

EXAM 1: INFORMATION**Potentially Useful Formulas**

De Broglie Wavelength: $\lambda = \frac{h}{p}$ **Uncertainty Principle:** $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

An Hermitian operator satisfies the relation: $\int \psi_j^* \hat{A} \psi_i d\tau = \int \psi_i (\hat{A} \psi_j)^* d\tau$

One Dimensional Schrödinger Equation: $H = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi$

One Dimensional PIB Energies: $E_n = \frac{n^2 \hbar^2}{8ma^2} \quad n = 1, 2, 3, \dots$

Momentum Operators: $\hat{p} = \frac{\hbar}{i} \frac{d}{dx} \quad \hat{p}^2 = -\hbar^2 \frac{d^2}{dx^2}$

Kinetic Energy: $KE = \frac{1}{2} mv^2 = \frac{p^2}{2m}$

Constants and Conversions:

$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s} = 6.63 \times 10^{-34} \text{ kg}\cdot\text{m}^2/\text{s}$

$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s} = 1.05 \times 10^{-34} \text{ kg}\cdot\text{m}^2/\text{s}$

$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$

$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$

$k \cdot N_A = R$

$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$

$k = 1.38 \times 10^{-23} \text{ J/K}$

$1 \text{ atm.} = 1.013 \times 10^5 \text{ Pa}$

$R = 8.31 \text{ J/mol}\cdot\text{K}$

$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$

$R = 8.31 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$

$1 \text{ Å} = 10^{-10} \text{ m}$

$m_e = 9.11 \times 10^{-31} \text{ kg (electron mass)}$

$m_p = 1.67 \times 10^{-27} \text{ kg (proton mass)}$

Name Solomon

- (18) 1. **Short Answer:** (2 points each) Just the answers, no explanations are required on any part

(a) Is the operator, e^{2ix} Hermitian? No

(b) Is the operator, $\frac{\hbar^2}{i^2} \frac{d^2}{dx^2}$, Hermitian? Yes

(c) True/False: It is necessary that the operators in Quantum Mechanics be Hermitian in order to ensure that the wavefunctions are real.

False

(d) True/False: Nondegenerate eigenfunctions of the same operator are orthogonal.

True

(e) True/False: A linear combination of two nondegenerate eigenfunctions of an operator is also an eigenfunction of the operator.

False

(f) True/False: If a wavefunction is simultaneously the eigenfunction of two operators, it will also be an eigenfunction of the product of the two operators.

True

(g) Which of the following functions are eigenfunctions of $\frac{d^2}{dx^2}$

e^{3ix} yes

xe^{-5x} No

1. (Cont'd.)

- (h) True/False: The operator, $x \cdot \int () dx$, [Integrate and then multiply by x] is a linear operator.

True

- (i) True/False: The derivative, $\frac{d\psi}{dx}$, must be continuous at boundaries in which the potential energy is finite ($V < \infty$)

True

- (08) 2. What is the mass of a particle which has a kinetic energy of 40 eV and a de Broglie wavelength of 0.25 Å.

$$KE = 40 \text{ eV} \times 1.60 \times 10^{-19} \frac{\text{J}}{\text{eV}} = 6.4 \times 10^{-18} \text{ J} = \frac{p^2}{2m}$$

$$\lambda = \frac{h}{p} \rightarrow p = \frac{h}{\lambda} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{0.25 \times 10^{-10} \text{ m}} = 2.652 \times 10^{-23} \frac{\text{J}\cdot\text{s}}{\text{m}}$$

$$KE = \frac{p^2}{2m} \rightarrow m = \frac{p^2}{2(KE)} = \frac{(2.652 \times 10^{-23} \frac{\text{J}\cdot\text{s}}{\text{m}})^2}{2(6.4 \times 10^{-18} \text{ J})} = 5.56 \times 10^{-29} \text{ kg}$$

Check: $\frac{\text{J}\cdot\text{s}^2}{\text{m}^2} = \frac{\text{J}\cdot\frac{\text{s}^2}{\text{m}^2}}{\text{J}} = \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2} \cdot \frac{\text{s}^2}{\text{m}^2} = \text{kg}$

