EPR Course
NTU
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Lecture 7

Spin Hamiltonian for a typical free radical

$$\mathcal{H}_S = \underbrace{-\vec{\mu}_S \cdot \vec{H} - \vec{\mu}_L \cdot \vec{H}}_{\text{electron Zeeman}} \underbrace{- \sum_N \vec{\mu}_N \cdot \vec{H}}_{\text{nuclear Zeeman}} + \underbrace{\sum_N a_N \vec{I}_N \cdot \vec{S}}_{\substack{\text{isotropic} \\ \text{nuclear hyperfine} \\ \text{interaction}}}$$

$$+ \underbrace{\sum_N \left\{ \frac{(\vec{\mu}_S + \vec{\mu}_L) \cdot \vec{\mu}_N}{r_N^3} - \frac{3\left[(\vec{\mu}_S + \vec{\mu}_L) \cdot \vec{r}_N\right]\left[\vec{r}_N \cdot (\vec{\mu}_S + \vec{\mu}_L)\right]}{r_N^5} \right\}}_{\substack{\text{electron-nuclear dipolar} \\ \text{interaction}}}$$

$$+ \lambda \vec{L} \cdot \vec{S}$$

spin-orbit coupling

$$\mathcal{H}_S \cong + g_S \beta \vec{S} \cdot \vec{H} - \sum_N g_N \beta_N \vec{I}_N \cdot \vec{H} + \sum_N a_N \vec{I}_N \cdot \vec{S}$$

$$+ \sum_N \left[\frac{\vec{\mu}_S \cdot \vec{\mu}_N}{r_N^3} - \frac{3(\vec{\mu}_S \cdot \vec{r}_N)(\vec{r}_N \cdot \vec{\mu}_N)}{r_N^5} \right] + \lambda \vec{L} \cdot \vec{S}$$

$$+ g_L \beta \vec{L} \cdot \vec{H}$$

strong field $= g_S \beta S_z H_0 - \sum_N g_N \beta_N I_z^N H_0 + \sum_N a_N I_z^N S_z + \sum_N \vec{I}_N \cdot \underset{\sim}{T}_N \cdot \vec{S}$

$$+ \lambda \vec{L} \cdot \vec{S} + g_L \beta L_z H_0$$

? = direction of magnetic field

In solution,

$$E_S \cong g_s \beta m_S H_0 - \sum_N g_N \beta_N m_I^N H_0 + \sum_N a_N m_I^N m_S$$

where we have invoked

$$\langle \mu_L \rangle \sim 0$$

$$\langle \vec{\mu}_e \rangle = \langle \vec{\mu}_S + \vec{\mu}_L \rangle = \langle \vec{\mu}_S \rangle$$

and $\underset{\sim}{T}_N = 0$ for free radical in solution

$$\underset{\sim}{T}_N = \left(-g_s g_N \beta \beta_N\right) \cdot$$

$$\begin{pmatrix} \left\langle\left\langle \frac{r_N^2 - 3x_N^2}{r_N^5} \right\rangle\right\rangle & \left\langle -\frac{3x_N y_N}{r_N^5} \right\rangle & \left\langle -\frac{3x_N z_N}{r_N^5} \right\rangle \\ \left\langle -\frac{3x_N y_N}{r_N^5} \right\rangle & \left\langle\left\langle \frac{r_N^2 - 3y_N^2}{r_N^5} \right\rangle\right\rangle & \left\langle -\frac{3y_N z_N}{r_N^5} \right\rangle \\ \left\langle -\frac{3x_N z_N}{r_N^5} \right\rangle & \left\langle -\frac{3y_N z_N}{r_N^5} \right\rangle & \left\langle \frac{r_N^2 - 3z_N^2}{r_N^5} \right\rangle \end{pmatrix}$$

Dipolar coupling tensor

$$\langle L \rangle = 0 \quad \text{and} \quad \langle \lambda L \cdot S \rangle = 0$$

Define nuclear hyperfine interaction tensor $\underset{\sim}{A}_N$

$$\underset{\sim}{A}_N = a + \underset{\sim}{T}_N = \begin{pmatrix} a + T_{\alpha\alpha}^N & T_{\alpha\beta}^N & T_{\alpha\gamma}^N \\ T_{\beta\alpha}^N & a + T_{\beta\beta}^N & T_{\beta\gamma}^N \\ T_{\gamma\alpha}^N & T_{\gamma\beta}^N & a + T_{\gamma\gamma}^N \end{pmatrix}$$

Spin-orbit Interaction & $\underline{\underline{g}}$-Tensor

So far, we have assumed that electron wavefunction for unpaired electron is just a single product of a spatial function and a spin function; i.e., the spatial and spin parts are separable.

$$\underline{\Psi}(\vec{r}, \vec{s}) = \phi(\vec{r}) \cdot \begin{matrix} \alpha \\ \beta \end{matrix} \qquad \text{(one electron only!)}$$

Introduce $\mathcal{H}_{SO} = \lambda \vec{L} \cdot \vec{S}$.

