

## 9. Multipole couplings and static external fields

So far, we have considered the electronic, vibrational, and rotational energy of molecules, in descending order of magnitude. There are also smaller terms in the Hamiltonian, which can nevertheless yield important spectroscopic clues to the structure and dynamics of molecules.

The presence of unpaired electron spins provides further fine structure in the energy levels, usually on a scale of a few  $\text{cm}^{-1}$  (meV) for light atoms to thousands of  $\text{cm}^{-1}$  (0.5 eV) for very heavy atoms such as iodine or uranium. The presence of nuclear spin provides even smaller hyperfine structure, which generally lies in the  $<0.001 \text{ cm}^{-1}$  for lighter nuclei, due to the smaller size of the nuclear magneton (0.00076 MHz/Gauss) as compared to the Bohr magneton (1.4 MHz/Gauss).

Nuclear and electronic spin levels can also be tuned in the presence of external fields, leading to EPR and NMR spectroscopies: the spins act as magnetic dipoles (or higher order multipoles for nuclei with  $I > 1/2$ ). Finally, the molecular charge cloud has monopole (ions), dipole and higher multipole moments which can interact with external magnetic and electric fields, leading to effects such as ion cyclotron resonance (a mass spectrometry technique) or the DC Stark effect. The external fields may also be provided by other individual molecules, leading to long range forces which may broaden or distort spectral lines.

Generally, most of these effects are small enough that their contributions to the Hamiltonian can be derived perturbatively via multipole electromagnetic interactions. To calculate dynamics of these small energy terms, perturbation theory is sufficient in some cases, while a full density matrix treatment may be more useful in others (e.g. NMR spectroscopy). In this section we consider the *derivation* of the most important such terms in the Hamiltonian. Perturbation techniques for extracting energies and dynamics from such terms have been covered in the previous semester, while density matrix techniques will be illustrated with optical excitation in section 11.

### 9.1 Angular momenta

Multipole couplings are generally associated with an angular momentum. The total angular momentum of a molecular system is given by

$$F = I + S + P + \underbrace{R + L}_N \quad 9-1$$

$\underbrace{\hspace{10em}}_J$

where  $I$  is the nuclear-spin,  $S$  the electron-spin,  $\ell$  the vibrational,  $R$  the rotational, and  $L$  the electronic angular momentum. These angular momenta are either associated with intrinsic magnetic moments or with rotating charge distributions that create magnetic fields. Consider the following three examples:

$$\text{ex: } \mu_s = g_e \beta_e \hat{S} \text{ where } g_e \approx 2 \text{ and } \beta_e = \frac{e\hbar}{2mc} \text{ is the Bohr magneton } (\hat{S} \text{ is unitless}). \quad 9-2$$

$$\text{ex: } \mu_I = g_N \beta_N I \text{ where } g_N \text{ is the nuclear } g\text{-factor, } \beta_N \text{ is the nuclear magneton } \frac{e\hbar}{2m_H c} \quad 9-3$$

ex: The magnetic field created by a rotating charge is (see eq. 9-26 for derivation of the magnetic moment  $\mu_M$  and 9-27 for the full derivation of the magnetic field):

$$B_L = \frac{1}{c} \frac{\mu_M}{r^3} = \left(\frac{q}{2c}\right) \frac{\mathbf{r} \times \mathbf{v}}{r^3}, \quad 9-4$$

This is the Biot-Savart law (inverse square law for magnetic field generated by a current  $I = qv$ . Using  $\mathbf{L} = m\mathbf{r} \times \mathbf{v}$ , this becomes for an electron ( $q = -e$ )

$$B_L = -\left(\frac{e}{2mc}\right) \frac{\mathbf{L}}{r^3} = -\left(\frac{e\hbar}{2mc}\right) \frac{L}{r^3} = -g_L \beta_e \frac{L}{r^3} \quad 9-5$$

in the absence of an external field, so  $\mathbf{A}_{\text{ext}} = 0$  and  $\mathbf{p} = m\mathbf{v}$ . The  $g_L$ -factor for the orbital angular momentum is 1 in this classical electrodynamic picture. For spin, it was originally predicted to be 2 by Dirac (*i.e.* a spin  $S = 1/2$  creates the same magnetic moment as an orbital angular momentum  $L = 1$ ). The actual value is closer to 2.00232 because of self-energy corrections that require quantum electrodynamics to evaluate; it can take on yet other values because the electron is not “free” in a molecule, *i.e.* perturbations from excited electronic states can modify its value.) Note:  $\mathbf{L}$  has units of angular momentum, while  $L$  is the usual unitless angular momentum vector with  $L^2$  having expectation value  $L(L+1)$ ,  $L = 0, 1, 2, \dots$ . The  $\hbar$  factor has been pulled out into the Bohr magneton.

ex: If  $I \geq 1$ , then  $eQ_N$ , the nuclear quadrupole moment (derived below), may be nonzero.

