

2021 Spring CH211 Physical Chemistry I

Final Exam

(June 16th (Wednesday), Time: 9:00 am – 11:20 am)

Total 170 pts (150 full pts + 20 bonus pts)

Problem 1. 10 pts

Problem 2. 10 pts

Problem 3. 15 pts

Problem 4. 25 pts

Problem 5. 15 pts

Problem 6. 20 pts

Problem 7. 15 pts

Problem 8. 10 pts

Problem 9. 25 pts

Problem 10. 10 pts

Problem 11. 15 pts

You may refer to the following information.

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

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

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$$

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

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

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

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

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

$$1 \text{ hartree} = 27.2114 \text{ eV}$$

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

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

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

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

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

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

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

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

$$\sin x = x - \frac{1}{6}x^3 + \dots$$

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

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

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

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

$$e^{ix} = \cos x + i \sin x$$

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

$$dx dy dz = 4\pi r^2 dr$$

$$\mu = QR$$

$$V = \frac{Q_1 Q_2}{4\pi\epsilon_0 r}$$

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

$$\alpha = 4\pi\epsilon_0\alpha'$$

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

$$P_m = \left(N_A / 3\epsilon_0 \right) \left(\alpha + \mu^2 / 3kT \right)$$

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

$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\epsilon_0 r^3} \text{ where } f(\theta) = 1 - 3\cos^2\theta$$

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

$$E_p = -A \times \frac{|z_A z_B| N_A e^2}{4\pi\epsilon_0 d}$$

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

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

$$\frac{e^2}{2\epsilon_0 h} = \frac{c}{137}$$

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

$$a_0 = 4\pi\epsilon_0 \hbar^2 / me^2$$

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

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

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

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

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

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

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

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

$$E = h\nu = \frac{hc}{\lambda}$$

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

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

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

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau}$$

For 1-D particle in a box,

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

and

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

$$\mu_z(x) = \mu_0 + \left(\frac{\partial \mu}{\partial x} \right)_{x=0} x + \dots$$

$$xH_v(x) = vH_{v-1}(x) + \frac{1}{2}H_{v+1}(x)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

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

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

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

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

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

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (-1 < x \leq 1)$$

$$\sinh x = \frac{e^x - e^{-x}}{2}$$

Final Exam

1. (Total 10 pts)

(a) Derive the expression for the standard deviation of the bond length of a diatomic molecule with \hbar , c , $\tilde{\nu}$, and μ when it is in its ground state. (5 pts for the correct answer. 0 pt otherwise)

(b) What is the standard deviation for the bond length of carbon monoxide ($^{12}\text{C}^{16}\text{O}$) in its ground state? For $^{12}\text{C}^{16}\text{O}$, $\tilde{\nu} = 2170 \text{ cm}^{-1}$. (5 pts for the correct answer. 2 pts for the answer with a simple mistake. 0 pt otherwise)

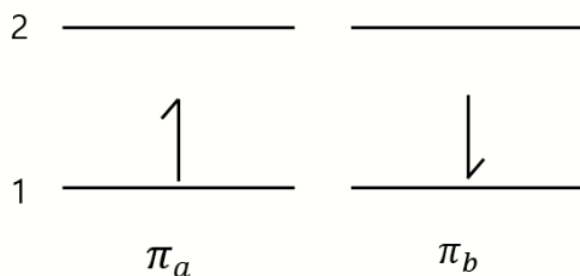
2. (Total 10 pts)

(a) Write the rate equation for the population of $N_1(t)$ and $N_2(t)$ for a nondegenerate two-level system in terms of N_1 , N_2 , B_{12} , A_{21} , B_{21} , and $\rho_\nu(\nu_{12})$. (5 pts for the correct answer, 0 pt otherwise)

(b) Assume that all the atoms are in the ground state at time $t = 0$ so that $N_1(t = 0) = N_{total}$, $N_2(t = 0) = 0$. Then solve the equation and get $N_2(t)$. (Express $N_2(t)$ in terms of Einstein coefficients, N_{total} , $\rho_\nu(\nu_{12})$, and t) (5 pts for the correct answer, 0 pt otherwise)

Final Exam

3. (Total 15 pts) Consider the following orbital configuration in a molecule.



