Chemistry 3PA3 - Midterm

November 6, 2015 7-9 pm

A Casio FX991 calculator, and 1 $8\frac{1}{2} \times 11"$ sheet written on both sides, are the only aids allowed.

$$h = 4.136 \times 10^{-15} \text{ eV s}$$

Question	**Out of ...**	**Your Mark**
1	10	
2	15	
3	20	
4	15	
5	20	
Total	**80**	

1. Which of the following statements are **true**? For statements that are false, **change** one (or a few) word(s) or number(s) to make it a true statement. [2 mark each + 1 mark for each corrected false statement]

a. Scanning tunneling microscopy (STM) achieves atomic-level resolution because of the exponential sensitivity of electron tunneling probability.

b. Every pair of observables in quantum mechanics is subject to an uncertainty principle such that if one observable has well-defined value, the other is completely uncertain.

c. The number of peaks observed in a low energy electron diffraction (LEED) experiment increases as the speed of the electrons increases.

d. Energy eigenstates are unaltered by time evolution in accord with the time dependent Schrödinger equation.

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a. True.

b. False. Only pairs of observables represented by non-commuting operators have an uncertainty principle - i.e., some pairs of observables have an uncertainty principle.

c. True.

d. False. Under time evolution, energy eigenstates vary - but only via a time dependent phase factor, $\exp(-iE_n t/\hbar)$, where E_n is the associated energy eigenvalue.

2. Consider a system with an observable, $\mathcal{A}$, represented by Hermitian operator, $\hat{A}$. Operator $\hat{A}$ has four normalized eigenfunctions, $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$ and $\psi_4(x)$, such that

$$\left(\hat{A}\psi_j\right)(x) = j\psi_j(x), \qquad j = 1, 2, 3 \text{ or } 4.$$

The wavefunction,

$$\psi(x) = \frac{1}{\sqrt{2}}\left(\psi_1(x) + \psi_4(x)\right)$$

represents a specific state of this system.

a. What are the **possible outcomes** of a measurement of $\mathcal{A}$, for **all possible system states**? [5 marks]

b. What are the **possible outcomes** of a measurement of $\mathcal{A}$, if the system is in **state** $\psi(x)$? Explain. [5 marks]

c. What is the **expectation value** of $\mathcal{A}$ for the system in state $\psi(x)$? How is this expectation value of $\mathcal{A}$ **related** to the outcomes of measurements of $\mathcal{A}$? [5 marks]

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a. The possible outcomes of a measurement of $\mathcal{A}$, for all possible system states, are the four eignevalues of $\hat{A}$, 1, 2, 3 and 4.

b. For the system in state, $\psi(x)$, the possible outcomes of a measurement of $\mathcal{A}$ are 1 and 4. This is because $\psi(x)$ is orthogonal to $\psi_2(x)$ and $\psi_3(x)$. The probability of a measurement yielding 2 is

$$\begin{aligned}
\rho_2 &= \left|\langle\psi_2|\psi\rangle\right|^2 \\
&= \left|\left\langle\psi_2\left|\frac{1}{\sqrt{2}}(\psi_1 + \psi_4)\right.\right\rangle\right|^2 \\
&= \frac{1}{2}\left|\underbrace{\langle\psi_2|\psi_1\rangle}_{=0} + \underbrace{\langle\psi_2|\psi_4\rangle}_{=0}\right|^2 \\
&= 0.
\end{aligned}$$

The inner products are zero because they are inner products of distinct eigenfunctions of a Hermitian operator. The probability of outcome 3 is similarly zero.

