The Schrödinger equation: the quantum description of one massive, slow-moving particle

To establish a probability wave equation for one photon, it was useful to note that probability density and electromagnetic energy density were proportional. The governing equation for EM radiation fields is the Maxwell wave equation, which is also the governing equation for photon probability wave functions. Converting from EM radiation to photon information is made plausible by identifying energy and momentum operators with time- and space-derivatives, respectively. Thus, the Maxwell wave equation can be interpreted as being equivalent to the energy-momentum relation for photons. Though we don't have a "Maxwell wave equation" to start with for massive particles, we *do* have an energy-momentum relation, so borrowing the energy and momentum operators from photons leads to an analogous wave equation for massive particles.

Thus, start with the relativistic energy-momentum relation (Notes Fn2):
$E = \sqrt{(pc)^2 + (mc^2)^2}$, for a free particle, and $E = \sqrt{(pc)^2 + (mc^2)^2} + U$, for a particle experiencing external forces described by a position dependent potential energy, U. If the particle's speed is much less than c, $pc \ll mc^2$, and the square root can be expanded as a binomial expansion (see Appendix I below) to yield $E \simeq \dfrac{p^2}{2m} + mc^2 + U$. The classical dynamics of a massive particle depends on applied forces, which, in turn, are spatial derivatives of U. That is, only changes in U are important, not the value of U itself. It is conventional, therefore, to incorporate the constant rest energy, mc^2, into U because that doesn't produce any force. As a result, the slow, massive particle wave equation is

$$E_{op}\Psi = \frac{1}{2m} p_{op}^2 \Psi + U\Psi, \tag{1}$$

where the potential energy operator is defined as just "multiply by U." Note that, in general, p_{op}^2 is a sum of three momentum-squared operators corresponding to the three directions the particle can move in. Equation (1) is known as the *Schrödinger Equation* (after Erwin Schrödinger who published the equation in 1926 and received the Nobel Prize for it in 1933); it is the basis for Lederman's assertion that a third of the world's economy is due to quantum mechanics.

Example: A **free particle** moves only in the $+x$ direction with a well-defined constant momentum magnitude, p, and a well-defined constant energy, E. Substituting $E_{op} = i\hbar \partial/\partial t$ and

$p_{x,op} = -i\hbar \partial/\partial x$ and setting $U = 0$ in (1) yields $i\hbar \dfrac{\partial \Psi}{\partial t} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2 \Psi}{\partial x^2} = E\Psi$. As long as the

independent variables x and t are not mixed (by a time-changing potential energy) this partial differential equation can be solved by the method of *separation of variables*—which **converts the partial derivatives into ordinary ones**. The method starts by assuming $\Psi(x,t)$ can be written as a product: $\Psi(x,t) = X(x)T(t)$. Substituting this into the partial differential equation leads to

$$i\hbar X \frac{dT}{dt} = -\frac{\hbar^2}{2m} T \frac{d^2 X}{dx^2} = EXT .$$

The partial derivatives are now ordinary derivatives because X only depends on x and T only depends on t. The separation of the variables follows from dividing by XT:

$$i\hbar \frac{1}{T}\frac{dT}{dt} = E \text{ and also } -\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} = E.$$

The former equation only depends on time, the latter only depends on space. The time part of the partial differential equation and the space part have been separated and **the *constant of separation* is the particle's energy, E.**

The time equation can be integrated directly to find T: i.e., $\int \frac{dT}{T} = \frac{E}{i\hbar}\int dt$ implies that

