4.1.4 Electric quadrupole interaction

If the nucleus does not have a spherically symmetric charge distribution, it probably has a non-zero electric quadrupole moment

$$Q = \frac{1}{e}\int d^3r\rho(\boldsymbol{r})[3z^2 - r^2] \tag{4.35}$$

which is < 0 for an oblate charge distribution. In contrast to the nuclear magnetic dipole, which is predominantly determined by the unpaired nucleons, Q is sensitive to collective deformations of the nucleus. Some nuclei are observed with 30% differences between polar and equatorial axes, so Q can be comparable to $\langle r^2\rangle$, i.e. $\approx 10^{-24}$ cm^2.

The interaction energy of the quadrupole moment Q with the electron can be found by expanding the term $|\boldsymbol{r}_e - \boldsymbol{r}_N|^{-1}$ in spherical harmonics and evaluating the resulting expressions in terms of Clebsch-Gordon coefficients. The resulting energy shifts are then

$$E^{\mathrm{Q}}_{hf} = BC(C+1) \tag{4.36}$$

where

$$B = \frac{3(Q/a_o^2)}{8I(2I-1)J(J+1)}\langle\frac{1}{r^3}\rangle R_\infty \tag{4.37}$$

and

$$C = [F(F+1) - J(J+1) - I(I+1)] \tag{4.38}$$

[Note that $\boldsymbol{I}\cdot\boldsymbol{J}/\hbar^2$, which was involved in $H^{\mathrm{hf}}_{\mathrm{mag}}$, is equal to $C/2$].

The preceding expressions, like the corresponding ones for the magnetic interactions, have several significant omissions. The most important are relativistic corrections and core shielding corrections. Calculations of core shielding have been made by Sternheimer [2], and the quadrupole shielding by the core is sometimes prefixed by his name.

The following is a detailed explanation of the form of the electric quadrupole interaction.

4.1.5 Multipole expansion

Electrostatic interaction between a charged nucleus and the charged electrons (and other nuclei in molecules)

$$\begin{aligned} H_E &= \int \mathrm{d}^3r_n\,\rho_n(\boldsymbol{r}_n)\,\varphi(\boldsymbol{r}_n) && \rho_n \text{ - charge density of nucleus} \\ &= \int \mathrm{d}^3r_n \int \mathrm{d}^3r_e \frac{\rho_n(\boldsymbol{r}_n)\rho_e(\boldsymbol{r}_e)}{|\boldsymbol{r}_n - \boldsymbol{r}_e|} && \varphi \text{ - el. potential at location } \boldsymbol{r}_n \end{aligned}$$

Consider charges exterior to nucleus, so restrict $|\boldsymbol{r}_e| > R_N \geq |\boldsymbol{r}_n|$, where R_N

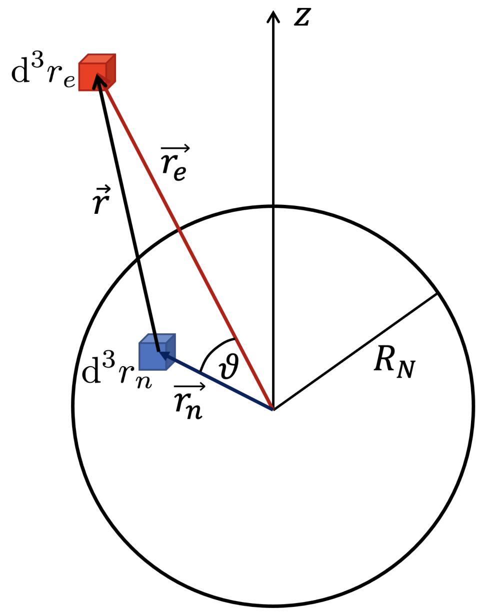

Figure 12. Setup for calculation of electrostatic interaction between electrons and nucleus.

is the radius of the nucleus. With $\boldsymbol{r} = \boldsymbol{r}_e - \boldsymbol{r}_n$ we have

$$\begin{aligned}\frac{1}{r} &= \frac{1}{\sqrt{r_e^2 + r_n^2 - 2\, r_e r_n \cos\vartheta}} \\ &= \frac{1}{r_e} + \frac{r_n}{r_e^2} P_1 + \frac{r_n^2}{r_e^3} P_2 + \frac{r_n^3}{r_e^4} P_3 + \ldots\end{aligned}$$

P_k - Legendre polynomials of $\cos\vartheta$.

