2021 Spring CH211 Physical Chemistry I

Midterm Exam

(April 21st (Wednesday), Time: 9:00 am – 11:20 am)

Total 155 pts (135 full pts + 20 bonus pts)

Problem 1. 15 pts

Problem 2. 10 pts

Problem 3. 10 pts

Problem 4. 20 pts

Problem 5. 10 pts

Problem 6. 15 pts

Problem 7. 10 pts

Problem 8. 10 pts

Problem 9. 30 pts

Problem 10. 10 pts

Problem 11. 15 pts

You may refer to the following information.

$e = 1.602 \times 10^{-19}\ C$

$1\ D = 3.33564 \times 10^{-30}\ C\ m$

$\varepsilon_0 = 8.854 \times 10^{-12}\ J^{-1}\ C^2\ m^{-1}$

$\mu_0 = 4\pi \times 10^{-7} J\ s^2\ C^{-2}\ m^{-1}$

$N_A = 6.022 \times 10^{23}\ mol^{-1}$

$R = 8.3141\ J\ K^{-1}\ mol^{-1}$

$k = 1.381 \times 10^{-23}\ J\ K^{-1}$

$h = 6.626 \times 10^{-34}\ J\ s$

$1\ hartree = 27.2114\ eV$

$\hbar = 1.0545 \times 10^{-34}\ J\ s$

$1\ eV = 1.602 \times 10^{-19}\ J$

$m_e = 9.109 \times 10^{-31}\ kg$

$c = 2.998 \times 10^8\ m\ s^{-1}$

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = (\pi/a)^{1/2}$$

$$\int_0^{\infty} xe^{-ax^2} dx = \frac{1}{2a}$$

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{4a^{3/2}}$$

$$\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

$$\int_0^{\infty} x^4 e^{-ax^2} dx = \frac{3}{8}(\frac{\pi}{a^5})^{1/2}$$

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$sinx = x - \frac{1}{6}x^3 + \cdots$$

$$(1 + x^2)^{1/2} = 1 + \frac{1}{2}x^2 - \frac{1}{8}x^4 + \cdots$$

$$(1 + x)^{-1} = 1 - x + x^2 - x^3 + x^4 \cdots$$

$$(1 + x)^{-1/2} = 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \frac{15}{48}x^3 + \frac{105}{384}x^4 \cdots$$

$$cos^2 x = \frac{1 + cos2x}{2}$$

$$e^{ix} = cosx + isinx$$

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \cdots$$

$$dxdydz = 4\pi r^2 dr$$

$$\mu = QR$$

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

$$\alpha = 4\pi\varepsilon_0 \alpha'$$

$$(\varepsilon_r - 1)/(\varepsilon_r + 2) = \rho P_m / M$$

$$P_m = \left({N_A}/{3\varepsilon_0}\right)\left(\alpha + {\mu^2}/{3kT}\right)$$

$$n_r = \varepsilon_r^{\frac{1}{2}}$$

$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\varepsilon_0 r^3} \quad \text{where} \quad f(\theta) = 1 - 3cos^2\theta$$

$$V = 4\varepsilon\{({r_0}/{r})^{12} - ({r_0}/{r})^6\}$$

$$E_p = -A \times \frac{|z_A z_B| N_A e^2}{4\pi\varepsilon_0 d}$$

$$\mathrm{pV} = \frac{1}{3} nMc^2$$

$$4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$$

$$\frac{e^2}{2\varepsilon_0 h} = \frac{c}{137}$$

$$\int \psi_i^* \hat{A} \psi_j \, d\tau \; = \; \int \psi_j (\hat{A}\psi_i)^* \, d\tau$$