Note that the orbitals are labeled $1\pi_a$, $1\pi_b$, $2\pi_a$, and $2\pi_b$, as indicated in the diagram, and the electron spins are indicated by up and down arrows.

(a) This configuration corresponds to a Slater determinant (*a. k. a. determinantal wave function*). Write down the corresponding Slater determinant with the correct normalization constant.

(8 pts for the correct answer, 4 pts for a partial answer with minor mistakes, 0 pt otherwise)

(b) Does the Slater determinantal wavefunction in a) describe a singlet or triplet spin state? Or Neither? Explain. (7 pts for the correct answer, 3 pts for a partial answer with minor mistakes, 0 pt otherwise)

(Hint: deriving the term symbol for $(1\pi_a)^2$ electron configuration will be helpful.)

Final Exam

4. (Total 25 pts) Here is a definition of the *variational principle* :

"If an arbitrary is used to calculate the energy, the value calculated is never less than the true energy"

(a) Now let us consider a trial wavefunction $\Psi_{\text{trial}} = \sum_{n=0} c_n \psi_n$, where ψ_n are true wavefunctions of the system, and c is a real-number parameter. The trial wavefunction is normalized so that $\sum_n |c_n|^2 = 1$. Starting with the expectation value $\langle E_{\Psi_{\text{trial}}} \rangle = \int \Psi_{\text{trial}}^* H \Psi_{\text{trial}} d\tau$, show that the true lowest energy E_0 is always less than the expectation value of the energy of the trial function. (10 pts for the correct answer, 5 pts for a partial answer with minor mistakes, 0 pt otherwise)

b) According to the variational principle, any function ϕ that we substitute for the real eigenfunction of the ground state will have greater energy E_ϕ than the ground-state energy E_0 . That is,

$$\langle E_\phi \rangle = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

Applying the property, show that if a trial function ψ_1 gives a certain energy E_1 , then a new function $\psi_1 + c\psi_2$, where c is a variational parameter, cannot give a higher trial energy. For simplicity, assume that ψ_1 and ψ_2 are orthonormalized ($\int \psi_1^* \psi_2 d\tau = 0$ and $\int \psi_1^* \psi_1 d\tau = 1$), c is real, and $\int \psi_1^* H \psi_2 d\tau = \int \psi_2^* H \psi_1 d\tau = 0$. (15 pts) (15 pts for the correct answer, 5 pts for partial answers with minor mistakes, 0 pt otherwise)

Final Exam

5. (Total 15 pts) Cyclopentadienyl anion, $[\text{C}_5\text{H}_5]^-$, is formed when cyclopentadiene is deprotonated.

(a) Write down the Hückel secular determinant (matrix form) for cyclopentadienyl anion. Use α and β to denote the Coulomb integrals and the resonance integrals, respectively, as commonly used in the Hückel approximation. (5 pts) (5 pts for the correct answer, 2 pts with an answer with a minor mistake, 0 pt otherwise)

(b) Draw the ground-state electron configuration of the π electrons in cyclopentadienyl anion with the energy levels in terms of α and β . (10 pts) (10 pts for the correct answer, 5 pts with an answer with a minor mistake, 0 pt otherwise)

Final Exam

6. (Total 20 pts)

(a) Write down the ground-state electron configuration of B_2^+ . (5 pts) (5 pts for the correct answer, 0 pt otherwise)

(b) Write down the term symbol of B_2^+ at (a). (5 pts) (5 pts for the correct answer, 0 pt otherwise)

(c) Write down the ground-state electron configuration of O_2^- . (5 pts) (5 pts for the correct answer, 0 pt otherwise)

(d) Write down the term symbol of O_2^- at (c). (5 pts) (5 pts for a correct answer, 0 pt otherwise)

7. (Total 15 pts)

