Lecture 11 – Electric Quadrupole Interaction (suite), Atoms/Molecules in DC electric fields

Example: Nuclear Quadrupole Interaction in ^{23}Na

$I = \frac{3}{2}$, $S = \frac{1}{2}$; $3^2S_{1/2}$ ground-state: $F = 1$ and $F = 2$,

hyperfine splitting $1.77\ \mathrm{GHz} = 2\,a_{hf} \Rightarrow a_{hf} = 885\ \mathrm{MHz}$

Excited states: $3\,^2P_{1/2}$ $\quad J = \frac{1}{2} \Rightarrow F = 1$ and 2

$a_{1/2} = 94.4\ \mathrm{MHz}$

No electric quadrupole interaction. ($J = \frac{1}{2}$!)

$3^2P_{3/2}$ $\quad J = \frac{3}{2} \Rightarrow F = 0, 1, 2, 3$

$a_{3/2} = \frac{1}{5}\,a_{1/2}$.

b – electric quadrupole interaction $= 2.72\ \mathrm{MHz}$

Why $a_{3/2} = \frac{1}{5}\,a_{1/2}$? Magnetic hyperfine interaction:

$$h a = \frac{\mu_I}{I}\frac{\vec{B}_J \cdot \vec{J}}{|J|^2}$$

$$= \frac{\mu_I}{I}\frac{\vec{J}}{J(J+1)} \cdot 2\mu_0\left(\frac{\vec{L}}{r^3} - \frac{\vec{S}}{r^3} + \frac{3(\vec{S}\cdot\hat{r})\hat{r}}{r^3}\right)$$

$$= \frac{\mu_I}{I}\frac{2\mu_0}{J(J+1)}\left\langle\frac{1}{r^3}\right\rangle \underbrace{\underbrace{\left((\vec{L}-\vec{S})\cdot(\vec{L}+\vec{S}) + 3(\vec{S}\cdot\hat{r})^2\right)}_{\vec{L}^2 - \vec{S}^2 + 3\frac{1}{4}}}_{L(L+1)}$$

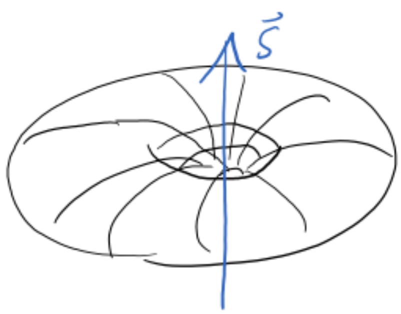
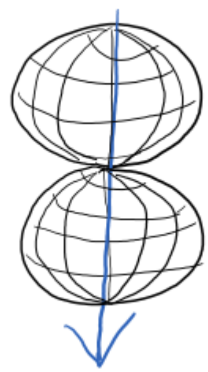
$$= 2\mu_0\frac{\mu_I}{I}\left\langle\frac{1}{r^3}\right\rangle\frac{L(L+1)}{J(J+1)} \qquad \Rightarrow \vec{B}_J\cdot\vec{J} \text{ only depends on } L!$$

$$= 2\mu_0\frac{\mu_I}{I}\frac{Z^3}{n^3 a_0^3}\frac{1}{(L+\frac{1}{2})J(J+1)}$$

So $$\frac{a_{1/2}}{a_{3/2}} = \frac{\frac{3}{2}(\frac{3}{2}+1)}{\frac{1}{2}(\frac{1}{2}+1)} = \frac{3\cdot 5}{1\cdot 3} = 5$$

Application to ^{23}Na: No electric quadrupole interaction in $^2S_{1/2}$ and $^2P_{1/2}$. Both of these have spherical charge distributions (!) So $q_{J=\frac{1}{2}} = 0$.

In particular, consider the angular part of $^2P_{1/2}$.
It is
$$|J=\tfrac{1}{2}, m_J=\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|L=1, m_L=1, S=\tfrac{1}{2}, m_S=-\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\,|L=1, m_L=0, S=\tfrac{1}{2}, m_S=+\tfrac{1}{2}\rangle$$
So
$$\langle\vartheta,\varphi|J=\tfrac{1}{2}, m_J=\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,Y_{11}(\vartheta,\varphi)\,|S=\tfrac{1}{2}, m_S=-\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\,Y_{10}(\vartheta,\varphi)\,|S=\tfrac{1}{2}, m_S=+\tfrac{1}{2}\rangle$$

