Electron Paramagnetic Resonance: *g*-values and *g*-tensors

Chem 634

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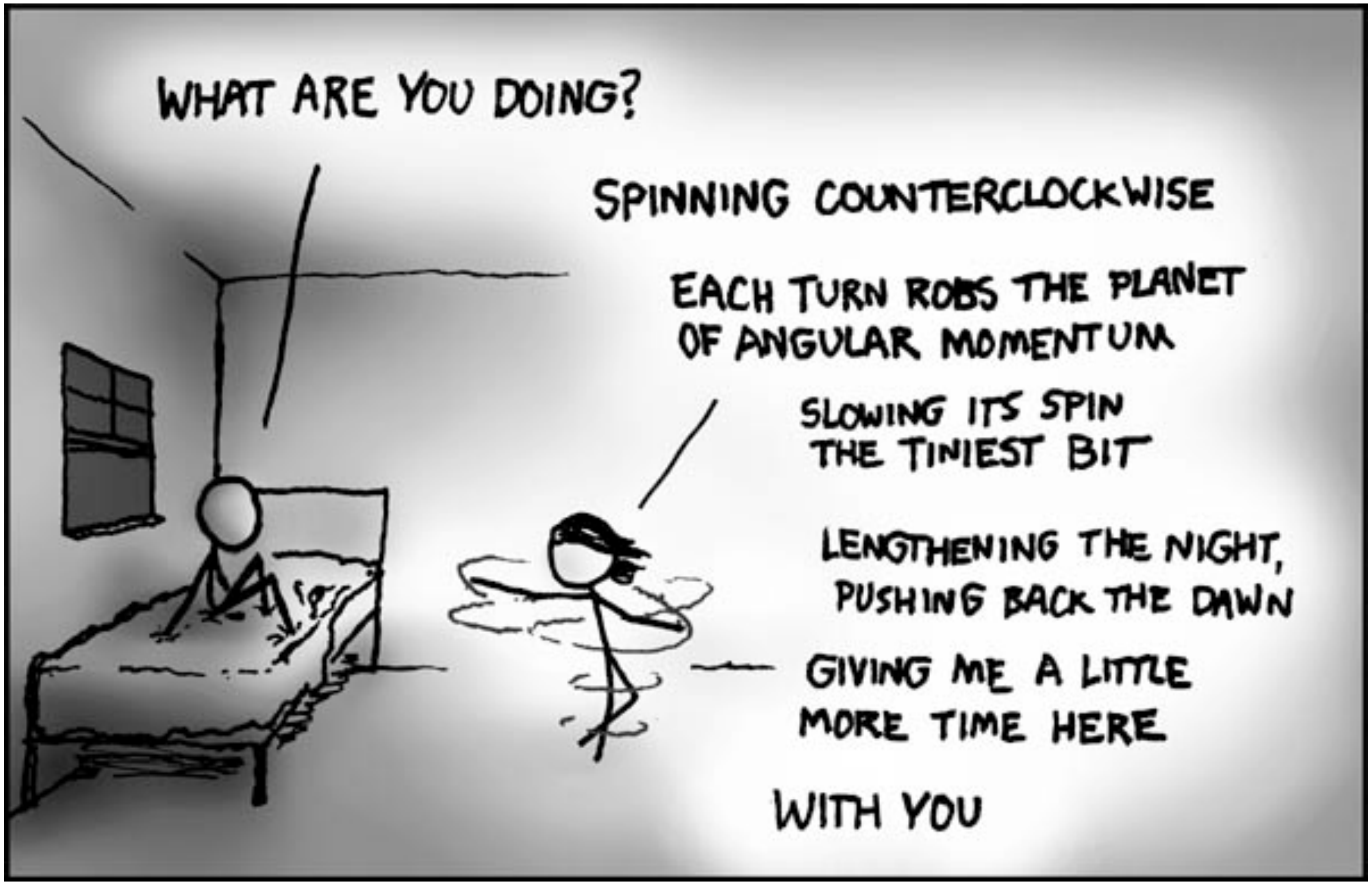
Angular Momentum

The effect of human angular momentum can alter the strength of the Earth's spin angular momentum.

$$\mathcal{H}_{\text{Human}} = \mu_B g_{insane} \mathbf{H} \bullet \mathbf{S}$$



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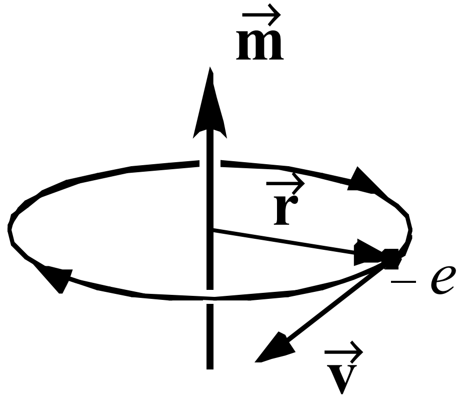
http://xkcd.com/c162.html

Magnetic Moments in Atoms

Classical orbital moment for charge $-e$ in circular orbit of radius r :



$$\vec{\mathbf{m}} = \frac{-e}{2c}(\vec{\mathbf{r}} \times \vec{\mathbf{v}})$$

$$\vec{\mathbf{r}} \times \vec{\mathbf{p}} = \vec{\mathbf{L}}$$

$$\boxed{\vec{\mathbf{m}} = \frac{-e}{2mc}\vec{\mathbf{L}}}$$

Quantum mechanical operator for electronic orbital moment :

$$\mathbf{M}_{orb} = \frac{-e}{2mc}\hbar\mathbf{L} = -\mu_B\mathbf{L}$$

$$\mu_B = \frac{e\hbar}{2mc} \quad \text{Bohr magneton}$$

$$\mu_B = 9.2740092 \times 10^{-21} \text{ erg/G}$$

$$= 9.2740092 \times 10^{-24} \text{ J/T}$$

Operator for electronic spin moment:

$$\mathbf{M}_{spin} = -g_e\mu_B\mathbf{S}$$

$$g_e = 2.0023193043618\text{2}(52)^*$$

The Hamiltonian that accounts for interaction between both the orbital and spin magnetic moments and the applied field is given by:

$$\mathcal{H} = -\mathbf{H} \bullet \left(\mathbf{M}_{orb} + \mathbf{M}_{spin}\right) = \mu_B\mathbf{H} \bullet (\mathbf{L} + g_e\mathbf{S})$$

*most accurately known physical constant: **physics.nist.gov/constants**

Atomic Structure

Most of what you know about atomic configurations and states derive from usual kinetic and potential energy terms of the Hamiltonian:

$$\mathcal{H}_0 = \sum_i h_i + \sum_{i<j} \frac{e^2}{r_{ij}} \; ; \quad \text{where} \quad h_i = \frac{-\hbar^2}{2m}\nabla_i^2 - \frac{Ze}{r_i}$$

and second group of terms are the $e^- - e^-$ repulsions

However, the spin and orbital magnetic moments interact:

Defining **L** and **S** so that they are dimensionless ($\mathbf{L},\mathbf{S} \rightarrow \hbar\mathbf{L},\hbar\mathbf{S}$):

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{Spin-Orbit}}$$

$$\mathcal{H}_{\text{S-O}} = Z\left(\frac{e^2\hbar^2}{2m^2c^2}\right)\left\langle\frac{1}{r^3}\right\rangle \mathbf{L}\bullet\mathbf{S} = \left[Z\left\langle\frac{1}{r^3}\right\rangle\right]\left(2\mu_B^2\right)\mathbf{L}\bullet\mathbf{S}$$

$$2\mu_B{}^2 = 2\left(\frac{e\hbar}{2mc}\right)^2$$

note: in these definitions of **L** and **S**:

$\mathbf{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)Y_{lm}(\theta,\varphi)$; $\mathbf{S}^2 \left|S\right\rangle = s(s+1)\left|S\right\rangle$

(factors of $\hbar^2$ are *not* in the eigenvalues)

How Big is S-O Coupling?

$$\mathcal{H}_{\text{S-O}} = \left[Z \left\langle \frac{1}{r^3} \right\rangle \right] \left(2\mu_B^2 \right) \mathbf{L} \bullet \mathbf{S}$$

For hydrogenic orbitals, $\left\langle \frac{1}{r^3} \right\rangle \sim Z^3$

$$\mathcal{H}_{\text{S-O}} = \left[Z \left\langle \frac{1}{r^3} \right\rangle \right] \left(2\mu_B^2 \right) \mathbf{L} \bullet \mathbf{S} \sim Z^4 \text{ (replace with } Z_{eff} \text{ for many-electron atoms)}$$

For a $2p$, $3d$, or $4f$ hydrogenic orbital: $\left\langle \frac{1}{r^3} \right\rangle = \frac{(2n-3)!}{(2n)!} \left(\frac{2Z_{eff}}{na_0} \right)^3$

See A. F. Orchard, "Magnetochemistry"

(n = principal quantum number)

more generally, for any n, l: $\left\langle \frac{1}{r^3} \right\rangle = \frac{2}{n^3 l(l+1)(2l+1)} \left(\frac{Z_{eff}}{a_0} \right)^3$

These are too small for 3d by about a factor of 2

$$\mathcal{H}_{\text{S-O}} = Z_{eff}^4 \left(0.2438 \text{ cm}^{-1} \right) \mathbf{L} \bullet \mathbf{S} \qquad \text{for } 2p \text{ electrons}$$

$$= Z_{eff}^4 \left(0.0145 \text{ cm}^{-1} \right) \mathbf{L} \bullet \mathbf{S} \qquad \text{for } 3d \text{ electrons}$$

$$= Z_{eff}^4 \left(0.00218 \text{ cm}^{-1} \right) \mathbf{L} \bullet \mathbf{S} \qquad \text{for } 4f \text{ electrons}$$

Z_{eff} for 1st-Row T.M.s

	s_{3d}	Z_{eff}	ζ_{calc}
Sc^{2+}	13.5894	7.41	44 cm^{-1}
Ti^{2+}	13.8587	8.14	64 cm^{-1}
V^{2+}	14.128	8.87	90 cm^{-1}
Cr^{2+}	14.3973	9.6	123 cm^{-1}
Mn^{2+}	14.6666	10.33	165 cm^{-1}
Fe^{2+}	14.9359	11.06	217 cm^{-1}
Co^{2+}	15.2052	11.79	280 cm^{-1}
Ni^{2+}	15.4745	12.53	357 cm^{-1}
Cu^{2+}	15.7438	13.26	448 cm^{-1}

$$s_{3d} = 13.5894 + 0.2693[\mathrm{N(3d)} - 1]$$

$$\zeta_{\mathrm{calc}} = 0.0145\ \mathrm{cm}^{-1} \cdot (Z_{eff})^4$$

Details

$$\mathcal{H}_{\text{S-O}} = \left[Z \left\langle \frac{1}{r^3} \right\rangle \right] \left(2\mu_B^2 \right) \mathbf{L} \bullet \mathbf{S}$$

For a 2p, 3d, or 4f hydrogenic orbital (n = principal quantum number):

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{(2n)!} \left(\frac{2Z}{na_0} \right)^{2n+1} \int_0^\infty \frac{r^{2n-2} e^{-2Zr/na_0}}{r^3} r^2 dr$$

$$x = \frac{2Z}{na_0} r$$

$$r^{2n-3} dr = \left(\frac{na_0}{2Z} \right)^{2n-2} x^{2n-3} dx$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{(2n)!} \left(\frac{2Z}{na_0} \right)^3 \int_0^\infty x^{2n-3} e^{-x} dx$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{(2n-3)!}{(2n)!} \left(\frac{2Z}{na_0} \right)^3$$

$$= \frac{1}{24} \left(\frac{Z}{a_0} \right)^3 \text{ for } 2p; \quad = \frac{1}{405} \left(\frac{Z}{a_0} \right)^3 \text{ for } 3d; \quad = \frac{1}{2688} \left(\frac{Z}{a_0} \right)^3 \text{ for } 4f$$

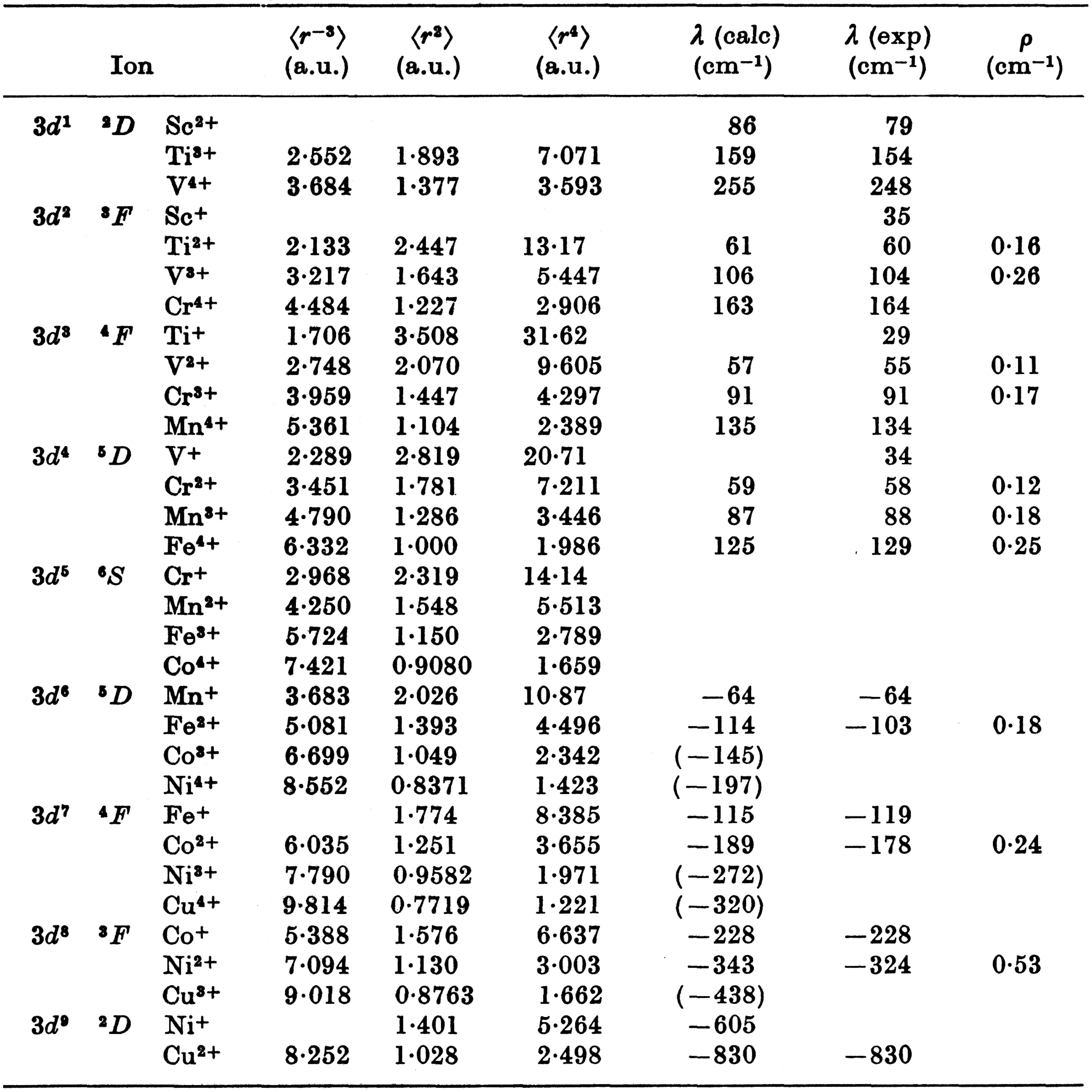
$$\mathcal{H}_{\text{S-O}} = \lambda \mathbf{L} \bullet \mathbf{S}$$

$$\lambda = \pm \frac{\zeta}{2S}$$

$+ < 1/2$-filled

$- > 1/2$-filled

ζ increases from 120 cm^{-1} for Ti^{2+} to 830 cm^{-1} for Cu^{2+} .



