Chem 120A Midterm 1

Justin Yeung

TOTAL POINTS

22 / 30

QUESTION 1

1 Question 1 **3 / 3**

- ✓ + **1 pts** **Correct boundary conditions (wavefunction is 0 at edges of box), statement must be explicit to receive credit. Statement about the wavefunction being 0 outside the box without an additional statement about the edges is not acceptable.**
- ✓ + **1 pts** **Statement of the general probability equation (Pr(x) = |Psi(x)|^2, not just the PIB probability expression) or explicit statement of why probability is 0 at boundaries that is based on the wavefunction (statement that probability of finding particle in box is 1 is not acceptable because this question is asking why that statement is true)**
- ✓ + **1 pts** **Particle cannot be outside the box because of infinite potential**
- \+ **0 pts** Incorrect

QUESTION 2

2 Question 2 **1 / 2**

- ✓ + **1 pts** **H Psi = E Psi**
- \+ **1 pts** Complete explanation (all definitions and statements must be correct, must involve the word "eigenvalue")
- \+ **0 pts** Incorrect

💬 Statement in words needs to be relating to H Psi = E Psi

QUESTION 3

3 Question 3 **3 / 3**

- \+ **1 pts** Statement of how to normalize
- \+ **1 pts** Mostly correct work, minor error that led to incorrect answer
- ✓ + **3 pts** **N = 1/3**
- \+ **0 pts** Incorrect

QUESTION 4

4 Question 4 **2 / 2**

- ✓ + **1 pts** **Energies (all or nothing)**
- ✓ + **1 pts** **Probabilities (all or nothing)**
- \+ **0 pts** Incorrect

QUESTION 5

5 Question 5 **2 / 2**

- ✓ + **2 pts** **Full credit**
- \- **1 pts** Signage wrong, assignment correct
- \- **2 pts** Row/Column assignment incorrect
- \- **2 pts** Wrong signs/numbers/assignment/inclusion of perturbation

QUESTION 6

6 Question 6 **1 / 1**

- ✓ + **1 pts** **Correct**
- \+ **1 pts** Added correct perturbation to whatever existing matrix was in place for Question 5
- \+ **0 pts** Any deviation from above, including incorrect sign

QUESTION 7

7 Question 7 **3 / 3**

- ✓ + **3 pts** **Fully correct**
- \+ **2 pts** Eigenvalue procedure done correctly for wrong matrix
- \+ **1 pts** Correctly set up determinant, in equation and/or matrix form
- \+ **1 pts** For each correct eigenvalue
- \+ **1 pts** Eigenvalues correct except for sign
- \+ **0 pts** Incorrect

QUESTION 8

8 Question 8 **2 / 2**

- ✓ + **2 pts** **Chooses correct lowest eigenvalue, solves**

for eigenvector

+ **2 pts** Applies Hamiltonian to given vector to yield lowest energy eigenvalue

+ **1 pts** Solves for eigenvector, but work is incomplete

+ **0 pts** Either 1 or 2 done incorrectly or inadequately, or attempted with incorrect matrix

+ **0 pts** Begins correct procedure, but work is half-hearted or inadequate

QUESTION 9

9 Question 9 **0 / 2**

+ **1 pts** Pr(Li2s) = |< Li2s|1 >|^2 = 4/13

+ **1 pts** Li is less electronegative than H; hence, results are consistent with chemical intuition

✓ + **0 pts** **incorrect**

QUESTION 10

10 Question 10 **0 / 2**

+ **2 pts** Correct qualitative: some acceptable combination of reasoning. Li(2s) is not an eigenstate of H. This state is a superposition of eigenvectors one and two, thus causing time dependent interference.

+ **2 pts** Correct quantitative: illustrates proper superposition with time dependent coefficients, including appropriate eigenvector components. Demonstrates that the probability expression yields interference, and is thus time dependent.

+ **1 pts** Either qualitative or quantitative explanation is partially correct, or inadequate

+ **1 pts** Provides an acceptable answer based on good chemical intuition, but with no discussion of the Hamiltonian or eigenstates.

