# ADVANCED CHEMISTRY - 2008
## WINTER QUARTER - QUANTUM MECHANICS MID-TERM EXAM

**STUDENT NAME** Answer Key

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ANSWER ALL THE QUESTIONS. **PLEASE SHOW ALL WORK.**

1.

(a) Using words only (no equations) describe the Heisenberg uncertainty principle.

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In a quantum mechanical system there are some physical observables that cannot be determined accurately, simultaneously. Example: position & momentum. High accuracy in one of these results in a necessarily high degree of uncertainty in the other.

(b) Using equations only (no words) describe what you understand by the phrase "a set of orthonormal wave functions"

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$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, d\tau = \delta_{ij}$$

(c) Show that the quantum mechanical operators for position and momentum (in one dimension only) do not commute.

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$$[\hat{P}_x, \hat{x}]\psi = [\hat{P}_x \hat{x} - \hat{x}\hat{P}_x]\psi = \hat{P}_x[\hat{x}\psi] - \hat{x}[\hat{P}_x\psi]$$

$$= -i\hbar \frac{d}{dx}(x\psi) - x\left(-i\hbar \frac{d\psi}{dx}\right)$$

$$= -i\hbar\left[x\frac{d\psi}{dx} + \psi\frac{dx}{dx}\right] + i\hbar x \frac{d\psi}{dx}$$

$$= \cancel{-i\hbar x\frac{d\psi}{dx}} - i\hbar\psi + \cancel{i\hbar x\frac{d\psi}{dx}} = -i\hbar\psi$$

$[\hat{P}_x, \hat{x}] = -i\hbar \neq 0 \quad \therefore \hat{x}$ and $\hat{P}_x$ do not commute.

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2. Calculate the wavelength (in nm) of the first spectral line of the Paschen series for the hydrogen atom. The Rydberg formula is

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

For the Paschen series $n_1 = 3$
for the first spectral line $n_2 = 4$

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$$\frac{1}{\lambda} = 1.09737 \times 10^5 \text{ cm}^{-1}\left[\frac{1}{3^2} - \frac{1}{4^2}\right] = 5334.44 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{5334.44} \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = \underline{\underline{1874.61 \text{ nm}}}$$

3. Using the de Broglie formula, derive the energy expression for a particle in a one-dimensional box.

de Broglie formula $\lambda = \frac{h}{p}$ $\quad p = \frac{h}{\lambda}$

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For a particle in a box, energy $= K.E. = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

For a particle in a box of length $a$; $\quad a = \frac{n\lambda}{2}$

$$\Rightarrow \lambda = \frac{2a}{n}$$

$$\Rightarrow E = \frac{h^2}{2m}\left(\frac{n}{2a}\right)^2 = \underline{\underline{\frac{n^2h^2}{8ma^2}}}$$

$n = 1, 2, 3, \ldots$
$h =$ Planck's constant
$m =$ mass of the particle

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4. The following function $\psi(x)$ can be used to describe a free particle of mass "m" moving in the x direction. Potential energy for a free particle is zero everywhere. Determine the momentum and the energy of this particle.

$\psi(x) = A\, e^{inx}$ where A is a constant, n is the quantum number

$$\hat{P}\psi(x) = -i\hbar \frac{d}{dx}\left(A e^{inx}\right) = -i\hbar\left(A\, in\, e^{inx}\right)$$

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$$= \hbar n \left(A e^{inx}\right) = \hbar n \psi$$

$\therefore$ momentum $= \hbar n$

$$\text{Energy}\quad \hat{H} = \hat{T} + \hat{V} = \frac{1}{2} m \hat{v}^2 + 0 = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\hat{p}\cdot\hat{p}$$

$$= \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(A e^{inx}\right) = -\frac{\hbar^2}{2m}\frac{d}{dx}\left[\frac{d}{dx} A e^{inx}\right]$$

$$= \frac{-\hbar^2}{2m}\frac{d}{dx}\left[inA\, e^{inx}\right] = -\frac{\hbar^2}{2m}(inA)\left[in\, e^{inx}\right]$$

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$$= \frac{\hbar^2}{2m} n^2 \left(A e^{inx}\right) = \frac{n^2\hbar^2}{2m}\psi(x)$$

$$\therefore \text{Energy} = \frac{n^2\hbar^2}{2m}$$

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5. Use your knowledge of the particle in a 1-dimensional box to:
   a. Write a wavefunction for a particle in a 2-dimensional box. Define all terms used.

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a}\right) x \qquad \psi(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b}\right) y$$

where $a$ = length of box
$b$ = width of box
7 $n_x, n_y = 1, 2, 3, 4, \ldots$ (quantum numbers)

$$\psi(x,y) = \sqrt{\frac{2}{a}} \sqrt{\frac{2}{b}} \left[\sin\left(\frac{n_x \pi}{a}\right) x\right] \left[\sin\left(\frac{n_y \pi}{b}\right) y\right]$$

   b. Write the energy expression for a particle in a 2-dimensional box. Define all terms used.

$$E_x = \frac{n_x^2 h^2}{8ma^2} \qquad E_y = \frac{n_y^2 h^2}{8mb^2}$$

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$$E(x,y) = E_x + E_y = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

$m$ = mass of the particle
$h$ = Planck's constant.