Ion			$\langle r^{-3}\rangle$ (a.u.)	$\langle r^{2}\rangle$ (a.u.)	$\langle r^{4}\rangle$ (a.u.)	λ (calc) (cm^{-1})	λ (exp) (cm^{-1})	ρ (cm^{-1})
$3d^1$	^2D	Sc^{2+}				86	79	
		Ti^{3+}	2·552	1·893	7·071	159	154	
		V^{4+}	3·684	1·377	3·593	255	248	
$3d^2$	^3F	Sc^{+}					35	
		Ti^{2+}	2·133	2·447	13·17	61	60	0·16
		V^{3+}	3·217	1·643	5·447	106	104	0·26
		Cr^{4+}	4·484	1·227	2·906	163	164	
$3d^3$	^4F	Ti^{+}	1·706	3·508	31·62		29	
		V^{2+}	2·748	2·070	9·605	57	55	0·11
		Cr^{3+}	3·959	1·447	4·297	91	91	0·17
		Mn^{4+}	5·361	1·104	2·389	135	134	
$3d^4$	^5D	V^{+}	2·289	2·819	20·71		34	
		Cr^{2+}	3·451	1·781	7·211	59	58	0·12
		Mn^{3+}	4·790	1·286	3·446	87	88	0·18
		Fe^{4+}	6·332	1·000	1·986	125	129	0·25
$3d^5$	^6S	Cr^{+}	2·968	2·319	14·14			
		Mn^{2+}	4·250	1·548	5·513			
		Fe^{3+}	5·724	1·150	2·789			
		Co^{4+}	7·421	0·9080	1·659			
$3d^6$	^5D	Mn^{+}	3·683	2·026	10·87	−64	−64	
		Fe^{2+}	5·081	1·393	4·496	−114	−103	0·18
		Co^{3+}	6·699	1·049	2·342	(−145)		
		Ni^{4+}	8·552	0·8371	1·423	(−197)		
$3d^7$	^4F	Fe^{+}		1·774	8·385	−115	−119	
		Co^{2+}	6·035	1·251	3·655	−189	−178	0·24
		Ni^{3+}	7·790	0·9582	1·971	(−272)		
		Cu^{4+}	9·814	0·7719	1·221	(−320)		
$3d^8$	^3F	Co^{+}	5·388	1·576	6·637	−228	−228	
		Ni^{2+}	7·094	1·130	3·003	−343	−324	0·53
		Cu^{3+}	9·018	0·8763	1·662	(−438)		
$3d^9$	^2D	Ni^{+}		1·401	5·264	−605		
		Cu^{2+}	8·252	1·028	2·498	−830	−830	

“Electron Paramagnetic Resonance of Transition Ions”, Abragam & Bleaney

$$\mathcal{H}_{\text{S-O}} = \lambda \mathbf{L} \bullet \mathbf{S}$$

$$\lambda = \pm \frac{\zeta}{2S}$$

$$+ < 1/2\text{-filled}$$

$$- > 1/2\text{-filled}$$

ζ increases from 300 cm^{-1} for Y^{2+} to 1600 cm^{-1} for Pd^{2+} .

		$\langle r^{-3} \rangle$ (a.u.)	$\langle r^{2} \rangle$ (a.u.)	$\langle r^{4} \rangle$ (a.u.)	ζ (exp) (cm^{-1})	ζ (calc) (cm^{-1})
$4d^1$	Y^{2+}	2·034	5·588	59·00	300	312
	Zr^{3+}	3·160	3·857	25·33	500	507
	Nb^{4+}				750	
	Mo^{5+}				1030	
$4d^2$	Zr^{2+}	2·706	4·526	37·86	425	432
	Nb^{3+}	3·913	3·308	18·60	670	644
	Mo^{4+}				950	
$4d^3$	Nb^{2+}	3·414	3·829	26·98	555	560
	Mo^{3+}	4·707	2·905	14·39	800	812
	Tc^{4+}				(1150)	
$4d^4$	Mo^{2+}	4·175	3·319	20·22	695	717
	Tc^{3+}				(990)	
	Ru^{4+}				(1350)	
$4d^5$	Mo^{+}	3·662	3·954	32·98	(630)	
	Tc^{2+}	5·015	2·903	15·41	(850)	
	Ru^{3+}	6·496	2·313	9·17	(1180)	1197
	Rh^{4+}				(1570)	
$4d^6$	Ru^{2+}	5·858	2·628	12·87	1000	1077
	Rh^{3+}	7·447	2·117	7·79	1400	1416
$4d^7$	Rh^{2+}	6·804	2·374	10·60	1220	1291
	Pd^{3+}	8·487	1·939	6·59	1640	1664
$4d^8$	Pd^{2+}	7·814	2·158	8·83	1600	1529
	Ag^{3+}	9·611	1·782	5·61	1930	1940
$4d^9$	Ag^{2+}	8·905	1·972	7·41	1840	1794

“Electron Paramagnetic Resonance of Transition Ions”, Abragam & Bleaney

Spin-Orbit Energies; Atoms

- For atoms and most of the lanthanides, the magnetic properties are fundamentally derived from the lowest J state, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and $J = L + S, L + S - 1, \ldots, |L - S|$. The spin-orbit energies of J states that are derived from a single Russell-Saunders term, ${}^{2S+1}L$, are given by the Landé interval formula:

$$\lambda \mathbf{L} \bullet \mathbf{S} \Psi(J; L, S) = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\Psi(J; L, S)$$

where $\lambda = \pm\zeta/2S$, + for < half-filled shell, – for > half-filled shell,

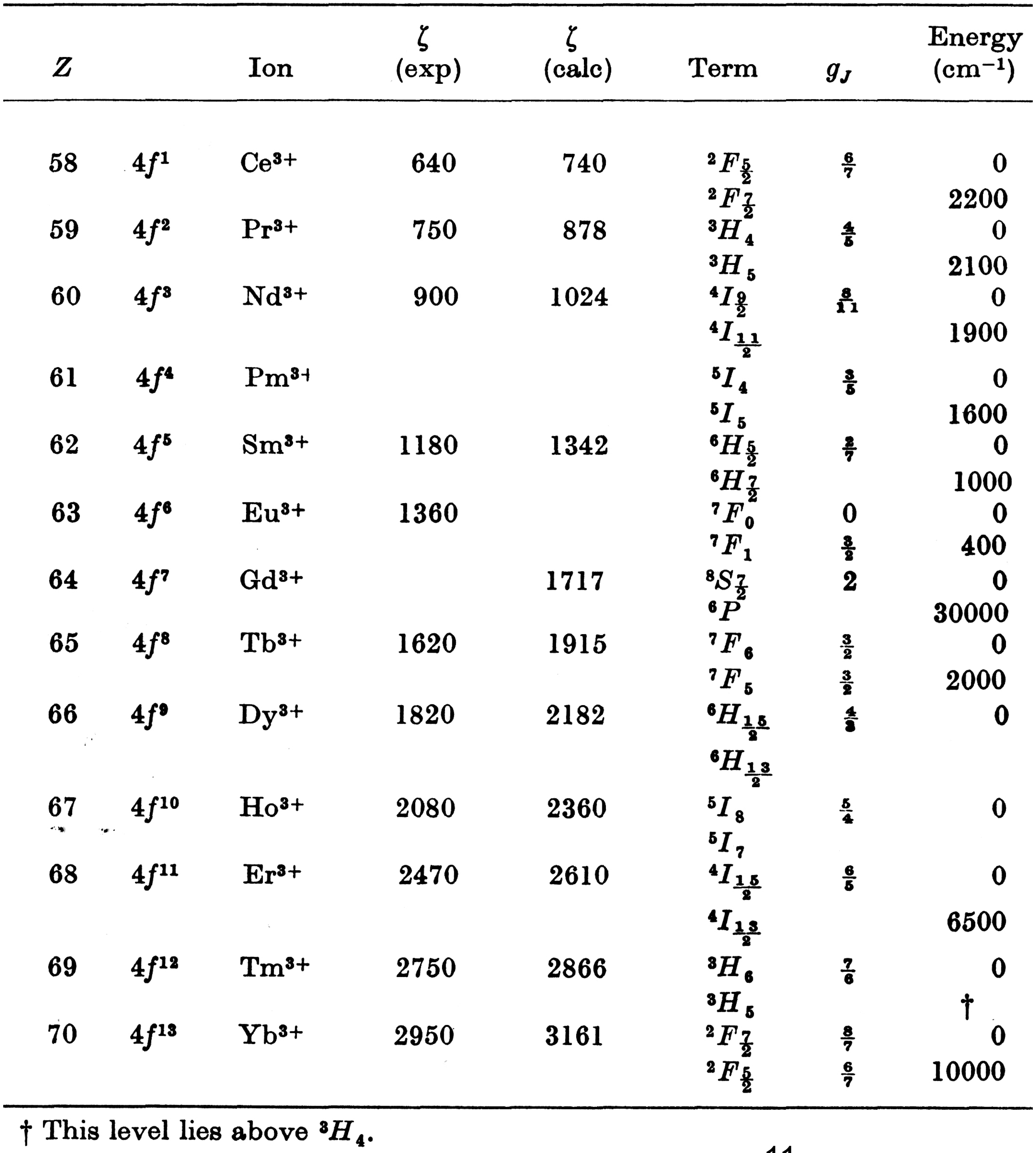
$$\mathcal{H}_{\text{S-O}} = \lambda \mathbf{L} \bullet \mathbf{S}$$

$$\lambda = \pm \frac{\zeta}{2S}$$

$$+ < 1/2\text{-filled}$$

$$- > 1/2\text{-filled}$$

ζ increases from 640 cm^{-1} for Ce^{3+} to 2950 cm^{-1} for Tb^{3+}.



Z		Ion	ζ (exp)	ζ (calc)	Term	g_J	Energy (cm^{-1})
58	$4f^1$	Ce^{3+}	640	740	$^2F_{\frac{5}{2}}$	$\frac{6}{7}$	0
					$^2F_{\frac{7}{2}}$		2200
59	$4f^2$	Pr^{3+}	750	878	$^3H_4$	$\frac{4}{5}$	0
					$^3H_5$		2100
60	$4f^3$	Nd^{3+}	900	1024	$^4I_{\frac{9}{2}}$	$\frac{8}{11}$	0
					$^4I_{\frac{11}{2}}$		1900
61	$4f^4$	Pm^{3+}			$^5I_4$	$\frac{3}{5}$	0
					$^5I_5$		1600
62	$4f^5$	Sm^{3+}	1180	1342	$^6H_{\frac{5}{2}}$	$\frac{2}{7}$	0
					$^6H_{\frac{7}{2}}$		1000
63	$4f^6$	Eu^{3+}	1360		$^7F_0$	0	0
					$^7F_1$	$\frac{3}{2}$	400
64	$4f^7$	Gd^{3+}		1717	$^8S_{\frac{7}{2}}$	2	0
					^6P		30000
65	$4f^8$	Tb^{3+}	1620	1915	$^7F_6$	$\frac{3}{2}$	0
					$^7F_5$	$\frac{3}{2}$	2000
66	$4f^9$	Dy^{3+}	1820	2182	$^6H_{\frac{15}{2}}$	$\frac{4}{3}$	0
					$^6H_{\frac{13}{2}}$		
67	$4f^{10}$	Ho^{3+}	2080	2360	$^5I_8$	$\frac{5}{4}$	0
					$^5I_7$		
68	$4f^{11}$	Er^{3+}	2470	2610	$^4I_{\frac{15}{2}}$	$\frac{6}{5}$	0
					$^4I_{\frac{13}{2}}$		6500
69	$4f^{12}$	Tm^{3+}	2750	2866	$^3H_6$	$\frac{7}{6}$	0
					$^3H_5$		†
70	$4f^{13}$	Yb^{3+}	2950	3161	$^2F_{\frac{7}{2}}$	$\frac{8}{7}$	0
					$^2F_{\frac{5}{2}}$	$\frac{6}{7}$	10000

† This level lies above $^3H_4$.

“Electron Paramagnetic Resonance of Transition Ions”, Abragam & Bleaney

Landé Interval Rule; Derivation

$$J^2 = \mathbf{J} \bullet \mathbf{J} = \left(\mathbf{L} + \mathbf{S}\right) \bullet \left(\mathbf{L} + \mathbf{S}\right) = L^2 + S^2 + 2\mathbf{L} \bullet \mathbf{S}$$

So, we can rearrange to get a completely general *operator identity*:

$$\mathbf{L} \bullet \mathbf{S} = \tfrac{1}{2}\left(J^2 - L^2 - S^2\right)$$

<u>If we can consider *J*-states derived from a single Russell-Saunders term</u>, then we can assume that all the *J*-states have well-defined values of L and S (i.e., L and S are still good approximate quantum numbers). In that case, we can operate on any one of the *J*-states, $\Psi(J;L,S)$, using the above identity to obtain the basis for the Landé interval rule:

$$\lambda \mathbf{L} \bullet \mathbf{S} \Psi(J;L,S) = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\Psi(J;L,S)$$

where $\lambda = \pm\zeta/2S$, + for < half-filled shell, – for > half-filled shell.

$$E_J^{s.o.} - E_{J-1}^{s.o.} = \lambda J$$

Summary - S.O. Coupling in Atoms

- Neither S nor L are strictly "good quantum numbers" in the presence of S.O. coupling, but J is. Nevertheless, spin-orbit splittings are usually small compared to term splittings, so J-states are usually overwhelmingly derived from a single ${}^{2S+1}L$ term.
- ζ increases from 120 cm^{-1} for Ti^{2+} to 830 cm^{-1} for Cu^{2+} ($3d$), from 300 cm^{-1} for Y^{2+} to 1600 cm^{-1} for Pd^{2+} ($4d$), and from 640 cm^{-1} for Ce^{3+} to 2950 cm^{-1} for Tb^{3+} ($4f$).

Magnetic Moments of Atoms

As we've seen, the Zeeman Hamiltonian has the form:

$$\mathcal{H}_{\text{Zeeman}} = -\mu_B \mathbf{H} \bullet \left(\mathbf{M}_{orb} + \mathbf{M}_{spin} \right) = \mu_B \mathbf{H} \bullet (\mathbf{L} + g_e \mathbf{S})$$

It is customary to express the Zeeman interaction in terms of the *total* angular momentum, J, and to define an effective "g-value", g_J, for this purpose. Of course, the effective Hamiltonian has to give the same results as if we used the true magnetic moment operator, so they are set equal:

$$\mathcal{H}_{\text{Zeeman}} = g_J \mu_B \mathbf{H} \bullet \mathbf{J} \ = \mu_B \mathbf{H} \bullet (\mathbf{L} + g_e \mathbf{S})$$

$\therefore \quad g_J \mathbf{J} = \mathbf{L} + g_e \mathbf{S}$, which is a *definition* of g_J.

