Electric quadrupole interaction

Multipole expansion: Electrostatic interaction between a charged nucleus and the charged electrons. (and other nuclei in molecules)

$$H_E = \int d\vec{r}_n^{\,3} \rho_n(\vec{r}_n)\, \varphi(\vec{r}_n)$$

ρ_n – charge density of nucleus

$$= \int d\vec{r}_n^{\,3} \int d\vec{r}_e^{\,3} \frac{\rho_n(\vec{r}_n)\, \rho_e(\vec{r}_e)}{|\vec{r}_n - \vec{r}_e|}$$

φ – electrostatic potential at location $\vec{r}_n$

Consider charges exterior to nucleus, so restrict $|\vec{r}_e| > R_N \geq |\vec{r}_n|$, where R_N is radius of nucleus.
With $\vec{r} = \vec{r}_e - \vec{r}_n$ we have

$$\frac{1}{r} = \frac{1}{(r_e^2 + r_n^2 - 2 r_e r_n \cos\vartheta)^{1/2}}$$

$$= \frac{1}{r_e} + \frac{r_n}{r_e^2} P_1 + \frac{r_n^2}{r_e^3} P_2 + \frac{r_n^3}{r_e^4} P_3 + \dots$$

P_k – Legendre polynomials of $\cos\vartheta$

$P_0 = 1$ $\qquad$ $P_2 = \frac{1}{2}(3\cos^2\vartheta - 1)$

$P_1 = \cos\vartheta$ $\qquad$ $P_3 = \frac{1}{2}(5\cos^3\vartheta - 3\cos\vartheta)$

$$P_\ell = \frac{1}{2^\ell \ell!} \frac{d^\ell}{(d\cos\vartheta)^\ell} (\cos^2\vartheta - 1)^\ell$$

$$\Rightarrow \quad H_E = \sum_\ell H_{E\ell}$$

ρ_e^e – charge density external to R_N.

$$H_{E\ell} = \int d\vec{r}_n^{\,3} \int d\vec{r}_e^{\,3} \frac{\rho_e^e(\vec{r}_e)\, \rho_n(\vec{r}_n)}{r_e} \left(\frac{r_n}{r_e}\right)^\ell P_\ell(\cos\vartheta)$$

Interaction energy from multipole moment of order 2^ℓ.

Seems difficult to do as ϑ depends on $\vec{r}_n$ and $\vec{r}_e$.
But we can actually write $P_\ell(\cos\vartheta)$ in terms of ϑ_n and ϑ_e angles that $\vec{r}_n$ and $\vec{r}_e$ make with the z-axis

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

$$\Rightarrow \quad H_{E\ell} = Q^{(\ell)} \cdot F^{(\ell)}$$

$$= \sum_{m=-\ell}^{\ell} (-1)^m Q_m^{(\ell)} F_{-m}^{(\ell)}$$

$$Q_m^{(\ell)} = \sqrt{\frac{4\pi}{2\ell+1}} \int d^3 r_n \; \rho_n(\vec{r}_n)\, r_n^{\ell}\, Y_{\ell m}(\vartheta_n, \varphi_n)$$

$$F_m^{(\ell)} = \sqrt{\frac{4\pi}{2\ell+1}} \int d^3 r_e \; \rho_e^e(\vec{r}_e)\, r_e^{-(\ell+1)}\, Y_{\ell m}(\vartheta_e, \varphi_e)$$

$\ell = 0$: Monopole interaction $\quad H_{E0} = Ze\,\varphi^e$

$$Ze = Q_0^{(0)} = \int d^3 r_n \; \rho_n(\vec{r}_n) \qquad \text{total nuclear charge}$$

$$\varphi^e = F_0^{(0)} = \int d^3 r_e \; \frac{\rho_e(\vec{r}_e)}{r_e}$$

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

$\ell = 1$: Dipolar interaction (will turn out to be zero):

$$H_{E1} = -p_z E_z^e - \tfrac{1}{2} p_+ E_-^e - \tfrac{1}{2} p_- E_+^e$$

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

– z-component of nuclear electrical dipole moment

$$p_\pm = p_x \pm i p_y = \pm\sqrt{2}\, Q_{\pm 1}^{(1)}$$

$$= \int d^3 r_n \; \rho_n \,(x_n \pm i y_n)$$

E_z^e – electric field at nucleus due to external charges.

