

Lecture 4, January 25, 2006**Solved Homework**

If an electron has a de Broglie wavelength of 1 Å (0.1 nm), then we can compute its momentum as

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s}}{1.0 \times 10^{-10} \text{ m}} = 6.626 \times 10^{-24} \text{ kg m s}^{-1}$$

The kinetic energy of an electron having this momentum is

$$T = \frac{p^2}{2m} = \frac{(6.626 \times 10^{-24} \text{ kg m s}^{-1})^2}{2 \times 9.11 \times 10^{-31} \text{ kg}} = 2.41 \times 10^{-17} \text{ J}$$

The energy of an electron subjected to one volt of accelerating potential is 1 eV. The conversion from eV to J is 1 eV = 1.602 × 10⁻¹⁹ J. The kinetic energy of the electron is thus 150.4 eV. So, an accelerating potential of roughly 150 V is required.

The Wave Function for a Material System

Erwin Schrödinger, in 1926, proposed a way to meld the many quantum observations up to that point with a wavelike description of matter. In particular, he started from the classical wave equation (shown here for a single dimension)

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2} \quad (4-1)$$

where Ψ is a wave function which has an amplitude for any specification of x (position) and t (time), and c is the velocity of the wave (wavelength times frequency). A general solution to this equation is

$$\Psi(x, t) = C e^{2\pi i \left(\frac{x}{\lambda} - \nu t \right)} \quad (4-2)$$

where C is an arbitrary multiplicative constant, i is the square root of negative one (a base for the complex numbers), λ is the wavelength and ν is the frequency. To verify, note that

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{4C\pi^2}{\lambda^2} e^{2\pi i \left(\frac{x}{\lambda} - \nu t \right)} \quad (4-3)$$

and

$$\frac{\partial^2 \Psi(x,t)}{\partial t^2} = -4C\pi^2 \nu^2 e^{2\pi i \left(\frac{x}{\lambda} - \nu t \right)} \quad (4-4)$$

and $c = \lambda\nu$.

Schrödinger decided to use the de Broglie wavelength for λ and to relate the frequency to the Planck energy. That is, he looked for a differential equation having the solution

$$\Psi(x,t) = Ce^{i \left(\frac{xp - Et}{\hbar} \right)} \quad (4-5)$$

where p is the momentum and E is the energy. For notational simplicity, from now on we will take the arbitrary constant C as one.

If we consider differentiating eq. 4-5 once with respect to time we have

$$\frac{\partial \Psi(x,t)}{\partial t} = -\frac{iE}{\hbar} e^{i \left(\frac{xp - Et}{\hbar} \right)} \quad (4-6)$$

or

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = E\Psi(x,t) \quad (4-7)$$

The total energy E at a given time may be expressed as a sum of kinetic and potential energy, both of which depend only on x and not on t . Thus, we have

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = \left[\frac{p^2}{2m} + V(x) \right] \Psi(x,t) \quad (4-8)$$

where p is the momentum, m is the mass, and V is the potential energy, which may be thought of as an outside influence on the system being described by the wave function Ψ .

Note that the idea here is to have Ψ be a function that contains information about the system contained within it. That is, we would like things like momentum and energy to be themselves *determinable* from the wave function. Let us consider how we might

determine the momentum from our wave function eq. 4-5. If we differentiate once with respect to x we have

$$\frac{\partial \Psi(x,t)}{\partial x} = \frac{i p}{\hbar} e^{i\left(\frac{x p - E t}{\hbar}\right)} \quad (4-9)$$

We may write this in what is known as "operator" formalism as

$$\frac{\partial}{\partial x} \Psi(x,t) = \frac{i p}{\hbar} \Psi(x,t) \quad (4-10)$$

or

$$\frac{\hbar}{i} \frac{\partial}{\partial x} = p \quad (4-11)$$

which is to say that the *operator* that can be applied to the wave function in order to *determine* the momentum is to differentiate once with respect to x and then multiply by \hbar over i . In this case, it is straightforward to show that the *square* of the momentum (needed for the kinetic energy) can be derived from operating *twice* with the momentum operator, i.e.,

$$-\hbar^2 \frac{\partial^2}{\partial x^2} = p^2 \quad (4-12)$$

If we include this result in equation 4-8 we have

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi(x,t) \quad (4-13)$$

This is the one-dimensional, time-dependent Schrödinger equation.

To generalize the Schrödinger equation to multiple dimensions (e.g., three), one replaces the partial second derivative operator with the more general Laplacian operator. In the usual 3 cartesian dimensions, the Laplacian, called "del-squared", is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (4-14)$$

So, the general form of the time-dependent Schrödinger equation in 3 dimensions is

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,y,z,t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x,y,z) \right] \Psi(x,y,z,t) \quad (4-15)$$

Memorize this equation. Really. Memorize it.

