

QUANTUM MECHANICS BASIC TO BIOPHYSICAL METHODS

William Fink

*Department of Chemistry,
University of California Davis*

2.1. QUANTUM MECHANICS POSTULATES

It is critical that I begin by stating that, if you have never before completed a course in quantum mechanics and its applications, I would strongly encourage you to do so. While the material I incorporate in this chapter will brush quickly over the subject, there is an emphasis on brush and quickly. It is probably more useful as a review and reference than as a primary study source. The essential material is commonly offered in first-year graduate courses in both physics and chemistry departments. Physics courses will emphasize clear comprehension of the fundamentals of quantum mechanics and plumb its depths with the exactly soluble problems and its formalism. Chemistry courses will spend less time on the exactly soluble problems and the formalism, but will emphasize the approximate solution of problems and have a molecular perspective. If you will use spectroscopic methods as your major tool to study biophysics, you will need a greater grounding in quantum mechanics than this chapter will provide.

With that caveat out of the way, let us state an acceptable set of postulates for quantum mechanics:

1. For every dynamical system there exists a state function, a solution of the Schrödinger equation, $\Psi(r_1, r_2, \dots, r_n, t)$ that fully describes the system.
2. Observables of the system are represented by operators corresponding to the classical concepts of position and momentum that satisfy the commutation relations

$$[q, p_{q'}] = i\hbar\delta_{q,q'}, \quad [q, q'] = 0, \quad [p_q, p_{q'}] = 0,$$

where q is a coordinate operator and p_q is its corresponding momentum:

$$p_q = -i\hbar(\partial / \partial q).$$

3. When a system is described by the state function Ψ , the mean value of a very large number of measurements of the property Ω on the system will be given by

$$\langle \Omega \rangle = \frac{\int \Psi^* \Omega \Psi d\tau}{\int \Psi^* \Psi d\tau}.$$

Here we have taken care to use the complex conjugate of the function to the left of the operator and the original function to the right of the operator. The complex conjugate is obtained by changing i to $-i$ wherever it appears in the function. If the state function should be a completely real function, then its complex conjugate is simply equal to itself. The result of each measurement will be one of the eigenvalues of Ω : $\Omega \varphi_n = \omega_n \varphi_n$. This equation is a statement of the operator eigenvalue problem. It asks that you find that collection of functions $\{\varphi_n\}$ that have the property that when operated upon by Ω , result in simply a constant, ω_n , times the original function itself. While each individual measurement of the property Ω must result in one of the eigenvalues, ω_n , the average of a large number of these measurements will be given by the formula above, which is called the expectation value.

4. The probability of finding the system in the configuration lying between r_1, r_2, \dots, r_n and $r_1 + dr_1, r_2 + dr_2, \dots, r_n + dr_n$ at a time lying between t and $t + dt$ is proportional to

$$|\Psi(r_1, r_2, \dots, r_n, t)|^2 dr_1 dr_2 \dots dr_n dt.$$

This is the Born interpretation.

5. The state function (or wavefunction) evolves in time according to the equation

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

Here H is the operator corresponding to the total energy of the system, called the Hamiltonian operator. It is the sum of the kinetic and potential energy operators.

6. Particles come in two intrinsic types: bosons and fermions. They each contain internal degrees of freedom that have properties analogous to those of angular momentum. We call this internal degree of freedom of a particle its spin. Fermions are identified with half-integral values of the spin and bosons are identified with integral values of the spin. Electrons are fermions and have spin $1/2$.
7. Systems composed of many fermions will have wavefunctions that are antisymmetric with respect to the interchange of any two fermions' coordinates. Systems composed of many bosons will have wavefunctions that are symmetric with respect to the interchange of any two bosons' coordinates.

As you have probably gathered from reading through the postulates, their implications and implementations are not transparent. Unfortunately, some nonlinearity in the presentation seems necessary. We need to continue to elaborate somewhat to learn how to build this theory of quantum mechanics.

1. The solution of the Schrödinger equation is at the heart of the theory.
 - a. The state function or wavefunction gives us everything we can know about a system. This assumption implies that wavefunctions have continuity over all space and are mathematically well behaved. We can draw upon those properties to aid in problem solution. We can require our solutions to be continuous, smooth, etc. as needed.
 - b. Notice that the wavefunction form depends only on coordinates. It has no dependence on momenta. The solution to a classical mechanical problem gives evolution of both coordinates and momenta (velocities) independently in time. We are clearly going to find some anomalies in the relationship between coordinates and momenta when compared with classical mechanical systems.
2. Operators for observables:
 - a. Write the classical property of interest in its simplest, most symmetrical form in terms of Cartesian coordinates and momenta.
 - b. Make the operator replacements:

$$x \rightarrow x\bullet$$

where $x\bullet$ means multiply by x ;

$$p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x},$$

where $\partial/\partial x$ means take the partial derivative with respect to x .

- c. Collect expressions into commonly used vector operator definitions and convert these to the coordinate system of interest.
- d. Most of the net operators one needs:
 1. Kinetic energy for a single particle

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\}.$$

Drop unneeded derivatives for lower dimensions.

2. Potential energy: these will be functions of the coordinates only, so simply remember that the expression is to multiply whatever it is operating on.
3. Multipole moments:
 - a. dipole moment

$$\begin{aligned}\mu_x &= qx\bullet \\ \mu_y &= qy\bullet \\ \mu_z &= qz\bullet\end{aligned}$$

where q will usually be e , the elementary charge.

- b. higher moments by analogy with the dipole moment, coordinates repeated as necessary for each component.

4. Momenta
 a. linear

$$\vec{p} = \frac{\hbar}{i} \vec{\nabla} = -i\hbar \vec{\nabla} = -i\hbar \left\{ \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right\}.$$

Again drop terms for lower dimensions than three.

- b. angular, $\vec{L} = \vec{r} \times \vec{p}$:

$$\begin{aligned} L_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \\ L_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \\ L_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \end{aligned}$$

- e. An important aspect of quantum mechanics is the development of the algebra of operators. Unlike the algebra of numbers, operator algebra is non-commuting and in fact is very parallel to matrix algebra and one formulation of quantum mechanics, which is perhaps more useful for molecular electronic structure problems, casts all of quantum mechanics into matrices and is therefore called matrix mechanics. We will not pursue that topic here, but the founder of matrix mechanics was Heisenberg, and Dirac showed that the Heisenberg formulation and the Schrödinger formulation were equivalent, and were both representations of the Hilbert space of functions that carries both representations. The most important characterization of the operator algebra is quantification of the noncommuting property. For this purpose, the commutator is defined:

$$[A, B] = AB - BA.$$

Here A and B are two operators, and the commutator is the operator that represents the difference between the order of application of the operators. We will also not show, but simply state, that when two operators commute ($[A, B] = 0$), then it is possible to find functions that are simultaneously eigenfunctions of both operators. It is especially valuable for the case of operators that commute with the Hamiltonian operator, because then we can know that the state vector can also be characterized by the eigenfunctions of these commuting operators. Often these operators' eigenvalue problems are simpler than is the S. equation. A great deal of understanding about the system of interest may be obtained by examining these eigenfunctions and eigenvalues without having to solve the more difficult S. equation. The set of operators that commute with the Hamiltonian are typically symmetry operations, and their corresponding eigenvalues are constants of the motion, the analogue of the classical mechanical conservation theorems, i.e., conservation of linear momentum and conservation of angular momentum.

3. Measurement of observables:

For any operator Ω , corresponding to an observable property, we can pose its eigenvalue problem:

$$\Omega\phi_n(x) = \omega_n\phi_n(x),$$

Where ω_n are the eigenvalues and $\phi_n(x)$ are the eigenfunctions.

