(|\frac{1}{2}, \frac{1}{2}\rangle\). We can easily construct two states by requiring them to be symmetric or antisymmetric with respect to interchange of the first two spins. This gives the states

\[
\begin{align*}
|\frac{1}{2}, \frac{1}{2}\rangle_S &= \frac{1}{\sqrt{6}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) - \frac{2}{\sqrt{6}}|\uparrow\uparrow\rangle \\
|\frac{1}{2}, -1/2\rangle_S &= -\frac{1}{\sqrt{6}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) + \frac{2}{\sqrt{6}}|\downarrow\uparrow\rangle
\end{align*}
\]

and

\[
\begin{align*}
|\frac{1}{2}, \frac{1}{2}\rangle_A &= \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle) \\
|\frac{1}{2}, -1/2\rangle_A &= -\frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle).
\end{align*}
\]

The state (A-62a) with the values of \(a, b, c\) found above can be written as a superposition of the \(S\) and \(A\) states with \(M = 1/2\).

**Four spins**

For four spins we have \(2^4 = 16\) states. The total angular momentum is \(J = 2, 1, 0\) giving \(5 + 3 + 1 = 9\) states. The remaining seven states are in additional multiplets since

\[
\begin{align*}
\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} &= \left[ \frac{3}{2} \oplus \left( \frac{1}{2} \right)_A \oplus \left( \frac{1}{2} \right)_B \right] \otimes \frac{1}{2} \\
&= 2 \oplus 1_C \oplus 1_A \oplus 1_A \oplus 1_B \oplus 0_B. \quad (A-63)
\end{align*}
\]
A.9 Values of Clebsch-Gordan coefficients and symmetry properties

So there is one \( J = 2 \) multiplet, three with \( J = 1 \), and two with \( J = 0 \), giving 16 states.

Let’s concentrate on finding the six states with \( M = 0 \). Starting with \( |2, 2\rangle \) and applying lowering operators we find

\[
|2, 0\rangle = \frac{1}{\sqrt{6}} (|\uparrow\uparrow\downarrow\downarrow\rangle + |\downarrow\downarrow\uparrow\uparrow\rangle + |\uparrow\uparrow\downarrow\rangle + |\downarrow\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle + |\uparrow\uparrow\rangle).
\]

There are two more \( M = 0 \) states that are symmetric on particle exchange corresponding to \( J = 0 \) and three antisymmetric states corresponding to \( J = 1 \). With a little thought we can construct these in the form

\[
|1, 0\rangle_1 = \frac{1}{\sqrt{2}} (|\uparrow\uparrow\downarrow\downarrow\rangle - |\downarrow\downarrow\uparrow\uparrow\rangle)
\]

\[
|1, 0\rangle_2 = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\uparrow\uparrow\rangle - |\downarrow\uparrow\down\rangle)
\]

\[
|1, 0\rangle_3 = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\downarrow\rangle)
\]

and

\[
|0, 0\rangle_1 = \frac{1}{\sqrt{12}} (|\uparrow\uparrow\downarrow\uparrow\rangle + |\downarrow\downarrow\uparrow\uparrow\rangle) + \frac{1}{\sqrt{12}} (|\uparrow\down\down\up\rangle + |\down\up\down\rangle) - \frac{2}{\sqrt{12}} (|\up\up\down\down\rangle + |\down\down\up\up\rangle)
\]

\[
|0, 0\rangle_2 = \frac{1}{2} (|\up\up\down\down\rangle + |\down\down\up\up\rangle) - \frac{1}{2} (|\up\down\down\up\rangle + |\down\up\up\down\rangle).
\]

It can be checked that \( \hat{J}_\pm |0, 0\rangle_1, 2 = 0 \). Only the \( |0, 0\rangle \) state is invariant to global spin rotations. Such a state is in general a linear superposition of \( |0, 0\rangle_1 \) and \( |0, 0\rangle_2 \).

A.9 Values of Clebsch-Gordan coefficients and symmetry properties

There exist a number of explicit expressions for the Clebsch-Gordan coefficients. An expression due to Wigner is

\[
C^{cγ}_{αabβ} = \delta_{γ, a+β} \Delta(abc) \left[ \frac{(c+γ)!(c-γ)!(2c+1)}{(a+α)!(a-α)!(b+β)!(b-β)!} \right]^{1/2} \times \sum_z \frac{(-1)^{b+β+z}(c+b+α-z)!(a-α+z)!}{z!(c-a+b-z)!(c+γ-z)!(a-b-γ+z)!}
\]

where

\[
\Delta(abc) = \sqrt{\frac{(a+b-c)!(a-b+c)!(a+b+c)!}{(a+b+c+1)!}}
\]

