

Constants and integrals you may need

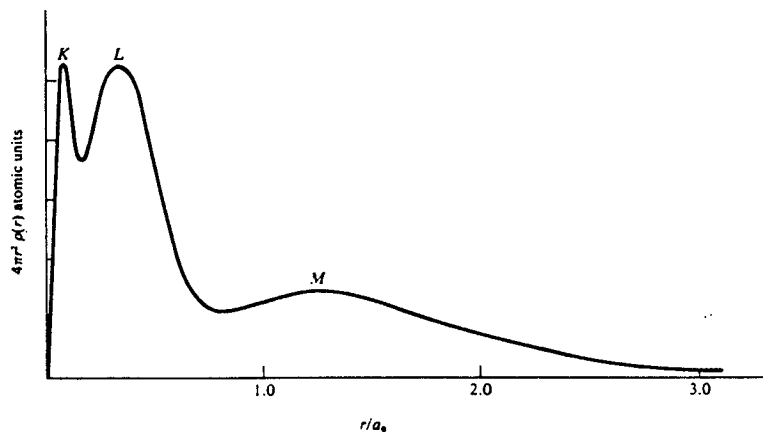
$$h = 6.63 \times 10^{-34} \text{ J s}$$

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

$$\int \sin^2 x dx = \frac{1}{2}x - \frac{1}{4} \sin 2x$$

$$\int_0^L \sin \frac{n\pi x}{L} \cos \frac{m\pi x}{L} dx = 0$$

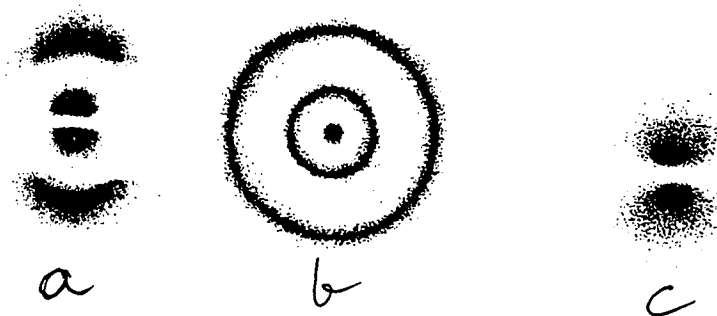
1. (15 points) Given the radial distribution function $r^2|\psi|^2$ for the Ar atom shown below,



- a. explain why the 1s electrons are more effective than the 3s electrons in shielding the nuclear charge from the 3p electrons.

- b. explain why the 2s electrons are not completely effective in shielding the nuclear charge from the 3p electrons.

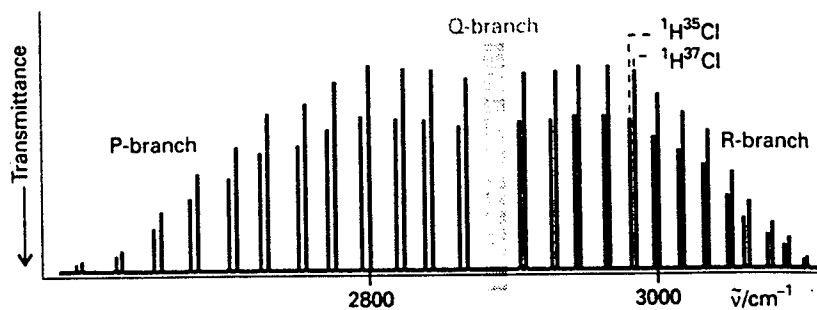
2. (15 points) Shown below are schematic probability functions, $\psi^*\psi$, for H orbitals.



a. Do these correspond to total wave functions $|\psi(r)\psi(\theta,\phi)|^2$, or just the angular part, $|\psi(\theta,\phi)|^2$? Why?

b. What are the values of the principle quantum number, n , corresponding to each of these? Explain your answer.

3. (15 points) a. The rotational-vibrational absorption spectrum for HCl ($\Delta v = 1$) is given below. Why does the intensity fall off for $\tilde{\nu} > 2950 \text{ cm}^{-1}$ and $\tilde{\nu} < 2800 \text{ cm}^{-1}$? Why is there no absorption at $\sim 2890 \text{ cm}^{-1}$?



- b. Write a determinantal wavefunction that satisfies the Pauli Exclusion Principle for the ground state of the Li atom.

4. (15 points) a. Write an expression that is proportional to the probability that absorption of electromagnetic radiation will induce a transition in a quantum mechanical system from state ψ_n to state ψ_m .

b. How can this expression be used to determine selection rules for a given spectroscopy? How can you obtain overtone spectra for HCl in the infrared given that we found that the selection rule is $\Delta v = \pm 1$?

c. Why aren't selection rules for all spectroscopies the same?

5. (40 points) In homework #19, you expressed the valence molecular orbitals for the HF molecule as linear combinations of a 1s orbital on the H atom and a $2p_z$ orbital on the F atom. The secular determinant which gave you the best energies of the molecular orbitals attainable by varying the relative magnitudes of the two coefficients in the molecular orbital is

$$\begin{vmatrix} H_{hh} - ES_{hh} & H_{hf} \\ H_{hf} & H_{ff} - ES_{ff} \end{vmatrix} = 0$$

- a. Give a mathematical expression for H_{ff} . What is H_{ff} in words? What are its units? Is it greater or less than zero? Why?

- b. Give a mathematical expression for S_{ff} . What are its units? What numerical value did you use for S_{ff} ? Why?

- c. What values of E are obtained in the limit $H_{hf} \rightarrow 0$. Explain.
- d. If you had solved the determinant for the two values E , how would you decide which is the bonding orbital? How would you calculate the coefficients of the H and F atomic orbitals in the bonding molecular orbital for HF?