The most important interactions can be classified as

- 1) Dipolar couplings: energy of 2 interacting dipoles;
- 2) Fermi contact interaction:  $H \approx I \cdot S \delta(\mathbf{r})$ ; part of 1);
- 3) Quadrupole couplings:  $Q_N \neq 0$  if  $I \geq 1$  due to nuclear shape being nonspherical; a nonspherical molecule may also have a quadrupole moment;
- 4) Zeeman or Stark couplings to external fields;
- 5) Scalar (through-bond) couplings: higher-order effects due to interactions of  $\mathbf{I}_N$  with  $\mathbf{S}$  and  $\mathbf{L}$ ;
- 6) Others:  $\mathbf{L} \cdot \mathbf{S}$  spin-orbit coupling,  $\mathbf{R} \cdot \mathbf{S}$  spin-rotation coupling; etc...

To understand how these arise, we consider in the following sections:

- a) Fields generated by electric or magnetic multipoles;
- b) Interaction energy of multipole with a field (either external or from another multipole).
- c) The terms 1)-6) in the Hamiltonian that arise by combining a) and b)

## 9.2 Fields generated by multipoles

### i) Electric multipoles

The electric field (Coulomb field) of a discrete charge distribution is

$$V(\mathbf{r}) = \sum_i \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|} \quad 9-6$$

for a continuous charge distribution one therefore has

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad 9-7$$

Using a point charge density  $\rho = q\delta(\mathbf{r} - \mathbf{r}')$ , eq. 9-7 is easily shown to be the solution to the inhomogeneous Poisson equation  $\nabla^2 V = -4\pi\rho$  by the Green function technique of Appendix A. If the distribution  $\rho$  is localized, we can assume that  $|\mathbf{r}'| \ll |\mathbf{r}|$  and expand in a multipole series (fig. 9-1):

$$\begin{aligned}
\frac{1}{|\mathbf{r} - \mathbf{r}'|} &= \{r^2 + r'^2 - 2r r' \cos \theta\}^{-1/2} \\
&= \frac{1}{r} \left\{ 1 + \left(\frac{r'}{r}\right)^2 - 2 \frac{\mathbf{r}' \cdot \mathbf{r}}{r^2} \right\}^{-1/2} \\
&= \frac{1}{r} \left[ 1 - \frac{1}{2} \left( \left(\frac{r'}{r}\right)^2 - 2 \frac{\mathbf{r}' \cdot \mathbf{r}}{r^2} \right) + \frac{3}{8} \left( \left(\frac{r'}{r}\right)^2 - 2 \frac{\mathbf{r}' \cdot \mathbf{r}}{r^2} \right)^2 + \dots \right] \\
&= \frac{1}{r} + \frac{\mathbf{r}' \cdot \mathbf{r}}{r^3} - \frac{1}{2} \frac{r'^2}{r^3} + \frac{3}{2} \frac{(\mathbf{r}' \cdot \mathbf{r})^2}{r^5} + \dots
\end{aligned} \tag{9-8}$$

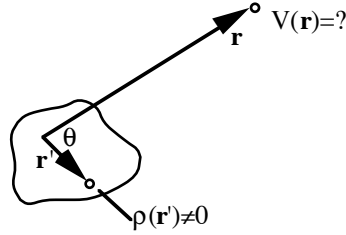


Fig. 9-1. Multipole expansion of a localized charge distribution

Inserting this expansion into eq. 9-7 for  $V(\mathbf{r})$ ,

$$V(\mathbf{r}) = \frac{1}{r} \int \rho' d\mathbf{r}' \left\{ 1 + \frac{\mathbf{r}' \cdot \mathbf{r}}{r^2} + \frac{1}{2r^2} \left( 3 \frac{(\mathbf{r}' \cdot \mathbf{r})^2}{r^2} - \frac{r'^2 \cdot r^2}{r^2} \right) + \dots \right\} \tag{9-9}$$

$$= \frac{Q}{r} + \frac{\boldsymbol{\mu} \cdot \mathbf{r}}{r^3} + \frac{1}{2} \sum_{i,j} Q_{ij} \frac{r_i r_j}{r^5} + \dots \tag{9-10}$$

where

$$Q = \int \rho' d\mathbf{r}' \tag{9-11}$$

is the monopole moment or total charge,

$$\boldsymbol{\mu} = \int \rho' \mathbf{r}' d\mathbf{r}' \tag{9-12}$$

is the dipole moment, and

$$Q_{ij} = \int \rho' (3r'_i r'_j - r'^2 \delta_{ij}) d\mathbf{r}' \tag{9-13}$$

is the quadrupole tensor.

$$\text{Eq. 9-13 follows from 9-9 and 9-10 since } (\mathbf{r}' \cdot \mathbf{r})^2 = \sum_{i,j} r'_i r'_i r'_j r'_j \text{ and } r'^2 r^2 = \sum_{i,j} r'^2 r_i r_j \delta_{ij}. \tag{9-14}$$

