Midterm 1 Solutions
Chemistry 120A, Fall 2011

Written by David Stück, Samuel Penwell, and Nicholas Esker

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1. (40 pts) A particle of mass m is confined to the region between x=0 and x=L, and in this region, it has no potential energy. The stationary state wave functions in that region obey the eigenfunction equation $(-\hbar^2/2m)\, d^2\psi/dx^2 = E\psi(x)$ with the boundary conditions $\psi(0) = \psi(L) = 0$. The set of solutions to this equation coincide with the quantized energy eigenvalues $E_n = \hbar^2 k_n^2/2m$, where $k_n = n\pi/L$, with $n = 1, 2, 3, ...$ and $\psi_n(x) = (\sqrt{2/L}) sin(k_n x)$. Consider that the particle in the box is prepared in a properly normalized, non-stationary state of the first and third energy levels (the ground state and the second excited state):

$$\psi(x,0) = (1/\sqrt{2})(\psi_1(x) + \psi_3(x))$$

   (a) A single measurement of energy is carried out. What values of energy could be measured and with what probabilities?

   Solution:

   From examination or intuition: Since the wavefunction is a superposition of the first and third energy eigenstates, the only energies we can detect are E_1 or E_3. Furthermore, since the coefficients in the expansion are the same, there is an equal probability of observing either energy.

   Proof: The postulates of quantum mechanics tell us that the we will only ever measure an eigenvalue of the operator corresponding to an observable with probability given by the square of the coefficient when we represent the wavefunction in the eigenfunction basis. We see that our wavefunction is already written as a sum of energy eigenfunctions:

$$\psi(x,0) = \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_3(x)$$

   So we know that we will measure eigenvalue E_1 with probability $(1/\sqrt{2})^2 = 1/2$ and likewise measure E_3 with probability $1/2$.

   (b) A single measurement of momentum is carried out. What values of momentum could be measured and with what probabilities?

   Solution:

Again, we must write our wavefunction out in terms of eigenfunctions, but this time they are eigenfunctions of $\hat{p}$, the momentum operator, which look like:

$$\phi_n = \frac{1}{\sqrt{L}} e^{ik_n x}$$

with corresponding eigenvalues $\hbar k$. Using the fact that,

$$\sin(kx) = \frac{e^{ikx} - e^{-ikx}}{2i}$$

We can write our wave function out as a sum of momentum eigenstates:

$$\begin{aligned}\psi(x,0) &= \frac{1}{2i\sqrt{L}} \left(e^{ik_1 x} - e^{-ik_1 x} + e^{ik_3 x} - e^{-ik_3 x} \right) \\ &= \frac{1}{2i} \left(\phi_1 - \phi_{-1} + \phi_3 - \phi_{-3} \right)\end{aligned}$$

Thus we have probability $\left| \frac{1}{2i} \right|^2 = \frac{1}{4}$ of measuring a momentum of $\pm \hbar k_1$ or $\pm \hbar k_3$.

(c) Determine the expectation value of energy, $< H >$, at a later time t.

Solution: The expectation value is independent of time. Recall that the expectation value is a weighted average of the allowed energy values. Thus the expression for the expectation value will show us the allowed energies and their relative probabilities

Proof:

$$\begin{aligned}< \psi|\hat{H}|\psi > &= \frac{1}{2} < \sin(k_1 x) e^{\imath \frac{E_1}{\hbar} t)} + \sin(k_3 x) e^{\imath \frac{E_3}{\hbar} t)} |\hat{H}| \sin(k_1 x) e^{\imath \frac{E_1}{\hbar} t)} + \sin(k_3 x) e^{\imath \frac{E_3}{\hbar} t)} > \\ &= \frac{1}{2} [< \sin(k_1 x)|\hat{H}| \sin(k_1 x) > + < \sin(k_1 x)|\hat{H}| \sin(k_3 x) > e^{\imath \frac{E_3 - E_1}{\hbar} t)} \\ &+ < \sin(k_3 x)|\hat{H}| \sin(k_1 x) > e^{\imath \frac{E_1 - E_3}{\hbar} t)} + < \sin(k_3 x)|\hat{H}| \sin(k_3 x) >] \\ &= \frac{1}{2} [E_1 < \sin(k_1 x)| \sin(k_1 x) > + E_3 < \sin(k_1 x)| \sin(k_3 x) > e^{\imath \frac{E_3 - E_1}{\hbar} t)} \\ &+ E_1 < \sin(k_3 x)| \sin(k_1 x) > e^{\imath \frac{E_1 - E_3}{\hbar} t)} + E_3 < \sin(k_3 x)| \sin(k_3 x) >] \\ &= \frac{1}{2} [E_1 + E_3]\end{aligned}$$

(d) Write out the expectation value of position, $< x >$, at a later time t (you do not need to calculate spatial integrals). With what frequency does it oscillate?