$$\mathrm{a}_0 = 4\pi\epsilon_0 \hbar^2 / me^2$$

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

$$Y_0^0 = 1/(4\pi)^{\frac{1}{2}}$$

$$\mathrm{G} = 6.672 \times 10^{-11} m^3 kg^{-1} s^{-2}$$

$$d\rho(v,T) = \rho_v(T) dv = \frac{8\pi h}{c^3} \frac{\mathrm{v}^3 dv}{\mathrm{e}^{\frac{\mathrm{hv}}{\mathrm{k_B T}}} - 1}$$

$$d\rho(\lambda,T) = \rho_\lambda(T) d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{\mathrm{e}^{\frac{\mathrm{hc}}{\lambda \mathrm{k_B T}}} - 1}$$

$$\lambda_{max} T = \frac{hc}{4.965 \mathrm{k_B}}$$

$$\tilde{v} = 109680 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \; cm^{-1}$$

$$\lambda = \frac{h}{mv}$$

$$\Delta_r G^0 = -RT \left[\frac{\Delta \bar{V}}{RT}(P-1)\right]$$

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

$$\tilde{v} = 2\tilde{B}(J+1)$$

$$E = hv = \frac{hc}{\lambda}$$

$$KE = \frac{1}{2} mv^2 = hv - \phi$$

$$\int \psi^* \psi \; d\tau = 1$$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

$$< A > \; = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau}$$

In 1-d particle in a box, $E = \frac{\mathrm{n}^2 \pi^2 \hbar^2}{2mL^2}$

And wavefunction $\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$

TABLE 4.1
Classical-mechanical observables and their corresponding quantum-mechanical operators.

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
	$\mathbf{r}$	$\hat{\mathbf{R}}$	Multiply by $\mathbf{r}$
Momentum	p_x	$\hat{P}_x$	$-i\hbar\frac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{P}}$	$-i\hbar\left(\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
			$=-\frac{\hbar^2}{2m}\nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x, y, z)$	$\hat{V}(\hat{x}, \hat{y}, \hat{z})$	Multiply by $V(x, y, z)$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
			$+\ V(x, y, z)$
			$=-\frac{\hbar^2}{2m}\nabla^2+V(x, y, z)$
Angular momentum	$L_x = yp_z - zp_y$	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	$L_y = zp_x - xp_z$	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	$L_z = xp_y - yp_x$	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

1. (Total 15 pts) Solve the following sub-problems, (a), (b), and (c).

(a) By calculating the equation below, show that the total energy emitted by the blackbody radiation is dependent on T^4. (5 pts) (5 pts for a correct answer, 0 pt otherwise)

$x = \frac{h\nu}{k_B T} \to \nu^3 = \left(\frac{k_B T}{h}\right)^3 x$

$dx = \frac{h}{k_B T} d\nu$

$$\int_0^\infty \frac{8\pi h}{c^3} \frac{v^3 dv}{e^{\frac{hv}{k_B T}} - 1}$$

$\frac{8\pi h}{c^3}\left(\frac{k_B T}{h}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx \to \pi^4/15$

$d\rho(v, T) = \rho_v(T)dv = \frac{8\pi h}{c^3}\frac{v^3 dv}{e^{\frac{hv}{k_B T}}-1}$

$d\rho(\lambda, T) = \rho_\lambda(T)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{\frac{hc}{\lambda k_B T}}-1}$

$\lambda_{max} T = \frac{hc}{4.965 k_B}$

(b) When a clean surface of silver is irradiated with light of wavelength 267 nm, the kinetic energy of the ejected electrons is found to be 0.374 eV. Calculate the work function and the threshold frequency of silver. (5 pts) (5 pts for a correct answer, 0 pt otherwise)

$K.E. = \frac{hc}{\lambda} - \phi \qquad \phi = hf_0$

(c) Compare a wavelength of 9.3 keV X-ray with a de Broglie wavelength of neutron at 1% of the speed of light. (5 pts) (5 pts for a correct answer with correct values, 0 pt otherwise)

$\lambda = \frac{h}{p}$

2. (Total 10 pts) Suppose that λ and μ are two distinct eigenvalues of operator $\hat{A}$ and let x and y be eigenvectors corresponding to λ and μ, respectively.

