Solved Homework

We are given that A is a Hermitian operator such that $A\phi_1 = a\phi_1$, $A\phi_2 = b\phi_2$, $A\phi_3 = b\phi_3$, and $A\phi_4 = c\phi_4$, $a \neq b \neq c$, and Z is some other operator for which $[A,Z] = 0$. We may then state whether the following integrals are definitely zero, or may be nonzero

(a) $<\phi_1 | \phi_4>$ Equals zero, because non-degenerate eigenfunctions of a Hermitian operator are orthogonal.

(b) $<\phi_2 | \phi_4>$ Equals zero, because non-degenerate eigenfunctions of a Hermitian operator are orthogonal.

(c) $<\phi_2 | \phi_3>$ May or may not be zero. Degenerate eigenfunctions are not necessarily orthogonal, even though orthogonal functions having identical eigenvalues *can* be constructed from linear combinations of them.

(d) $<\phi_3 | \phi_4>$ Equals zero, because non-degenerate eigenfunctions of a Hermitian operator are orthogonal.

(e) $<\phi_1 | A | \phi_3>$ Equals zero. $<\phi_1 | A | \phi_3> = <\phi_1 | b\phi_3> = b<\phi_1 | \phi_3>$ and we know $<\phi_1 | \phi_3> = 0$ because non-degenerate eigenfunctions of a Hermitian operator are orthogonal.

(f) $<\phi_2 | A | \phi_3>$ May or may not be zero. $<\phi_2 | A | \phi_3> = <\phi_2 | b\phi_3> = b<\phi_2 | \phi_3>$ and we know from (c) above that this overlap integral need not be zero.

(g) $<\phi_1 | Z | \phi_4>$ Equals zero. If the commutator of two operators is zero, then they share common eigenfunctions and we were told that the functions ϕ belong to this set. Thus, $<\phi_1 | Z | \phi_4> = <\phi_1 | d\phi_4> = d<\phi_1 | \phi_4>$ where d is an eigenvalue of Z and we know from (a) above that this overlap integral is zero.

(h) $<\phi_2 | Z | \phi_3>$ May or may not be zero. Continuing from our above logic, $<\phi_2 | Z | \phi_3> = <\phi_2 | e\phi_3> = e<\phi_2 | \phi_3>$ and we know from (c) above that this overlap integral need not be zero.

(i) $<\phi_2 + \phi_3 | Z | \phi_2 - \phi_3>$ May or may not be zero. This one is a bit tricky. If we expand the integral, we get $<\phi_2 | Z | \phi_2> - <\phi_2 | Z | \phi_3> + <\phi_3 | Z | \phi_2> - <\phi_3 | Z | \phi_3>$. The first question is, just because ϕ_2 and ϕ_3 are degenerate for the Hamiltonian, are they necessarily degenerate for the operator Z? The answer is, yes. We can prove this by noting that, by the turnover rule, $<\phi_2 | Z | \phi_3> = <Z\phi_2 | \phi_3> = f<\phi_2 | \phi_3>$ where f is the appropriate eigenvalue for Z. But, we already showed in (h) above that $<\phi_2 | Z | \phi_3> = e<\phi_2 | \phi_3>$, so e must be equal to f.

So, if we pull all of the eigenvalues out from our sum of 4 integrals we have $e<\phi_2 \mid \phi_2 > - e<\phi_2 \mid \phi_3 > + e<\phi_3 \mid \phi_2 > - e<\phi_3 \mid \phi_3 >$. Assuming that ϕ_2 and ϕ_3 are normalized, the first and last terms cancel as $e - e$. However, since ϕ_2 and ϕ_3 are degenerate, they are not necessarily orthogonal. Let us say that the overlap integral $<\phi_2 \mid \phi_3 > = c$. Then $<\phi_3 \mid \phi_2 > = <\phi_2 \mid \phi_3 >^* = c^*$. For a complex number, $c \neq c^*$ unless c is simply a real number. So, the second and third terms of the sum do *not* necessarily cancel and we cannot say that the integral is necessarily zero.

(j) $<\phi_2 + \phi_3 \mid A \mid \phi_2 - \phi_3 >$ May or may not be zero. Same answer as (i) but with A and its eigenvalue b in place of Z and its eigenvalue e.

(k) $<\phi_2 + \phi_3 \mid \phi_2 - \phi_3 >$ May or may not be zero. Same answer as (i) above, but no need to pull out eigenvalues from the sum of the 4 intermediate integrals.

