

A brief introduction to quantum mechanics

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Abstract

Some notes on the basic formalism of quantum mechanics.

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I. WAVE FUNCTION AND SCHRÖDINGER EQUATION

Associating a definite trajectory $(x(t), p(t))$ with a particle is not consistent with experimental data from, e.g. the two-slit experiment. In quantum mechanics we instead describe the state of a particle in terms of a wavefunction $\psi(\mathbf{r}, t)$. The interpretation is then that

$$P(\mathbf{r}) = |\psi(\mathbf{r}, t)|^2$$

is the probability to find the particle at position \mathbf{r} at time t and

$$d^3P(\mathbf{r}) = |\psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$$

is the probability to find the particle in an infinitesimal volume $d^3\vec{r}$ centered at \vec{r} at time t .

Note the probability amplitude is complex: $\psi(\mathbf{r}, t) = \psi_r(\mathbf{r}, t) + i\psi_i(\mathbf{r}, t)$ and

$$|\psi(\mathbf{r}, t)|^2 = \psi(\mathbf{r}, t)\psi^*(\mathbf{r}, t) = [\psi_r(\mathbf{r}, t) + i\psi_i(\mathbf{r}, t)][\psi_r(\mathbf{r}, t) - i\psi_i(\mathbf{r}, t)] = \psi_r(\mathbf{r}, t)^2 + \psi_i(\mathbf{r}, t)^2.$$

A quantum state is completely determined¹ by the wavefunction $\psi(\mathbf{r}, t)$. The wavefunction is arbitrary up to a global phase. Making the change $\psi \rightarrow e^{i\alpha}\psi$ does not change the probability distribution:

$$P'(\mathbf{r}) = |e^{i\alpha}\psi|^2 = |\psi|^2 = P(\mathbf{r}),$$

since $|e^{i\alpha}|^2 = 1$ for any real α .

To calculate probabilities of events when there are multiple pathways we add the amplitudes and then square. So if $\psi = \psi_1 + \psi_2 + \dots$ the probability of an event is

$$P = |\psi|^2 = |\psi_1 + \psi_2 + \dots|^2$$

and interference occurs due to the cross terms $\psi_1\psi_2^* + \psi_1^*\psi_2$, etc. This is the wave-like interference of particles travelling through slit one or two in the two-slit experiment.

A. Position measurement

Let's assume some classical apparatus measures a particle at time t to be in some region δ^3r around \mathbf{r} . The precision of the apparatus is δ^3r . If we prepare N particles all in the same state ψ the distribution of \mathbf{r}_i , $i = 1 \dots N$ will be given by

$$d^3P(\mathbf{r}) = |\psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$$

¹ When there are additional degrees of freedom such as spin we need additional quantum numbers to fully describe the state.

and the expected value of the measurement of \mathbf{r} will be

$$\langle \mathbf{r} \rangle = \int d^3\mathbf{r} P(\mathbf{r}) \mathbf{r} = \int d^3\mathbf{r} |\psi(\mathbf{r})|^2 \mathbf{r}.$$

The variance or mean square deviation of the measurement is

$$\begin{aligned} \langle (\mathbf{r} - \langle \mathbf{r} \rangle)^2 \rangle &= \langle \mathbf{r} \cdot \mathbf{r} - 2\mathbf{r} \cdot \langle \mathbf{r} \rangle + \langle \mathbf{r} \rangle \cdot \langle \mathbf{r} \rangle \rangle \\ &= \langle r^2 \rangle - 2\langle \mathbf{r} \rangle \cdot \langle \mathbf{r} \rangle + \langle \mathbf{r} \rangle \cdot \langle \mathbf{r} \rangle \\ &= \langle r^2 \rangle - \langle \mathbf{r} \rangle^2 \\ &\equiv (\Delta \mathbf{r})^2. \end{aligned}$$

We will consistently use the notation $(\Delta f)^2$ to denote the variance of a quantity f . The standard deviation is then given by

$$\Delta_f = \sqrt{(\Delta f)^2}.$$

Thus if we are interested in the variance of a measurement of say the x coordinate of a particle, it is given by

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 = \int d^3\mathbf{r} |\psi(\mathbf{r})|^2 x^2 - \left[\int d^3\mathbf{r} |\psi(\mathbf{r})|^2 x \right]^2.$$

Note that there are two different integrals here: one has x^2 as part of the integrand and the other one has only x .

B. deBroglie waves

Photons have energy (Einstein, 1905) $E = h\nu = \hbar\omega$, with $\hbar = h/2\pi$, $\omega = 2\pi\nu$ and momentum (Einstein, 1917) $p = h/\lambda = \hbar k$, with $k = 2\pi/\lambda$. The phase velocity is given by

$$v_\phi = \lambda\nu = \omega/k.$$

Photons have $v_\phi = c$ the speed of light.

deBroglie suggested that $p = h/\lambda = \hbar k$, or in vectorial form $\mathbf{p} = \hbar\mathbf{k}$, is also true for massive particles. Consider a particle of mass m and velocity \mathbf{v} , so classically $\mathbf{p} = m\mathbf{v}$. Combining these relations we see that

$$\mathbf{p} = \hbar\mathbf{k} \quad \text{and} \quad \mathbf{p} = m\mathbf{v}$$

imply

$$\mathbf{k} = \frac{m\mathbf{v}}{\hbar}$$

for the effective wavevector of a particle. The deBroglie wavelength is then

$$\lambda_{\text{dB}} = \frac{2\pi}{|\mathbf{k}|} = \frac{2\pi\hbar}{m|\mathbf{v}|} = \frac{h}{mv}.$$

We will describe the particle by a plane wave $\psi(\mathbf{r}, t) = \psi_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$. The particle has a definite momentum given by $\mathbf{p} = \hbar\mathbf{k}$ but is completely delocalized in space, since ψ is everywhere nonzero and $|\psi|^2 = 1$ and is constant. This is consistent with the Heisenberg uncertainty principle ($\Delta p = 0$ so we must have $\Delta x = \infty$).

For a free particle the energy is $E = p^2/2m$ so $\omega = E/\hbar = p^2/2m\hbar$ and the deBroglie wave is

$$\psi = \psi_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} = \psi_0 e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - \frac{p^2}{2m}t\right)}.$$

Note that the phase velocity is

$$v_\phi = \frac{\omega}{k} = \frac{p^2/2m\hbar}{p/\hbar} = \frac{p}{2m} \neq v_{\text{classical}} = \frac{p}{m}.$$

The phase velocity is not equal to the classical velocity. However the group velocity is

$$v_g \equiv \frac{d\omega}{dk} = \frac{d}{dp} \frac{p^2}{2m} = \frac{p}{m} = v_{\text{classical}}.$$

As we will see later the group velocity gives the rate of transport of the probability density which corresponds to the classical velocity.

We could use these waves to describe the results of a two-slit experiment with particles. If ψ_1 is the solution with only slit 1 open, and ψ_2 is the solution with only slit 2 open then $\psi_c = \psi_1 + \psi_2$ is the solution with both slits open and

$$|\psi_c(\mathbf{r})|^2 = (|\psi_1|^2 + |\psi_2|^2) + (\psi_1\psi_2^* + \psi_1^*\psi_2)$$

gives the probability distribution on the output screen. We can interpret this as the first term being “particle like” and the second term which shows interference being “wave like”.

You might be wondering why we have to use a complex ψ instead of writing for the free particle

$$\psi = A \sin(kz - \omega t)$$

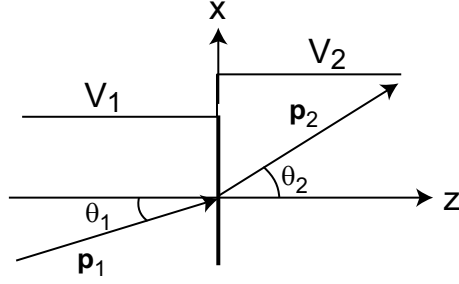


FIG. 1. Particle with momentum \mathbf{p}_1 is incident from the left at angle θ_1 . The potential step at $z = 0$ results in transmission of a particle with momentum \mathbf{p}_2 at angle θ_2 .

which describes a wave traveling along z . The trouble is

$$|\psi|^2 = A^2 \sin^2(kz - \omega t)$$

so the probability distribution is not uniform, it is a function of z . So, although we can prepare states like this, they do not describe a free particle. (What kind of situation does the sin function describe? We will find out in more detail in a few lectures.)

C. More on free particle deBroglie waves

Consider the situation shown in the figure where there is a potential step. The potential is V_1 for $z < 0$ and V_2 for $z > 0$. The deBroglie wave can be written as

$$\psi = Ae^{i(\mathbf{p}\cdot\mathbf{r}/\hbar - Et/\hbar)}$$

where the energy is $E = p^2/2m + V$ and the momentum is $p = \sqrt{2m(E - V)}$. So for $z < 0$, $p_1 = \sqrt{2m(E - V_1)}$ and for $z > 0$, $p_2 = \sqrt{2m(E - V_2)}$. The relative index of refraction of the two regions is defined as the ratio of the phase velocities or

$$n = \frac{v_{\phi,2}}{v_{\phi,1}} = \frac{p_2}{p_1} = \sqrt{\frac{E - V_2}{E - V_1}}.$$

Snell's law of refraction then says that the change in direction of the wave at the interface is given by $\sin \theta_1 = n \sin \theta_2$ so

$$\frac{\sin \theta_1}{\sin \theta_2} = n = \sqrt{\frac{E - V_2}{E - V_1}}$$

where $n = n_2/n_1$ is the relative index of refraction.

Let's check if this is consistent with classical particle mechanics? The interface gives a force on the particle $\mathbf{F} = -\nabla V$ and since $V = V(z)$, \mathbf{F} has only a z component perpendicular to the interface. Therefore p_x must be constant which says $p_1 \sin \theta_1 = p_2 \sin \theta_2$. Therefore

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{p_2}{p_1} = \sqrt{\frac{E - V_2}{E - V_1}}$$

which is consistent with what we found using a deBroglie wave and Snell's law. It is generally true that for motion in a piecewise constant potential where the energy is positive the same motion is found using Newtonian mechanics or wave mechanics. We will see however, that there are also differences between classical and quantum mechanics. Classically the particle is always transmitted as long as it has enough energy. Quantum mechanically there is a finite probability of particle reflection.

D. Schrödinger equation

If we ask the question what wave equation are the deBroglie waves the solution of we find the Schrödinger equation (it is surprising that deBroglie did not find this equation). The demonstration is simple. For a particle in a potential $V(\mathbf{r})$, the energy is $E = p^2/2m + V(\mathbf{r})$, and the wave is $\psi = \psi_0 e^{(i/\hbar)(\mathbf{p}\cdot\mathbf{r} - Et)}$. We can check that

$$\frac{\partial \psi}{\partial t} = -i \frac{E}{\hbar} \psi, \quad \text{and} \quad \nabla^2 \psi = -\frac{p^2}{\hbar^2} \psi.$$

Thus

$$i\hbar \frac{\partial \psi}{\partial t} + \frac{\hbar^2}{2m} \nabla^2 \psi = E\psi - \frac{p^2}{2m} \psi = V\psi$$

so

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

which is Schrödinger's wave equation.

The Hamiltonian is the sum of kinetic and potential energy

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}).$$

We can then write the Schrödinger equation as

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi.$$

When there is no potential $H = -\frac{\hbar^2}{2m}\nabla^2$ and we get the equation for a free particle

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi.$$

We see that the existence of deBroglie waves implies the Schrödinger equation. We can also go the other way. If we assume a wave of the form $\psi = \psi_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ then the Schrödinger equation implies $\hbar\omega = \hbar^2 k^2/2m = p^2/2m$ and we get deBroglie waves. It is important to recognize that the Schrödinger equation is linear. If ψ_1 and ψ_2 are solutions then $\psi = c_1\psi_1 + c_2\psi_2$ is also a solution for arbitrary constants c_1, c_2 .

