

Name:

## Chemistry 3PA3 – Midterm

November 4, 2016 7-9 pm

Any calculator, and 1 8 ½ × 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	25	
3	20	
4	25	
Total	80	

1. The electron diffraction pattern is measured for two substances, A and B, with two electron beams - slow and fast, with velocities  $v$  and  $2v$  respectively. Substance A has the smaller atomic spacing, by a factor of 1.2. Order the diffraction patterns, A-slow, A-fast, B-slow and B-fast ordering to the number of peaks observed - from lowest number of peaks to highest. Explain. [10 marks]

The von Laue equation(s) provides the angles of reflection,  $\theta_r$ , that produce diffraction peaks due to constructive interference.

$$\frac{n\lambda}{a} = \cos(\theta_i) + \cos(\theta_r)$$

where  $\theta_i$  is the angle of incidence,  $\lambda$  is the particle (electron) de Broglie wavelength,  $a$  is the lattice spacing and  $n$  is a positive integer – distinct for each diffraction peak. The right side of the equation is bounded between  $-2$  and  $+2$ . Thus,

$$|n| \leq 2 \frac{a}{\lambda} = 2 \frac{amv}{h} = \frac{2m}{h} av,$$

and the number of distinct diffraction peaks is proportional to  $av$  – i.e., proportional to the spacing, and to the velocity of the incoming electrons. Thus, the number of distinct diffraction peaks increases as follows:

$$A\text{-slow} < B\text{-slow} < A\text{-fast} < B\text{-fast}$$

The faster electron beam produces the most peaks. The velocity changes by a factor of 2, while the spacing changes only by the factor, 1.2.

2.

(a) Show that the “localized plane wave”,

$$\varphi_n(x) = \begin{cases} 0, & x < 0 \\ \frac{1}{\sqrt{L}} \exp(in\pi x / L), & 0 \leq x \leq L \\ 0, & L < x \end{cases}$$

is a normalized eigenfunction of the momentum operator (exclude the  $x = 0$  and  $x = L$  boundary points from the derivative evaluation). What is the associated momentum eigenvalue? [10 marks]

(b) Suppose that a particle is in the state,  $\psi(x) = \frac{1}{\sqrt{5}}(2\varphi_1(x) + \varphi_2(x))$ . What are the possible outcomes, if the momentum of this particle is measured? Explain.[5 marks]

(a) Apply the momentum operator to the localized plane wave:

$$\hat{p} \varphi_n(x) = -i\hbar \frac{d}{dx} \varphi_n(x) = \begin{cases} 0, & x < 0 \\ \frac{-i\hbar}{\sqrt{L}} \frac{d}{dx} \exp(in\pi x / L), & 0 \leq x \leq L \\ 0, & L < x \end{cases}$$

$$\begin{aligned} \frac{-i\hbar}{\sqrt{L}} \frac{d}{dx} \exp(in\pi x / L) &= \frac{-i\hbar \times in\pi}{\sqrt{L}L} \exp(in\pi x / L) \\ &= \frac{\hbar n\pi}{L} \frac{1}{\sqrt{L}} \exp(in\pi x / L) \end{aligned}$$

So,

$$\begin{aligned} \hat{p} \varphi_n(x) &= \begin{cases} 0, & x < 0 \\ \frac{\hbar n\pi}{L} \varphi_n(x), & 0 \leq x \leq L \\ 0, & L < x \end{cases} \\ &= \frac{\hbar n\pi}{L} \varphi_n(x), \text{ for all } x \end{aligned}$$

The localized plane wave is an eigenfunction of the momentum operator, with associated

eigenvalue,  $\frac{\hbar n\pi}{L}$ .