Free Particle Wave Function

The time-independent Schrödinger equation in one dimension is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right) \Psi(x) = E\Psi(x) \tag{7-1}$$

For a free particle, the potential energy V is everywhere zero. This leads to a simplified equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - E \right) \Psi(x) = 0 \tag{7-2}$$

This has a slightly simpler looking form if we select a constant

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{7-3}$$

in which case we may write eq. 7-2 as

$$\left(\frac{d^2}{dx^2} + k^2 \right) \Psi(x) = 0 \tag{7-4}$$

This is one of the simplest possible differential equations. It has solutions of the form

$$\Psi(x) = Ae^{ikx} + Be^{-ikx} \tag{7-5}$$

(you should be able to verify this readily). A and B are arbitrary constants for the general case of eq. 7-4. If we wish to ensure normalization, there are some rather tricky details that arise, but we will ignore them for this particular system as they don't really matter.

Let's focus on the important details of this wave function. First, there is no quantization. From eq. 7-3, it is apparent that all positive values of E are allowed (positive because the particle has only kinetic energy, and kinetic energy is bounded from below by zero).

Some of you may not be familiar with the function e^{ix}. If we use its series expansion, we obtain

$$e^{ix} = 1 + ix - \frac{1}{2!}x^2 - \frac{1}{3!}ix^3 + \frac{1}{4!}x^4 + \frac{1}{5!}ix^5 + \cdots$$

$$= \left(1 - \frac{1}{2!}x^2 + \frac{1}{4!}x^4 - \cdots\right) + i\left(x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 + \cdots\right) \tag{7-6}$$

$$= \cos x + i\sin x$$

Thus, if we were to take $A = B$ in eq. 7-5, we would have

$$\Psi(x) = N\cos kx \tag{7-7}$$

and if we were to take $A = -B$ in eq. 7-5, we would have

$$\Psi(x) = N\sin kx \tag{7-8}$$

where N is some arbitrary normalization constant.

So, a free particle has a wave function that can be represented as either a sine or cosine function, which is to say, it is highly delocalized. The wavelength of the wave function decreases with higher energy and with greater mass (recall the definition of k)—results we expect.

Because the free particle is not quantized, we sometimes say it is 'in the continuum", meaning that there is a continuous range of energies available to it. The free particle wave function is readily generalized to three dimensions with no change in qualitative interpretation.

The Particle in a Box

What if instead of a particle being free over all space, it is free only within a box of length L, outside of which the potential energy is infinite, i.e., the particle is totally confined? We then have (in one dimension)

$$V(x) = \begin{cases} \infty, & x < 0 \\ 0, & 0 \le x \le L \\ \infty, & L < x \end{cases} \tag{7-9}$$

Since the particle cannot exist in regions of infinite potential energy, we can be certain that

$$\Psi(x) = \begin{cases} 0, & x < 0 \\ 0, & L < x \end{cases} \tag{7-10}$$

and, from the requirement that the wave function be continuous, that further mandates that

$$\Psi(x) = \begin{cases} 0, & x = 0 \\ 0, & L = x \end{cases} \tag{7-11}$$

Within the length of the box, however, the particle looks like a typical free particle, which suggests that it should have a sine or cosine wave function. Given our choice of $x = 0$ as one wall of the box, we cannot use the cosine function (since $\cos(0) = 1$, not 0), so we will need a function having the form of eq. 7-8. Moreover, to ensure that $\Psi = 0$ at position L, we can only use arguments of the sine function that are guaranteed to be integral multiples of π at position L. That is, if we require $\sin(kL) = 0$, we require

$$k = \frac{n\pi}{L} \tag{7-12}$$

where n is an integer. So, besides eq. 7-10 (which specifies the wave function to be identically zero outside the box) we have

$$\Psi(x) = C\sin\left(\frac{n\pi x}{L}\right) \tag{7-13}$$

where C is an integration constant. Since we can now insist on normalization, we enforce

$$
\begin{aligned}
1 &= \int_0^L \left[C\sin\left(\frac{n\pi x}{L}\right) \right]^* \left[C\sin\left(\frac{n\pi x}{L}\right) \right] dx \\
&= C^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx \\
&= C^2 \left(\frac{L}{2}\right)
\end{aligned}
\tag{7-14}
$$

so that it is apparent that $C = (2/L)^{1/2}$. Thus, within the box, the particle in a box has the wave function

$$\Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{7-15}$$

If we plug this wave function into the time-independent Schrödinger equation, we have

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = E_n\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \tag{7-16}$$

Taking the derivative on the l.h.s. provides

$$\left(\frac{n^2\pi^2\hbar^2}{2mL^2}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = E_n\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \tag{7-17}$$

or, after canceling Ψ from both sides

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \tag{7-18}$$

The energy levels of the particle in a box are thus quantized, since n is an integer (we may as well say a positive integer, since we are dealing with n^2).