If we assume that $g_e = 2$, and again assume that L and S are good quantum numbers, we can derive a formula for g_J:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Derivation

$g_J \mathbf{J} \simeq \mathbf{L} + 2\mathbf{S} = \mathbf{J} + \mathbf{S}$, if we take $g_e = 2$.

dot both sides with **J**: $g_J \mathbf{J} \bullet \mathbf{J} = \mathbf{J} \bullet \left(\mathbf{J} + \mathbf{S} \right)$

$g_J J^2 = J^2 + \mathbf{J} \bullet \mathbf{S} = J^2 + \left(\mathbf{L} + \mathbf{S} \right) \bullet \mathbf{S} = J^2 + S^2 + \mathbf{L} \bullet \mathbf{S}$

Now plug in the operator identity, $\mathbf{L} \bullet \mathbf{S} = \frac{1}{2}\left(J^2 - L^2 - S^2 \right)$, and solve

$\left(g_J - \frac{3}{2} \right) J^2 = \frac{1}{2}\left(S^2 - L^2 \right)$ which is an *operator* identity (if $g_e = 2$).

The operator identity is applied to $\Psi(J; L, S)$ to obtain the formula:

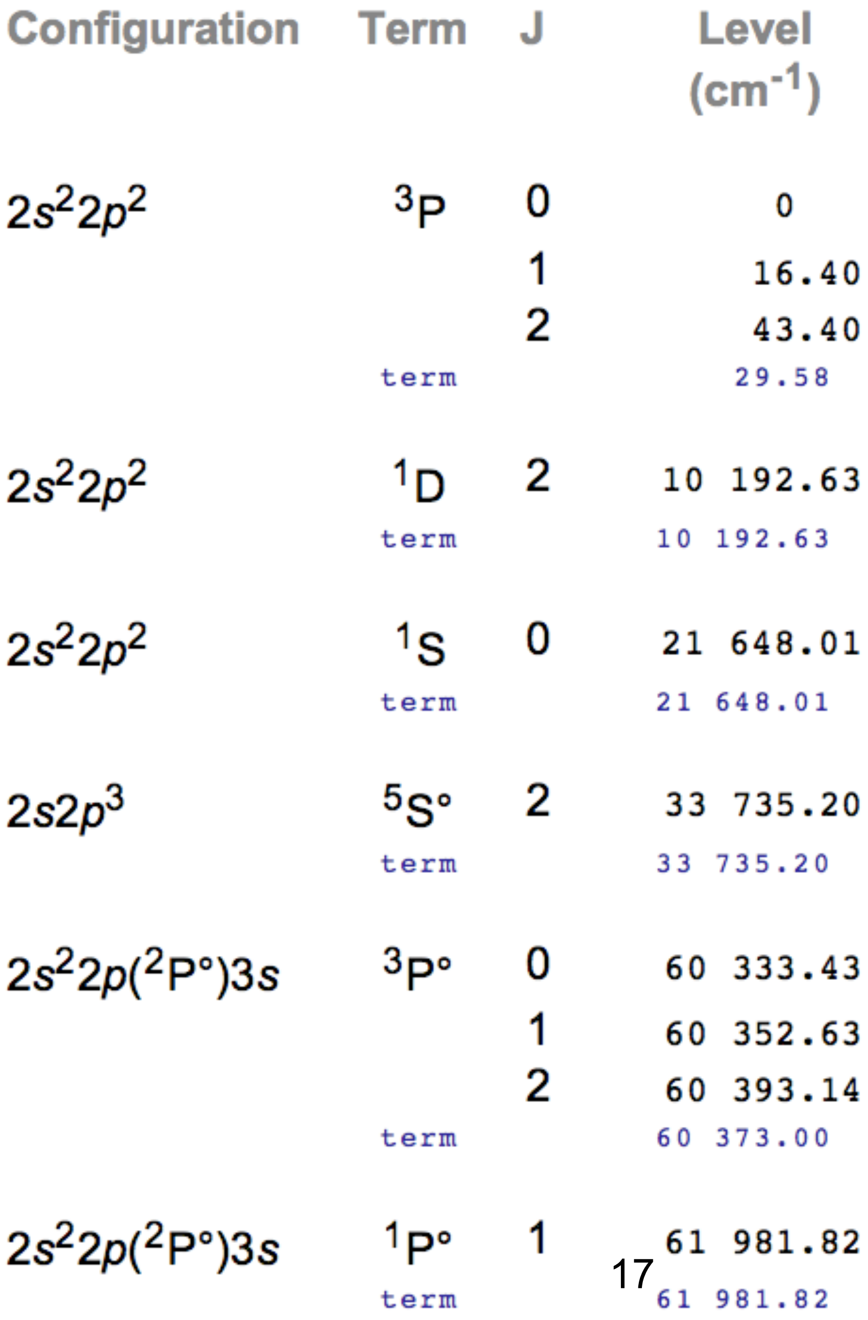
$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Why use a g_J value at all?

- The Zeeman splitting splits each J-state into $2J+1$ levels, each associated with M_J, which takes on the values $-J, -J+1, \ldots, J-1, J$. We therefore want to think about the Zeeman splitting of these $2J+1$ levels.
- Although magnetic moment operator, $(\mathbf{L} + g_e\mathbf{S})$, is not changed by spin-orbit coupling, the Zeeman interaction *is* changed and $\mathbf{J}$ is not equal to $\mathbf{L} + g_e\mathbf{S}$.

Carbon: Atomic Energy Levels

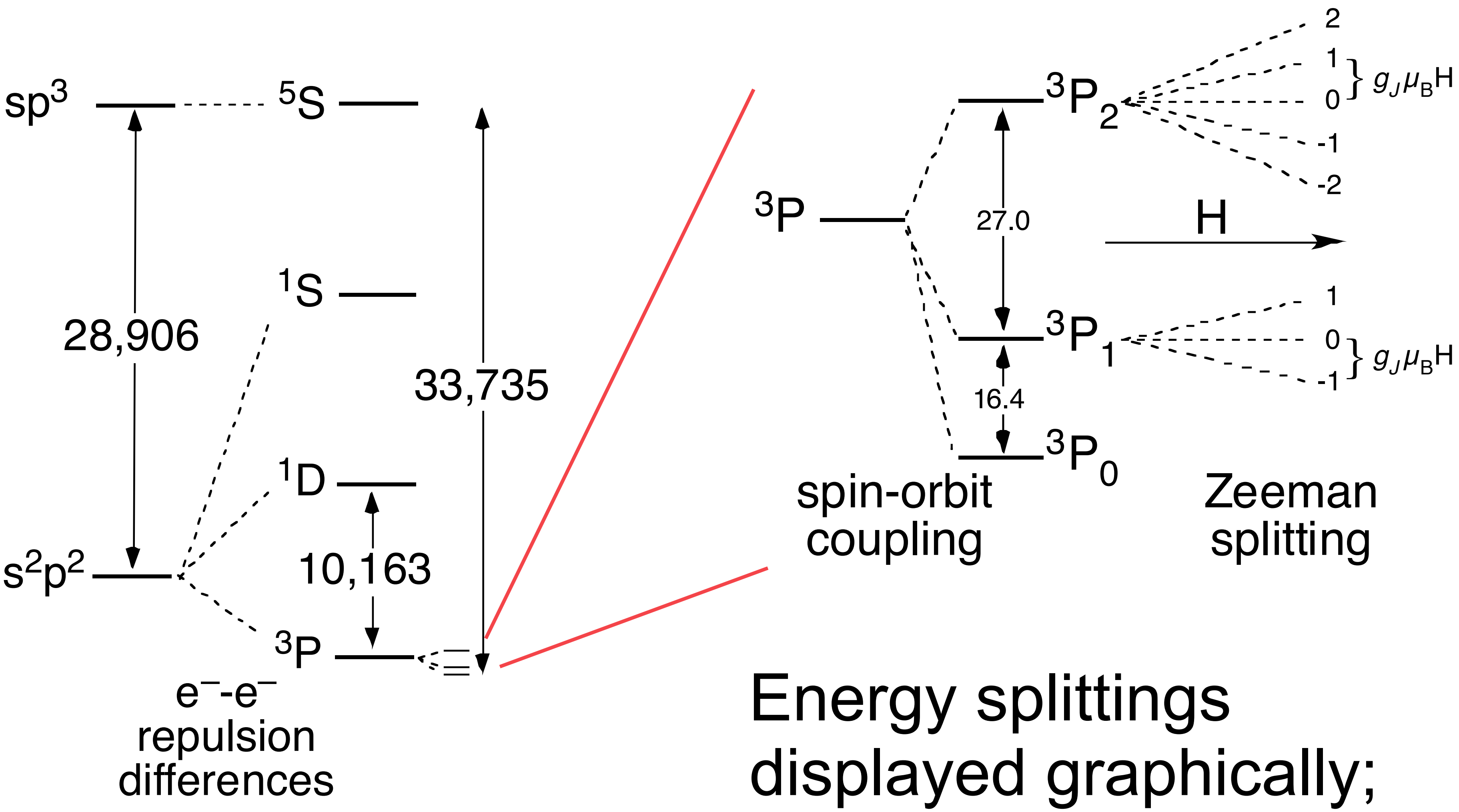
Experimental atomic energy levels are shown, with energies in cm^{-1}.



Configuration	Term	J	Level (cm^{-1})
$2s^2 2p^2$	^{3}P	0	0
		1	16.40
		2	43.40
	term		29.58
$2s^2 2p^2$	^{1}D	2	10 192.63
	term		10 192.63
$2s^2 2p^2$	^{1}S	0	21 648.01
	term		21 648.01
$2s2p^3$	^{5}S°	2	33 735.20
	term		33 735.20
$2s^2 2p(^2$P°$)3s$	^{3}P°	0	60 333.43
		1	60 352.63
		2	60 393.14
	term		60 373.00
$2s^2 2p(^2$P°$)3s$	^{1}P°	1	61 981.82
	term		61 981.82