c. The expectation value of $\mathcal{A}$ for the system in state $\psi(x)$ is

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\begin{aligned}
\langle \psi | \hat{A}\psi \rangle &= \left\langle \frac{1}{\sqrt{2}}(\psi_1 + \psi_4) \middle| \hat{A}\frac{1}{\sqrt{2}}(\psi_1 + \psi_4) \right\rangle \\
&= \frac{1}{2}\langle \psi_1 + \psi_4 | \hat{A}\psi_1 + \hat{A}\psi_4 \rangle \\
&= \frac{1}{2}\langle \psi_1 + \psi_4 | \psi_1 + 4\psi_4 \rangle \\
&= \frac{1}{2}\Big(\underbrace{\langle \psi_1 | \psi_1 \rangle}_{=1} + 4\underbrace{\langle \psi_1 | \psi_4 \rangle}_{=0} + \underbrace{\langle \psi_4 | \psi_1 \rangle}_{=0} + 4\underbrace{\langle \psi_4 | \psi_4 \rangle}_{=1} \Big) \qquad \psi_1 \text{ and } \psi_4 \text{ are normalized} \\
&= \frac{1}{2}(1+4) = \frac{5}{2}.
\end{aligned}
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The expectation value of $\mathcal{A}$ is the average of many measurements of $\mathcal{A}$ for systems in the same state (in this case, $\psi(x)$). Here, it is the equally-weighted average of eigenvalues 1 and 4.

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3. Suppose there are four electrons in a well with depth, $V_{\mathrm{d}} = 17.00$ eV. The electrons can be treated as independent particles with particle-in-a-box energy levels and energy eigenstates. The well width, L, is such that $\pi^2\hbar^2/(2mL^2) = 1.00$ eV, where m is the mass of an electron.

a. What is the **energy** of the ground state of this four electron system? [5 marks]

b. What is the **ionization energy** of this system? [5 marks]

c. What is the **electron affinity** of this system? [5 marks]

d. What **dipole-allowed transitions** are possible for this system? What are the associated transition **frequencies**? **Sketch** the spectrum. [5 marks].

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a. In the ground state, the four electrons occupy the lowest two energy levels,

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} = 1.00 \text{ eV}$$

and

$$E_2 = \frac{2^2\pi^2\hbar^2}{2mL^2} = 4.00 \text{ eV},$$

with two electrons in each of the two associated orbitals. Thus,

$$\begin{aligned} E_{\text{g.s.}} &= 2 \times E_1 + 2 \times E_2 \\ &= 10.00 \text{ eV}. \end{aligned}$$

b. The ionization energy is the energy of the ground state of the cation and an unbound electron with energy, V_{d}, minus the energy of the ground state of the neutral species. Specifically,

$$\begin{aligned} I &= E_{\text{g.s. cat.}} + V_{\mathrm{d}} - E_{\text{g.s.}} \\ &= 2 \times E_1 + E_2 + V_{\mathrm{d}} - E_{\text{g.s.}} \\ &= 6.00 + 17.00 - 10.00 \text{ eV} \\ &= 13.00 \text{ eV}. \end{aligned}$$

c. The electron affinity is the energy of the ground state of the anion minus the energy of the ground state of the neutral species and an unbound electron with energy, V_{d}. Specifically,

$$\begin{aligned} A &= E_{\text{g.s. an.}} - (E_{\text{g.s.}} + V_{\mathrm{d}}) \\ &= 2 \times E_1 + 2 \times E_2 + E_3 - (E_{\text{g.s.}} + V_{\mathrm{d}}) \\ &= 10.00 + 9.00 - (10.00 + 17.00) \text{ eV} \\ &= -8.00 \text{ eV}. \end{aligned}$$

d. The allowed transitions are one electron transitions. There are four energy levels - the lowest two are filled, and the highest two are empty. The lowest energy transition is the 2 to 3 transition. The 2 to 4 transition is dipole-forbidden (it is even to even). The 1 to 3 transition is also dipole-forbidden (it is odd to odd). The remaining transition, 1 to 4 is dipole-allowed - though it has small intensity. The transition frequencies of the dipole-allowed transitions are

$$\nu_{2\text{ to }3} = \frac{E_3 - E_2}{h} = \frac{9.00 - 4.00\text{ eV}}{4.136\times 10^{-15}\text{ eV s}}$$
$$= 1.21\times 10^{15}\text{ s}^{-1}$$
$$= 1.21\text{ PHz}$$

and

$$\nu_{1\text{ to }4} = \frac{E_4 - E_1}{h} = \frac{16.00 - 1.00\text{ eV}}{4.136\times 10^{-15}\text{ eV s}}$$
$$= 3.63\text{ PHz.}$$

A sketch of the spectrum shows two peaks. The second peak has 3× the frequency of the first peak, and it has much smaller amplitude.