✓ + **0 pts** **Either qualitative or quantitative explanation is incorrect and/or inadequate**

QUESTION 11

11 Question 11 **1 / 2**

+ **1 pts** Evaluated TX and XT properly

✓ + **1 pts** **Evaluated T and X commutator**

+ **0 pts** Incorrect

QUESTION 12

12 Question 12 **2 / 2**

✓ + **1 pts** **delta x = L**

✓ + **1 pts** **delta p = hbar/2L**

+ **0 pts** Incorrect

QUESTION 13

13 Question 13 **2 / 2**

✓ + **2 pts** **Showing A and B have common eigenfunctions**

+ **1 pts** Set up correctly, but didn't prove

+ **0 pts** Incorrect

QUESTION 14

14 Question 14 **0 / 2**

+ **1 pts** Stating T and X don't commute or uncertainty principle

+ **1 pts** Describing states of alternating measurement

✓ + **0 pts** **Incorrect**

Chemistry 120A

Spring Semester, 2019; Prof. Head-Gordon
1st Mid-Term Exam: Thursday February 21

Name: Justin Yeung

Instructions: (1) Keep calm, write clearly so we can give partial credit! Do all questions.
(2) The exam is closed book.
(3) The exam has 5 pages (use blank back sides as scratch paper (not graded).

Grade:	Problem 1: Particle in a box (10 points)	________________
	Problem 2: Two-level system (12 points)	________________
	Problem 3: Uncertainty principle (8 points)	________________
	Total (30 points)	________________

Useful facts and figures:

$h=6.626755\times10^{-34}$ J s

$k=1.380658\times10^{-23}$ J K^{-1}

$N_A=6.022137\times10^{23}$ mol^{-1}

1 eV = 1.60219×10^{-19} J

$\hbar = h/(2\pi)$

$$ax^2+bx+c=0$$

$$\Rightarrow x=\left(-b\pm\sqrt{b^2-4ac}\right)\Big/2a$$

$$\hat{H}=\frac{\hat{p}^2}{2m}+V(x)$$

$$\hat{p}=\frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\hat{H}|\psi\rangle=\frac{-\hbar}{i}\frac{\partial}{\partial t}|\psi\rangle$$

$$\Delta p\Delta x\geq\hbar/2$$

$$\left[\hat{A},\hat{B}\right]=\hat{A}\hat{B}-\hat{B}\hat{A}$$

Question I. A particle in a 1-dimensional box of length L with potential:

$$V(x)=\begin{cases} 0 & \text{for } 0<x<L \\ \infty & \text{for } x\le 0,\ x\ge L \end{cases}$$

The energy eigenvalues and normalized eigenfunctions are as follows;

$$E_n=\frac{n^2\pi^2\hbar^2}{2mL^2}; \qquad \phi_n(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad n=1,2,3\ldots$$

1. (3 points) What boundary conditions must a valid state vector obey for the particle in a box problem? Give a brief explanation of the origin of those conditions in terms of probability.

In Particle in a box, the $\phi_n(r)$ must be zero when @ the ends of the box, so $x=0$, and $x=L$. This is because we need the potential @ the ends to be infinite, so no wavefcn can^not^ reside at these ends, so their probabilities must be zero also.
Not to mention, probability of finding ϕ in ^entire^ box must be $=1$ and normalized, so $\sqrt{\frac{2}{L}}$ is there for this reason.

2. (2 points) What property must a ket (or wavefunction) have in order to be an energy eigenfunction? Answer with an equation, clearly defining any terms you introduce.

$$\hat{H}|\Psi\rangle = E_n|\Psi\rangle$$

① Closure/superposition: if a & b ^& c^ are arbitrary constants, & f is just any space: ^if^ $a|\Psi_1\rangle \in f$, $b|\Psi_2\rangle \in f$ then → $a|\Psi_1\rangle + b|\Psi_2\rangle = c|\Psi_3\rangle \in f$

② Scalar product exists: $\langle\Psi_i|\Psi\rangle$ bra, or a ket in complex space

③ Orthogonal basis: $\langle\Psi_i|\Psi_j\rangle = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i\neq j \end{cases}$

④ $|\Psi(x,t)\rangle$ must be separable such that $=\Psi(x)\Psi(t)$ or $\Psi(x)e^{-iEt/\hbar}$

3. (3 points) Find the value of the constant N which will normalize the following state vector:

$$|\Psi\rangle = N\left\{2|\phi_{n=1}\rangle - 2i|\phi_{n=2}\rangle + |\phi_{n=3}\rangle\right\}$$

$$||\Psi\rangle| = \sqrt{2^2+(-2i)(2i)+1^2} = \sqrt{4+1+4} = 3$$

$$\boxed{N = 1/3}$$

4. (2 points) The energy of the state given above is measured. What are the possible values of the energy can be obtained, and their probabilities? $Pr = c^*c = |c|^2$

$$E_1 = \frac{1^2\pi^2\hbar^2}{2mL^2} = \frac{1}{2}\frac{\pi^2\hbar^2}{mL^2} \Rightarrow Pr(\phi_{n=1}) = \left(\frac{2}{3}\right)^2 = \frac{4}{9}$$

$$E_2 = \frac{2^2\pi^2\hbar^2}{2mL^2} = 2\frac{\pi^2\hbar^2}{mL^2} \rightarrow Pr(\phi_{n=2}) = \left(\frac{-2i}{3}\right)\left(\frac{2i}{3}\right) = \frac{4}{9}$$

$$E_3 = \frac{3^2\pi^2\hbar^2}{2mL^2} = \frac{9}{2}\frac{\pi^2\hbar^2}{mL^2} \rightarrow Pr(\phi_{n=3}) = \left(\frac{1}{3}\right)^2 = \frac{1}{9}$$