and in the summation \( z \) assumes all integer values for which the factorial arguments are nonnegative. The Clebsch-Gordan coefficients satisfy the following unitarity relations

\[
\sum_{m_1 m_2} C^{jm}_{j_1 m_1 j_2 m_2} C^{j'm}_{j_1 m_1' j_2 m_2'} = \delta_{jj'} \delta_{mm'}
\]

\[
\sum_{jm} C^{jm}_{j_1 m_1 j_2 m_2} C^{jm}_{j_1 m_1' j_2 m_2'} = \delta_{m_1 m_1'} \delta_{m_2 m_2'}.
\]
Some additional sums of products
\[ \sum_\alpha \sum_\beta |C_{\alpha\beta}^{c\alpha+\beta}|^2 = 2c + 1, \quad (c = a - 1, a, \text{ or } a + 1, ) \]
\[
\sum_\alpha \sum_\beta C_{\alpha\beta}^{c\gamma} C_{\alpha\beta}^{c\gamma'} = \delta_{\beta,\beta'} \frac{2c + 1}{2b + 1},
\]
\[
\sum_\alpha \sum_\beta C^{a\alpha}_{\alpha\beta} C^{b\beta}_{\gamma'\alpha} = \delta_{c,c'} \delta_{\gamma,\gamma'} (-1)^{b-a-\gamma} \sqrt{\frac{(2a+1)(2b+1)}{2c+1}}.
\]

There are a large number of symmetry relations involving permutations of indices. Some of them are:
\[ C_{a\alpha b\beta}^{c\gamma} = (-1)^{a+b-c} C_{b\beta a\alpha}^{c\gamma} = (-1)^{a-a} \sqrt{\frac{2c+1}{2b+1}} C_{c\alpha a\gamma}^{b\beta} = (-1)^{b+\beta} \sqrt{\frac{2c+1}{2a+1}} C_{a\alpha c\gamma}^{b\beta} = (-1)^{a+\gamma} \sqrt{\frac{2c+1}{2a+1}} C_{a\alpha b\beta}^{c\gamma}
\]

When one of the momenta is zero:
\[ C_{a\alpha b\beta}^{00} = (-1)^{a-a} \frac{\delta_a \delta_{a-b}}{\sqrt{2a+1}},
\]
\[ C_{a\alpha 00}^{c\gamma} = \delta_{a\gamma} \delta_{a\gamma}
\]

When the third momentum is the maximum possible:
\[ C_{a\alpha b\beta}^{a+b\alpha+\beta} = \left[ \frac{(2a)! (2b)! (a+b+\alpha+\beta)! (a+b-\alpha-\beta)!}{(2a+2b)! (a+\alpha)! (a-\alpha)! (b+\beta)! (b-\beta)!} \right]^{1/2}
\]

When all the \( m \)'s are zero:
\[ C_{a\alpha 0b}^{a+b} = \frac{(a+b)!}{a!b!} \left[ \frac{(2a)! (2b)!}{(2a+2b)!} \right]^{1/2}
\]
\[ C_{a\alpha 0b}^{a-b} = (-1)^b \frac{a!}{b! (a-b)!} \left[ \frac{(2b)! (2a-2b+1)!}{(2a+1)!} \right]^{1/2}
\]

In particular when \( b = 1 \)
\[ C_{j010}^{j+10} = \pm \sqrt{\frac{j_{\text{max}}}{2j+1}}, \quad (A-64)
\]
where \( j_{\text{max}} \) is the larger of \( j, j+1 \).

The coefficients for the cases when one of the momenta is 1/2 or 1 are often needed in atomic calculations. The \( b = 1/2 \) cases are:
\[ C_{a\alpha 1/2+1/2}^{a+1/2} = \sqrt{\frac{a+\alpha+1}{2a+1}}
\]
\[ C_{a\alpha 1/2+1/2}^{a-1/2} = \mp \sqrt{\frac{a+\alpha}{2a+1}}
\]
The \( b = 1 \) cases are:

\[
\begin{align*}
C_{aa10}^{\alpha+1} &= \sqrt{(a + \alpha + 1)(a - \alpha + 1)} \frac{a(2a + 1)(a + 1)}{(a + 1)(a + 2a + 1)}, \\
C_{aa10}^{\alpha+1} &= \sqrt{(a + \alpha + 1)(a - \alpha + 2)} \frac{2(2a + 1)(a + 1)}{2(a + 1)(a + 2a + 1)} \\
C_{aa10}^{\alpha-1} &= -\sqrt{(a + \alpha)(a - \alpha)} \frac{a(2a + 1)(a + 1)}{(a + 1)(a + 2a + 1)}, \\
C_{aa11}^{\alpha+1} &= \sqrt{(a + \alpha + 1)(a + \pm \alpha)} \frac{2a(a + 1)}{2a(a + 1)}. \\
C_{aa11}^{\alpha-1} &= \sqrt{(a - \alpha - 1)(a + \alpha)} \frac{2a(a + 1)}{2a(a + 1)}. \\
\end{align*}
\]