$\phi_n(x)$ constitutes a complete set of functions, so that any function of x may be expanded in terms of them. Indeed, the state function for a system may be so expanded, and we may write

$$\Psi(x) = \sum_n c_n \phi_n(x), \quad \int_{-\infty}^{+\infty} \Psi^*(x) \Psi(x) dx = 1,$$

and

$$\int_{-\infty}^{+\infty} \phi_n^*(x) \phi_m(x) dx = \delta_{n,m}, \quad \delta_{n,m} = \begin{cases} 0, & n \neq m \\ 1, & n = m \end{cases}.$$

Using these,

$$\begin{aligned} \langle \Omega \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x) \Omega \Psi(x) dx = \int_{-\infty}^{+\infty} \sum_n c_n^* \phi_n^*(x) \Omega \sum_m c_m \phi_m(x) dx \\ &= \sum_n \sum_m c_n^* c_m \int_{-\infty}^{+\infty} \phi_n^*(x) \Omega \phi_m(x) dx = \sum_n \sum_m c_n^* c_m \omega_m \delta_{n,m} \\ &= \sum_n c_n^* c_n \omega_n. \end{aligned}$$

And we conclude that all possible values of ω_n times the probability of the occurrence of that value gives the average of a very large number of measurements of the observable. This average value is called the expectation value.

4. The Born interpretation:

The effect of postulate 4 is that our quantum mechanics will not be a deterministic theory. At its heart is a probabilistic result; hence there will be no result that carries absolute certainty as there is in classical mechanics, where the trajectories evolve unequivocally in time. A particle is known to be at a particular point with a certain velocity at a given time with no ambiguity in classical mechanics. The only limits on knowledge are because of measurement error. Here instead, we have a theory that describes its results with a probability distribution right away. More modern versions of the interpretation consider the possibility of evolving parallel universes. The Born interpretation presents enough of an intellectual challenge for our purposes.

A consequence of this probabilistic interpretation is that our state vectors must be square integrable:

$$\int_{\text{allspace}} |\Psi|^2 d\tau < \infty.$$

Consequently, we must have

$$\lim_{x \rightarrow \infty} \Psi(x) = 0.$$

This presents some difficulties that must be recognized and dealt with for the case of unimpeded translational motion for a particle.

- a. Put it in a very large enclosing box with impenetrable walls.
 - b. Express all results as normalized to an incident flux of particle density.
- Beam experiments, laser fluence will utilize this option.

5. Time dependence of the Schrödinger equation:

The general treatment of time dependence in quantum mechanics is not simple, but for problems for which there is no explicit dependence of the Hamiltonian operator on time, there is a universal solution of the time dependence, which results in separation of time variables from space variables. We write $\Psi(\vec{r}, t) = \psi(\vec{r})U(t)$ and insert this trial form into the equation. The partial differential equation separates into an equation for the time function $U(t)$ and a separate equation for the space function. The separation constant turns out to be the total energy of the system, the eigenvalue of the spatial equation. These two equations are:

$$i\hbar \frac{dU(t)}{dt} = EU(t), \quad (1)$$

$$H\psi(\vec{r}) = E\psi(\vec{r}). \quad (2)$$

Equation (2) is the time-independent form of the Schrödinger equation. The explicit solution for Eq. (1) is available. This is an ordinary differential equation that asks the question, what function do you know that has the property that its derivative is a constant times the original function? The exponential function has that property and the solution is

$$U(t) = e^{-i\frac{E}{\hbar}t}.$$

Since $e^{i\omega t} = \cos \omega t + i \sin \omega t$, with ω being the angular frequency of oscillation, the time dependence modifies the spatial part as an amplitude giving a real and an imaginary component that vary sinusoidally with angular frequency E/\hbar . We call state vectors with this time dependence stationary states, because the spatial part of the state vector never changes in time, and the probability is constant in time since $U^* U = 1$.

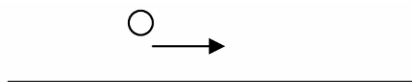
Postulates 6 and 7 speak to another aspect of nature that arises only in the treatment of systems with many particles. Since our molecular level particles cannot carry labels, they are all indistinguishable. This indistinguishability forces us to treat them by considering all possible permutations of labels to particles. State vectors must then be classified into an irreducible representation of the permutation group. Particles belonging to the antisymmetric representation are called

fermions, the most important one of which for us is the electron. Particles belonging to the symmetric representation are called bosons. We will reserve the treatment of this property until after we have described single-particle problems.

2.2. ONE-DIMENSIONAL PROBLEMS

2.2.1. Description of the Motion of an Unimpeded Particle

Classical motion:



The particle moves in one dimension with no forces acting on it. We let T stand for kinetic energy and V for potential energy. The position of the particle is the variable x ; its mass is m and its speed v ; its position at time $t = 0$ is x_0 , and its momentum is p :

$$x = vt + x_0, \quad T = (1/2)mv^2 = \frac{p^2}{2m}, \quad p = mv,$$

$$x = \frac{p}{m}t + x_0, \quad E = T + V; \quad V = 0, \quad E = T,$$

$$E = \frac{p^2}{2m}; \quad p = \sqrt{2mE}.$$

Quantum problem:

$$H\Psi(x,t) = E\Psi(x,t); \quad H = T + V = T;$$

$$\frac{-\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi; \quad \frac{d^2\Psi(x)}{dx^2} = \frac{-2mE}{\hbar^2} \Psi(x).$$

This is a second-order ordinary differential equation. What function do you know that has the property that when it is differentiated twice the result is a negative number times the original function? The possible solutions are

$$\sin(kx), \quad \cos(kx), \quad e^{\pm ikx} \dots$$

In this case, since the particle is freely translating, we will probably want to characterize the system by its linear momentum as well as its energy since we expect that to be a constant of the motion since $[H, p_x] = 0$. Only the imaginary exponential form is also an eigenfunction of

$$p_x \Psi(x) = k\Psi(x), \quad p_x = -i\hbar \frac{d}{dx}, \quad -i\hbar \frac{d}{dx} (e^{\pm ikx}) = \pm k\hbar e^{\pm ikx}.$$

For the solution of our problem, we then choose $\Psi(x) = Ae^{+ikx} + Be^{-ikx}$.

For the full time-dependent wavefunction, we have

$$\Psi(x,t) = \Psi(x)e^{-i\frac{E}{\hbar}t} = Ae^{i(kx - \frac{E}{\hbar}t)} + Be^{-i(kx + \frac{E}{\hbar}t)}.$$

Notice the form of the arguments of the imaginary exponentials.

We want to extract a physical interpretation of each of the two terms on the right-hand side (rhs). Since the imaginary exponential is composed of a cosinusoidal real part and a sinusoidal imaginary part, let us examine the real part

$\cos(kx - \omega t)$ at $t = 0$ and at $t = \delta/\omega$ (Fig. 2.1)

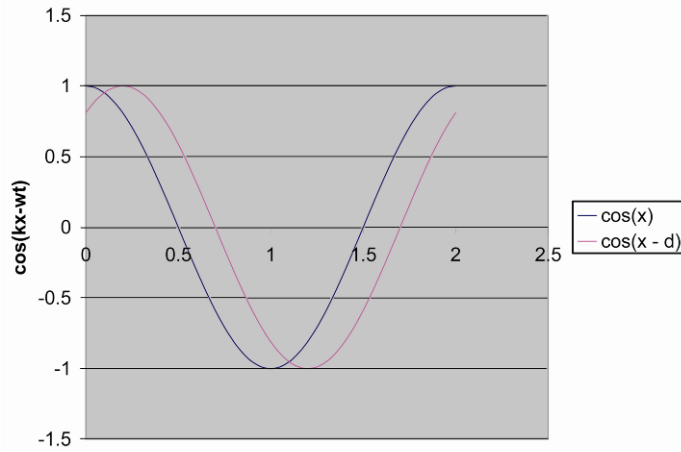


Figure 2.1. An oscillating function with argument $(kx - \omega t)$ moves to the right as time advances. Please visit <http://www.springer.com/series/7845> to view a high-resolution full-color version of this illustration.

and $\cos(kx + \omega t)$ at $t = 0$ and at $t = \delta/\omega$ (Fig. 2.2).

