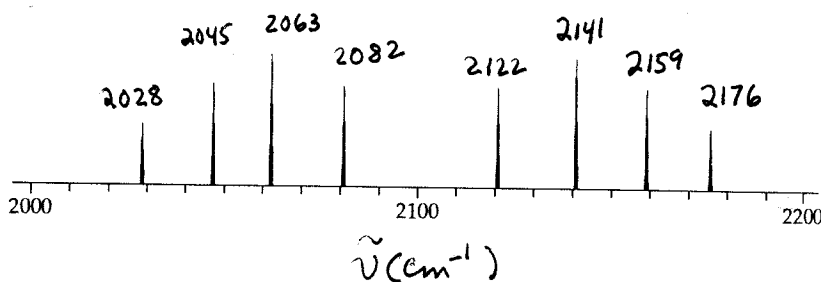


Chem1410 (Spring 2006) Second Exam

You may use your text book and class notes. Other material is not allowed. Good luck!!

1. (20pts) (a) The zero point energy of the 2D rigid rotor is $\hbar^2/\mu r_0^2$. T F
- (b) \hat{L}_z commutes with \hat{H} for the He^+ (Helium ion). T F
- (c) All rotational energy levels of the 3D rigid rotor are degenerate. T F
- (d) All vibrations of Na_3 in an equilateral triangular geometry are infrared inactive. T F
- (e) $\psi = r e^{-r/2a_0} \sin \phi \sin \theta$ is an eigenfunction of \hat{L}_z for a one-electron atom. T F

2. (16 pts) Consider the following IR spectrum of a diatomic molecule. What are the values of the vibrational frequency and rotational constant in cm^{-1} ?



$$\tilde{\nu}_{\text{vib}} = \frac{2122 + 2082}{2} = 2102 \text{ cm}^{-1}$$

$$2\tilde{B} = 19 \text{ cm}^{-1} \Rightarrow \tilde{B} = 9.5 \text{ cm}^{-1}$$

3. (20 pts) The Hamiltonian for an H atom in an electric field in the z direction is $\hat{H} = \hat{H}_0 + e\epsilon z$, where ϵ is the electric field, and \hat{H}_0 is the Hamiltonian in the absence of the field.

- (4) a) Does \hat{L}_z commute with this Hamiltonian? (State why or why not.)
 Yes $z = r \cos \theta$ and $L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$. The system has cylindrical symmetry.
- (4) b) Does \hat{L}^2 commute with this Hamiltonian? (State why or why not.)
 No, the Hamiltonian does not have spherical symmetry.

(4) c) Does \hat{S}^2 commute with this Hamiltonian? (State why or why not.)

Yes, there is no spin operator in \hat{H}

Consider the trial function $\Phi = c_1\psi_{1s} + c_2\psi_{2pz}$, where ψ_{1s} and ψ_{2pz} denote orbitals of the H atom in the absence of the field.

(4) d) Write the energy of this trial function as a function of c_1 and c_2 using $H_{11} = \langle \psi_{1s} | H | \psi_{1s} \rangle$, $H_{12} = \langle \psi_{1s} | H | \psi_{2pz} \rangle = \langle \psi_{2pz} | H | \psi_{1s} \rangle$, $H_{22} = \langle \psi_{2pz} | H | \psi_{2pz} \rangle$

$$E = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + c_2^2}$$

(4) e) Evaluate $\frac{\partial E}{\partial c_1}$ and $\frac{\partial E}{\partial c_2}$. (You do not have to solve the resulting equations for c_1 and c_2 .)

$$\frac{\partial E}{\partial c_1} = \frac{2c_1 H_{11} + 2c_2 H_{12}}{c_1^2 + c_2^2} + \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{(c_1^2 + c_2^2)^2} (-2c_1)$$

$$\frac{\partial E}{\partial c_2} = \frac{2c_1 H_{12} + 2c_2 H_{22}}{c_1^2 + c_2^2} + \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{(c_1^2 + c_2^2)^2} (-2c_2)$$

4. (12 pts) Consider the following electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4p$. What electronic states are possible (e.g., S, P, D, F, G, etc)? Be sure to specify the multiplicities.

$$L = 3, 2, 1 \Rightarrow {}^3F, {}^1F, {}^3D, {}^1D, {}^3P, {}^1P$$

5. (10 pts) Write the wavefunction of the $1s2p$ singlet state of He including the spin part of the function.

$$\left[1s(\vec{r}_1) 2p(\vec{r}_2) + 2p(\vec{r}_1) 1s(\vec{r}_2) \right] (\alpha(\sigma_1) \beta(\sigma_2) - \beta(\sigma_1) \alpha(\sigma_2))$$

6. (10 pts) The rotational constant of HF is 21.0 cm^{-1} . What is the rotational constant of DF in cm^{-1} ? (D is deuterium.)

$$\frac{\tilde{B}(\text{DF})}{\tilde{B}(\text{HF})} = \frac{\mu(\text{HF})}{\mu(\text{DF})} \Rightarrow \tilde{B}(\text{DF}) = (21.0) \frac{0.95}{1.809} = 11.0 \text{ cm}^{-1}$$

The vibrational frequency of HF is 4138 cm^{-1} . What is the vibrational frequency of DF in cm^{-1} ?

$$\frac{\tilde{\nu}(\text{DF})}{\tilde{\nu}(\text{HF})} = \sqrt{\frac{\mu(\text{DF})}{\mu(\text{HF})}} = \sqrt{\frac{1.809}{0.95}} \Rightarrow \tilde{\nu}(\text{DF}) = 2998 \text{ cm}^{-1}$$

7. (12 pts) The expression for the energy levels of an H atom also apply to positronium (e^- , e^+), where e^- denotes an electron and e^+ a positron, provided the correct reduced mass is used. Note that the positron has the same mass but opposite charge from the electron.

a) What is the energy of the ground state of positronium?

$$E = -\frac{1}{2} \frac{1}{2} \frac{1}{n^2} \text{ in a.u.} \quad \text{ground state} = -\frac{1}{4} \text{ a.u.} = -6.8 \text{ eV}$$

↑ reduced mass

b) What is the energy of the first dipole allowed excited state?

$$E = -\frac{1}{4} \frac{1}{4} \text{ a.u.} = -1.7 \text{ eV}$$