It's  + 

And
$$\left|\langle\vartheta,\varphi|J=\tfrac{1}{2}, m_J=\tfrac{1}{2}\rangle\right|^2 = \frac{2}{3}\,|Y_{11}(\vartheta,\varphi)|^2 + \frac{1}{3}\,|Y_{10}(\vartheta,\varphi)|^2$$
$$= \frac{2}{3}\cdot\frac{3}{8\pi}\sin^2\vartheta + \frac{1}{3}\,\frac{3}{4\pi}\cos^2\vartheta$$
$$= 1 = \text{const.}$$

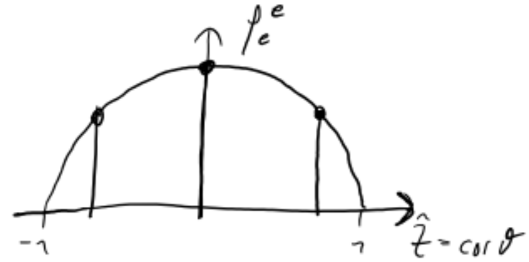
=  a sphere!

Of course, we shouldn't be surprised that a $J=\frac{1}{2}$ state doesn't have an electric field gradient at the nucleus. An electric field gradient is a tensor of rank 2, and I cannot combine $\frac{1}{2}$ and $\frac{1}{2}$ to make total angular momentum 2. Or again more colloquially, $J=\frac{1}{2}$ gives only 2 orientations, up and down, and these two won't allow me to distinguish a <u>gradient</u> in the electric field. An observed energetic splitting like

$$\begin{array}{l} \text{——— } m_J=+\tfrac{1}{2} \\[1em] \text{——— } m_J=-\tfrac{1}{2} \end{array}$$

could always be interpreted as an effective <u>magnetic</u> dipole interaction.

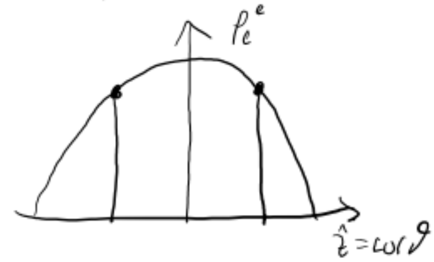
To see a gradient in E, i.e. a <u>curvature</u> in ρ_e^e, I need to measure in at least $\underline{\underline{3}}$ places:



3 measurements at 3 values of $\hat{z}=\cos\vartheta$

$\Rightarrow$ curvature!

e.g. $J=1$, $m_J=\pm 1, 0$



2 measurements at 2 values of $\hat{z}=\cos\vartheta$

$\Rightarrow$ don't see the curvature.

e.g. $J=\frac{1}{2}$, $m_J=\pm\frac{1}{2}$.

With $J=\frac{1}{2}$ I could in principle detect an electric field, i.e. a gradient of the potential. This does not occur for electronic wavefunctions of definite parity, as then

$$|\Psi_e(\vec{r})|^2 = |\Psi_e(-\vec{r})|^2 \quad \text{and} \quad \int d^3r_e \, \frac{\rho_e(\vec{r})}{r_e^2}\cos\vartheta_e = 0.$$

Ok, so no el. quadrupole interaction in $^2S_{1/2}$ and $^2P_{1/2}$.

Now: $^2P_{3/2}$. $J = \frac{3}{2} \longrightarrow$ can give electric field gradient

for ^{23}Na: $I = \frac{3}{2} \longrightarrow$ can possess electric quadrupole moment.

$$q_J = -\left\langle \frac{3\cos^2\vartheta_e - 1}{r_e^3} \right\rangle_{JJ}$$ due to single valence electron.

$$= -\left\langle \frac{1}{r_e^3} \right\rangle \left\langle 3\cos^2\vartheta_e - 1 \right\rangle_{JJ}$$

$$\left\langle 3\cos^2\vartheta_e - 1 \right\rangle_{JJ} = 0 \text{ for } J = \tfrac{1}{2} \text{ (as it should)}$$

$$= \int d\Omega \, |Y_{11}|^2 \cdot (3\cos^2\vartheta - 1)$$

$$= \frac{3}{8\pi} \cdot 2\pi \int d\vartheta \sin\vartheta \cdot \sin^2\vartheta \, (3\cos^2\vartheta - 1)$$

$$= \frac{3}{4} \int_{-1}^{1} d(\cos\vartheta) \, (1 - \cos^2\vartheta)(3\cos^2\vartheta - 1)$$

$$= \frac{3}{4} \int_{-1}^{1} dz \, (-3z^4 + 4z^2 - 1)$$

$$= \frac{3}{4}\left(-\frac{3}{5}\cdot 2 + \frac{4}{3}\cdot 2 - 2\right)$$

$$= \frac{1}{2}\left(-\frac{9}{5} + \frac{20}{5} - \frac{5}{5}\right)$$

$$= \frac{1}{2}\left(-\frac{4}{5}\right)$$

$$= -\frac{2}{5}$$

$$\left\langle \frac{1}{r_e^3} \right\rangle = \frac{Z^3}{n^3 a_0^3} \frac{1}{\ell(\ell+1)(\ell+\frac{1}{2})}$$ with Z and n effective values.

