Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

Spring Semester 2006

Christopher J. Cramer

Lecture 8, February 3, 2006

Solved Homework *(Homework for grading is also due today)*

Evaluate <x> and <x^2> for a particle-in-a-box wave function. These expectation values are, generically

$$\langle x\rangle = \frac{2}{L}\int_0^L \left[\sin\left(\frac{n\pi x}{L}\right)\right]^* x\sin\left(\frac{n\pi x}{L}\right)dx$$

$$\langle x^2\rangle = \frac{2}{L}\int_0^L \left[\sin\left(\frac{n\pi x}{L}\right)\right]^* x^2\sin\left(\frac{n\pi x}{L}\right)dx$$

Noting that the complex conjugate in this case is simply the sine function (since the function is real) and using the trigonometric identity given as a hint in the assignment, these simplify to

$$\langle x\rangle = \frac{1}{L}\int_0^L x\left[1-\cos\left(\frac{2n\pi x}{L}\right)\right]dx$$

$$\langle x^2\rangle = \frac{1}{L}\int_0^L x^2\left[1-\cos\left(\frac{2n\pi x}{L}\right)\right]dx$$

Additional simplification leads to

$$\begin{aligned}\langle x\rangle &= \frac{1}{L}\left[\int_0^L xdx - \int_0^L x\cos\left(\frac{2n\pi x}{L}\right)dx\right]\\ &= \frac{L}{2} - \frac{1}{L}\int_0^L x\cos\left(\frac{2n\pi x}{L}\right)dx\\ \langle x^2\rangle &= \frac{1}{L}\left[\int_0^L x^2dx - \int_0^L x^2\cos\left(\frac{2n\pi x}{L}\right)dx\right]\\ &= \frac{L^2}{3} - \frac{1}{L}\int_0^L x^2\cos\left(\frac{2n\pi x}{L}\right)dx\end{aligned}$$

The remaining integrals can be solved by integration by parts (or by reference to a good integral table). To demonstrate the former, let us consider the first case

$$\int_0^L x\cos\left(\frac{2n\pi x}{L}\right)dx$$

Integration by parts uses the relationship

$$\int u\,dv = uv - \int v\,du$$

If we choose

$$u = x \qquad v = \frac{L}{2n\pi}\sin\left(\frac{2n\pi x}{L}\right)$$
$$du = dx \quad dv = \cos\left(\frac{2n\pi x}{L}\right)$$

we have

$$\begin{aligned}\int_0^L x\cos\left(\frac{2n\pi x}{L}\right)dx &= \frac{xL}{2n\pi}\sin\left(\frac{2n\pi x}{L}\right)\Bigg|_0^L - \frac{L}{2n\pi}\int_0^L \sin\left(\frac{2n\pi x}{L}\right)dx \\ &= 0 - 0 - \frac{L^2}{4n^2\pi^2}\cos\left(\frac{2n\pi x}{L}\right)\Bigg|_0^L \\ &= -\frac{L^2}{4n^2\pi^2} + \frac{L^2}{4n^2\pi^2} \\ &= 0\end{aligned}$$

The final result, then, is that

$$\langle x\rangle = \frac{L}{2}$$

Happily, this is a completely intuitive result. The average position is the center of the box! If we look at the plotted wave functions from last lecture, this *should* be obvious, as all have square moduli that are symmetric about the box center.

To solve the integral remaining in $<x^2>$ requires two successive integrations by parts. The calculus is straightforward, if tedious, and is not shown here. An integral table can also be used to find

$$\int x^2\cos(ax)dx = \frac{2x\cos ax}{a^2} + \frac{a^2x^2 - 2}{a^3}\sin ax$$

If we plug in the appropriate values for a and evaluate over the integration limits 0 to L we have the remaining contribution to $<x^2>$ and our final result is

$$\langle x^2\rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

The *classical* result is the *first* term on the r.h.s., which makes sense (the probability is uniform across the entire box (that is, $P(x) = 1/L$) for the classical case, but not the quantum case—when n approaches infinity, the rapid oscillation of the wave function again makes the probability essentially uniform and, as it should be, we see that the classical limit is recovered). The appearance of n in this expectation value reflects the highly *non*-uniform probability distribution of the lower-energy particle-in-a-box wavefunctions, which have *reduced* expectation values for $\langle x^2\rangle$, since those wave functions have low probabilities near the walls and higher probabilities near the center. This effect is larger as L gets larger, since more and more of the distances far from the center are disadvantaged compared to distances near the center. [Note that these results would be slightly more intuitive if we had transformed our coordinate system by $L/2$, so that the center of the box was zero, but the physics doesn't change.]