1. Conservation of probability

The Schrödinger equation conserves the total probability for the particle to be somewhere. Normalized solutions satisfy

$$\int d^3\mathbf{r} P = \int d^3\mathbf{r} |\psi|^2 = 1.$$

This equation has to be interpreted in a different way for free particles, since in that case the integral of $|\psi|^2$ diverges and is δ function normalized. We will clarify this point later on. Nevertheless, we can always calculate the time rate of change of the probability integral. We have

$$\begin{aligned} \frac{d}{dt} \int d^3\mathbf{r} |\psi|^2 &= \int d^3\mathbf{r} \left(\psi \frac{d\psi^*}{dt} + \frac{d\psi}{dt} \psi^* \right) \\ &= \int d^3\mathbf{r} \left[\psi \frac{i}{\hbar} \left(\frac{-\hbar^2}{2m} \nabla^2 \psi^* + V^* \psi^* \right) + \psi^* \left(\frac{-i}{\hbar} \right) \left(\frac{-\hbar^2}{2m} \nabla^2 \psi + V \psi \right) \right] \\ &= \frac{i}{\hbar} \int d^3\mathbf{r} (V^* - V) |\psi|^2 + \left(\frac{-i\hbar}{2m} \right) \int d^3\mathbf{r} (\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi). \end{aligned}$$

Assume V is real so $V^* - V = 0$. We are left with

$$\begin{aligned} \int d^3\mathbf{r} (\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi) &= (\psi \nabla \cdot \psi^* - \psi^* \nabla \cdot \psi) |_{\text{boundary}} \\ &\quad - \int d^3\mathbf{r} (\nabla \cdot \psi \nabla \cdot \psi^* - \nabla \cdot \psi^* \nabla \cdot \psi) \\ &= (\psi \nabla \cdot \psi^* - \psi^* \nabla \cdot \psi) |_{\text{boundary}}. \end{aligned}$$

Assuming that the wavefunction vanishes on a boundary at infinity we get zero for the the integral so probability is conserved.

II. DIRAC NOTATION AND RULES OF QUANTUM MECHANICS

Dirac notation provides an abstract representation theory of quantum mechanics. The notation is elegant and powerful and widely used. The authoritative reference is Dirac's book on quantum mechanics². The theory employs three types of objects: states, operators, and c -numbers (complex numbers). In the following we give a brief introduction to the main notational rules and ideas.

A. States and operators

A quantum state is represented by the ket $|\psi\rangle$. The ket should be thought of as an abstract symbol for a quantum state. It is not the same as $\psi(x)$ which is the position space representation of the state. We will soon see how to calculate $\psi(x)$ from $|\psi\rangle$.

The Hermitian conjugate is the bra $\langle\psi|$. The inner product called a bra-ket or bracket is

$$\langle\phi|\psi\rangle = c \text{ (a number)}. \quad (1)$$

If $c = \langle\phi|\psi\rangle$ then the complex conjugate is $c^* = \langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle$. Kets and bras exist in a Hilbert space which is a generalization of the three dimensional linear vector space of Euclidean geometry to a complex valued space with possibly infinitely many dimensions.

The inner product is linear

$$\langle\phi|(a_1|\psi_1\rangle + a_2|\psi_2\rangle) = \langle\phi|a_1|\psi_1\rangle + \langle\phi|a_2|\psi_2\rangle = a_1\langle\phi|\psi_1\rangle + a_2\langle\phi|\psi_2\rangle. \quad (2)$$

Operators are denoted by a hat \hat{A} .

$$\hat{A}(c_1|\psi_1\rangle + c_2|\psi_2\rangle) = c_1\hat{A}|\psi_1\rangle + c_2\hat{A}|\psi_2\rangle.$$

The matrix element of an operator is

$$\langle\phi|\hat{A}|\psi\rangle = \langle\phi|(\hat{A}|\psi\rangle) = (\langle\phi|\hat{A})|\psi\rangle = c \text{ (a number)}. \quad (3)$$

The complex conjugate of the matrix element is

$$\langle\phi|\hat{A}|\psi\rangle^* = \langle\psi|\hat{A}^\dagger|\phi\rangle = c^* \quad (4)$$

² P. A. M. Dirac, *The Principles of Quantum Mechanics*, 4th Ed., Oxford University Press, Oxford (1958).

where \hat{A}^\dagger is the Hermitian conjugate of \hat{A} . When \hat{A} is represented by a matrix the Hermitian conjugate is found by transposing the matrix and then taking the complex conjugate of each matrix element. The operation of taking the Hermitian conjugate of a combination of numbers, states, and operators involves changing $c \rightarrow c^*$, $|\psi\rangle \rightarrow \langle\psi|$, $\langle\psi| \rightarrow |\psi\rangle$, $\hat{A} \rightarrow \hat{A}^\dagger$ and reversing the order of all elements. For example

$$\left(c_1 \hat{A}^\dagger \langle\phi|\hat{B}|\psi\rangle\langle\xi|\right)^\dagger = c_1^* |\xi\rangle\langle\psi|\hat{B}^\dagger|\phi\rangle\hat{A}.$$

The combination of a ket and a bra is an operator

$$|\phi\rangle\langle\psi|.$$

When dealing with a finite dimensional Hilbert space we can represent kets as column vectors, bras as row vectors and matrix elements as inner products:

$$|\psi\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ a_n \end{pmatrix}, \quad \langle\psi| = \left(a_1^* \ a_2^* \ \cdot \ \cdot \ \cdot \ a_n^*\right),$$

$$\langle\psi|\psi\rangle = \left(a_1^* \ a_2^* \ \cdot \ \cdot \ \cdot \ a_n^*\right) \begin{pmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ a_n \end{pmatrix} = |a_1|^2 + |a_2|^2 + \dots + |a_n|^2.$$

The outer product is therefore a matrix

$$|\psi\rangle\langle\psi| = \begin{pmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ a_n \end{pmatrix} \left(a_1^* \ a_2^* \ \cdot \ \cdot \ \cdot \ a_n^*\right) = \begin{pmatrix} |a_1|^2 & a_1 a_2^* & \cdot \ \cdot & a_1 a_n^* \\ a_1^* a_2 & |a_2|^2 & \cdot \ \cdot & a_2 a_n^* \\ \cdot & \cdot & \cdot \ \cdot & \cdot \\ \cdot & \cdot & \cdot \ \cdot & \cdot \\ a_1^* a_n & a_2^* a_n & \cdot \ \cdot & |a_n|^2 \end{pmatrix}.$$

Note that $|\psi\rangle\langle\psi|$ has real, nonnegative entries on the diagonal. This is not the case for the more general operator $|\phi\rangle\langle\psi|$.

It is important to understand that c -numbers obey the usual associative and commutative rules of multiplication so that

$$\langle a|b\rangle\langle c|d\rangle = \langle c|d\rangle\langle a|b\rangle$$

and

$$\langle a|b\rangle|c\rangle\langle d| = |c\rangle\langle d|\langle a|b\rangle$$

but operators do not satisfy the commutative rule so in general

$$(|a\rangle\langle b|)(|c\rangle\langle d|) \neq (|c\rangle\langle d|)(|a\rangle\langle b|).$$

Operators do satisfy the associative rule so that

$$(|a\rangle\langle b|)(|c\rangle\langle d|) = |a\rangle(\langle b|c\rangle)\langle d| = |a\rangle\langle b|c\rangle\langle d| = \langle b|c\rangle|a\rangle\langle d|.$$

B. Observables

Observables are represented by Hermitian operators which satisfy $\hat{A}^\dagger = \hat{A}$. Hermitian operators are also referred to as self-adjoint. The expectation value of a Hermitian operator is real:

$$a^* = \langle \hat{A} \rangle^* = \langle \psi | \hat{A} | \psi \rangle^* = \langle \psi | \hat{A}^\dagger | \psi \rangle = \langle \psi | \hat{A} | \psi \rangle = a. \quad (5)$$

Denote the eigenstates of a Hermitian operator by $|n\rangle$. They satisfy

$$\hat{A}|n\rangle = a_n|n\rangle.$$

The eigenvalues are real since

$$\langle m | \hat{A} | m \rangle = \langle m | a_m | m \rangle = a_m \langle m | m \rangle = a_m$$

and

$$a_m^* = \langle m | \hat{A} | m \rangle^* = \langle m | \hat{A}^\dagger | m \rangle = \langle m | \hat{A} | m \rangle = a_m.$$

States corresponding to different eigenvalues are orthogonal. We assume the states are normalized so that $\langle m | n \rangle = \delta_{mn}$. To prove orthogonality we calculate

$$\langle m | \hat{A} | n \rangle = \langle m | a_n | n \rangle = a_n \langle m | n \rangle$$

and

$$\langle m|\hat{A}|n\rangle = \left(\langle m|\hat{A}\right)|n\rangle = \left(\hat{A}^\dagger|m\rangle\right)^\dagger|n\rangle = (a_m|m\rangle)^\dagger|n\rangle = a_m^*\langle m|n\rangle = a_m\langle m|n\rangle.$$

Thus

$$(a_m - a_n)\langle m|n\rangle = 0$$

so $\langle m|n\rangle = 0$ if $m \neq n$. We can write this as $\langle m|n\rangle = \delta_{mn}$ when the kets are normalized.

The eigenstates $|n\rangle$ of a Hermitian operator form a complete set. Therefore for an arbitrary ket $|\psi\rangle$

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|n\rangle \quad (6)$$

where

$$\langle n|\psi\rangle = \langle n|\sum_{j=0}^{\infty} c_j|j\rangle = \sum_{j=0}^{\infty} c_j\langle n|j\rangle = \sum_{j=0}^{\infty} c_j\delta_{nj} = c_n.$$

Thus

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|n\rangle = \sum_{n=0}^{\infty} \langle n|\psi\rangle|n\rangle = \sum_{n=0}^{\infty} |n\rangle\langle n|\psi\rangle = \left(\sum_{n=0}^{\infty} |n\rangle\langle n|\right)|\psi\rangle.$$

Since this is true for arbitrary $|\psi\rangle$ we can write the identity operator as

$$\hat{I} = \sum_{n=0}^{\infty} |n\rangle\langle n|. \quad (7)$$

A component of $|\psi\rangle$ can be found by operating with the projection operator $\hat{P}_n = |n\rangle\langle n|$.

We have

$$\hat{P}_n|\psi\rangle = |n\rangle\langle n|\sum_{j=0}^{\infty} c_j|j\rangle = |n\rangle\sum_{j=0}^{\infty} c_j\langle n|j\rangle = |n\rangle\sum_{j=0}^{\infty} c_j\delta_{nj} = c_n|n\rangle. \quad (8)$$

The projection operator is idempotent:

$$(\hat{P}_n)^2 = \hat{P}_n\hat{P}_n = (|n\rangle\langle n|)(|n\rangle\langle n|) = |n\rangle(\langle n|n\rangle)\langle n| = |n\rangle\langle n| = \hat{P}_n. \quad (9)$$

The inner product of two states can be expressed in terms of the coefficients of their decomposition. We write $|\psi\rangle = \sum_n c_n|n\rangle$, $|\phi\rangle = \sum_n b_n|n\rangle$. Then

$$\langle\phi|\psi\rangle = \sum_m b_m^*\langle m|\sum_n c_n|n\rangle = \sum_m \sum_n b_m^*c_n\delta_{mn} = \sum_n b_n^*c_n. \quad (10)$$

The spectral representation of an operator is found from

$$\begin{aligned}\hat{A} &= \hat{I}\hat{A}\hat{I} = \left(\sum_m |m\rangle\langle m| \right) \hat{A} \left(\sum_n |n\rangle\langle n| \right) = \sum_m \sum_n |m\rangle\langle m| a_n |n\rangle\langle n| \\ &= \sum_m \sum_n a_n |m\rangle\delta_{mn}\langle n| = \sum_n a_n |n\rangle\langle n|.\end{aligned}$$

Thus

$$\hat{A} = \sum_n a_n |n\rangle\langle n|. \quad (11)$$

The representation (11) is diagonal since we have expressed \hat{A} in a basis of the eigenvectors of \hat{A} . If we choose some other set of basis vectors $\{|m\rangle\}$ (not the eigenvectors of \hat{A}) then the representation will not be diagonal. Thus

$$\begin{aligned}\hat{A} &= \sum_n a_n |n\rangle\langle n| \\ &= \sum_n a_n \left(\sum_m |m\rangle\langle m| \right) |n\rangle\langle n| \left(\sum_{m'} |m'\rangle\langle m'| \right) \\ &= \sum_{n,m,m'} a_n |m\rangle c_{mn} c_{nm'} \langle m'| \\ &= \sum_{m,m'} u_{mm'} |m\rangle\langle m'|.\end{aligned}$$

where $c_{mn} = \langle m|n\rangle$ and $u_{mm'} = \sum_n a_n c_{mn} c_{nm'}$.