The electric field in the absence of oscillating external fields is obtained by differentiation of the potential (setting  $\mathbf{r} = r\hat{n}$ )

$$\mathbf{E} = -\frac{\partial V}{\partial \mathbf{r}} = \frac{Q\hat{n}}{r^2} + \frac{3\hat{n}(\bar{\boldsymbol{\mu}} \cdot \hat{n}) - \bar{\boldsymbol{\mu}}}{r^3} - \frac{4\pi}{3} \bar{\boldsymbol{\mu}} \delta(\mathbf{r}) + \text{quadrupole and higher terms.} \tag{9-15}$$

The third term is due to a singularity of the dipole field at  $\mathbf{r}=0$  for a point dipole, and is required for the surface integral of a point dipole electric field to have the proper value in agreement with Gauss' law (Maxwell's first equation in section 2b).

ii) Magnetic multipoles

The field of a magnetic multipole distribution can be obtained in a similar fashion. We first motivate the concept of magnetization by considering the magnetostatic case. In the absence of oscillating electric charges and fields, the second and fourth of Maxwell's equations in section 2 become

$$\nabla \cdot \mathbf{B} = 0 \text{ and} \quad 9-16$$

$$\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j}. \quad 9-17$$

Unlike charges, there are no magnetic monopoles since  $\nabla \cdot \mathbf{B} = 0$ . From section 2,  $\mathbf{B} = \nabla \times \mathbf{A}$ , and from eq. 9-17,  $\nabla \times \nabla \times \mathbf{A} = \frac{4\pi}{c} \mathbf{j}$ . Using vector identity 2-34c and the Coulomb gauge 2-51, this yields

$$\nabla^2 \mathbf{A} = -\frac{4\pi}{c} \mathbf{j}. \quad 9-18$$

The Green function method in Appendix A then yields the solution

$$\mathbf{A} = \frac{1}{c} \int \frac{\mathbf{j}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad 9-19$$

Assuming that the current  $\mathbf{j}(\mathbf{r}')$  is localized near the origin at  $|\mathbf{r}'| \ll |\mathbf{r}|$ , we again expand the denominator in the multipole series 9-8 such that

$$A_i = \frac{1}{cr} \int J_i(r') d\mathbf{r}' + \frac{\mathbf{r} \cdot}{cr^3} \int \mathbf{r}' J_i(\mathbf{r}') d\mathbf{r}' + \dots \quad 9-20$$

in analogy to eq. 9-9. If the current is indeed localized inside the surface bounding the integration volume ( $\mathbf{J} = 0$  at the surface), then no charge flows out of the surface and by continuity the first integral vanishes since there can be no average current flow in any direction inside the volume. (This can also be shown by setting  $f=1$  and  $g=x_i'$  in eq. A-78.) The second integral can also be rewritten using identity A-80 to yield

$$\mathbf{A} = -\frac{\mathbf{r}}{2cr^3} \times \int \mathbf{r}' \times \mathbf{j} d\mathbf{r}' + \dots \quad 9-21$$

or

$$\mathbf{A} = \frac{\boldsymbol{\mu}_M \times \mathbf{r}}{r^3} + \dots \quad 9-22$$

if we define

$$\boldsymbol{\mu}_M(\mathbf{r}') = \int \mathbf{M}(\mathbf{r}') d\mathbf{r}' = \frac{1}{2c} \int \mathbf{r}' \times \mathbf{j} d\mathbf{r}'. \quad 9-23$$

Eq. 9-22 is the magnetic analog of eq. 9-10. The vector  $\mathbf{M}$  is the magnetic dipole density, and  $\boldsymbol{\mu}_M$  is the magnetic dipole moment, in analogy to the electric dipole  $\boldsymbol{\mu}$  of eq. 9-10.

To interpret  $\boldsymbol{\mu}_M$  physically, consider a small circular loop of current  $I$  centered about  $\mathbf{r}' = 0$ . Eq. 9-23 would then become

$$\boldsymbol{\mu}_M = \frac{1}{2c} \int \mathbf{r}' \times (I d\mathbf{l}) = \frac{I}{c} \int d\mathbf{a} = \frac{I}{c} \mathbf{a} \quad 9-24$$

since 1)  $\mathbf{r}'$  is perpendicular to the circular current flow  $\mathbf{J} = I d\mathbf{l}$  such that  $\mathbf{r}' \times d\mathbf{l} = r' d\mathbf{l}$ ; 2) we need integrate only along the circle of the loop, since  $I=0$  elsewhere; 3)  $da = r' dl/2$  as shown in fig. 9-2 for the triangular integration area increment.  $\boldsymbol{\mu}_M$  is thus the current flow times the area of the current loop, and the current loop creates the lowest order contribution to the vector potential, namely a magnetic dipole potential as in eq. 9-22.