Note that $\langle x\rangle^2 \neq \langle x^2\rangle$ because the eigenfunctions of the Hamiltonian are *not* eigenfunctions of the position operator. Put differently (but equivalently) $[H,x] \neq 0$. Delocalization of the wave function makes fairly obvious that the wave function cannot be an eigenfunction of the position operator. [For the mathematically inclined, the Dirac delta function $\delta(x)$ is the eigenfunction of the position operator. That function has an infinite first derivative, meaning that the expectation value of the momentum operator would be infinite, as required by the Heisenberg uncertainty principle!]

It is trivial to compute $\langle H\rangle^2$ and $\langle H^2\rangle$. We already know that the particle-in-a-box wave functions are *eigenfunctions* of the Hamiltonian having energy levels

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

When this eigenvalue is pulled out of $\langle H\rangle$, all that is left is an integral of $|\Psi|^2$, and by normalization this is one. So, the expectation value of H is the energy above. Applying H twice in a row just gives the square of this value, again pulled out front of a normalized integral, so we have $\langle H\rangle^2 = \langle H^2\rangle$. This is the requirement when the wave function is an eigenfunction of the operator, as is the case here.

Parity

Often in quantum mechanics we face a fairly simple question with respect to a given integral: Is it zero or can it be non-zero? It can be surprisingly easy to answer this question by taking advantage of a property known as parity. If it is the case that a function of a given variable changes sign when the variable changes sign but does not change in magnitude, i.e.,