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

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

$l=2$: Electric quadrupole interaction

$$H_{E2} = \sum_{m=-2}^{2} (-1)^m Q_m \, (\nabla E^e)_{-m}$$

Q_m – nuclear electrical quadrupole tensor

$(\nabla E^e)_m$ – electric field gradient tensor

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

$$Q_{\pm1} = Q_{\pm1}^{(2)} = \mp\sqrt{\frac{3}{2}}\int d^3r_n \, \rho_n \, z_n (x_n \pm i y_n)$$

$$Q_{\pm2} = Q_{\pm2}^{(2)} = \sqrt{\frac{3}{8}}\int d^3r_n \, \rho_n \, (x_n \pm i y_n)^2$$

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

$$(\nabla E^e)_{\pm1} = \pm\frac{1}{\sqrt6}\frac{\partial E_\pm^e}{\partial z} \quad ; \quad (\nabla E^e)_{\pm2} = -\frac{\sqrt6}{12}\left(\frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y}\right) E_\pm^e$$

Alternatively, we could use cartesian components

$$H_{E2} = -\frac{1}{6}\sum_{i=x,y,z}\sum_{j=x,y,z} Q_{ij}\,(\nabla E^e)_{ij}$$

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

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

Theoretical restrictions on multipole orders:

Nucleus of definite spin I, orientation fully specified by orientation of spin angular momentum $\vec{I}$.

1. Parity consideration:

If all nuclear electrical effects arise from electrical charges, if there is no degeneracy of nuclear states with different parity, and if the nuclear hamiltonian is unaltered by an inversion of coordinates ($\vec{r} \to -\vec{r}$):

$\Rightarrow$ No odd (l odd) electrical multipole can exist.

$\Rightarrow$ No electric dipole or octupole moment

Sketch of proof: Wave function of nucleus must obey

$$\Psi(\vec{r}_1, \ldots, \vec{r}_A) = \pm\, \Psi(-\vec{r}_1, \ldots, -\vec{r}_A)$$

$$\Rightarrow |\Psi(\vec{r}_1, \ldots, \vec{r}_A)|^2 = |\Psi(-\vec{r}_1, \ldots, -\vec{r}_A)|^2$$

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

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

Purcell and Ramsey, Phys. Rev. 78, 699 (1950)

search for neutron EDM

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

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

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

$$Q_m^{(l)} = \int d\vec{r}_n^3 \; \psi_n^* r_n^l Y_{lm} \psi_n$$

Y_{lm} – orbital wavefunction for orbital angular momentum l

ψ_n – wave function of angular momentum I.

$\Rightarrow$ $Y_{lm}\psi_n$ – wave function of a system with angular momentum between $|l-I|$ and $l+I$.

ψ_n^* and $\psi_n^* r_n^l$ – angular momentum I.

$\Rightarrow$ I must lie between $|l-I|$ and $l+I$.

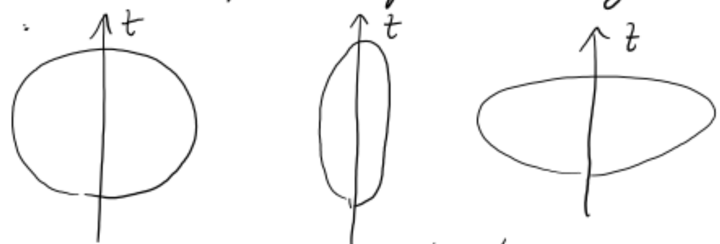
$\Rightarrow$ $l \leq 2I$

I, I and l must satisfy triangle rule

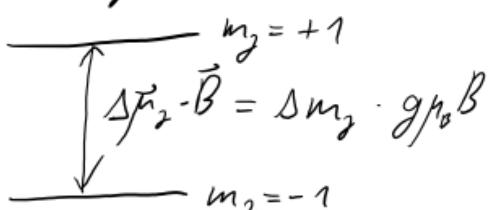
Analogously: For atoms or molecules with angular momentum J, the field tensor $F_m^{(l)}$ is zero unless $l \leq 2J$.