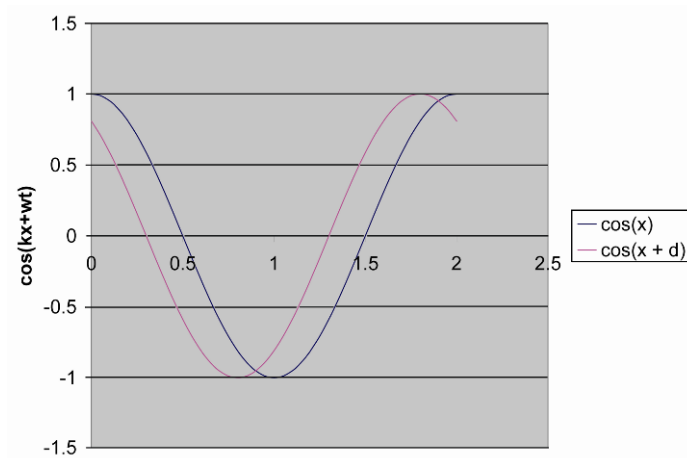


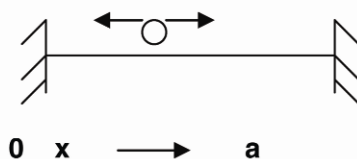
Figure 2.2. An oscillating function with argument $(kx + \omega t)$ moves to the left as time advances. Please visit <http://www.springer.com/series/7845> to view a high-resolution full-color version of this illustration.

A function with argument $(kx - \omega t)$ moves to the right (in the positive sense, a forward moving wave) as time advances, whereas a function with argument $(kx + \omega t)$ moves to the left (in the negative sense, a backward moving wave) as time advances. Therefore, the term multiplied by A , (e^{ikx}) in our solution is the forward-moving wave and the term multiplied by B , (e^{-ikx}) in our solution is the backward-moving wave. These are associated with positive momentum ($p_x e^{ikx} = k(\hbar/2\pi)e^{ikx}$) and negative momentum, so we have recovered the natural algebraic signs for the direction of movement.

2.2.2. Problems with Step-Function Changes in the Potential

With this much mathematics and a lot of tedium, one can address lots of one-dimensional problems where the potential is changed by step-functions, so that the solution will always be representable in terms of the trigonometric or imaginary exponential functions. The problems are solved by matching the value of the wavefunction and its derivative, if required, at each boundary where the value of the potential changes. The most informative, the simplest, and the least tedious of these is the solution of the particle in a box, also called a particle in a well.

The classical model for a particle in a well might be a bead on a wire mounted between two absolutely impermeable steel walls:



The potential to describe this problem would have the value zero for values of $0 < x < a$, and have an infinite value for all other values of x . The infinite value implies that there is a force so strong that the particle would never enter that region of space. There are then three regions of this one-dimensional space: the region to the left of the origin (I), the region between the origin and a (II), and the region to the right of a (III). In regions I and III, our wavefunction must be zero, because the potential is so strong that the particle will never be there; consequently, it has zero probability of being found there. This zero probability for the entire region can only be achieved if our wavefunction is zero in that region. In region II, the solution must be composed of the sine, and cosine, or alternatively of the imaginary exponentials. In this case, it is more convenient to use the trigonometric functions, since linear momentum will not be conserved in the classical problem and there is no need to expect that the QM solution will be an eigenfunction of linear momentum. One tries the form $\Psi = A \cos(\omega x) + B \sin(\omega x)$ in the S. equation, and finds that to satisfy the S. equation,

$$\omega = \frac{\sqrt{2mE}}{\hbar}.$$

Application of the boundary condition that $\Psi_I(0) = \Psi_{II}(0)$ eliminates the cosine function as a possible form to include since it has value of 1 at zero. Application of the boundary condition that $\Psi_{II}(a) = \Psi_{III}(a)$, can only be satisfied if the argument of the sine function is a multiple of π .

This latter condition will be satisfied only if the energy takes on the specific values

$$E = \frac{n^2 \hbar^2 \pi^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}. \text{ Using this in the expression for } \omega, \text{ and normalizing the solution to 1}$$

gives: $\Psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$, $0 \leq x \leq a$, $n = 1, 2, 3, \dots$ Notice that n may not be zero. If it

were zero, the entire function would be zero for all values of x ; $|\Psi|^2 = 0$ also, for all values of x . There is no probability of finding the particle anywhere, and, therefore, somehow the particle vanished. The energy can therefore also not be zero. This is a general result in quantum mechanics. Particles never have zero energy; there is always a finite value to the first possible energy level.

This zero point energy is closely related to the Heisenberg uncertainty relationship between momentum and position. The uncertainty principle may be stated $\Delta x \bullet \Delta p \geq \hbar/2$. The product of the uncertainty of position and the uncertainty of momentum is always larger or equal to $\hbar/2$. If the energy were to be zero, the particle would be at rest, its position would be precisely known, and so would its momentum (zero). Such a condition for a system would violate this general relationship, and consequently never occurs.

Let's take a look at the nature of these solutions. On the next page is plotted a representation of the first three solutions. Notice that the energy level spacing increases as the energy gets higher in the well. This is an unusual behavior that is unique to this problem and occurs because the well is infinitely high and has straight sides. In this figure the wavefunction and corresponding probability density have been superimposed in the energy well at the energy level corresponding with that wavefunction. The vertical scales for the wavefunction and probability density are not shown, but both are referenced to zero at the horizontal line corresponding to the energy level. There are several points worth noting: 1) the number of nodes in the wavefunctions increases with increasing energy; 2) the solutions are either even ($\psi(x) = \psi(-x)$) or odd ($\psi(x) = -\psi(-x)$) with respect to the center of the well, even for n odd, and odd for n even; we should have expected the solutions to have this symmetry, since the potential is symmetric about the center of the well; 3) the probability densities, of course, go to zero at the nodes of the wavefunction; this observation can lead to a conundrum worth discussing.

In the second energy level, the probability density is appreciable on either side of the center point, but is exactly zero at the center point. From a classical perspective, one might wonder how a particle can get from the left half of the well to the right half of the well without passing through the center. The resolution of this paradox is that making that observation is attempting to impose a classical mechanical concept, that of a trajectory, onto the solution of a quantum mechanical problem. In quantum mechanics, the trajectory is not the fundamental nature of the solution, but the wavefunction. QM says that, if you make observations of where the particle is in the well, then the probability of finding it at such times of observation is given by the probability density. It makes no statement about how the particle is moving either before or after the observation, and it is artificial to cling to the classical concept of a trajectory. To impose the classical concept of a trajectory on the problem is a logical mistake. It is like asking for the angle between two matrices. The concept of angle comes from geometry and does not apply in the linear algebra of matrices without further development of the concept. Likewise, we can recover a trajectory in quantum mechanics by taking a superposition of the stationary states, each with time-varying amplitude, but to do so one will necessarily need to have an ill-defined energy.