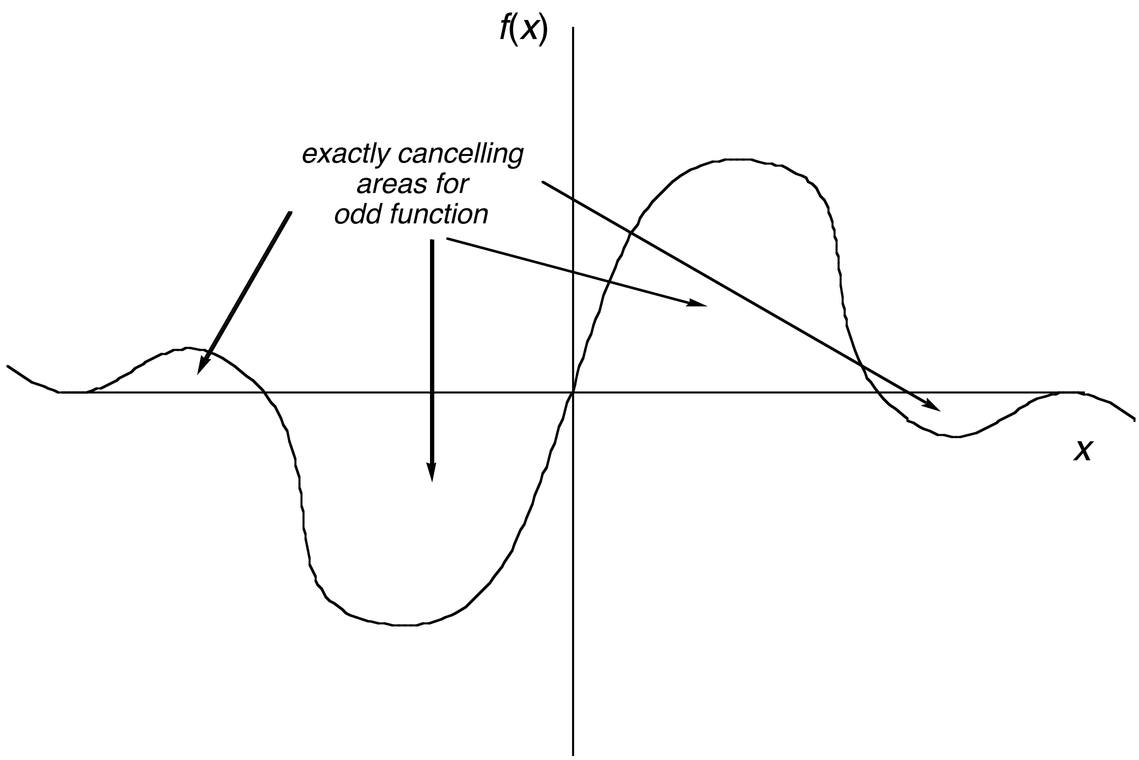
$$-f(x) = f(-x) \tag{8-1}$$

we say the function has "odd" parity. If, on the other hand, it neither changes in magnitude nor in sign, i.e.,

$$f(x) = f(-x) \tag{8-2}$$

we say that it has "even" parity. [Note that $f(x) = 0$ is a rather odd beast that has both even *and* odd parity, but it is so boring a function that we won't worry about it any longer.]

Parity is a useful quality because any integral that equally spans either side of zero may be non-zero if the function being integrated has even parity, and it will be zero if the function being integrated has odd parity. If these statements are not intuitively obvious, quick graphical examples should make things clear.



From inspection of eq. 8-1 it is clear that an odd function must pass through the origin, and that the areas on the left and right sides of the origin will exactly cancel one another. For an even function (not shown above), the area on one side will exactly equal (not cancel) the area on the other side, so the integral may be non-zero. A simple example of a trivial even function is $f(x) = C$ where C is a constant (i.e., no dependence on x). In that case, the area defined by the integral from $-a$ to a is simply $2aC$, which is not zero except in the boring case of $C = 0$.

Note that an arbitrary function does not have to have any parity at all. For instance, $f(x) = e^x$ is neither even nor odd. We can actually regard parity as having an associated operator, call it Π, where the operator replaces every coordinate variable with its negative. That is,

$$\Pi f(x,y,z) = f(-x,-y,-z) \qquad (8\text{-}3)$$

From generalizing eqs. 8-1 and 8-2, it should be clear that odd and even functions are eigenfunctions of the parity operator having eigenvalues −1 and 1, respectively. [These are also the only possible eigenvalues if the function f is required to be differentiable at x=0.]

Now, let us consider whether the parity operator commutes with the Hamiltonian for the particle in a box. Put differently, does $[H,\Pi] = 0$? For the particle in a box, the Hamiltonian is simply the kinetic energy operator. If we evaluate the commutator for an arbitrary function (of one variable, for simplicity) we have

$$\begin{aligned}
[H,\Pi]f(x) &= H\Pi f(x) - \Pi H f(x) \\
&= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} f(-x) - \Pi\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right) f(x) \\
&= (-1)(-1)\left(-\frac{\hbar^2}{2m}\right) f''(-x) - \Pi\left(-\frac{\hbar^2}{2m}\right) f''(x) \qquad (8\text{-}4) \\
&= \left(-\frac{\hbar^2}{2m}\right) f''(-x) - \left(-\frac{\hbar^2}{2m}\right) f''(-x) \\
&= 0
\end{aligned}$$

The kinetic energy operator and the parity operator commute. Since the eigenfunction of one Hermitian operator is also an eigenfunction for all Hermitian operators with which the first one commutes, it is required that the particle-in-a-box wave functions be either even or odd (the only two possibilities for Π). We'll look at the wave functions in a moment to decide when they are even or odd, but we need to do one more thing with parity first.

Parity has a multiplication rule associated with it, and it is the same rule that is true for arithmetic addition. The product of either two odd functions or two even functions is always an even function, just as the sum of two even numbers or two odd numbers is always even. Conversely, the product of an even function with an odd function is always odd, just as the sum of an even number and an odd number is always odd. Staring at some graphs will help you see these product relationships, if they aren't immediately clear.