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c. If the 2-dimensional box is a square, determine the energy of the first six energy states and their degeneracies. $a = b$

| $n_x$ | $n_y$ | energy | degeneracy |
|---|---|---|---|
| 1 | 1 | $2h^2/8ma^2$ | 1 |
| 1<br>2 | 2<br>1 | $5h^2/8ma^2$ | 2 |
| 2 | 2 | $8h^2/8ma^2$ | 1 |
| 3<br>1 | 1<br>3 | $10h^2/8ma^2$ | 2 |

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total of 6 states

d. Draw a ladder type energy diagram to show the energies of the above system (for the first six energy states). Identify each quantum state with its quantum numbers.

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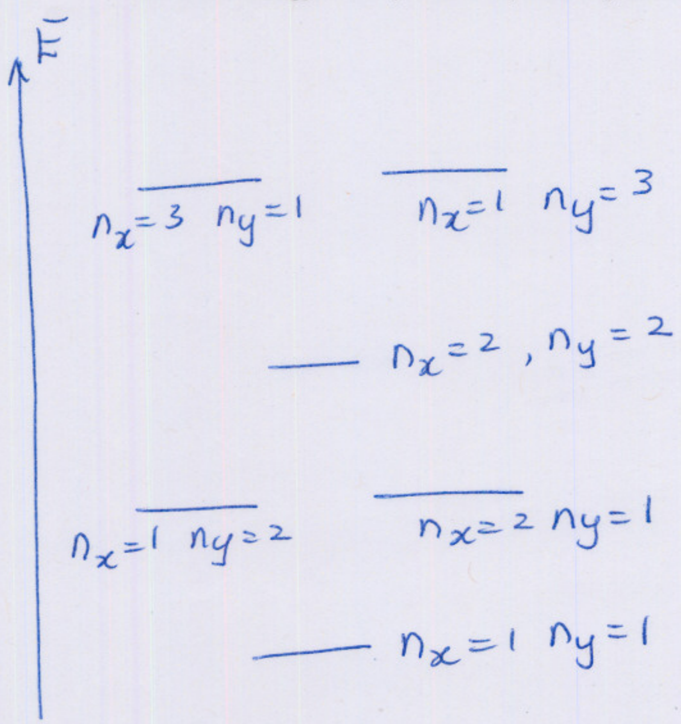

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6. The fundamental vibrational frequency for $^{1}H^{79}Br$ molecule is 2559.03 cm$^{-1}$. Evaluate the fundamental vibrational frequency of the $^{2}H^{81}Br$ molecule in cm$^{-1}$ units assuming that the bond in each isotopic molecule is identical.

$$\tilde{\nu}_1 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_1}} \qquad \tilde{\nu}_2 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_2}}$$

$$\Rightarrow \frac{\tilde{\nu}_2}{\tilde{\nu}_1} = \sqrt{\frac{\mu_1}{\mu_2}} \Rightarrow \tilde{\nu}_2 = \tilde{\nu}_1\sqrt{\frac{\mu_1}{\mu_2}}$$

$$\mu_1(^{1}H^{79}Br) = \frac{1\times 79}{1+79}\text{ amu} = \frac{79}{80}\text{ amu}$$

$$\mu_2(^{2}H^{81}Br) = \frac{2\times 81}{2+81}\text{ amu} = \frac{162}{83}\text{ amu}$$

$$\tilde{\nu}_2(^{2}H^{81}Br) = 2559.03\text{ cm}^{-1}\left(\frac{79}{80}\times\frac{83}{162}\right)^{1/2}$$

$$= \underline{\underline{1820.23\text{ cm}^{-1}}}$$

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7. The wavefunctions for the $2p_{-1}$ $(n=2, \ell=1, m_\ell=-1)$, $2p_0$ $(n=2, \ell=1, m_\ell=0)$, $2p_1$ $(n=2, \ell=1, m_\ell=1)$, orbitals are given by $\psi_{2p_{-1}}, \psi_{2p_0}, \psi_{2p_1}$ respectively. These orbitals are known to be degenerate in the hydrogen atom, with energy = ε. Prove that a linear combination of the above wavefunctions given by: $\phi = a_1 \psi_{2p_{-1}} + a_2 \psi_{2p_0} + a_3 \psi_{2p_1}$ is also an eigen function of the energy operator with the eigen value ε. Note that $a_1$, $a_2$, $a_3$ are constants.

$\hat{\mathcal{H}} \psi_{2p_{-1}} = \epsilon \psi_{2p_{-1}}$ $\quad \hat{\mathcal{H}} \psi_{2p_0} = \epsilon \psi_{2p_0}$ $\quad \hat{\mathcal{H}} \psi_{2p_1} = \epsilon \psi_{2p_1}$

$$\hat{\mathcal{H}} \phi = \hat{\mathcal{H}} \left( a_1 \psi_{2p_{-1}} + a_2 \psi_{2p_0} + a_3 \psi_{2p_1} \right)$$

$$= a_1 \hat{\mathcal{H}} \psi_{2p_{-1}} + a_2 \hat{\mathcal{H}} \psi_{2p_0} + a_3 \hat{\mathcal{H}} \psi_{2p_1}$$

$$= a_1 \left( \epsilon \psi_{2p_{-1}} \right) + a_2 \left( \epsilon \psi_{2p_0} \right) + a_3 \left( \epsilon \psi_{2p_1} \right)$$

$$= \epsilon \left( a_1 \psi_{2p_{-1}} + a_2 \psi_{2p_0} + a_3 \psi_{2p_1} \right)$$

$$= \epsilon \phi$$

$\therefore$ $\phi$ is an eigen function of $\hat{\mathcal{H}}$ (energy operator) with the same eigen value $\epsilon$.