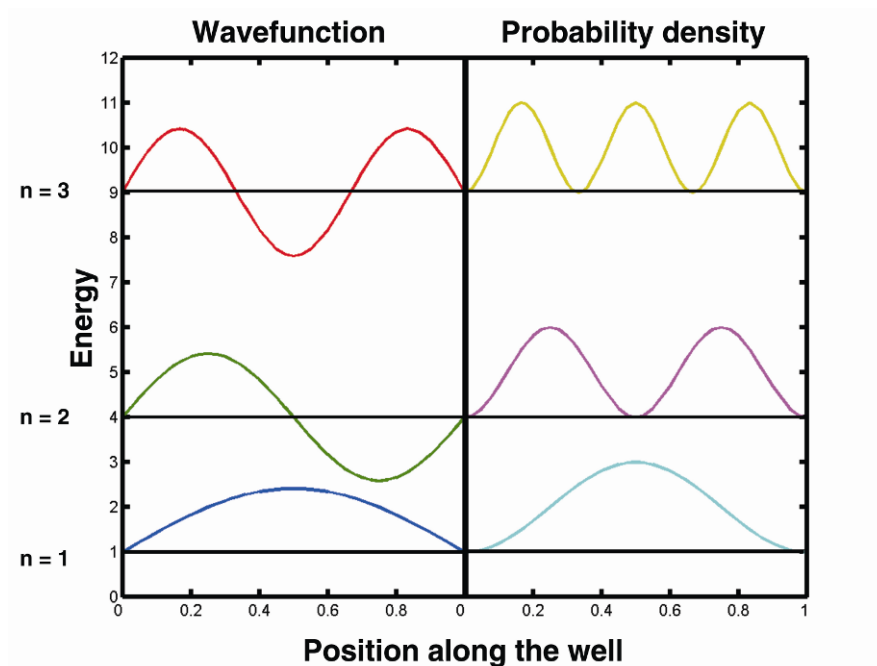
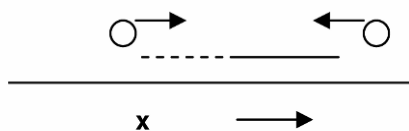


Figure 2.3. The first three solutions to the Schrödinger equation for the one-dimensional particle-in-a-well problem are displayed placed at their respective energies in the well. The wavefunction amplitude axis and probability density axis are not shown but are referenced to a zero horizontal at the energy corresponding to $n = 1, 2, 3$. Notice the increasing numbers of nodes in the solution as the energy increases. Please visit <http://www.springer.com/series/7845> to view a high-resolution full-color version of this illustration.

2.3. THE HARMONIC OSCILLATOR

The single model that has been most successful for depicting the essence of many physical situations is the harmonic oscillator model. Its versatility stems largely from the fact that it is the first two terms of the Taylor expansion for any arbitrary function. Higher terms that improve the representation of the potential may be added, but just the simple harmonic oscillator captures an enormous amount of the physics of many problems.

2.3.1. The Problem



A particle is subject to a restoring force that tends to return it to the origin whenever it is displaced away from the origin, $F = -kx$.

Since

$$F = -\frac{dV}{dx}; \quad V = \frac{1}{2}kx^2,$$

$$H = T + V = \frac{p^2}{2m} + \frac{1}{2}kx^2.$$

2.3.2. The Classical Solution

$$F = ma = m \frac{d^2x}{dt^2} = -kx, \quad \frac{d^2x}{dt^2} = -\frac{k}{m}x,$$

$$x = A \cos \omega t + B \sin \omega t, \quad \omega = \sqrt{\frac{k}{m}}, \quad \omega^2 = \frac{k}{m},$$

where ω is the angular frequency in radians/sec. It is common to define a cycle frequency, complete cycles per second given the symbol ν . Since there are 2π radians in one complete circle (cycle), then $\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$. To give complete form to our solution, let us say that $x = 0$ at $t = 0$, so that $x = B \sin \omega t$.

The maximum value of x occurs for a maximum value of $\sin \omega t = 1$. $x_{\max} = B$. The nature of the constant B is then clear; it represents x_{\max} or the amplitude of the motion. When $x = x_{\max} = B$, $v = dx/dt = \omega B \cos \omega t$.

But when $x = x_{\max} = B$, then $\sin \omega t = 1$ and $\cos \omega t = 0$,

$$E = T + V = \frac{1}{2}m \left(\frac{dx}{dt} \right)^2 + \frac{1}{2}kx^2 = 0 + \frac{1}{2}kB^2.$$

Then B , which is the measure of the amplitude of the oscillation, determines (or is determined by) the total energy of the system.

When $x = 0$, $B \sin \omega t = 0$, $\omega B \cos \omega t = \omega B$. Then the particle is moving its fastest at $x = 0$. There, $T = \frac{1}{2}mv^2 = \frac{1}{2}m\omega^2 B^2 = \frac{1}{2}m \frac{k}{m} B^2 = \frac{1}{2}kB^2$, and $V = \frac{1}{2}kx^2 = \frac{1}{2}k(0)^2 = 0$. And all the energy is kinetic.

When $x = B$, $T = 0$, $V = \frac{1}{2}kB^2$, and the energy is all potential, the particle is at rest. The points $x = \pm B$ are called the turning points, since the motion stops and turns around there. The motion is confined to the region $-B \leq x \leq B$.

It is useful for comparison with the quantum mechanical result to consider the probability that a particle executing simple harmonic oscillator motion will be at each value of the coordinate when the motion is averaged over many oscillations. First, we should scale the coordinate so that we express it as a fraction of the maximum amplitude $u = x/B$. By considering one period of oscillation, and finding the length of time the particle requires to traverse each infinitesimal length du , the probability of occurrence of each location will be that time divided by the entire period. The resulting expression is

$$P(u)du = \frac{du}{2\pi\sqrt{1-u^2}}$$

Notice that this expression has singularities at $u = \pm 1$, where the value rises indefinitely. These are the turning points, and it is, of course, most likely that since the particle stops and turns around there, that it is extremely likely that the particle will be found at the turning points if one makes randomly selected observations.

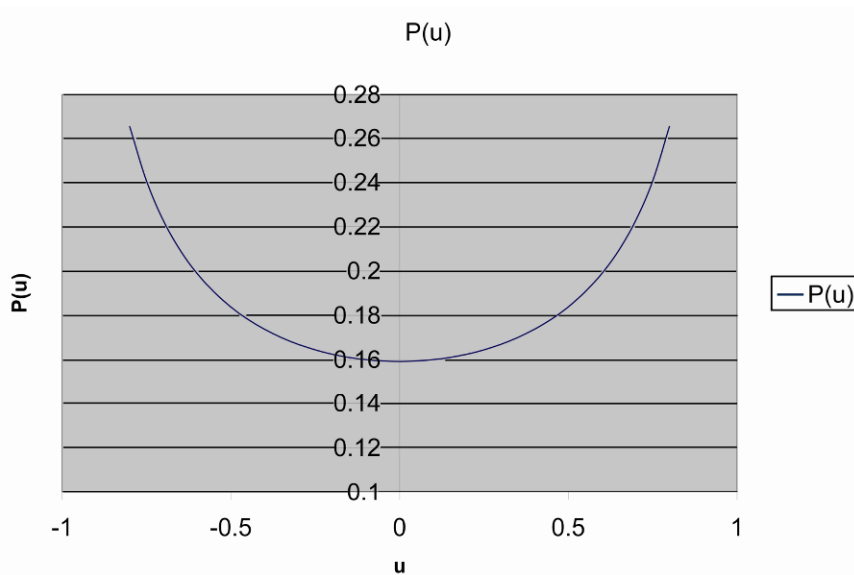


Figure 2.4. The probability of locating a particle executing classical harmonic oscillator motion measured along its trajectory. There are infinities at the endpoints of the trajectory that are called “turning points.” It is most likely that a classical particle will be observed at the turning points as the particle slows down, comes to rest, and reverses its direction of motion there. Please visit <http://www.springer.com/series/7845> to view a high-resolution full-color version of this illustration.