There are many other important qualitative features of this wave function that are worth taking note of:

1)   The lowest possible energy is *not* zero, but rather $h^2/(8mL^2)$ for $n = 1$. This energy is called zero-point energy. The reason the energy cannot be zero is that if $n = 0$, we see from eqs. 7-10 and 7-15 that $\Psi = 0$ *everywhere*. That is an allowed wave function, but it corresponds to no particle at all (it obviously integrates to zero over all space) which is hardly very interesting... Note that zero-point energy is an intrinsically quantum mechanical phenomenon. A classical particle can certainly be "at rest" (have no energy) in a box, but *not* a quantum particle. Note that if the QM particle *were* to be at rest, we would simultaneously know its position *and* its momentum, but the uncertainly principle tells us that we can *never* know that!

2)   As the box length L becomes infinite, the spacing between levels becomes zero and we recover the continuum.

3)   As the mass becomes infinite, the spacing between levels becomes zero and we recover the continuum, which is certainly well known as the classical limit.

Representing Wave Functions

When we work with wave functions, there are various convenient ways to express them graphically. A typical illustration is shown below.
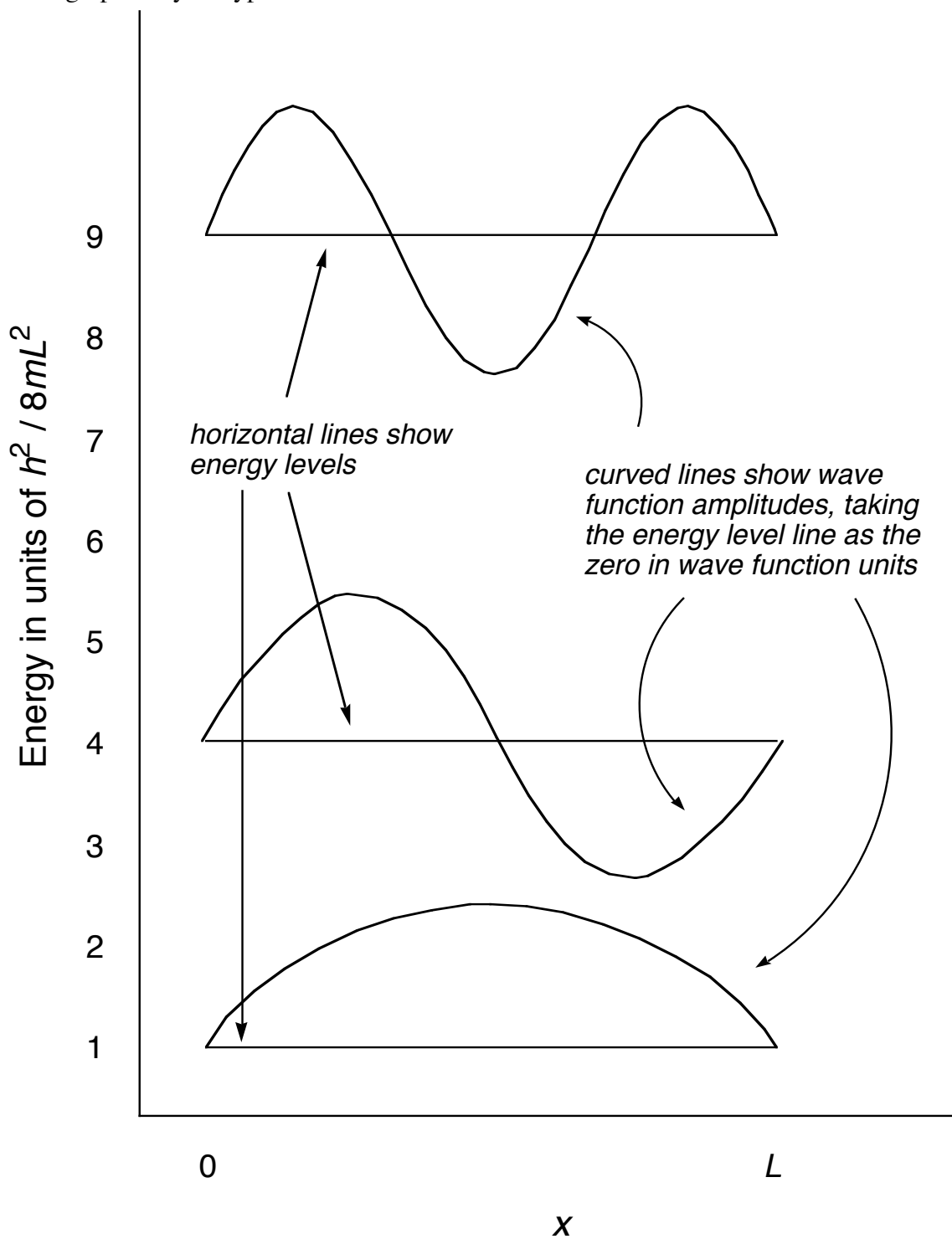
Note that the lowest energy wave function ($n = 1$) has no nodes. The next higher energy wave function has one node, etc.