$$\begin{aligned}P_0 &= 1 \\ P_1 &= \cos\vartheta \\ P_2 &= \frac{1}{2}\left(3\cos^2\vartheta - 1\right) \\ P_3 &= \frac{1}{2}\left(5\cos^3\vartheta - 3\cos\vartheta\right) \\ P_l &= \frac{1}{2^l l!}\frac{\mathrm{d}^l}{(d\cos\vartheta)^l}(\cos^2\vartheta - 1)^l\end{aligned}$$

So we get the multipole expansion of H_E:

$$\begin{aligned}H_E &= \sum_l H_{E,l} \\ H_{E,l} &= \int \mathrm{d}^3 r_n \int \mathrm{d}^3 r_e \frac{\rho_e^e(\boldsymbol{r}_e)\rho_n(\boldsymbol{r}_n)}{r_e}\left(\frac{r_n}{r_e}\right)^l P_l(\cos\vartheta)\end{aligned}$$

where r_e^e is the charge density external to R_N. $H_{E,l}$ represents the interaction energy from the multipole moment of order 2^l.

It seems difficult to do the integral as ϑ depends on $\boldsymbol{r}_n$ and $\boldsymbol{r}_e$. But we can actually write $P_l(\cos\vartheta)$ in terms of ϑ_n and ϑ_e angles that $\boldsymbol{r}_n$ and $\boldsymbol{r}_e$ make with the z-axis. (This must be so, as $\cos\vartheta$, as any function of it, is, for fixed angles ϑ_n, φ_n, a function of ϑ_e, φ_e, i.e. a function on the unit sphere. I can decompose any function on the unit sphere by spherical harmonics).

$$P_l(\cos\vartheta) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l}(-1)^m Y_{l,-m}(\vartheta_n,\varphi_n)\,Y_{lm}(\vartheta_e,\varphi_e)$$

We thus get the decomposition

$$\begin{aligned}
H_{E,l} &= \mathcal{Q}^{(l)}\cdot\mathcal{F}^{(l)} \\
&= \sum_{m=-l}^{l}(-1)^m Q_m^{(l)} F_{-m}^{(l)} \\
Q_m^{(l)} &= \sqrt{\frac{4\pi}{2l+1}}\int \mathrm{d}^3 r_n\,\rho_n(\boldsymbol{r}_n)\,r_n^l\,Y_{lm}(\vartheta_n,\varphi_n) \\
F_m^{(l)} &= \sqrt{\frac{4\pi}{2l+1}}\int \mathrm{d}^3 r_e\,\rho_e(\boldsymbol{r}_e)\,r_e^{-(l+1)}\,Y_{lm}(\vartheta_e,\varphi_e)
\end{aligned}$$

$l=0$**: Monopole interaction** We have

$$H_{E,0} = Ze\,\phi^e$$

with

$$Ze = Q_0^{(0)} = \int \mathrm{d}^3 r_n \rho_n(\boldsymbol{r}_n)$$

the total nuclear charge and

$$\phi^e = F_0^{(0)} = \int \mathrm{d}^3 r_e \frac{\rho_e^e(\boldsymbol{r}_e)}{r_e}$$

the electrostatic potential from external charges ($r_e > R_N$) at the nucleus.

$l=1$ **Dipolar interaction (will turn out to be zero)**

$$H_{E,1} = -p_z E_z^e - \frac{1}{2}p_+ E_-^e - \frac{1}{2}p_- E_+^e$$

with

$$p_z = Q_0^{(1)} = \int \mathrm{d}^3 r_n\,\rho_n(\boldsymbol{r}_n)\,\boldsymbol{r}_n\,\cos\vartheta_n = \int \mathrm{d}^3 r\,\rho_n(\boldsymbol{r}_n) z_n$$

which is the z-component of the nuclear electrical dipole moment, and

$$p_{\pm 1} \equiv p_x \pm i p_y = \pm\sqrt{2}\,Q_{\pm 1}^{(1)} = \int \mathrm{d}^3 r_n\,\rho_n(\boldsymbol{r}_n)(x_n \pm i y_n)$$

E_z^e is the electric field at the nucleus due to external charges, given by

$$E_z^e = -F_0^{(1)} = -\int \mathrm{d}^3 r_e \frac{\rho_e^e(\boldsymbol{r}_e)}{r_e^2} \cos\vartheta_e = -\int \mathrm{d}^3 r_e \frac{\rho_e^e(\boldsymbol{r}_e)}{r_e^3} z_e = -\frac{\partial \varphi_e^e}{\partial z}$$

.

