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Spin-rotational Hamiltonian for diatomic radicals in $^2\Sigma_{1/2}$ state

[includes two spins, dipole and quadrupole hfs and anapole moment]

$$H_p = W_{\underline{P}}\, \varkappa\, \bar{n}\times\bar{s}\cdot\bar{I}_1 \equiv W_{\underline{P}}\, \varkappa\, \bar{v}\cdot\bar{I}_1\,; \quad \bar{v} = \bar{n}\times\bar{s}$$

$$H_{hfs} = (\hat{A}\cdot\bar{S})\cdot\bar{I}_1 \longleftarrow$$ identical structure

Molecular spin-rotational WF:

$|J\Omega, F_1, F_2 M_2\rangle$; $\bar{F}_1 = \bar{J}+\bar{I}_1$; $\bar{F}_2 = \bar{F}_1 + \bar{I}_2$

- No parity QN ! $\left(|p\rangle = \frac{1}{\sqrt{2}}\left(|\Omega\rangle + \chi p|-\Omega\rangle\right), \chi\text{-phase}\right)$

Both H_p and H_{hfs} are of the form $\bar{v}\cdot\bar{I}_1$, $\begin{cases} \bar{v} = \bar{n}\times\bar{s}, H_p \\ \bar{v} = \hat{A}\bar{s}, H_{hfs} \end{cases}$

So, we look for ME

$$\langle J'\Omega' F_1' F_2' M_2' |\, \bar{v}\cdot\bar{I}_1 \,| J\Omega F_1 F_2 M_2\rangle$$

$$= \delta_{M_2' M_2}\,\delta_{F_2', F_2}\, \langle J'\Omega' F_1' M_1' |\, \bar{v}\bar{I}_1 \,| J\Omega F_1 M_1\rangle$$

$$= \delta_{M_2' M_2}\,\delta_{F_2' F_2}\,\delta_{M_1' M_1}\,\delta_{F_1' F_1}\, \langle J'\Omega' F_1 M_1 |\, \bar{v}\bar{I}_1 \,| J\Omega F_1 M_1\rangle \checkmark$$

$\langle J'\Omega' F_1 M_1 | \vec{V}\,\vec{I}_1 | J\Omega F_1 M_1\rangle = $ (S 14.63)

$$= (-1)^{J+I_1+F_1} \begin{Bmatrix} J' & I_1 & F_1 \\ I_1 & J & 1 \end{Bmatrix} \langle J'\Omega' \| V \| J\Omega\rangle \langle I_1 \| I_1 \| I_1\rangle$$

$$= (-1)^{J+I_1+F_1} \begin{Bmatrix} J' & I_1 & F_1 \\ I_1 & J & 1 \end{Bmatrix} \sqrt{I_1(I_1+1)(2I_1+1)}\ \langle J'\Omega' \| V \| J\Omega\rangle$$

All we need is (see LL-III)

$$\langle J'\Omega' \| V \| J\Omega\rangle = (-1)^{J'-\Omega'} \sqrt{(2J'+1)(2J+1)} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q' & \Omega \end{pmatrix} \langle \Omega' | V_{q'} | \Omega\rangle \quad (*)$$

Thus

$$\langle J'\Omega' F_1 M_1 | \vec{V}\cdot\vec{I}_1 | J\Omega F_1 M_1\rangle = (-1)^{J+J'+I_1+F_1-\Omega'} \sqrt{I_1(I_1+1)(2I_1+1)(2J'+1)(2J+1)}$$
$$\begin{Bmatrix} J' & I_1 & F_1 \\ I_1 & J & 1 \end{Bmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q' & \Omega \end{pmatrix} \langle \Omega' | V_{q'} | \Omega\rangle$$

where

$\langle \Omega' | V_{q'} | \Omega\rangle$, q' - spherical ~~[illegible]~~ component $0, \pm 1$

is ME in the molecular frame and does not depend on J's and F's.

