Chemistry 120A, Spring 2009

Midterm 1 Solutions

February 20, 2009

Problems

Question 1: Multiple choice problems: $7 \times 3 = 21$ points

1. At a finite potential step, the 2nd derivative of the wavefunction $\frac{\partial \Psi}{\partial x}$, exhibits:

   (a) continuity   (b) a finite step   (c) an infinite step   **B**

2. All else constant, a smaller force constant for the harmonic oscillator will cause the wavelength corresponding to the energy difference between levels to:

   (a) increase   (b) decrease   (c) stay the same   **A**

3. Can a particle in quantum mechanics pass through a potential barrier that is smaller than its kinetic energy?

   (a) always   (b) sometimes   (c) never   **B**

4. Which of the following is the quantity $|\phi\rangle\langle\psi|$?

   (a) a number   (b) a ket   (c) an operator   **C**

5. Which of the following is the quantity $\langle\phi|\psi\rangle$?

   (a) a number   (b) a ket   (c) an operator   **A**

6. All else being equal, if one compares two wavefunctions, the one with the smaller curvature $\left(\frac{\partial^2 \Psi}{\partial x^2}\right)$ will have an energy which is:

   (a) higher   (b) lower   (c) either is possible   **B**

7. Which of the following has the longest de Broglie wavelength?

   (a) a 1 eV He atom   (b) a 1 eV photon   (c) a 1 eV electron   **B**

Question 2: (15 points) Consider applying the Heisenberg uncertainty principle, $\Delta p \Delta x \geq \frac{\hbar}{2}$, to the problem of a particle in a one-dimensional box, with box length a.

(a) (5 points) Estimate the uncertainties that are expected in the position (from box size) and momentum (from Heisenberg), Δx and Δp

(1) Because the particle is in the box, we know that $\boxed{\Delta x \leq a}$
(Any answer in the range $0.1a \leq \Delta x \leq a$ is acceptable)

(2) Then, from the Heisenberg uncertainty principle,

$$\Delta p \Delta x \geq \frac{\hbar}{2} \Rightarrow \Delta p \geq \frac{\hbar}{2\Delta x} \Rightarrow \boxed{\Delta p \geq \frac{\hbar}{2a}}$$

(b) (5 points) From your estimate of Δp estimate the lowest possible energy of the system.

The lowest allowed energy level for the particle in a box has a non-zero kinetic energy. This kinetic energy can be estimated from Δp:

$$KE = \frac{p^2}{2m} \cong \frac{(\Delta p)^2}{2m} \cong \frac{\left(\frac{\hbar}{2a}\right)^2}{2m} \cong \boxed{\frac{\hbar^2}{8ma^2}}$$

(c) (5 points) Compare your result for the lowest energy of the particle in a box with the result from classical mechanics and discuss the effect of increasing the mass of the particle.

From quantum, we have the lowest energy of $\frac{\hbar^2}{8ma^2}$.
From classical mechanics, we have the lowest energy of 0, $\left(\text{from } E = \frac{1}{2}mv^2, \text{ for } v = 0\right)$
In classical mechanics, the particle can be totally at rest ($v = 0$), and can have an energy of zero. In quantum mechanics, the lowest energy the particle can have is a non-zero number (the zero-point energy). But, as mass is increased in the quantum mechanical model, the zero-point energy decreases, approaching the classical limit of zero as $m \to \infty$.

Question 3: (18 points). Commutators and measurement. The commutator of two operators is defined as $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$, and, if this is zero, we say that the two operators commute. Commuting and non-commuting operators have very different properties, which this problem explores.

(a) (6 points) Prove that two commuting operators have common eigenfunctions (conversely two non-commuting operators do not).