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4. Consider a single particle, with mass m, subject to the potential energy,

$$V(x) = \begin{cases} \infty, & x \le 0 \\ 0, & 0 < x < L \\ V_{\mathrm{d}}, & L \le x \end{cases}.$$

a. What is the **general solution** (i.e., do not yet apply the boundary conditions) to the Schrödinger equation for (i) $0 < x < L$, and (ii) $L \le x$? [5 marks]

b. **Simplify** the general solutions of part a by applying boundary conditions at $x = 0$ and $x = \infty$. [5 marks]

c. Apply boundary conditions at $x = L$ to **determine** a quantization equation for a particle in a well. The energies that solve this equation are the energy eigenvalues. [5 marks].

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a. The general solutions to the Schrödinger equation: (i) For $0 < x < L$,

$$\psi(x) = A\sin\left(\frac{\sqrt{2mE}\,x}{\hbar}\right) + B\cos\left(\frac{\sqrt{2mE}\,x}{\hbar}\right)$$

(ii) For $L < x$,

$$\psi(x) = C\exp\left(\frac{\sqrt{2m(V_{\mathrm{d}} - E)}\,x}{\hbar}\right) + D\exp\left(-\frac{\sqrt{2m(V_{\mathrm{d}} - E)}\,x}{\hbar}\right).$$

b. The boundary condition at $x = 0$ is the continuity condition,

$$\psi(0) = 0,$$

since $\psi(x) = 0$ for $x < 0$. This condition simplifies $\psi(x)$, for $0 < x < L$. Specifically,

$$\psi(x) = A\sin\left(\frac{\sqrt{2mE}\,x}{\hbar}\right).$$

The boundary condition at $x = \infty$ is the condition that the wavefunction must be bounded. Since $\exp\left(\sqrt{2m(V_{\mathrm{d}} - E)}\,x/\hbar\right) \to \infty$, as $x \to \infty$, coefficient C must be zero. Therefore, for $L < x$,

$$\psi(x) = D\exp\left(-\frac{\sqrt{2m(V_{\mathrm{d}} - E)}\,x}{\hbar}\right).$$

c. There are two boundary conditions at $x = L$, continuity of $\psi(x)$ and $d\psi(x)/dx$ The continuity condition gives

$$A\sin\left(\frac{\sqrt{2mE}\,L}{\hbar}\right) = D\exp\left(-\frac{\sqrt{2m(V_{\mathrm{d}} - E)}\,L}{\hbar}\right).$$

The continuity of derivative condition gives

$$\frac{\sqrt{2mE}}{\hbar} A\cos\left(\frac{\sqrt{2mE}\,L}{\hbar}\right) = -\frac{\sqrt{2m(V_\mathrm{d}-E)}}{\hbar} D\exp\left(-\frac{\sqrt{2m(V_\mathrm{d}-E)}\,L}{\hbar}\right).$$

Dividing the first equation by the second gives

$$\frac{\hbar}{\sqrt{2mE}}\tan\left(\frac{\sqrt{2mE}\,L}{\hbar}\right) = -\frac{\hbar}{\sqrt{2m(V_\mathrm{d}-E)}}$$

or

$$\tan\left(\frac{\sqrt{2mE}\,L}{\hbar}\right) = -\sqrt{\frac{E}{V_\mathrm{d}-E}}\,.$$

The solutions to this equation, E_n, are the energy eigenvalues of the particle in a well.