These rules allow us to state, for instance, that $|\Psi|^2$ is typically non-zero for eigenfunctions of the parity operator because $|\Psi|^2$ is an integral over the product of either two even or two odd functions, and thus the product must be even, and the integral of an even function is typically non-zero.

Spectroscopic Transitions

Later in the course, we will hopefully have a chance to prove the following statement. Until then, just accept it as fact. A quantum mechanical system cannot be induced to go from state *m* to state *n* if it is true that

$$\int_{-\infty}^{\infty} \Psi_m^*(\mathbf{r}) e\mathbf{r} \Psi_n(\mathbf{r}) d\mathbf{r} = 0 \tag{8-5}$$

where *e* is the charge on an electron (just a constant) and **r** is the coordinate operator (*x* in one dimension, **r** in 3 dimensions). Because the operator *e***r** has units of charge times distance, it is called the “electric dipole moment operator” $\boldsymbol{\mu}$. The probability of a spectroscopic transition is proportional to the absolute value of $< \Psi_m \mid \boldsymbol{\mu} \mid \Psi_n >$, and this value is called the transition dipole moment, also written $<\boldsymbol{\mu}_{mn}>$.

If the transition dipole moment is zero, we say that the transition is "forbidden". If it is non-zero, we say that the transition is "allowed". For allowed transitions between states *m* and *n*, increases in energy require absorption of a photon of frequency ν and decreases in energy involve emission of a photon of frequency ν, where ν satisfies the Bohr condition

$$\left| E_m - E_n \right| = h\nu \tag{8-6}$$

where *h* is Planck's constant.

Let us use parity to determine whether the transition dipole moment for two particle-in-a-box wave functions is zero. Note that the dipole moment operator is an eigenfunction of the parity operator, and it is an odd function (multiplying something by $-x$ or by $(-x\mathbf{i},-y\mathbf{j},-z\mathbf{k})$ results in the negative of multiplying by x or by $(x\mathbf{i},y\mathbf{j},z\mathbf{k})$). So, for the transition dipole moment integral to be non-zero, the product of the two particle-in-a-box wave functions must be an odd function too. Thus, we need one odd particle-in-a-box wave function and one even one. Is that possible?

To answer that question, we first need to recast our particle-in-a-box wave functions into a form such that the transition dipole moment is integrated from $-a$ to a. In this case, a will be $L/2$ where L is the length of the box. If we take our normalized particle-in-a-box wave function

$$\Psi(x') = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x'}{L}\right) \tag{8-7}$$

and make the substitution $x = x' - L/2$, we have

$$\Psi(x) = \sqrt{\frac{2}{L}}\sin\left[\frac{n\pi\left(x+\frac{L}{2}\right)}{L}\right] = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}+\frac{n\pi}{2}\right) \tag{8-8}$$

If we now use the trigonometric identity for the sine of a sum, we have

$$\Psi(x) = \sqrt{\frac{2}{L}}\left[\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi}{2}\right)+\cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi}{2}\right)\right] = \begin{cases} (-1)^{(n-1)/2}\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right), & n \text{ odd} \\ (-1)^{n/2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), & n \text{ even} \end{cases} \tag{8-9}$$

Notice the distinction in the functions depending on whether n is odd or even (arithmetically, in this case, not a reference to parity!). That is because the cosine and sine terms that are *not* dependent on x are equal to zero for odd and even values of n respectively, so one term in the sum disappears. In the other term, the non-x dependent trigonometric functions are either 1 or −1 depending on the precise value of n as indicated by the preceding powers of −1 in the final expression.