Then spatial or orbital and spin parts will be mixed.

According to perturbation theory in quantum mechanics

$\underline{\Psi}_0(\vec{r}, \vec{s})$ to first order

$$= |\Phi_0^{(1)} \alpha\rangle - \sum_n{}' \frac{\langle n | \lambda \vec{L} \cdot \vec{S} | \phi_0(\vec{r}) \alpha \rangle}{E_n - E_0} |n\rangle$$

($|n\rangle$: excited state wavefunction including spin)

$$= \phi_0(\vec{r}) \alpha + \sum_n{}' c_n^{\alpha} \underline{\Psi}_n(\vec{r}, \vec{s})$$

($\phi_0(\vec{r}) \alpha$: $\underline{\Psi}_0(\vec{r}, \vec{s})$)

$$\text{where } c_n^{\alpha,\beta} = - \frac{\int \underline{\Psi}_n^*(\vec{r}, \vec{s}) \left[\lambda \vec{L} \cdot \vec{S} \right] \phi_0(\vec{r}) \alpha \, d\vec{r} \, d\zeta_s}{E_n - E_0}$$
$$\beta$$

E_0 = energy of $\phi_0(\vec{r}) \alpha$ or $\underline{\Psi}_0(\vec{r}, \alpha)$

E_n = energy of $\underline{\Psi}_n(\vec{r}, \vec{s})$ — could be α or β

With corrected wavefunction, the Zeeman energy is

$$\int \Psi_0^*(\vec{r},\vec{\lambda})\left(g_s\beta\vec{S}\cdot\vec{H}+g_L\beta\vec{L}\cdot\vec{H}\right)\Psi_0(\vec{r},\vec{\lambda})\,d\tau_s\,d\vec{r}$$

$$\vec{\lambda}=\alpha\,\alpha\,\beta$$

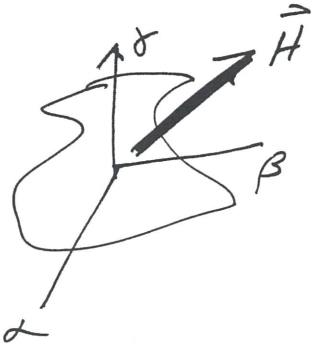
$$=\int \Phi_0^*(\vec{r},\vec{\lambda})\left(g_s\beta\vec{S}\cdot\vec{H}+g_L\beta\vec{L}\cdot\vec{H}\right)\Phi_0(\vec{r},\vec{\lambda})\,d\tau_s\,d\vec{r}$$

$$-2\sum_n{}'\frac{\langle n|\delta\vec{L}\cdot\vec{S}|0\vec{\lambda}\rangle}{E_n-E_0}\int\Phi_0^*(\vec{r},\vec{\lambda})\left[g_s\beta S\cdot\vec{H}+g_L\beta\vec{L}\cdot\vec{H}\right]\Phi_m(\vec{r},\vec{\lambda})\,d\xi\,d\vec{r}$$

$$=\int\Phi_0^*(\vec{r},\vec{\lambda})\,g_s\beta\vec{S}\cdot\vec{H}\,\Phi_0(\vec{r},\vec{\lambda})\,d\tau_S\,dr$$

$$-2\sum_n{}'\frac{\langle n|\delta\vec{L}\cdot\vec{S}|0\rangle\langle 0|g_L\beta\vec{L}\cdot\vec{H}|n\rangle}{E_n-E_0}$$

second term also linear in $\vec{S}\propto\vec{H}$! just like spin zeeman



Pick a set of axes fixed in molecule

1st term ⇒ Regular spin Zeeman ; isotropic !

$$\int\Phi_0(\vec{r},\vec{\lambda})\,g_s\beta\,\vec{S}\cdot\vec{H}\,\Phi_0(\vec{r},\vec{\lambda})\,d\tau_S\,d\vec{r}$$

$$-\int\phi_0^*(\vec{r})\,\phi_0(\vec{r})\,d\vec{r}\cdot\int_\beta^\alpha\left(g_s\beta\vec{S}\cdot\vec{H}\right)_\beta^\alpha d\vec{r}$$