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5. Consider a particle in a box of width, L.

a. **Show** that the "plane wave",

$$\varphi(x) = \frac{1}{\sqrt{L}} \exp(ikx),$$

is a normalized eigenfunction of the momentum operator. What is the associated momentum **eigenvalue**? [10 marks]

b. Let the particle be in its ground state. What are the **possible outcomes** of a measurement of **momentum** of the particle? [5 marks]

c. What is the **probability** that a measurement of momentum of the particle yields the value, $\hbar\pi/L$? [5 marks]

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a.

$$\begin{aligned}(\hat{p}\varphi)(x) &= -i\hbar\frac{d}{dx}\varphi(x) \\ &= -i\hbar\frac{d}{dx}\frac{1}{\sqrt{L}}\exp(ikx) \\ &= \frac{-i\hbar}{\sqrt{L}}\frac{d}{dx}\exp(ikx) \\ &= \frac{-i\hbar}{\sqrt{L}} ik\exp(ikx) \\ &= \hbar k\frac{1}{\sqrt{L}}\exp(ikx) \\ &= \hbar k\varphi(x);\end{aligned}$$

i.e., $\varphi(x)$ is an eigenfunction of $\hat{p}$. The associated eigenvalue is $\hbar k$. To see that this state is normalized, consider

$$\langle\varphi|\varphi\rangle = \int_0^L |\varphi(x)|^2 dx$$

b. The ground state of the particle in a box is

$$\begin{aligned}\psi_1(x) &= \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right) \\ &= \frac{1}{2i}\sqrt{\frac{2}{L}}\left(\exp\left(i\frac{\pi x}{L}\right) - \exp\left(-i\frac{\pi x}{L}\right)\right) \\ &= \frac{1}{\sqrt{2}\,i}\sqrt{\frac{1}{L}}\left(\exp\left(i\frac{\pi x}{L}\right) - \exp\left(-i\frac{\pi x}{L}\right)\right)\end{aligned}$$

It is written above as a superposition of two normalized momentum eigenstates. The associated momentum eigenvalues are $\hbar\pi/L$ and $-\hbar\pi/L$. These are the possible outcomes of a measurement of momentum of the particle.

c. The probability that a measurement of momentum yields $\hbar\pi/L$ equals $1/2$. This can be deduced from the fact that there are only two momentum outcomes possible, and they are equally likely - the coefficients of the two associated momentum eigenstates have equal modulus. Alternatively, we can calculate the probability directly as follows:

$$\begin{aligned}
\rho_+ &= |\langle\varphi_+|\psi_1\rangle|^2 \\
&= \left|\int_0^L \varphi_+^*(x)\psi_1(x)\,dx\right|^2 \\
&= \left|\int_0^L \frac{1}{\sqrt{L}}\exp\left(-i\frac{\pi x}{L}\right)\sqrt{\frac{2}{L}}\,\sin\left(\frac{\pi x}{L}\right)dx\right|^2 \\
&= \left|\frac{\sqrt{2}}{2iL}\int_0^L \exp\left(-i\frac{\pi x}{L}\right)\left(\exp\left(i\frac{\pi x}{L}\right)-\exp\left(-i\frac{\pi x}{L}\right)\right)dx\right|^2 \\
&= \frac{1}{2}\left|\frac{1}{L}\int_0^L\left(1-\exp\left(-2i\frac{\pi x}{L}\right)\right)dx\right|^2 \\
&= \frac{1}{2}\left|\frac{1}{L}\left(\int_0^L dx-\int_0^L \exp\left(-2i\frac{\pi x}{L}\right)dx\right)\right|^2 \\
&= \frac{1}{2}\left|\frac{1}{L}\left(L+\frac{L}{2i\pi}\left[\exp\left(-2i\frac{\pi x}{L}\right)\right]_0^L\right)\right|^2 \\
&= \frac{1}{2}\left|1+\frac{1}{2i\pi}\left[\underbrace{\exp(-2i\pi)}_{=1}-1\right]\right|^2 \\
&= \frac{1}{2}.
\end{aligned}$$

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