C. Degeneracy

Each eigenvalue a_α may be associated with a subspace of dimension $n_\alpha > 1$. The n_α degenerate eigenvectors can be orthonormalized to span the subspace. In this case we label the eigenvectors with an additional parameter r as $|\alpha, r\rangle$ where $r = 1, 2, \dots, n_\alpha$ and $\langle \beta, s | \alpha, r \rangle = \delta_{\alpha\beta} \delta_{rs}$. The eigenvalue relation is then

$$\hat{A}|\alpha, r\rangle = a_\alpha |\alpha, r\rangle \text{ for } r = 1, \dots, n_\alpha. \quad (12)$$

The identity operator can be written as

$$\hat{I} = \sum_{\alpha=0}^{\infty} \sum_{r=1}^{n_\alpha} |\alpha, r\rangle\langle \alpha, r|. \quad (13)$$

The spectral decomposition of the operator is

$$\hat{A} = \sum_{\alpha=0}^{\infty} \sum_{r=1}^{n_\alpha} a_\alpha |\alpha, r\rangle\langle \alpha, r|. \quad (14)$$

D. Norm

The norm of a state can be defined as

$$|| |a\rangle || = \sqrt{\langle a|a\rangle}.$$

Similarly the norm of an operator \mathcal{O} acting on a state is

$$||\mathcal{O}|a\rangle|| = \sqrt{\langle a|\mathcal{O}^\dagger\mathcal{O}|a\rangle}.$$

This clearly depends on the choice of $|a\rangle$. A definition that is independent of the state is the supremum norm,

$$||\mathcal{O}||_s = \sup_{|a\rangle} \frac{||\mathcal{O}|a\rangle||}{|| |a\rangle ||} = \sup_{|a\rangle} \frac{\sqrt{\langle a|\mathcal{O}^\dagger\mathcal{O}|a\rangle}}{\sqrt{\langle a|a\rangle}}$$

where $\sup_{|a\rangle} \dots$ means the maximum of \dots for all possible nonzero $|a\rangle$.

III. CONTINUOUS BASIS

A Dirac ket $|\psi\rangle$ should be thought of as an abstract symbol for a quantum state. It is not tied to any particular representation. By taking inner products we can find a representation in terms of a discrete set of basis states as in Eq. (6). This can also be generalized to a continuous basis $|\xi\rangle$ using the orthogonality condition

$$\langle \xi' | \xi \rangle = \delta(\xi - \xi')$$

and the representation of the unit operator

$$\hat{I} = \int d\xi |\xi\rangle\langle\xi|.$$

An arbitrary state $|\psi\rangle$ can be expanded as

$$|\psi\rangle = \hat{I}|\psi\rangle = \left(\int d\xi |\xi\rangle\langle\xi| \right) |\psi\rangle = \int d\xi \langle\xi|\psi\rangle |\xi\rangle = \int d\xi \psi(\xi) |\xi\rangle$$

where we have introduced the wavefunction $\psi(\xi) = \langle\xi|\psi\rangle$. The wavefunction $\psi(\xi)$ gives the amplitude of the decomposition of the state $|\psi\rangle$ into the basis ket $|\xi\rangle$.

Using a continuous basis we can calculate the matrix elements of operators as follows. Consider a general operator $\hat{A}(\hat{\xi}, \frac{\partial}{\partial \xi})$ that is some function of $\hat{\xi}$ and $\frac{\partial}{\partial \xi}$. For arbitrary states

$|\psi\rangle, |\phi\rangle$ we have

$$\begin{aligned}\langle\phi|\hat{A}|\psi\rangle &= \left(\int d\xi''|\xi''\rangle\langle\xi''|\phi\rangle\right)^\dagger \hat{A}\left(\hat{\xi}, \frac{\partial}{\partial\hat{\xi}}\right) \left(\int d\xi'|\xi'\rangle\langle\xi'|\psi\rangle\right) \\ &= \int d\xi''d\xi'\langle\phi|\xi''\rangle\langle\xi''|\hat{A}\left(\hat{\xi}, \frac{\partial}{\partial\hat{\xi}}\right)|\xi'\rangle\langle\xi'|\psi\rangle.\end{aligned}\quad (15)$$

Now the matrix element in the middle of the last expression is

$$\langle\xi''|\hat{A}\left(\hat{\xi}, \frac{\partial}{\partial\hat{\xi}}\right)|\xi'\rangle = A\left(\xi, \frac{\partial}{\partial\xi}\right)\langle\xi''||\xi'\rangle = A\left(\xi, \frac{\partial}{\partial\xi}\right)\delta(\xi'' - \xi') = A\left(\xi', \frac{\partial}{\partial\xi'}\right)\delta(\xi'' - \xi').$$

Thus (15) becomes

$$\begin{aligned}\langle\phi|\hat{A}|\psi\rangle &= \int d\xi''d\xi'\langle\phi|\xi''\rangle\delta(\xi'' - \xi')A\left(\xi', \frac{\partial}{\partial\xi'}\right)\langle\xi'|\psi\rangle \\ &= \int d\xi'\langle\phi|\xi'\rangle A\left(\xi', \frac{\partial}{\partial\xi'}\right)\langle\xi'|\psi\rangle \\ &= \int d\xi\phi^*(\xi)A\left(\xi, \frac{\partial}{\partial\xi}\right)\psi(\xi).\end{aligned}\quad (16)$$

Equation (16) gives the general formula for evaluating a matrix element in terms of an expansion in a continuous basis.

A. Representation of Derivatives

Given a ket $|\psi\rangle$ we can define another ket $|d\psi/d\xi\rangle$ whose representation is the derivative of the original one. This new ket is the result of transforming the original one with an operator and we write the transforming operator as $\frac{d}{d\hat{\xi}}$ so

$$\frac{d}{d\hat{\xi}}|\psi\rangle = \left|\frac{d\psi}{d\xi}\right\rangle.$$

The matrix element of the differential operator is

$$\langle\phi|\frac{d}{d\hat{\xi}}|\psi\rangle = \int d\xi'\langle\phi|\frac{d}{d\hat{\xi}}|\xi'\rangle\langle\xi'|\psi\rangle = \int d\xi'\langle\phi|\frac{d}{d\hat{\xi}}|\xi'\rangle\psi(\xi') = \int d\xi'\phi^*(\xi')\frac{d\psi(\xi')}{d\xi'}.\quad (17)$$

Assuming the wavefunctions vanish at infinity an integration by parts gives

$$\int d\xi'\phi^*(\xi')\frac{d\psi(\xi')}{d\xi'} = -\int d\xi'\frac{d\phi^*(\xi')}{d\xi'}\psi(\xi').\quad (18)$$

Comparing (17) and (18) we get

$$\langle\phi|\frac{d}{d\hat{\xi}}|\xi'\rangle = -\frac{d\phi^*(\xi')}{d\xi'} = -\left\langle\frac{d\phi}{d\hat{\xi}}|\xi'\right\rangle$$

so

$$\langle \phi | \frac{d}{d\hat{\xi}} = -\langle \frac{d\phi}{d\hat{\xi}} | \quad (19)$$

and

$$\left(\frac{d}{d\hat{\xi}} \right)^\dagger = -d/d\hat{\xi}.$$

The minus sign in this equation is important. It guarantees that the position representation of the momentum is Hermitian, and a valid observable since $\left(id/d\hat{\xi} \right)^\dagger = id/d\hat{\xi}$ and e.g. the momentum operator $-i\hbar d/d\hat{x}$ is a Hermitian operator.

If you find the steps from (17) - (19) unnecessarily complicated an alternative is to simply note that

$$\begin{aligned} \langle \phi | \frac{d}{d\hat{\xi}} | \psi \rangle &= \langle \phi | \left(\frac{d}{d\hat{\xi}} | \psi \rangle \right) \\ &= \int d\xi \phi^* \frac{d\psi}{d\xi} \\ &= - \int d\xi \frac{d\phi^*}{d\xi} \psi \\ &= -\langle \frac{d\phi}{d\hat{\xi}} | \psi \rangle \\ &= \left(\langle \phi | \frac{d}{d\hat{\xi}} \right) | \psi \rangle. \end{aligned}$$

Thus

$$\langle \phi | \frac{d}{d\hat{\xi}} = -\langle \frac{d\phi}{d\hat{\xi}} |.$$

B. Position and momentum representations

We can use the above results for a continuous basis to find the relation between the position and momentum wavefunctions $\psi(x)$ and $\phi(p)$. Consider position and momentum eigenkets: $\hat{x}|x\rangle = x|x\rangle$ and $\hat{p}|p\rangle = p|p\rangle$. The matrix element of \hat{p} between different basis kets is

$$\langle x | \hat{p} | p \rangle = \langle x | p | p \rangle = p \langle x | p \rangle.$$

Using the position representation of the momentum operator we can also write this as

$$\langle x | \hat{p} | p \rangle = \langle x | \left(-i\hbar \frac{\partial}{\partial \hat{x}} \right) | p \rangle = -i\hbar \frac{\partial}{\partial x} \langle x | p \rangle. \quad (20)$$

This follows also from the general expression for matrix elements Eq. (16)³.

Comparing we see that

$$\frac{\partial}{\partial x} \langle x|p\rangle = \frac{ip}{\hbar} \langle x|p\rangle$$

which has solution

$$\langle x|p\rangle = N e^{ipx/\hbar}$$

with N a normalization constant.

We then observe that

$$\psi(x) = \langle x|\psi\rangle = \langle x| \left(\int dp |p\rangle \langle p| \right) |\psi\rangle = N \int dp e^{ipx/\hbar} \psi(p)$$

and

$$\psi(p) = \langle p|\psi\rangle = \langle p| \left(\int dx |x\rangle \langle x| \right) |\psi\rangle = N^* \int dx e^{-ipx/\hbar} \psi(x).$$

Requiring that $\int dx |\psi(x)|^2 = \int dp |\psi(p)|^2$ gives $|N|^2 = 1/h$. We choose N to be real and obtain

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int dp e^{ipx/\hbar} \psi(p) \\ \psi(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int dx e^{-ipx/\hbar} \psi(x), \end{aligned}$$

which demonstrates that $\psi(x)$ and $\psi(p)$ are related by a Fourier transform. For clarity we sometimes write $\phi(p)$ instead of $\psi(p)$.

IV. COMMUTING OBSERVABLES

If a state $|\psi\rangle$ is an eigenstate of two observables \hat{A} and \hat{B} with eigenvalues α and β then

$$\hat{A}\hat{B}|\psi\rangle = \alpha\beta|\psi\rangle = \beta\alpha|\psi\rangle = \hat{B}\hat{A}|\psi\rangle. \quad (21)$$

A necessary and sufficient condition for \hat{A} and \hat{B} to have a common complete set of eigenstates is that \hat{A} and \hat{B} commute:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0. \quad (22)$$

³ To see this use $|x\rangle = \int d\xi |\xi\rangle \langle \xi|x\rangle = \int d\xi \delta(\xi - x)|\xi\rangle$, so (16) gives $\langle x|\hat{p}|p\rangle = -i\hbar \langle x|\frac{\partial}{\partial x}|p\rangle = -i\hbar \int d\xi \delta(\xi - x) \frac{\partial}{\partial \xi} \langle \xi|p\rangle = -i\hbar \frac{\partial}{\partial x} \langle x|p\rangle$.

The uncertainty (variance) of an operator is

$$\langle(\Delta\hat{A})^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2. \quad (23)$$

The generalized uncertainty relation for two noncommuting observables is

$$(\Delta A)(\Delta B) \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle| \quad (24)$$

where $\Delta A = \sqrt{\langle(\Delta\hat{A})^2\rangle}$, $\Delta B = \sqrt{\langle(\Delta\hat{B})^2\rangle}$.