(05) 3. Simplify the complex quantity, $\frac{10-6i}{4+3i}$. Your final result should be of the form $a+bi$

$$\frac{10-6i}{4+3i} \cdot \frac{4-3i}{4-3i} = \frac{40-24i-30i+18i^2}{4^2-3^2} = \boxed{\frac{22-54i}{25}}$$

$$= \boxed{\frac{22}{25} - \frac{54}{25}i} = \boxed{0.88 - 2.16i}$$

Any of these 3 is fine

(08) 4. Evaluate the commutator: $\left[\frac{d}{dx}, x \frac{d}{dx} \right] = [A, B]$

$$\left[\frac{d}{dx}, x \frac{d}{dx} \right] \phi = \frac{d}{dx} \left(x \frac{d\phi}{dx} \right) - x \frac{d}{dx} \left(\frac{d\phi}{dx} \right)$$

$$= \left(x \frac{d^2\phi}{dx^2} + \frac{d\phi}{dx} \frac{dx}{dx} \right) - x \frac{d^2\phi}{dx^2}$$

$$= \frac{d\phi}{dx} \rightarrow \boxed{\left[\frac{d}{dx}, x \frac{d}{dx} \right] = \frac{d}{dx}}$$

- (08) 5. Consider the wavefunction of a particle moving freely through space with the wavefunction, $\psi = Ae^{ikx-i\omega t}$, $k = 1.5 \times 10^{10} \text{ m}^{-1}$

Show that this is an eigenfunction of the momentum operator and calculate the eigenvalue (i.e. the momentum), in $\text{kg}\cdot\text{m/s}$:-

$$\hat{p}\psi = p\psi$$

$$\hat{p}\psi = \frac{\hbar}{i} \frac{d}{dx} Ae^{ikx-i\omega t}$$
$$= \frac{\hbar}{i} Ae^{ikx-i\omega t} (ik)$$

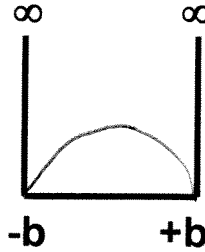
$$= \frac{\hbar}{i} ik\psi = \hbar k\psi$$

$$\therefore p = \hbar k = (1.05 \times 10^{-34} \text{ kg m}^2/\text{s}) (1.5 \times 10^{10} \text{ m}^{-1})$$

$$= 1.58 \times 10^{-24} \text{ kg m/s}$$

- (18) 6. Consider a particle in a box, defined by the potential

$$\begin{aligned} V(x) &= 0 & -b \leq x \leq +b \\ V(x) &\rightarrow \infty & x < -b, x > +b \end{aligned}$$



One of the normalized wavefunctions for this particle is:

$$\psi = C \cos\left(\frac{3\pi}{2b}x\right), \quad C = \sqrt{\frac{1}{b}}$$

- (9) a) Calculate the probability that the particle will be found in the region between $x=0$ and $x=+b/2$.

Note: You should arrive at a numerical value for the probability.

$$\begin{aligned} P(0 \leq x \leq b/2) &= \int_0^{b/2} \psi^2 dx = C^2 \int_0^{b/2} \cos^2\left(\frac{3\pi}{2b}x\right) dx \\ &= C^2 \int_0^{b/2} \cos^2 kx dx \quad \text{where } k = \frac{3\pi}{2b} \\ &= C^2 \left[\frac{1}{2}x + \frac{1}{4k} \sin 2kx \right]_0^{b/2} \\ &= C^2 \left[\left\{ \frac{1}{2} \cdot \frac{b}{2} + \frac{1}{4k} \sin\left(2k \cdot \frac{b}{2}\right) \right\} - \left\{ \frac{1}{2} \cdot 0 + \frac{1}{4k} \sin 0 \right\} \right] \\ &= C^2 \left[\frac{b}{4} + \frac{1}{4\left(\frac{3\pi}{2b}\right)} (-1) - 0 - 0 \right] \\ &= \left(\frac{1}{\sqrt{b}}\right)^2 \left[\frac{b}{4} - \frac{b}{6\pi} \right] = \frac{1}{4} - \frac{1}{6\pi} \\ &= 0.197 \approx 0.20 \end{aligned}$$