For H_{hfs} $V_q = (AS)_q$ and for ${}^2\Sigma_\Omega$ state $\Omega = \Sigma \Rightarrow$

$$\langle \Omega' | S_{q'} | \Omega\rangle = \begin{cases} \delta_{\Omega'\Omega} \cdot \Omega, & q' = 0 \\ \delta_{\Omega', -\Omega} \cdot \sqrt{2}\,\Omega, & q' = \Omega' - \Omega = \pm 1 \end{cases}$$

For H_p $\quad V_{q'} = (n \times S)_{q'}$

Now $\vec{n} = (0, 1, 0)$ $(q' = -1, 0, 1)$

Vector product in sph. basis:

$$\begin{cases} (n\times S)_1 = i\, n_0 S_1 \\ (n\times S)_0 = 0 \\ (n\times S)_{-1} = -i\, n_0 S_{-1} \end{cases}$$

$\Rightarrow$

$$\langle \Omega' | (n\times S)_{q'} | \Omega \rangle = \begin{cases} 0, & \Omega' = \Omega \\ i q' \langle \Omega' | n_0 | \Omega' \rangle \langle \Omega' | S_{q'} | \Omega \rangle \end{cases}$$

$$= i q' \cdot 1 \cdot \sqrt{2}\, \Omega$$

E and B fields

$$H_E = -D\,\bar{n}\cdot\bar{E} \equiv \vec{V}\cdot\vec{E}$$

$$H_B = \mu_0\,\vec{B}\cdot(\hat{G}\vec{S}) \equiv \vec{V}'\vec{B}$$

So, we need ME of electron vector $\vec{V}$

$$\langle J'\Omega' F_1' F_2' M_2' | V_q | J\Omega F_1 F_2 M_2\rangle = (-1)^{F_2'-M_2'}\begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & q & M_2\end{pmatrix}\langle J'\Omega' F_1' F_2' \| V \| J\Omega F_1 F_2\rangle$$

$$(S14.69) = (-1)^{F_2'-M_2'}\begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & q & M_2\end{pmatrix}\sqrt{(2F_2'+1)(2F_2+1)}\begin{Bmatrix} F_1' & F_2' & I_2 \\ F_2 & F_1 & 1\end{Bmatrix}\langle J'\Omega' F_1' \| V \| J\Omega F_1\rangle (-1)^{F_1'+I_2+F_2+1}$$

$$(S14.69) = (-1)^{F_2'-M_2'}\begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & q & M_2\end{pmatrix}\sqrt{(2F_2'+1)(2F_2+1)(2F_1'+1)(2F_1+1)}\begin{Bmatrix} F_1' & F_2' & I_2 \\ F_2 & F_1 & 1\end{Bmatrix}\begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & 1\end{Bmatrix}$$

$$(-1)^{F_1'+I_2+F_2+\cancel{1}}(-1)^{J'+I_1+F_1+\cancel{1}}\langle J'\Omega' \| V \| J\Omega\rangle$$

We use LL-III or (*) from p 2:

$$= (-1)^{F_2'+F_2+F_1'+F_1+I_1+I_2-M_2'+\Omega'}\begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & q & M_2\end{pmatrix}\sqrt{(2F_2'+1)(2F_2+1)(2F_1'+1)(2F_1+1)(2J'+1)(2J+1)}$$

$$\begin{pmatrix} J' & 1 & J \\ -\Omega' & q' & \Omega\end{pmatrix}\begin{Bmatrix} F_1' & F_2' & I_2 \\ F_2 & F_1 & 1\end{Bmatrix}\begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & 1\end{Bmatrix}\langle \Omega' | V_{q'} | \Omega\rangle$$

For H_E: $\vec{V} = \vec{n} = (0,1,0)$

$$\langle \Omega' | V_{q'} | \Omega\rangle = \begin{cases} 1, & q'=0 \\ 0, & q'=\pm 1\end{cases}$$

H_B: $\vec{V} = \hat{G}\cdot\vec{S}$ $\left(\hat{G} = \begin{pmatrix} G_\perp & & \\ & G_\perp & \\ & & G_\parallel\end{pmatrix}\right)$

$$\langle \Omega' | V_{q'} | \Omega\rangle = \begin{cases} G_\parallel \cdot \Omega, & q'=0 \\ \sqrt{2}\,G_\perp \Omega, & q'=\pm 1\end{cases}$$

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Zeeman effect for nuclear spins in diatomics

