Many electron atoms

We have learned how to approximately calculate energy levels of He. Going beyond two electrons we need a more general formalism.

A first approximation is provided by CFA - Central Field Approximation. This describes the multi-electron problem keeping only the $e^--e^-$ Coulomb interaction as a perturbation. Higher order spin dependent terms are not included.

The stationary problem is $H \Psi = E \Psi$ with

\[
H = \sum_i \left( - \frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z \phi_i}{r_i} \right) + \sum_{i<j} \frac{\phi_i \phi_j}{r_{ij}}
\]

\[
H_0 = k + V \quad H_1
\]

\[
r_{ij} = | \vec{r}_i - \vec{r}_j | = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}
\]

We can't solve $H \Psi = E \Psi$ exactly due to $H_1$.

If $\langle H_1 \rangle \ll \langle H_0 \rangle$ we could use perturbation theory. As we saw with Helium this does not work well since $\langle H_1 \rangle$ is not small.
The CFA regroups terms in a useful way. The origin of the coordinate system is at the nucleus. Then \( H_i = \sum_{j=1}^{\infty} \frac{q_i q_j}{r_{ij}} \) can be written as \( H_i = \sum_i H_{ii} \)

\[
H_{ii} = \sum_{j=1}^{\infty} \frac{q_i q_j}{r_{ij}} = \sum_i \frac{q_i^2}{r_i^2} = \sum_i |\psi_i|^2 \frac{q_i^2}{r_i^2}
\]

Each contribution \( H_{ii} \) is the sum of \( i=1 \) terms, each of which gives forces that have radial and non-radial components:

\[
\vec{F}_i = -\nabla H_{ii}
\]

If we decompose \( \vec{F}_i \) there will be a radial part along \( \hat{r}_i \) (from the origin) and a non-radial part.

Note that the contribution to \( H_{ii} \) from the electrons in a filled shell give only a radial force since

\[
\sum |\psi_m(\theta, \phi)|^2 = \frac{2zH_\text{nl}}{4\pi} \quad \text{is not a fn. (}\theta, \phi)\text{.}
\]

Call the radial part of \( H_i \) \( \sum_i S(r_i) \)
Then the central potential is

\[ \sum_i \left( \frac{-Zq^2}{r_i} + S(r_i) \right) = \sum_i V(r_i) \]

This motivates putting \( \tilde{H} = \tilde{H}_0 + \tilde{H}_1 \) with

\[ \tilde{H}_0 = \sum_i \frac{-Zq^2}{2m} \frac{\partial^2}{\partial r_i^2} + \sum_i V(r_i) = H_0 + \sum_i S(r_i) \]

\[ \tilde{H}_1 = \sum_{i \neq j} \frac{q^2}{r_{ij}} - \sum_i S(r_i) \]

\[ = \sum_{i \neq j} \frac{q^2}{r_{ij}} - \sum_i \left( V(r_i) + \frac{Zq^2}{r_i} \right) = H_1 - \sum_i S(r_i) \]

Clearly \( \tilde{H} = H \). This may be useful if

\[ \langle \tilde{H}_1 \rangle \ll \langle \tilde{H}_0 \rangle \]

so we can use perturbation theory.

In zeroth order solve \( H_0 \psi_0 = E_0 \psi_0 \) (drop \( \tilde{\psi} \))

\[ H_0 = \sum_i \left( \frac{-Zq^2}{2m} \frac{\partial^2}{\partial r_i^2} + V(r_i) \right) \]

Since \( H_0 = \sum_i H_{0i} \) the solution will be

separable \( \psi = \prod_i \psi_i \) but properly antisymmetrized

with a Slater determinant
For each electron we need to solve

\[
\left[ \frac{-\hbar^2}{2m} \nabla^2 + U(r) \right] \Psi_{n\ell m_\ell m_s} = E_{n\ell} \Psi_{n\ell m_\ell m_s}
\]

This is the same as for H atom except

\[-\frac{2\epsilon}{r} \rightarrow U(r) \]

radial (central) potential

so \( E = E_{n\ell} \). However \( U(r) \) is not known - it depends on \( S(r) \), the radial part of the interaction terms.

The basic method to solve this problem is due to Hartree, and is called self-consistent field.