$\phi_{n=1}$: $E = \frac{5.205\cdot 10^{-34}}{mL^2}$
$Pr = 4/9$

$\phi_{n=2}$: $E = \frac{2.0819\cdot 10^{-33}}{mL^2}$
$Pr = 4/9$

$\phi_{n=3}$: $E = \frac{4.684\cdot 10^{-33}}{mL^2}$
$Pr = 1/9$

Question II. Let's make a toy model (as a 2-level system) of the chemical bond between two elements like Li and H that each have one unpaired electron, with different electronegativities. Let us say that the ionization energy of H is 10 eV and the ionization energy of Li is 5 eV (these are not quite the truth, but will make later calculations easier). For simplicity we will assume that these levels are orthogonal to each other.

5. (2 points) Write the 2x2 Hamiltonian matrix describing the H and Li atoms when they are not interacting with each other. Use the first row and column for H, and the second for Li. Be careful with signs!

$$\boxed{\begin{bmatrix} -10 & 0 \\ 0 & -5 \end{bmatrix}}$$

- Since Li has the lower IP, it's easier to remove the e⁻ from system, so Li is HOMO. H thus takes the electron, and is the LUMO.

HOMO : -IP

LUMO : -EA

6. (1 point) Let us now permit the Li atom and the H atom to interact with each other, with an off-diagonal coupling that is -6 eV in strength. Write the perturbed Hamiltonian matrix that includes the interaction between Li and H.

$$\begin{bmatrix} -10 & -6 \\ -6 & -5 \end{bmatrix}$$

7. (3 points) Find the eigenvalues of the perturbed Hamiltonian, which will represent the energy levels (molecular orbital energies) of LiH modeled as a 2-level system

$$\lambda = \bar{E} \pm \sqrt{\Delta^2 + \omega^2}$$

$$\bar{E} = \tfrac{1}{2}(E_1 + E_2)$$

$$\Delta = \tfrac{1}{2}(E_1 - E_2)$$

$$\lambda = \frac{1}{2}(-10-5) \pm \sqrt{\left(\frac{-10+5}{2}\right)^2 + (-6)^2}$$

$$= \frac{-15}{2} \pm \sqrt{\frac{25}{4} + 36}$$

$$\boxed{\lambda = -1 \quad \text{and} \quad \lambda = -14}$$

8. (2 points) Show that the eigenvector associated with the lowest energy level is:

$$13^{-1/2}\begin{bmatrix} 3 \\ 2 \end{bmatrix}$$

$\lambda = -14$

$$\begin{bmatrix} -10+14 & -6 \\ -6 & -5+14 \end{bmatrix} = \begin{bmatrix} 4 & -6 \\ -6 & 9 \end{bmatrix} = \begin{bmatrix} 2 & -3 \\ 2 & -3 \end{bmatrix}$$

$$\text{nul}\begin{bmatrix} 2 & -3 \\ 0 & 0 \end{bmatrix} \Rightarrow 2x_1 - 3x_2 = 0$$

$$x_1 = \tfrac{3}{2}x_2 \quad \phi = \begin{bmatrix} \frac{3}{2} \\ 1 \end{bmatrix} x_2 \overset{\times 2}{\Rightarrow} \phi = \begin{bmatrix} 3 \\ 2 \end{bmatrix} \overset{\text{normalize}}{\Rightarrow}$$

$|\phi| = \sqrt{3^2+2^2}$

$|\phi| = \sqrt{13}$

$$\Downarrow$$

$$\boxed{\phi = \frac{1}{\sqrt{13}}\begin{bmatrix} 3 \\ 2 \end{bmatrix}}$$

9. (2 points) If the system is placed in the lowest energy level, what is the probability that it is localized on the 2s orbital of Li? Discuss whether or not your result is consistent with chemical intuition.

$$Pr = |\langle \phi | \psi \rangle|^2$$

2s orbital: $\begin{bmatrix} 0 \\ -5 \end{bmatrix}$

→ the energy needed to remove e^- @ the valence orbital, or 2s orbital.

$$= \left(\frac{1}{\sqrt{13}}\begin{bmatrix} 3 & 2 \end{bmatrix}\begin{bmatrix} 0 \\ -5 \end{bmatrix}\right)^2$$

$$= \frac{1}{13}(-10) = \frac{10}{13} = \boxed{\frac{100}{169}}$$

Chemical intution tells us that we should expect or be nearly certain that the valence e^- resides in the 2s orbital, since it's the next orbital to occupy after 1s, and Li only has $3e^-$. Thus, the result slightly fits with intution, however, the probability should be closer to or basically equal to 1.