2.3.3. The Quantum Mechanical Solution

The Schrödinger equation becomes

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

This is an ordinary differential equation that has a long history in applied mathematics. The solutions turn out to be the Hermite polynomials:

$$\psi_v(x) = N_v H_v(\alpha x) e^{-(\alpha x)^2/2}, \quad N_v = \left(\frac{\alpha}{\sqrt{\pi} 2^v v!} \right)^{1/2}, \quad \alpha = \left(\frac{mk}{\hbar^2} \right)^{1/4} = \left(\frac{m\omega}{\hbar} \right)^{1/2},$$

$$E_\nu = \left(\nu + \frac{1}{2} \right) \hbar \omega, \quad \hbar \omega = \frac{h}{2\pi} \sqrt{\frac{k}{m}} = h \left(\frac{1}{2\pi} \sqrt{\frac{k}{m}} \right) = h\nu, \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}},$$

In the above, the index ν takes on values 0, 1, 2, 3, ...

You will see both the $\hbar\omega$ and $h\nu$ forms used extensively.

The following remarks are worth noting:

1. Energy is quantized; only these specific values of the energy lead to acceptable solutions of the S. equation. One method of finding the specific polynomial forms imposes the quantized energy condition in order that the wavefunction be finite at infinite values of the coordinate. The quantization arises naturally and intrinsically, not as an ad-hoc addition or postulate.
2. The functions $H_\nu(u)$ are polynomials. For even index they are even; for odd index they are odd with respect to the origin. An index of zero just gives a constant; index 1 is simply u ; index 2 is $(2u^2 - 1)$, etc. The wavefunction is this polynomial multiplied by a gaussian centered at the origin. The gaussian ensures that the wavefunction goes to zero at large absolute values of u .
3. There is a finite zero-point energy of $\frac{1}{2}h\nu$ for the lowest energy level. This is another illustration of finite zero-point energies in quantum mechanical solutions.
4. Because there is a definition for the wavefunction that has a nonzero value at all positions of the coordinate, there is some (small) probability that the particle will be found outside the classically allowed region ($|x| > 2E/k$). This is our first encounter with the phenomenon of quantum mechanical tunneling, that is, there is a finite probability of the particle being in a classically forbidden region where the potential energy is greater than the total energy.
5. The number of nodes increases with increasing E . Plots of $|\psi|^2$ for high values of the index ν will show higher probabilities at the edges of the well (turning points) than in the center; one thus sees a tendency toward the classical probability at high energies. This is an illustration of the correspondence principle that quantum mechanics tends toward the classical solution at high energies and large masses. However, the lowest energy level has a probability distribution that peaks in the middle of the well, very different from the classical result.

2.4. THE HYDROGEN ATOM

For problems with spherical symmetry, the angular portion of the one-particle Schrödinger equation has the same solution regardless of the radial part of the problem. The general problem is

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

Here we have written the mass with the Greek symbol μ because it will typically be a reduced mass after removal of the translational problem of the center of mass. The simplest of these problems is for $V(r) = 0$. This would be the case for a particle constrained to move only on the

surface of a sphere, or a more physical problem, that of a rigid rotor, two mass points attached to the ends of a rigid rod. We use the expression for the Laplacian after it has been converted to spherical polar coordinates, a painful exercise best done once in a lifetime. The result is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)_{r, \theta}$$

For the rigid rotor, r is a constant, $\mu = m_1 + m_2$, and $\mu r^2 = I$, the moment of inertia, so that

$$H = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] = \frac{L^2}{2I},$$

where the latter equality comes from recognizing that the classical form involves only kinetic energy and that for angular motion the angular momentum L plays the role that linear momentum plays for translational motion. We conclude that the quantum mechanical form of the operator for the square of the angular momentum is

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right].$$

Since the angular variables are unit-less, the correct units of angular momentum are those of Planck's constant, erg-seconds, and the natural size of the unit is multiples of \hbar . The S. equation for the rigid rotor is equivalent to finding the eigenfunctions of the square of the angular momentum. The square of the angular momentum plays an enormous role in the development and understanding of quantum mechanics since it applies to every spherical problem. The two variables are the two angles that will specify the orientation of the rigid rod. The solution to the eigenvalue problem $L^2 Y(\theta, \phi) = \Lambda Y(\theta, \phi)$ are the spherical harmonics with eigenvalues $\Lambda = (\ell(\ell+1))\hbar^2$.

Apart from an arbitrarily chosen complex phase, the spherical harmonics are of the form

$$Y_{l,m}(\theta, \phi) = \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{\frac{1}{2}} P_l^{|m|}(\cos \theta) e^{im\phi},$$

where $P_l^{|m|}(x)$ are the associated Legendre functions, another famous set of functions from applied mathematics that are also just polynomials. Here, l is the same as ℓ in the expression for Λ , and takes on values 0, 1, 2, ...

The values m takes on are $-l \leq m \leq l$; $Y_{l,m}(\theta, \phi)$ are also eigenfunctions of the z -component of the angular momentum $L_z = -i\hbar \frac{\partial}{\partial \phi}$, with eigenvalue $m\hbar$. The quantum mechanical angular momentum is commonly thought of in terms of a quantized vector model.

The angular momentum may be thought of as a vector precessing about the z -axis on the surface of a cone. (Its x and y components are not constants of the motion.) It has a length $\hbar\sqrt{l(l+1)}$ and possible projections along the z -axis of integer multiples of \hbar from $-l$ to $+l$. When there is more than one particle in a spherical potential, the individual values of their an-

gular momentum may couple together to form a total angular momentum for the entire system. The problem of coupling multiple angular momenta leads to an elegant study of its own. This is the domain of books on angular momentum. The simplest coupling scheme is that of successive additions of the momenta and leads to relative weightings available in tables called Clebsch-Gordon Coefficients, Wigner Coefficients, or Vector-Coupling Coefficients, depending on who the author wishes to give credit for their creation, or if the author prefers to be descriptive rather than honor the history of the algebra.

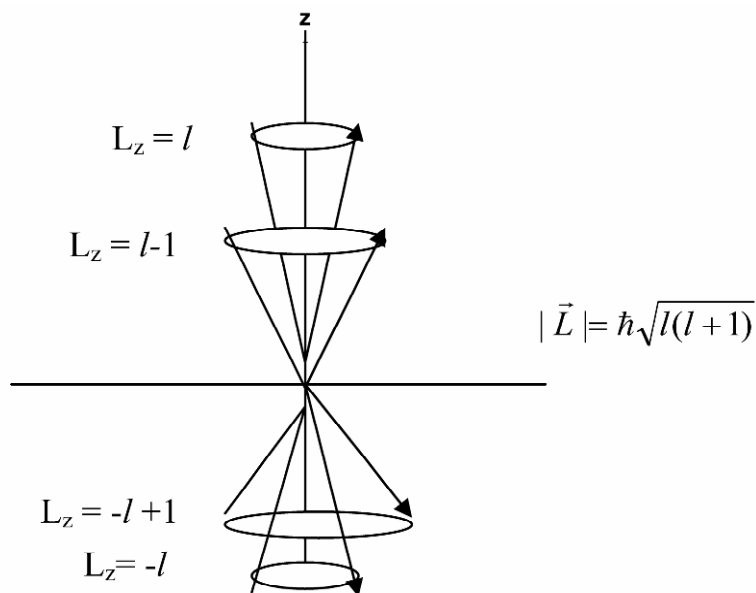


Figure 2.5. The angular momentum viewed as a vector precessing on the surface of a cone. The projection along the z -axis is quantized in units of \hbar from L to $-L$. The length of the vector along the cone surface is $\sqrt{l(l+1)}\hbar$.