$\boldsymbol{\mu}_M$  is also related to the angular momentum of the charged particles causing the current to flow in the loop. For discrete charges, it was seen in section 2 that

$$\mathbf{j} = \sum q_i \mathbf{v}_i \delta(\mathbf{x} - \mathbf{x}_i) \quad 9-25$$

Inserting this into eq. 9-23 yields

$$\boldsymbol{\mu}_M = \frac{1}{2c} \sum q_i (\mathbf{r}_i \times \mathbf{v}_i) = \sum \frac{q_i}{2m_i c} \mathbf{L}_i \quad 9-26$$

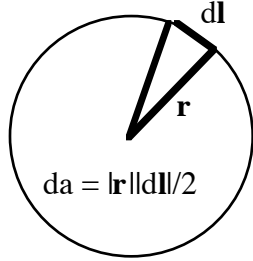


Fig. 9-2. Area element of the integration leading to the magnetic moment  $\mathbf{m}$

This clearly shows the linear relationship between  $\boldsymbol{\mu}_M$  and the associated angular momentum, of which examples were given in a). For a spin angular momentum, such a classical analog in terms of a current loop does not apply, of course.

We can now use eq. 9-22 for  $\mathbf{A}$  to derive the leading terms in  $\mathbf{B}(\mathbf{r})$  by taking the curl of  $\mathbf{A}$ :

$$\mathbf{B} = \nabla \times \mathbf{A} = \frac{3\hat{\mathbf{n}}(\boldsymbol{\mu} \cdot \hat{\mathbf{n}}) - \boldsymbol{\mu}}{r^3} + \frac{8\pi}{3} \boldsymbol{\mu} \delta(\mathbf{r}) + \text{quadrupole and higher terms} \quad 9-27$$

in analogy to eq. 9-15. Again, there is a delta-function term due to the discontinuity of the dipole field at  $\mathbf{r}=0$ , in order to satisfy the magnetic field boundary conditions imposed by eqs. 9-16 and 9-17.

Finally, in the magnetostatic case eq. 9-17 can be made analogous to the modified Maxwell's equations in section 2 where the electric dipole was considered explicitly. Consider a distribution of magnetic dipole density  $\mathbf{M}(\mathbf{r}')$ . Integrating eq. 9-22 over such a distribution to get the total vector potential yields

$$\begin{aligned} \mathbf{A}(\mathbf{r}) &= \frac{1}{c} \int d\mathbf{r}' \frac{c\mathbf{M}(\mathbf{r}') \times (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \\ &= \frac{1}{c} \int d\mathbf{r}' c\mathbf{M}(\mathbf{r}') \times \nabla' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{1}{c} \int d\mathbf{r}' \frac{c\nabla' \times \mathbf{M}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \quad 9-28$$

The first step can be verified easily by calculating the gradient of  $1/\sqrt{[(x-x')^2+(y-y')^2+(z-z')^2]}$ , which is simply  $(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3$ . The second step follows from integration by parts if the magnetization density  $\mathbf{M}(\mathbf{r}')$  vanishes on the surface (i.e. is localized at small  $\mathbf{r}'$ ).

Comparing eq. 9-28 to 9-19 shows that  $\mathbf{j}_{\text{dip}} = c\nabla \times \mathbf{M}$  is a "magnetic dipole current"; the total current can therefore be decomposed into

$$\mathbf{j} = \mathbf{j}_0 + c\nabla \times \mathbf{M} = \mathbf{j}_0 + \mathbf{j}_{\text{dip}} \quad 9-29$$

where  $\mathbf{j}_0$  is a dc current with no dipole contributions (loops), and  $\mathbf{j}_{\text{dip}}$  takes into account any current loops in the total current density. Inserting into eq. 9-17,

$$\begin{aligned} \nabla \times \mathbf{B} &= \frac{4\pi}{c} \mathbf{j}_0 + 4\pi \nabla \times \mathbf{M} \dots \text{or} \\ \nabla \times \mathbf{H} &= \frac{4\pi}{c} \mathbf{j}_0 \text{ where } \mathbf{H} = \mathbf{B} - 4\pi \mathbf{M} \end{aligned} \quad 9-30$$

In the absence of a dc current (only the dipoles are present), the curl of  $\mathbf{H}$  therefore vanishes, and  $\mathbf{H}$  can be written in terms of a magnetic scalar potential:

$$\mathbf{H} = -\nabla V_M$$

From 9-16 it then follows that

$$\begin{aligned}\nabla \cdot \mathbf{B} &= \mathbf{0} = \nabla \cdot (\mathbf{H} + 4\pi\mathbf{M}) \Rightarrow \\ \nabla^2 V_M &= -4\pi(-\nabla \cdot \mathbf{M}) \equiv -4\pi\rho_M\end{aligned}\tag{9-31}$$

where  $\rho_M$  is an effective "magnetic charge", which is given by the negative divergence of the magnetic dipole density. Of course  $\rho_M$  does not have a monopole component in the magnetic case; however, the same kind of expansion is possible in the electric field case, in which case there can be a monopole component and  $\rho = \rho_0 - \nabla \cdot \mathbf{P} + \dots$ . In section 2, this led to a modification of the vacuum Maxwell's equations in analogy to eq. 9-30, e.g.  $\nabla \mathbf{E} = 4\pi\rho/c \rightarrow \nabla \mathbf{D} = 4\pi\rho_0/c$  where  $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ .

The solution to the right hand inhomogeneous equation 9-31 is given by the Green function method in Appendix A, and is identical in structure to eq. 9-7 for the electric potential:

$$\begin{aligned}V_M &= \int \frac{\rho_M(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= \int \frac{-\nabla' \cdot \mathbf{M}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= \int \mathbf{M}(\mathbf{r}') \cdot \nabla' \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= -\nabla \cdot \int \frac{\mathbf{M}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &\approx -\nabla \cdot \frac{1}{r} \int \mathbf{M}(\mathbf{r}') d\mathbf{r}' = \frac{\mathbf{r}}{r^3} \cdot \int \mathbf{M}(\mathbf{r}') d\mathbf{r}'\end{aligned}\tag{9-32}$$

The third line is obtained by integration by parts using the fact that  $\mathbf{M}$  vanishes on the boundary, while the last step again uses the first term in the multipole expansion of  $1/|\mathbf{r} - \mathbf{r}'|$ . From eq. 9-23 follows that

$$V_M = \frac{\boldsymbol{\mu}_M \cdot \mathbf{r}}{r^3} + \dots\tag{9-33}$$

where  $\boldsymbol{\mu}_M$  is the total magnetic dipole moment in the volume. The negative gradient of eq. 9-33 yields the  $\mathbf{B}$  of eq. 9-27 everywhere except at the location of the magnetic dipole  $\boldsymbol{\mu}_M$ , where the expression again diverges and the same corrective term as in eq. 9-27 must be added.

### 9.3 Interaction energy of a multipole with a field

We now know how to decompose a charge or current distribution into multipoles, and the electric or magnetic fields created by such multipoles. Next, we calculate the interaction energy of a multipole moment located at  $\mathbf{r}$  with an external potential at  $V(\mathbf{r})$ .

#### 9.3.1 Electrostatic energy

For an isolated charge  $U = qV$ . For a distribution of charges we therefore can write, by Taylor expanding  $V(\mathbf{r})$  about  $\mathbf{r}=0$

$$\begin{aligned}U &= \int \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \\ &= \int \rho(\mathbf{r}) \{ V(0) + \mathbf{r} \cdot \nabla V(0) + \frac{1}{2} \sum_{i,j} r_i r_j \frac{\partial^2 V}{\partial r_i \partial r_j} \Big|_{\mathbf{r}=0} + \dots \} d\mathbf{r} \\ &= \int \rho(\mathbf{r}) \{ V(0) - \mathbf{r} \cdot \mathbf{E}(0) - \frac{1}{2} \sum_{i,j} r_i r_j \frac{\partial E_j}{\partial r_i} \Big|_0 + \dots \} d\mathbf{r} \quad (\text{since } \mathbf{E} = -\nabla V)\end{aligned}$$

$$\begin{aligned}
&= QV(0) - \mu \cdot \mathbf{E}(0) - \frac{1}{6} \sum_{i,j} \left\{ \int d\mathbf{r} \rho(3r_i r_j - r^2 \delta_{ij}) \right\} \frac{\partial E_j}{\partial r_i} \Big|_{\mathbf{r}=0} + \dots \\
&= QV(0) - \mu \cdot \mathbf{E}(0) - \frac{1}{6} \sum_{i,j} Q_{ij} \frac{\partial E_j}{\partial r_i} \Big|_0 + \dots
\end{aligned} \tag{9-34}$$

To proceed from the third to the penultimate step,  $r^2 \nabla \cdot \mathbf{E} / 6 = 0$  was added: the divergence of  $\mathbf{E}$  is zero if one assumes that the sources of the external field  $\mathbf{E}$  do not lie at  $\mathbf{r}=0$ , where the multipole in question is located. Eq. 9-34 gives the interaction energy up to the quadrupole term, including the familiar dipole interaction and monopole potential energy.