10. (2 points) If the system is placed in the 2s orbital of Li at time zero, explain qualitatively (or quantitatively if you can) how the probability of finding the system localized on Li changes with time.

The probability should be time-independent since the energy has been localized on lithium. When localized, the state fcn of the 2s orbital remains unchanged, and so the probabilities should not depend on time. in the equation above, $Pr = \left(\frac{1}{\sqrt{13}}\begin{bmatrix} 3 & 2 \end{bmatrix}\begin{bmatrix} 0 \\ -5 \end{bmatrix}\right)^2$. Since $\begin{bmatrix} 0 \\ -5 \end{bmatrix}$ will remain the same, as well as the eigenfcn since the bond has already been made, Pr will remain the same. The probability changes if the system has been perturbed, such as the chemical bond breaks or a new bond is formed.

Question III: Uncertainty principle, 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….

11. (2 points) Evaluate the commutator of the operators for kinetic energy and position (see front page for definitions).

$$[\hat{K},\hat{x}] = \hat{K}\hat{x} - \hat{x}\hat{K}$$

$$= -\frac{\hbar^2}{2m}\underbrace{\frac{d^2}{dx^2}(x)}_{=0 \text{ b/c } \frac{d^2}{dx^2}(x)=0} - \underbrace{x\left(\frac{-\hbar^2}{2m}\right)\frac{d^2}{dx^2}}_{=0 \text{ b/c } \frac{d^2}{dx^2}(1)=0}$$

$$\boxed{[\hat{K},\hat{x}]=0}$$

12. (2 points) For a particle in a box of length *L*, estimate the uncertainties that are expected in the position (from box-size) and momentum (from Heisenberg), Δx and Δp.

$$\Delta p \Delta x \geq \hbar/2$$

$\boxed{\Delta p \geq \frac{\hbar}{2L}}$ ← uncertainty from momentum

PIB: $V = \begin{cases} 0 & 0<x<L \\ \infty & x\leq 0,\ x\geq L \end{cases}$

$\boxed{0<\Delta x<L}$ ← uncertainty in position

13. (2 points) Prove that two commuting operators have common eigenfunctions (conversely two non-commuting operators do not).

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

$$\hat{A}|\psi_1\rangle = a_1|\phi_1\rangle \quad \text{and} \quad \hat{B}|\psi_1\rangle = b_2|\phi_2\rangle$$

$$\Downarrow \qquad\qquad \Downarrow$$

① $\hat{B}\hat{A}|\psi_1\rangle = \hat{B}a_1|\phi_1\rangle$ ② $\hat{A}\hat{B}|\psi_1\rangle = \hat{A}b_2|\phi_2\rangle$

① - ② $\cancel{\hat{B}\hat{A}|\psi_1\rangle - \hat{A}\hat{B}|\psi_1\rangle} = \hat{B}a_1|\phi_1\rangle - \hat{A}b_2|\phi_2\rangle$

=0 since commutator $\hat{B}\hat{A}-\hat{A}\hat{B}=0$

$$\hat{B}a_1|\phi_1\rangle - \hat{A}b_2|\phi_2\rangle = 0$$

$$b_2\hat{A}|\phi_2\rangle = a_1\hat{B}|\phi_1\rangle$$

if $|\phi_2\rangle = |\phi_1\rangle$

$b_2 a_1 = a_1 b_2$

- They must be same eigenfunctions in order for equality $b_2\hat{A}|\phi_2\rangle = a_1\hat{B}|\phi_1\rangle$ to work

In essence,
$\hat{B}|\phi_1\rangle = b_2$
and
$\hat{A}|\phi_2\rangle = a_1$
so
$|\phi_1\rangle = |\phi_2\rangle$

14. (2 points) Using your results from the questions 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.

From question 11, we see that $[\hat{k}, \hat{x}] = 0$, so that K.E. and position <u>do</u> commute. With that said, the two also have common eigenfunctions. Because of these results, we know that we <u>can</u> simultaneously know KE and position values. This is the case because commuting operators do <u>not</u> change the state of the system, so the system constantly is the same after $\hat{k}$ or $\hat{x}$ measurements are taken, so we can evaluate both K.E and position @ the same time with no consequences. In othe words, we can continually break down the space to 1D with $\hat{k}$ and $\hat{x}$ since state isn't changing.