There are many ways to prove this, e.g. with the Schwarz inequality. Here is an alternative approach. Define $\hat{A}' = \hat{A} - \langle\hat{A}\rangle$ so $\langle\hat{A}'\rangle = 0$,

$$\langle(\Delta\hat{A}')^2\rangle = \langle\hat{A}'^2\rangle = (\Delta A)^2$$

and similarly for $\hat{B}' = \hat{B} - \langle\hat{B}\rangle$. We note that $[\hat{A}', \hat{B}'] = [\hat{A}, \hat{B}]$.

Consider an arbitrary ket $|\psi\rangle$ and the quantity $(\hat{A}' + i\lambda\hat{B}')|\psi\rangle$ with λ real. The square of the norm is

$$\begin{aligned} \|(\hat{A}' + i\lambda\hat{B}')|\psi\rangle\|^2 &= \langle\psi|(\hat{A}' - i\lambda\hat{B}')(\hat{A}' + i\lambda\hat{B}')|\psi\rangle \\ &= \langle\psi|\hat{A}'^2|\psi\rangle + \lambda^2\langle\psi|\hat{B}'^2|\psi\rangle + i\lambda\langle\psi|[\hat{A}', \hat{B}']|\psi\rangle \\ &= \lambda^2(\Delta B)^2 + i\lambda\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle + (\Delta A)^2 \\ &\geq 0. \end{aligned}$$

The last term is the commutator of two Hermitian operators which is anti-Hermitian (it has imaginary eigenvalues), so i times the commutator is a Hermitian operator. The above expression is therefore a quadratic function of λ with real coefficients, and is therefore strictly real. It is non-negative for all values of λ , and therefore must not have two different real roots, since if that were the case the expression would have to change sign and be somewhere negative. For this to be so the discriminant must be negative or zero which corresponds to

$$(\Delta A)(\Delta B) \geq \frac{1}{2}|\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle|.$$

Since this is true for any $|\psi\rangle$ we can write

$$(\Delta A)(\Delta B) \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|$$

as desired.

As an example of application of the commutation relation (24) consider \hat{x} and \hat{p} . Their commutator can be evaluated in the position representation as

$$\begin{aligned}
\langle \psi | [\hat{x}, \hat{p}] | \psi \rangle &= \langle \psi | (\hat{x}\hat{p} - \hat{p}\hat{x}) | \psi \rangle \\
&= -i\hbar \int dx \psi^* \left(x \frac{\partial}{\partial x} - \frac{\partial}{\partial x} x \right) \psi \\
&= -i\hbar \int dx \psi^* \left(x \frac{\partial \psi}{\partial x} - \psi - x \frac{\partial \psi}{\partial x} \right) \\
&= i\hbar \int dx \psi^* \psi \\
&= \langle \psi | i\hbar | \psi \rangle.
\end{aligned}$$

Since $|\psi\rangle$ is an arbitrary ket we have $[\hat{x}, \hat{p}] = i\hbar$ and using (24)

$$(\Delta x)(\Delta p) \geq \frac{\hbar}{2}$$

which is the usual position-momentum form of the uncertainty relation.

V. EVOLUTION IN TIME

Time evolution is governed by the Hamiltonian \hat{H} and

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle. \quad (25)$$

For a particle of mass m in the coordinate representation $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$ and we get the Schrödinger equation

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}, t) + V(\mathbf{r}) \psi(\mathbf{r}, t). \quad (26)$$

The formal solution for time evolution is

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle$$

where the time evolution operator is

$$\hat{U}(t, t_0) = \exp \left[-\frac{i}{\hbar} \int_{t_0}^t dt' \hat{H}(t') \right]_+ \quad (27)$$

and $[\dots]_+$ indicates time ordering of operator products: $[\hat{A}(t_1) \dots \hat{A}(t_n)]_+ = \hat{A}(t_1) \dots \hat{A}(t_n)$ when $t_1 \geq t_2 \geq \dots \geq t_n$.

When \hat{H} is not explicitly time dependent this simplifies to

$$\hat{U}(t, t_0) = \exp \left[-\frac{i}{\hbar} \hat{H}(t - t_0) \right]. \quad (28)$$

The time evolution operator is unitary which means $\hat{U}^\dagger = \hat{U}^{-1}$ so

$$\hat{U}^\dagger \hat{U} = \hat{U} \hat{U}^\dagger = \hat{I}. \quad (29)$$

The time evolution of an initial state $|\psi(t_0)\rangle$ can be determined explicitly by expanding in energy eigenfunctions $\hat{H}|n\rangle = E_n|n\rangle$. Assume the initial state

$$|\psi(t_0)\rangle = \sum_n \langle n|\psi(t_0)\rangle |n\rangle = \sum_n c_{n0} |n\rangle$$

and the time dependent state

$$|\psi(t)\rangle = \sum_n \langle n|\psi(t)\rangle |n\rangle = \sum_n c_n(t) |n\rangle.$$

Plugging in to the Schrödinger equation gives

$$i\hbar \sum_n \frac{dc_n}{dt} |n\rangle = \sum_n \hat{H} c_n |n\rangle = \sum_n E_n c_n |n\rangle.$$

Projecting out the m^{th} component by operating on both sides with $\langle m|$ gives

$$i\hbar \frac{dc_m}{dt} = E_m c_m$$

which is solved by

$$c_m(t) = c_{m0} e^{-iE_m(t-t_0)/\hbar}.$$

Thus

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle = \sum_n c_{n0} e^{-iE_n(t-t_0)/\hbar} |n\rangle.$$

A. Schrödinger and Heisenberg pictures

There are several different ways of working with time evolution.

In the Schrödinger picture the state $|\psi(t)\rangle_S$ is a function of time while all observables \hat{A}_S are constant. The state vector evolves according to the Schrödinger equation $i\hbar \frac{d|\psi\rangle_S}{dt} = \hat{H}_S |\psi\rangle_S$ and the expectation value of an operator at time t is

$$\begin{aligned} a(t) &= \langle \hat{A}_S \rangle \\ &= {}_S \langle \psi(t) | \hat{A}_S | \psi(t) \rangle_S. \end{aligned}$$

Here the subscripts S refer to the Schrödinger picture.

We can cast this in a different form as follows. The expectation value of an operator at time t is

$$\begin{aligned} a(t) &= \langle \hat{A}_S \rangle \\ &= {}_S \langle \psi(t) | \hat{A}_S | \psi(t) \rangle_S \\ &= \langle \psi(0) | \hat{U}^\dagger(t) \hat{A}_S \hat{U}(t) | \psi(0) \rangle. \end{aligned}$$

We can define a time dependent operator by $\hat{A}_H = \hat{U}^\dagger(t) \hat{A}_S \hat{U}(t)$, and time independent states by $|\psi\rangle_H = |\psi(0)\rangle$ such that

$$a(t) = {}_H \langle \psi | \hat{A}_H | \psi \rangle_H.$$

This is the Heisenberg picture in which the kets are stationary but the operators evolve in time. The equation of motion for the operator is found from

$$\begin{aligned} \frac{d\hat{A}_H(t)}{dt} &= \frac{d}{dt} \left(\hat{U}^\dagger(t) \hat{A}_S \hat{U}(t) \right) + \frac{\partial \hat{A}_H}{\partial t} \\ &= \frac{d\hat{U}^\dagger(t)}{dt} \hat{A}_S \hat{U}(t) + \hat{U}^\dagger(t) \hat{A}_S \frac{d\hat{U}(t)}{dt} + \frac{\partial \hat{A}_H}{\partial t} \\ &= \left(\frac{i}{\hbar} \hat{U}^\dagger \hat{H} \right) \hat{A}_S \hat{U}(t) + \hat{U}^\dagger(t) \hat{A}_S \left(\frac{-i}{\hbar} \hat{H} \hat{U}(t) \right) + \frac{\partial \hat{A}_H}{\partial t} \\ &= \frac{i}{\hbar} [\hat{H}, \hat{A}_H] + \frac{\partial \hat{A}_H}{\partial t} \end{aligned}$$

where the last line follows from $[\hat{U}, \hat{H}] = 0$, and for completeness we have included the possibility of an explicit time dependence (not due to $\hat{U}(t)$) in \hat{A}_H . Thus

$$\frac{d\hat{A}_H}{dt} = -\frac{i}{\hbar} [\hat{A}_H, \hat{H}] + \frac{\partial \hat{A}_H}{\partial t}, \quad (30)$$

which is referred to as the Heisenberg equation (although it was first written down by Dirac). This equation is usually more difficult to solve than the Schrödinger equation. However, it provides a clear picture of the correspondence between quantum and classical mechanics.

B. Quantum - Classical correspondence and Ehrenfest's theorem

In classical mechanics we can describe a dynamical system by coordinates q_j and momenta p_j . The Hamiltonian of the system is a function $H(q_j, p_j)$ of the coordinates and momenta

which satisfy Hamilton's equations

$$\frac{\partial q_j}{\partial t} = \frac{\partial H}{\partial p_j}, \quad \frac{\partial p_j}{\partial t} = -\frac{\partial H}{\partial q_j}.$$

For a particle in a potential $V(\mathbf{r})$, $H = \mathbf{p}^2/2m + V(\mathbf{r})$ so Hamilton's equations give $d\mathbf{r}/dt = \mathbf{p}/m$ and $d\mathbf{p}/dt = -\nabla V(\mathbf{r})$.

For any two dynamical quantities A, B we define the Poisson bracket $\{A, B\}$ by

$$\{A, B\} = \sum_j \left(\frac{\partial A}{\partial q_j} \frac{\partial B}{\partial p_j} - \frac{\partial A}{\partial p_j} \frac{\partial B}{\partial q_j} \right).$$

Clearly $\{A, B\} = -\{B, A\}$.

The time derivative of the quantity A is

$$\begin{aligned} \frac{dA}{dt} &= \sum_j \left(\frac{\partial A}{\partial q_j} \frac{\partial q_j}{\partial t} + \frac{\partial A}{\partial p_j} \frac{\partial p_j}{\partial t} \right) + \frac{\partial A}{\partial t} \\ &= \sum_j \left(\frac{\partial A}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial A}{\partial p_j} \frac{\partial H}{\partial q_j} \right) + \frac{\partial A}{\partial t} \\ &= \{A, H\} + \frac{\partial A}{\partial t}. \end{aligned} \tag{31}$$

The similarity between the quantum equation (30) and the classical equation (31) is remarkable. We see that the quantum equation of motion for the operator \hat{A} can be found by writing down the classical equation for the dynamical variable A in terms of Poisson brackets and making the substitution

$$\{A, H\} \rightarrow -\frac{i}{\hbar} [\hat{A}_H, \hat{H}]. \tag{32}$$

Alternatively, we may think of quantum mechanics as the more fundamental theorem which classical mechanics is an approximation to. In the limit of $\hbar \rightarrow 0$ the transformation

$$-\frac{i}{\hbar} [\hat{A}_H, \hat{H}] \rightarrow \{A, H\} \tag{33}$$

reveals the limiting classical equation of motion. Note that while (32) should always lead to a valid quantum equation, the substitution (33) may be meaningless since there are quantum problems for which no classical analog exists. A prime example is the spin of an electron.

Finally, we note that the time evolution of the expectation value of a quantum variable has a close analogy with the time evolution of the corresponding classical quantity. This analogy is already apparent in equations (30,31), which when written in terms of expectation values is referred to as Ehrenfest's theorem.