The harmonic oscillator wavefunctions are $\psi_v(x) = N_v H_v\left(\alpha^{1/2}x\right) e^{-\alpha x^2/2}$, where $H_v\left(\alpha^{1/2}x\right)$ is a Hermitian polynomial and $\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$. The transition dipole moment for electromagnetic radiation polarized along the z axis is $(\mu_z)_{v,v'} = \int_{-\infty}^{\infty} N_v N_{v'} H_{v'}\left(\alpha^{1/2}x\right) e^{-\alpha x^2/2} \mu_z H_v\left(\alpha^{1/2}x\right) e^{-\alpha x^2/2} dx$. Derive the vibrational selection rule from the equations above. (15 pts for the correct answer, 7 pts for an answer with a simple miscalculation, 0 pt otherwise)

Hint 1) The transition moment can be expanded as, $\mu_z(x) = \mu_0 + \left(\frac{\partial \mu}{\partial x}\right)_{x=0} x + \dots$. (Use only to the second term.)

Final Exam

8. (10 pts) An atom with orbital angular momentum L and spin angular momentum S often has a term in its Hamiltonian of the form $A(L \cdot S)$ called the spin-orbit coupling term. Since the total angular momentum $J = L + S$ commutes with the Hamiltonian, the states of this atom can be labeled with the eigenvalues of J^2 , J_z , L^2 , and S^2 . Note that $L \cdot S = \frac{1}{2}(J^2 - L^2 - S^2)$ so that the eigenvalue of $L \cdot S$ is $\frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$. The spin-orbit coupling can lead to observable energy level splitting. For example, the excited states of an alkali atom with the outermost electron excited from the s to the next higher p orbital will have $L=1$ and $S=1/2$, which lead to two possible J values: $3/2$ and $1/2$.

Calculate the energy level splitting due to spin-orbit coupling. (10 pts for the correct answer, 0 pt otherwise)

(A is a constant number)

Final Exam

9. (Total 25 pts)

(a) How many microstates are there for the nd^2 electron configuration? (5 pts) (5 pts for the correct answer. 0 pt otherwise)

(b) What are the term symbols for the nd^2 electron configuration? Write down all term symbols considering S and L. (10 pts) (10 pts for the correct answer, 5 pts for an answer with minor mistakes, 0 pt otherwise)

(c) What are the values of J associated with each of these term symbols at (b)? (5 pts) (5 pts for the correct answers. 0 pt otherwise)

(d) Which term symbol represents the ground state? (5 pts for the correct answer, 0 pt otherwise)

Final Exam

10. (10 pts) Use the 1st order correction of the perturbation theory to calculate the ground-state energy of a particle constrained to move within the region $0 \leq x \leq a$ in a potential given by

$$V = \epsilon \text{ in } 0 \leq x \leq \frac{a}{2}$$
$$= 0 \text{ in } \frac{a}{2} \leq x \leq a$$

The energy and wave function of 1D particle-in-a-box are as follows: $E = \frac{n^2 h^2}{8ma^2}$, $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$

(10 pts for the correct answer, 5 pts for a partial answer with minor mistakes, 0 pt otherwise)

Final Exam

11. (Total 15 pts) a) The ground-state term symbol for O_2^+ is $^2\Pi_g$. The first electronic excited state has an energy of 38795 cm^{-1} above that of the ground state and has a term symbol of $^2\Pi_u$. Is the radiative $^2\Pi_u \rightarrow ^2\Pi_g$ decay of the O_2^+ molecule an example of fluorescence or phosphorescence? Also provide the justification for your answer.

(5 pts for the correct answer, 0 pt otherwise)

b) (10 pts) A titanium sapphire (Ti:sapphire) laser operating at 780 nm produces pulses at a repetition rate of 100 MHz. If each pulse is 25 fs in duration and the average radiant power of the laser is 1.4 W, calculate the radiant power of each laser pulse. How many photons are produced by this laser in one second? (10 pts)(5 pts for the correct answer, 5 pts for a partial answer with minor mistakes, 0 pt otherwise)