

**MASSACHUSETTS INSTITUTE OF TECHNOLOGY**  
**Department of Chemistry**

5.61 Quantum Mechanics

Fall 2013

Problem Set #6

Reading Assignment: McQuarrie 7.1-7.9, 9.1-9.5)

(● = Easier   ■ = More Challenging   ◆ = Most Challenging)

1. ■/◆ *Measurement of the internuclear distance dependence of an electronic property from the  $v, J$  dependence of the energy levels in the spectrum.  $\hat{A}$  is an electronic property:*

$$\hat{A} = A_0 + \frac{dA}{dQ} \hat{Q} + \frac{d^2A}{dQ^2} \hat{Q}^2$$

where the derivatives are evaluated at  $Q=0$ . As you change the vibrational and rotational state of the molecule, the average value of  $\hat{A}$  changes as:

$$A_{v,J} = A_0 + \alpha_A (v + 1/2) + A_D J(J + 1)$$

Determine  $\alpha_A$  and  $A_D$  using perturbation theory as discussed in class. You may wish to make use of the following relationships:

$$\hat{Q} = \left[ \frac{\hbar}{4\pi c \mu \omega_e} \right]^{1/2} (\hat{a} + \hat{a}^\dagger) \quad B(\hat{Q}) = B_e \left[ 1 - \frac{2\hat{Q}}{R_e} + \frac{3\hat{Q}^2}{R_e^2} \right]$$

$$\frac{2\hat{Q}}{R_e} = \left[ \frac{4B_e}{\omega_e} \right]^{1/2} (\hat{a} + \hat{a}^\dagger) \quad \frac{3\hat{Q}^2}{R_e^2} = \frac{3B_e}{\omega_e} (\hat{a} + \hat{a}^\dagger)^2$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

$$\hat{H}^{(0)} = hc\omega_e (\hat{N} + 1/2) + hcB_e J(J + 1) \quad H^{(1)} = hc \left[ A_0 + \frac{dA}{dQ} \hat{Q} \right] + hcB_e J(J + 1) \left[ -\frac{2\hat{Q}}{R_e} \right]$$

2. ■ Compute each of the following in MKS (meter-Kilogram-seconds) units:
- The average distance between the electron and the nucleus in a 3s orbital for  $\text{He}^+$ .
  - The energy of a 3p<sub>x</sub> electron in  $\text{Li}^{2+}$
  - The root mean square velocity of the 1s electron in  $\text{Th}^{+89}$  (i.e. a thorium atom with one electron). Compare this velocity with the speed of light. Is there a problem here?
3. ● Compute each of the following in atomic units:
- The distance from your dorm room or apartment to 4-237.
  - The energy content of one Hostess Twinkie<sup>®</sup> snack cake.
  - The average velocity of a winning boat in the Head of the Charles Regatta.
4. ● What did you learn from questions 1&2?

5. ● List the possible outcomes for each of the following measurements in a hydrogenic atom:
- Measuring the total angular momentum for a 3p electron.
  - Measuring the total angular momentum for a 4p electron.
  - Measuring the z component of the angular momentum for a 3d electron.
  - Measuring the z component of the angular momentum for a 3f electron.
6. ●/■ The virial theorem gives us a very simple relationship between the potential energy of the hydrogen atom and its total energy. To be precise, the virial theorem implies that, for any eigenstate of the hydrogen atom the average potential energy is equal to twice the total energy:  $\langle U \rangle = 2\langle E \rangle$ . Use the virial Theorem to derive an expression for  $\left\langle \frac{1}{r} \right\rangle$  that is valid for any  $Z$ , and any quantum numbers  $nlm$ .
7. ■ In each of the following cases, state which of the two quantities is larger. Justify your answers. You need not do any integrals here.
- The average value of  $r$  for a 2s electron versus a 2p electron.
  - The average value of  $1/r$  for a 2s electron versus a 2p electron.
  - The average value of  $r$  for a 2s electron in  $\text{He}^+$  versus a 1s electron in H.
  - The average value of  $r$  for a 3d electron in  $\text{Fe}^{25+}$  versus a 1s electron in  $\text{C}^{5+}$ .
  - The number of radial nodes in an 8g orbital versus the number of angular nodes in an 8g orbital.
  - The spacing between the radial nodes for a 14s orbital versus the spacing between the radial nodes for a 16d orbital.
8. ◆ In class, we solved for the eigenstates of the Hydrogen atom Hamiltonian

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

$$E_{nlm} = -\frac{e^2}{8\pi^2\epsilon_0 a_0 n^2} \quad \Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

For various reasons, real Hydrogen atoms are not exactly represented by this Hamiltonian. For each of the following effects, **qualitatively characterize** how you think the new term will affect i)  $E_{nlm}$  ii)  $R_{nl}(r)$  iii)  $Y_l^m(\theta, \phi)$  and iv) the selection rules for absorption. Sketch the resulting spectra for each case. You need not do any integrals to justify your answers.

- The proton is not a point particle, but has a finite size ( $r_p \sim 10^{-15}$  m). Thus, a better approximation to the potential would be

$$V(\hat{r}) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{\sqrt{\hat{r}^2 + r_p^2}}$$

- According to special relativity, the kinetic energy is actually given by

$$\hat{T} = \frac{mc^2}{\sqrt{1 - \hat{\mathbf{p}}^2 / m^2 c^2}} - mc^2 \approx \frac{\hat{\mathbf{p}}^2}{2m} + \frac{3\hat{\mathbf{p}}^4}{8m^3 c^2} + \dots$$

- The electron spin (**S**) and proton spin (**I**) are coupled by a small magnetic hyperfine interaction

$$\hat{H}_1 \propto \delta(r) \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} = \delta(r) (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z).$$

- d. About 0.01% of the time, the hydrogen nucleus is not a proton, but a deuteron (one proton and one neutron).

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