To see this note that for any differentiable operator function $\hat{F} = F(\hat{q}_j, \hat{p}_j)$ we have the following commutators

$$[\hat{q}_j, \hat{F}] = i\hbar \frac{\partial \hat{F}}{\partial \hat{p}_j}, \quad [\hat{p}_j, \hat{F}] = -i\hbar \frac{\partial \hat{F}}{\partial \hat{q}_j}.$$

From (30) with $\hat{F} = \hat{H}$ we obtain

$$\frac{d}{dt} \langle \hat{q}_j \rangle = \left\langle \frac{\partial \hat{H}}{\partial \hat{p}_j} \right\rangle, \quad \frac{d}{dt} \langle \hat{p}_j \rangle = - \left\langle \frac{\partial \hat{H}}{\partial \hat{q}_j} \right\rangle.$$

Thus for a particle in potential $V(\hat{\mathbf{r}})$ with $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}})$ we get

$$\frac{d}{dt} \langle \hat{\mathbf{r}} \rangle = \frac{\langle \hat{\mathbf{p}} \rangle}{m}, \quad \frac{d}{dt} \langle \hat{\mathbf{p}} \rangle = - \langle \nabla V(\hat{\mathbf{r}}) \rangle. \quad (34)$$

The first of Eqs. (34) is identical to the corresponding classical equation obtained by putting $\langle \hat{\mathbf{r}} \rangle \rightarrow \mathbf{r}$, $\langle \hat{\mathbf{p}} \rangle \rightarrow \mathbf{p}$. However, the second equation differs from the corresponding classical equation

$$\frac{d}{dt} \langle \hat{\mathbf{p}} \rangle = \nabla V(\mathbf{r})|_{\mathbf{r}=\langle \hat{\mathbf{r}} \rangle}$$

since, in general,

$$\langle \nabla V(\hat{\mathbf{r}}) \rangle \neq \nabla V(\mathbf{r})|_{\mathbf{r}=\langle \hat{\mathbf{r}} \rangle}.$$

The difference between these two expressions is negligible provided the potential is close to constant over the extent of the deBroglie wave packet of the particle. When the potential is constant over the extent of the deBroglie wave packet the expectation values of the quantum variables agree with the results of a classical description.

VI. MEASUREMENTS

Consider an observable \hat{A} with eigenspectrum $|n\rangle$ satisfying $\hat{A}|n\rangle = a_n|n\rangle$. An arbitrary state $|\psi\rangle$ can be expanded as $|\psi\rangle = \sum_{n=0}^{\infty} c_n|n\rangle$. The result of a measurement of the observable A is

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \sum_m c_m^* \langle m | \hat{A} \sum_n c_n | n \rangle = \sum_m \sum_n c_m^* c_n a_n \langle m | n \rangle = \sum_n |c_n|^2 a_n. \quad (35)$$

The probability of the measurement result being the eigenvalue a_n is

$$P(a_n) = |c_n|^2 = |\langle n | \psi \rangle|^2 = \| \hat{P}_n | \psi \rangle \|^2 = \langle \psi | \hat{P}_n | \psi \rangle. \quad (36)$$

After \hat{A} has been measured and given the result a_n the new state of the system is

$$|\psi'\rangle = \frac{\hat{P}_n|\psi\rangle}{\|\hat{P}_n|\psi\rangle\|} = \frac{c_n}{|c_n|}|n\rangle. \quad (37)$$

A subsequent measurement of $\langle\hat{A}\rangle$ will return a_n with unit probability.

The uncertainty in the measurement of an operator depends on the state being measured. Recall the definition of the variance

$$\langle(\Delta\hat{A})^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2.$$

Let us assume $|\psi\rangle = a|0\rangle + b|1\rangle$ describes a two-state particle and that \hat{A} has eigenvalues $\hat{A}|0\rangle = \lambda_0|0\rangle$, $\hat{A}|1\rangle = \lambda_1|1\rangle$. The variance of \hat{A} is

$$\begin{aligned} \langle(\Delta\hat{A})^2\rangle &= \lambda_0^2|a|^2 + \lambda_1^2|b|^2 - (\lambda_0|a|^2 + \lambda_1|b|^2)^2 \\ &= \lambda_0^2(|a|^2 - |a|^4) + \lambda_1^2(|b|^2 - |b|^4) - 2\lambda_0\lambda_1|a|^2|b|^2. \end{aligned}$$

If $a = 0$ or $b = 0$ we are in an eigenstate of \hat{A} and $\langle(\Delta\hat{A})^2\rangle = 0$. If $a = b = 1/\sqrt{2}$ then $\langle(\Delta\hat{A})^2\rangle = \lambda_0^2/4 + \lambda_1^2/4 - 2\lambda_0\lambda_1/4$. This variance is often referred to as quantum projection noise. Variation of the measurement variance as the state changes is a signature of a quantum limited measurement.

VII. PRINCIPLES OF QUANTUM MECHANICS

We can summarize the formalism given above in a small set of principles.

1. A physical system is associated with a Hilbert space \mathcal{E}_H containing ket vectors. At time t the physical state is completely described by a ket $|\psi(t)\rangle$ residing in \mathcal{E}_H .
2. Any physical quantity A is associated with a Hermitian operator \hat{A} that acts on kets in \mathcal{E}_H . The result of a measurement of A is always one of the eigenvalues a_n of \hat{A} . The probability of measuring a_n is $P(a_n) = \|\hat{P}_n|\psi\rangle\|^2$ where $\hat{P}_n = |n\rangle\langle n|$ is the projector onto the ket $|n\rangle$. After the measurement the system will be in the new state $|\psi'\rangle = \frac{\hat{P}_n|\psi\rangle}{\|\hat{P}_n|\psi\rangle\|}$.
3. Time evolution is governed by the Hamiltonian according to $i\hbar\frac{d|\psi(t)\rangle}{dt} = \hat{H}|\psi(t)\rangle$. The solution can be written in terms of a time evolution operator \hat{U} as $|\psi(t)\rangle = \hat{U}(t, t_0)|\psi(t_0)\rangle$ with \hat{U} a unitary operator.

How to translate these simple rules into explicit procedures is often far from obvious, and learning how to do so constitutes a course in Quantum Mechanics.

VIII. DENSITY MATRIX THEORY

When we have a statistical mixture of states the state vector $|\psi\rangle$ is equal to one of the set $\{|\psi_i\rangle\}$ with probability P_i . If the state is described by any one of the $|\psi_i\rangle$ the quantum mechanical expectation value of an operator \hat{O} is simply $\langle\hat{O}\rangle_i = \langle\psi_i|\hat{O}|\psi_i\rangle$. When we have a statistical mixture we define the expectation value of an operator as

$$\langle\hat{O}\rangle = \sum_i P_i \langle\hat{O}\rangle_i = \sum_i P_i \langle\psi_i|\hat{O}|\psi_i\rangle. \quad (38)$$

It should be emphasized that the probabilistic nature of the expectation value $\langle\hat{O}\rangle$ is not quantum mechanical in origin but arises from our imperfect knowledge of the state $|\psi\rangle$. This could for example be due to imperfect preparation of the state. In addition there is the quantum mechanical uncertainty due to the probabilistic interpretation of $\langle\hat{O}\rangle_i$. The probabilities satisfy $0 \leq P_i \leq 1$, $\sum_i P_i = 1$, and $\sum_i P_i^2 \leq 1$. A pure state refers to the situation where only one $P_i = 1$ and all the other P_i vanish. In this case $\langle\hat{O}\rangle = \langle\hat{O}\rangle_i$ and we recover our usual quantum mechanical result. If this is not the case we refer to the state as a mixed state.

In order to deal with situations where we only have statistical knowledge of the wave function we introduce the density matrix defined by

$$\hat{\rho} = \sum_i P_i |\psi_i\rangle\langle\psi_i|.$$

For a pure state this reduces to $\hat{\rho} = |\psi\rangle\langle\psi|$. We now introduce a complete set of orthonormal basis states $|n\rangle$ using which we can write

$$|\psi_i\rangle = \hat{I}|\psi_i\rangle = \left(\sum_n |n\rangle\langle n| \right) |\psi_i\rangle = \sum_n \langle n|\psi_i\rangle |n\rangle = \sum_n c_{in} |n\rangle$$

with $c_{in} = \langle n|\psi_i\rangle$. The trace of the density matrix is the sum of the diagonal components

which is

$$\begin{aligned}
\text{Tr}[\hat{\rho}] &= \sum_n \langle n | \hat{\rho} | n \rangle \\
&= \sum_n \langle n | \sum_i P_i |\psi_i\rangle \langle \psi_i | n \rangle \\
&= \sum_i P_i \sum_{n, n', n''} c_{in'} c_{in''}^* \langle n | n' \rangle \langle n'' | n \rangle \\
&= \sum_i P_i \sum_n c_{in} c_{in}^* \\
&= \sum_i P_i = 1.
\end{aligned} \tag{39}$$

which corresponds to conservation of probability. Some important properties of density matrices are $\hat{\rho} = \hat{\rho}^\dagger$, and $\langle j | \hat{\rho}^2 | i \rangle \leq \langle j | \hat{\rho} | i \rangle$. The equality holds for pure states with $\hat{\rho}^2 = \hat{\rho}$ in which case the density matrix is referred to as idempotent.

The expectation value of an arbitrary operator \hat{O} is given by

$$\begin{aligned}
\langle \hat{O} \rangle &= \sum_i P_i \langle \psi_i | \hat{O} | \psi_i \rangle \\
&= \sum_i P_i \sum_{n', n''} \langle \psi_i | (|n'\rangle \langle n'|) \hat{O} (|n''\rangle \langle n''|) | \psi_i \rangle \\
&= \sum_i P_i \sum_{n', n''} \langle \psi_i | n' \rangle \langle n' | \hat{O} | n'' \rangle \langle n'' | \psi_i \rangle \\
&= \sum_i P_i \sum_{n', n''} \langle n'' | \psi_i \rangle \langle \psi_i | n' \rangle \langle n' | \hat{O} | n'' \rangle \\
&= \sum_{n''} \langle n'' | \left(\sum_i P_i |\psi_i\rangle \langle \psi_i| \right) \sum_{n'} |n'\rangle \langle n'| \hat{O} | n'' \rangle \\
&= \sum_{n''} \langle n'' | \hat{\rho} \sum_{n'} |n'\rangle \langle n'| \hat{O} | n'' \rangle \\
&= \sum_{n''} \langle n'' | \hat{\rho} \hat{O} | n'' \rangle \\
&= \text{Tr} \left[\hat{\rho} \hat{O} \right].
\end{aligned}$$

It can be shown that the trace is unchanged with cyclic reordering of the operators so for any operator

$$\langle \hat{O} \rangle = \text{Tr} \left[\hat{\rho} \hat{O} \right] = \text{Tr} \left[\hat{O} \hat{\rho} \right]. \tag{40}$$

Equation (40) defines the expectation value of an operator when the state is only known statistically. The equation of motion for the density matrix is

$$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar} [\hat{\rho}, \hat{\mathcal{H}}]. \tag{41}$$

This can be derived by plugging the definition of $\hat{\rho}$ into the Schrödinger equation. Comparing with (30) for the time evolution of a Heisenberg frame operator we see that Eq. (41) is of the same form but differs by a minus sign.

A physically admissible density matrix must satisfy three conditions

$$\text{Tr}[\rho] = 1, \quad (42a)$$

$$\rho^\dagger = \rho, \quad (42b)$$

$$\langle \psi | \rho | \psi \rangle \geq 0 \quad \forall |\psi\rangle. \quad (42c)$$

The first condition is conservation of probability, the second says ρ is Hermitian which is apparent from the definition of a mixed state density operator $\rho = \sum_i P_i |\psi_i\rangle\langle\psi_i|$, with the P_i non-negative real numbers, and the third condition says that ρ is a positive operator. This last condition follows from

$$\langle \psi | \rho | \psi \rangle = \langle \psi | \left(\sum_i P_i |\psi_i\rangle\langle\psi_i| \right) | \psi \rangle = \sum_i P_i \langle \psi | \psi_i \rangle \langle \psi | \psi_i \rangle^* = \sum_i P_i |\langle \psi | \psi_i \rangle|^2 \geq 0.$$

A density operator describing the quantum state in a D dimensional basis can be represented as a $D \times D$ matrix with D^2 elements. There are D real entries on the diagonal and $D^2 - D$ off-diagonal complex coherences giving a total of $D + 2(D^2 - D)$ real values. There is one constraint from $\text{Tr}[\rho] = 1$ and $2(D^2 - D)\frac{1}{2} = D^2 - D$ constraints from $\rho^\dagger = \rho$. The density matrix can thus be described by $D + 2(D^2 - D) - 1 - (D^2 - D) = D - 1 + D^2 - D = D^2 - 1$ independent real parameters. If the quantum system of interest is N spin 1/2 particles then $D = 2^N$ and the density matrix has $2^{2N} - 1$ independent real parameters. An arbitrary bipartite density matrix of two spins can thus be described by $2^4 - 1 = 15$ real parameters.

