Chemistry 1410
Exam #2

The exam is open text and open notes.

1. Which of the following statements are true? (25 pts)

   a. The linear momentum operator $\hat{p}_z$ commutes with $\hat{H}$ for the hydrogen atom. T (F)

   b. It requires more energy to ionize D than to ionize H. (T) F

   c. The first excitation energy of He^+ is 40.8 eV. (T) F

   d. The bondlength of a molecule determined from pure rotational spectroscopy corresponds to the minimum of the potential energy curve. T (F)

   e. The molecule Cl_2 displays a pure rotational spectrum. T (F)

2. Consider the wavefunction $\Phi = \left(1/\sqrt{2}\right)(\psi_{2s} + \psi_{2pz})$ for the H atom where ψ_{2s} and ψ_{2pz} are eigenfunctions of the Hamiltonian for the H atom. (25 pts)

   a. What is the energy (in eV) associated with Φ?

   $$E = \frac{-13.6\ eV}{4} = -3.4\ eV$$

   b. Is Φ an eigenfunction of $\hat{L}^2$, where $\hat{L}$ is the angular momentum operator?

   $$\hat{L}^2(\psi_{2s} + \psi_{2pz}) = \hbar^2(0\,\psi_{2s} + 2\,\psi_{2pz}) \neq \text{constant}(\psi_{2s} + \psi_{2pz})$$

   No, it is not an eigenfunction of $\hat{L}^2$.

   c. Is Φ an eigenfunction of $\hat{L}_z$?

   Yes, since both ψ_{2s} and ψ_{2pz} have $m_\ell = 0$.

3. Calculate the frequency (in cm^{-1}) of the $J = 2 \rightarrow 3$ rotational transition of $^{12}C^{16}O$ given that the bond length is 112.81 pm. (25 pts)

$E_J = \tilde{B}J(J+1)$, $E_2 = \tilde{B}(2)(3)$, $E_3 = \tilde{B}(3)(4)$.

$E_3 - E_2 = 6 \cdot \tilde{B} = 6(1.85\ cm^{-1}) = 11.10\ cm^{-1}$

↑ calculate this using the bond length

What is the energy separation between the P and R branches in the vibrational/rotational spectrum of CO?

$\Delta E = 4\tilde{B}_e = 4(1.85) = 7.40\ cm^{-1}$.

4. The $n = 0 \rightarrow 1$ and $n = 1 \rightarrow 2$ vibrational transitions of a molecule occur at 2000 and 1900 cm^{-1}. Assuming that the molecule is described by the Morse potential (25 pts)

a. What is the fundamental frequency (in cm^{-1})?

$E_n = \tilde{\omega}_e(n+\frac{1}{2}) - \widetilde{\omega_e x_e}(n+\frac{1}{2})^2$

$E_0 = \frac{1}{2}\tilde{\omega}_e - \frac{1}{4}\widetilde{\omega_e x_e}$

$E_1 = \frac{3}{2}\tilde{\omega}_e - \frac{9}{4}\widetilde{\omega_e x_e}$

$E_2 = \frac{5}{2}\tilde{\omega}_e - \frac{25}{4}\widetilde{\omega_e x_e}$

$E_1 - E_0 = \tilde{\omega}_e - 2\widetilde{\omega_e x_e} = 2000$

$E_2 - E_1 = \tilde{\omega}_e - 4\widetilde{\omega_e x_e} = 1900$

$\Rightarrow \widetilde{\omega_e x_e} = 50\ cm^{-1}$, $\tilde{\omega}_e = 2100\ cm^{-1}$

b. What is the anharmonicity (in cm^{-1})?

← (see $\widetilde{\omega_e x_e} = 50\ cm^{-1}$ above)

c. What is the zero point energy (in cm^{-1})?

$E_0 = \frac{1}{2}\tilde{\omega}_e - \frac{1}{4}\widetilde{\omega_e x_e} = \frac{1}{2}(2100) - \frac{1}{4}(50) = 1038\ cm^{-1}$

d. What is the energy of the $v = 2 \rightarrow 3$ transition (in cm^{-1})?

$E_3 - E_2 = \tilde{\omega}_e - 6\widetilde{\omega_e x_e} = 1800\ cm^{-1}$