$\boxed{\Rightarrow \text{Even a nucleus with large } I \text{ and a nuclear quadrupole moment can have no electric quadrupole interaction energy with an atom whose } J = \tfrac{1}{2}.}$

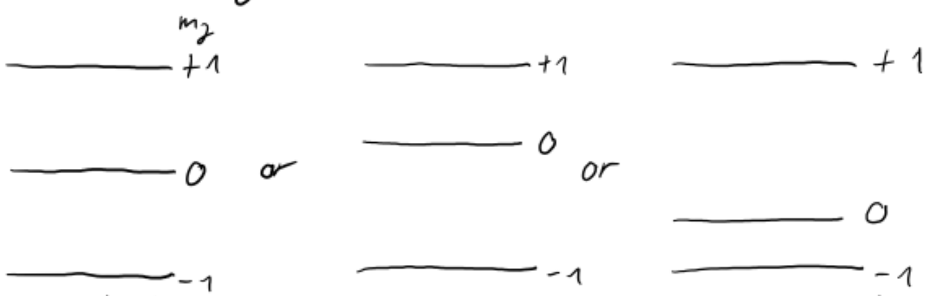
More colloquially, $J=\frac{1}{2}$ only gives us two orientations, e.g. either up or down. That's not sufficient to distinguish a sphere from a cigar or a pancake.



All I get are at most two energy values, which I can associate with a magnetic moment in some B-field



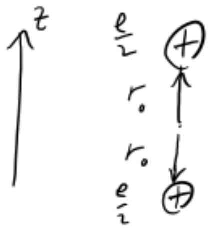
The two m_J values (corresponding semiclassically to only two values of $\cos\vartheta$) are not enough to tell me about directions transverse to this $\vec{B}$-field.
But take $J = 1$. Now we can have



These situations can be modelled as $\vec{\mu}_J \cdot \vec{B} + C \cdot m_J^2$ with $C = 0$, $C < 0$, $C > 0$ respectively. But $m_J^2 = \cos^2\vartheta$, which can be expressed as a quadrupole interaction plus a constant.

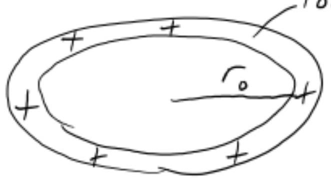
Simple examples for a non-zero quadrupole moment:

$$Q \equiv \frac{1}{e} \int d^3 r_n \, \rho_n \left(3z^2 - r^2\right) \quad \text{quadrupole moment}$$



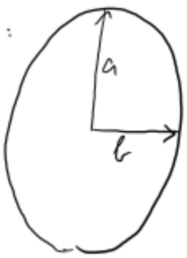
gives $Q = 2 r_0^2 > 0$

total charge e



gives $Q = - r_0^2 < 0.$

Ellipsoid:



uniform density, $\frac{x^2+y^2}{b^2} + \frac{z^2}{a^2} = 1$

gives $\rho_n \int dz \int d^2 r_\perp \left(2z^2 - r_\perp^2\right)$

$$= \rho_n b^2 a \int d\tilde{z} \, d^2\tilde{r}_\perp \left(2a^2 \tilde{z}^2 - b^2 \tilde{r}_\perp^2\right)$$

$$= \rho_n b^2 a \left(2a^2 \cdot \int d^3\tilde{r} \, \tilde{z}^2 - b^2 \int d^3\tilde{r} \, \tilde{r}_\perp^2\right)$$

$$\int d^3\tilde{r} \, \tilde{z}^2 = \frac{1}{3} \int d^3\tilde{r} \, \tilde{r}^2 = \frac{4\pi}{3} \int d\tilde{r} \, \tilde{r}^4 = \frac{4\pi}{15}$$

$$\int d^3\tilde{r} \, \tilde{r}_\perp^2 = \frac{2}{3} \int d^3\tilde{r} \, \tilde{r}^2 = \frac{8\pi}{15}.$$

$$\Rightarrow \quad Q = \frac{1}{e} \frac{8\pi}{15} \rho_n b^2 a \left(a^2 - b^2\right)$$

but $e = \frac{4\pi}{3} b^2 a \rho_n$

$$\Rightarrow \quad Q = \frac{2}{5} \left(a^2 - b^2\right) > 0$$

$Q < 0$ as $a < b$.