As a note of historical interest, Schrödinger derived his eponymous equation while vacationing in a mountain cabin with a female companion other than his wife. The identity of the woman has never been determined and remains a favorite subject of speculation by scientific historians (some of whom wonder if he got the idea from her...) Schrödinger and his wife, Annemarie, had what might be called an “open” marriage and were well known as *bons vivants* in Berlin (she was fond of various foreign ambassadors). Schrödinger was not burdened with modesty, having once said “I have never slept with a woman who did not afterwards wish to live with me forever”. These biographical details somehow never seem to make it into standard quantum chemistry textbooks.

The Time-independent Schrödinger Equation

The operator which returns the energy E is called the Hamiltonian operator, and it is written as H . Thus, a more shorthand way to write eq. 4-15 is

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = H\Psi \quad (4-16)$$

Let us now consider whether there may be simple forms for Ψ that permit the time variable to be separated from the position variables, i.e.,

$$\Psi(x, y, z, t) = \psi(x, y, z)\varphi(t) \quad (4-17)$$

If we employ the form on the r.h.s. of eq. 4-17 in eq. 4-16, we have

$$\psi \left(-\frac{\hbar}{i} \frac{d\varphi}{dt} \right) = \varphi(H\psi) \quad (4-18)$$

We may rearrange this to

$$-\frac{1}{\varphi} \frac{\hbar}{i} \frac{d\varphi}{dt} = \frac{1}{\psi} (H\psi) \quad (4-19)$$

Note that the l.h.s. of eq. 4-19 depends only on t while the r.h.s. depends only on the position coordinates. For the equality to hold, then, neither side can vary as a function of its variables, i.e., the two sides must equal the same constant.

If we solve the differential equation implied by setting the r.h.s. of eq. 4-19 equal to a constant we have

$$C = \frac{1}{\psi}(H\psi) \quad (4-20)$$

or

$$H\psi = C\psi \quad (4-21)$$

Note, however, that this equation is in the form of an operator equation. By operating on the wave function with the Hamiltonian, we obtain the wave function back multiplied by a constant. The Hamiltonian is the operator that returns the energy, so C is then E . That is

$$H\psi = E\psi \quad (4-22)$$

This is the time-*independent* Schrödinger equation. It too should be memorized. Note that, in terms of nomenclature, this is a case where we say that ψ is an “eigenfunction” of H and E is an “eigenvalue”.

Let us return now to the l.h.s. of eq. 4-19, which must also be equal to E . That is

$$-\frac{\hbar}{i} \frac{d\varphi}{dt} = E\varphi \quad (4-23)$$

A simple solution to this first-order differential equation is

$$\varphi(t) = e^{-iEt/\hbar} \quad (4-24)$$

So, a general form for an acceptable wavefunction can be written

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-iEt/\hbar} \quad (4-25)$$

So, What Is a Wave Function?

Discussion of wave functions seems terribly abstract, even if the mathematics are clear. What is the physical *meaning* of the wave function? Put fairly simply, the wave function is a probability map. That is, since waves have amplitudes, we may state that where our wave function’s spatial amplitude (the part depending on x , y , and z) is large, there is a good chance of finding our system there if we look for it. Conversely, if the wave function has small amplitude at a certain position, we are unlikely to find it there. The key point to bear in mind is that our system is spread out in some continuous fashion *until* we look for it. Because of wave-particle duality, if we look for a particle with an experiment that detects particles, we will find it in that form. But, the likelihood of finding it in any particular place at a particular time is dictated by the wave function.

Now, the wave function can be complex valued, but the probability of finding a particle in some arbitrary volume of space at a specific time t is a real number between zero and one. Thus, the wave function itself does *not* have units of probability density, but rather its square modulus, $\Psi^*\Psi$ (also written $|\Psi|^2$) does. Recall that for a complex number $c = a + bi$, where a and b are real numbers, the complex conjugate c^* is given by $c^* = a - bi$, so that $c^*c = a^2 + b^2$, which is a real number.

This relationship between the square modulus of the wave function and the probability density imposes a constraint on the arbitrary multiplicative constant that has been showing up here and there in some of our differential equations. In particular, the probability of finding our system if we search *all* of space must be one. That is

$$1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\Psi^* \Psi) dx dy dz \quad (4-26)$$

A wave function that satisfies eq. 4-26 is said to be "normalized". Note that it is trivial to construct a normalized wave function from one that is *not* normalized. One simply creates a new wave function that is $A^{-1/2}$ times the old wave function, where A is the value of the square modulus of the old wave function integrated over all space. Such prefactors designed to ensure normalization are called normalization constants.