⟶ spin hamiltonian $\quad g_s\beta\sum_\lambda S_\lambda H_\lambda$

2nd term $\Longrightarrow$ correction to spin Zeeman

$$= -2 \sum_n{}' \frac{1}{E_n - E_0} \left[\int \phi_0^{*\alpha}_{\beta} \left(g_L \beta \vec{L} \cdot \vec{H} \right) \phi_n^{\alpha}_{\beta} \, d\vec{r} \, d\tau_S \cdot \int \phi_n^{*\alpha}_{\beta} \left(\Delta \vec{L} \cdot \vec{S} \right) \phi_0^{\alpha}_{\beta} \, d\vec{r} \, d\tau_S \right]$$

$$= -2 \sum_\lambda \sum_\eta \sum_n{}' \left(\frac{1}{E_n - E_0} \right) \left[\int \phi_0^*(\vec{r}) \, g_L \beta L_\lambda H_\lambda \, \phi_n(\vec{r}) \int \beta^{*\alpha} \beta^{\alpha} \, d\tau_S \right.$$

$$\left. \cdot \int \phi_n^*(\vec{r}) \, \Delta L_\eta \, \phi_0(\vec{r}) \, d\vec{r} \cdot \int \beta^{*\alpha} S_\eta \, \beta^{\alpha} \, d\tau_S \right]$$

$$= -2 g_L \beta \Delta \sum_\lambda \sum_\eta H_\lambda S_\eta \left[\sum_n{}' \frac{1}{E_n - E_0} \int \phi_0^*(\vec{r}) L_\lambda \, \phi_n(\vec{r}) \, d\vec{r} \cdot \int \phi_n^*(\vec{r}) \, L_\eta \, \phi_0(\vec{r}) \, d\vec{r} \right]$$

$\int \beta^{*\alpha} S_\eta \, \beta^{\alpha} \, d\tau_S$

$$= \sum_\lambda \sum_\eta H_\lambda S_\eta (\Delta g_{\lambda\eta}) \beta$$

with $\boxed{(\Delta g_{\lambda\eta})\beta = -2 g_L \beta \Delta \sum_n{}' \frac{1}{E_n - E_0} \int \phi_0^*(\vec{r}) L_\lambda \, \phi_n(\vec{r}) \, d\vec{r} \cdot \int \phi_n^*(\vec{r}) \, L_\eta \, \phi_0(\vec{r}) \, d\vec{r}}$

Therefore, after correcting for spin-orbit interaction, effective Zeeman interaction

$$\sum_{\lambda,\eta} H_\lambda S_\eta \left[\delta_{\lambda\eta} \left(g_s \beta \right) + \Delta g_{\lambda\eta} \beta \right]$$

$\delta_{\lambda\eta} = 0$ if $\lambda \neq \eta$

$= 1$ if $\lambda = \eta$

$$= \beta \sum_{\lambda,\eta} H_\lambda S_\eta \left(g_s \delta_{\lambda\eta} + \Delta g_{\lambda\eta} \right)$$

$$\beta (H_x \quad H_\beta \quad H_\gamma) \begin{pmatrix} g_s + \Delta g_{xx} & \Delta g_{x\beta} & \Delta g_{x\gamma} \\ \Delta g_{\beta x} & g_s + \Delta g_{\beta\beta} & \Delta g_{\beta\gamma} \\ \Delta g_{\gamma x} & \Delta g_{\gamma\beta} & \Delta g_{\gamma\gamma} + g_s \end{pmatrix} \begin{pmatrix} S_x \\ S_\beta \\ S_\gamma \end{pmatrix}$$

$=$

Symmetric 3×3 matrix

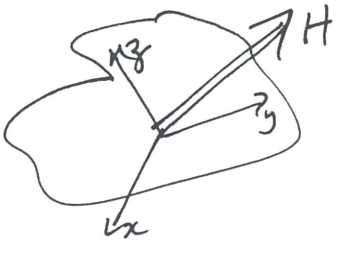
Tensor interaction!

or $$\beta (H_x \quad H_\beta \quad H_\gamma) \begin{pmatrix} g_{xx} & g_{x\beta} & g_{x\gamma} \\ g_{\beta x} & g_{\beta\beta} & g_{\beta\gamma} \\ g_{\gamma x} & g_{\gamma\beta} & g_{\gamma\gamma} \end{pmatrix} \begin{pmatrix} S_x \\ S_\beta \\ S_\gamma \end{pmatrix}$$

or

$$\boxed{\begin{aligned} \mu_x &= g_{xx} S_x + g_{x\beta} S_\beta + g_{x\gamma} S_\gamma \\ \mu_\beta &= g_{\beta x} S_x + g_{\beta\beta} S_\beta + g_{\beta\gamma} S_\gamma \\ \mu_\gamma &= g_{\gamma x} S_x + g_{\gamma\beta} S_\beta + g_{\gamma\gamma} S_\gamma \end{aligned}}$$

Since $\underset{\sim}{g}$ is a symmetric matrix, can always diagonalize by rotating axes!