Remember that the probability of finding a particle at a given position is $\Psi(x)^*\Psi(x)$. Noting the convention that the zeroes of the individual wave functions are where they cross their respective energy lines (it is as though each is drawn with its own right-hand ordinate have the zero at the energy level), it is straightforward to sketch $\Psi(x)^*\Psi(x)$. In this case, Ψ is real, not complex, so we simply square the function. Thus, it is zero at the nodes (the walls, and any internal nodes), and positive everywhere else, with maximum probability at the positions of maximum amplitude in Ψ in either the positive or negative directions.

There are some interesting observations from this analysis. First, the lowest energy wave function has a non-zero probability at every position inside the box, but higher energies have zero probabilities at nodal positions. In addition, the lowest energy wave function has the lowest probability of being found near the walls (stare at the graph until you see this). As the energy increases, the probability of being found near the wall increases.

It is a worthwhile exercise to check whether our wave functions are orthogonal (we know that, as eigenfunctions of a Hermitian operator, they *should* be). The generic overlap between any two particle-in-a-box wave functions is

$$\langle \Psi_m | \Psi_n \rangle = \int_0^L \left[\sqrt{\frac{2}{L}} \sin\left(\frac{m\pi x}{L}\right) \right]\left[\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right] dx$$

$$= \frac{2}{L}\left(\frac{L}{2}\delta_{mn} \right) \tag{7-19}$$

$$= \delta_{mn}$$

(the integral solution is available in any good integral table). Thus, the wave functions are indeed orthonormal.

Now, let us consider the expectation value of the momentum for a particle-in-a-box wave function. We determine this as

$$\langle p_x \rangle = \int_0^L \left[\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right] \frac{\hbar}{i} \frac{d}{dx} \left[\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right] dx$$

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

$$= \frac{n\pi\hbar}{iL^2} \int_0^L \sin\left(\frac{2n\pi x}{L}\right) dx \qquad\qquad (7\text{-}20)$$

$$= -\frac{\hbar}{2iL} \cos\left(\frac{2n\pi x}{L}\right)\Big|_0^L$$

$$= -\frac{\hbar}{2iL}(0-0)$$

$$= 0$$

Irrespective of the quantum number, the expectation value of the momentum is zero. Intuitively, if we had thought about it, we probably would have realized that this was the necessary result. Any time we sample the system, the probability that we will find a particle moving from left to right with some momentum is equal, by symmetry, to the probability that we will find it moving from right to left! This is the perfect example of a superposition of states.

Of course, if we evaluated p^2 we would expect a different, non-zero result. In this case, however, we need not do the integration because again we already know the answer. The entire energy for *any* particle-in-a-box wave function is kinetic energy, and the kinetic energy is simply $p^2/2m$. So, $<p^2>$ is simply $2m$ times the value from eq. 7-18, i.e., $n^2h^2/4L^2$.

Homework

To be solved in class:

(a) Evaluate $<x>$ and $<x^2>$ for the particle in a box as a function of quantum number n.

(b) Why does only one of the answers in part (a) depend on n?

(c) Why isn't $<x^2>$ equal to $<x>^2$?

(d) Determine $<H>$ and $<H^2>$ and compare the latter with $<H>^2$. Contrast the result with your answer to part (c).

Hints:

$$\sin\alpha \sin\beta = \frac{1}{2}\left[\cos(\alpha - \beta) - \cos(\alpha + \beta)\right]$$

In the absence of a nice integral table you will need to recall how to integrate by parts, namely

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

To be turned in for possible grading Feb. 3:

For the particle in a box of length L, what is the probability of finding the particle in the intervals $0.45L$ to $0.55L$ for the following levels:

(a) $n = 1$

(b) $n = 2$

(c) $n = 7{,}503$

(d) The Bohr correspondence principle states that quantum mechanics should reduce to classical mechanics for very large quantum numbers. Is your final answer consistent with classical mechanics? Explain the direction of deviations from the classical answer, if any, for cases (a), (b), and (c).