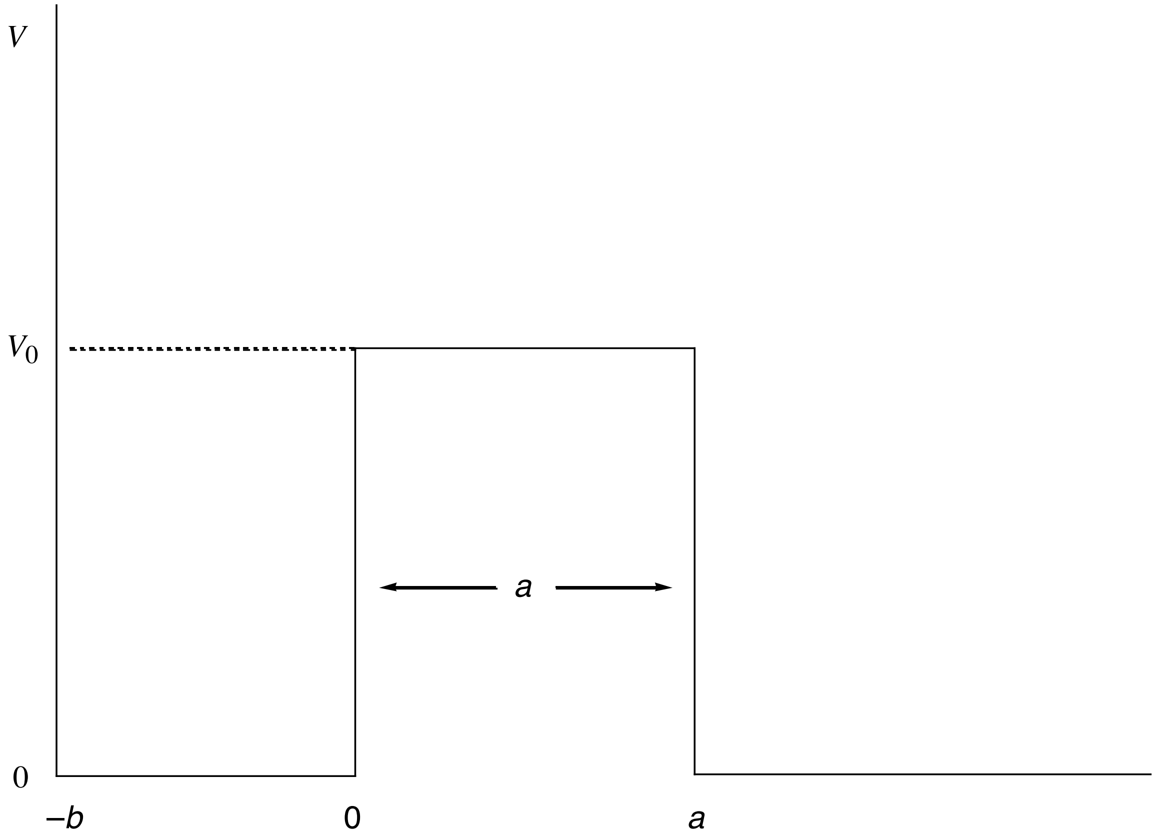
What about the parity of the two possible wave functions? From trigonometry we know that

$$\begin{aligned} \cos(x) = \cos(-x) \quad &\Rightarrow \quad \text{even function} \\ -\sin(x) = \sin(-x) \quad &\Rightarrow \quad \text{odd function} \end{aligned} \tag{8-10}$$

So, it is the case that when n is odd, our particle-in-a-box wave functions are of even parity, while when n is even, they are of odd parity. Thus, as noted above, transitions between levels will be allowed if and only if one level has an even quantum number and the other an odd one, since the product of the two wave functions will then have odd parity.

Tunneling

One of the strangest and most fascinating phenomena allowed in the quantum mechanical world but not in the classical world is called quantum mechanical tunneling, or simply, tunneling. Imagine that you place a classical particle in a box. On one side of the box (let's say the left side) there is a barrier of infinite height. On the other side is a barrier of finite height and width (let's say it is square topped) beyond which the potential returns to zero forever. If we provide our classical particle with an amount of kinetic energy that is less than the potential energy barrier height of the right side of the box, it will bounce around inside forever (assuming no energy loss to friction, collisional heating, etc.) and it will never, never escape. The quantum mechanical particle, on the other hand, given enough time will always find its way out. It is as though it "tunnels" through the barrier.