Zeeman interaction

$$\beta \begin{pmatrix} H_x & H_y & H_z \end{pmatrix} \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$

$$= \beta \begin{pmatrix} H_x & H_y & H_z \end{pmatrix} \begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_{\perp'} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$

Note x, y, z molecular axes.

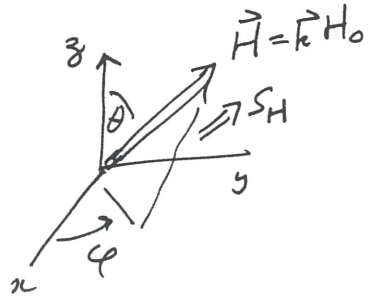
So $g_\perp, g_{\perp'}, g_\parallel$ are properties of radical!

Energy Levels

For illustration purposes, first pick $g_\perp = g_{\perp'} = g_\parallel = g_S$

Then Zeeman interaction

$$= g_S \beta \begin{pmatrix} H_x & H_y & H_z \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$



assume spin is quantized along magnetic field

$$= g_S \beta \begin{pmatrix} H_0 \sin\theta\cos\varphi & H_0 \sin\theta\sin\varphi & H_0 \cos\theta \end{pmatrix} \begin{pmatrix} S_H \sin\theta\cos\varphi \\ S_H \sin\theta\sin\varphi \\ S_H \cos\theta \end{pmatrix}$$

$$= g_S \beta H_0 \left(\sin^2\theta\cos^2\varphi + \sin^2\theta\sin^2\varphi + \cos^2\theta \right) S_H$$

$= g_S \beta H_0 S_H$ and $\langle S_H \rangle = m_S = \pm \frac{1}{2}$

same result as we obtain before!

Now for anisotropic $\underset{\sim}{g}$ tensor

For arbitrary orientations of $\vec{H}$ vis a vis x, y, z

$$\beta \vec{H} \cdot \underset{\sim}{g} \cdot \vec{S} = \beta (H_x \; H_y \; H_z) \underbrace{\begin{pmatrix} g_\perp & & \\ & g_\perp' & \\ & & g_\parallel \end{pmatrix}}_{\text{row vector}} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$

Denote the direction of $\vec{H} \cdot \underset{\sim}{g}$ by unit vector $\hat{h}$ and its magnitude by $H_0 g_{eff}$

Then $\hat{h} H_0 g_{eff} = \hat{H} \cdot \underset{\sim}{g}$

So that $H_0^2 g_{eff}^2 = \hat{H} \cdot \underset{\sim}{g} \cdot \underset{\sim}{g} \cdot \vec{H} = \vec{H} \cdot \underset{\sim}{g}^2 \cdot \vec{H}$

$$= H_0^2 (\sin\theta\cos\phi \;\; \sin\theta\sin\phi \;\; \cos\theta) \cdot \underset{\sim}{g}^2 \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

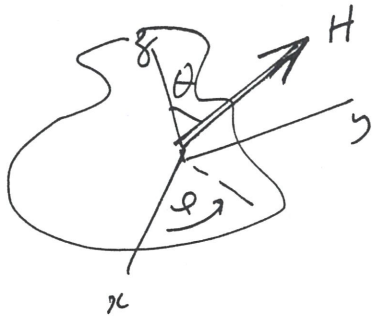
$$= H_0^2 (\sin\theta\cos\phi \;\; \sin\theta\sin\phi \;\; \cos\theta) \begin{pmatrix} g_\perp^2 & 0 & 0 \\ 0 & g_\perp'^2 & 0 \\ 0 & 0 & g_\parallel^2 \end{pmatrix} \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

$$= H_0^2 \left[(\sin^2\theta\cos^2\phi) g_\perp^2 + (\sin^2\theta\sin^2\phi) g_\perp'^2 + \cos^2\theta \, g_\parallel^2 \right]$$

$$\text{or } g_{eff} = \left[g_\perp^2 \sin^2\theta \cos^2\varphi + g_{\perp'}^2 \sin^2\theta \sin^2\varphi + g_{\parallel}^2 \cos^2\theta \right]^{1/2}$$

and EPR transition occurs at

$$\boxed{h\nu = g_{eff}\,\beta H_0 = \left[g_\perp^2 \sin^2\theta \cos^2\varphi + g_{\perp'}^2 \sin^2\theta \sin^2\varphi + g_{\parallel}^2 \cos^2\theta \right]^{1/2} \beta H_0}$$



$g_\perp, g_{\perp'}, g_\parallel$ obtained by EPR of radical in <u>single crystal</u>!

