

Chem 542  
Homework for Part 2: Multipoles

1. Show that  $\nabla^2(1/r) = -4\pi\delta(r)$ , where  $\delta$  is the Dirac "delta function." Start by showing that  $\nabla^2(1/r) = 0$  when  $r \neq 0$ . [Hint: use the del-square operator in polar coordinates, and the fact that  $1/r$  does not depend on  $\theta$  and  $\phi$ .] Then show that the function cannot be zero at  $r=0$  by using Gauss' law. [Hint: Gauss' law in integral form is discussed in appendix B.]

Similar discontinuities also produce the delta functions in the dipole electric and magnetic field, see for example "Jackson, *Classical Electrodynamics* 2<sup>nd</sup> edition, eq. 4-18 in the multipole chapter for the full proof.

Because molecular couplings from our lectures on "multipoles" are usually small compared to rovibronic energies, they can be dealt with by time-independent perturbation theory, which you mastered in Chem 540.

2. Using the approach of section 9 (eq. 9-32) which relates the magnetic dipole to a "magnetic charge density" (no monopoles here, of course), derive the multipole expansion in section 2b for the electric charge density and current up to the dipole terms

$$\rho = \rho_0 - \nabla \cdot \mathbf{P} + \dots$$

$$\mathbf{j} = \mathbf{j}_0 + \frac{\partial \mathbf{P}}{\partial t} + \dots$$

(Hint: if you get stuck, take a look at Jackson or another upper division E&M book from the reading list on the 542 web site).

3. Ammonia is a symmetric top molecule, and several of its rotational levels show a pronounced Stark effect  $-\mu \cdot \mathbf{E}$ . ( $\mathbf{E}$  here is the electric field).
- Write down the Stark Hamiltonian in terms of space-fixed axes, assuming the E-field is  $E_z$ .
  - Rewrite the dipole term in a. in terms of the molecule-fixed dipole and Euler angles. You may neglect vibrational displacements, i.e. the dipole vector is that of rigid ammonia along the  $z_b$  axis going through the nitrogen atom.
  - Assuming a weak electric field, use first order perturbation theory to calculate the energy shift of a  $|JKM\rangle$  symmetric top rotational eigenstate of ammonia. You may find the following formulas useful:

$$|JKM\rangle = \left\{ \frac{2J+1}{8\pi^2} \right\}^{1/2} Y_{M,K}^{J*}(\varphi, \vartheta, \chi) = (-1)^{M-K} \left\{ \frac{2J+1}{8\pi^2} \right\}^{1/2} Y_{-M,-K}^J(\varphi, \vartheta, \chi)$$

$$Y_{00}^1 = \cos \vartheta$$

$$\int d\varphi d\vartheta \sin \vartheta Y_{M_3, M_3}^{J_3} Y_{M_2, M_2}^{J_2} Y_{M_1, M_1}^{J_1} = 8\pi^2 \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}.$$

You can look up Clebsch-Gordan coefficients or 3-J symbols in an angular momentum book, e.g. Zare, Brink & Satchler on the Chem 542 web book list: the things that look like 2x3 matrices in the above formula are actually functions  $f(J_1, \dots, M_3)$

d. Do the  $J=1, K=0$  levels have a first-order Stark effect? The  $J=1, K=\pm 1$  levels?

4. Consider the NMR scalar coupling  $H_{\text{scalar}} = \mathbf{I}_1 \cdot \mathbf{I}_2$  between two nuclear spins in more detail. This cannot arise from a direct coupling between the two nuclear spins because nuclei are separated by too large a distance for their weak magnetic fields to interact directly.

There are several dipole-dipole, orbit-nuclear spin, etc. terms that contribute to give  $H_{\text{scalar}}$ . We consider the dipole contact Hamiltonian, which turns out to be largest for electrons in sigma-orbitals of molecules:

$$H_J = \frac{8\pi}{3} g\beta g_N \beta_N I_{zA} (S_{z1} \delta(\mathbf{r}_1 - \mathbf{r}_A) + (S_{z2} \delta(\mathbf{r}_2 - \mathbf{r}_A))) + \frac{8\pi}{3} g\beta g_N \beta_N I_{zB} (S_{z1} \delta(\mathbf{r}_1 - \mathbf{r}_B) + (S_{z2} \delta(\mathbf{r}_2 - \mathbf{r}_B)))$$

This is the contact interaction between two electrons of spins  $S_{z1,2}$  at positions  $\mathbf{r}_{1,2}$  with two nuclei of spin  $I_{zA,B}$  at positions  $\mathbf{r}_{A,B}$ . The two electrons are in  $\sigma$ -orbitals (for example,  $\sigma(\mathbf{r}) \sim s_A(\mathbf{r}) + s_B(\mathbf{r})$ ,  $\sigma^*(\mathbf{r}) \sim s_A(\mathbf{r}) - s_B(\mathbf{r})$ ) with their spins paired, so their total ground state wavefunction with  $M_S = 0$  is

$$\Psi = \frac{1}{\sqrt{2}} \sigma(\mathbf{r}_1) \sigma(\mathbf{r}_2) \{ |M_{S1} = 1/2\rangle |M_{S2} = -1/2\rangle - |M_{S1} = -1/2\rangle |M_{S2} = 1/2\rangle \},$$

and the first excited triplet wavefunction with  $M_S = 0$  is

$$\Psi' = \frac{1}{2} \{ \sigma(\mathbf{r}_1) \sigma^*(\mathbf{r}_2) - \sigma(\mathbf{r}_1)^* \sigma(\mathbf{r}_2) \} \{ |1/2\rangle |-1/2\rangle + |-1/2\rangle |1/2\rangle \}.$$

a. Write down the second order perturbation expression for  $H_{\text{scalar}}$ . (Hint: when you calculate matrix elements of the kind  $\langle \Psi | H_J | \Psi' \rangle$ , only electron positions and spins are integrated over, so  $I_1$  and  $I_2$  remain as variables you can pull out, yielding the effective Hamiltonian  $H_{\text{scalar}}$  with  $J$  given by a perturbation summation.)

b. Using  $E' - E = \Delta E$ , evaluate the perturbation term for states  $\Psi$  and  $\Psi'$ , showing that approximately

$$J = \left( \frac{8\pi}{3} g\beta g_N \beta_N \right)^2 \frac{\sigma(\mathbf{r}_A) \sigma^*(\mathbf{r}_A) \sigma(\mathbf{r}_B) \sigma^*(\mathbf{r}_B)}{\Delta E}$$

c. Look up the nuclear and Bohr magnetons, assume the g-factors are about 2, and a typical excited triplet state energy difference is about  $E/hc = 20,000 \text{ cm}^{-1}$ . What is the coupling constant  $J$  in Hertz?

5. Spin-orbit coupling arises because the orbital angular momentum of an electron creates a dipolar magnetic field:

$$\mathbf{B} = g_e \beta \frac{\mathbf{L}}{r^3}.$$

- Write down the lowest order (dipole-field) interaction energy between the electron magnetic field and spin magnetic moment  $\mu_s = g_e \beta \mathbf{S}$ .
- In a doublet Pi ( $^2\Pi$ ) radical such as OH, the electronic angular momentum lies mainly along the internuclear axis,  $L_z = \Lambda = 1$ . The electron spin is coupled to it, so  $S_{x,y}$  average to zero. What is the spin orbit energy of the  $^2\Pi$  state to first order in perturbation?