(a) If a and b are nonzero numbers, then prove that $ax + by$ is not an eigenvector of $\hat{A}$. (5 pts) (5 pts for a perfect answer, 2 pts for an answer with a slight mistake, 0 pt otherwise)

(Hint) Two eigenvectors corresponding to distinct eigenvalues are linearly (x, y) independent.

$\hat{A}x = \lambda x$

$\hat{A}y = \mu y$

$\hat{A}(ax+by) = \hat{A}(ax) + \hat{A}(by) = a\lambda x + b\mu y$

If it is eigenvector; $\hat{A}(ax+by) = \varepsilon(ax+by)$

$a(\lambda-\varepsilon)x + b(\mu-\varepsilon)y = 0$

$a(\lambda-\varepsilon) = 0 \qquad b(\mu-\varepsilon) = 0$

(b) Suppose that two eigenvectors, ψ_1 and ψ_2, of an operator $\hat{A}$ have the same eigenvalue λ. Prove that any linear combination of ψ_1 and ψ_2 has the same eigenvalue λ. (5 pts) (5 pts for a perfect answer, 0 pt otherwise)

$\hat{A}\psi_1 = \lambda\psi_1$

$\hat{A}\psi_2 = \lambda\psi_2$

$\hat{A}(a\psi_1 + b\psi_2) = a\hat{A}(\psi_1) + b\hat{A}(\psi_2)$

$= a\lambda\psi_1 + b\lambda\psi_2$

$= \lambda(a\psi_1 + b\psi_2)$

3. (Total 10 pts) According to the postulate 2,

"To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics"

$\hat{A}\psi_1 = \mu\psi_1 \quad \hat{A}\psi_2 = \lambda\psi_2$

Prove that the linear Hermitian operator has real eigenvalues and eigenfunctions of the Hermitian operator with different eigenvalues are orthogonal. (10 pts) (10 pts for a perfect answer, 5 pts for a correct partial answer, 0 pt otherwise)

(Hint: for any Hermitian operator $\hat{A}$, $\int \psi_i^* \hat{A}\psi_j \, d\tau = \int \psi_j (\hat{A}\psi_i)^* \, d\tau$. Here * refers to conjugate transpose. You may start the prove with this relation.)

$\int \psi_1^* (\lambda\psi_2)\, d\tau = \int \psi_2 (\mu\psi_1)^* \, d\tau$

$\lambda \int \psi_1^*\psi_2 \, d\tau - \mu^* \int \psi_2 \psi_1^* \, d\tau = 0$

$\int \psi_1^* \psi_2 \, d\tau \, (\lambda - \mu^*) = 0$

since $\lambda \neq \mu$; $\int \psi_1^* \psi_2 \, d\tau = 0$

4. (Total 20 pts) For an aromatic ring compound, we can apply a simple crude model, called particle on a 1-dimensional (1D) ring to its pi conjugated system. The Schrödinger equation for a free particle which is restricted to a ring is

$$\mathrm{H}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi = \mathrm{E}\psi$$

Using polar coordinates on the 1D ring of radius r, the wave function depends only on the angular coordinate, and ∇^2 can be expressed as follows.

$$\nabla^2 = 1/r^2 \frac{\partial^2}{\partial\theta^2}$$

(a) By applying $\psi(\theta) = e^{\lambda\theta}$ in the Schrödinger equation above, express λ with $E, m, \hbar, r$. (5 pts)

(5 pts for a perfect answer, 0 pt otherwise)

$\frac{\partial}{\partial\theta}\psi(\theta) = \lambda e^{\lambda\theta}$

$\frac{\partial^2}{\partial\theta^2}\psi(\theta) = \lambda^2 e^{\lambda\theta} = \lambda^2 \psi(\theta)$

$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\right)\lambda^2 \psi(\theta) = E\psi(\theta)$