The algebra of angular momentum incorporates another set of operators, the raising and lowering operators $L_{\pm} = L_x \pm iL_y$. They have the properties $(L_{\pm})^{\dagger} = L_{\mp}$. If we denote a $Y_{lm}(\theta, \phi) = |l, m\rangle$ containing just the two quantum numbers, then these operators change the m quantum number by one unit $L_{\pm}|l, m\rangle = \{l(l+1) - m(m \pm 1)\}^{1/2} \hbar |l, m \pm 1\rangle$. It is worth remarking that all of the algebra of angular momentum eigenvalues will work for half-integral quantum numbers. In some sense this foreshadows the need for the postulation of spin angular momentum intrinsic to the particles of quantum mechanics. We do not have time to go into the details of the coupling of angular momentum in quantum mechanics, but for many spectroscopies it is very important in working out models for the spectra.

For understanding of molecular electronic structure, there is no problem in quantum mechanics as important as the solution of the hydrogen atom. It provides us with the pattern for understanding the entire periodic table of the elements, and with the best first approximation to the representation of bonding in molecules. In SI units the Hamiltonian for the system is

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r},$$

where $\mu = m_e m_n / (m_e + m_n)$, and m_e, m_n are the masses of the electron and nucleus. Of course, for the hydrogen atom itself $Z = 1$, the nuclear charge. When the Laplacian is expanded in spherical polar coordinates, the angular part of the problem is identical with that for the rigid rotor, when a trial form of $\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ is inserted and the partial differential equation separated into ordinary differential equations in single variables, and the solutions are the spherical harmonics. Only the radial part is different and needs to be solved. The radial equation is

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} R(r) + \frac{\hbar^2}{2\mu r^2} l(l+1)R(r) = ER(r),$$

and the solutions are

$$R_{n,l}(r) = \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{\frac{1}{2}} e^{-\frac{Z}{na_0}r} \left(\frac{2Z}{na_0}r \right)^l L_{n-l-1}^{2l+1} \left(\frac{2Z}{na_0}r \right), \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}.$$

The $L_{n-l-1}^{2l+1}(x)$, are the Laguerre functions. They are a particular set of polynomials of order $n-l-1$. The first one is of order zero, a constant. The energy must be quantized to the values

$$E_n = -\frac{Z^2\mu}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2}, \quad n = 1, 2, \dots$$

The hydrogen atom quantum numbers n, l, m , are called the principal quantum number, the angular momentum quantum number, and the magnetic or azimuthal quantum number, respectively. Notice that E depends only on the n quantum number. The other quantities in the expression are the nuclear charge Z , the reduced mass of the nucleus μ , the elementary charge, the permittivity of space, and Planck's constant. There is a further restriction connecting n and l , namely that $n > l$. This means that for $n = 1$, only $l = 0$ is permitted; for $n = 2$, $l = 0, 1$ occur; for $n = 3$, $l = 0, 1, 2$ arise. These restrictions are the origin of the atomic orbital energy levels 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, etc. There is an association between the values of $l = 0, 1, 2, 3, 4, 5, \dots$ and the letters s, p, d, f, g, h, i, j, k, l, ... The first four are historical, being a description of the nature of the emission lines from states of that angular momentum type as sharp, principal, diffuse, and fine. The rest of the alphabet is used in sequence, omitting *i*. Since the order of the polynomials will increase with n , there will be increasing numbers of radial nodes as n increases. You should examine an introductory quantum text to see the nature of the hydrogenic solutions.

2.5. APPROXIMATE METHODS

Because the exact solution of the Schrödinger equation can only be obtained for a very few problems, it becomes important to have methods of obtaining approximate solutions of the equation. The methods should be capable of improving the quality of the solution in a se-

ries of known steps so that we can get as accurate a solution as is desired. In principle, we can continue to improve the approximate solution until it is equal to the exact solution. There are two fundamental approaches to such approximate solutions: perturbation theory and the variational principle.

2.5.1. Perturbation Theory

The essential ideas behind perturbation theory involve the assumption that we have in hand the solution to a problem that is close to the one that we would really like to solve so that we can use it as a basis for starting to describe the final system. Formally we write:

$$H = H_0 + \lambda H',$$

which is the problem we seek to solve, and

$$H_0 \varphi_k^0 = E_k^0 \varphi_k^0.$$

We have these solutions in hand, and they have the property $\langle \varphi_k^0 | \varphi_l^0 \rangle = \delta_{k,l}$. λ is a scaling parameter that enables us to turn on the perturbation. When $\lambda = 0$, we are in the limit of our zeroth-order solution, and when $\lambda = 1$ we have turned on our perturbation completely so that the Hamiltonian is the one we seek to solve:

$$H \psi_k = E_k \psi_k.$$

We proceed by expanding ψ_k and E_k in a series of increasing powers of λ :

$$\psi_k = \varphi_k^0 + \sum_{j=1} \lambda^j \psi_k^j \quad \text{and} \quad E_k = E_k^0 + \sum_{j=1} \lambda^j E_k^j.$$

We require $\langle \psi_k^j | \psi_k^i \rangle = 0$, so that we have orthogonality between the successive terms of correction. This guarantees that each successive correction will add a linearly independent new quality to the solution. We insert these forms into the S. equation, gather powers of λ together on each side of the equation, and invoke the theorem from algebra that the coefficients of each order of two equal polynomials must be equal. Applying this theorem for the case of our polynomial in λ , we obtain equations for the successive powers of λ :

$$\lambda^0 : H^0 \varphi_k^0 = E_k^0 \varphi_k^0 \quad \text{in zeroth order, we recover the equation we have in hand.}$$

•
•

$$\lambda^n : H^0 \psi_k^n + H' \psi_k^{n-1} = \sum_{j=0}^n E_k^{n-j} \psi_k^j$$

Now we can attack each of these individual order equations, one at a time, obtain the correction to the energy and the wavefunction through that order, and work our way up a bit at a time to achieve as accurate a solution as we are willing to work toward.

The zeroth-order equation gives us nothing new to work with; it is just the unperturbed problem. The first-order equation is

$$H_0 \psi_k^1 + H' \varphi_k^0 = E_k^0 \psi_k^1 + E_k^1 \varphi_k^0.$$

Multiplying this equation by φ_k^{0*} and integrating over all space and simplifying gives $E_k^1 = \langle \varphi_k^0 | H' | \varphi_k^0 \rangle$. This says that the first-order correction to the energy is given by the expectation value of the perturbing Hamiltonian over the zeroth-order wavefunction.