### 9.3.2 Magnetostatic energy

The energy can be derived from the vector potential  $\mathbf{A}$ , but it is easiest in the magnetostatic case to derive it using the magnetic charge density  $\rho_M = -\nabla \cdot \mathbf{M}$ . Let  $V_M$  be the magnetic potential created by a source dipole density, and let  $\rho_M$  be the dipole density interacting with this potential. In analogy to the electrostatic potential equation at the top of 9-34

$$\begin{aligned}
U &= \int \rho_M(\mathbf{r}) V_M(\mathbf{r}) d\mathbf{r} \\
&= - \int \nabla \cdot \mathbf{M}(\mathbf{r}) V_M(\mathbf{r}) d\mathbf{r} \\
&= + \int \mathbf{M}(\mathbf{r}) \cdot \nabla V_M(\mathbf{r}) d\mathbf{r} \quad (\text{integrate by parts, } V_M \rightarrow 0 \text{ as } r \rightarrow \infty, \text{ so does } \mathbf{M}) \\
&= - \int \mathbf{M}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r} \\
&= - \int \mathbf{M}(\mathbf{r}) \cdot (\mathbf{B}(0) + \dots) d\mathbf{r} \\
&= -\mu \cdot \mathbf{B} + \dots
\end{aligned} \tag{9-35}$$

To obtain the fourth line, it is assumed that  $\mathbf{B} = \mathbf{H} = -\nabla V_M$ ; the first of these equalities is true only if no external magnetization is present at  $\mathbf{r}$ . In the last step, it is assumed that  $\mathbf{B}(\mathbf{r})$  is essentially constant, or slowly varying, at the location of the dipole.

## 9.4 Terms in the molecular Hamiltonian

We can now discuss molecular energy terms arising due to multipole moments, according to the list presented in a).

### 9.4.1 Dipole-dipole couplings

For two spins with magnetic moments  $\mu_1$  and  $\mu_2$ , the interaction energy is given by eqs. 9-27 and 9-35 for one dipole in the field of the other dipole:

$$\begin{aligned}
H_{DD} &= -\mu_1 \cdot \mathbf{B}_{\mu_2} = -\frac{3(\mu_1 \cdot \hat{\mathbf{n}})(\hat{\mathbf{n}} \cdot \mu_2) - \mu_1 \cdot \mu_2}{r^3} - \frac{8\pi}{3} \delta(\mathbf{r}_1 - \mathbf{r}_2) \mu_1 \cdot \mu_2. \\
&= \tilde{\mu}_1 \cdot D \cdot \mu_2 - \frac{8\pi}{3} \delta(\mathbf{r}_1 - \mathbf{r}_2) \mu_1 \cdot \mu_2
\end{aligned} \tag{9-36}$$

where

$$D = \frac{1}{r^5} \begin{pmatrix} r^2 - 3x^2 & -3xy & -3xz \\ -3xy & r^2 - 3y^2 & -3yz \\ -3xz & -3yz & r^2 - 3z^2 \end{pmatrix} \tag{9-37}$$

is the dipole tensor. Note that its trace reduces according to  $A_1$  in  $SU(2)$ , and would contribute to  $U$  even in a spherically averaged environment. However,  $\text{Tr}(D) = 0$ , so the dipolar coupling

makes no contribution to the energy if  $\mu_1, \mu_2, \& \hat{n}$  are randomly oriented (e.g. liquid NMR). It could make a contribution if  $\mu_1 \propto \hat{I}$  and  $\mu_2 \propto \hat{S}$ , where there is a nonspherical molecular electronic distribution (most molecules). Dipole couplings can still contribute to linewidths in isotropic environments, as they allow energy transfer between the spins.

### 9.4.2 Fermi contact interaction

The second term in eq. 9-36 is known as the Fermi contact interaction. It requires the two dipoles to come into contact. This is not possible for nuclear spins, but quite possible for an electronic and a nuclear spin if the electron wave function has s-character. In that case, letting  $\mu_1 \propto \hat{I}$  and  $\mu_2 \propto \hat{S}$ ,

$$H_{FC} = -\frac{8\pi}{3} g_N \beta_N g \beta I \cdot S \delta(\mathbf{r}). \quad 9-38$$

This is nonzero only if  $\Psi_e(0) \neq 0$ ; then the diagonal matrix element (first order perturbation theory) becomes:

$$E_{FC} = -\frac{8\pi}{3} g_N \beta_N g \beta I \cdot S \langle \Psi_e | \delta(\mathbf{r}) | \Psi_e \rangle = -\frac{8\pi}{3} g_N \beta_N g \beta I \cdot S |\Psi_e(0)|^2 \quad 9-39$$

