Chemistry 1410
Exam 2

1. (25 points) True or False

   a. The zero-point energy of the 2D rigid rotor is zero. T F

   b. The symmetric stretch vibration of CO_2 is IR active. T F

   c. At a temperature of 100 K, most rotational spectra will display a single line. T F

   d. $f \rightarrow p$ transitions are forbidden for the H atom. T F

   e. The average of $\hat{l}_z$ for the $2p_z$ orbital of H is $\hbar$. T F

2. (20 points) Consider a diatomic molecule with a fundamental vibrational frequency of 300 cm^{-1} and an anharmonicity of 30 cm^{-1}. Assuming that the potential energy curve is well described by a Morse potential:

   a. In cm^{-1}, what is the $n = 0 \rightarrow 1$ transition "energy"?

$$\tilde{E}_n = \tilde{\nu}(n+\tfrac{1}{2}) - \widetilde{\nu_e x_e}(n+\tfrac{1}{2})^2$$

$$n=0: \ \tilde{E}_0 = \tfrac{1}{2}(300) - \tfrac{1}{4}(30) = 142.5 \text{ cm}^{-1}$$

$$n=1: \ \tilde{E}_1 = \tfrac{3}{2}(300) - \tfrac{9}{4}(30) = 382.5 \text{ cm}^{-1}$$

$$\tilde{E}_1 - \tilde{E}_0 = 240 \text{ cm}^{-1}$$

   b. What is the zero-point energy in cm^{-1}?

$$ZPE = \tfrac{1}{2}(300) - \tfrac{1}{4}(30) = 142.5 \text{ cm}^{-1}$$

   c. Estimate the dissociation energy in eV.

$$\text{anharmonicity} = \widetilde{\nu_e x_e} = \frac{\tilde{\nu}^2}{4\tilde{D}_e}$$

$$\Rightarrow \tilde{D}_e = \tilde{\nu}^2/4\widetilde{\nu_e x_e} = (300)^2/4(30) = 750 \text{ cm}^{-1}$$

3. (20 points) Consider the Li^{+} ion with electrons in the 1s and $2p_z$ orbitals.

a. Write out the full wavefunction for the M_s=0 component of the triplet state.

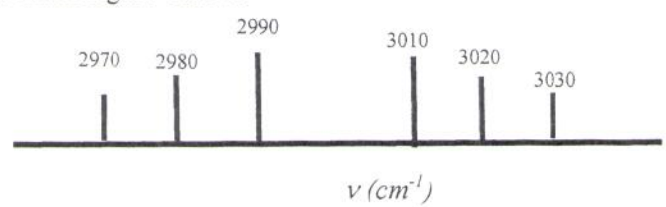
$$\Psi = [1s(r_1)\,2p_z(r_2) - 2p_z(r_1)\,1s(r_2)]\,(\alpha\beta + \beta\alpha)$$

b. Write out the expression for one-electron Fock operator for the 1*s* orbital.

$$h = -\frac{1}{2}\nabla^2 - \frac{3}{r} + \int |\phi_{2p_z}(2)|^2 \frac{1}{r_{12}}\, dr_2 - \text{Exchange integral}$$

(exchange integral exchanges ϕ_{1s} and ϕ_{2p_z})

4. (15 points) You are presented the spectrum shown in the figure below.



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

Average of $J=0 \to 1$ and $J=1 \to 0$ transitions =

$$\frac{1}{2}(2990 + 3010) = 3000\ \text{cm}^{-1}$$

b. What is the rotational constant (cm^{-1})?

$$4\tilde{B}_e = 20\ \text{cm}^{-1} \Rightarrow \tilde{B}_e = 5\ \text{cm}^{-1}$$

5. (20 points) Consider an electron in a spherical box of radius a. with the potential V equal to zero inside the box and V = ∞ for r > a.

a. Write the Schrodinger equation in atomic units for this system

$$\underbrace{-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)}\psi = E\psi \quad \text{inside the box where } V=0$$

$$\hookrightarrow -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr}$$

b. Show that $\frac{\sin(kr)}{r}$ is a solution to this Schrodinger equation when $\ell=0$.

$$\frac{d}{dr}\frac{\sin kr}{r} = \frac{k\cos kr}{r} - \frac{\sin kr}{r^2}$$

$$\frac{d^2}{dr^2}\frac{\sin kr}{r} = -k^2\frac{\sin kr}{r} - \frac{2k\cos kr}{r^2} + \frac{2\sin kr}{r^3}$$

$$\left[-\frac{1}{2}\left(-\frac{k^2\sin kr}{r} - \frac{2k\cos kr}{r^2} + \frac{2\sin kr}{r^3}\right) - \frac{1}{r}\left(\frac{k\cos kr}{r} - \frac{\sin kr}{r^2}\right)\right]$$

$$= E\frac{\sin kr}{r}$$

$$\frac{1}{2}\frac{k^2\sin kr}{r} + \cancel{\frac{k\cos kr}{r^2}} - \cancel{\frac{\sin kr}{r^3}} - \cancel{\frac{k\cos kr}{r^2}} + \cancel{\frac{\sin kr}{r^3}} = E\frac{\sin kr}{r}$$

$$\Rightarrow \frac{1}{2}k^2 = E$$

$$\psi(a) = \frac{\sin ka}{a} = 0 \Rightarrow ka = n\pi, \; n = 1, 2, 3, \ldots$$

for $n=1$, $ka = \pi$, $k = \pi/a$

$E = \frac{1}{2}\frac{\pi^2}{a^2}$ in atomic units