$\ln(T) = const - \frac{iEt}{\hbar}$ or $T = const \cdot \exp(-iEt/\hbar)$; here $\frac{1}{i} = -i$ has been used, and the $const$ part is a constant of integration. The space equation is a little more difficult because it involves two

derivatives. Rewriting it as $\frac{d^2X}{dx^2} = -k^2X$ where $k^2 = 2mE/\hbar^2$ reminds us of the simple harmonic

oscillator (SHO) from elementary mechanics. (That is, the SHO equation of motion for a mass

attached to a spring is *mass* x *acceleration = Hooke's Law restoring force* or $\frac{d^2q}{dt^2} = -\frac{k_{spring}}{m}q$,

where q is the position of the oscillator mass.) The solutions to the SHO problem are sines, cosines, and, via Euler, complex exponentials: $X \rightarrow \sin(kx), \cos(kx), \exp(\pm ikx)$. We can't use the sine or cosine because the free particle has a well-defined momentum: i.e., X satisfies the eigenvalue equation $p_{x,op}X = \pm pX$, where p is the momentum magnitude, $k = p/\hbar$, and the $\pm$ indicates the momentum direction. The momentum operator involves a derivative with respect to x, so it changes sin to cos and cos to sin; sines and cosines are *not* eigenfunctions of momentum—they both contain two momenta, p and $-p$. The correct solution is the exponential with $+k$, corresponding to momentum in the $+x$ direction. Consequently,

$$\Psi(x,t) = \Psi_{max}\exp[i(\frac{px}{\hbar} - \frac{Et}{\hbar})].$$

Note that p can take any value and that $E = p^2/2m$. Note also that $|\Psi|^2$ is the probability density

of finding the particle at some point in space. But, for this wavefunction $|\Psi|^2 = \Psi_{max}^2$ (assuming

Ψ_{max} is real), which is the same value everywhere. The free particle's wavefunction is spread out over all space (and has been and will be for all time, also) so we can't say anything about where it is likely to be. Obviously, (like lunches) **there are *no free particles*.**

The infinite square well

An important toy example of **bound states** is a massive particle trapped in an **infinite square well**. This problem, for a massive particle trapped in *quantum wire* (see Sc3 p2), is analogous to the photon trapped in a fiber optic cable discussed in Fn3. In this problem, the particle is not free; it experiences a potential energy $U(x) = 0$, for $0 < x < L$, and infinite otherwise. This is depicted to the right: position runs along the horizontal axis, energy along the vertical. In regions *I* and *III*, Equation (1) has the unpleasant potential energy terms, $\infty \cdot \Psi$. In order to have finite solutions
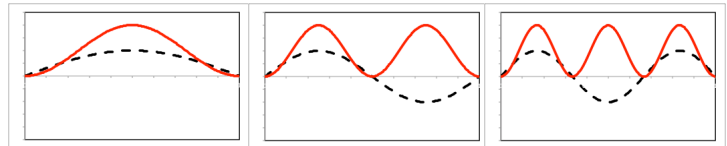

$U = \infty$ $U = 0$ $U = \infty$

I   *II*   *III*

$x = 0$ $x = L$
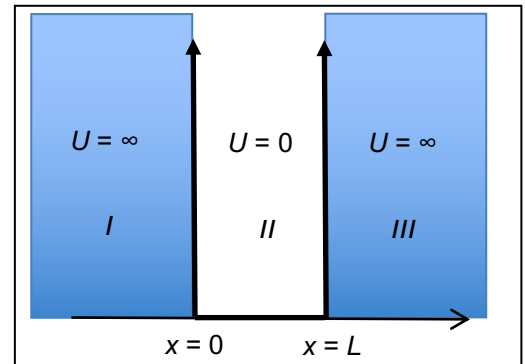
everywhere, Ψ is taken to be zero in regions *I* and *III*, including at the "boundaries" $x = 0$ and $x = L$. The calculation now proceeds identically to the previous example. When we get to the point of choosing which of $X \to \sin(kx), \cos(kx), \exp(\pm ikx)$ is correct, we note that Ψ has to vanish at $x = 0$ and $x = L$, and so does X. As in the trapped photon example in Fn3, the correct choice is $\sin(kx)$. The sine vanishes automatically at $x = 0$ and will do so also at $x = L$ provided $k_n L = n\pi$ or $p_n = n\pi\hbar/L$. **The fact that the particle is trapped in a finite region of space means that only certain discrete values of wavelength and momentum magnitude are allowed**. This result is identical to the trapped photon example. What *is* different, however, is the set of allowed energies. For the photon, $E_n = cp_n = (\pi c\hbar/L)n$, whereas for the massive particle