To calculate the quadrupole moment tensor, we need to rotate the tensor in the nuclear frame into the lab frame, where the orientation of the nucleus is given by I and m_I. Now conveniently, the components of the coordinate vector $\vec{r}_n$ transform just like the components of $\vec{I}$, and products like $(x_n \pm i y_n) \cdot z_n$ transform like the properly symmetrized $\frac{1}{2}(I_\pm I_z + I_z I_\pm)$.

So we have

$$Q_0 = \frac{1}{2} \int d^3 r_n \, \rho_n \, (3 z_n^2 - r_n^2) = C \cdot \frac{1}{2} \left(3 I_z^2 - \vec{I}^2\right)$$

$$Q_{\pm 1} = \mp \sqrt{\frac{3}{2}} \, C \cdot \frac{1}{2} \left(I_z I_\pm + I_\pm I_z\right)$$

$$Q_{\pm 2} = \sqrt{\frac{3}{8}} \, C \, I_\pm^2$$

Define
$$Q \equiv \frac{1}{e} \int d^3 r_n \, \rho_{nII} \, (3 z_n^2 - r_n^2) \quad \text{"the" quadrupole moment}$$
$$= \frac{1}{e} \int d^3 r_n \, \rho_{nII} \, r_n^2 \, (3 \cos^2 \vartheta_n - 1)$$
$$= \langle r_n^2 (3 \cos^2 \vartheta_n - 1) \rangle_{II}$$

ρ_{nII} - charge density when nucleus is in the orientation state with $m_I = I$. $\langle \ldots \rangle_{II}$ - average in $|II\rangle$

$$Q = \frac{2}{e} \langle II | \, Q_0 \, | II \rangle$$
$$= \frac{C}{e} \left(3 I^2 - I(I+1)\right) = \frac{C}{e} \, I \, (2I - 1)$$

$$\Rightarrow \quad Q_0 = \frac{eQ}{2I\,(2I-1)} \left(3 I_z^2 - I(I+1)\right)$$

$$Q_{\pm 1} = \mp \frac{\sqrt{6}}{2} \, \frac{eQ}{2I\,(2I-1)} \left[I_z I_\pm + I_\pm I_z\right]$$

$$Q_{\pm 2} = \frac{\sqrt{6}}{2} \, \frac{eQ}{2I\,(2I-1)} \, I_\pm^2$$

Diagonalization of the electric quadrupole interaction:

Need to diagonalize $3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - \vec{I}^2\vec{J}^2$

Use $\vec{F} = \vec{J} + \vec{I}$

$$\vec{J}\cdot\vec{I} = \frac{1}{2}\left(F(F+1) - I(I+1) - J(J+1)\right) \equiv \frac{1}{2}C$$

$$\Rightarrow 3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - \vec{I}^2\vec{J}^2 = \frac{3}{4}C(C+1) - I(I+1)J(J+1)$$

$$\Rightarrow \boxed{H_{E2} = \frac{e^2 q_J Q}{2I(2I-1)J(2J-1)}\left(\frac{3}{4}C(C+1) - I(I+1)J(J+1)\right)}$$

(Note that for $F = I+J$, $H_{E2} = \frac{e^2 q_J Q}{4}$)

The last term with $\vec{I}^2\vec{J}^2$ is a constant and often omitted or included in the reference energy.

$$\rightarrow \boxed{H_{E2}' = h\,b\;2\vec{I}\cdot\vec{J}\,(2\vec{I}\cdot\vec{J} + 1)}$$

which in the $|F, m_F\rangle$ basis is just

$$\boxed{\langle F, m_F | H_{E2} | F, m_F\rangle = h\,b\;C\,(C+1)}$$

Together with the magnetic dipole moment interaction $a\,\vec{I}\cdot\vec{J}$ this gives

$$\langle F, m_F | H_{HF} | F, m_F\rangle = h\,\frac{a}{2}\,C + h\,b\,C(C+1)$$

with $C = F(F+1) - I(I+1) - J(J+1)$