Now, consider the average value of some property that depends on the position of the system in space. In quantum mechanics, we call such average values "expectation values" and indicate them by surrounding " \langle " and " \rangle " symbols. To compute them is straightforward: one integrates over all spatial coordinates the value of the property at each position times the probability that the system will ever *be* at that position (determined from the square modulus of the wave function). So, if one would like to know the average of the product of the x and y coordinates, xy , one would compute this using

$$\langle xy \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} xy (\Psi^* \Psi) dx dy dz \quad (4-27)$$

Note that x and y may be thought of as multiplicative *operators*. Their operation seems rather trivial, as they simply multiply the wave function by the variable. However, it is helpful to take an operator viewpoint because there are other properties, like momentum, that quantum mechanically involve differential operators (see above). When we seek expectation values of such properties, we must evaluate the integral resulting from the operator acting on the wave function. Thus, the average value of the system's momentum in the x direction (see eq. 4-11 for the operator) is computed from

$$\langle p_x \rangle = \frac{\hbar}{i} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(\Psi^* \frac{\partial}{\partial x} \Psi \right) dx dy dz \quad (4-28)$$

Remember that the partial derivative of Ψ will give $ip\Psi/\hbar$ (assuming Ψ is a momentum eigenfunction, see eq. 4-10), where p is now a number, so the net result will indeed be an average of p times the square modulus just as it is for a multiplicative operator.

The association of a wave function with a probability density imposes certain requirements on Ψ . These are:

1. Ψ must be quadratically integrable. That is, the integral of $|\Psi|^2$ over all space must be a finite number (so that it can be normalized).
2. Ψ must be single valued (otherwise the probability density at the same position in space could take on two or more values, which would not correspond to reality).
3. Ψ must be continuous (it is not physically reasonable for the probability density to change in a discontinuous fashion over an infinitesimally small distance in space).

Collapse of the Wave Function

For a particular system, there may be many solutions to the time-independent Schrödinger equation. Consider the hydrogen atom, for example. There are an infinite number of allowed orbits in the Bohr model (since n can be any whole number), each having different energy and a different associated wave function. A wave function that would satisfy the time-dependent Schrödinger equation is

$$\Psi(x, y, z, t) = \sum_{n=1}^{\infty} c_n \psi_n(x, y, z) e^{-iE_n t / \hbar} \quad (4-29)$$

where the $\{c\}$ are arbitrary constants (possibly depending on time) and the $\{\psi\}$ are the various so-called “stationary” (i.e., unchanging in time) spatial wave functions satisfying the time-independent Schrödinger equation. (You might try proving to yourself that the Ψ of eq. 4-29 really does satisfy eq. 4-15).

This suggests that the time-dependent wave function is really a “wave packet”, that is, it is composed of a linear combination of products of various stationary-state wave functions with the time-dependent exponential. One also says that the system exists as a “superposition” of states. However, at the moment that the system is sampled by some experimental probe, it *must* take on a single state characterized by a single value of the observable. That is, it must have only a single energy, a single momentum, etc. Exactly what the values are is dictated by the stationary-state wave function, but it would not correspond to physical reality if the observable properties were not single valued.

This effect of sampling is sometimes referred to as “collapsing” the wave function. The most famous and provocative thought experiment illustrating some of the seeming paradoxes of quantum mechanics is the so-called Schrödinger's cat experiment.

Imagine that a cat is placed in a box with a sealed vial of poison gas. Next to the vial is a single atom of a radioactive element. When that element decays, its ejected beta particle will be detected by a Geiger counter that is attached to a hammer that will smash the vial, killing the cat.

We seal the box so that we cannot know what is happening inside. Note that the time required for a single atom of a radioactive element to decay is unknowable; we know the time it takes on average for half of a *huge* number of atoms to decay very accurately, but the time for *one* atom is completely random. So, with the box closed, the question at any moment in time may be asked, “Is the cat dead or alive?” For those who believe in some objective reality to the Universe, the answer is certainly one or the other. They realize that they do not know which answer is correct, but they will insist that there *is* a definite answer.

In quantum mechanics, on the other hand, the cat is neither alive nor dead. It exists as a superposition of those two states. Until *you* open the box and collapse the wave function by observation, it chooses neither the alive option nor the dead one.

This raises all sorts of fascinating philosophical questions. Can the cat not collapse its own wave function? In its box, it knows whether it is alive or dead, but outside of it, we see it as a superposition of states. Is “consciousness” the ability to collapse a wave function? When the wave function *does* collapse, could it be that it undergoes all *possible* collapses, each one generating a new, distinct universe (this is called the “many-worlds hypothesis” of quantum mechanics)? In that case, our lives are simply particular world-lines following one collapse event to the next.

Homework

To be solved in class:

Let the probability that a variable x has a value between $-x$ and x be given by

$$P(x) = Ne^{-ax^2}$$

where a is a positive constant (this is a so-called “normal” probability distribution). Show that N is equal to $\sqrt{a/\pi}$ when $P(x)$ is normalized. Sketch the appearance of $P(x)$ as a function of x . Where do the points of inflection occur? For the normalized function, what is $\langle x \rangle$? What is $\langle x^2 \rangle$? Why does $\langle x^2 \rangle \neq \langle x \rangle^2$? Note that recourse to integral tables will probably be helpful for this problem.

To be turned in for possible grading Jan. 27:

Which of the following functions are eigenfunctions of the operator d^2/dx^2 , and what are their corresponding eigenvalues if they are? (a) $ae^{-3x} + be^{-3ix}$, (b) \sin^2x , (c) e^{-x} , (d) $\cos(ax)$, (e) $\sin x + \cos x$.