$\Rightarrow$ reorienting crystal about $\vec{H}$! and fitting ν or $H_{resonance}$ to above formula. $\Rightarrow$ locate $\perp, \perp', \parallel$ on x, y, z relative to <u>a b c</u> (crystal axes)

In general, expect 1 set of unique resonances per unit cell.

<u>Spectrum</u>

<u>So</u> for a given ν_0, $H_{resonance}$ will depend on θ and φ.

For simplicity, pick axial case, namely $g_\perp = g_{\perp'}$

For axial case, $H_{resonance}$ depends on θ only!

$$h\nu = \left[g_\perp^2 (\sin^2\theta \cos^2\varphi + \sin^2\theta \sin^2\varphi) + g_\parallel^2 \cos^2\theta \right]^{1/2} \beta H_0$$

$$\text{or } \frac{h\nu_0}{\beta H_{resonance}} = \left[g_\perp^2 \sin^2\theta + g_\parallel^2 \cos^2\theta \right]^{1/2}$$

$$\text{or } \frac{h\nu_0}{\beta\left(g_\perp^2 \sin^2\theta + g_\parallel^2 \cos^2\theta\right)^{1/2}} = H_{resonance}$$

$H_{resonance}$ will sweep from $\frac{h\nu_0}{\beta g_\perp}$ to $\frac{h\nu_0}{\beta g_\parallel}$ as

θ is varied from 0 to 2π! actually from 0 to $\frac{\pi}{2}$.

The above expressions give the resonance fields in single crystal studies, when $\vec{H}$ is oriented at defined orientations with respect to x, y, z (molecular axes) or principal axes of g-tensor.

Powder Spectrum

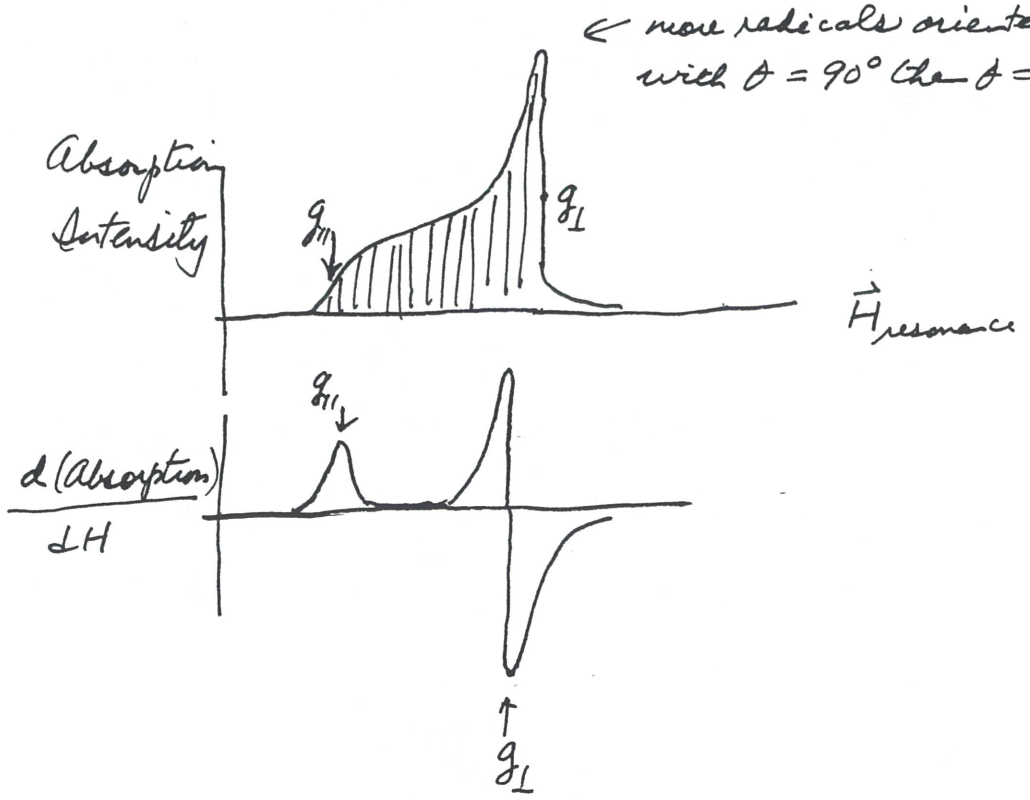
All orientations of x, y, z with respect to $\vec{H}$ are present in a powder sample. So EPR spectrum observed is a superposition of absorption from all possible orientations $\Rightarrow$ so-called powder spectrum.