$$E_\pm^e = E_x^e \pm i E_y^e = \pm F_\pm^{(1)} = -\int \mathrm{d}^3 r_e \frac{\rho_e^e}{r_e^3}(x_e \pm i y_e) = -\frac{\varphi_e^e}{\partial x} \mp i \frac{\partial \varphi_e^e}{\partial y}$$

$l = 2$: **Electric quadrupole interaction**

$$H_{E,2} = \sum_{m=-2}^{2} (-1)^m Q_m (\boldsymbol{\nabla} E^e)_{-m}$$

Q_m is the nuclear electric quadrupole tensor, $(\boldsymbol{\nabla} E^e)_m$ the electric field gradient tensor. The various components of Q_m are

$$Q_0 = Q_0^{(2)} = \frac{1}{2}\int \mathrm{d}^3 r_n \rho_n(\boldsymbol{r}_n)\, r_n^2\,(3\cos^2\vartheta_n - 1) = \frac{1}{2}\int \mathrm{d}^3 r_n \rho_n\,(3z_n^2 - r_n^2)$$

$$Q_{\pm 1} = Q_{\pm 1}^{(2)} = \mp\sqrt{\frac{3}{2}}\int \mathrm{d}^3 r_n \rho_n\, z_n (x_n \pm i y_n)$$

$$Q_{\pm 2} = Q_{\pm 2}^{(2)} = \sqrt{\frac{3}{8}}\int \mathrm{d}^3 r_n \rho_n\,(x_n \pm i y_n)^2$$

For the elctric field gradient tensor, we have

$$(\boldsymbol{\nabla} E^e)_0 = F_0^{(2)} = \frac{1}{2}\int \mathrm{d}^3 r_e \frac{\rho_e}{r_e^3}(3\cos^2\vartheta - 1) = -\frac{1}{2}\frac{\partial E_z^e}{\partial z}$$

$$(\boldsymbol{\nabla} E^e)_{\pm 1} = \pm\frac{1}{\sqrt{6}}\frac{\partial E_\pm^e}{\partial z}$$

$$(\boldsymbol{\nabla} E^e)_{\pm 2} = -\frac{\sqrt{6}}{12}\left(\frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y}\right) E_\pm^e$$

Using the above representation of the nuclear electric quadrupole tensor and the electric field gradient tensor is efficient, given by five numbers, without redundancies. Alternatively, we could also use cartesian components Q_{ij} and $(\boldsymbol{\nabla} E^e)_{ij}$ with i and $j = x, y, z$. These are 3×3 matrices. When demanding them to be traceless and symmetric, they each again are described by five numbers. One has

$$H_{E,2} = -\frac{1}{6}\sum_{i=x,y,z}\sum_{j=x,y,z} Q_{ij} (\boldsymbol{\nabla} E^e)_{ij}$$

$$Q_{ij} = \int \mathrm{d}^3 r_n\, \rho_n\,(3 x_{ni} x_{nj} - \delta_{ij} r_n^2)$$

$$(\boldsymbol{\nabla} E^e)_{ij} = -\int \mathrm{d}^3 r_e \frac{\rho_e^e}{r_e^5}(3\, x_{ei} x_{ej} - \delta_{ij}\, r_e^2) = -\frac{\partial^2 \varphi_e^e}{\partial x_i \partial x_j}$$

4.1.6 Theoretical restrictions on multipole orders

The nucleus, having definite spin I, has its orientation fully specified by the orientation of the spin angular momentum $\boldsymbol{I}$.

Parity consideration **<u>If</u>**

- all nuclear electrical effects arise from electrical charges
- there is no degeneracy of nuclear states with different parity
- the nuclear Hamiltonian is unaltered by an inversion of coordinates ($\boldsymbol{r} \to -\boldsymbol{r}$)

<u>then</u> no odd (l odd) electrical multipole can exist. So there is no electric dipole or octupole moment.

Sketch of proof: The wave function of the nucleus must obey

$$\begin{aligned} \psi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_A) &= \pm\psi(-\boldsymbol{r}_1, \dots, -\boldsymbol{r}_A) \\ \Rightarrow |\psi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_A)|^2 &= |\psi(-\boldsymbol{r}_1, \dots, -\boldsymbol{r}_A)|^2 \end{aligned}$$

Now for even l, the Y_{lm} is unchanged by inversion, but for odd l, Y_{lm} reverses sign.

$$\Rightarrow \int \mathrm{d}^3 r_n\, \rho_n(\boldsymbol{r}_n)\, Y_{lm}(\vartheta_n, \varphi_n) = 0 \qquad \text{for odd } l.$$

See Purcell and Ramsey, Phys. Rev. 78, 699 (1950). Search for neutron EDM. Outcome:

$$d_{\text{neutron}} < e \cdot 5 \cdot 10^{-20}\,\text{cm}$$

Constraint on observable multiple order For nuclear spin I it is impossible to observe a nuclear multipole moment of order 2^l for $l > 2I$.