### 9.4.3 Quadrupole couplings

Molecular electrons create an electric field gradient at the nucleus. This gradient can interact with the nuclear quadrupole moment according to eq. 9-34. As a simple example, consider a molecule with cylindrical symmetry ( $D_{\infty h}$  or  $C_{\infty v}$ ). In that case, the only nonzero gradient component in eq. 9-34 is  $\partial E / \partial z \neq 0$ . Therefore

$$U_{QP} = -\frac{1}{6} Q_{zz} (\hat{I}) \frac{\partial E_z}{\partial z} \quad 9-40$$

where  $Q_{zz}$  is the molecule-fixed z component of the quadrupole tensor, which depends on the orientation of the nucleus in the molecule fixed frame. Looking at the definition of the quadrupole in eq. 9-13, we have  $Q_{zz} = \int dV \rho_{nuc} (3z^2 - r^2) = \int dV \rho_{nuc} r^2 (3\cos^2 \theta - 1)$ , where  $\rho_{nuc}$  is the nuclear charge distribution. The expectation value of this nuclear operator can be evaluated using the  $|IM_I\rangle$  basis and the Wigner-Eckart theorem from chapter 5:  $\langle IM_I | Q_{zz} | IM_I \rangle = \frac{3}{2} eQ [3M_I^2 - I(I+1)] / [3I^2 - I(I+1)]$ , where Q is a nuclear shape-dependent constant. Replacing the electric field by the potential gradient, we obtain the final expression

$$U_{QP} = \frac{1}{4} eQ \frac{\partial^2 V}{\partial z^2} \frac{[3M_I^2 - I(I+1)]}{[3I^2 - I(I+1)]} \quad 9-41$$

The associated energy shift can be evaluated by first order perturbation theory, by simply calculating the electronic matrix element  $\langle \Psi_e | \partial^2 V / \partial z^2 | \Psi_e \rangle$ , the expectation value of the potential gradient created by the electron distribution. Note that electron distributions are often approximately cylindrically symmetric about the bond axis, so eqs. 9-41 work approximately even when the molecule does not have cylindrical symmetry.

### 9.4.4 Zeeman and Stark couplings to external fields

Molecules with unpaired electrons or  $I > 0$  nuclear spins will show a splitting of the energy levels in a magnetic field, depending on the  $M_S$  or  $M_I$  components of the spins along the quantization axis provided by the field (Zeeman effect). Similarly, molecules with a nonzero



dipole moment will interact with an applied electric field. The resulting Stark effect can be used to measure the magnitude of molecular dipole moments. In very strong electric fields, the rotational states of a molecule actually become "pendular states", as the dipole locks in to have its positive end point towards the negative field terminal.

For the Zeeman effect, eq. 9-35 yields

$$H_Z = -\vec{\mu}_{spin} \cdot \mathbf{B}_{local} = -\mu_Z B_Z = -g_N \beta_N I_Z B_Z \text{ (nucleus) NMR} \quad 9-42$$

$$\text{or } H_Z = -g_e \beta_e S_Z B_Z \text{ (electron) ESR} \quad 9-43$$

$\mathbf{B}_{local}$  is usually taken to be the externally applied field. However, an applied field can induce electron currents in a molecule, whose field in turn counteracts the applied field. The nuclei therefore usually see a field  $\mathbf{B}_{local}$  which is slightly weaker than the actual applied field. A particularly dramatic case is benzene, in which the  $\pi$  electron system flows in a ring current under the influence of an external field, creating a dipole field according to eq. 9-27. The energy splitting in eq. 9-41 is thus shifted to smaller values, and

$$H_Z = -\vec{\mu}_{spin} \cdot \mathbf{B}_{local} = -g_N \beta_N \mathbf{I} \cdot (1 - 10^{-6} \sigma) \mathbf{B}_{applied} \quad 9-44$$

where  $\sigma$  is the chemical shift in ppm.

Here we briefly sketch how one would compute shielding constants from the ground and excited electronic state wavefunctions of the molecule. Several effects contribute, but let us consider the one caused by a field induced electronic angular momentum  $L$ . The external magnetic field induces a Zeeman effect on the electron via  $L$ , creating a small nonzero  $\langle L \rangle$  via mixing-in of excited electronic states. Then the magnetic field associated with  $\langle L \rangle \neq 0$  interacts with the nucleus via the dipole energy  $-\mu_n \mathbf{B}(L)$ . The relevant interaction terms in the Hamiltonian are

$$H_{shift} = -g_e \beta_e \mathbf{B}_{ext} \cdot \mathbf{L} - g_e \beta_e g_n \beta_n \frac{\mathbf{L}}{r^3} \cdot \mathbf{I}. \quad 9-45$$

The second order perturbation theory cross-term, calld the "paramagnetic term," is

$$E_{shift}^{(2)} = -\mathbf{B}_{ext} \cdot \left\{ - (g_e \beta_e)^2 \sum_{n=1} \frac{\langle \Psi_{e0} | \mathbf{L} | \Psi_{en} \rangle \langle \Psi_{en} | \mathbf{L} / r^3 | \Psi_{e0} \rangle}{E_n - E_0} \right\} \cdot g_n \beta_n \mathbf{I}. \quad 9-46$$

The term in curly brackets is in general a second rank tensor with all possible combination  $L_i L_j$ . However for random orientations of closed-shell ( $\langle L \rangle = 0$  in the ground state) molecules it averages out to a diagonal matrix of equal diagonal matrix elements, or the value  $\sigma$  shown in eq. 9-44. For a typical excited state splitting of  $30,000 \text{ cm}^{-1}$ ,  $\langle 1/r^3 \rangle \approx \langle r \rangle^{-3} \approx 0.2 \text{ \AA}^{-3}$  for typical orbital sizes, and  $L_{0n} \approx 1$  for the unitless angular momentum coupling operator, this evaluates to about  $10^{-5} = 10 \text{ ppm}$ , as expected for the size of a typical chemical shift. Atoms that support low-lying excited electronic states, such as  $^{19}\text{F}$ , will have particularly large chemical shifts.