http://physics.nist.gov/PhysRefData/ASD/index.html

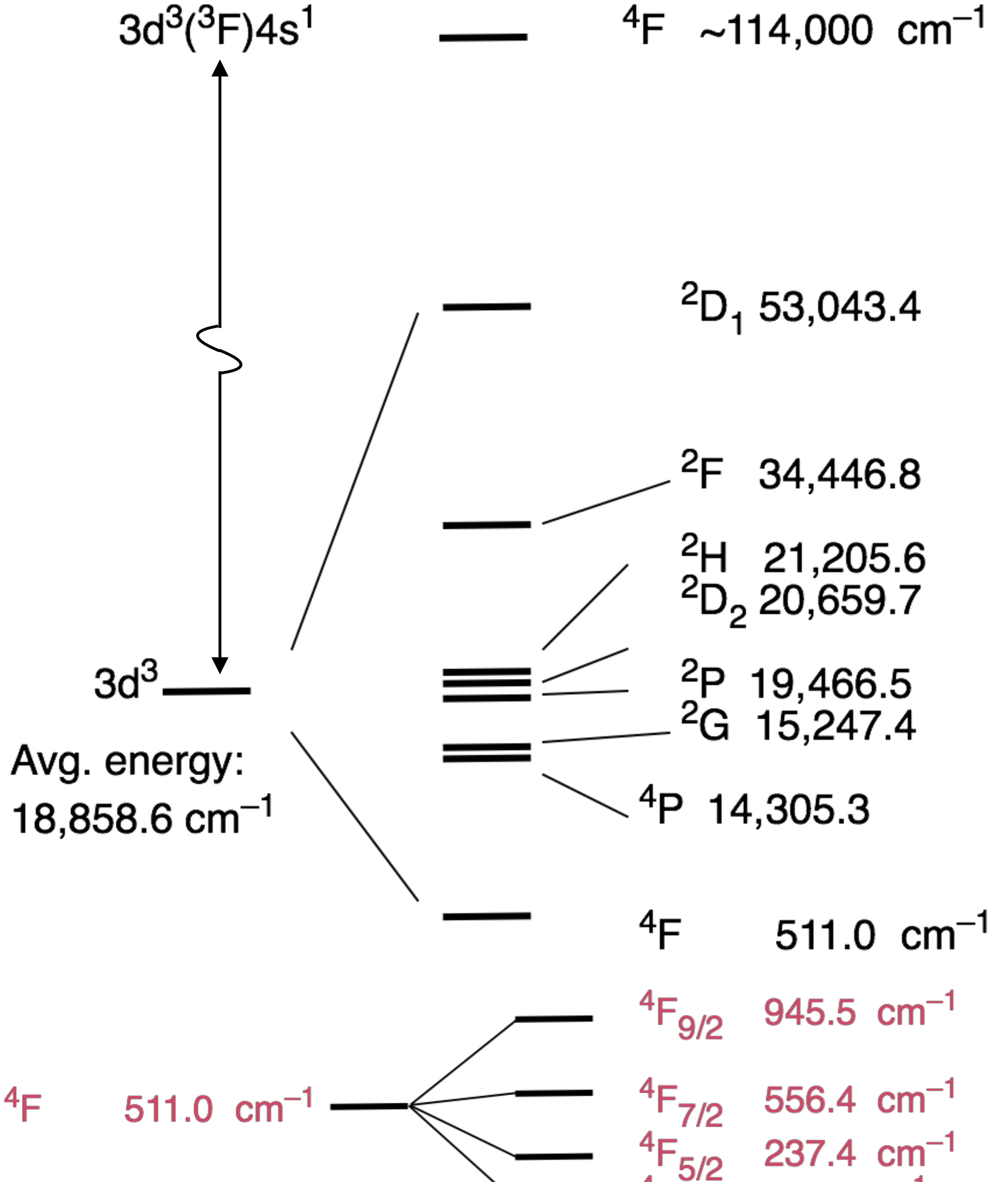
Carbon Atom energies

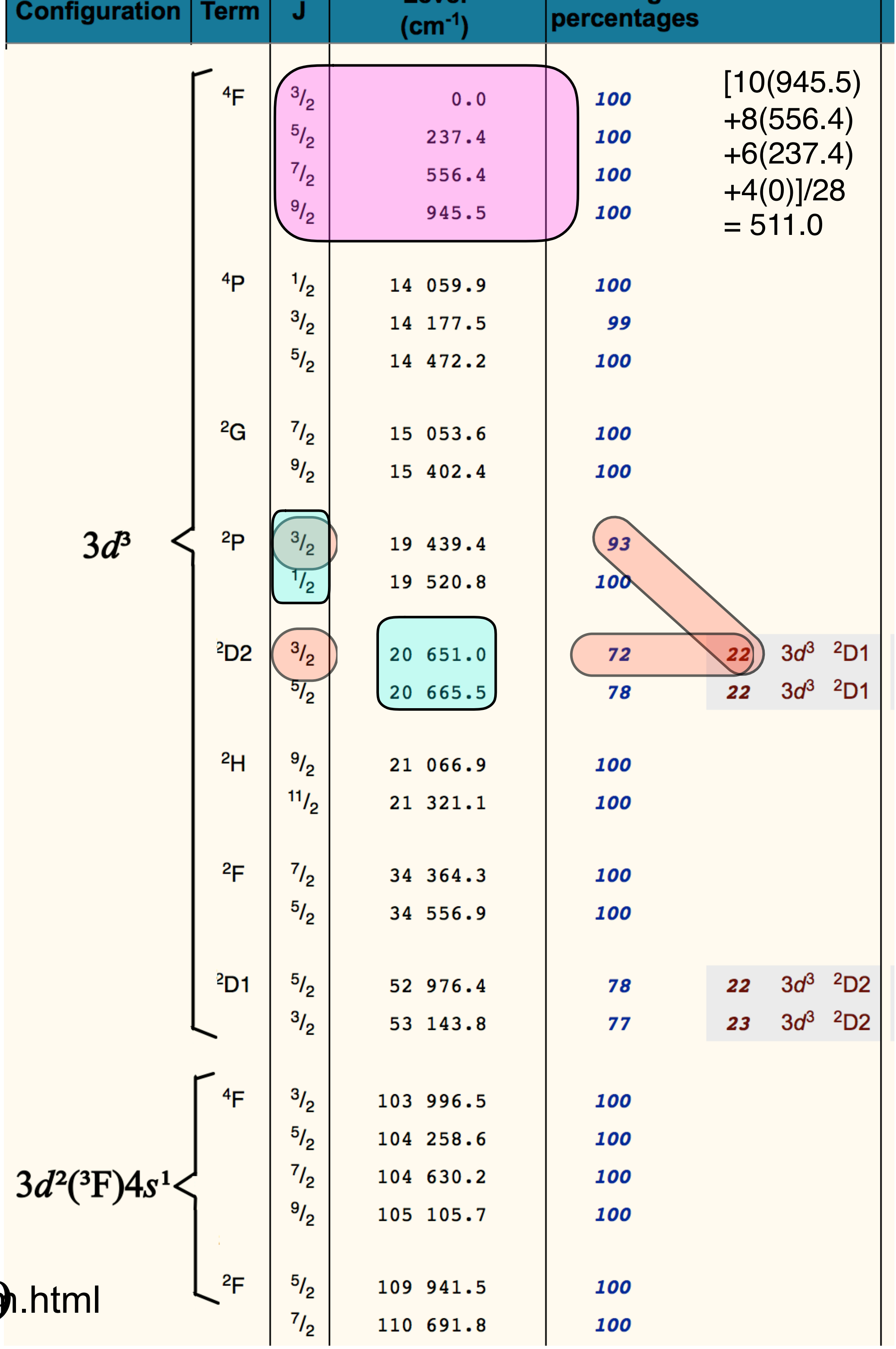


Energy splittings displayed graphically; energies in cm^{-1}

$$\mu_B H = 5.6711\times 10^{-5}\ \text{eV} \sim\ 0.4574\ \text{cm}^{-1},\ \text{at}\ H = 1.0T$$

Cr(III): Electronic Energy Levels





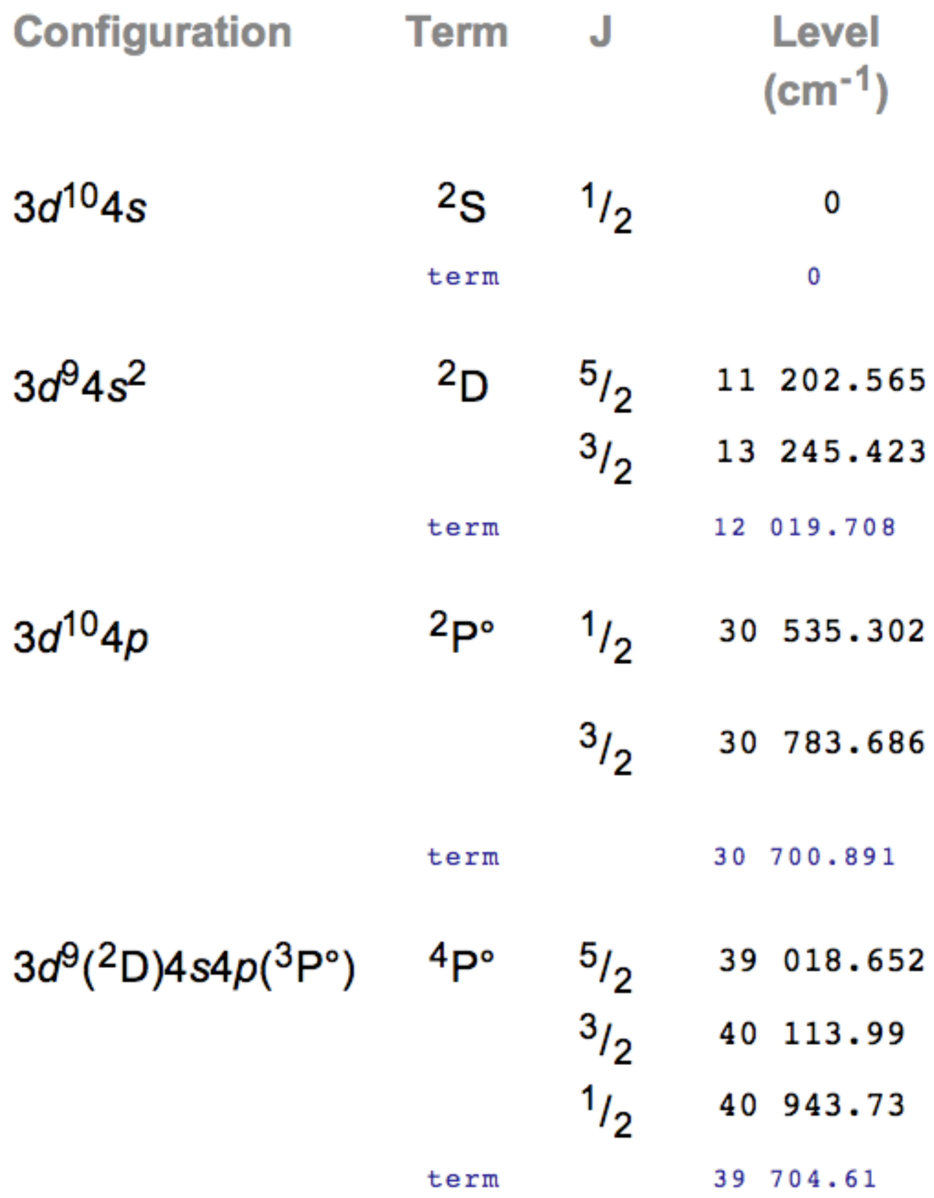
Configuration	Term	J	Level (cm^{-1})	percentages			
$3d^3$	^4F	3/2	0.0	100			
		5/2	237.4	100			
		7/2	556.4	100			
		9/2	945.5	100			
	^4P	1/2	14 059.9	100			
		3/2	14 177.5	99			
		5/2	14 472.2	100			
	^2G	7/2	15 053.6	100			
		9/2	15 402.4	100			
	^2P	3/2	19 439.4	93			
		1/2	19 520.8	100			
	$^2D2$	3/2	20 651.0	72	22	$3d^3$	$^2D1$
		5/2	20 665.5	78	22	$3d^3$	$^2D1$
	^2H	9/2	21 066.9	100			
		11/2	21 321.1	100			
	^2F	7/2	34 364.3	100			
		5/2	34 556.9	100			
	$^2D1$	5/2	52 976.4	78	22	$3d^3$	$^2D2$
		3/2	53 143.8	77	23	$3d^3$	$^2D2$
$3d^2(^3F)4s^1$	^4F	3/2	103 996.5	100			
		5/2	104 258.6	100			
		7/2	104 630.2	100			
		9/2	105 105.7	100			
	^2F	5/2	109 941.5	100			
		7/2	110 691.8	100			

[10(945.5)
+8(556.4)
+6(237.4)
+4(0)]/28
= 511.0

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Copper: Atomic Energy Levels

For TM *atoms*, energy differences between configurations with varying numbers of *n*d and (*n*+1)s electrons can be comparable to state energy differences within a configuration.



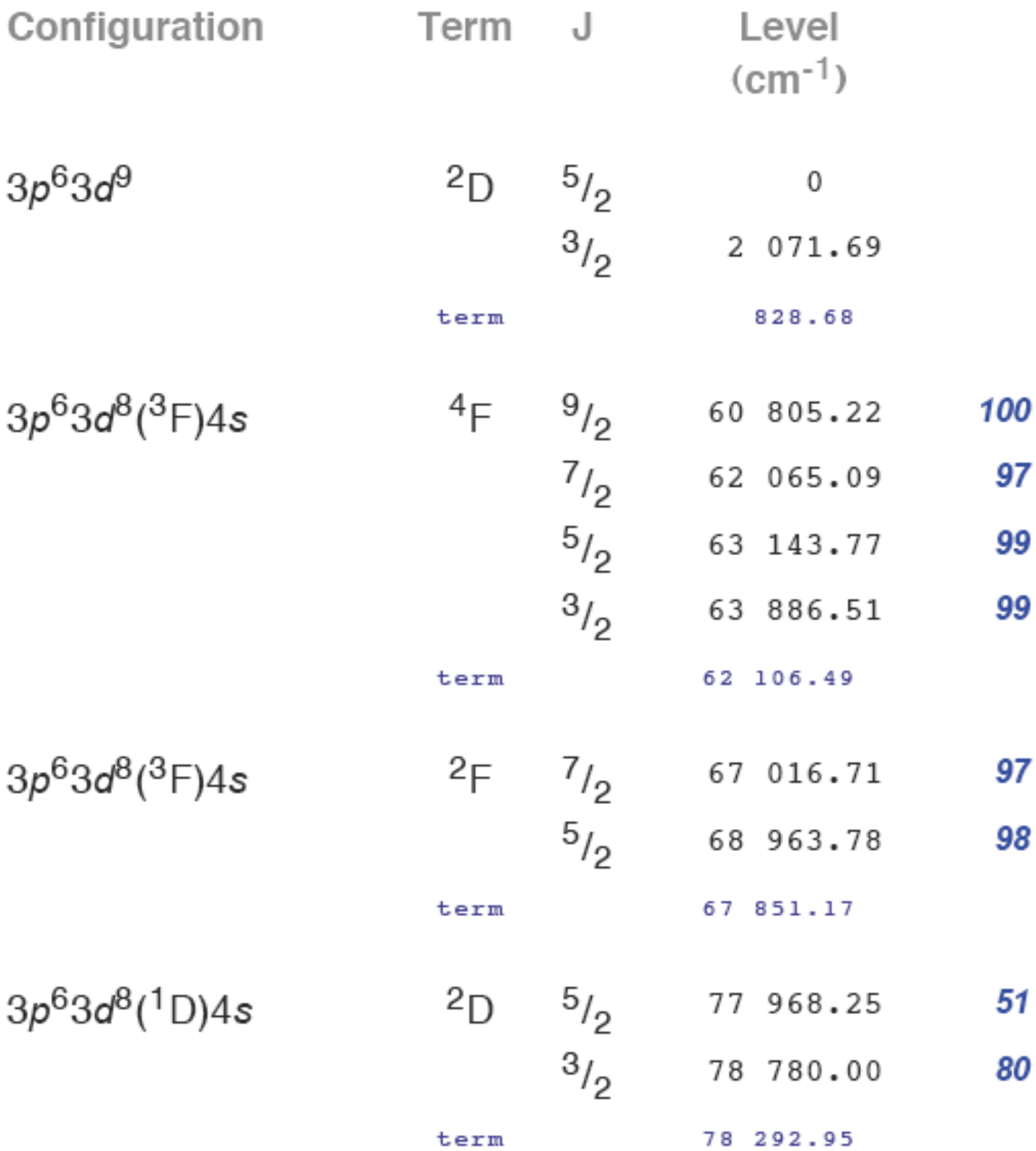
Configuration	Term	J	Level (cm^{-1})
$3d^{10}4s$	^2S	$^1/_2$	0
	term		0
$3d^94s^2$	^2D	$^5/_2$	11 202.565
		$^3/_2$	13 245.423
	term		12 019.708
$3d^{10}4p$	$^2P°$	$^1/_2$	30 535.302
		$^3/_2$	30 783.686
	term		30 700.891
$3d^9(^2D)4s4p(^3P°)$	$^4P°$	$^5/_2$	39 018.652
		$^3/_2$	40 113.99
		$^1/_2$	40 943.73
	term		39 704.61

http://physics.nist.gov/PhysRefData/ASD/index.html

Cu^{2+} ion: Energy Levels

For TM *cations*, energies of configurations with (*n*+1)s electrons are usually high.

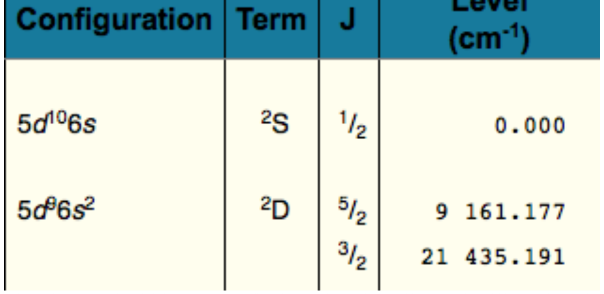
Note the large spin-orbit coupling for Cu, due to an increased Z_{eff} at the end of the T.M. series.



Configuration	Term	J	Level (cm^{-1})	
$3p^6 3d^9$	^2D	$^5/_2$	0	
		$^3/_2$	2 071.69	
	term		828.68	
$3p^6 3d^8(^3F)4s$	^4F	$^9/_2$	60 805.22	100
		$^7/_2$	62 065.09	97
		$^5/_2$	63 143.77	99
		$^3/_2$	63 886.51	99
	term		62 106.49	
$3p^6 3d^8(^3F)4s$	^2F	$^7/_2$	67 016.71	97
		$^5/_2$	68 963.78	98
	term		67 851.17	
$3p^6 3d^8(^1D)4s$	^2D	$^5/_2$	77 968.25	51
		$^3/_2$	78 780.00	80
	term		78 292.95	

http://physics.nist.gov/PhysRefData/ASD/index.html

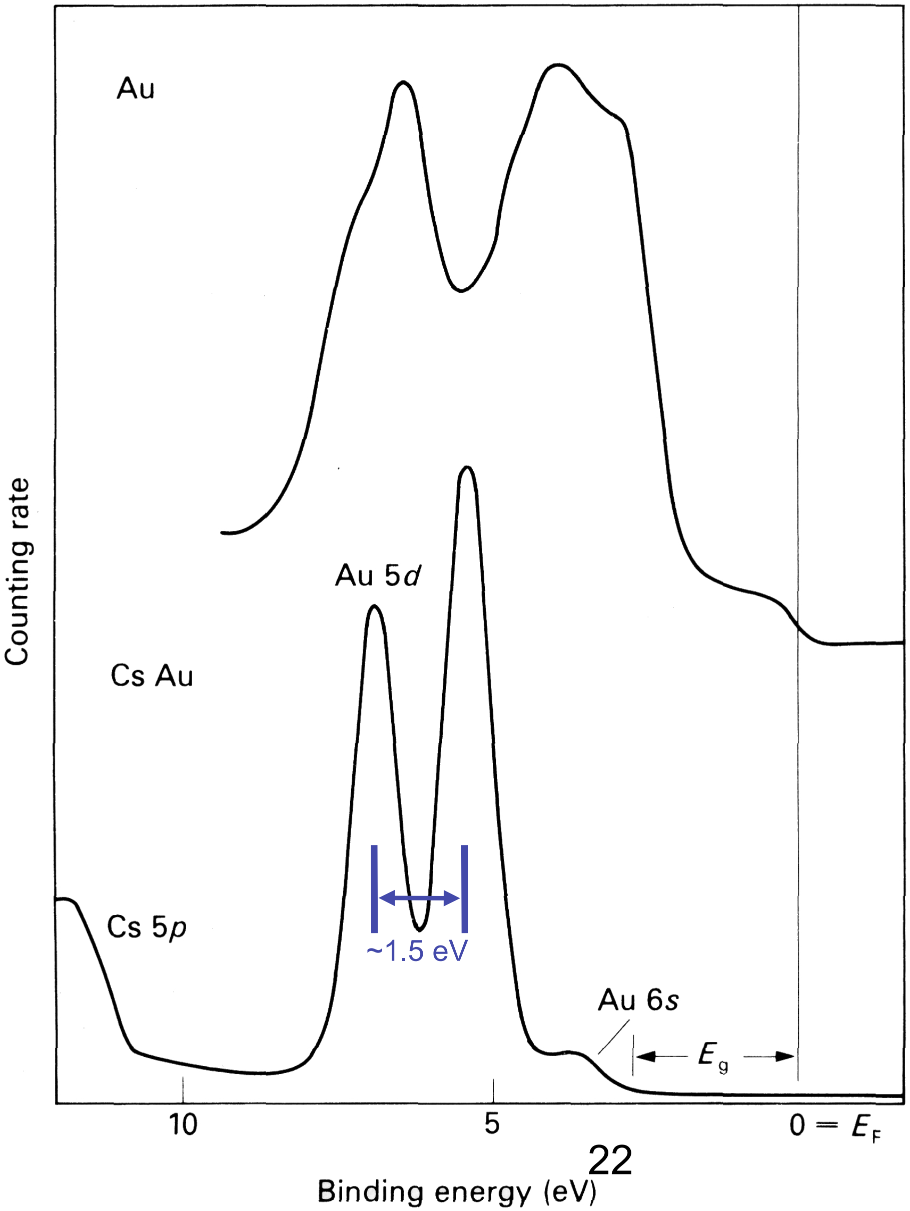
Au 5d electrons (CsAu)