To construct a wave function that explains this, we need to piece together in a continuous, differentiable fashion, wave functions for the three different regions. The relevant Schrödinger equations are

$$
\begin{aligned}
&-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) = E\Psi(x), && -b \le x \le 0 \\
&\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_0\right)\Psi(x) = E\Psi(x), && 0 \le x \le a \\
&-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) = E\Psi(x), && a \le x
\end{aligned}
\tag{8-11}
$$

All of these may be rearranged into the generic form

$$\left(\frac{d^2}{dx^2} + k^2\right)\Psi(x) = 0 \tag{8-12}$$

where

$$\begin{aligned} k^2 &= \frac{2mE}{\hbar^2}, && -b \le x \le 0 \\ k^2 &= -\frac{2m(V_0 - E)}{\hbar^2}, && 0 \le x \le a \\ k^2 &= \frac{2mE}{\hbar^2}, && a \le x \end{aligned} \tag{8-13}$$

Recall that the general solution for eq. 8-12 is

$$\Psi(x) = Ae^{ikx} + Be^{-ikx} \tag{8-14}$$

If we use A and B as the multiplicative constants for the box region, there will be an analogous F and G for the rightmost region (we reserve C and D for the barrier region and skip E to avoid confusion with the particle energy). The solution for the barrier region is slightly tricky insofar as k^2 is a negative number (since $V_0 > E$). Rather than work with an imaginary k, we can simply rewrite the differential equation as

$$\left(\frac{d^2}{dx^2} - K^2\right)\Psi(x) = 0 \tag{8-15}$$

where

$$K^2 = \frac{2m(V_0 - E)}{\hbar^2} \tag{8-16}$$

The solution to eq. 8-15 is as straightforward as that for eq. 8-12. It is

$$\Psi(x) = Ce^{Kx} + De^{-Kx} \tag{8-17}$$

Prior to doing any more work to determine the constants A to G, let us take a moment to evaluate the momentum operator over the two exponential components of the first and third wave functions. For the first component, we have

$$\begin{aligned}\langle p_x\rangle &= |A|^2\int\left(e^{ikx}\right)^*\left(\frac{\hbar}{i}\frac{d}{dx}\right)\left(e^{ikx}\right)dx \\ &= \hbar k|A|^2\int\left(e^{ikx}\right)^*\left(e^{ikx}\right)dx \\ &= \hbar k|A|^2\int dx \\ &\geq 0\end{aligned} \tag{8-18}$$

and for the second component

$$\begin{aligned}\langle p_x\rangle &= |B|^2\int\left(e^{-ikx}\right)^*\left(\frac{\hbar}{i}\frac{d}{dx}\right)\left(e^{-ikx}\right)dx \\ &= -\hbar k|B|^2\int\left(e^{-ikx}\right)^*\left(e^{-ikx}\right)dx \\ &= -\hbar k|B|^2\int dx \\ &\leq 0\end{aligned} \tag{8-19}$$

So, the momentum associated with the first term is always positive if A is non-zero and that with the second term is always negative if B is non-zero. We may view the two-term wave function, then, as a superposition of right-moving (positive momentum) and left-moving (negative momentum) particles.

If tunneling occurs, that means that F must be non-zero. That is, right-moving particles are present in the open region. The intensity of a beam of such particles would be related to the ratio of $|F|^2$ to $|A|^2$. This ratio is called the "transmission coefficient" κ and is a measure of the efficiency of tunneling. Our goal is to compute κ. Moreover, since the likelihood of any particles coming back and tunneling *into* the box is effectively zero (since the free space to the right is infinite) we can be confident that $G = 0$ in the wave function for the open region.

For the two points at which the wave functions are stitched together, using $G = 0$ and the requirement for a continuous, differentiable wave function provides the following boundary conditions (several e^0 terms are not shown as they are simply one)

$$\begin{aligned}&A + B = C + D \\ &Ce^{Ka} + De^{-Ka} = Fe^{ika} \\ &ik(A - B) = K(C - D) \\ &K\left(Ce^{Ka} - De^{-Ka}\right) = ikFe^{ika}\end{aligned} \tag{8-20}$$

These are 4 equations in 5 unknowns. To make the whole thing more tractable, we may assume that C is zero. To rationalize this, consider the wave function of eq. 8-17. As a particle enters a region whose potential energy exceeds its kinetic energy, do we expect the probability of being there to increase exponentially as we go further in (the *C* term) or to drop off exponentially as we go further in (the *D* term). Obviously the latter is the case.