Let's now look at a few examples. Consider a single atom with two levels in a pure state. The density matrix is $\hat{\rho} = |\psi\rangle\langle\psi|$ and using $|\psi\rangle = c_g|g\rangle + c_e|e\rangle$ gives

$$\hat{\rho} = \begin{pmatrix} |c_g|^2 & c_g c_e^* \\ (c_g c_e^*)^* & |c_e|^2 \end{pmatrix}.$$

The maximum possible value of the off-diagonal entries occurs for $|c_g| = |c_e| = 1/\sqrt{2}$ giving an off-diagonal entry with magnitude 1/2. If the atom is in a coherent superposition of ground and excited states $|\psi\rangle = (1/\sqrt{2})(|g\rangle + |e\rangle)$, and the density matrix is

$$\hat{\rho} = \sum_i P_i |\psi_i\rangle\langle\psi_i| = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}.$$

The nonzero off-diagonal elements are referred to as coherences. They show that the expectation value of for example the dipole operator $\hat{\mathbf{d}} = e\hat{\mathbf{r}}$ will be nonzero. On the other hand an atom that is prepared in an incoherent mixture of ground and excited states has density matrix

$$\hat{\rho} = \sum_i P_i |\psi_i\rangle\langle\psi_i| = \frac{1}{2}|g\rangle\langle g| + \frac{1}{2}|e\rangle\langle e| = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}.$$

The off-diagonal elements are zero and there is no coherence. Note that measurements of the probabilities of the ground and excited states do not distinguish between the two cases.

As a second example of a mixed state consider a two-level atom in thermal equilibrium at temperature T . The probability of occupation of state $|j\rangle$ is proportional to $\langle e^{-\hat{H}/k_B T} \rangle = e^{-E_j/k_B T}$. Taking the energy of the ground state to be 0 and the energy of the excited state to be $\hbar\omega_a$ the correctly normalized density operator is

$$\begin{aligned} \hat{\rho} &= \frac{e^{-\hat{H}/k_B T}}{\text{Tr} [e^{-\hat{H}/k_B T}]} \\ &= \frac{1}{1 + e^{-\hbar\omega_a/k_B T}} \begin{pmatrix} 1 & 0 \\ 0 & e^{-\hbar\omega_a/k_B T} \end{pmatrix} \\ &= \frac{1}{2 \cosh(\hbar\omega_a/2k_B T)} \begin{pmatrix} e^{\hbar\omega_a/2k_B T} & 0 \\ 0 & e^{-\hbar\omega_a/2k_B T} \end{pmatrix}. \end{aligned}$$

In the case of a sample of N atoms the wavefunction can be written as

$$|\psi\rangle = c_0|1_g 2_g \dots N_g\rangle + (c_1|1_e 2_g \dots N_g\rangle + \dots) + C_{N+2}|1_e 2_e \dots N_g\rangle + \dots + C_{2N}|1_e 2_e \dots N_e\rangle.$$

When N is large this is a very complicated wavefunction with 2^N coefficients. When the atoms are uncorrelated, that is to say the state of any atom is not dependent on the states of the other atoms, the total density matrix is just the product of the density matrices of the individual atoms,

$$\rho = \prod_i \rho^{(i)} = \rho^{(1)} \otimes \rho^{(2)} \otimes \dots \otimes \rho^{(N)}.$$

A system of N two-level atoms is described by a composite density matrix of dimensions $2^N \times 2^N$. For N large we have approximately $2^{2N}/2$ independent complex quantities which highlights the difficulty of solving quantum dynamical many body problems.

A. Composite systems

Density matrices are important for describing composite quantum systems. Consider two subsystems A, B in the product state

$$|\psi\rangle = |\phi\rangle_A \otimes |\chi\rangle_B.$$

Here \otimes denotes the tensor product. We will often omit the \otimes symbol and write

$$|\psi\rangle = |\phi\rangle_A |\chi\rangle_B \text{ or } |\psi\rangle = |\phi_A \chi_B\rangle \text{ or } |\psi\rangle = |\phi\chi\rangle.$$

In this last version the subsystems are identified by their ordering in the ket. The corresponding bra is

$$\langle\psi| = |\psi\rangle^\dagger = \langle\phi|_A \langle\chi|_B \text{ or } \langle\psi| = \langle\phi_A, \chi_B| \text{ or } \langle\psi| = \langle\phi\chi|.$$

Unfortunately the other convention is also in use for which

$$\langle\psi| = \langle\chi|_B \langle\phi|_A = \langle\chi\phi|.$$

In many cases the ordering will be clear from the context. If not, then it is a good idea to be explicit by using subscripts to indicate the subsystems.

Using the partial trace the density matrix of the joint state ρ_{AB} can be reduced to give

$$\rho_A = \text{Tr}_B(\rho_{AB}) \text{ or } \rho_B = \text{Tr}_A(\rho_{AB}).$$

The reduced density matrices ρ_A or ρ_B encapsulate what we know about the subsystems individually. In many applications of density matrices the composite system may consist of a material object A such as an electron or an atom or a piece of condensed matter containing many atoms. The second half of the system B may be the set of oscillator modes describing a radiation field that is coupled to the matter. We are often interested in the state and the dynamics of the matter, but have only statistical knowledge of the radiation field B . In this case the result of measurements performed on the matter are found using the reduced density matrix $\hat{\rho}_A$.

As an example of a basic composite system consider the two-particle Bell state

$$|\psi\rangle = \frac{|01\rangle + |10\rangle}{\sqrt{2}}. \tag{43}$$

If we measure one of the particles individually we will get the answer 0 or 1 with 50% probability. However, we will also know that a measurement of the other particle would reveal the opposite state. This type of behavior, where there is no local certainty, but strong two-particle correlations is characteristic of entanglement, and is revealed by contrasting the full density matrix with the reduced density matrices. We find

$$\begin{aligned}
 \rho_{AB} &= |\psi\rangle\langle\psi| \\
 &= \frac{|01\rangle + |10\rangle}{\sqrt{2}} \frac{\langle 01| + \langle 10|}{\sqrt{2}} \\
 &= \frac{|01\rangle\langle 01| + |01\rangle\langle 10| + |10\rangle\langle 01| + |10\rangle\langle 10|}{2} \\
 &= \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}
 \end{aligned}$$

which displays the maximum possible coherence. Indeed the Bell state (43) is a maximally entangled state of two, two-level objects.

On the other hand

$$\begin{aligned}
 \rho_A &= \text{Tr}_B(\rho_{AB}) \\
 &= \sum_x {}_B\langle x| \frac{|01\rangle\langle 01| + |01\rangle\langle 10| + |10\rangle\langle 01| + |10\rangle\langle 10|}{2} |x\rangle_B \\
 &= \frac{|0\rangle\langle 0| + |1\rangle\langle 1|}{2} \\
 &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
 \end{aligned}$$

is a mixed state with no coherence.

For reference let's calculate the partial trace for an arbitrary mixed state of two spin 1/2 objects. The most general 4×4 matrix is

$$\rho_{AB} = \begin{pmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \\ m & n & o & p \end{pmatrix}.$$

Of course the coefficients have to satisfy the conditions (42) for this to be a valid density matrix. The reduced density matrices are

$$\rho_A = \text{Tr}_B(\rho_{AB}) = \begin{pmatrix} a + f & c + h \\ i + n & k + p \end{pmatrix}$$

and

$$\rho_B = \text{Tr}_A(\rho_{AB}) = \begin{pmatrix} a + k & b + l \\ e + o & f + p \end{pmatrix}.$$

IX. TIME EVOLUTION OF OPEN QUANTUM SYSTEMS

The unitary evolution of the density operator is described by

$$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}] \quad (44)$$

with $\hat{\mathcal{H}}$ the Hamiltonian. Since $\hat{\mathcal{H}}$ is a hermitian operator the solution for $\hat{\rho}(t)$ is described by a unitary transformation

$$\hat{\rho}(t) = U(t, t_0)\hat{\rho}(t_0)U^\dagger(t, t_0)$$

with U the unitary time evolution operator. Unitary time evolution is characteristic of “closed” quantum systems that are isolated from the environment.

On the other hand we often deal with “open” quantum systems that interact with the environment. This is depicted qualitatively in Fig. 2. In such cases we may observe non-unitary evolution. A familiar example is the decay of an excited atomic level. The atom decays to a lower level and emits a photon, but is never observed to spontaneously transition from a lower to a higher level in the absence of some source of energy in the environment. The dynamics is therefore non-unitary since independent of the initial conditions the atom is always observed in the lower level at long times.

This apparent departure from unitary evolution can be understood from different points of view. If we believe that quantum mechanics applies to everything then the non-unitary dynamics is simply an expression of our lack of knowledge of the environment. If we had a complete description of the environment, i.e. knew the Hamiltonian, there should be a unitary description of the combined dynamics of the system and the environment. In the example of the decaying atom the emitted photon, after rattling around in the environment,

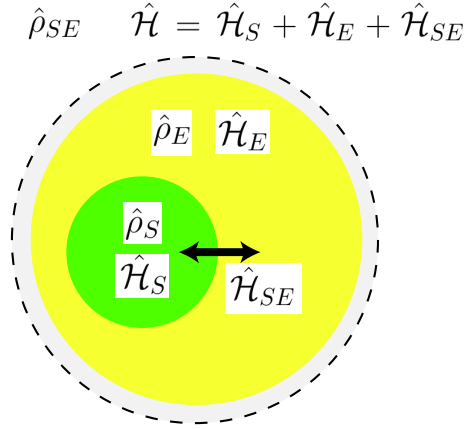


FIG. 2. Quantum system and environment. The total Hamiltonian $\hat{\mathcal{H}}$ and the combined density operator $\hat{\rho}_{SE}$ consist of parts describing the system, the environment, and their interaction.

should eventually return to the atom and have the possibility of exciting it to a higher level, thereby restoring unitary dynamics.

An alternative viewpoint is that quantum mechanics only applies to systems of a finite size, and that at some point we have to give up the quantum description and use classical mechanics. Otherwise we would predict quantum behavior in macroscopic objects, which is never observed. This is the famous Schrödinger's cat paradox. A problem with this point of view is that there is no obvious scale at which to insert a boundary between quantum and classical behavior. Indeed experimental advances of the last few decades have succeeded in observing quantum behavior in larger and larger objects.

Whatever our point of view about these questions, it is true that we often wish to predict the evolution of a quantum system without full knowledge of the environment. This leads to a generalization of Eq. (44) to describe effectively non-unitary evolution. Let's now make these ideas more precise⁴. Consider a quantum system S and an environment E . The density matrix describing system and environment is $\hat{\rho}_{SE}$ and the Hamiltonian is $\hat{\mathcal{H}} = \hat{\mathcal{H}}_S + \hat{\mathcal{H}}_E + \hat{\mathcal{H}}_{SE}$. Here $\hat{\mathcal{H}}_S$ is the system Hamiltonian, $\hat{\mathcal{H}}_E$ is the Hamiltonian of the environment, and $\hat{\mathcal{H}}_{SE}$ describes the coupling between the system and the environment.

Let's assume that the system and the environment are initially in a separable state,

⁴ We primarily draw on the treatment in B. Schumacher and M. Westmoreland, *Quantum processes systems, & information*, Cambridge University Press, Cambridge (2010).

$\hat{\rho}_{SE}(t_0) = \hat{\rho}_S(t_0) \otimes \hat{\rho}_E(t_0)$. At a later time t we have

$$\hat{\rho}_{SE}(t) = U\hat{\rho}_{SE}(t_0)U^\dagger$$

where the time evolution operator U is defined by the total Hamiltonian $\hat{\mathcal{H}}$. The state of the system alone at a later time is

$$\hat{\rho}_S(t) = \text{Tr}_E[\hat{\rho}_{SE}] = \text{Tr}_E[U\hat{\rho}_{SE}(t_0)U^\dagger] = \text{Tr}_E[U\hat{\rho}_S(t_0) \otimes \hat{\rho}_E(t_0)U^\dagger].$$

The evolution of the system density operator can be formally described as due to the action of a superoperator \mathcal{E} ,

$$\hat{\rho}_S(t) = \mathcal{E}[\hat{\rho}_S(t_0)].$$

The map \mathcal{E} is referred to as a quantum process, or as a superoperator, since it maps operators to operators.