Configuration	Term	J	Level (cm^{-1})
$5d^{10}6s$	^2S	$^1/_2$	0.000
$5d^96s^2$	^2D	$^5/_2$	9 161.177
		$^3/_2$	21 435.191

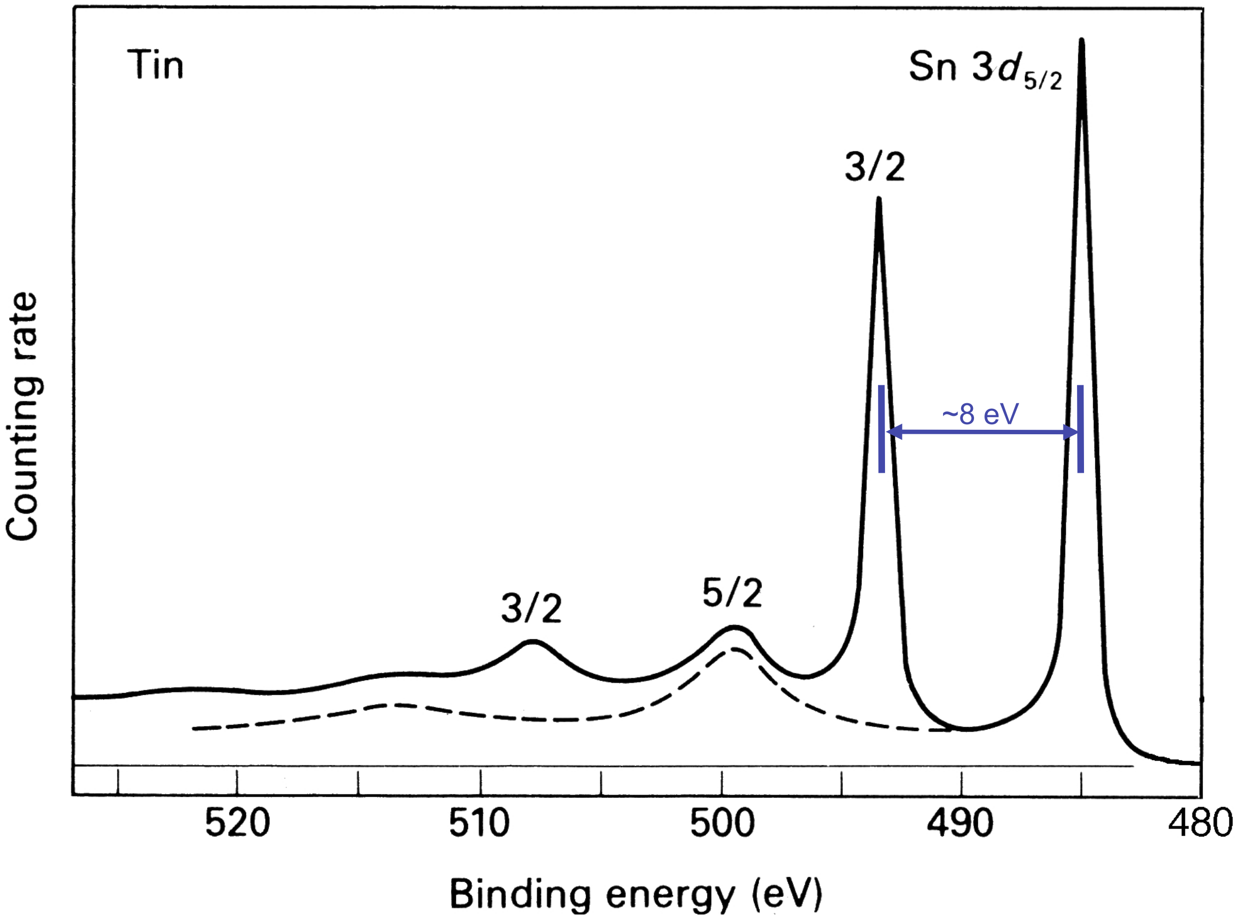
The width of the 5d band in elemental gold is mostly determined by 5d-5d overlap. In CsAu, it is spin-orbit coupling. (The splitting is $^5/_2\lambda$ = $^5/_2\zeta$ = 1.5 eV for the $5d^96s^2$ configuration of the Au atom.)

G. K Wertheim, in “Solid State Chemistry: Techniques”, Cheetham & Day, Eds.



Sn 3d core electrons

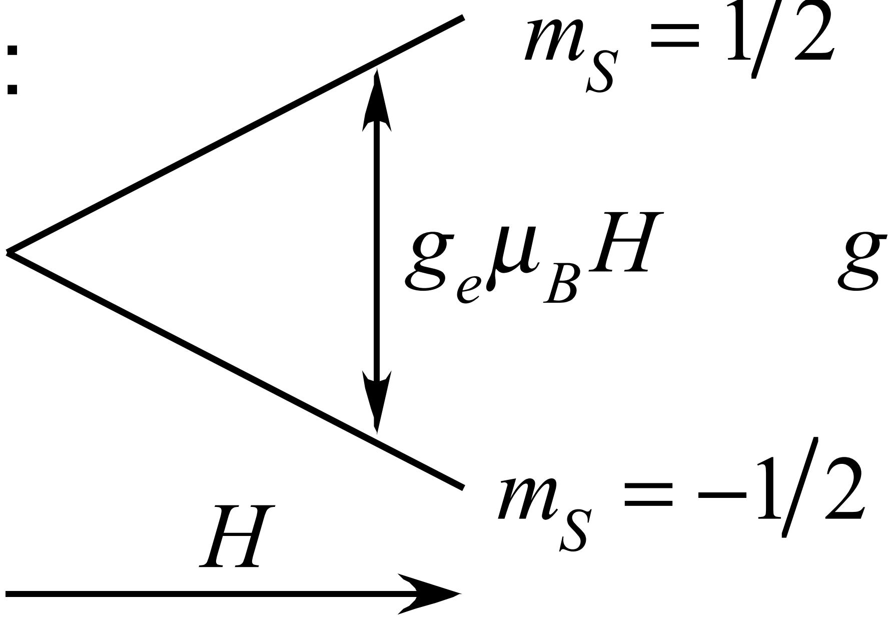
The 3d core electrons in tin experience a large effective nuclear charge (Z_{eff}). Consequently, the spin-orbit coupling is large. (The splitting is $^5/_2\lambda$ = $^5/_2\zeta$ = 8 eV)



XPS for Sn. See G. K Wertheim, in “Solid State Chemistry: Techniques”, Cheetham & Day, Eds.

Zeeman interaction for H-atom

If a hydrogen atom is placed in a magnetic field, $\mathbf{H} = H_z\,\hat{\mathbf{z}}$, the electron's energy will depend on its m_S value. The Zeeman interaction between the applied field and the magnetic moment of the electron is illustrated as:



$$g_e = 2.00232\ldots$$

Nuclear spin neglected!

Zeeman splitting for molecules

- The Zeeman splitting one observes for a molecule can depend on the direction that the applied magnetic field, **H**, makes with the molecular axes

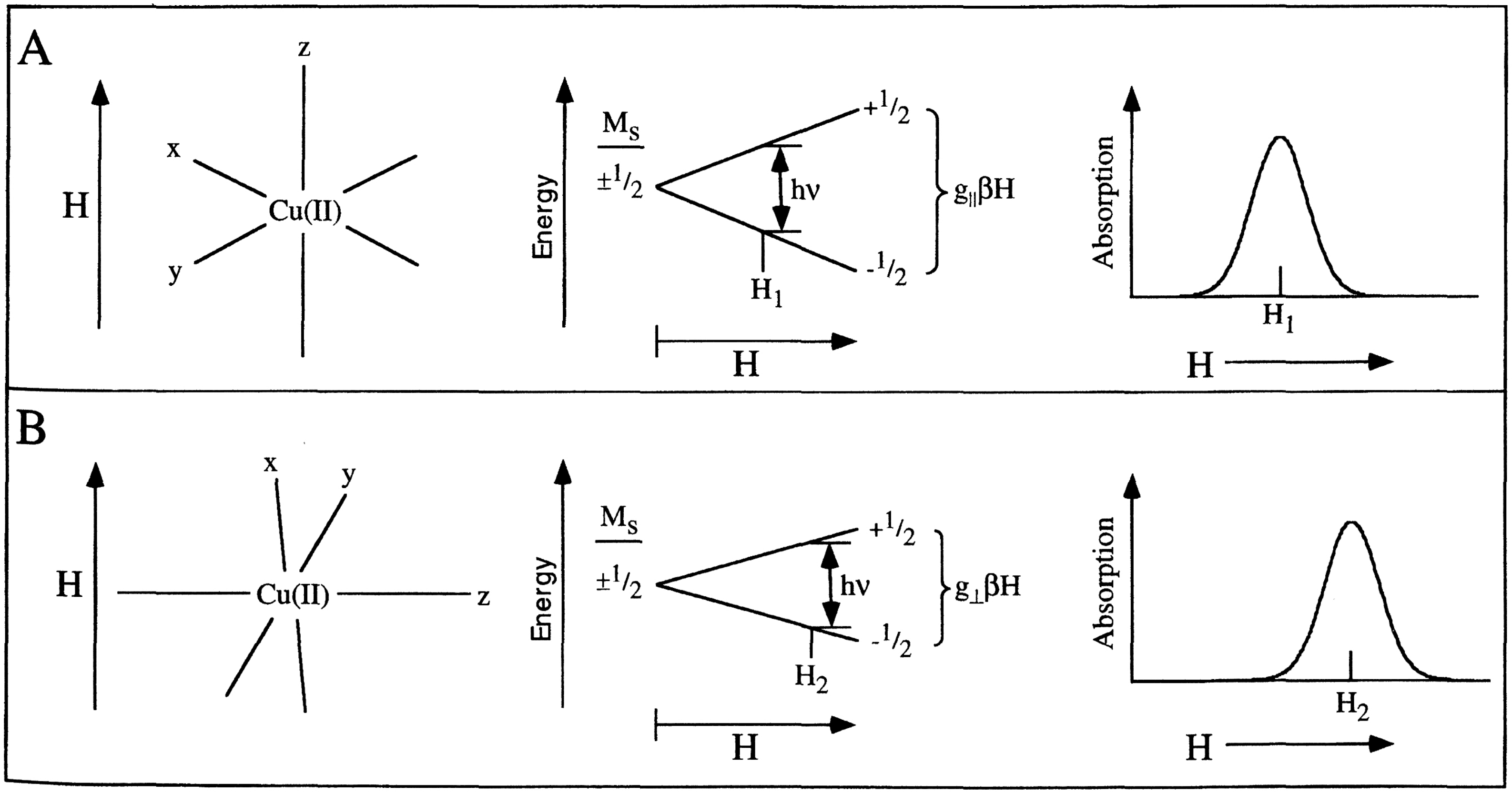


Figure 3. EPR experiment for a tetragonal Cu(II) complex A) with $H \parallel z$ and B) with $H \perp z$. Left: orientation of complex; center: associated energy splitting in a magnetic field; right: EPR absorption spectrum.

Why is the *g*-value directional?

- The spin “coordinate” of an electron doesn’t depend spatial coordinates, so how can the *direction* of the applied field be make any difference in the Zeeman splitting?
- Ans: There is an internal orbital contribution to the magnetic field “felt” by the electron. For molecules with nondegenerate SOMOs, the orbital contribution arises from orbital mixing due to spin-orbit coupling.

The ***g*** Tensor

- To account for the anisotropy of the Zeeman response to an applied magnetic field, an “effective” Hamiltonian using a so-called “***g*** tensor” is used:

$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \mathbf{S} = \mu_B \begin{bmatrix} H_x & H_y & H_z \end{bmatrix} \begin{bmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

The ***g*** Tensor

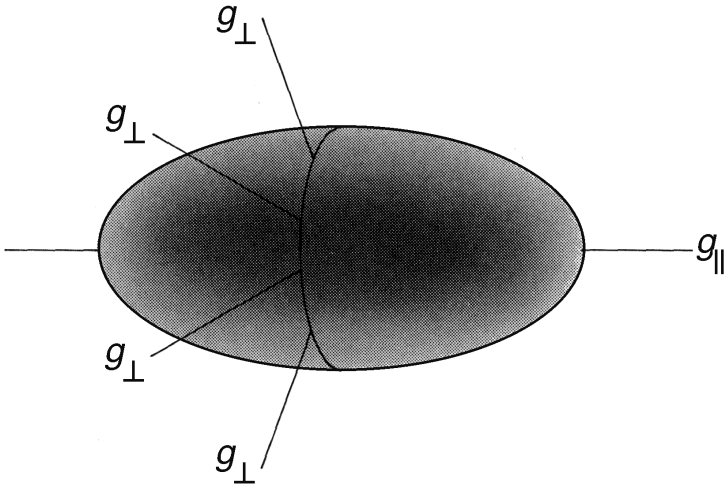
- The g-tensor is symmetric: $g_{ij} = g_{ji}$.
- In the laboratory coordinate system, the *g*-tensor can, in principle and sometimes in practice, be measured for a single crystal by measuring the Zeeman splitting as a function of the angle that the applied field makes with the crystallographic directions:

$$\begin{aligned} g_{eff}^2 &= \left(g^2\right)_{xx} \cos^2\theta_{Hx} + \left(g^2\right)_{yy} \cos^2\theta_{Hy} + \left(g^2\right)_{zz} \cos^2\theta_{Hz} \\ &= \left(g^2\right)_{xx} l_x^2 + \left(g^2\right)_{yy} l_y^2 + \left(g^2\right)_{zz} l_z^2 \end{aligned}$$

The *g* Tensor

- The g-tensor is symmetric: $g_{ij} = g_{ji}$.
- In the right coordinate system, i.e., using the principal axes, the *g*-tensor is diagonalized:

$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \mathbf{S} = \mu_B \begin{bmatrix} H_x & H_y & H_z \end{bmatrix} \begin{bmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$



The *g* Tensor

- While the form just shown is common, it isn't *really* correct. We know that when the electron possesses spin angular momentum only, the ***g*** tensor is isotropic. Therefore, **S** in the previous cannot represent the true spin, so we might add a 'cap' for this *fictitious spin*:

$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \hat{\mathbf{S}} = \mu_B \begin{bmatrix} H_x & H_y & H_z \end{bmatrix} \begin{bmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{bmatrix} \begin{bmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{bmatrix}$$

The *fictitious spin* operators will be defined later!