Note: $\sin\left(2k \cdot \frac{b}{2}\right) = \sin\left(2 \cdot \frac{3\pi}{2b} \cdot \frac{b}{2}\right) = \sin\left(\frac{3\pi}{2}\right) = -1$

Problem #6: Continued

(9) b) Calculate the expectation value for the kinetic energy, $\left\langle \frac{p^2}{2m} \right\rangle$,

as a function of $\hbar$, b , and m .

$$\psi = C \cos\left(\frac{3\pi}{2b}x\right) = C \cos(\alpha x) \quad \alpha = \frac{3\pi}{2b}$$

$$\frac{d\psi}{dx} = -\alpha (\sin \alpha x) \rightarrow \frac{d^2\psi}{dx^2} = -\alpha^2 C \cos(\alpha x)$$

$$\langle p^2 \rangle = \int_{-b}^b \psi(-\hbar^2) \frac{d^2\psi}{dx^2} dx$$

$$= \int_{-b}^b C \cos \alpha x (-\hbar^2) (-\alpha^2 C \cos \alpha x) dx$$

$$= +\hbar^2 \alpha^2 C^2 \int_{-b}^b \cos^2 \alpha x dx$$

$$= \hbar^2 \alpha^2 C^2 \left[\frac{1}{2}x + \frac{1}{4\alpha} \sin(2\alpha x) \right]_{-b}^b$$

$$= \hbar^2 \alpha^2 C^2 \left[\left(\frac{1}{2}b + 0 \right) - \left(-\frac{1}{2}b + 0 \right) \right]$$

$$= \frac{\hbar^2}{4\pi^2} \left(\frac{9\pi^2}{4b^2} \right) \left(\frac{1}{b} \right) (b) = \frac{9}{16} \frac{\hbar^2}{b^2}$$

$$\langle KE \rangle = \frac{\langle p^2 \rangle}{2m} = \boxed{\frac{9 \hbar^2}{32 m b^2}}$$

$$\sin(2\alpha b) = \sin\left(2 \cdot \frac{3\pi}{2b} b\right) = \sin(2\pi) = 0$$

$$\sin(2\alpha(-b)) = \sin\left(2 \cdot \frac{3\pi}{2b} (-b)\right) = \sin(-2\pi) = 0$$

(18) 7. Consider a particle in a two dimensional box of length of length $\frac{1}{2}b$ in the x direction and b in the y direction; i.e. the dimensions are: $\frac{1}{2}b \times b$

(9) a) Draw a diagram containing the lowest 6 energy **levels*** of a particle in a two dimensional box of dimensions $\frac{1}{2}b \times b$. Put the energies in units of $\frac{h^2}{8mb^2}$, and give the degeneracy of each level.

(*Note: A doubly degenerate level would count as only 1 of the 6 levels)

$$E_{n_x, n_y} = \frac{n_x^2 h^2}{8m(\frac{b}{2})^2} + \frac{n_y^2 h^2}{8mb^2} = \frac{4n_x^2 h^2}{8mb^2} + \frac{n_y^2 h^2}{8mb^2}$$

$$= (4n_x^2 + n_y^2) \left(\frac{h^2}{8mb^2} \right)$$

n_x	n_y	$E \left(\frac{h^2}{8mb^2} \right)$
1	1	5
1	2	8
1	3	13
2	1	17
1	4	20
2	2	20
2	3	25

25	23 g=1
20	14 22 g=2
17	21 g=1
13	13 g=1
8	12 g=1
5	11 g=1

Problem #7: Continued

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$b = 8 \text{ \AA} \times 10^{-10} \text{ m/\AA} = 8 \times 10^{-10} \text{ m}$$

- (9) b) The 10 π electrons in naphthalene can be treated as particles in a two dimensional box of dimensions $\frac{1}{2}b \times b$, where $b = 8 \text{ \AA}$. Use your diagram above to calculate the wavelength, in $\text{\AA}$, of the lowest energy $\pi \rightarrow \pi^*$ electronic transition in naphthalene.

$$E (\text{J}/8mb^2)$$

25	1	25	1
20	1	20	1
17	1	17	1
13	1	13	1
8	1	8	1
5	1	5	1
π		π^*	

$$\Delta E = \frac{25 h^2}{8mb^2} - \frac{20 h^2}{8mb^2} = \frac{5 h^2}{8mb^2}$$

$$E_{ph} = \Delta E = \frac{5 (6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}{8 (9.11 \times 10^{-31} \text{ kg}) (8 \times 10^{-10} \text{ m})^2}$$