The 3j symbols are given by

\[
\begin{align*}
\left( \begin{array}{ccc} a & b & c \\ \alpha & \beta & \gamma \end{array} \right) &= (-1)^{2a+\gamma+ \alpha} \frac{1}{\sqrt{2c + 1}} C_{a \alpha \beta \gamma}^{\gamma},
\end{align*}
\]

Matrix elements of \( \sin(\theta), \sin^2(\theta) \)

\[
\sin(\theta) = \sum_{k=0}^{\infty} a_k Y_{k0}(\theta, \phi)
\]

with

\[
\begin{align*}
a_k &= -\frac{\pi^{3/2} \sqrt{2k + 1}[k(k - 1)]!^2}{2^k(k + 2)(k - 1)[(k/2)!]^2}, & k \text{ even} \\
a_k &= 0, & k \text{ odd}
\end{align*}
\]

The first few numerical values of \( a_k \) are:

\[
\begin{align*}
a_0 &= 2.78 \\
a_2 &= -.778 \\
a_4 &= -.131 \\
a_6 &= -.0490 \\
a_8 &= -.0245 \\
a_{10} &= -.0143
\end{align*}
\]

Thus

\[
\langle l'm'|\sin(\theta)|lm\rangle = \delta_{m'm} \sum_{k=0}^{l+l'} a_k \left[ \frac{(2k + 1)(2l + 1)}{4\pi(2l' + 1)} \right]^{1/2} C_{l0k0}^{l'} C_{l0k0}^{l'm'}.
\]

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Some sample matrix elements for \( l = m = 80 \) are:

\[
\begin{array}{c|c}
  l' & \langle l'| \sin(\theta) | l \rangle \\
  \hline
  80 & 0.99692 \\
  82 & -4.3 \times 10^{-3} \\
  84 & -2.3 \times 10^{-5} \\
  86 & -3.8 \times 10^{-7} \\
  88 & -1.0 \times 10^{-8} \\
  90 & -4.1 \times 10^{-10}
\end{array}
\]

Use \( \sin^2(\theta) = 1 - \cos^2(\theta) = \frac{4\sqrt{\pi}}{3} Y_{00} - \frac{4\sqrt{\pi}}{3\sqrt{5}} Y_{20} \)

Thus

\[
\langle l'm'| \sin^2(\theta) | lm \rangle = \delta_{ll'} \delta_{mm'} + \frac{4\sqrt{\pi}}{3} \delta_{mm'} \left[ \langle l'm'| Y_{00} | lm \rangle - \frac{1}{\sqrt{5}} \langle l'm'| Y_{20} | lm \rangle \right]
\]

\[
= \delta_{mm'} \delta_{ll'} \left[ 1 - \frac{1}{3\sqrt{4\pi}} \right] - \delta_{mm'} \delta_{ll'} \frac{4\sqrt{\pi}}{3\sqrt{5}} \sqrt{\frac{5(2l + 1)}{4\pi(2l' + 1)}} C_{t020}^{l00} C_{tm20}^{l'm'}.
\]
There are many good texts on atomic physics and related topics, some of which are listed here.

**General references**


C. Foot, *Atomic physics*, (Oxford University Press, Oxford, 2004). Written by an experimentalist, with applications to modern topics such as laser cooling and quantum computing.


Comprehensive treatment of highly excited Rydberg atoms.


Pedagogical and modern treatment. Some additional topics, but less detail compared to Woodgate.

Detailed coverage of optical pumping, uses non-standard notation.


Advanced level, including numerical techniques.

Advanced treatment of group theoretical methods.


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Includes much detail on the Hydrogen atom, angular momentum algebra, and collision theory.

Contains an excellent treatment of the interaction of atoms with radiation fields

Good reference for diagrammatic method in angular momentum calculations.


Advanced treatment of many electron atoms.


Intermediate level treatment, much material on collision processes.


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Older texts


Covers a wealth of material. Excellent reference.

This is a classic. Advanced treatment of atomic structure.

G. Herzberg, *Atomic spectra and atomic structure, 2nd Ed.*, (Dover, New York, 1944).
Good introductory treatment

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Comprehensive treatment of quantum mechanics and applications to atoms. Includes extensive bibliographies.

Collision theory


Angular momentum theory


### Astrophysical Applications


### Other Applications


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Covers interaction of atoms with external fields, and applications to laser cooling.

Includes a self-contained treatment of laser cooling and atomic collision theory.
Bibliography


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