If two operators commute, then $\hat{A}\hat{B} = \hat{B}\hat{A}$. If the eigenfunctions/eigenvectors of $\hat{A}$ are given by:

$$\hat{A}\left|\phi_n\right\rangle = a_n\left|\phi_n\right\rangle$$

Then:

$$\hat{A}\left[\hat{B}\left|\phi_n\right\rangle\right] = \hat{A}\hat{B}\left|\phi_n\right\rangle = \hat{B}\hat{A}\left|\phi_n\right\rangle = \hat{B}a_n\left|\phi_n\right\rangle = a_n\hat{B}\left|\phi_n\right\rangle = a_n\left[\hat{B}\left|\phi_n\right\rangle\right]$$

$\Rightarrow$ We can see that $\hat{B}\left|\phi_n\right\rangle$ is also an eigenfunction of $\hat{A}$ **<u>if</u>** $\hat{A}$ and $\hat{B}$ commute.

$\Rightarrow$ Therefore, we must have $\hat{B}\left|\phi_n\right\rangle \propto \left|\phi_n\right\rangle$, as they are both eigenfunctions of $\hat{A}$.

$\Rightarrow$ The only way this can be true is if $\hat{B}\left|\phi_n\right\rangle$ is equal to a constant times the eigenfunction $\left|\phi_n\right\rangle$ (In other words, $\hat{B}$ cannot cause the eigenfunction $\left|\phi_n\right\rangle$ to be changed)

$\Rightarrow$ We can now see that we must have $\hat{B}\left|\phi_n\right\rangle = b_n\left|\phi_n\right\rangle$, which shows that $\left|\phi_n\right\rangle$ is also an eigenfunction of $\hat{B}$, with eigenvalue b_n.

$\Rightarrow$ Hence, commuting operators $\hat{A}$ and $\hat{B}$ must have common eigenfunctions.

(b) (6 points) Evaluate the commutator of the operators for kinetic energy and position.

The operators for kinetic energy and position are $\hat{x} = x$ and $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{aligned}
\left[\hat{T}, \hat{x}\right]\psi(x) &= \hat{T}\hat{x}\psi(x) - \hat{x}\hat{T}\psi(x) \\
&= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}x\psi(x) - x\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\psi(x) \\
&= -\frac{\hbar^2}{2m}\left(\frac{d}{dx}\left\{\frac{d}{dx}x\psi(x)\right\} - x\frac{d^2}{dx^2}\psi(x)\right) \\
&= -\frac{\hbar^2}{2m}\left(\frac{d}{dx}\left\{\psi(x) + x\frac{d\psi(x)}{dx}\right\} - x\frac{d^2\psi(x)}{dx^2}\right) \\
&= -\frac{\hbar^2}{2m}\left(\left\{\frac{d\psi(x)}{dx} + \frac{d\psi(x)}{dx} + x\frac{d^2\psi(x)}{dx^2}\right\} - x\frac{d^2\psi(x)}{dx^2}\right) \\
&= -\frac{\hbar^2}{2m}\left(2\frac{d\psi(x)}{dx} + x\frac{d^2\psi(x)}{dx^2} - x\frac{d^2\psi(x)}{dx^2}\right) \\
\left[\hat{T}, \hat{x}\right]\psi(x) &= -\frac{\hbar^2}{m}\frac{d\psi(x)}{dx} \Rightarrow \boxed{\left[\hat{T}, \hat{x}\right] = -\frac{\hbar^2}{m}\frac{d}{dx}}
\end{aligned}$$

Another way this can done is:

$$\begin{aligned}
\left[\frac{\hat{p^2}}{2m}, \hat{x}\right] &= \frac{\hat{p}^2}{2m}\hat{x} - \hat{x}\frac{\hat{p}^2}{2m} \\
&= \frac{1}{2m}\left(\hat{p}^2\hat{x} - \hat{x}\hat{p}^2\right) \\
&= \frac{1}{2m}\left(\hat{p}\hat{p}\hat{x} - \hat{x}\hat{p}\hat{p}\right) \\
&= \frac{1}{2m}\left(\hat{p}\hat{p}\hat{x} - \hat{p}\hat{x}\hat{p} + \hat{p}\hat{x}\hat{p} - \hat{x}\hat{p}\hat{p}\right) \\
&= \frac{1}{2m}\left(\hat{p}\left\{\hat{p}\hat{x} - \hat{x}\hat{p}\right\} + \left\{\hat{p}\hat{x} - \hat{x}\hat{p}\right\}\hat{p}\right) \\
&= \frac{1}{2m}\left(\hat{p}\left[\hat{p}, \hat{x}\right] + \left[\hat{p}, \hat{x}\right]\hat{p}\right) \\
&= \frac{1}{2m}\left(-i\hbar\hat{p} - i\hbar\hat{p}\right) \\
&= \frac{1}{2m}\left(-2i\hbar\hat{p}\right) \\
&= -\frac{i\hbar}{m}\hat{p} \\
&= -\frac{i\hbar}{m} \cdot \frac{\hbar}{i}\frac{d}{dx} \\
&= -\frac{\hbar^2}{m}\frac{d}{dx}
\end{aligned}$$