$\lambda^2 = \frac{-2Emr^2}{\hbar^2}$

$\lambda = \frac{i}{\hbar}\sqrt{2Emr^2}$

$$\psi(\theta) = e^{\lambda\theta} \qquad \lambda = \frac{i}{\hbar}\overset{A}{\sqrt{2Emr^2}}$$

(b) As we assumed that the particle is restricted to a ring, we can set an initial condition for $\psi(\theta)$ as the following equation.

$$\psi(\theta) = \psi(\theta + 2\pi) \qquad \cdots \ (1)$$

Using this initial condition (1) and the relation $e^{i\theta} = \cos\theta + i\sin\theta$, express the energy of the system with $m, \hbar, r, and\ integer\ n$. (5 pts) (5 pts for a perfect answer, 2 pts for a correct partial answer, 0 pt otherwise)

$$\psi(\theta + 2\pi) = e^{\lambda(\theta+2\pi)} = e^{\lambda\theta}$$

$$e^{\lambda 2\pi} = e^{2iA\pi} = \cos(A2\pi) + i\sin(A2\pi) = 1$$

$$A2\pi = 2n\pi\ ; \ n = 0, \pm 1, 2, \ldots$$

$$\frac{\sqrt{2Emr^2}}{\hbar} = 2n$$

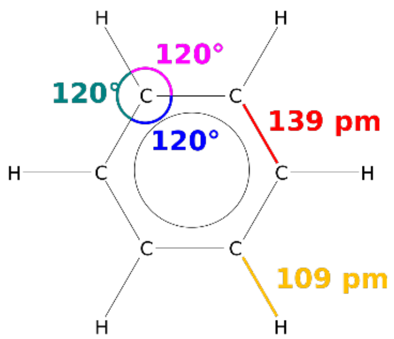
$$E = \frac{n^2\hbar^2}{2mr^2}$$

(c) By far, we derived the energy of the system and we can now realize the $\psi(\theta)$ we applied is an eigenfunction of the system. But the function is not normalized. Find the normalization coefficient of $\psi(\theta)$. (5 pts) (5 pts for a correct answer, 0 pt otherwise)

$$\int_0^{2\pi} \psi(\theta)\psi^*(\theta)\, d\theta = 1$$

$$N^2 \int_0^{2\pi} e^{iA} \cdot e^{-iA}\, d\theta = N^2(2\pi) = 1 \longrightarrow N = \frac{1}{\sqrt{2\pi}}$$

(d) The structure of Benzene, one of the simplest aromatic compounds, is shown below. Calculate the HOMO-LUMO energy gap of benzene **in eV** by approximating benzene as a particle in a 1D ring model. Note that six π electrons are evolved in the π conjugated system of benzene. (5 pts) (5 pts for a perfect answer, 2 pts for a correct partial answer, 0 pt otherwise)



LUMO $n = \pm 2$

HOMO $n = \pm 1$

$n = 0$

$$\Delta E = (4-1)\frac{\hbar^2}{2mr^2}$$

$r = 139$ pm

5. (Total 10 pts) There is a free particle with the following wavefunction:

$$\psi(x) = ae^{ikx} + be^{-ikx}$$

(a) $\psi(x)$ is an eigenfunction of $\hat{H}$. Find the eigenvalue of $\hat{H}$. (5 pts) (5 pts for a correct answer, 0 pt otherwise)

$\frac{\partial^2}{\partial x^2} = -kae^{ikx} - kbe^{-ikx}$

$= -k\,\psi(x)$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$\frac{\hbar^2 k}{2M}$

(b) What is the expectation value of $\hat{H}$? (5 pts) (5 pts for a correct answer, 0 pt otherwise)

$E\,\psi(x)$

6. (Total 15 pts) Solve the following sub-problems, (a), (b), and (c).