$$E_n = p_n^2/2m = [(\pi c\hbar/L)^2/2mc^2]n^2. \tag{2}$$

The allowed energies for the trapped photon are $E_1 = \pi c\hbar/L$, $2E_1$, $3E_1$, …; for the trapped massive particle they are $E_1 = (\pi c\hbar/L)^2/2mc^2$, $4E_1$, $9E_1$, … . For a photon and electron both trapped in an interval 1 nm long, E_1 is about 600 eV for a photon, and about 0.4 eV for an electron. Regardless, the *n* = 1 state is called **the "ground state"; there is no allowed energy less than** E_1**.** The states for *n* > 1 are "**excited states.**" In general, **all quantum systems that occupy a finite region of space (such as electrons in atoms or neutrons and protons in nuclei) have ground states. They cannot make transitions to lower energy states because there are none**.

The figures to the right show the spatial parts of the first three infinite square well eigenfunctions—the dotted curves—and the corresponding probability densities— the solid curves. (There are n probability density *maxima* for quantum state n.) The wavefunctions are not physically measurable, but the probability densities are. A small detector of length Δx placed at x records the particle with an approximate probability $|\Psi(x)|^2 \Delta x$. Some places have high probability of detecting the particle, other places (such as the middle of the well for n = 2) have zero. **According to the standard interpretation of quantum mechanics, the act of measurement "collapses" the particle's wavefunction from its original eigenstate form to a sharp narrow bump inside the detector immediately after detection. Nobody actually knows how the wavefunction collapse happens. It's one of the important unsolved problems of contemporary physics**. The figure to the right shows a particle wavefunction and probability density in a high n state. (Can you say what n is?) A small detector of length Δx (though longer than half a wavelength) detects the particle essentially equally everywhere. This is what one expects for a classical particle bouncing back and forth between rigid walls. This is a general rule: **classical physics emerges from quantum physics when the excitation levels are high**.
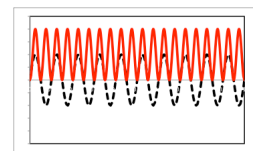
Expectation values

If it is known that the Schrödinger Equation describes *one* particle then the integral of the probability density over all space must equal 1—i.e., there's 100% probability of finding the particle somewhere:

$$\int_{all\ space} |\Psi|^2 dV = 1. \tag{3}$$

Here dV is an infinitesimal element of volume. When (3) is true, the expected, or average, value of a measurement (done over and over, each time starting in the same state, Ψ) on the particle is **defined** as

$$\langle M \rangle = \int_{all\,space} \Psi^*[M_{op}\Psi]dV. \qquad (4)$$

In general, the outcome of M might differ from measurement to measurement. Thus, the standard deviation—the "root mean square of the deviations from the mean"—of the spread of outcomes is

$$\Delta M = [\langle (M - \langle M \rangle)^2 \rangle]^{1/2} = [\langle M^2 \rangle - \langle M \rangle^2]^{1/2}. \qquad (5)$$

Note: The following examples, all for the infinite square well problem, use the integrals tabulated in the Appendix II below.

Example: Let's apply (3)-(5) to the particle in the infinite square well. Suppose the particle is in the state n with wavefunction $\Psi_n(x,t) = \Psi_{max}\sin(n\pi x/L)\exp(-iE_n t/\hbar)$. How do we guarantee that $\int_{all\,space} |\Psi|^2 dV = 1$?