Introducing the representation of the first-order correction to the wavefunction in terms of an expansion over the zeroth-order solutions into the second-order equation gives the second-order correction to the energy as

$$E_k^2 = \sum_{\substack{i=0 \\ i \neq k}} \frac{\langle \varphi_k^0 | H' | \varphi_i^0 \rangle \langle \varphi_i^0 | H' | \varphi_k^0 \rangle}{E_k^0 - E_i^0},$$

and to the wavefunction as

$$\psi_k^1 = \sum_{\substack{i=0 \\ i \neq k}} \frac{\langle \varphi_i^0 | H' | \varphi_k^0 \rangle}{E_k^0 - E_i^0} \varphi_i^0.$$

This latter form is often used to describe the extent to which the zeroth-order functions will mix under the perturbation. The weight of mixing being inversely proportional to the energy separation between the levels, i.e., energy levels close to the one of interest will mix more under the perturbation than will those that differ a lot in energy.

The above expressions are valid only if the energy level being perturbed is not degenerate. If the energy level of interest is degenerate, then one is often interested in how the perturbation affects the degeneracy. The degenerate problem must be handled more delicately, by first finding those forms of the zeroth-order solution that are approached in the zero limit of the perturbation. (Since we are applying a perturbation on a previously solved problem, there is no reason to expect that the solutions we obtained earlier are the correct limiting forms for the new perturbation) The correct linear combination is found from a secular equation:

$$\sum_{j=1}^m c_{ji} (H'_{lj} - E_{ki}^1 \delta_{lj}) = 0;$$

repeat for $l = 1, 2, \dots, n$, the order of the degeneracy. This is a set of n homogeneous linear equations in n unknowns c_{ji} . There is a nontrivial solution only if

$$\det \left\{ \sum_{j=1}^m c_{ji} (H'_{lj} - E_{ki}^1 \delta_{lj}) \right\} = 0.$$

This determinant will be zero only for very specific, unique values of E_{ki}^1 . There are n such unique values, the roots of the determinant, which are then the first-order correction to the energies for the perturbed problem. Higher-order degenerate perturbation theory is possible, but the expressions get very messy. The only widely available source that even considers it, of which I am aware, is D.R. Bates (ed.), *Quantum theory, I: elements*. New York: Academic Press, 1961.

2.5.2. The Variational Principle

The big idea behind the variational principle is to find some quantity the value of which you know cannot possibly get smaller than some result, which is of interest. This quantity can then be used as a criterion for minimizing the form to yield the best possible answer within the approximation of the form assumed. In bound-state quantum mechanics the quantity is the expectation value of the Hamiltonian for the system, which is bounded by the ground state energy for the system. It is fairly easy to prove that

$$\frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0,$$

where E_0 is the ground state energy for the system. This equality holds iff $\Phi = \Psi$.

With this as a criterion, we may assume any form that contains adjustable parameters for Φ , find the values of the parameters that minimize this expression, and we can know that we have then found the best possible (lowest possible energy) for the system using the assumed form. Probably the most powerful of these approaches is the linear variation, since it is most widely applicable. We expand a trial form as a linear combination of assumed functions,

$$\varphi_\alpha = \sum c_{j\alpha} f_j(x), \quad \langle f_i | f_j \rangle = S_{ij},$$

and choose the φ_α to be normalized to 1 right away. This normalization constitutes a constraint that can be incorporated by the method of undetermined multipliers. We define a new criterion, $W = \langle \varphi_\alpha | H | \varphi_\alpha \rangle - \lambda_\alpha \langle \varphi_\alpha | \varphi_\alpha \rangle$, and find the minimum of this expression with respect to $c_{j\alpha}$. As in the degenerate perturbation theory case, we are led to a secular equation (the term “secular equation” comes from the use of such equations in the study of the motion, and therefore time evolution sense of secular, of the planets):

$$\sum_i [c_{i\alpha} (H_{ii} - \lambda_\alpha S_{ii})] = 0, \quad i = 1, 2, \dots, n.$$

There are powerful algorithms that have been developed in applied mathematics for solving equations of this type. The most elementary approach is to find the values of λ_α first by requiring that the determinant of the expression in parentheses be zero. Expansion of the determinant gives a polynomial of order n in λ_α . The roots of this polynomial are the allowed values of λ_α , which turn out to be the approximate energies. This procedure where the assumed set of functions, the $\{f_i\}$, are atomic orbitals centered on the nuclei, becomes the molecular orbital approximation for the description of bonding in molecules.

2.6. MANY ELECTRON ATOMS AND MOLECULES

The final postulates of quantum mechanics require us to entertain the idea of an internal degree of freedom to particles. Since we tend to conceptualize our particles as tiny spheres, it is natural to think about this internal degree of freedom as that of the tiny sphere rotating about some axis passing through it, and thus is spinning. We therefore call this internal degree of freedom *spin*. It turns out that this internal degree of freedom does have all the aspects of an angular momentum, so thinking about it as a spin is very appropriate. This spin is quantized in quantum mechanics just as orbital motion angular momentum is quantized, but now it can take on half-integral as well as integral values. For an electron the spin has a value of $\frac{1}{2}$,

$$S^2 = s(s+1)\hbar^2 = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 = \frac{3}{4}\hbar^2,$$

and we need to create two functions, commonly called α and β , with the properties

$$\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha, \quad \hat{S}_z\beta = -\frac{1}{2}\hbar\beta, \quad \hat{S}^2\alpha = \frac{3}{4}\hbar^2\alpha, \quad \hat{S}^2\beta = \frac{3}{4}\hbar^2\beta.$$

These spin functions multiply an electron's spatial orbital to form a spin-orbital. They are merely a formal construct defined to be symbols that carry the above properties and furthermore will be both normalized and orthogonal:

$$\langle\alpha|\alpha\rangle=1, \quad \langle\beta|\beta\rangle=1, \quad \langle\alpha|\beta\rangle=0.$$

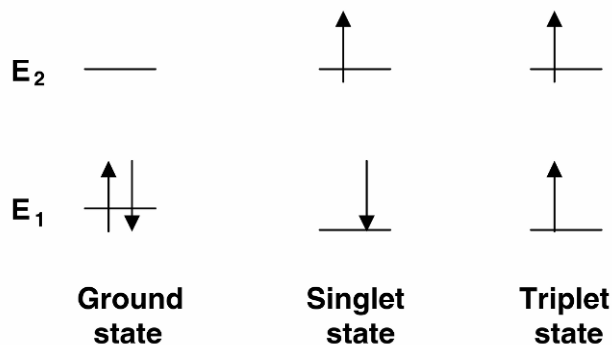
The Pauli principle states that, for a system composed of many electrons, the wavefunction must be antisymmetric with respect to the interchange of any two electrons' space-spin coordinates. A determinant composed by indexing the rows of the determinant with the spin-orbital index and the columns by the electron space-spin coordinates, when expanded, will provide this antisymmetry. Recall that a determinant has the property that interchanging any two rows or columns will change the sign of the determinant. To be specific, for two electrons:

$$\Psi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) \\ \phi_2(1) & \phi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2!}} (\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)).$$

You may confirm that by interchanging (1) and (2) that the wavefunction changes sign. Writing out the full expanded form of the determinant is obviously tedious, even the condensed square form is cumbersome, so it is common to simply write the diagonal down and to suppress the $1/\sqrt{n!}$. $\Psi(1,2,3,\dots,n) = |\phi_1(1)\phi_2(2)\dots\phi_n(n)|$. These determinantal wavefunctions are commonly called Slater determinants. Uncommonly they are called *detors*.