Note that fine structure splitting is $\delta = \mu_0^2 \left\langle \frac{1}{r^3} \right\rangle (2\ell+1) Z$

So $\left\langle \frac{1}{r^3} \right\rangle = \frac{\delta}{\mu_B^2 (2\ell+1) Z} \Longrightarrow q_J = \frac{2}{15} \frac{\delta}{\mu_B^2 Z}$

A better value of $\langle \frac{1}{r^3} \rangle$ comes directly from the measured hyperfine structure:

$$\langle \frac{1}{r^3} \rangle = \frac{h\, a}{\mu_B \left(\frac{\mu_I}{I}\right)} \frac{J(J+1)}{2L(L+1)} \qquad \mu_I = g_I \mu_N I$$

$$\Rightarrow \quad q_{J=\frac{3}{2}} = \frac{2}{5} \frac{h\, a_{J=\frac{3}{2}}\ \frac{3}{2}\cdot\frac{5}{2}}{\mu_B\, g_I \mu_N\ 2\cdot 2}$$

$$= \frac{3}{8} \frac{h\, a_{J=\frac{3}{2}}}{\mu_B\, g_I \mu_N} = \frac{3}{40} \frac{h\, a_{J=\frac{1}{2}}}{\mu_B\, g_I \mu_N}$$

$$h\, b = \frac{3}{8} \frac{e^2 q_J\, Q}{I(2I-1)J(2J-1)}$$

$$= \frac{3}{8} \frac{e^2 q_J\, Q}{\frac{3}{2}(3-1)\frac{3}{2}(3-1)} = \frac{1}{24} e^2 q_J\, Q$$

$$= \frac{1}{320} h\, a_{J=\frac{1}{2}} \frac{e^2 Q}{g_I \mu_B^2 \left(\frac{m}{M_p}\right)} \qquad \mu_B = \frac{e\hbar}{2mc}$$

$$= \frac{4}{320} h\, a_{J=\frac{1}{2}} \frac{Q}{\lambda_c^2} \frac{M_p}{m\, g_I} \qquad \frac{\mu_B}{e} = \frac{\hbar}{2mc} = \lambda_c \frac{1}{2}$$

$$\Rightarrow \frac{Q}{\lambda_c^2} = 80 \frac{b}{a_{J=\frac{1}{2}}} g_I \frac{m}{M_p}$$

$$g_I \frac{m}{M_p} = 0.0008\ ; \quad 24 \cdot b = 2.72\ \text{MHz} = \frac{e^2 q_J Q}{h}\ ; \quad a_{J=\frac{1}{2}} = 94.4\ \text{MHz}$$

$$\Rightarrow \quad \frac{Q}{\lambda_c^2} = \frac{10}{3} \frac{e q Q}{h\, a_{J=\frac{1}{2}}} g_I \frac{m}{M_p} = 7.7 \cdot 10^{-5}$$

$$Q = 0.11 \cdot 10^{-24}\ \text{cm}^2 = 0.11\ \text{barn} > 0$$

First measured by Perl, Rabi, Senitzky, Phys. Rev. 97, 838 (1954)

Structure of $^2P_{3/2}$ $\quad 24b = e^2 q_z Q/h = 2.72\ \text{MHz}$

$J = \frac{3}{2},\ I = \frac{3}{2}\ ;\quad a_{3/2} = 18.5\ \text{MHz}\ \left(\approx \frac{1}{5} a_{1/2}\right)$

$F=0 \Rightarrow C = -\frac{3}{2}\cdot\frac{5}{2}\cdot 2 = -\frac{15}{2} \qquad \cdot 1 \qquad -15$

