

Chem 542
Homework for Part 2: Multipoles

1. Show that $\nabla^2(1/r) = -4\pi\delta(r)$, where δ 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 θ and ϕ .] 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* 2nd 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:

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

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

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

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_{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 σ -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_{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_{scalar} with J given by a perturbation summation.)

b. Using $E' - E = \Delta E$, evaluate the perturbation term for states Ψ and Ψ' , 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:

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

- a. Write down the lowest order (dipole-field) interaction energy between the electron magnetic field and spin magnetic moment $\mu_s = g_s \beta \mathbf{S}$.
- b. 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?