The True (Zeeman) Hamiltonian

- When an electron has angular momentum, **L**, as well as spin angular momentum, **S**, the true Hamiltonian for the interaction with an applied field is given by:

$$\mathcal{H}_{\text{Zeeman}} = \mu_B(\mathbf{H} \bullet \mathbf{L} + g_e \mathbf{H} \bullet \mathbf{S}) = \mu_B \mathbf{H} \bullet (\mathbf{L} + g_e \mathbf{S})$$

- The ***g*** tensor must be constructed such that the energies obtained with the effective Hamiltonian (containing ***g*** and the “fictitious” spin) are the same as one would get with the true Hamiltonian.

Huh? Can you clarify…?

The effect of the *internal* molecular orbital angular momentum can alter the strength of an external field necessary to produce the Zeeman splitting so that an electron’s spin ‘flips’ at a given excitation frequency.

$$\mathcal{H}_{\text{Zeeman}} = \mu_B \mathbf{H} \bullet (\mathbf{L} + g_e \mathbf{S})$$

The ***g*** tensor must be constructed so that the effect of the *internal* orbital angular momentum is accounted for correctly. As a consequence, the ***g*** tensor contains information about the wavefunction of the molecule in its electronic ground state.

Nondegenerate HOMO case

- Suppose we have a molecule, like a d^9 square-planar complex, with a single unpaired electron with wavefunction $\psi_0(\mathbf{r})$ with either spin α or β. We calculate the Zeeman energy as follows:

$$\text{states:} \quad \left|\psi_0\alpha\right\rangle \text{ or } \left|\psi_0\beta\right\rangle; \quad \text{we take } \mathbf{H} = H_z\hat{\mathbf{z}}$$

$$E_\alpha = \left\langle \psi_0\alpha \right| \mu_B(\mathbf{H}\bullet\mathbf{L} + g_e\mathbf{H}\bullet\mathbf{S}) \left| \psi_0\alpha \right\rangle$$

$$= \mu_B \left\langle \psi_0\alpha \right| H_z L_z + g_e H_z S_z \left| \psi_0\alpha \right\rangle$$

$$= \mu_B H_z \left\langle \psi_0 \right| L_z \left| \psi_0 \right\rangle + g_e \mu_B H_z \left\langle \alpha \right| S_z \left| \alpha \right\rangle$$

$$E_\alpha = \mu_B H_z \left\langle \psi_0 \right| L_z \left| \psi_0 \right\rangle + \frac{1}{2} g_e \mu_B H_z$$

$$\text{likewise, } E_\beta = \mu_B H_z \left\langle \psi_0 \right| L_z \left| \psi_0 \right\rangle - \frac{1}{2} g_e \mu_B H_z$$

$E_\alpha - E_\beta = g_e \mu_B H_z$ but this is just same as the usual Zeeman splitting!

Nondegenerate HOMO case

- Where did we go wrong?

In the presence of S.-O. coupling, $|\psi_0\alpha\rangle$ and $|\psi_0\beta\rangle$ are not correct wavefunctions! Instead, we should use perturbed wavefunctions where S.-O. coupling is taken into account:

$$\left|+\right\rangle = \left|\psi_0\alpha\right\rangle + \sum_n \frac{\left\langle n\middle|\lambda\mathbf{L}\bullet\mathbf{S}\middle|\psi_0\alpha\right\rangle}{E_n - E_0}\left|n\right\rangle$$

$$\lambda = \pm\frac{\zeta}{2S},$$

$$\left|-\right\rangle = \left|\psi_0\beta\right\rangle + \sum_n \frac{\left\langle n\middle|\lambda\mathbf{L}\bullet\mathbf{S}\middle|\psi_0\beta\right\rangle}{E_n - E_0}\left|n\right\rangle$$

In the perturbed wavefunction, excited unperturbed states are "mixed" into ground state by the s-o coupling.

+ for < half-filled shell,

– for > half-filled shell

$$\mathbf{L}\bullet\mathbf{S} = L_zS_z + \tfrac{1}{2}\left(L_+S_- + L_-S_+\right)$$

$$\left|+\right\rangle = \left|\psi_0\alpha\right\rangle - \frac{\zeta}{2S}\left[\sum_n \frac{\left\langle n\middle|L_z\middle|\psi_0\right\rangle}{E_n - E_0}\left|\psi_n\alpha\right\rangle + \sum_n \frac{\left\langle n\middle|L_x + iL_y\middle|\psi_0\right\rangle}{E_n - E_0}\left|\psi_n\beta\right\rangle\right]$$

$$\left|-\right\rangle = \left|\psi_0\beta\right\rangle + \frac{\zeta}{2S}\left[\sum_n \frac{\left\langle n\middle|L_z\middle|\psi_0\right\rangle}{E_n - E_0}\left|\psi_n\beta\right\rangle - \sum_n \frac{\left\langle n\middle|L_x - iL_y\middle|\psi_0\right\rangle}{E_n - E_0}\left|\psi_n\alpha\right\rangle\right]$$

See: Carrington & McLachlan, *Introduction to Magnetic Resonance*

Fictitious Spin Definition

The fictitious spin operators are defined so that they operate on $|+\rangle$ and $|-\rangle$ in exactly the same way the true spin operators, S_x, S_y, S_z, operate on $|\alpha\rangle$ and $|\beta\rangle$.

$$\hat{S}_z\left|+\right\rangle = \frac{1}{2}\left|+\right\rangle, \quad \hat{S}_z\left|-\right\rangle = \frac{1}{2}\left|-\right\rangle$$
$$\hat{S}_+\left|-\right\rangle = \left|+\right\rangle, \quad \hat{S}_-\left|+\right\rangle = \left|-\right\rangle$$
$$\hat{S}_+\left|+\right\rangle = 0, \quad \hat{S}_-\left|-\right\rangle = 0$$

and so on…

like

$$S_z\left|\alpha\right\rangle = \tfrac{1}{2}\left|\alpha\right\rangle, \quad S_z\left|\beta\right\rangle = -\tfrac{1}{2}\left|\beta\right\rangle$$
$$S_+\left|\beta\right\rangle = \left|\alpha\right\rangle, \quad S_-\left|\alpha\right\rangle = \left|\beta\right\rangle$$
$$S_+\left|\alpha\right\rangle = 0, \quad S_-\left|\beta\right\rangle = 0$$

and so on…

When the field is aligned along z ($H_x = H_y = 0$), the effective Hamiltonian (containing the $\mathbf{g}$ tensor) simplifies:

$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \hat{\mathbf{S}} = \mu_B \begin{bmatrix} 0 & 0 & H_z \end{bmatrix} \begin{bmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{bmatrix} \begin{bmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{bmatrix} =$$

$$\mathcal{H}_{eff} = \mu_B H_z \left(g_{zx}\hat{S}_x + g_{zy}\hat{S}_y + g_{zz}\hat{S}_z \right)$$

The Hamiltonians' Matrices Must be Equivalent

If the effective Hamiltonian means anything, in the basis of the "true" wavefunctions, $|+\rangle$ and $|-\rangle$, its matrix must be equal to the Zeeman Hamiltonian in the same basis:

$$\mathcal{H}_{eff} = \mu_B H_z\left(g_{zx}\hat{S}_x + g_{zy}\hat{S}_y + g_{zz}\hat{S}_z\right) \quad ; \; \mathcal{H}_{\text{Zeeman}} = \mu_B(H_z L_z + g_e H_z S_z)$$

$$\begin{bmatrix} \left\langle + \middle| \mathcal{H}_{eff} \middle| + \right\rangle & \left\langle + \middle| \mathcal{H}_{eff} \middle| - \right\rangle \\ \left\langle - \middle| \mathcal{H}_{eff} \middle| + \right\rangle & \left\langle - \middle| \mathcal{H}_{eff} \middle| - \right\rangle \end{bmatrix} = \begin{bmatrix} \left\langle + \middle| \mathcal{H}_{\text{Zeeman}} \middle| + \right\rangle & \left\langle + \middle| \mathcal{H}_{\text{Zeeman}} \middle| - \right\rangle \\ \left\langle - \middle| \mathcal{H}_{\text{Zeeman}} \middle| + \right\rangle & \left\langle - \middle| \mathcal{H}_{\text{Zeeman}} \middle| - \right\rangle \end{bmatrix} \quad \text{or} \quad \left[\mathcal{H}_{eff}\right] = \left[\mathcal{H}_{\text{Zeeman}}\right]$$

Now we evaluate all the matrix elements

$$\left[\mathcal{H}_{eff}\right] = \begin{bmatrix} \tfrac{1}{2}\mu_B H_z g_{zz} & \tfrac{1}{2}\mu_B H_z\left(g_{zx} - ig_{zy}\right) \\ \tfrac{1}{2}\mu_B H_z\left(g_{zx} - ig_{zy}\right) & -\tfrac{1}{2}\mu_B H_z g_{zz} \end{bmatrix} = \mu_B H_z \begin{bmatrix} \tfrac{1}{2} g_{zz} & \tfrac{1}{2}\left(g_{zx} - ig_{zy}\right) \\ \tfrac{1}{2}\left(g_{zx} + ig_{zy}\right) & -\tfrac{1}{2} g_{zz} \end{bmatrix}$$

$$\left[\mathcal{H}_{\text{Zeeman}}\right] = \mu_B H_z \begin{bmatrix} \left\langle + \middle| L_z + g_e S_z \middle| + \right\rangle & \left\langle + \middle| L_z + g_e S_z \middle| - \right\rangle \\ \left\langle - \middle| L_z + g_e S_z \middle| + \right\rangle & \left\langle - \middle| L_z + g_e S_z \middle| - \right\rangle \end{bmatrix}$$

We can now set the matrix elements equal, to obtain

$$g_{zz} = 2\left\langle + \middle| L_z + g_e S_z \middle| + \right\rangle \quad ; \quad g_{zx} + ig_{zy} = 2\left\langle - \middle| L_z + g_e S_z \middle| + \right\rangle$$

Gory Details

We can now set the matrix elements equal, to obtain

$$g_{zz} = 2\left\langle + \middle| L_z + g_e S_z \middle| + \right\rangle \quad ; \quad g_{zx} + i g_{zy} = 2\left\langle - \middle| L_z + g_e S_z \middle| + \right\rangle$$

$$g_{zz} = 2\left\langle + \middle| L_z + g_e S_z \middle| + \right\rangle \quad - \quad \text{evaluate to first order in } \zeta$$

$$\begin{aligned} g_{zz} &= 2\left\langle \psi_0\alpha \middle| \left(L_z + g_e S_z\right) \middle| \psi_0\alpha \right\rangle \\ &-\zeta\left[\sum_n \frac{\left\langle n \middle| L_z \middle| \psi_0 \right\rangle}{E_n - E_0}\left\langle \psi_0\alpha \middle| \left(L_z + g_e S_z\right) \middle| \psi_n\alpha \right\rangle + \sum_n \frac{\left\langle n \middle| L_x + iL_y \middle| \psi_0 \right\rangle}{E_n - E_0}\left\langle \psi_0\alpha \middle| \left(L_z + g_e S_z\right) \middle| \psi_n\beta \right\rangle\right] \\ &-\zeta\left[\sum_n \frac{\left\langle n \middle| L_z \middle| \psi_0 \right\rangle}{E_n - E_0}\left\langle \psi_n\alpha \middle| \left(L_z + g_e S_z\right) \middle| \psi_0\alpha \right\rangle + \sum_n \frac{\left\langle n \middle| L_x + iL_y \middle| \psi_0 \right\rangle}{E_n - E_0}\left\langle \psi_n\beta \middle| \left(L_z + g_e S_z\right) \middle| \psi_0\alpha \right\rangle\right] \end{aligned}$$

$$g_{zz} = g_e - \zeta\left[\sum_n \frac{\left\langle \psi_n \middle| L_z \middle| \psi_0 \right\rangle\left\langle \psi_0 \middle| L_z \middle| \psi_n \right\rangle}{E_n - E_0}\right] - \zeta\left[\sum_n \frac{\left\langle \psi_n \middle| L_z \middle| \psi_0 \right\rangle\left\langle \psi_n \middle| L_z \middle| \psi_0 \right\rangle}{E_n - E_0}\right]$$

$$g_{zz} = g_e - 2\zeta\left[\sum_n \frac{\left\langle \psi_n \middle| L_z \middle| \psi_0 \right\rangle\left\langle \psi_0 \middle| L_z \middle| \psi_n \right\rangle}{E_n - E_0}\right]$$

$$g_{ij} = g_e - 2\zeta\sum_n \frac{\left\langle \psi_0 \middle| L_i \middle| \psi_n \right\rangle\left\langle \psi_n \middle| L_j \middle| \psi_0 \right\rangle}{E_n - E_0}$$

Interpreting *g*-values

$$g_{ij} = g_e - 2\zeta \sum_n \frac{\langle \psi_0 | L_i | \psi_n \rangle \langle \psi_n | L_j | \psi_0 \rangle}{E_n - E_0}$$

In the nondegenerate case, the departure of the *g*-values from g_e (≈ 2.00232) is due to the mixing of some orbital angular momentum into the ground state by spin-orbit coupling. The factors determining this mixing are:

- The change in orbital angular momentum (the numerator) is ±1 when L_x and L_y are involved, and zero when L_z is involved (more explanation below).
- The larger ζ is, the larger the mixing and the larger the *g* shift from 2.00232.
- The smaller the energy gaps are, the larger the mixing and the larger the *g* shift from 2.00232.

d-orbital conversions

- In coordination complexes, the ligand field splits the *d*-orbitals into familiar “ligand field diagrams”.
- *g*-tensor expressions involve orbital angular momentum operators that are evaluated with complex orbitals.
- To interconvert,

$$\sqrt{\frac{15}{8\pi}} \times f(r) \times \begin{cases} \frac{1}{4}\sin^2\theta e^{2i\varphi} = \left|2\right\rangle \\ -\sin\theta\cos\theta e^{i\varphi} = \left|1\right\rangle \\ \frac{1}{\sqrt{6}}(3\cos^2\theta - 1) = \left|0\right\rangle \\ +\sin\theta\cos\theta e^{-i\varphi} = \left|-1\right\rangle \\ \frac{1}{4}\sin^2\theta e^{-2i\varphi} = \left|-2\right\rangle \end{cases}$$

$$\left|z^2\right\rangle = \left|0\right\rangle$$

$$\left|xz\right\rangle = \frac{1}{\sqrt{2}}\left[-\left|1\right\rangle + \left|-1\right\rangle\right]$$

$$\left|yz\right\rangle = \frac{i}{\sqrt{2}}\left[\left|1\right\rangle + \left|-1\right\rangle\right]$$

$$\left|x^2 - y^2\right\rangle = \frac{1}{\sqrt{2}}\left[\left|2\right\rangle + \left|-2\right\rangle\right]$$

$$\left|xy\right\rangle = \frac{-i}{\sqrt{2}}\left[\left|2\right\rangle - \left|-2\right\rangle\right]$$

