KEY

First Exam (90 pts. possible)

Please budget your time carefully and show all work for partial credit. Read each problem carefully!

$h = 6.62608 \times 10^{-34}$ J s $\quad N_A = 6.02214 \times 10^{23}$ mol^{-1}
$m_e = 9.10939 \times 10^{-31}$ kg $\quad$ 1 nm = 1×10^{-9} m
$c = 2.99792 \times 10^{8}$ m/s

(1) (10 pts) Concisely explain what the "ultraviolet catastrophe" was in regards to the blackbody radiation problem and what Max Planck proposed that reconciled theory and experiment.

Classical theory (Raleigh-Jeans) was able to describe the low frequency part of the emission distribution but blew-up at high frequencies, i.e., even at low T the blackbody was predicted to emit radiation of all frequencies.
Planck proposed the oscillators of the blackbody could only exchange energy in units of $h\nu$

(2) (10 pts) Consider the photoelectric effect on zinc metal, which has a work function Φ of 5.816×10^{-19} J (i.e., a threshold frequency $\nu_0 = 8.777 \times 10^{14}$ s^{-1}). Use conservation of energy to calculate the maximum kinetic energy (in J) of an emitted electron when light of wavelength 140.0 nm strikes the surface of a sample of zinc metal.

Conservation of energy: $\quad K.E\ e^-\text{'s} = h\nu - \Phi$

$$h\nu = \frac{hc}{\lambda} = \frac{(6.62608 \times 10^{-34})(2.99792 \times 10^{8})}{140.0 \times 10^{-9}\ \text{m}}$$

$$= 1.41889 \times 10^{-18}\ \text{J}$$

$$K.E = 1.41889 \times 10^{-18} - 5.816 \times 10^{-19}$$

$$= 8.373 \times 10^{-19}\ \text{J}$$

(3) (10 pts) Show that the linear combination $\hat{B}+i\hat{C}$ is <u>not</u> hermitian if $\hat{B}$ and $\hat{C}$ <u>are</u> hermitian operators.

Show $\int \psi^*(B+iC)\phi\, d\tau \neq \int (B+iC)^*\psi^*\phi\, d\tau$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$\int \psi^* B\phi\, d\tau + i\int \psi^* C\phi\, d\tau \qquad\qquad \int B^*\psi^*\phi\, d\tau - i\int C^*\psi^*\phi\, d\tau$$

$\downarrow$ hermitian $\qquad$ $\downarrow$ hermitian

$$\int B^*\psi^*\phi\, d\tau + i\int C^*\psi^*\phi\, d\tau \qquad \neq$$

✓

(4) (10 pts) Evaluate the commutator $\left[\frac{1}{x^2}, p_x^2\right]$, where $p_x^2 = -\hbar^2 \frac{d^2}{dx^2}$

$$\left[\frac{1}{x^2}, p_x^2\right] = -\hbar^2\left[\frac{1}{x^2}, \frac{d^2}{dx^2}\right]$$

$$-\hbar^2\left[\frac{1}{x^2}, \frac{d^2}{dx^2}\right]f = -\hbar^2\left(\frac{1}{x^2}\frac{d^2f}{dx^2} - \frac{d}{dx}\frac{d}{dx}\frac{1}{x^2}f\right)$$

$$= -\hbar^2\left(\frac{1}{x^2}\frac{d^2f}{dx^2} - \frac{d}{dx}\left(\frac{1}{x^2}\frac{df}{dx} + -2x^{-3}f\right)\right)$$

$$= -\hbar^2\left(\frac{1}{x^2}\frac{d^2f}{dx^2} - \left(\frac{1}{x^2}\frac{d^2f}{dx^2} - 2x^{-3}\frac{df}{dx} + 6x^{-4}f - 2x^{-3}\frac{df}{dx}\right)\right)$$

$$= -\hbar^2\left(\frac{4}{x^3}\frac{df}{dx} - \frac{6}{x^4}f\right)$$

$$\therefore \left[\frac{1}{x^2}, p_x^2\right] = \left(\frac{4}{x^3}\frac{d}{dx} - \frac{6}{x^4}\right)(-\hbar^2)$$

(5) (25 pts) Consider a particle in a one-dimensional, infinitely deep box of length L with energies and wave functions given by $E_n = \frac{n^2h^2}{8mL^2}$ and $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$, where $n = 1, 2, 3, \ldots$

(a) Why do we ignore the solution with $n = 0$?

for $n=0$, $\psi=0$ everywhere $\Rightarrow$ we have no particle in the box

(b) The lowest allowable energy is non-zero. How does this relate to the Heisenberg Uncertainty Principle? (be brief)

if E could be zero, Δp (uncertainty in p) $= 0$

but we know Δx to within L

$\therefore \quad \Delta x \Delta p \geq \frac{\hbar}{2}$ is violated

(c) Briefly describe two examples that demonstrate the Bohr Correspondence Principle for this system.

as $L \to \infty$, the energy spacing $\to 0$ continuous E

as $m \to \infty$, same

as $n \to \infty$, $|\psi|^2 \to$ constant

(d) Give a single expression that would allow you to calculate the total probability of finding the particle in either the left 1/4 or right 1/4 of the box. Label carefully but do not solve.

$$\text{prob} = \int_0^{L/4} |\psi|^2 dx + \int_{\frac{3L}{4}}^{L} |\psi|^2 dx$$

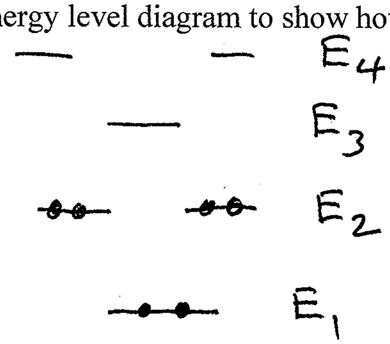
$$= \frac{2}{L}\int_0^{L/4} \sin^2\left(\frac{n\pi}{L}x\right)dx + \frac{2}{L}\int_{3L/4}^{L} \sin^2\left(\frac{n\pi}{L}x\right)dx$$

(6) (25 pts.) One can use an alternative free electron molecular orbital (FEMO) model for molecules like benzene by using a 2-dimensional box and assuming the area of the box is the same as the cross-sectional area of the molecule. Let's use a square box to describe the π electrons in benzene.

(a) Based on what you know about the 1-dimensional case given in problem (5), give the quantum numbers (n_x, n_y), energies (in units of $\frac{h^2}{8mL^2}$), and degeneracies of the first 4 energy levels of this 2-dimensional square box. I've filled in the 1st entry for you.

Level	(n_x, n_y) of all states in the level	Energy	Degeneracy
1	(1,1)	2	1
2	(2,1) (1,2)	5	2
3	(2,2)	8	1
4	(3,1) (1,3)	10	2

(b) Draw and label an energy level diagram to show how benzene's 6 π electrons fill the box.



(c) The lowest energy excitation of benzene (highest filled orbital to lowest unfilled) is observed at a wavelength of 200 nm. Using the FEMO model above, what box area (in nm^2) would correspond to this wavelength?

$$\Delta E = (8-5)\frac{h^2}{8mL^2} = \frac{3h^2}{8mA} \qquad \text{where area} = A = L^2$$

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{3h^2}{8mA}$$

$$A = \frac{3h\lambda}{8mc} = \frac{(3)(6.62608\times10^{-34})(200\times10^{-9})}{(8)(9.10939\times10^{-31})(2.99792\times10^{8})}$$

$$= 1.8197\times10^{-19}\ m^2 = 0.182\ nm^2$$