We use basis set $|J\Omega I_1 F_1 I_2 F_2 M_2\rangle \equiv |J\Omega F_1 F_2 M_2\rangle$ (1)

$$H_{B,nuc} = -(\vec{\mu}_1+\vec{\mu}_2)\vec{B} = -\mu_n B_z (g_1 I_{1,z} + g_2 I_{2,z}) \quad (2)$$

So, we need to calculate $\langle I_z\rangle$ for states (1)

By analogy with p4 ~~of SR Hamiltonian 1.pdf~~.

$$\langle J'\Omega' F_1' F_2' M_2 | I_{1,z} | J\Omega F_1 F_2 M_2\rangle =$$
$$= \delta_{J'J}\, \Omega_{\Omega'\Omega} (-1)^{F_2'-M_2} \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2 & 0 & M_2 \end{pmatrix}$$
$$(-1)^{2F_1'+I_1+I_2+J+F_2} \sqrt{(2F_1'+1)(2F_1+1)(2F_2'+1)(2F_2+1)}$$
$$\begin{Bmatrix} F_1' & F_2' & I_2 \\ F_2 & F_1 & 1 \end{Bmatrix} \begin{Bmatrix} I_1 & F_1' & J \\ F_1 & I_1 & 1 \end{Bmatrix} \sqrt{I_1(I_1+1)(2I_1+1)} \quad (3)$$

$$\langle J'\Omega' F_1' F_2' M_2 | I_{2,z} | J\Omega F_1 F_2 M_2\rangle =$$
$$= \delta_{J'J}\, \delta_{\Omega'\Omega}\, \delta_{F_1'F_1} (-1)^{F_2'-M_2} \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2 & 0 & M_2 \end{pmatrix}$$
$$(-1)^{F_1+I_2+F_2'+1} \sqrt{(2F_2'+1)(2F_2+1)} \quad (4)$$
$$\begin{Bmatrix} I_2 & F_2' & F_1 \\ F_2 & I_2 & 1 \end{Bmatrix} \sqrt{I_2(I_2+1)(2I_2+1)}$$

Expressions (2), (3), and (4) can be used to calculate Zeeman matrix in the basis set (1)

For 2^{nd} hyperfine term $\qquad J' I_1' = F_1$

$$\langle J'\Omega' F_1' F_2' M_2' | \vec{V}\cdot\vec{I}_2 | J\Omega F_1 F_2 M_2\rangle =$$

$$= (-1)^{F_1' + I_2 + F_2} \begin{Bmatrix} F_1' & I_2 & F_2 \\ I_2 & F_1 & 1 \end{Bmatrix} \langle F_1'\Omega' \| V \| F_1\,\Omega\rangle \langle I_2 \| I \| I_2\rangle \quad ✓$$

$$= (-1)^{F_1+I_2+F_2} \begin{Bmatrix} F_1' & I_2 & F_2 \\ I_2 & F_1 & 1 \end{Bmatrix} (-1)^{J'+I_1+\cancel{F_1}+1} \langle J'\Omega' \| V \| J\Omega\rangle \sqrt{(2F_1+1)(2F_1'+1)}$$

$$\cdot \begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & 1 \end{Bmatrix} \sqrt{I_2(I_2+1)(2I_2+1)} \quad \langle J'\Omega' \| V \| J\Omega\rangle \quad ✓$$

$$= (-1)^{2F_1 + I_1 + I_2 + F_2 + J' + 1} \begin{Bmatrix} F_1' & I_2 & F_2 \\ I_2 & F_1 & 1 \end{Bmatrix} \begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & 1 \end{Bmatrix} \sqrt{(2F_1+1)(2F_1'+1)} \sqrt{I_2(I_2+1)(2I_2+1)}$$

$$\cdot \langle J'\Omega' \| V \| J\Omega\rangle \text{ from } (*)$$

(J' is $\frac{1}{2}$ integer)

$$= (-1)^{2F_1 + I_1 + I_2 + F_2 - \Omega'} \sqrt{(2F_1+1)(2F_1'+1)(2J'+1)(2J+1)\, I_2(I_2+1)(2I_2+1)}$$

$$\cdot \begin{Bmatrix} F_1' & I_2 & F_2 \\ I_2 & F_1 & 1 \end{Bmatrix} \begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & 1 \end{Bmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q' & \Omega \end{pmatrix} \langle \Omega' | V_{q'} | \Omega\rangle \quad ✓$$