(signs have to be consistent)

To help crank things out…

Effect of orbital angular momentum operators on the real *d* orbitals

$$\begin{array}{ccc}
L_x d_{xz} = -i d_{xy} & L_y d_{xz} = -i\sqrt{3} d_{z^2} + i d_{x^2-y^2} & L_z d_{xz} = i d_{yz} \\
L_x d_{yz} = i\sqrt{3} d_{z^2} + i d_{x^2-y^2} & L_y d_{yz} = i d_{xy} & L_z d_{yz} = -i d_{xz} \\
L_x d_{xy} = i d_{xz} & L_y d_{xy} = -i d_{yz} & L_z d_{xy} = -2i d_{x^2-y^2} \\
L_x d_{x^2-y^2} = -i d_{yz} & L_y d_{x^2-y^2} = -i d_{xz} & L_z d_{x^2-y^2} = 2i d_{xy} \\
L_x d_{z^2} = -i\sqrt{3} d_{yz} & L_y d_{z^2} = i\sqrt{3} d_{xz} & L_z d_{z^2} = 0
\end{array}$$

Reference: Ballhausen, C. J. *Introduction to Ligand Field Theory*

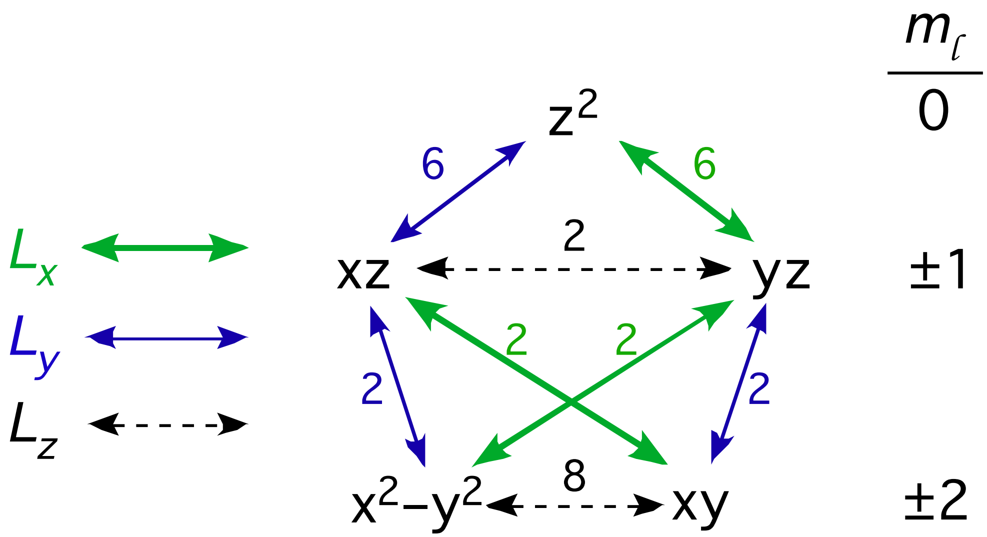
Examples:

$$L_x\left|z^2\right\rangle = \tfrac{1}{2}\left(L_+ + L_-\right)\left|0\right\rangle = \sqrt{\frac{3}{2}}\left[\left|1\right\rangle + \left|-1\right\rangle\right] = -i\sqrt{3} \times \frac{i}{\sqrt{2}}\left[\left|1\right\rangle + \left|-1\right\rangle\right] = -i\sqrt{3}\left|yz\right\rangle$$

$$L_z\left|x^2-y^2\right\rangle = \frac{1}{\sqrt{2}}\left[L_z\left|2\right\rangle + L_z\left|-2\right\rangle\right] = \frac{1}{\sqrt{2}}\left[2\left|2\right\rangle - 2\left|-2\right\rangle\right] = 2\frac{1}{\sqrt{2}}\left[\left|2\right\rangle - \left|-2\right\rangle\right] = 2i \times \frac{-i}{\sqrt{2}}\left[\left|2\right\rangle - \left|-2\right\rangle\right] = 2i\left|xy\right\rangle$$

Magic Pentagon - for S = $^1/_2$ systems

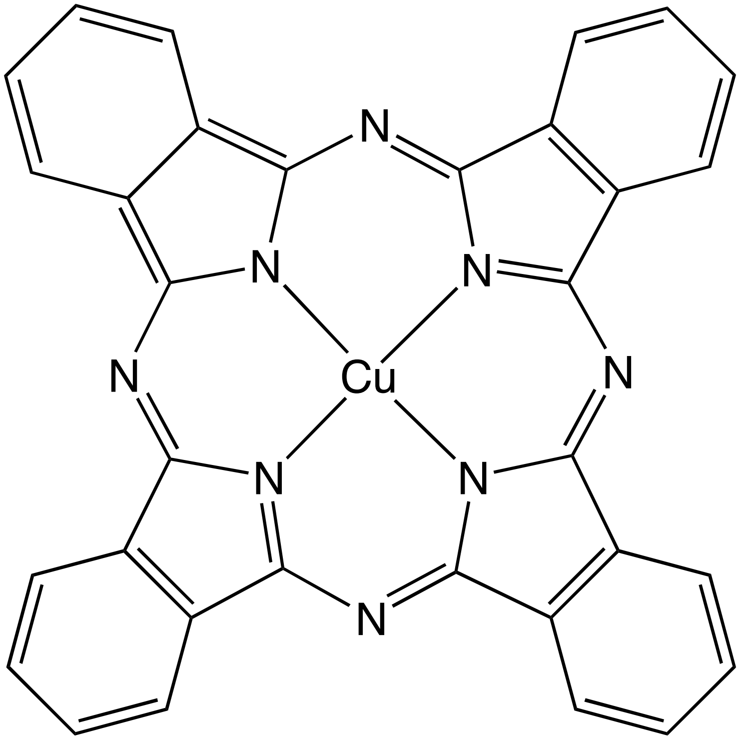
$$g = g_e + \frac{\mathbf{n}\zeta}{E_n - E_0}$$

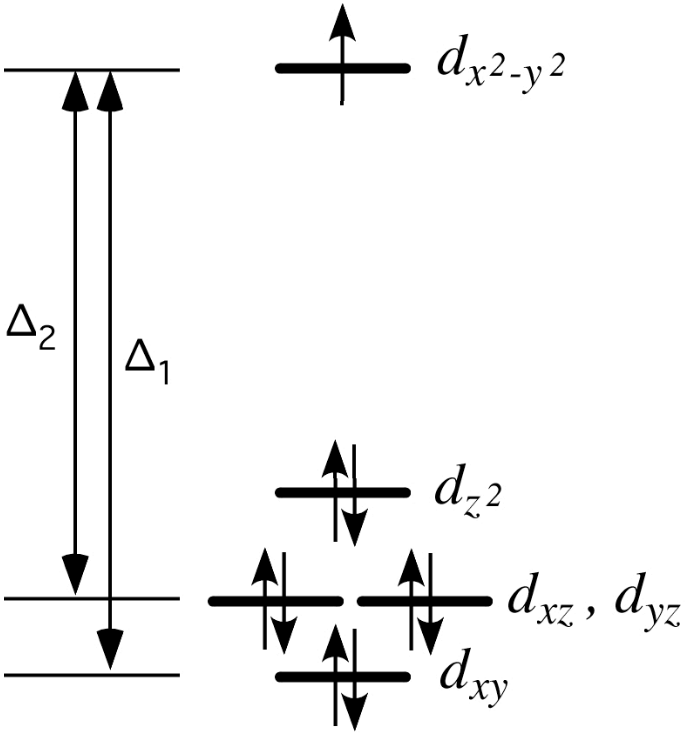


- The pentagon gives values of **n**, but remember the horizontal connections apply to L_z and the vertical connections apply to L_x and L_y. The L_x and L_y operators that couple the orbitals are shown.

(Again, *z* is the principal axis!)

Example: Cu(phthalocyanine)





Observed g-values are: $g_{||}$ = 2.165 and $g_{\perp}$ = 2.045.

What are Δ_1 and Δ_2?

What information is needed?

ζ = 830 cm^{-1} for Cu^{2+} .

Table 3 Calculated g Values for d^n Ions in Pseudo-Octahedral Coordination

Configuration	S	Ground State	obs.[a]	g_x	g_y	g_z
d^1	1/2	$^2T_{2g}$	E	$g_e - 2\lambda/\Delta_1{}^{b}$	$g_e - 2\lambda/\Delta_2{}^{b}$	$g_e - 8\lambda/\Delta_3{}^{b}$
d^2	1	$^3T_{1g}$	VD	$g_e - 9\lambda/2\Delta^{c}$	$g_e - 9\lambda/2\Delta^{c}$	g_e
d^3	3/2	$^4A_{2g}$	E	$g_e - 8\lambda/\Delta_1{}^{d}$	$g_e - 8\lambda/\Delta_2{}^{d}$	$g_e - 8\lambda/\Delta_3{}^{d}$
d^4 HS	2	^5E_g	VD	$-6\lambda/\Delta_1{}^{e}$ $-2\lambda/\Delta_1{}^{f}$	$-6\lambda/\Delta_2{}^{e}$ $-2\lambda/\Delta_2{}^{f}$	g_e $-8\lambda/\Delta_3{}^{f}$
d^5 HS	5/2	$^6A_{1g}$	E	g_e	g_e	g_e
d^5 LS	1/2	$^2T_{2g}$	D	$2[-2\alpha\gamma + \beta^2 + k\beta(\alpha^2 - \gamma^2)]^{g}$	$2[-2\alpha\gamma - \beta^2 - k\beta(\alpha^2 - \gamma^2)]^{g}$	$2[\alpha^2 - \beta^2 + \gamma^2 + k(\alpha^2 - \gamma^2)]^{g}$
d^6 HS	2	$^5T_{2g}$	VD	$g_e + 2\lambda/\Delta_1{}^{h}$	$g_e + 2\lambda/\Delta_1{}^{h}$	$g_e + 8\lambda/\Delta_2{}^{h}$
d^7 HS	3/2	$^4T_{2g}$	D	$2(5-\gamma)/3^{i}$ 0^{ℓ} 4^{m}	$2(5-\gamma)/3^{i}$ 0^{ℓ} 4^{m}	$2(5-\gamma)/3^{i}$ $2(3-\gamma)^{\ell}$ 2^{m}
d^8	1	$^3A_{2g}$	VD	$g_e + 8\lambda/\Delta_1{}^{n}$	$g_e + 8\lambda/\Delta_2{}^{n}$	$g_e + 8\lambda/\Delta_3{}^{n}$
d^9	1/2	^2E_g	E	$g_e + 2\lambda/\Delta_1{}^{o}$ $g_e + 6\lambda/\Delta_1{}^{p}$	$g_e + 2\lambda/\Delta_2{}^{o}$ $g_e + 6\lambda/\Delta_2{}^{p}$	$g_e + 8\lambda/\Delta_3{}^{o}$ g_e

[a] E = easy to observe: generally at room temperature; D=difficult to observe: usually liquid helium temperature is required; VD=very difficult to observe: zero field splitting can be large to prevent observation except in very high magnetic fields. The x and y axes of the reference system bisect the equatorial L-M-L angle. The symmetries of the d orbitals are: $|xy\rangle$, $|xz\rangle$, $|yz\rangle \in T_{2g}$ and $|x^2 - y^2\rangle$, $|z^2\rangle \in E_g$. λ should be taken as positive in any case.

[b] Ground state $|xy\rangle$. Δ_1 and Δ_2 are the energies of $|yz\rangle$ and $|xz\rangle$ (degenerate in tetragonal symmetry); Δ_3 is the energy of $|x^2 - y^2\rangle$.

[c] Δ is the splitting of the ground term in tetragonal symmetry.

[d] Δ_1 are the states arising from the splitting of the $^4T_{2g}$ state. The **g** tensor is generally nearly isotropic even in distorted chromophores.

[e] Ground state configuration: $(t_{2g})^3(e_g)^1 \equiv (|xy\rangle)^1\ (|xz\rangle)^1\ (|yz\rangle)^1\ (x^2 - y^2\rangle)^1\ (|z^2\rangle)^0$; Δ_1 and Δ_2 are the energies of the excitations $|yz\rangle \rightarrow |z^2\rangle$ and $|xz\rangle \rightarrow |z^2\rangle$ respectively. They are degenerate in tetragonal symmetry.

[f] Ground state configuration: $(t_{2g})^3(e_g)^1 \equiv (|xy\rangle)^1\ (|xz\rangle)^1\ (|yz\rangle)^1\ (x^2 - y^2\rangle)^0\ (|z^2\rangle)^1$; Δ_1 and Δ_2 are the energies of the excitations $|yz\rangle \rightarrow |xy\rangle$ and $|xz\rangle \rightarrow |xy\rangle$ respectively. They are degenerate in tetragonal symmetry.

[g] The ground Kramers doublet arising form the $^2T_2$ state is written as $|^2T_2, \pm\rangle = \pm\alpha|\pm1, \pm\rangle + \frac{1}{2}\beta\sqrt{2}[|2, \mp\rangle - |-2, \mp\rangle] \pm \gamma|\mp1, \pm\rangle$. (After Griffith, J.S. *Mol. Phys.* **1971**, *21*, 135).

[h] Elongated tetragonal. Ground state $^5B_2$. Δ_1 and Δ_2 are the energies of the excitations to ^5E and $^5B_1$.

[i] O_h symmetry. $\gamma = -1$ in strong ligand fields and $-3/2$ in weak fields.

[l] Tetragonal elongated complexes.

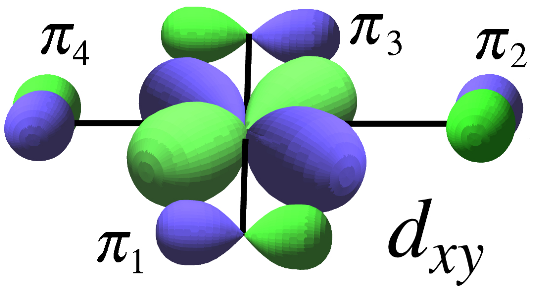
[m] Tetragonal compressed complexes.

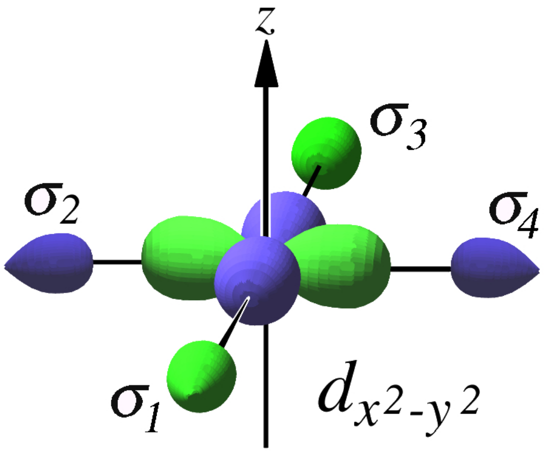
[n] Δ_i are the states arising from the splitting of the $^3T_{2g}$ excited state. $\Delta_1 \equiv {}^3B_{3g}$; $\Delta_2 \equiv {}^3B_{2g}$; $\Delta_3 \equiv {}^3B_{1g}$; Δ_1 and Δ_2 are degenerate in tetragonal symmetries.