For the Stark effect, eq. 9-34 yields

$$H_S = -\mu \cdot \mathbf{E}_{ext} = -\mu_Z E_Z = -\mu_z(r_i) \cos \theta E_Z \quad 9-47$$

where  $\mu(r_i)$  is the molecular dipole along the z-axis for a symmetric top molecule. In the general case, the dipole does not lie along the molecule-fixed z-axis, and the full direction cosine matrix from section 5 must be used to transform  $\mu$  from the molecule to the space-fixed frame. This is also true in NMR and EPR spectroscopy, particularly in the latter, where an anisotropic 3 by 3 g-tensor is usually required to describe the lineshapes if the molecule is not tumbling freely in solution or spinning of the sample is used to average out off-diagonal couplings.

## 9.4.5 Scalar couplings

Scalar interactions directly between nuclei, of type  $U = J_{12} \mathbf{I}_1 \cdot \mathbf{I}_2$  (first described by Herb Gutowsky at UIUC) also arise as higher-order perturbation effects; the direct coupling is too weak because nuclear spin magnetic fields are so small. Instead, the nuclear spin  $\hat{\mathbf{I}}_1$  couples to the electron spin  $\mathbf{S}$ . For a closed shell molecule,  $\langle S \rangle = 0$  in the absence of  $-\hat{\mathbf{S}} \cdot \hat{\mathbf{B}}(\mathbf{I}_1)$  coupling, where  $\mathbf{B}(\mathbf{I})$  is the magnetic field caused by the nuclear spin near the electron. However, this term introduces a small admixture of excited electronic states with  $S \neq 0$ . This small  $S$  then interacts with the second nucleus via Fermi-contact  $\approx |\Psi'_e(0)|^2 \mathbf{I}_2 \cdot \mathbf{S}$ , where  $\Psi'_e(0)$  is the nuclear-spin perturbed electronic wavefunction. Second order perturbation theory with electronic matrix elements averaging over all contributing electronic states eliminates the  $\hat{\mathbf{S}}$  dependence and leaves the effective Hamiltonian  $H = J_{12} \mathbf{I}_1 \cdot \mathbf{I}_2$ . Instead of  $S$ , the magnetic moment associated with a nonzero  $L$  (eq. 9-5) can also contribute to this scalar coupling. Scalar couplings introduce splittings among nuclear spins, arising from the various  $M_{S1}M_{S2}$  combinations. For example, for spin 1 being in its ground state, spin 2 can be in  $M_1 = \pm 1/2$ , splitting the ground state into two levels; likewise for the excited state of spin 1. There are thus two transitions with  $M_{S1} = -1/2 \rightarrow 1/2$  which may differ slightly in energy because of the  $J$  term, leading to a doublet splitting in the spectrum.

#### 9.4.6 Other couplings

Many other couplings are possible, including effects as esoteric as shifts in rotational energy levels induced by the independent rotation of electrons in the nuclear frame, which allows one to measure the sign of the molecular dipole moment (not possible by the Stark effect). We consider just two more couplings explicitly.

Spin-orbit coupling arises when electron spins couple to the magnetic field generated by orbital angular momentum (eq. 9-5). In large atoms such as iodine, these splittings can amount to 1000's of  $\text{cm}^{-1}$ , and are certainly not a minor perturbation. From eqs. 9-5 and 9-35, the energy of the electron spin in the field created by circulation of the electrons is

$$H_{SO} = -\mu\beta S \cdot B_{orbit} = \left(\frac{e}{c}\right) \frac{\mu\beta}{r^3} L \cdot S \quad 9-48$$

It is particularly strong in diatomic molecules where  $L_z \neq 0$  and  $S_z \neq 0$ , such as the  $^2\Pi$  states of NO or OH radical.

Spin-rotation coupling was discussed in section 5 for  $^2\Sigma$  molecules, and the Hamiltonian is  $H_{SR} = B_{rot} \mathbf{N} \cdot \mathbf{S}$ . The fact that  $B_{rot}$  should be proportional to the rotational angular momentum  $N$  is clear from eqs. 9-26 and 9-27, which show that the magnetic moment  $\boldsymbol{\mu}$  generated by  $N$  is proportional to  $N$ , and the magnetic field generated by  $\boldsymbol{\mu}$  is proportional to  $\boldsymbol{\mu}$ .