Procedure:

1) Guess \( U(r) \)

2) Solve for \( \Psi(r_i) \), \( i = 1, \ldots, N \)

3) update \( U(r_k) \rightarrow -\frac{2\epsilon}{r_k} + \sum_i \frac{\epsilon_i^2}{r_k} \left\langle \Psi_i \right| \Psi_k \left| \Psi_i \right\rangle \)

angular average to make spherically symmetric

Repeat 1), 2), 3) until \( U(r_k) \) converges.
Using \( \Psi = \prod_i \phi_i \) is called Hartree method with correct antisymmetrization (Slater det.) its called Hartree-Fock including relativistic terms in \( H \) (spin-spin, spin-orbit, spin-other orbit, etc.) its called Dirac-Fock.

In general solving these equations must be done on a computer. Book by Cowan is an authoritative reference. "Cowan code" is freely available but not simple to use.

**Slater determinant**

Suppose we have \( N \) electrons

\[ \phi(1), \phi(2), \ldots, \phi(N) \]

with coordinates \( \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N \). So the above is shorthand for

\[ \psi(\vec{r}_1), \psi(\vec{r}_2), \ldots, \psi(\vec{r}_N) \]
Each electron has a wave function specified by the quantum numbers \( n, l, m_l, m_s \).

The different combinations that occur define wavefunctions \( \psi_1, \psi_2, \ldots, \psi_N \).

The Slater determinant wave function is

\[
\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{c}
\psi_1(1) & \psi_2(1) & \ldots & \psi_N(1) \\
\psi_1(2) & \psi_2(2) & \ldots & \psi_N(2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(N) & \psi_2(N) & \ldots & \psi_N(N)
\end{array} \right|
\]

This way of writing the wave function ensures the correct \((-1)^{ij}\) factor upon exchange of coordinates of two electrons and vanishes if any two wave functions are the same, which enforces the Pauli principle.

For 2 electrons we get

\[
\psi = \frac{1}{\sqrt{2}} \left| \begin{array}{c}
\psi_a(1) & \psi_a(2) \\
\psi_b(1) & \psi_b(2)
\end{array} \right| = \frac{1}{\sqrt{2}} \left( \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \right)
\]

which is antisymmetric on exchange.
This representation as a Slater determinant corresponds to a configuration of electrons, i.e., a specification of the individual electron quantum numbers in an uncoupled basis.

Recall that a particular configuration can lead to different states. For example, in a He excited state we could have \( n_d = 1, \ell_d = 0, m_d = 0, m_{sd} = \frac{1}{2} \)

\( n_p = 2, \ell_p = 1, m_p = 0, m_{sp} = \frac{1}{2} \)

States corresponding to \( S = 0 \) (singlet) or \( S = 1 \) (triplet) are different linear combinations of Slater determinants for the underlying configurations.

We gave some examples of this last week.

In LS coupling a multielectron level specified by \( ^{2S+1}L_J \) is called a term. The levels \( ^{2S+1}L_J \) \( 1 \leq S \leq 2 + S \) are fine structure levels within a term.
If we are given an electron configuration which terms are possible?

We need to distinguish two cases: inequivalent and equivalent electrons.

Inequivalent electrons have different \( n, l \) values for each orbital.

**Example** Si atom, atomic number 14

electron configuration: \( 1s^2 2s^2 2p^6 3s^2 3p^2 \)

excited states have one of the 3\( p \) electrons excited.

One possibility is \( [1s^2 2s^2 2p^6 3s^2] 3p^4 \)

The valence electrons are \( n_1 = 3, \ l_1 = 1, s_1 = \frac{1}{2} \)
\( n_2 = 4, \ l_2 = 1, s_2 = \frac{1}{2} \)

\( L = 0, 1, \text{ or } 2 \)

\( S = 0, 1 \)

So we can have \( ^1S ^3S ^1P ^3P ^1D ^3D \)

six possible terms.
Another possibility is \([1s^2 2s^2 2p^6 3s^2] 3p 4s\)

Valence electrons:
- \(n_1 = 3, l_1 = 1, s_1 = \frac{1}{2}\)
- \(n_2 = 4, l_2 = 0, s_2 = \frac{1}{2}\)

\(L = 1, S = 0, 1\)

We can have \(\frac{1}{2} P^1, 3 P^0\) two possible terms.

More systematically, we can keep track of the multiplicities as follows.

Start from closed shell \(L = S = 0\). The term is \(\frac{1}{2} S\).