Quadrupole HFS

$$H_Q = -3\frac{q_0 Q_1}{8I_1(2I_1-1)}\,\vec{n}\,\hat{T}_1\,\vec{n}$$

Note, that in mol. frame

$$H_Q = -\frac{q_0 Q_1}{12 I_1(2I_1-1)}\left(3I_{1z}^2 - I_1(I_1+1)\right)$$

This is 3 times smaller than in Ryzlewicz et.al. (82)

Here $\hat{T}_1 = I^1_i I^1_k + I^1_k I^1_i - \frac{2}{3}\delta_{ik} I_1(I_1+1)$

We can rewrite $\vec{n}\hat{T}\vec{n}$ as (we can add this because T_{ik} is traceless)

$$n_i T_{ik} n_k = T_{ik} n_i n_k = T_{ik}\left(n_i n_k - \frac{1}{3}\delta_{ik}\right) \equiv T_{ik}P_{ik}$$

$$= (-1)^q T^{(2)}_q P^{(2)}_{-q}$$

We already worked out expression for the scalar products of this type;

$$\langle J'\Omega' F_1' F_2' M_2' | T^{(2)}\cdot P^{(2)} | J\Omega F_1 F_2 M_2\rangle$$

$$= \delta_{M_2'M_2}\delta_{F_2'F_2}\delta_{M_1'M_1}\delta_{F_1'F_1}\langle J'\Omega' F_1 M_1 | T^{(2)}\cdot P^{(2)} | J\Omega F_1 M_1\rangle$$

$$= \delta_{M_2'M_2}\delta_{F_2'F_2}\delta_{F_1'F_1}(-1)^{J+I_1+F_1}\begin{Bmatrix} J' & I_1 & F_1 \\ I_1 & J & 2 \end{Bmatrix}\langle J'\Omega' \| P^{(2)} \| J\Omega\rangle \langle I_1 \| T^{(2)} \| I_1\rangle$$

Using (*):

$$\langle J'\Omega' \| P^{(2)} \| J\Omega\rangle = (-1)^{J'-\Omega'}\sqrt{(2J'+1)(2J+1)}\begin{pmatrix} J' & 2 & J \\ -\Omega' & q' & \Omega \end{pmatrix}\langle \Omega' | P^{(2)}_{q'} | \Omega\rangle$$

$\cancel{P^{(2)} = \left(-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}\right)}$

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From Red Notebook

$$\langle I_1 \| T^{(2)} \| I_1\rangle = \sqrt{\frac{2}{3}}\sqrt{I_1(I_1-1)(2I_1+1)(2I_1-1)(2I_1+3)}$$

(This was checked against WE-theorem)

§4 What is P^2_0 ? RdN, p 41:

$$P^2_0 = \frac{\sqrt{6}}{3} = \sqrt{\frac{2}{3}}$$

So

$$\langle \Omega' | P^2_0 | \Omega \rangle = \delta_{\Omega',\Omega} \cdot \sqrt{\frac{2}{3}}$$

Final answer for Quadrupole HFS:

accounts for (-) in the operator H_Q

$$\langle J'\Omega' F_1' F_2' M_2' | H_Q | J \Omega F_1 F_2 M \rangle$$

$$= \delta_{M_2' M_2} \delta_{F_2' F_2} \delta_{F_1' F_1} \delta_{\Omega' \Omega} (-1)^{J+J'+I_1+F_1+\Omega'} \sqrt{(2J'+1)(2J+1)}$$

$$\begin{pmatrix} J' & 2 & J \\ -\Omega & 0 & \Omega \end{pmatrix} \begin{Bmatrix} J' & I_1 & F_1 \\ I_1 & J & 2 \end{Bmatrix} 3 \cdot \frac{2}{3} \sqrt{I_1(I_1-1)(2I_1+1)(2I_1-1)(2I_1+3)} \; \frac{q_0 Q}{8 I_1 (2I_1 - 1)}$$