With this final simplifying assumption, we can solve for κ (the tedious algebra is not shown). Our final result is

$$\kappa = \frac{16}{\left(Z^2 + 2 + Z^{-2}\right)} e^{-\left[\frac{2a}{\hbar}\sqrt{2m\left(V_0 - E\right)}\right]} \tag{8-21}$$

where *Z* is *k*/*K* or

$$Z = \sqrt{\frac{V_0 - E}{V_0}} \tag{8-22}$$

Note the key qualitative features in eq. 8-21. First, for κ to be zero (no possibility of escape by tunneling) either the width *a*, or the mass *m*, or the barrier height V_0, must be infinity. For a given barrier height, tunneling increases for smaller widths, lighter masses, and smaller differences between *E* and V_0. We may summarize these in a sensible way:

1) Tunneling is more efficient the narrower the barrier.

2) Tunneling is more efficient for lighter particles.

3) Tunneling is more efficient near the top of the barrier than further down.

Note that real chemistry barriers tend to be thicker at the bottom than the top, so points 1 and 3 often combine their effects.

Tunneling is intrinsically quantum mechanical, but it is an everyday phenomenon, as exotic as it may seem (exotic because, in the barrier region, the particle must, by conservation of energy, have *negative* kinetic energy (imaginary momentum?)) Tunneling is the mechanism by which certain radioactive nuclei emit α particles (the nuclear binding potential is always vastly greater than the α particle's kinetic energy). Electron transfer in biological processes like photosynthesis involves electrons tunneling from one metal center to another. Finally, protons and hydrogen atoms are still light enough to tunnel effectively in many instances, and liver alcohol dehydrogenase (the enzyme responsible for detoxifying those who have overimbibed) achieves a part of its reactivity owing to tunneling of this light nucleus.

Homework (n/a — Study for exam I — see below)

Some Sample Exam Questions:

a. Which of the following statements about the de Broglie wavelength λ are *true*?

(a)	λ decreases as mass increases if velocity is constant	(e)	A particle that has zero velocity has an infinite de Broglie wavelength
(b)	$\lambda = h / p$	(f)	All of the above
(c)	λ decreases as momentum increases	(g)	(a), (b) and (e)
(d)	λ increases as kinetic energy decreases	(h)	(c) and (d)

b. Which of the below equations can be *false* for an arbitrary, possibly complex, pair of orthonormal functions f and g?

(a)	$< \|f\|^2 >< \|g\|^2 > = 1$	(e)	$f^*g - g^*f = 0$
(b)	$< f \| H \| g > = 0$	(f)	(a) and (c)
(c)	$< f \| g > = 0$	(g)	(b), (d) and (e)
(d)	$fg = 0$	(h)	All of the above

c. Which of the below expectation values are zero? f and g are arbitrary, possibly complex, functions.

(a)	$< \sin x \| x \| \cos x >$	(e)	$< f \| g > - < g \| f >$
(b)	$< \sin^2 x \| x \| \cos^2 x >$	(f)	$<\mu_{mn}>$ for a forbidden transition
(c)	$< f \| [A,B] \| g >$ where A and B commute	(g)	(b), (d) and (f)
(d)	$< \Psi \| H \| \Psi >$ where Ψ is a stationary state	(h)	(b), (c), and (f)

d. Given a particle of mass m in a box of length L having the wave function $\Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$, what is the energy of the level corresponding to n = 8?

(a)	Since this wave function is not an eigenfunction of the Hamiltonian the question cannot be answered	(e)	$\frac{16\pi^2\hbar^2}{mL^2}$
(b)	64 times the energy of the ground state	(f)	(c) and (d)
(c)	$< \Psi \| p_x^2 \| \Psi >$	(g)	(b) and (d)
(d)	$8h^2 / mL^2$	(h)	None of the above