To see that it is normalized, consider the integral of  $|\varphi_n(x)|^2$  from 0 to  $L$ . The integral from  $-\infty$  to  $+\infty$  reduces to the integral from 0 to  $L$  because, the wavefunction is zero outside this interval.

$$\begin{aligned} \int_0^1 dx |\varphi_n(x)|^2 &= \int_0^1 dx \varphi_n^*(x) \varphi_n(x) \\ &= \frac{1}{L} \int_0^1 dx \exp(-in\pi x / L) \exp(in\pi x / L) \\ &= \frac{1}{L} \int_0^L dx \exp(-in\pi x / L + in\pi x / L) \\ &= \frac{1}{L} \int_0^L dx \exp(0) = \frac{1}{L} \int_0^L dx 1 = \frac{1}{L} [x]_0^L = \frac{L}{L} = 1 \end{aligned}$$

The given localized plane wave is normalized.

(b) The state,

$$\psi(x) = \frac{1}{\sqrt{5}} (2\varphi_1(x) + \varphi_2(x)),$$

is a superposition of  $\varphi_1(x)$  and  $\varphi_2(x)$ . The  $\varphi_n(x)$  are the distinct eigenfunctions of a Hermitian linear operator. You can assume that they are orthogonal. The probability of observing the eigenvalue,  $\frac{\hbar n \pi}{L}$ , is given by

$$\rho_n = \left| \left\langle \begin{array}{c} \varphi_n \\ \text{eigenfunction} \\ \text{associated with} \\ n \text{ th eigenvalue} \end{array} \middle| \begin{array}{c} \psi \\ \text{state of system} \end{array} \right\rangle \right|^2$$

Here,

$$\begin{aligned} \langle \varphi_n | \psi \rangle &= \frac{1}{\sqrt{5}} (2 \underbrace{\langle \varphi_n | \varphi_1 \rangle}_{=0, \text{ unless } n=1} + \underbrace{\langle \varphi_n | \varphi_2 \rangle}_{=0, \text{ unless } n=2}) \\ &= \frac{1}{\sqrt{5}} (2 \underbrace{\delta_{n,1}}_{=1, \text{ if } n=1, 0 \text{ otherwise}} + \underbrace{\delta_{n,2}}_{=1, \text{ if } n=2, 0 \text{ otherwise}}) \\ &= 0, \text{ unless } n = 1 \text{ or } 2. \end{aligned}$$

The only possible outcomes of a momentum measurement are the  $n = 1$  and  $2$  eigenvalues,

$$\frac{\hbar \pi}{L} \quad \text{and} \quad \frac{2\hbar \pi}{L}.$$

2. continued.

(c) What are the probabilities of the possible outcomes of the momentum measurement of part (b)? Explain. [5 marks]

(d) What are the possible outcomes of a measurement of energy of the particle in state  $\psi(x)$ ? Explain. [5 marks]

(c) Since

$$\begin{aligned} \langle \varphi_1 | \psi \rangle &= \frac{1}{\sqrt{5}} (2 \times 1 + 0) \\ &= \frac{2}{\sqrt{5}}, \\ \rho_1 &= |\langle \varphi_1 | \psi \rangle|^2 \\ &= \frac{4}{5} \end{aligned}$$

Similarly,

$$\begin{aligned}\rho_2 &= |\langle \varphi_2 | \psi \rangle|^2 \\ &= \left| \frac{1}{\sqrt{5}} \right|^2 = \frac{1}{5}\end{aligned}$$

The probability of observing  $\frac{\hbar\pi}{L}$  is 4/5, while the probability of observing  $\frac{2\hbar\pi}{L}$  is 1/5.

(d) Note that if we apply the Hamiltonian operator, for a free mass  $m$  particle, to  $\varphi_1(x)$  and  $\varphi_2(x)$ , separately, we get

$$\begin{aligned}\hat{H} \varphi_1(x) &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \frac{1}{\sqrt{L}} \exp(i\pi x / L) \\ &= -\frac{i^2 \pi^2 \hbar^2}{2mL^2} \frac{1}{\sqrt{L}} \exp(i\pi x / L) \\ &= \frac{\pi^2 \hbar^2}{2mL^2} \varphi_1(x)\end{aligned}$$

and

$$\hat{H} \varphi_2(x) = \frac{4\pi^2 \hbar^2}{2mL^2} \varphi_2(x)$$

Thus, the two components of  $\psi(x)$ ,  $\varphi_1(x)$  and  $\varphi_2(x)$ , are eigenfunction of the Hamiltonian (for a free particle). The associated energy eigenvalues are  $\frac{\pi^2 \hbar^2}{2mL^2}$  and  $\frac{4\pi^2 \hbar^2}{2mL^2} = \frac{2\pi^2 \hbar^2}{mL^2}$ , respectively. These are the possible energy measurement outcomes when the system is in a superposition of  $\varphi_1(x)$  and  $\varphi_2(x)$ . Other energy eigenstates are orthogonal to this superposition. No other energy measurement outcome is possible.