(a) Starting with $\langle x \rangle = \int \Psi^*(x,t)x\Psi(x,t)dx$

and the time-dependent Schrödinger equation, show that $\frac{d\langle x \rangle}{dt} = \int \Psi^* \frac{i}{\hbar}\left(\hat{H}x - x\hat{H}\right)\Psi dx$. (5 pts for a correct answer, 0 pt otherwise)

(b) Given that $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$, show that $\hat{H}x - x\hat{H} = -2\frac{\hbar^2}{2m}\frac{d}{dx} = -\frac{\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x = -\frac{i\hbar}{m}\hat{P}_x$. (5 pts for a correct answer, 0 pt otherwise)

(c) Finally, substitute this result into the equation for $\frac{d\langle x \rangle}{dt}$ to show that $m\frac{d\langle x \rangle}{dt} = \langle \hat{P}_x \rangle$. And interpret this result. (5 pts for a correct answer, 0 pt otherwise)

7. (Total 10 pts) What is the speed of the electron in Bohr's model for the hydrogen atom in the quantum state n = 2? Express it in terms of the speed of light, c. (10 pts) (10 pts for a correct answer, 0 pt otherwise)

8. (Total 10 pts) For the wavefunction of hydrogen atom $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, prove that $R_{10}(r)Y_0^0(\theta, \phi)$ is an eigenfunction of H with $l = 0$ and show the energy of the wavefunction. (10 pts) (10 pts for a correct answer, 0 pt otherwise)

(Hint: Schrodinger equation for the spherical harmonics: $H = -\frac{\hbar^2}{2m}\left\{\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right\} + \frac{\hbar}{2m}l(l+1) - \frac{Ze^2}{4\pi\epsilon_0 r}$)

9. (Total 30 pts) Answer the following questions.

(a) What is the difference between a "wavefunction" and an "orbital"? (5 pts) (5 pts for a correct answer, 0 pt otherwise)

(b) What are the quantum numbers n, l, and m of the following function? (5 pts) (5 pts for a correct answer, 0 pt otherwise)

$$\psi_{nml} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin\theta \cos\theta \, e^{-i\phi}, where \;\; \sigma = \frac{Zr}{a_0}.$$

(c) How many radial nodes and angular nodes does the wavefunction shown in (b)? How many nodes in total does it have? (5 pts) (5 pts for a correct answer, 0 pt otherwise)

(d) Write down the functional form of $R_{31}(r)$ in terms of r, θ, φ, and a_0 (Bohr radius). (5 pts) (5 pts for a correct answer, 2 pts for an answer with a slight mistake, 0 pt otherwise)

(e) Write down the functional form of $Y_1^{-1}(\theta, \phi)$ in terms of r, θ, φ, and a_0 (Bohr radius). (5 pts) (5 pts for a correct answer, 0 pt otherwise)

(f) Write down the functional form of the orbital with n = 3, l = 1, m = -1 in terms of r, θ, φ, and a_0 (Bohr radius). (5 pts) (5 pts for a correct answer, 0 pt otherwise)

10. (Total 10 pts) Write down the Schrodinger equation for "two" particles in 2-dimensional box where the potential energy is 0 inside the box and infinity outside the box. (10 pts for a perfect answer, 3 pts for an answer with a slight mistake, 0 pt otherwise)

11. (Total 15 pts) Answer the following questions.

(a) How many approximation methods were mentioned in the chapter 7 of the textbook? (5 pts) (5 pts for a correct answer, 0 pt otherwise)

(b) Write down the names of the approximation methods in (a). (5 pts) (5 pts for a correct answer, 0 pt otherwise)

(c) Write down the name of the approximation method stated below. (5 pts) (5 pts for a correct answer, 0 pt otherwise)

"If ϕ is any well-behaved function that satisfies the boundary conditions associated with the problem of interest, then the expectation value of H, calculated using ϕ, will obey the inequality

$< E_\phi > = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$, w*here E_0 is the exact ground-state energy."*