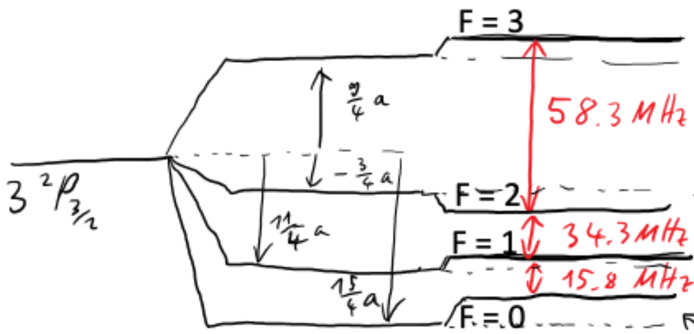
$F=1 \Rightarrow C = 2 - \frac{15}{2} = -\frac{11}{2} \qquad \cdot 3 \qquad -33$

$F=2 \Rightarrow C = 6 - \frac{15}{2} = -\frac{3}{2} \qquad \cdot 5 \qquad -15$

$F=3 \Rightarrow C = 12 - \frac{15}{2} = +\frac{9}{2} \qquad \cdot 7 \qquad 63$

$\overline{}$ 0 ✓

$$H_{HF} = \frac{ah}{2}\cdot C + bh\left(C(C+1) - \underbrace{\tfrac{4}{3} I(I+1) J(J+1)}_{\frac{4}{3}\cdot\frac{15}{4}\cdot\frac{15}{4} = \frac{75}{4}}\right)$$



$b\left(\frac{9\cdot 11}{2\cdot 2} - \frac{75}{4}\right) = b\cdot 6$

$b\left(\frac{3\cdot 1}{2\cdot 2} - \frac{75}{4}\right) = -b\cdot 18$

$b\left(\frac{11\cdot 9}{2\cdot 2} - \frac{75}{4}\right) = b\cdot 6$

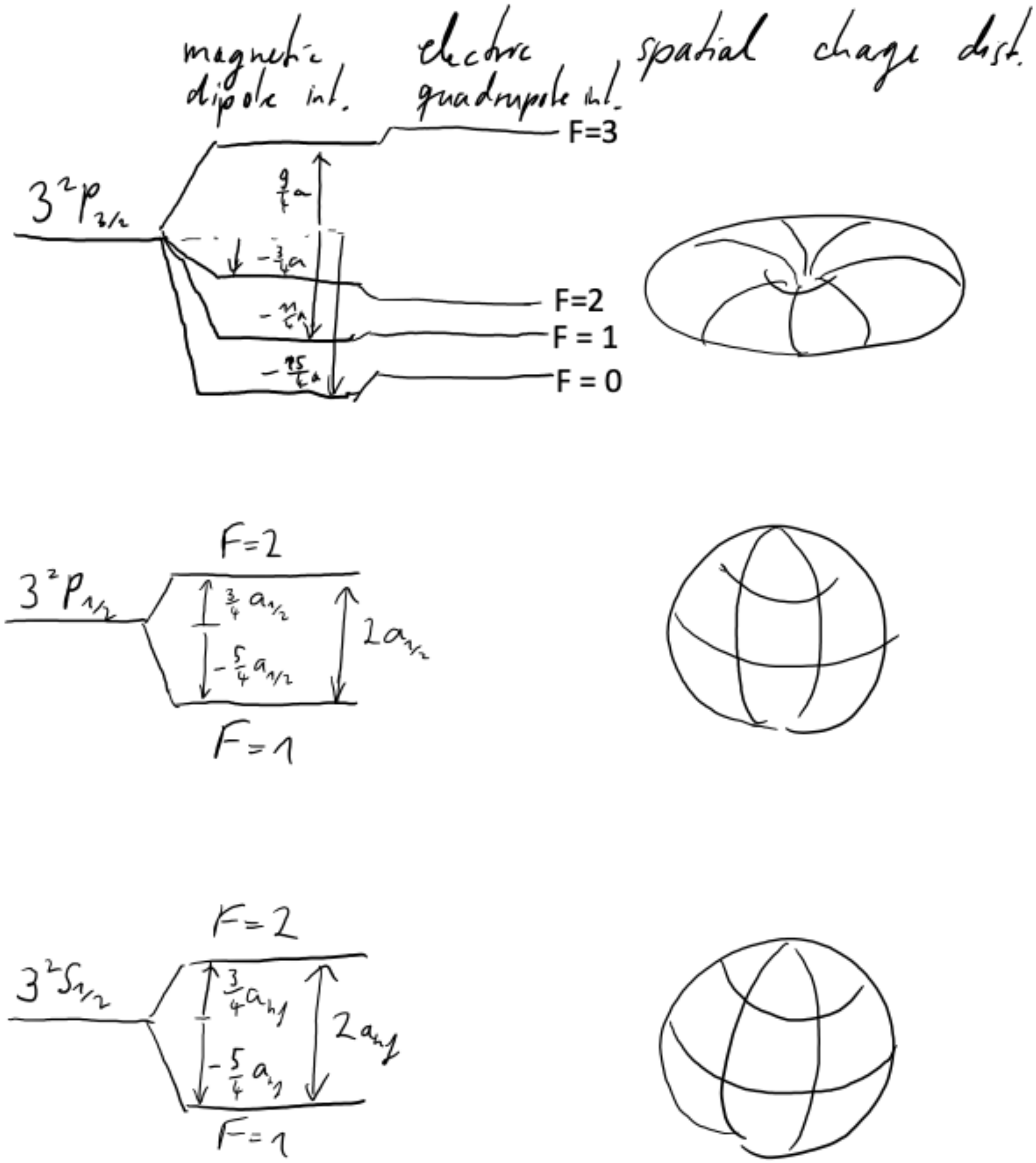
$b\cdot\left(\frac{15}{2}\cdot\frac{13}{2} - \frac{75}{4}\right) = b\cdot 30$