Solution:

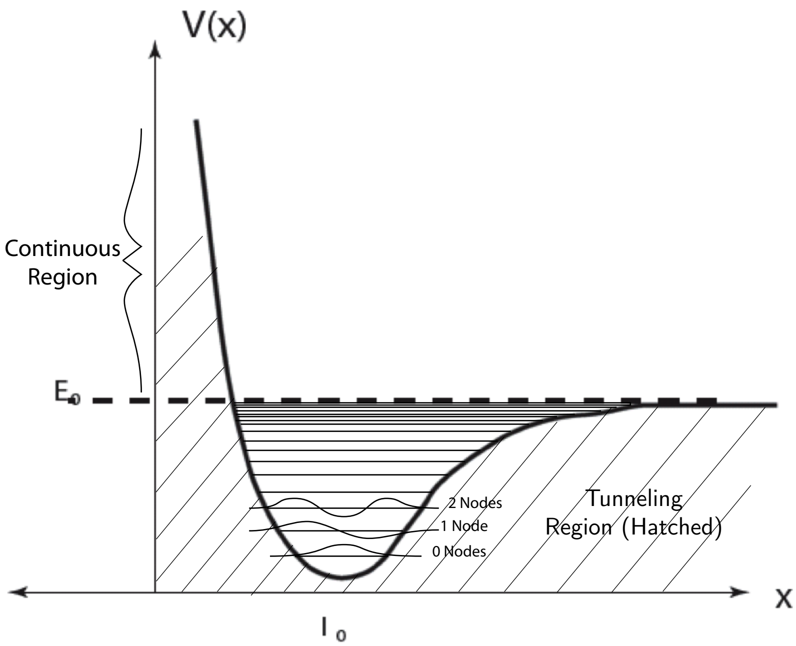
$$
\begin{aligned}
<\psi|\hat{x}|\psi> &= \frac{1}{2} < \sin(k_1 x) e^{\imath \frac{E_1}{\hbar} t)} + \sin(k_3 x) e^{\imath \frac{E_3}{\hbar} t)} |\hat{x}| \sin(k_1 x) e^{\imath \frac{E_1}{\hbar} t)} + \sin(k_3 x) e^{\imath \frac{E_3}{\hbar} t)} > \\
&= \frac{1}{2}[< \sin(k_1 x)|\hat{x}|\sin(k_1 x) > + < \sin(k_1 x)|\hat{x}|\sin(k_3 x) > e^{\imath \frac{E_3 - E_1}{\hbar} t)} \\
&+ < \sin(k_3 x)|\hat{x}|\sin(k_1 x) > e^{\imath \frac{E_1 - E_3}{\hbar} t)} + < \sin(k_3 x)|\hat{x}|\sin(k_3 x) >] \\
&= \frac{1}{2}[\mathbb{I}(x) + < \sin(k_1 x)|\hat{x}|\sin(k_3 x) > e^{\imath \frac{E_3 - E_1}{\hbar} t)} + < \sin(k_3 x)|\hat{x}|\sin(k_1 x) > e^{-\imath \frac{E_3 - E_1}{\hbar} t)}] \\
&= \mathbb{I}(x) + < \sin(k_1 x)|\hat{x}|\sin(k_3 x) > \cos(\omega_{31} t)
\end{aligned}
$$

Where $\mathbb{I}(x) =< \sin(k_1 x)|\hat{x}|\sin(k_1 x) > + < \sin(k_3 x)|\hat{x}|\sin(k_3 x) >$, which doesn't vary with time and $\omega_{31} = \dfrac{E_3 - E_1}{\hbar}$.

2. (28 pts) Consider a mass moving in the 1D potential shown in Figure 1.
   (a) Sketch the energy levels of the bound states.
   (b) Label the region of continuous states.
   (c) Sketch out the wavefunctions of the bound states for the lowest three energy levels. How many nodes does each have?
   (d) Label the region where quantum tunneling would be observed.