For our axial case, and $g_\parallel > g_\perp$

Solution Spectrum

Isotropic spectrum with rotational average g given by

$$\frac{1}{3}\left(g_\perp + g_\perp + g_\parallel\right)$$



$g_{\parallel} - g_{\perp}$ depends on Spin-orbit Coupling Constant

Atoms with p electrons (cm^{-1})

B	11	Na	11
C	28	P	299
N	76	S	382
O	151	Cl	586
F	270	Br	2460

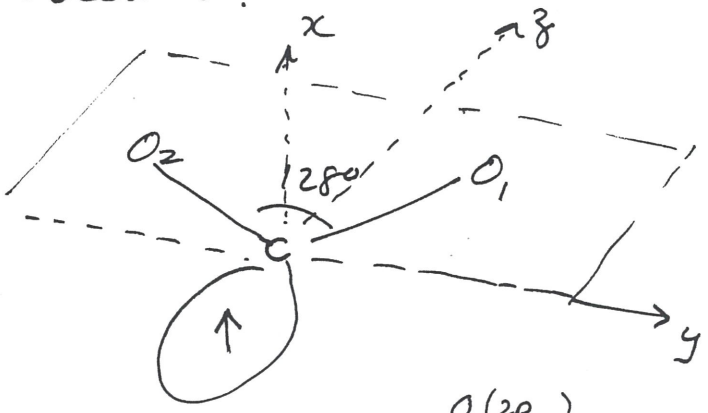
Atoms with d electrons (cm^{-1})

Ti^{3+}	$3d^1$	$\frac{5}{2}$	154	Fe^{2+}	$3d^6$	−410	2
V^{3+}	$3d^2$	1	209	Co^{3+}	$3d^6$	—	2
V^{2+}	$3d^3$	$\frac{3}{2}$	167	Co^{2+}	$3d^7$	−533	$\frac{3}{2}$
Cr^{3+}	$3d^3$		273	Ni^{2+}	$3d^8$	−649	1
Cr^{2+}	$3d^4$	2	230	Cu^{2+}	$3d^9$	−829	$\frac{1}{2}$
Mn^{3+}	$3d^4$	2	352				
Mn^{2+}	$3d^5$	$\frac{5}{2}$	347				
Fe^{3+}	$3d^5$	$\frac{5}{2}$	—				

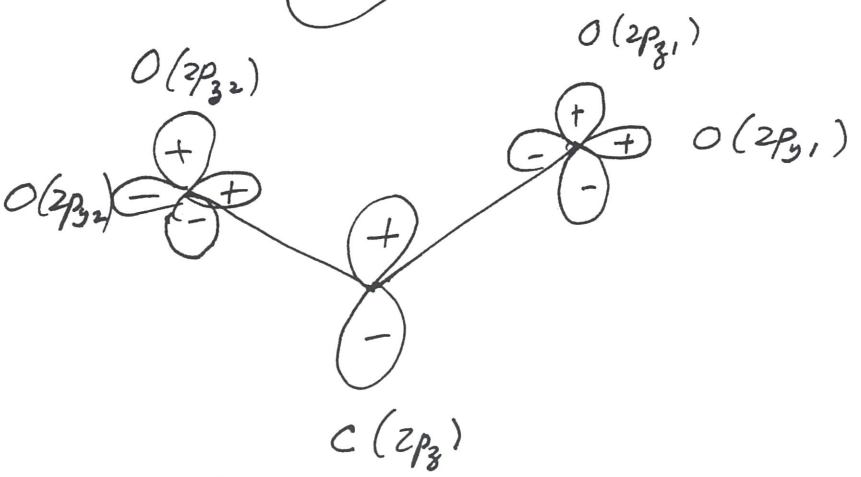
A few examples

The CO_2^- radical

Irradiation of a single crystal of sodium formate, $Na^+HCO_2^-$, with X rays results to loss of a hydrogen atom to form oriented CO_2^- radicals. The g-tensor is found to be anisotropic, and anisotropic hyperfine structure from ^{13}C is also observed.



structure of CO_2^-



definition of atomic orbitals

$$\mathcal{H}_{Spin} = \beta \vec{H} \cdot \underset{\sim}{g} \cdot \vec{S} + \vec{S} \cdot \underset{\sim}{A} \cdot \vec{I}$$

$g_{xx} = 2.0032$

$g_{yy} = 1.9975$

$g_{zz} = 2.0014$

$g_{av} = 2.0006$

$\underset{\sim}{A}$

$\frac{a}{h} = +468\ MHz$

$T_{xx}/h = T_1/h = -32\ MHz$

$T_{yy}/h = T_2/h = -46\ MHz$

$T_{zz}/h = T_3/h = +78\ MHz$

CO_2^- is isoelectronic with NO_2, so is expected to have a bent structure with C_{2v} symmetry.

x ⊥ plane of molecule

z axis bisects the O–C–O bond angle.

x, y, z define principal axes of $\underset{\sim}{g}$. Also $\underset{\sim}{A}$ or $\underset{\sim}{I}$.