2.6.1. Singlets and Triplets

Excited states of molecules are often describable in terms of just the highest-energy two electrons. The following energy level diagrams illustrate the ground state, and two different possible ways of describing an excited state:



We can use Slater determinants to write the wavefunctions for these states. Let ϕ_1 and ϕ_2 be the spatial orbitals associated with energy levels E_1 and E_2 . We will introduce a somewhat shorthand notation to depict the spin functions assigned. Let the unadorned spatial orbital mean that it is multiplied by the α spin function. We will use an overbar on the spatial orbital to mean that it is multiplied by the β spin function. The ground state of the system is then depicted by $|\phi_1(1)\phi_1(2)|$, the singlet state by $|\bar{\phi}_1(1)\phi_2(2)|$, and the triplet by $|\phi_1(1)\phi_2(2)|$. However, we will find that while the ground state and the triplet state are properly eigenfunctions of the combined spin operator S^2 , and $S_z = s_z(1) + s_z(2)$ (S^2 is composed of $S_x^2 + S_y^2 + S_z^2$, where S_x and S_y are similarly the sum of one such operator for each electron), there is a problem with the singlet state. Since for the singlet it is arbitrary whether the lower energy state is given up or down spin and likewise for the upper state, we should symmetrize the system by taking both possible spin assignments into the wavefunction for the singlet state:

$$\Psi_{\text{sing}} = \frac{1}{\sqrt{2}} \{ |\phi_1\bar{\phi}_2| - |\bar{\phi}_1\phi_2| \} \quad \text{and} \quad \Psi_{\text{triplet } 0} = \frac{1}{\sqrt{2}} \{ |\phi_1\bar{\phi}_2| + |\bar{\phi}_1\phi_2| \}.$$

The second form here is the $S_z = 0$ component of the triplet; the form we wrote earlier was the $S_z = +1$ component. We will also have an $S_z = -1$ component, where both spins are assigned down: $\Psi_{\text{triplet } -} = |\bar{\phi}_1\bar{\phi}_2|$. Expansion of the determinants will show that the singlet is symmetric in space coordinates but antisymmetric in spin coordinates, whereas the triplet is antisymmetric in space coordinates but symmetric in spin coordinates. While we have discussed these spin states for electronic levels, the same parallel arguments can be used to construct the spin states for protons. These descriptions of spin states for protons then constitute the beginning of the quantum treatment of the phenomenon of nuclear magnetic resonance and its very rich spectroscopies.

2.7. THE INTERACTION OF MATTER AND LIGHT

The correct way to handle the interaction of light and matter is to treat both the radiation field and the matter field as quantum objects. However, one can get nearly as satisfactory a picture of the interaction by treating the light wave as a perturbation on the quantized matter system, and we will follow that tack. The approach we follow is called the semi-classical theory of the interaction of light with matter.

The picture of a light wave that one gets from solution of Maxwell's equations for propagation through a vacuum is one that manifests the passage of both electric and magnetic fields sinusoidally varying in both space and time. The electric field is perpendicular to both the magnetic field and the direction of propagation. The magnetic field has the same properties. If the plane of the electric field is oriented along a spatially fixed axis perpendicular to the direction of propagation of the light, it is called plane-polarized. As this light wave passes through a molecule, the charged electrons and nuclei will interact with the electric field and their magnetic moments will interact with the magnetic field. The positively charged particles will move in the direction of the electric field and the negatively charged particles opposite the direction of the electric field. If the frequency of the field (the frequency of light) matches the Planck condition for the energy difference between two energy levels ($E_2 - E_1 = h\nu$), we can expect absorption of energy from the radiation field and the appearance of a molecular excited state. The process just described is the nature of the interaction between light and matter. Any frequency of "light" —

from radiowaves, microwaves, infrared, visible, ultraviolet, x-rays, and gamma-rays — is the same phenomenon and will interact with matter in this way. Radiowaves can have enormously long wavelengths and gamma rays incredibly short ones. Visible radiation has a wavelength of a few thousand Angstroms (in SI a few hundred thousand picometers or several hundred nanometers) and x-rays a wavelength of around a hundred picometers.

To make the interaction quantitative, we write that the energy of interaction between the electric field and the molecule is given by the negative of the dot product of the molecular dipole moment operator with the electric field vector:

$$H_{\text{interaction}} = -\hat{\vec{\mu}} \cdot \vec{E} = -\hat{\vec{\mu}} \cdot \vec{E}_0 \cos 2\pi \nu t .$$

We would then add this interaction term to the Hamiltonian for our system when it is interacting with a light wave as in a spectroscopic experiment. This new Hamiltonian now depends explicitly on time, and we must solve the time-dependent Schrödinger equation. We can do this approximately by doing a time-dependent perturbation treatment of the system, since we can regard the new interaction term as being a small perturbation on the original system. Treatment of a two-level system is a good treatment of the problem since we know the transitions occur appreciably only when the Planck condition is satisfied. The results yield the following:

1. A transition occurs between levels i and j only if there is a nonzero element of the dipole moment operator that connects the two levels. $\langle i | \hat{\vec{\mu}} | j \rangle \neq 0$. The conditions that must be met in order that the transition dipole is nonzero are commonly called “selection rules.” A transition for which the dipole matrix element is nonzero is called an “allowed” transition, and one for which it is zero is called a “forbidden” transition.
2. The intensity of the transition is proportional to the square of this transition dipole moment.
3. The probability of the transition is large only when the resonance frequency condition is met.
4. Transitions are not exact delta functions, but do have a finite width of energy.
5. If the transition dipole integral is zero, a transition may still occur, but by a much weaker mechanism than an electric dipole transition. We could consider additional models for the interaction that include higher multipole moments interacting with the electric field or magnetic dipoles interacting with the magnetic field of the light wave. The size of these interactions is one or two orders of magnitude smaller than the dipole-stimulated transitions.

PROBLEMS

- 2.1. Formalism of quantum mechanics – commutators.
 - a. Show that $[p_x, x] = -i\hbar$. (hint: when working commutator problems, provide a dummy function for the commutator to work on; then factor out that function to the right after simplifying the result)
 - b. Show that $[AB, C] = A[B, C] + [A, C]B$ is valid for any three operators.

- 2.2. Complete the solution of the particle in a well or box problem by explicitly carrying out the mathematical steps described in words in the text so that you arrive at the final form for the wavefunction and the energy level expression.
- 2.3. Sketch the wavefunctions for the harmonic oscillator for the first three energy levels. You may need to consult a quantum mechanics text to obtain the mathematical forms for the first three Hermite polynomials if you need more explicit forms than have been given in the text.
- 2.4. The harmonic oscillator is a reasonable approximation for the vibrational motion of a diatomic molecule. How would you expect the absorption frequency of HCl to be related to that of DCl? Which has the lower zero-point energy?
- 2.5. Show that $Y_{1,0} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$ and $Y_{1,1} = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{i\phi}$ are both normalized and orthogonal to each other. The volume element for angular integration is $\sin\theta d\theta d\phi$.

MORE PROBLEMS

- 2.6. Prove that the expectation value over an arbitrary trial wavefunction is necessarily greater than or equal to the ground state energy of the system. Use the exact solutions of the Schrödinger equation as an expansion set with which to expand the approximate trial function; then let the Hamiltonian work on the expanded forms. Lastly, argue for the inequality and you will immediately see when the equality holds.
- 2.7. Expand the symmetrized forms for the singlet and triplet electronic states and show that the wavefunction factors into a spatial part times a spin part. Notice that the spin part for the singlet function is antisymmetric with respect to interchange of the spin coordinates, but that the spin part for the triplet wavefunction is symmetric with respect to interchange of the spin coordinates.

REFERENCES AND FURTHER READING

Many magnificent books are available for an introduction to quantum mechanics. Here are a few of them.

Physics, first-year graduate texts

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