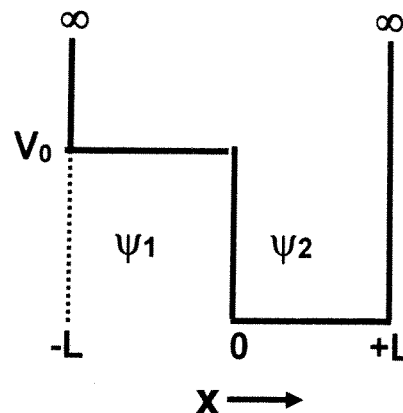
$$E_{ph} = 4.71 \times 10^{-19} \text{ J} = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E_{ph}} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s}) (3 \times 10^8 \text{ m/s})}{4.71 \times 10^{-19} \text{ J}}$$

$$= 4.22 \times 10^{-7} \text{ m} \times \frac{1 \text{ \AA}}{10^{-10} \text{ m}} = \boxed{4220 \text{ \AA}}$$

- (17) 8. Consider a particle in a box (right) with the potential energy defined by:

$$\begin{aligned} V(x) &\rightarrow \infty & -\infty < x < -L \\ V(x) &= V_0 & -L \leq x \leq 0 \\ V(x) &= 0 & 0 \leq x \leq +L \\ V(x) &\rightarrow \infty & x > +L \end{aligned}$$



For $E > V_0$, the wavefunctions in the two regions are of the form:

$$\psi_1 = A \sin[\alpha(x + L)] + B \cos[\alpha(x + L)] \quad \text{and}$$

$$\psi_2 = C \sin[\beta(L - x)]$$

α and β are positive constants.

- 8) (a) Apply the appropriate boundary condition at $x = -L$ to simplify ψ_1 and use your result for ψ_1 in the Schrödinger equation in Region 1 to develop an equation for α as a function of m , E , V_0 and $\hbar$. **SHOW YOUR WORK**

BC: $\psi_1(x = -L) = 0$

$$\begin{aligned} \psi_1 &= A \sin[\alpha \cdot 0] + B \cos[\alpha \cdot 0] \\ &= 0 + B \rightarrow \boxed{B = 0} \end{aligned}$$

$$\boxed{\psi_1 = A \sin[\alpha(x + L)]}$$

$$\frac{d\psi_1}{dx} = A \alpha \cos[\alpha(x + L)]$$

$$\begin{aligned} \frac{d^2\psi_1}{dx^2} &= A(-\alpha^2) \sin[\alpha(x + L)] \\ &= -\alpha^2 \psi_1 \end{aligned}$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_1}{dx^2} + V_0 \psi_1 = E \psi_1$$

$$-\frac{\hbar^2}{2m} (-\alpha^2 \psi_1) + V_0 \psi_1 = E \psi_1$$

$$\frac{\hbar^2}{2m} \alpha^2 + V_0 = E$$

$$\therefore \alpha^2 = \frac{2m}{\hbar^2} (E - V_0)$$

$$\boxed{\alpha = \sqrt{\frac{2m}{\hbar^2} (E - V_0)}}$$

Problem #8: Continued

- (9) (b) Apply the appropriate boundary conditions at $x = 0$ to develop two (2) relationships between the wavefunction parameters in the two regions

SHOW YOUR WORK

$$\psi_1 = A \sin[\alpha(x+L)]$$

$$\psi_2 = C \sin[\beta(L-x)]$$

$$\frac{d\psi_1}{dx} = \alpha A \cos[\alpha(x+L)]$$

$$\frac{d\psi_2}{dx} = -\beta C \cos[\beta(L-x)]$$

BC-1 $\psi_1(x=0) = \psi_2(x=0)$

∴ $A \sin(\alpha L) = C \sin(\beta L)$

BC-2

$$\left[\frac{d\psi_1}{dx} \right]_{x=0} = \left[\frac{d\psi_2}{dx} \right]_{x=0}$$

∴ $\alpha A \cos(\alpha L) = -\beta C \cos(\beta L)$