Add one \(e^-\) \(S' = S \pm \frac{1}{2}\) (for \(S > 0\))

\(2S' + 1 = 2S + 1 \pm 1\) multiplicity goes up or down by 1

Example: \(L = 0, S = 0\)

\(S = 0, S = \frac{1}{2}\)

\(\frac{1}{2} S_0, \frac{1}{2} S_{\frac{1}{2}}\)
There is a useful diagram for keeping track of the relative weight of the terms.

\[
\begin{array}{c}
2S+1 & \frac{5}{2} \\
5 & \frac{3}{2} \\
4 & 1 \\
3 & \frac{1}{2} \\
2 & 0 \\
1 & 0 \\
\end{array}
\]

# electrons

\[
\begin{array}{c}
1 \quad 1:1 \\
2 \quad 1:2 \\
3 \quad 1:3:2 \\
4 \quad \ldots \ldots \\
\end{array}
\]

relative weight of terms

even # of electrons gives singlets, triplets, quartets
odd # of electrons gives doublets, quartets, etc.

The number of terms is for a given configuration of inequivalent electrons is

\[
N = \prod_{i} 2 (2l_i + 1)
\]
or

\[
N = \sum_{J} (2J+1) = \sum_{l}^{l_{\text{term}}} (2l+1) (2S+1)
\]
Check:

\[
\prod_{i} 2(zL_i + 1) = 2(2+t) - 2(0+t) = 12
\]

\[
\sum_{S=0}^{2} 2S + 1 = (1 + 3 + 5) + 3 = 12
\]

\[
\sum_{\text{terms}} (2L+1)(2S+1) = 3\cdot 3 + 3\cdot 1 = 12
\]

---

\[
\prod_{i} 2(zL_i + 1) = 2(2+t) - 2(2+t) = 36
\]

\[
\sum_{S=0}^{2} 2S + 1 = 1 + 3 + 3 + 1 + 3 + 5 + 5 + 3 + 5 + 7 = 36
\]

\[
\sum_{\text{terms}} (2L+1)(2S+1) = 1\cdot 1 + 1\cdot 3 + 3\cdot 1 + 3\cdot 3 + 5\cdot 1 + 5\cdot 3 = 36
\]
Equivalent Electrons

When we have equivalent electrons, that is same n, l for more than one electron, finding the allowed terms is more complicated.

That is because not all terms will satisfy the Pauli exclusion principle. Therefore there will be fewer terms than for inequivalent electrons.

For example we saw that \((np)(n'p)\) gives 36 states.

Two equivalent \(p\) electrons, \(np^2\), gives only 15 states.

To find the allowed terms there is a procedure:

1) write down all terms for inequivalent \(e^-\), \(np \quad np'\) = \(\begin{align*} \ \ 5'p \quad 1D \quad 3S \\ 3p \quad 3D \quad \end{align*}\)

2) define \(N(5), N('p)\), etc. the allowed configurations for each term

3) write out allowed \(M_s, M_l\) values from most to least
4) Write out allowed determinantal product states with \( \sum_i m_i^s = M_s \) and \( \sum_i m_i^e = M_L \).

5) Count \# such states with given \( M_L, M_s \) this \# must be independent of representation so

6) Write \( \sum_{L,s} N (2s+1)L \) states and equate to \# from 5 \( \Rightarrow \) determines \( N \).

When doing this we will use a shorthand for determinantal product states

\[ \{ m_{s1}, m_{s2}, \ldots, m_{e1}, m_{e2}, \ldots \} \]

Pauli principle says no two pairs of symbols can be the same.
This is best illustrated with an example.

Configuration np². If inequivalent would be np + np' giving 3D, 1D, 3P, 1P, 3S, 1S.

<table>
<thead>
<tr>
<th>Ms</th>
<th>Ml</th>
<th>det. product</th>
<th># states</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>½</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>= N(3D) + N(3P)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>= N(3D) + N(3P) + N(1S)</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>1</td>
<td>= N(3D) + N(1D)</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>= N(3D) + N(1D) + N(3P) + N(1P)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td>= N(3D) + N(1S)</td>
</tr>
</tbody>
</table>

So,

\[ N(3D) = 0, \quad N(3P) = 1, \quad N(1S) = 0 \]
\[ N(1D) = 1, \quad N(1P) = 0, \quad N(1S) = 1 \]

allowed terms are \( ^3P, ^1D, ^3S \)

\# states is \( \sum_{\text{terms}} 2S + 1 = 1 + 3 + 5 + 5 + 1 = 15 \).