center of mass stays put:

$$6\cdot 7 - 18\cdot 5 + 6\cdot 3 + 30\cdot 1 = 0 \ ✓$$

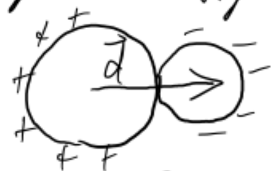
$^{23}Na:\quad I = \frac{3}{2}$

Summary


magnetic dipole int.
electric quadrupole int.
spatial charge dist.
$3^2P_{3/2}$
F=3
$\frac{9}{4}a$
$-\frac{3}{4}a$
$-\frac{11}{4}a$
$-\frac{15}{4}a$
F=2
F = 1
F = 0
$3^2P_{1/2}$
F=2
$\frac{3}{4}a_{1/2}$
$-\frac{5}{4}a_{1/2}$
$2a_{1/2}$
F=1
$3^2S_{1/2}$
F=2
$\frac{3}{4}a_{hf}$
$-\frac{5}{4}a_{hf}$
$2a_{hf}$
F=1

DC Stark Effect of a diatomic molecule

Molecule frame: Aligned, has dipole moment $\vec{d}$



Lab frame: ?

! Not aligned ! $\langle \vec{d} \rangle = 0$!

In the absence of degeneracies, every eigenstate has definite parity.

Proof: P parity operator; H hamiltonian, Eigenstate $|\Psi\rangle$

If $[H,P]=0$, then from $H|\Psi\rangle = E|\Psi\rangle$ we get

$$HP|\Psi\rangle = PH|\Psi\rangle = EP|\Psi\rangle$$

$\Rightarrow P|\Psi\rangle$ is also eigenstate of H with the same eigenenergy. So if there are no degeneracies, we can immediately conclude that

$$P|\Psi\rangle = \alpha|\Psi\rangle \quad \text{with some number } \alpha.$$

Since $P^2|\Psi\rangle = |\Psi\rangle$, we must have $\alpha^2 = 1 \Rightarrow \alpha = \pm 1$

Dipole operator $\hat{d} = d\hat{r}$ odd parity.

$$\Rightarrow \langle \underset{\text{even}}{\Psi} | \underset{\text{odd}}{\hat{d}} | \underset{\text{even}}{\Psi} \rangle = 0$$

Formally $P\hat{d}P = -\hat{d}$

$$\Rightarrow \langle\Psi|\hat{d}|\Psi\rangle = \langle\Psi|P\hat{d}P|\Psi\rangle = -\langle\Psi|\hat{d}|\Psi\rangle$$

$$\Rightarrow \langle\Psi|\hat{d}|\Psi\rangle = 0$$

Colloquially: No direction singled out in lab frame $\Rightarrow \langle \hat{d} \rangle = 0$.

Hamiltonian of a simple molecule, a "symmetric top" molecule:

$$H = \frac{\vec{J}^2}{2\Theta} \qquad \Theta - \text{Moment of inertia (more generally a tensor)}$$

$[H, P] = 0$ indeed. $\vec{J}$ - angular momentum operator.

Eigenstates: Spherical harmonics $Y_{JM}(\vartheta, \varphi)$

Eigenenergies: $E = \frac{\hbar^2 J(J+1)}{2\Theta} \equiv \underset{\uparrow}{B}\, J(J+1)$
rotational constant.

