

Chem 21a Midterm Exam

Distributed 2 pm, Friday November 2, 2007

Due Back by 5 pm, Friday, November 9, 2007 outside Noyes 120

You have 4 continuous hours in which to complete this exam. You may use your notes and homework sets from this class, homework sets and solutions from the class website, the textbook for this class (*Molecular Quantum Mechanics* by Atkins/Friedman), and standard mathematical tools (calculators, integral tables, Mathematica, etc.). Good luck!!

1. Modeling Spectroscopy of the Carbon Monoxide Molecule (30 points).

- a. Small amplitude vibrations of a diatomic molecule can be studied using the simple harmonic oscillator, $V(x)$, as a model for the molecular vibrational potential, where the force constant is approximately $k_f = 50 \text{ Jm}^{-2}$.

$$V(x) = 0.5 k_f x^2$$

- i. Calculate the value of the zero point vibrational energy of a carbon monoxide molecule.
 - ii. Calculate the energy spacing between the ground vibrational state and the first excited vibrational state of carbon monoxide.
 - iii. When the molecule relaxes from its first vibrational excited state to the vibrational ground state what is the energy, and wavelength of the emitted photon?
- b. Rotation of a diatomic molecule can be studied using a rigid rotor model. The molecule is treated as two point masses (the mass of carbon is $1.99 \times 10^{-26} \text{ kg}$ and oxygen is $2.66 \times 10^{-26} \text{ kg}$) separated at a fixed distance R (the equilibrium bond distance is $1.13 \times 10^{-10} \text{ m}$ for carbon monoxide), which are otherwise free to rotate. Use the rigid rotor model to study carbon monoxide as follows.
- i. Write down the quantum mechanical Hamiltonian for this model.
 - ii. What are the eigenfunctions of this Hamiltonian and the associated energy values.
 - iii. Calculate the energy difference between the ground rotational state and the first excited rotational state. What is the degeneracy of each of these states?
 - iv. What wavelength of light is required to excite carbon monoxide from its ground state to the first excited rotational state?
- c. Compare the relative spacings between vibrational and rotational states of carbon monoxide.

2. Spin and NMR (20 points).

- a. Just as electrons have intrinsic magnetic moments, nuclei do also, and the magnitude of a nuclear moment is given by

$$\mu = g \frac{e}{2m_N} S$$

where g is a factor characteristic of the particular nucleus, e is the proton charge, m_N is the mass of the nucleus, and S is the spin angular momentum of the nucleus. For example, a proton has a spin of $\frac{1}{2}$ and $g = 5.5849$. In a NMR experiment involving protons, the protons undergo transitions between the states $s_z = -\frac{1}{2}$ and $s_z = +\frac{1}{2}$. Calculate the frequency of radiation for such an experiment in a magnetic field of 11.7 Tesla.

- b. Given a particle with the normalized wave function:

$$\Psi = R(r) \left[\left(\frac{1}{3} \right)^{\frac{1}{2}} Y_{1,0}(\theta, \phi) \alpha + \left(\frac{2}{3} \right)^{\frac{1}{2}} Y_{1,1}(\theta, \phi) \beta \right]$$

and spin eigenfunctions (α and β) that satisfy the equations:

$$\hat{S}_z \alpha = \frac{\hbar}{2} \alpha$$

$$\hat{S}_z \beta = -\frac{\hbar}{2} \beta$$

show that the particle has a total component of angular momentum along the z-axis equal to $\frac{\hbar}{2}$, and orbital angular momentum $l = 1$. What is the probability for finding the particle with spin up at (r, θ, ϕ) ?

- c. For a two electron system with $\hat{S}_{total} = \hat{S}(1) + \hat{S}(2)$ prove:

$$\hat{S}_{total}^2 = \hat{S}^2(1) + \hat{S}^2(2) + \hat{S}_+(1)\hat{S}_-(2) + \hat{S}_-(1)\hat{S}_+(2) + \hat{S}_z(1)\hat{S}_z(2)$$

Consider the following spin functions:

$$\Psi_1 = \alpha(1)\alpha(2)$$

$$\Psi_2 = \beta(1)\beta(2)$$

$$\Psi_3 = \alpha(1)\beta(2)$$

$$\Psi_4 = \beta(1)\alpha(2)$$

$$\Psi_5 = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\Psi_6 = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Which are eigenfunctions of \hat{S}_{total}^2 ? Prove your answer and for all eigenfunctions state the eigenvalues.

Note that $\hat{S}(1)$ is the spin operator acting on only particle 1 and $\hat{S}(2)$ is the spin operator acting only on particle 2. Also, $\alpha(1)\beta(2)$ denotes the wavefunction describing particle 1 in the α eigenstate and particle 2 in the β eigenstate.

- d. You have a spin-1/2 system in the state

$$\Psi_{\alpha\beta} = A\{(15 + 20i)\alpha + (36 - 48i)\beta\}$$

where α is the spin-up state, β is the spin-down state, and A is a normalization constant. Suppose that you would like to subject this particle to a Stern-Gerlach measurement in such a way that the outcome of the measurement is $+\frac{\hbar}{2}$ with 100% certainty. In what direction must the magnetic field of the Stern-Gerlach apparatus be oriented?

3. Angular Momentum (20 points).

- a. Show that l_x, l_y, l_z commute with the hamiltonian operator (for the relative motion of the electron and nucleus) for the hydrogen atom in free space. What is the significance of this result?
- b. Show that the spherical harmonics are eigenfunctions of the operator: $l_x^2 + l_y^2$.
- c. Consider a general potential that is cylindrically symmetric ($V = V(\rho, z)$) about the z-axis. Show that l_z commutes with the hamiltonian for this potential and explain the significance. What is the maximum degeneracy allowed for the eigenstates of this potential?
- d. Show that the eigenfunctions of such a potential are separable into a product of three one-variable functions, if one extra condition is satisfied. What is this condition?

4. Wavefunctions (30 points)

- a. Consider the one-dimensional double potential well with the following properties: $V = \infty$ for $x < -a$ and for $x > a$, $V = 0$ for $-a < x < -b$ and for $b < x < a$, and $V = V_0$ for $-b < x < b$ where $a > b > 0$.
 - i. Sketch the potential.
 - ii. Use the general properties of wavefunctions we have discussed for a particle in a box and an harmonic oscillator to sketch the wavefunctions for the five lowest eigenstates of the Hamiltonian of a single particle in this potential. Briefly describe your reasoning for each drawing. Assume that V_0 is greater than the energy of the particle with $n=2$, but less than the energy of the particle with $n=3$.
 - iii. Repeat part ii with $V_0 = \infty$, but draw only wavefunctions for the lowest four states. Comment on the relationship between the energies of the third and fourth wavefunctions in this potential.
- b. Consider a one-dimensional potential V , which is defined by $V = \infty$ for $x < 0$, $V = \frac{1}{2} kx^2$ where $k > 0$ for $x > 0$, and $V = 0$ for $x = 0$.
 - i. Sketch the potential.
 - ii. Sketch the wavefunctions for the three lowest eigenstates of the Hamiltonian for this system.
 - iii. What are energy eigenvalues associated with these states?