3. Suppose there are three electrons in a well with depth,  $V_d = 16.00$  eV. The electrons can be treated as independent particles with particle-in-a-well energy levels. and energy eigenstates. You can use the approximate well energy eigenvalues - i.e., the particle-in-a-box levels scaled by  $\eta_d^2/(\eta_d+1/\pi)^2$ . The well width,  $L$ , is such that  $\pi^2 \hbar^2 / (2 m L^2) = 1.00$  eV, where  $m$  is the mass of an electron.

(a) What is the energy of the ground state of this three electron system? [5 marks]

(b) What is the ionization energy of the system? [5 marks]

(a) The ground state electron configuration is  $1^2 2^1$ ; i.e., there are two electrons (of opposite spin, in accord with the Pauli principle) in the lowest energy state ( $n = 1$ ), and one electron in the next lowest energy state ( $n = 2$ ). With the independent electron approximation, we can write the energy of the ground state as

$$\begin{aligned}
 E_{g.s.} &= 2E_1 + E_2 \\
 &= 2E_1 + 4E_1 = 6E_1
 \end{aligned}$$

Here, we used the fact that the well energy eigenvalues scale with  $n^2$  just like the particle in a box energy eigenvalues. The difference is that the well energies are (approximately) the box energies scaled by  $\eta_d^2/(\eta_d+1/\pi)^2$  where  $\eta_d^2 = 2m L^2 V_d / (\pi^2 \hbar^2) = V_d / \epsilon_1$ , where  $\epsilon_1 = 1.00$  eV is lowest energy level for the particle in a box of the same width as the well. Thus, the particle in the well energy levels are just

$$\begin{aligned}
 E_n &= \frac{16}{(\sqrt{16} + 1/\pi)} \epsilon_n \\
 &= 0.86n^2 \epsilon_1 \\
 &= 0.86n^2 \text{ eV} \\
 &= 0.86 \text{ eV}, 3.43 \text{ eV}, \dots
 \end{aligned}$$

So,

$$E_{g.s.} = 6E_1 = 5.15 \text{ eV} .$$

(b) The ionization energy is the difference in energy between the +1 cation ground state system with two electrons, plus a free electron with energy  $V_d = 16.00$  eV, and the neutral three electron system ground state; i.e., it is  $\Delta E$  for the ionization process,  $W \rightarrow W^+ + e^-$ , where  $W$  is the neutral three electron well.

$$\begin{aligned}
 I &= E_{\text{cation g.s.}} + 16.00 \text{ eV} - E_{g.s.} \\
 &= 2E_1 + 16.00 \text{ eV} - 5.15 \text{ eV} \\
 &= 1.72 + 16.00 - 5.15 \text{ eV} \\
 &= 12.57 \text{ eV}
 \end{aligned}$$

Because the electrons are independent, the ionization energy is more easily calculated as  $\Delta E$  for the electron which transitions from  $E_2$  to  $V_d$ . Specifically,

$$\begin{aligned}
 I &= 16.00 \text{ eV} - E_2 \\
 &= 16.00 - 3.43 \text{ eV} \\
 &= 12.57 \text{ eV}
 \end{aligned}$$

We get the same result as above because the energies of the other two electrons are the same in the cation ground state and in the neutral ground state. They cancel out. This is because of the independent electron approximation. If we accounted for electron repulsion, the ionization energy would come out lower because the electrons in the cation would have a reduced energy.

3. continued.