The Y_{JM}'s have definite parity:

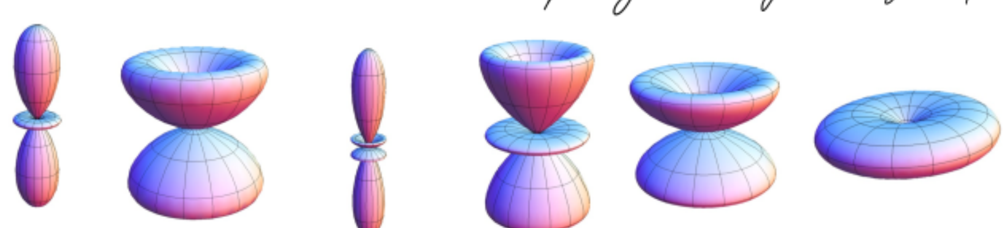
$$P\, Y_{JM}(\vartheta, \varphi) = Y_{JM}(\pi - \vartheta, \varphi + \pi) = (-1)^J\, Y_{JM}(\vartheta, \varphi)$$

And so indeed $\langle JM | \hat{d} | JM \rangle = d \int d\Omega\, Y_{JM}^* \,\hat{r}\, Y_{JM} = 0$

e.g. $\langle JM | \hat{z} | JM \rangle = \int d\Omega\, Y_{JM}^* \cos\vartheta\, Y_{JM} = 0$

As $P \cos\vartheta = \cos(\pi - \vartheta) = -\cos\vartheta$ odd.

$\Rightarrow$ Indeed, as expected on general grounds, the molecule has no "permanent" electric dipole moment in the lab frame. The orientation of the molecule (described by ϑ and φ) is arbitrary, any (ϑ, φ) pair as likely as $(\pi - \vartheta, \pi + \varphi)$. This is also clear when plotting a few $|Y_{JM}(\vartheta, \varphi)|^2$:



$J=2, M=0$ 2,1 3,0 3,1 3,2 3,3

For none of these you could say "they point this way".

Now let's apply an electric field in the (say) z-direction:

$$\vec{\mathcal{E}} = \mathcal{E}\hat{z} \Rightarrow \text{Interaction } V = -\hat{d}\cdot\vec{\mathcal{E}} = -d\mathcal{E}\cos\vartheta.$$

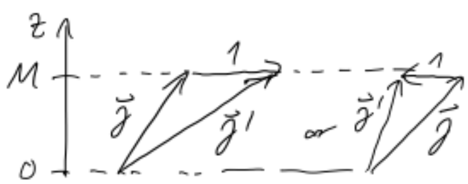
We immediately know that there won't be a first-order shift: $\langle JM|V|JM\rangle = 0$ as $\langle JM|\cos\vartheta|JM\rangle = 0$.

(side note: Obviously, there are degeneracies here, as the eigen-energies for given J are $2J+1$-fold degenerate. However, all eigenstates $|JM\rangle$ for given J have the same parity $(-1)^J$, so even any superposition of the $|JM\rangle$ for fixed J are parity eigenstates).

In order to orient our molecule, the $\mathcal{E}$-field will have to mix in states with different angular momentum J'. For second-order perturbation theory, we need matrix elements

$$\langle J'M'|\cos\vartheta|JM\rangle = \sqrt{\frac{4\pi}{3}}\int d\Omega\, Y^*_{J'M'}(\vartheta,\varphi)Y_{10}(\vartheta,\varphi)Y_{JM}(\vartheta,\varphi)$$

Now this gives selection rules $M' = M$ and $J' = J \pm 1$ (triangle rule)



One has indeed $Y_{10}Y_{JM} = b_{JM}Y_{J+1,M} + b_{J-1,M}Y_{J-1,M}$

with $b_{JM} = \sqrt{\frac{(J+M+1)(J-M+1)}{(2J+1)(2J+3)}}\sqrt{\frac{3}{4\pi}}$

So $\langle J-1, M|\cos\vartheta|J,M\rangle = \sqrt{\frac{J^2-M^2}{(2J-1)(2J+1)}}$ are the only non-zero matrix elements. $\Rightarrow$ state $|J,M\rangle$ is directly "connected" only to it's "neighbours" $|J-1,M\rangle$ and $|J+1,M\rangle$. But these in turn are mixed with $|J-2,M\rangle$ and $|J+2,M\rangle$. $\Rightarrow$ It's in principle an infinite matrix. But can truncate