здесь д.б. (I_1+1)
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$$= \delta_{M_2' M_2} \delta_{F_2' F_2} \delta_{F_1' F_1} \delta_{\Omega' \Omega} (-1)^{J+J'+I_1+F_1+\Omega_1'} \sqrt{\frac{(2J'+1)(2J+1)(I_1-1)(2I_1+1)(2I_1+3)}{I_1(2I_1-1)}}$$

$$\begin{pmatrix} J' & 2 & J \\ -\Omega & 0 & \Omega \end{pmatrix} \begin{Bmatrix} J' & I_1 & F_1 \\ I_1 & J & 2 \end{Bmatrix} \frac{1}{4} q_0 Q$$

Anapole moment in $|J\Omega p F M\rangle$ Basis $(I_1 = 1/2, \Omega = \pm 1/2)$ (Comparison with KLM(91))

$$|J\Omega p F M\rangle = \frac{1}{\sqrt{2}}\left(|J\Omega F M\rangle + p\,\chi_J |J -\Omega F M\rangle\right), \quad \chi_J = (-1)^{J+1/2}$$

$$\langle J' \tfrac{1}{2} + F M | H_p | J \tfrac{1}{2} \cancel{+} F M\rangle = \frac{1}{2}\left(-\chi_J \langle J' \tfrac{1}{2} F M | H_p | J -\tfrac{1}{2} F M\rangle + \chi_{J'} \langle J' -\tfrac{1}{2} F M | H_p | J \tfrac{1}{2} F M\rangle\right)$$

Use Eq. from p. (2):

$$\langle J'\Omega F M | H_p | J\Omega F M\rangle = (-1)^{J+J'+1/2+F-\Omega} \sqrt{\frac{3}{2}} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} J' & J & 1 \\ 1/2 & 1/2 & F \end{Bmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q' & \Omega \end{pmatrix}$$

$$i q' \sqrt{2}\, \Omega\, W_p \varkappa$$

Phase between $\langle 1/2 | H_p | -1/2\rangle$ and $\langle -1/2 | H_p | 1/2\rangle$:

$$(-1)^{\cancel{2\Omega}} (-1)^{J'+J+\cancel{1}} = (-1)^{J'+J} \Longrightarrow \left(\chi_J = (-1)^{J+1/2}\right)$$

$$\langle J' \tfrac{1}{2} + F M | H_p | J \tfrac{1}{2} - F M\rangle$$

$$= (-1)^{J-1/2} \langle J' \tfrac{1}{2} F M | H_p | J -\tfrac{1}{2} F M\rangle$$

$$= (-1)^{J-1/2+J+J'+\cancel{1/2}+F-\cancel{1/2}} \sqrt{\frac{3}{2}} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} J' & J & 1 \\ 1/2 & 1/2 & F \end{Bmatrix} \begin{pmatrix} J' & 1 & J \\ -1/2 & 1 & -1/2 \end{pmatrix} i\,1 \sqrt{2}\, \tfrac{1}{2} W_p \varkappa$$

$$= i\frac{\sqrt{3}}{2} (-1)^{J'+1/2+F} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} J' & J & 1 \\ 1/2 & 1/2 & F \end{Bmatrix} W_p \varkappa \begin{cases} (-1)^{J+1/2} (J+\tfrac{1}{2}) / \sqrt{2J(J+1)(2J+1)}, & J' = J \\ (-1)^{J+1/2} \dfrac{\sqrt{(J-\frac{1}{2})(J+\frac{1}{2})}}{\sqrt{2J(2J-1)(2J+1)}}, & J' = J-1 \end{cases}$$

$$= i\frac{\sqrt{3}}{4\sqrt{2}} (-1)^{J-J'+F} \begin{Bmatrix} J' & J & 1 \\ 1/2 & 1/2 & F \end{Bmatrix} W_p \varkappa \begin{cases} (2J+1)^{3/2} / \sqrt{J(J+1)}, & J' = J \\ \dfrac{\sqrt{(2J-1)(2J+1)}}{\sqrt{J}}, & J' = J-1 \end{cases}$$

This agrees with the paper KLM(91) Eq. (II.2)