(c) What is the electron affinity of the system? [5 marks]

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

(c) The electron affinity is the difference in energy between the  $-1$  anion ground state system with four electrons, and the neutral three electron system ground state plus a free electron with energy  $V_d = 16.00$  eV; i.e., it is  $\Delta E$  for the electron attachment process,  $W + e^- \rightarrow W^-$ .

$$\begin{aligned} I &= E_{\text{anion g.s.}} - (E_{\text{g.s.}} + 16.00 \text{ eV}) \\ &= 2E_1 + 2E_2 - (5.15 + 16.00 \text{ eV}) \\ &= 10E_1 - 21.15 \text{ eV} \\ &= 8.58 - 21.15 \text{ eV} \\ &= -12.57 \text{ eV} \end{aligned}$$

Again, because the electrons are independent, the electron affinity is more easily calculated as  $\Delta E$  for the electron which transitions from  $V_d$  to  $E_2$ . This is why the electron affinity comes out to be minus the ionization energy.

$$\begin{aligned} I &= E_2 - 16.00 \text{ eV} \\ &= -12.57 \text{ eV} \end{aligned}$$

(d) The dipole allowed transitions (treating the well states as box states) are odd to even and even to odd. The 1 to 2 transition is allowed here because there is a “hole” in the  $n = 2$  level (i.e., the  $n = 2$  level can accommodate one more electron). The 1 to 4 transition is also allowed. The 2 to 3 transition is also allowed. There are no higher level electrons to make transitions, and the final state cannot have  $n$  higher than 4 as that is the highest energy level in the well.

The transition frequency is  $\Delta E/h$ . For the three allowed transitions,

$$\Delta E_{1 \rightarrow 2}/h = (4 - 1) E_1/h = 622 \text{ THz}$$

$$\Delta E_{1 \rightarrow 4}/h = (16 - 1) E_1/h = 3112 \text{ THz}$$

$$\Delta E_{2 \rightarrow 3}/h = (9 - 4) E_1/h = 1037 \text{ THz}$$

There are two electrons that can transition from  $n = 1$ . However, only the electron that has spin opposite to that of the electron in  $n = 2$  can actually make the  $1 \rightarrow 2$  transition. The  $1 \rightarrow 4$  transition has much smaller intensity, though both electrons can make the transition. There is one electron that can make the  $2 \rightarrow 3$  transition. However, its intensity is lower than that of the  $1 \rightarrow 2$  transition due to the smaller transition matrix element – the transition matrix element decreases with increasing  $n_{\text{initial}}$  as  $n_{\text{initial}}^{-1}$ .

4. Consider a mass  $m$  particle in a box of width,  $L$ , in the state,  $\psi(x) = \frac{1}{\sqrt{2}}(\psi_1(x) + \psi_2(x))$ , where  $\psi_1$  and  $\psi_2$  are the lowest two energy eigenstates. Here,  $\pi^2 \hbar^2 / (2 m L^2) = 1.00 \text{ eV}$

(a) Determine the expectation value of momentum for this state. [10 marks]

(b) What are the possible outcomes of a measurement of energy of the particle? [5 marks]

(a) The expectation value of momentum is computed as follows:

$$\begin{aligned}
 \langle \psi | \hat{p} \psi \rangle &= \left\langle \frac{1}{\sqrt{2}}(\psi_1 + \psi_2) \left| \hat{p} \frac{1}{\sqrt{2}}(\psi_1 + \psi_2) \right. \right\rangle \\
 &= \frac{1}{2} \left( \underbrace{\langle \psi_1 | \hat{p} \psi_1 \rangle}_{=0 \text{ shown in class}} + \langle \psi_2 | \hat{p} \psi_1 \rangle + \langle \psi_1 | \hat{p} \psi_2 \rangle + \underbrace{\langle \psi_2 | \hat{p} \psi_2 \rangle}_{=0 \text{ shown in class}} \right) \\
 &= \frac{1}{2} \left( \langle \psi_2 | \hat{p} \psi_1 \rangle + \underbrace{\langle \hat{p} \psi_1 | \psi_2 \rangle}_{\hat{p} \text{ is Hermitian}} \right) \\
 &= \frac{1}{2} \left( \langle \psi_2 | (-i\hbar) \frac{d}{dx} \psi_1 \rangle + \left\langle (-i\hbar) \frac{d}{dx} \psi_1 \right| \psi_2 \right\rangle \right) \\
 &= \frac{1}{2} \left( -i\hbar \langle \psi_2 | \frac{d}{dx} \psi_1 \rangle + i\hbar \left\langle \frac{d}{dx} \psi_1 \right| \psi_2 \right\rangle \right) \\
 &= \frac{-i\hbar}{2} \left( \langle \psi_2 | \frac{d}{dx} \psi_1 \rangle - \underbrace{\langle \psi_2 | \frac{d}{dx} \psi_1 \rangle}_{\psi_1 \text{ and } \psi_2 \text{ are real}} \right) = 0
 \end{aligned}$$

In fact, any real wavefunction has zero momentum expectation. We could have deduced that the expectation is zero directly from the fact that  $\psi(x)$  is real.

(b) This state is a superposition of the two lowest energy eigenstates. The two associated eigenvalues are the only possible outcomes of an energy measurement. Specifically,

$$E_1 = \pi^2 \hbar^2 / (2 m L^2) \quad \text{and} \quad E_2 = 2^2 \pi^2 \hbar^2 / (2 m L^2) = 2 \pi^2 \hbar^2 / (m L^2)$$

are the possible outcomes of an energy measurement.

4. continued.

(c) What is the state of the system after time,  $t$ ? [5 marks]

(d) At what time,  $t$ , does the system state return to its original form,  $\psi(x)$ ? [5 marks]



(c) The time evolution of the system state – initially  $\psi(x)$  – is given formally as follows:

$$\begin{aligned}\Psi(x, t) &= \exp\left(-i \hat{H} t / \hbar\right) \Psi(x, 0) \\ &= \exp\left(-i \hat{H} t / \hbar\right) \psi(x)\end{aligned}$$

Because  $\psi_1(x)$  and  $\psi_2(x)$  are energy eigenstates – i.e., eigenfunctions of the Hamiltonian – they are also eigenfunctions of any function of the Hamiltonian. Thus,

$$\begin{aligned}\Psi(x, t) &= \exp\left(-i \hat{H} t / \hbar\right) \frac{1}{\sqrt{2}} (\psi_1(x) + \psi_2(x)) \\ &= \frac{1}{\sqrt{2}} (\exp\left(-i \hat{H} t / \hbar\right) \psi_1(x) + \exp\left(-i \hat{H} t / \hbar\right) \psi_2(x)) \\ &= \frac{1}{\sqrt{2}} (\exp(-i E_1 t / \hbar) \psi_1(x) + \exp(-i E_2 t / \hbar) \psi_2(x)) \\ &= \frac{1}{\sqrt{2}} (\exp(-i E_1 t / \hbar) \psi_1(x) + \exp(-4i E_1 t / \hbar) \psi_2(x))\end{aligned}$$

(d) The phase factors,  $\exp(-i E_1 t / \hbar)$  and  $\exp(-i E_2 t / \hbar)$  are periodic in time. They return to 1 when  $E_1 t / \hbar = 2\pi n_1$  and  $E_2 t / \hbar = 2\pi n_2$ , where  $n_1$  and  $n_2$  are integers. The state returns to original form when both of these conditions are satisfied. Specifically,

$$t = \frac{2\pi\hbar}{E_1} n_1 = \frac{2\pi\hbar}{4E_1} n_2$$

The first return time occurs for  $n_1 = 1$  and  $n_2 = 4$  (the  $\psi_2(x)$  term returns to its original form four times in the time it takes for the  $\psi_1(x)$  term to return once); i.e., the first return time is

$$\begin{aligned}t &= \frac{h}{E_1} = \frac{4.136 \times 10^{-15} \text{ eV s}}{1.00 \text{ eV}} \\ &= 4.136 \text{ ps}\end{aligned}$$