Recall $\underset{\sim}{I}$:

$$I_{xx} = \left\langle \frac{r^2 - 3x^2}{r^5} \right\rangle \cdot (-g_s g_N \beta \beta_N)$$

$$I_{yy} = \left\langle \frac{r^2 - 3y^2}{r^5} \right\rangle \cdot (-g_s g_N \beta \beta_N)$$

$$I_{zz} = \left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle \cdot (-g_s g_N \beta \beta_N)$$

g_N, β_N for ^{13}C here

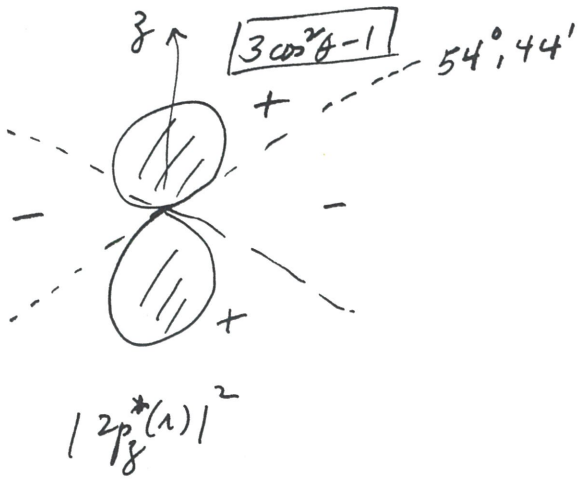
Dipolar Interaction for $2p_z$

$$2p_z = \sqrt{\frac{3}{4\pi}} \cos\theta \frac{f(r)}{r}$$

$$I_{zz} = g_s g_N \beta \beta_N \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} 2p_z * \frac{3z^2 - r^2}{r^5} 2p_z \, d\varphi \, d\theta \, r^2 \, dr$$

$$= g_s g_N \beta \beta_N \cdot \int_0^{\infty} \frac{f(r) f(r)}{r^3} dr \int_0^{\pi} (3\cos^2\theta - 1) \cos^2\theta \sin\theta \, d\theta \cdot \int_0^{2\pi} d\varphi \cdot \left(\frac{3}{4\pi}\right)$$

$$= \left(\frac{3}{4\pi}\right) g_s g_N \beta \beta_N \cdot \left\langle \frac{1}{r^3} \right\rangle (2\pi) \left(\frac{2}{5}\right) = \frac{4}{5} g_s g_N \beta \beta_N \left\langle \frac{1}{r^3} \right\rangle > 0$$



Thus, T_{xx}, T_{yy} < 0 and of the same order of magnitude.

Now $\frac{a}{h} = +468\ MHz$

arises from exchange coupling of $2p_z$ electron with paired 1s and 2s electrons of carbon atom?

$$\underline{\underline{a_{^{13}C}}} \cong Q_C \rho_\pi = 30\text{-}35\ \text{gauss} \cdot \rho_\pi \sim 100\ MHz$$

, so $\frac{a}{h}$ large for $^{13}CO_2$!

MO for unpaired electron:

$$\psi = c_1 C(2s) + c_2 C(2p_z) + c_3 O(2p_{z1} + {}^2p_{z2})$$

$4a_1$

MO symmetric towards reflection about xz + yz planes

$$= 0.374\, C(2s) - 0.832\, C(2p_z) + 0.397\, O(2p_{z1} + {}^2p_{z2})$$

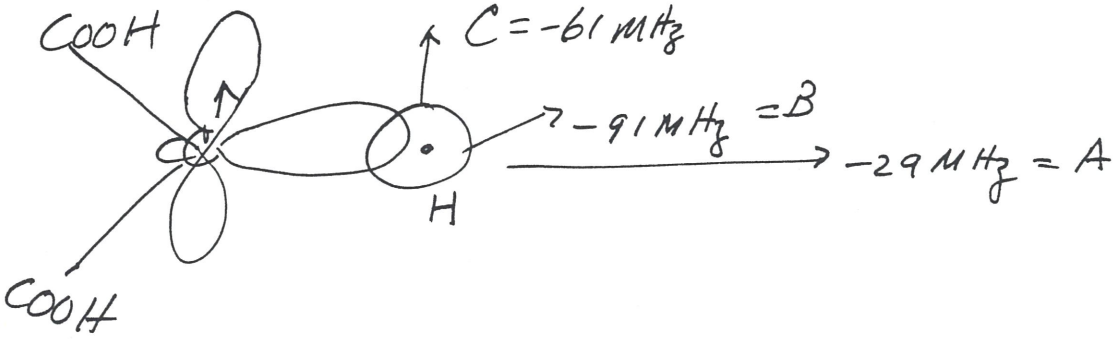
So large isotropic interaction due to unpaired spin density