(c) (6 points) Using your results from parts (a) and (b) above, and the way in which measurement affects a system in quantum mechanics, discuss whether or not it is possible to know the value of kinetic energy and position simultaneously based on alternating measurements of kinetic energy and position.

Kinetic energy and position do not commute, and therefore the cannot be measured simultaneously. This is because they do not share common eigenfunctions. A measurement of kinetic energy will changes the state of the system to the basis of kinetic energy eigenfunctions. A subsequent measurement of position will then switch the state into position eigenfunctions. Therefore, alternating these two operators will constantly change the basis the which the state is represented. This causes the state to be different each time a measurement is taken, and thus will never give a consistent value for alternating measurements of non-commuting operators.

Question 4: (16 Points) Suppose a two-level system is described by the Hamiltonian:

$$\hat{H} = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix}$$

Further, suppose that the following normalized state of the system is prepared:

$$|\psi\rangle = \frac{3}{5}|\phi_1\rangle - \frac{4}{5}|\phi_2\rangle$$

(a) (4 points) What is the probability of measuring the system to have the energy E_1 immediately after the above state is prepared?

$$\begin{aligned} |\psi\rangle &= \frac{3}{5}|\phi_1\rangle - \frac{4}{5}|\phi_2\rangle \\ \Pr(|\phi_1\rangle) = |\langle\phi_1|\psi\rangle|^2 &= \left|\frac{3}{5}\langle\phi_1|\phi_1\rangle - \frac{4}{5}\langle\phi_1|\phi_2\rangle\right|^2 \\ &= \left|\frac{3}{5}\right|^2 = \frac{9}{25} \end{aligned}$$

(b) (7 points) Solve for the wavefunction at time t, and hence discuss how the probability of finding the system in the state E_1 varies with time.

Solve for the wavefunction at time t, and hence discuss how the probability of finding the system in the state E_1 varies with time.

$$\begin{aligned} |\psi(t)\rangle &= \frac{3}{5}\exp(-iE_1t/\hbar)|\phi_1\rangle - \frac{4}{5}\exp(-iE_2t/\hbar)|\phi_2\rangle \\ \Pr(|\phi_1\rangle) &= |\langle\phi_1|\psi(t)\rangle|^2 \\ &= \left|\frac{3}{5}\exp(-iE_1t/\hbar)\langle\phi_1|\phi_1\rangle - \frac{4}{5}\exp(-iE_2t/\hbar)\langle\phi_1|\phi_2\rangle\right|^2 \\ &= \frac{3}{5} * \frac{3}{5}\exp(iE_1t/\hbar)\exp(-iE_1t/\hbar) = \frac{9}{25} \end{aligned}$$

$\therefore$ The probability of finding the system in the state E_1 is time-independent.

(c) (5 points) Discuss qualitatively, with equations as appropriate, how this would (or would not change) if the Hamiltonian were changed to:

$$\hat{H} = \begin{bmatrix} E_1 & w \\ w & E_2 \end{bmatrix}$$

Since a perturbation has been introduced to the system, $|\phi_1\rangle$ and $|\phi_2\rangle$ are no longer eigenstates of the Hamiltonian. In fact the new eigenstates of the Hamiltonian can be expressed as a superposition of the $|\phi_1\rangle$ and $|\phi_2\rangle$. From part b we know that an eigenstate has no time-dependence. However, since we are now dealing with states that are not eigenstates, the probability that the system will be in state $|\phi_1\rangle$ varies sinusoidally with time. A proof of this can be seen on pages 8 and 9 of chapter 3.