Solution: The particle in the infinite square well only moves along the x-axis and its wavefunction is zero outside the interval 0 to L. Consequently, dV reduces to dx and the "all space" integral reduces to $\int_0^L |\Psi|^2 dx = 1$. Taking the complex conjugate and multiplying yields $|\Psi|^2 = \Psi_{max}^2 \sin^2(n\pi x/L)$, assuming Ψ_{max} is real*. Note that time disappears: the probability density does not change in time. Since $\int_0^L \sin^2(n\pi x/L)dx = L/2$, $\Psi_{max} = \sqrt{2/L}$ for any n. The wavefunction has dimensions of (length)$^{-1/2}$ and the probability density (for motion in 1-dimension) has dimensions of (length)$^{-1}$.
(* Like any complex number, Ψ can be written as $R \cdot e^{i\theta}$, where R and θ are real. Consequently, $|\Psi|^2 = R^2$, irrespective of the wavefunction's phase, θ, which can be chosen arbitrarily. Setting Ψ_{max} to be real is equivalent to setting $e^{i\theta} = \pm 1$.)

Example: What is $\langle E \rangle$ for the state n?
Solution: The state n is an eigenstate of energy with eigenvalue equal to E_n: $E_{op}\Psi_n = E_n\Psi_n$.
Consequently, $\langle E \rangle = \int_0^L \Psi_n^*[E_{op}\Psi_n]dx = \int_0^L \Psi_n^*[E_n\Psi_n]dx = E_n\int_0^L \Psi_n^*\Psi_n dx = E_n$. Whenever energy is measured starting with the state n the result is always E_n. Clearly, $\langle E^2 \rangle = E_n^2$ and $\Delta E = 0$.

Example: What is $\langle p_x \rangle$ for the state n? (This is the expectation value of the momentum vector, not its magnitude.)
Solution: The momentum operator for this example is $p_{x,op} = -i\hbar\partial/\partial x$. Therefore,

$p_{x,op}\Psi_n = -i\hbar\frac{n\pi}{L}\sqrt{\frac{2}{L}}\cos(\frac{n\pi x}{L})\exp(-iE_n t/\hbar)$. Evaluating $\langle p_x \rangle$ requires employing the integral

$\int_0^L \sin(n\pi x/L)\cos(n\pi x/L)dx$, which is zero. Hence, $\langle p_x \rangle = 0$. This is so because half the time a

momentum measurement results in $+n\pi\hbar/L$ and half the time $-n\pi\hbar/L$ (because momentum is a vector and has direction).

Example: What is $\langle p_x^2 \rangle$ for the state n?

Solution: $p_{x,op}^2 = -\hbar^2 \partial^2/\partial x^2$, so $\langle p_x^2 \rangle = \frac{2}{L}\int_0^L (\frac{n\pi\hbar}{L})^2 \sin^2(n\pi x/L)dx = (\frac{n\pi\hbar}{L})^2$.

Example: What is Δp_x for the state n?

Solution: $\Delta p_x = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2} = [(n\pi\hbar/L)^2 - 0]^{1/2} = n\pi\hbar/L$

Example: What is $\langle x \rangle$ for the state n? (Position is also a vector, but here position is always a positive value.)
Solution: Operators corresponding to functions of position only (such as U) are *defined* as "multiply by:" $\langle x \rangle = \frac{2}{L}\int_0^L x\sin^2(n\pi x/L)dx = \frac{2}{L}\frac{L^2}{4} = \frac{L}{2}$.

Example: What is $\langle x^2 \rangle$ for the state n?

Solution: $\langle x^2 \rangle = \frac{2}{L}\int_0^L x^2\sin^2(n\pi x/L)dx = \frac{2}{L}L^3[1/6 - 1/(2n\pi)^2] = L^2(1/3 - 1/2n^2\pi^2)$.

Example: What is Δx for the state n?
Solution: $\Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = [L^2(1/3 - 1/2n^2\pi^2) - L^2/4]^{1/2} = L(1/12 - 1/2n^2\pi^2)^{1/2}$.

Example: What is $\Delta x\Delta p_x$ for the state n?
Solution: $\Delta x\Delta p_x = [n\pi(1/12 - 1/2n^2\pi^2)^{1/2}]\hbar$. For $n = 1$, for example, $\Delta x\Delta p_x = 0.57\hbar$.