   Solution:

Figure 1



3. (28 pts) This problem poses questions about the one-dimensional harmonic-oscillator system: a particle of mass m with the potential energy $V(x) = (1/2)k\,x^2$ oscillates with frequency $\omega_0 = \sqrt{k/m}$. The stationary-state solutions to Schrodinger's equation lead to the quantized energy levels of this system, $E_n = (1/2 + n)\hbar\omega_0,\ n = 0, 1, 2, ...$

   The normalized wave-function for the two lowest energy stationary states are

$$\psi_0(x) = (m\omega_0/\pi\hbar)^{1/4}\ \exp(-m\omega_0\,x^2\,/2\hbar)$$

   and

$$\psi_1(x) = (4m^3\omega_0^3/\pi\hbar^3)^{1/4}\ x\ \exp(-m\omega_0\,x^2\,/2\hbar),$$

   respectively. Circle which of the following is true about the harmonic oscillator:

   (a) The expectation value of x is zero in all eigenstates because they are either even or odd functions of x.

   (b) As the mass m increases, the spacing between adjacent energy levels increases.

(c) The uncertainty in position in the lowest energy eigenstate decreases with increasing mass, m.

(d) There are an even number of nodes with states of even n, and an odd number of nodes for states with odd n.

(e) The lowest energy eigenstate is $(1/2)\hbar\omega_0$ above the minimum energy of a classical mass in the same harmonic oscillator potential.

(f) If prepared in the non-stationary state $\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_0(x) + \psi_1(x)]$, the expectation value of position, $< x >$ oscillates with $2\omega_0$ (or $\cos(2\omega_0 \mathrm{t})$).

(g) It is possible to simultaneously measure momentum and energy for the stationary state solutions because the momentum operator commutes with the Hamiltonian.

Solutions: T,F,T,T,T,F,F

(a) True. The hermite polynomials are all even or odd, so squaring them gives an even function (you can also figure this out from the fact that the potential is symmetric, so the probability density must have the same symmetry). Taking this even probability density, multiplying by x (an odd function) and integrating gives zero.

(b) False. The spacing between energy levels is given by $\hbar\omega_0$ where we are given that $\omega_0 = \sqrt{k/m}$. Thus increasing m decreases the spacing.

(c) True. The important thing to notice is that the lowest energy eigenstate is purely a gaussian. Writing it in the form

$$\psi(x) = e^{-x^2/(4\sigma_x^2)}$$

gives us that $\sigma_x^2 = \dfrac{\hbar}{2m\omega_0} = \dfrac{\hbar}{2\sqrt{mk}}$. So we see that the uncertainty decreases with the fourth root of mass. Extra note: the 1/4 in the exponent is there instead of the 1/2 you see in a Gaussian distribution because it it the square of the wave function that gives the distribution, not the wave function itself.

(d) True. We know that the lowest energy eigenstate will have no nodes and nodes increase by one with energy quantum number. Since the first n is 0, we see that there is one node for $n = 1$, two for $n = 2$, and realize that even n gives even nodes, odd n gives odd number of nodes.

(e) True. The lowest state corresponds to $n = 0$ and an energy of $(1/2)\hbar\omega_0$. Classically, we know that the spring will oscillate back and forth, and when it is at the minimum will have a potential energy of 0.

(f) False. Since the wavefunctions are real, the oscillation in time will go as ,

$$\cos(\frac{E_2 - E_1}{\hbar}t) = \cos(\omega_0 t)$$

Explicitly:

$$\begin{aligned}
\langle\Psi|x|\Psi\rangle &= \frac{1}{2}\langle\psi_1|x|\psi_1\rangle + \frac{1}{2}\langle\psi_2|x|\psi_2\rangle + \frac{1}{2}\langle\psi_1|x|\psi_2\rangle + \frac{1}{2}\langle\psi_2|x|\psi_1\rangle \\
&= \mathbf{I}(x) + \frac{1}{2}\int_{-\infty}^{\infty}\psi_1^*(x)\psi_2(x)e^{-i(E_2-E_1)t/\hbar}xdx + \frac{1}{2}\int_{-\infty}^{\infty}\psi_1(x)\psi_2^*(x)e^{i(E_2-E_1)t/\hbar}xdx \\
&= \mathbf{I}(x) + \cos(\omega_0 t)\int_{-\infty}^{\infty}\psi_1(x)\psi_2(x)xdx
\end{aligned}$$

Here I have just called grouped the first two inner products into one term since neither are time-dependent.

(g) False. As shown in PS3, $[\hat{p}, \hat{H}] = 0$ if and only if $V(x)$ is constant over all x which it is not.