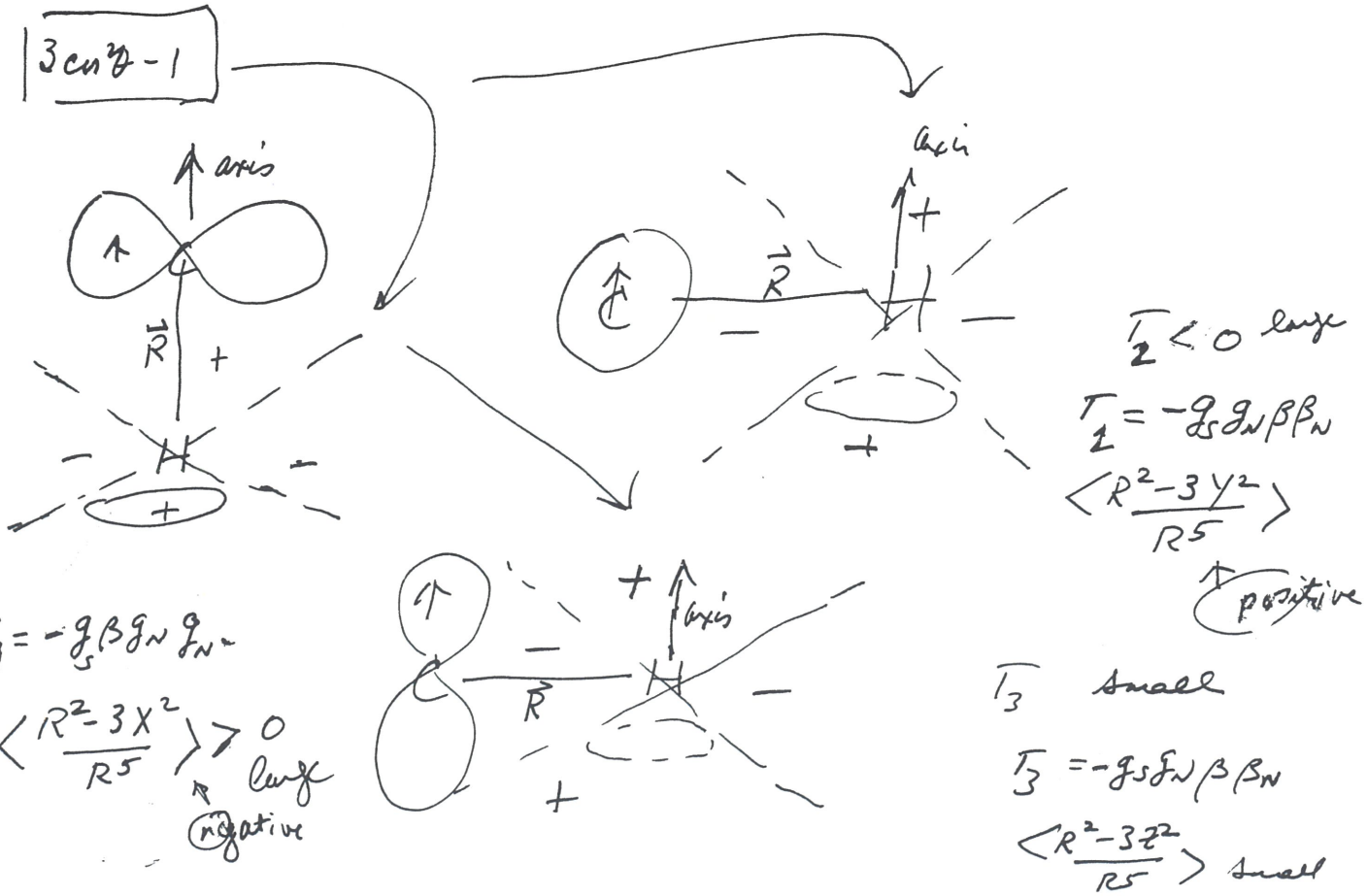
in 2s orbital of carbon. Isotropic splitting for a Hartree 2s atomic orbital is ~ 3300 MHz

$$\text{i.e.,}\quad \frac{a_{^{13}C}}{h} = \frac{4\pi}{3} g_s \beta g_{^{13}C} \beta_N \left|2s(0)\right|^2_{^{13}C}$$

$$c_1^2 \cong \frac{468}{3330} = 0.140 \quad \text{or} \quad c_1 \cong 0.374$$

Malonic acid Radical





$a = -60.3\ MHz$

$T_1 = 31.3\ MHz$

$T_2 = -30.7\ MHz$

$T_3 = -0.7\ MHz$