Please keep in mind that the above examples are all specific to the infinite square well potential energy. Situations involving other potential energies will require different sets of integral identities from those given in Appendix 2 and will result in different expressions for expectation values and uncertainties (with the distinct possibility that only numerical approximations might be available).

Heisenberg Uncertainty Principle

The last result above is a specific example of the **Heisenberg Uncertainty Principle** (HUP), which, in turn, is a direct consequence of a theorem in Fourier analysis. Fourier analysis says that almost any function can be represented as a sum of sines and cosines (or complex exponentials). Roughly, the relevant theorem states that the range of wavenumbers (inverse wavelengths) needed to do this is inversely proportional to the region over which the function is nonzero. Thus, for example, a perfect sine function needs only one sine function with a single wavenumber to represent it, but such a function is spread out over all of its independent variable. In terms of quantum mechanics, particles are described by wavefunctions that are spread out in

space (and in time) and the wavenumbers (or, in time, frequencies) of sines and cosines needed to represent them correspond to momenta (or energies). The HUP is expressed as

$$\Delta x \Delta p_x = \alpha_x \hbar, \tag{6}$$

for measurements of motion along the $x-$axis (or $y-$, or $z-$), and

$$\Delta t \Delta E = \alpha_t \hbar \tag{7}$$

for measurements of energy (see below). The quantities α are dimensionless numbers that depend on the wavefunction in question. According to the Fourier theorem, the smallest α can be is ½, which corresponds to a Gaussian shaped wavefunction. Apparently, the one-humped wavefunction for the $n=1$ state of the particle in the infinite square well is pretty close to a Gaussian (since for it $\alpha_x = 0.57$).

Some implications of the HUP are: (1) Certain pairs of variables (e.g., x and p_x, t and E) in the quantum realm cannot be measured simultaneously with perfect accuracy; this is unlike classical physics where, *in principle*, any pair of dynamic and kinematic variables can be measured with any accuracy. In the quantum realm if the position of a particle in a given direction is known with 100% certainty, the momentum of the particle in that direction is infinitely uncertain, and so on. (2) The smaller the region of space a particle is confined to, the faster it has to be moving (on average). To confine a particle requires a potential energy. The size of the region of confinement arises from an interplay between the potential energy and the particle's HUP-produced kinetic energy. The size of an atom, for example, is determined by the interplay between the potential energy of electrical attraction between the atom's electrons and its nucleus and the electrons' HUP-produced kinetic energy. (3) The Δt **in (7) is not the standard deviation of a sequence of time operator measurements**; rather it is related to the time available to measure the corresponding energy. If there is a limited time in which to measure the energy of a quantum system, then the energy will have an irreducible uncertainty given by Equation (7). This can happen for excited states that "decay" to lower energy somehow. The characteristic decay time fixes how well the energy can be measured. Conversely, if the system has a well-defined energy (i.e., is in an energy eigenstate) then Δt must be infinite. Energy eigenstates are permanent— until some influence outside the system changes the potential energy (such as a collision between an excited atom and another atom).

Appendix I: The binomial expansion. (**Memorize this**.)

If $A \gg B$, the binomial $(A+B)^x \approx A^x + xA^{x-1}B + \frac{1}{2}x(x-1)A^{x-2}B^2$, plus higher order (smaller) terms in B. (In the notes, $E = \sqrt{(pc)^2 + (mc^2)^2}$ is a binomial with $A = (mc^2)^2$, $B = (pc)^2$, and $x = 1/2$. So, what is E to first order in B?)

Appendix II: A short table of relevant integrals (where n and k are integers).

$$\int_0^L \sin^2(n\pi x/L)dx = L/2 \qquad\qquad \int_0^L x^2 \sin^2(n\pi x/L)dx = L^3[1/6 - 1/(2n\pi)^2]$$

$$\int_0^L \sin(n\pi x/L)\cos(n\pi x/L)dx = 0 \qquad\qquad \int_0^L \sin(n\pi x/L)\sin(k\pi x/L)dx = 0, n \neq k$$

$$\int_0^L x\sin^2(n\pi x/L)dx = L^2/4$$