Define a basis of environment states $|E_j\rangle$ then

$$\begin{aligned} \hat{\rho}_S(t) &= \text{Tr}_E[U\hat{\rho}_S(t_0) \otimes \hat{\rho}_E(t_0)U^\dagger] \\ &= \sum_j \langle E_j|U\hat{\rho}_S(t_0) \otimes \hat{\rho}_E(t_0)U^\dagger|E_j\rangle. \end{aligned}$$

Let the initial state of the environment be $\rho_E(t_0) = |E_0\rangle\langle E_0|$ and the initial system state be a pure state $\rho_S(t_0) = |S_0\rangle\langle S_0|$ then

$$\begin{aligned} \hat{\rho}_S(t) &= \sum_j \langle E_j|U|S_0\rangle\langle S_0| \otimes |E_0\rangle\langle E_0|U^\dagger|E_j\rangle \\ &= \sum_j \langle E_j|U|S_0\rangle|E_0\rangle \otimes \langle S_0|\langle E_0|U^\dagger|E_j\rangle \\ &= \sum_j \langle E_j|U|E_0\rangle|S_0\rangle \otimes \langle S_0|\langle E_0|U^\dagger|E_j\rangle. \end{aligned}$$

If we now define an operator \hat{A}_j by

$$\hat{A}_j|S_0\rangle = \langle E_j|U|E_0\rangle|S_0\rangle$$

then

$$\hat{\rho}_S(t) = \sum_j \hat{A}_j|S_0\rangle\langle S_0|\hat{A}_j^\dagger.$$

Since any density operator can be written as a sum of pure state density operators we arrive at

$$\hat{\rho}_S(t) = \mathcal{E}[\hat{\rho}_S(t_0)] = \sum_j \hat{A}_j\hat{\rho}_S(t_0)\hat{A}_j^\dagger. \quad (45)$$

The result of these manipulation is that we have an expression for the evolution of the system called the operator sum representation of the process \mathcal{E} . The \hat{A}_j are often called Kraus operators. There are two important things to note about Eq. (45). First, we have found a representation for the time evolution in terms of operators \hat{A}_j that act only on the system. Second, the operators are not unitary and the temporal dynamics of the system density matrix is therefore not unitary. The act of tracing over the environment effectively leads to non-unitary system evolution.

The Kraus operators satisfy a normalization condition since

$$1 = \text{Tr}[\hat{\rho}_S(t)] = \text{Tr}\left[\sum_j \hat{A}_j |S_0\rangle \langle S_0| \hat{A}_j^\dagger\right] = \text{Tr}\left[\langle S_0| \sum_j \hat{A}_j^\dagger \hat{A}_j |S_0\rangle\right] = \langle S_0| \sum_j \hat{A}_j^\dagger \hat{A}_j |S_0\rangle$$

must hold for any pure system state $|S_0\rangle$. Therefore

$$\sum_j \hat{A}_j^\dagger \hat{A}_j = \hat{I}.$$

We can now use the operator sum representation to find a general form for the time evolution of the system density operator when coupled to an environment. Consider an infinitesimal time evolution

$$\mathcal{E}[\hat{\rho}] = \hat{\rho} + \delta\hat{\rho} = \sum_j \hat{A}_j \hat{\rho} \hat{A}_j^\dagger \quad (46)$$

with $\delta\hat{\rho} \sim \delta t$. Here we have dropped the subscript S with the understanding that $\hat{\rho}$ is the reduced density operator of the system. Assume one of the Kraus operators \hat{A}_0 is dominant and is given by

$$\hat{A}_0 = \hat{I} + \hat{L}_0 \delta t$$

and the other operators are

$$\hat{A}_j = \hat{L}_j \sqrt{\delta t}, \quad j \neq 0.$$

Then

$$\hat{A}_0 \hat{\rho} \hat{A}_0^\dagger = \hat{\rho} + (\hat{L}_0 \hat{\rho} + \hat{\rho} \hat{L}_0^\dagger) \delta t + \mathcal{O}(\delta t^2)$$

and

$$\hat{A}_j \hat{\rho} \hat{A}_j^\dagger = \hat{L}_j \hat{\rho} \hat{L}_j^\dagger \delta t.$$

To order δt (46) becomes

$$\hat{\rho} + \delta\hat{\rho} = \hat{\rho} + \left(\hat{L}_0 \hat{\rho} + \hat{\rho} \hat{L}_0^\dagger + \sum_{j \neq 0} \hat{L}_j \hat{\rho} \hat{L}_j^\dagger \right) \delta t.$$

This implies the differential equation

$$\frac{d\hat{\rho}}{dt} = \hat{L}_0\hat{\rho} + \hat{\rho}\hat{L}_0^\dagger + \sum_{j \neq 0} \hat{L}_j\hat{\rho}\hat{L}_j^\dagger.$$

If we compare with (44) we see that in order to recover the Hamiltonian part of the dynamics we must put $\hat{L}_0 = -i\hat{\mathcal{H}}/\hbar + L'_0$ so that

$$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}] + \hat{L}'_0\hat{\rho} + \hat{\rho}\hat{L}'_0{}^\dagger + \sum_{j \neq 0} \hat{L}_j\hat{\rho}\hat{L}_j^\dagger.$$

Since $\text{Tr}[\hat{\rho}] = 1$ at all times we require $\text{Tr}[d\hat{\rho}/dt] = 0$ which results in the condition $\hat{L}'_0 = -\frac{1}{2}\sum_j \hat{L}_j^\dagger\hat{L}_j$. Plugging in we get

$$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar}[\hat{\rho}, \hat{\mathcal{H}}] + \sum_j \hat{L}_j\hat{\rho}\hat{L}_j^\dagger - \frac{1}{2}\hat{L}_j^\dagger\hat{L}_j\hat{\rho} - \frac{1}{2}\hat{\rho}\hat{L}_j^\dagger\hat{L}_j.$$

This is known as the Lindblad equation⁵ and is widely used to study open quantum system dynamics. The specific form of the Lindblad operators \hat{L}_j depends on the problem being treated. We will see an example for the interaction of atomic energy eigenstates with a radiation field.

⁵ G. Lindblad, *On the Generators of Quantum Dynamical Semigroups*, Commun. Math. Phys. **48**, 119 (1976).

X. ONE-DIMENSIONAL HARMONIC OSCILLATOR

The time independent Schrödinger equation for a one-dimensional harmonic oscillator is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi.$$

It is convenient to introduce a characteristic energy $E_0 = \hbar\omega$, length $x_0 = \sqrt{\hbar/(m\omega)}$, and dimensionless position coordinate $\xi = x/x_0$. In terms of these new variables we have

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{2E}{E_0} - \xi^2\right)\psi = 0. \quad (47)$$

To find solutions to this equation consider the limit $\xi \rightarrow \infty$ for which $\psi'' - \xi^2\psi = 0$, where prime denotes the derivative with respect to ξ . Asymptotic solutions are $\psi \sim e^{\pm\xi^2/2}$. To avoid a singularity at infinity we choose the decaying exponential and therefore seek a solution of (47) in the form $\psi = f(\xi)e^{-\xi^2/2}$. The function f then satisfies

$$f'' - 2\xi f' + 2\left(\frac{E}{E_0} - \frac{1}{2}\right)f = 0.$$

The solutions to this equation are the Hermite polynomials $H_n(\xi)$ with integer $n = E/E_0 - 1/2$. The energy eigenvalues are therefore $E_n = E_0(n + 1/2) = \hbar\omega(n + 1/2)$. The normalized eigenfunctions satisfying $\int_{-\infty}^{\infty} d\xi |\psi|^2 = 1$ are

$$u_n = \sqrt{\frac{1}{\pi^{1/2}n!2^n}} H_n(\xi) e^{-\xi^2/2}.$$

The first few Hermite polynomials are

$$H_0 = 1 \quad (48)$$

$$H_1 = 2x \quad (49)$$

$$H_2 = 4x^2 - 2. \quad (50)$$

A. One-dimensional Quartic Oscillator

The quartic oscillator with potential $U(x) = (aE_{ho}/2)(x/x_0)^4$ satisfies the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (aE_{ho}/2)(x/x_0)^4\psi = E\psi$$

where the constant a is dimensionless. Introducing $\xi = x/x_0$ gives

$$\psi'' + 2 \left(\frac{E}{E_{ho}} - \frac{a}{2} \xi^4 \right) \psi = 0$$

where $E_{ho} = \hbar\omega$. There are no closed form analytical solutions to this equation. We proceed by seeking an approximate solution in the form

$$\psi(\xi) = \sum_{n=0}^N c_n u_n(\xi)$$

where the u_n are normalized solutions to a harmonic oscillator and the c_n are constants to be determined. Using the differential equation for the harmonic oscillator we find

$$\sum_n \left(-a\xi^4 + \xi^2 - (2n+1) + \frac{2E}{E_{ho}} \right) c_n u_n = 0. \quad (51)$$

We can convert this into a set of linear equations for the coefficients c_n using the following integrals

$$\int_{-\infty}^{\infty} d\xi u_m \xi^2 u_n = \left(\frac{1}{2} + d_0 \right) \delta_{m,n} + d_{2+} \delta_{m,n+2} + d_{2-} \delta_{m,n-2} \quad (52)$$

$$\begin{aligned} \int_{-\infty}^{\infty} d\xi u_m \xi^4 u_n = & \left(\frac{3}{4} + \tilde{d}_0 \right) \delta_{m,n} + \tilde{d}_{2+} \delta_{m,n+2} + \tilde{d}_{2-} \delta_{m,n-2} \\ & + \tilde{d}_{4+} \delta_{m,n+4} + \tilde{d}_{4-} \delta_{m,n-4} \end{aligned} \quad (53)$$

where

$$\begin{aligned} d_0 = n, \quad d_{2+} = \frac{\sqrt{(n+1)(n+2)}}{2}, \quad d_{2-} = \frac{\sqrt{n(n-1)}}{2} \\ \tilde{d}_0 = \frac{3}{2}(n^2 + n), \quad \tilde{d}_{2+} = \frac{1}{2}(2n+3)\sqrt{(n+2)(n+1)}, \quad \tilde{d}_{2-} = \frac{(2n-1)\sqrt{n(n-1)}}{2} \\ \tilde{d}_{4+} = \frac{\sqrt{(n+4)(n+3)(n+2)(n+1)}}{4}, \quad \tilde{d}_{4-} = \frac{\sqrt{n(n-1)(n-2)(n-3)}}{4}. \end{aligned}$$

Multiplying by u_m and integrating over all space transforms Eq. (51) into a set of algebraic equations

$$\mathbf{M}\mathbf{c} = \lambda\mathbf{c} \quad (54)$$

where $\lambda = (-2E + \frac{3}{4}aE_{ho})/E_{ho} + 1/2$ and $\mathbf{c} = (c_0, c_1, \dots, c_N)$ is the vector of coefficients. The energy eigenvalues are therefore given by

$$E_n = \frac{E_{ho}}{2} \left(\frac{1}{2} + \frac{3}{4}a - \lambda_n \right)$$

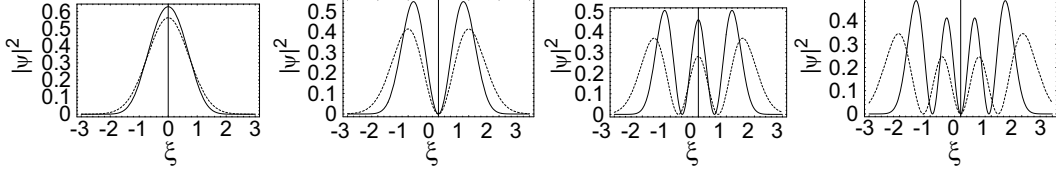


FIG. 3. Probability distributions of the first four eigenmodes for the quartic oscillator (solid lines) and the harmonic oscillator (dashed lines). In all cases the eigenfunctions have been normalized such that $\int_{-\infty}^{\infty} d\xi |\psi|^2 = 1$.

where λ_n is the n^{th} eigenvalue of Eq. (54). The elements of the matrix \mathbf{M} are

$$\begin{aligned}
 M_{mn} = & \left(-2n + d_0 - a\tilde{d}_0\right) \delta_{m,n} \\
 & + \left(d_{2+} - a\tilde{d}_{2+}\right) \delta_{m,n+2} + \left(d_{2-} - a\tilde{d}_{2-}\right) \delta_{m,n-2} \\
 & - a\tilde{d}_{4+} \delta_{m,n+4} - a\tilde{d}_{4-} \delta_{m,n-4} .
 \end{aligned}$$

As an example we can take $a = 1, E_{ho} = 2$. Using $N = 20$ I find the first few eigenvalues to be .1896, -2.550 , -6.206 and the corresponding energies are $E_0 = 1.06037$, $E_1 = 3.7997$, $E_2 = 7.4558$, $E_3 = 11.646$. These agree well with values published in the literature. As shown in Fig. 3 the eigenfunctions look quite similar to those of the harmonic oscillator, but are localized more strongly near the origin.