Proof: If $\rho_n = \psi_n^* \psi_n$ we have

$$Q_m^{(l)} = \int \mathrm{d}^3 r_n\, \psi_n^*\, r_n^l\, Y_{lm}\, \psi_n.$$

Now Y_{lm} is an orbital wavefunction for orbital angular momentum l. ψ_n is the wavefunction of angular momentum I. So $Y_{lm}\psi_n$ is the wavefunction of a system with angular momentum between $|l-I|$ and $l+I$. ψ_n^* and $\psi_n^* r_n^e$ represent wavefunctions of angular momentum I.

For the integral to be non-zero, we therefore have to have that I lies between $|l-I|$ and $l+I$. Therefore $l \le 2I$. In other words, I, I, and l must satisfy the triangle rule.

An analogous result holds for the electric field gradient tensor and the total angular momentum J of the electronic wavefunction: Atoms (or molecules) in an angular momentum state J, the field tensor $F_m^{(l)}$ is zero unless $l \le 2J$.

So for example, even a nucleus with a large I and a non-zero nuclear quadrupole moment cannot have an electric quadrupole interaction energy with an atom whose $J = \frac{1}{2}$.

More intuitively, a $J = \frac{1}{2}$ angular momentum state is a "sensor" allowing us to probe the nuclear charge distribution only using two alignments (say aligned and anti-aligned with the nuclear spin), giving us at most two different energy

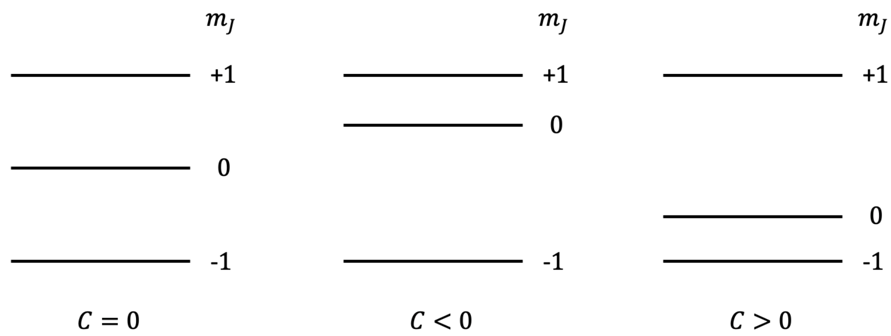

Figure 13. Three outcomes when probing a nucleus with $I \geq 1$ using a $J = 1$ electronic state. (Left) Without quadrupole moment all one can see is a splitting from an effective magnetic field (e.g. the actual magnetic field due to the magnetic moment of the nucleus). With quadrupole moment, one sees the central $m_J = 0$ level shifted up ($C < 0$, middle) or down ($C > 0$, right) with respect to the average of the two $m_J = \pm 1$ levels.

levels. That would be enough to see a nuclear electric dipole (but that is zero), and to sense the magnetic field created by the magnetic moment of the nucleus.

However, it is not enough information to distinguish a sphere from a cigar or a pancake-shaped charge distribution (they all would give the same energy for the two orientations of $\boldsymbol{J}$). The two orientations, i.e. the result for the two m_J values, which correspond semi-classically to two values of $\cos\vartheta$, are not enough to tell me about the nuclear shape along directions transverse to $\boldsymbol{I}$. But take instead $J = 1$. Now there are three alignments of our “sensor”, e.g. aligned, anti-aligned, and transverse to $\boldsymbol{I}$. Correspondingly, there are three energy levels (see Fig. 13). Generally, all possible outcomes can be modelled by an effective Hamiltonian $m_J g \mu_B B + C m_J^2$. The magnetic field will cause symmetric splitting of $m_J = \pm 1$ about $m_J = 0$, while the second term will shift $m_J = \pm 1$ together up ($C > 0$) or down ($C < 0$) with respect to $m_J = 0$. But m_J^2 comes from a term like $(\boldsymbol{I} \cdot \boldsymbol{J})^2 \propto \cos^2\vartheta$, which can be expressed as a quadrupole interaction plus a constant.