XI. TWO DIMENSIONAL HARMONIC OSCILLATOR

In two dimensions the harmonic oscillator potential can be written as $U = \frac{1}{2}m\omega^2 r^2 = \frac{1}{2}m\omega^2(x^2 + y^2)$. The Schrödinger equation is separable in Cartesian coordinates so the 2-D solutions can be written as products of 1-D solutions. The eigenfunctions and eigenvalues are labeled by two quantum numbers m, n and the energies are $E_{mn} = \hbar\omega(m + n + 1)$ with degeneracy $m + n + 1$.

Alternatively the 2-D harmonic oscillator can be solved using polar coordinates (r, ϕ) with $x = r \cos \phi$, $y = r \sin \phi$. This will be advantageous for studying anharmonic extensions since ρ^4 and higher potentials are not separable in Cartesian coordinates. In a polar representation we label the solutions with quantum numbers n, l where n refers to the radial dependence and l determines the azimuthal behavior. The requirement of a single valued

wavefunction will result in only integer values of l being admissible. We will find that for a given n there are $2n + 1$ degenerate solutions corresponding to $0 \leq |l| \leq n$.

The Schrödinger equation in polar coordinates is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} \right) + \frac{1}{2} m \omega^2 r^2 \psi = E \psi.$$

We seek solutions in the form $\psi = f(r)\Phi(\phi)$. Requiring that the angular dependence is single valued we use $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{il\phi}$ with l integer. The radial equation is then

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} - \frac{l^2}{r^2} R \right) + \frac{1}{2} m \omega^2 r^2 R = ER.$$

As in the one-dimensional case we introduce characteristic energy $E_0 = \hbar\omega$, length $r_0 = \sqrt{\hbar/(m\omega)}$, and dimensionless radial coordinate $\rho = r/r_0$. Using the new variables the radial equation can be written as

$$\left(\frac{d^2 R}{d\rho^2} + \frac{1}{\rho} \frac{dR}{d\rho} - \frac{l^2}{\rho^2} R \right) + \left(\frac{2E}{E_0} - \rho^2 \right) R = 0.$$

For small ρ , $\rho^2 R'' + \rho R' - l^2 R \sim 0$. This is solved by $R \sim \rho^l$. To prevent divergence at the origin we use $R \sim \rho^{|l|}$. For large ρ , $R'' - \rho^2 R \sim 0$. This is solved by $R \sim e^{\pm \rho^2/2}$. We therefore seek a solution in the form $R = f(\rho)\rho^{|l|}e^{-\rho^2/2}$. The function f satisfies

$$\rho f'' + (1 + 2|l| - 2\rho^2)f' + 2\left(\frac{E}{E_0} - |l| - 1\right)\rho f = 0.$$

To remove the terms in ρ^2 we make a change of variables $x = \rho^2$ and $g(x) = f(\rho)$. Then $f' = g'2\sqrt{x}$, $f'' = g''4x + 2g'$ and

$$xg'' + (1 + |l| - x)g' + (E/2E_0 - |l|/2 - 1/2)g = 0.$$

The solutions of this equation are the associated Laguerre polynomials $L_n^{|l|}(x)$ where $n = E/2E_0 - |l|/2 - 1/2$ is integer. The energy is $E_n = E_0(2n + |l| + 1)$.

The solutions of the Schrödinger equation can therefore be written

$$\begin{aligned} u_{nl}(\rho, \phi) &= R_{nl}(\rho)\Phi_l(\phi) \\ &= \left(L_n^{|l|}(\rho^2)\rho^{|l|}e^{-\rho^2/2} \right) \left(\frac{1}{\sqrt{2\pi}} e^{il\phi} \right). \end{aligned} \quad (55)$$

Although the wavefunctions written above are correct they do not provide the most convenient labeling and ordering of the states. We can order the energy eigenvalues in a

v	states in polar basis (v, l)	degeneracy	states in Cartesian basis (m, n)	degeneracy
0	(0,0)	1	(0,0)	1
1	(1,1), (1,-1)	2	(1,0), (0,1)	2
2	(2,2), (2,-2), (2,0)	3	(2,0), (0,2), (1,1)	3
3	(3,3), (3,-3), (3,1), (3,-1)	4	(2,1), (1,2), (3,0), (0,3)	4
4	(4,4), (4,-4), (4,2), (4,-2), (4,0)	5	(4,0), (0,4), (3,1), (1,3), (2,2)	5

TABLE I. Labeling of 2-D harmonic oscillator states in a polar (v, l) basis or Cartesian (m, n) basis.

manner that makes the analogy with the 1-D case more apparent by introducing an effective vibrational quantum $v = 2n + |l|$ so that

$$E_v = E_{ho}(v + 1).$$

The last term in parentheses is 1 as opposed to 1/2 in the 1-D case as we now have two units of ground state energy, one from the x motion and one from the y motion. We can therefore write the wavefunctions as

$$u_{vl}(\rho, \phi) = R_{vl}(\rho)\Phi_l(\phi) = \left(L_{\frac{v-|l|}{2}}^{|l|}(\rho^2)\rho^{|l|}e^{-\rho^2/2} \right) \left(\frac{1}{\sqrt{2\pi}}e^{il\phi} \right). \quad (56)$$

where $v = 0, 1, 2, \dots$ and $l = v, v - 2, v - 4, \dots, 1$ or 0 . States differing only in the sign of l are degenerate so the degeneracy of the eigenvalue E_v is $v + 1$. We can verify that the same degeneracy is obtained with a Cartesian representation of the 2-D harmonic oscillator solutions as shown in Table XI.

A. Two dimensional quartic oscillator

In two dimensions the quartic oscillator potential can be written as $U = \frac{aE_{ho}}{2}(r/r_0)^4$ with a a dimensionless number proportional to the energy scale which we take as the ground state of the harmonic oscillator $E_{ho} = \hbar\omega$, and $r_0 = \sqrt{\hbar/m\omega}$ is the characteristic length scale. The frequency ω sets the scale for the energy and the spatial dependence. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} \right) + \frac{aE_{ho}}{2r_0^4} r^4 \psi = E\psi.$$

Introducing $\rho = r/r_0$ we get

$$\left(\frac{\partial^2 \psi}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial \psi}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2 \psi}{\partial \phi^2} \right) + \left(\frac{2E}{E_{ho}} - a\rho^4 \right) \psi = 0.$$

The quartic term is diagonal in the azimuthal variable so l remains a good quantum number and we can seek approximate solutions in the form

$$\psi_l(\rho, \phi) = \Phi_l(\phi) \sum_{v=0}^N c_v R_{vl}(\rho).$$

This leads to the equation

$$\sum_{v=0}^N \left(-a\rho^4 + \rho^2 - 2(v+1) + \frac{2E}{E_{ho}} \right) c_v R_{vl} = 0. \quad (57)$$

To convert this into a set of linear equations for the coefficients c_v we use the integrals

$$\begin{aligned} \int_0^\infty dx L_m^k(x) L_n^k(x) x^k e^{-x} &= \frac{(n+k)!}{n!} \delta_{mn}, \\ \int_0^\infty dx [L_n^k(x)]^2 x^{k+1} e^{-x} &= \frac{(n+k)!}{n!} (2n+k+1), \end{aligned} \quad (58)$$

together with the recurrence relation

$$(n+1)L_{n+1}^k(x) = (2n+k+1-x)L_n^k(x) - (n+k)L_{n-1}^k(x). \quad (59)$$

It is then readily shown that

$$\begin{aligned} \int_0^\infty d\rho \rho R_{ml} R_{nl} &= d_0 \delta_{m,n}, \\ \int_0^\infty d\rho \rho R_{ml} \rho^2 R_{nl} &= d_0 d'_0 \delta_{m,n} + d_0 d'_{1+} \delta_{m,n+1} + d_0 d'_{1-} \delta_{m,n-1} \\ \int_0^\infty d\rho \rho R_{ml} \rho^4 R_{nl} &= d_0 d''_0 \delta_{m,n} + d_0 d''_{1+} \delta_{m,n+1} + d_0 d''_{1-} \delta_{m,n-1} \\ &\quad + d_0 d''_{2+} \delta_{m,n+2} + d_0 d''_{2-} \delta_{m,n-2} \end{aligned} \quad (60)$$

where

$$\begin{aligned} d_0 &= \frac{1}{2} \frac{(n+|l|)!}{n!}, \\ d'_0 &= (2n+|l|+1), \quad d'_{1+} = -(n+1), \quad d'_{1-} = -(n+|l|) \\ d''_0 &= [(k+2)(k+1) + 6n(n+k+1)], \quad d''_{1+} = -2(2n+|l|+2)(n+1), \\ d''_{1-} &= -2(2n+|l|)(n+|l|), \quad d''_{2+} = (n+2)(n+1), \quad d''_{2-} = (n+|l|)(n+|l|-1). \end{aligned} \quad (61)$$

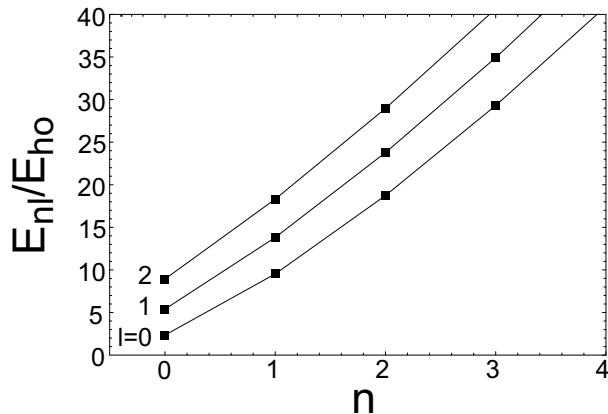


FIG. 4. Energy eigenvalues for the 2d quartic oscillator with $a = 1$, scaled to $E_{ho} = 2$.

With these results we transform Eq. (57) into the algebraic equations

$$\mathbf{M}\mathbf{c} = \lambda\mathbf{c} \quad (62)$$

where $\lambda = 2(|l| + 1) - 2E/E_{ho}$ and $\mathbf{c} = (c_0, c_1, \dots, c_N)$ is the vector of coefficients. The energy eigenvalues are therefore given by

$$E_{nl} = E_{ho} \left(|l| + 1 - \frac{\lambda_{nl}}{2} \right)$$

where λ_{nl} is the n^{th} eigenvalue of Eq. (62) evaluated with azimuthal quantum number l . The elements of the matrix \mathbf{M} are

$$\begin{aligned} M_{mn} = & (-4n + d'_0 - ad''_0) \delta_{m,n} \\ & + (d'_{1+} - ad''_{1+}) \delta_{m,n+1} + (d'_{1-} - ad''_{1-}) \delta_{m,n-1} \\ & - ad''_{2+} \delta_{m,n+2} - ad''_{2-} \delta_{m,n-2} . \end{aligned}$$

The first few energy values shown in Fig. 4 for $E_{ho} = 2$ and $a = 1$ are $E_{00} = 2.345$, $E_{10} = 9.530$, $E_{20} = 18.74$, $E_{01} = 5.394$, $E_{11} = 13.81$, $E_{21} = 23.78$, $E_{02} = 8.928$, $E_{12} = 18.31$, $E_{22} = 28.96$.