[o] Complexes having $|x^2 - y^2\rangle$ have the ground state (tetragonally elongated). Δ_1 and Δ_2 are the energies of $|xz\rangle$ and $|yz\rangle$ (degenerate in tetragonal symmetry); Δ_3 is the energy of $|xy\rangle$.

[p] Complexes having $|z^2\rangle$ have the ground state (tetragonally compressed). Δ_1 and Δ_2 are the energies of $|xz\rangle$ and $|yz\rangle$ (degenerate in tetragonal symmetry).

Effect of ligand delocalization





$$\kappa d_{x^2-y^2} + \frac{\sqrt{1-\kappa^2}}{2}\left(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4\right)$$

$$\kappa' d_{xy} + \frac{\sqrt{1-\kappa'^2}}{2}\left(\pi_1 - \pi_2 + \pi_3 - \pi_4\right)$$

- Delocalization reduces the effective spin-orbit coupling by a significant fraction (~κ •κ′)
- *g*-value shifts are therefore decreased in comparison to those expected for pure *d* orbitals.

The appearance of spectra

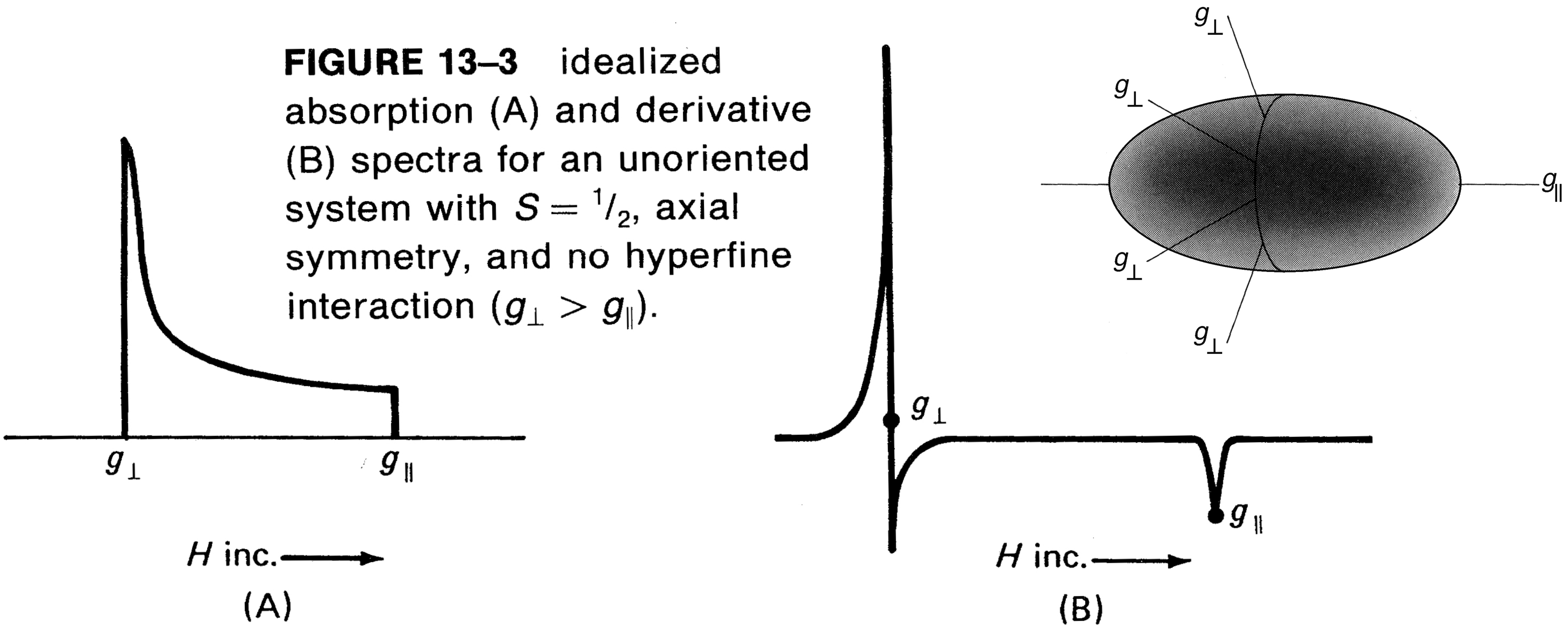
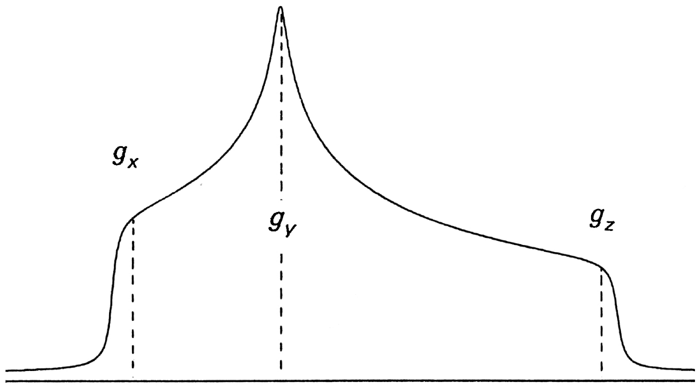


FIGURE 13–3 idealized absorption (A) and derivative (B) spectra for an unoriented system with $S = {}^1/_2$, axial symmetry, and no hyperfine interaction ($g_\perp > g_\parallel$).

- At left is an absorption spectrum for an axial system (e.g., D_{4h} or D_{3h}).
- EPR spectra are usually plotted as derivatives, to changes in slope and extrema more evident.

Orthorhombic case: g_x, g_y, and g_z

- $g_x < g_y < g_z$
- Most probable orientations have *g*-values near the “middle” *g*-value.



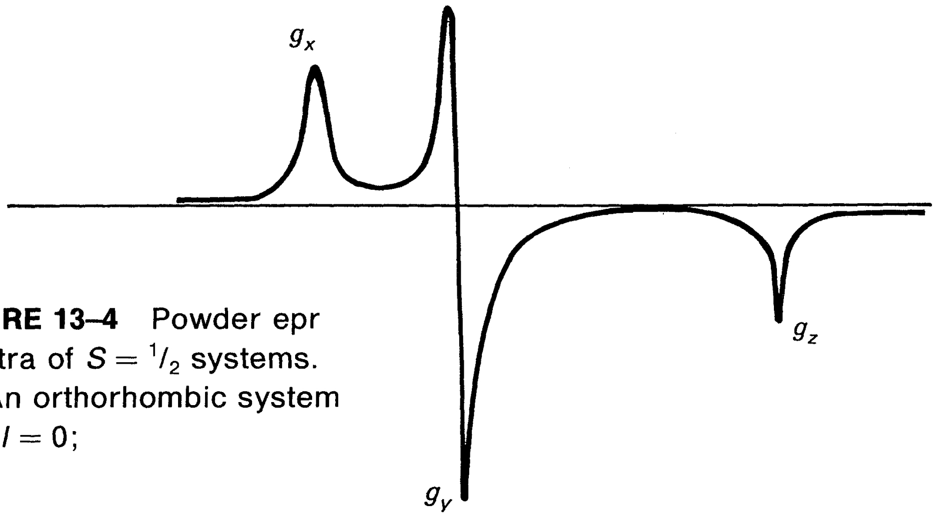
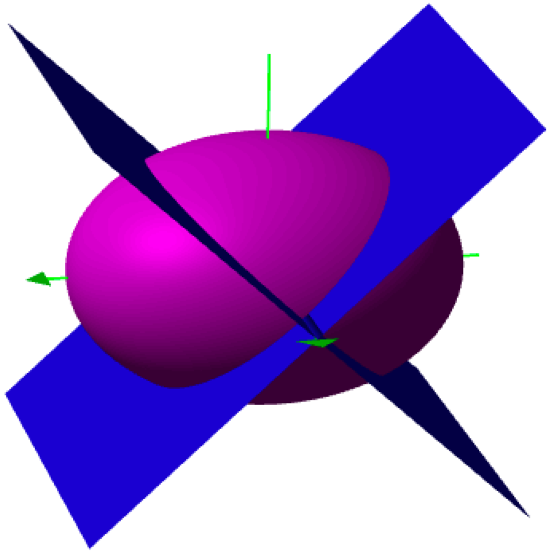
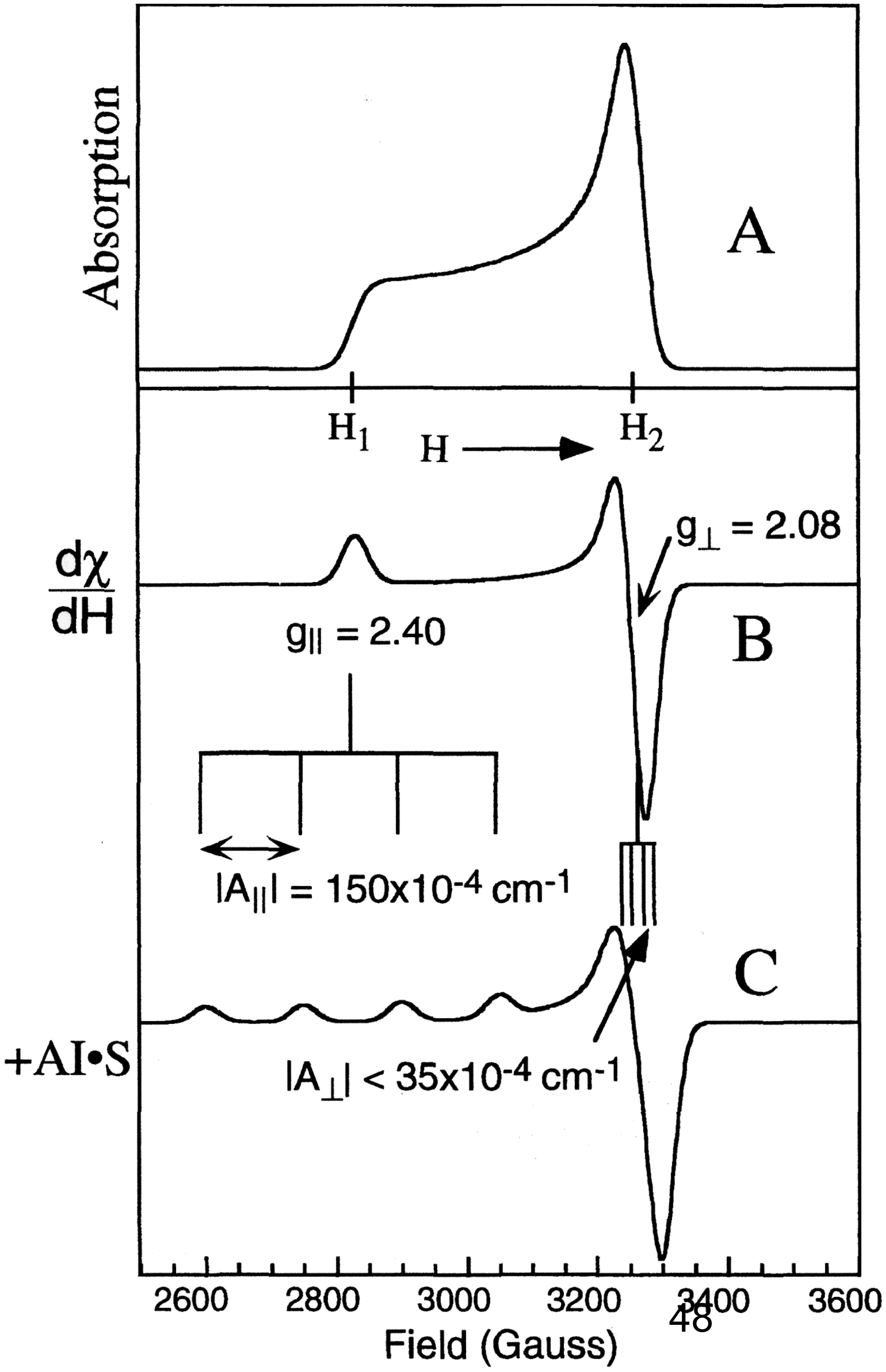


FIGURE 13–4 Powder epr spectra of $S = {}^1/_2$ systems. (A) An orthorhombic system with $I = 0$;

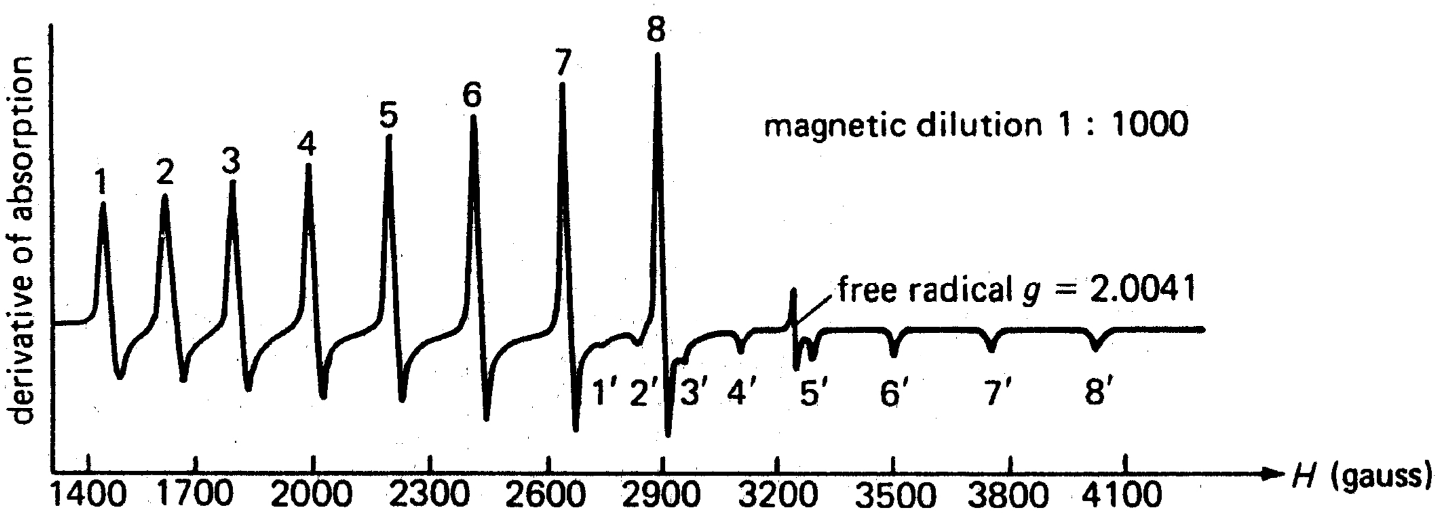


More reality…

Simulated EPR spectrum of a normal copper complex, tetragonal $Cu(H_2O)_6^{2+}$ (at X-band, n = 9.50 GHz). (A) EPR absorption; (B) first derivative spectrum without and (C) with copper hyperfine splitting.

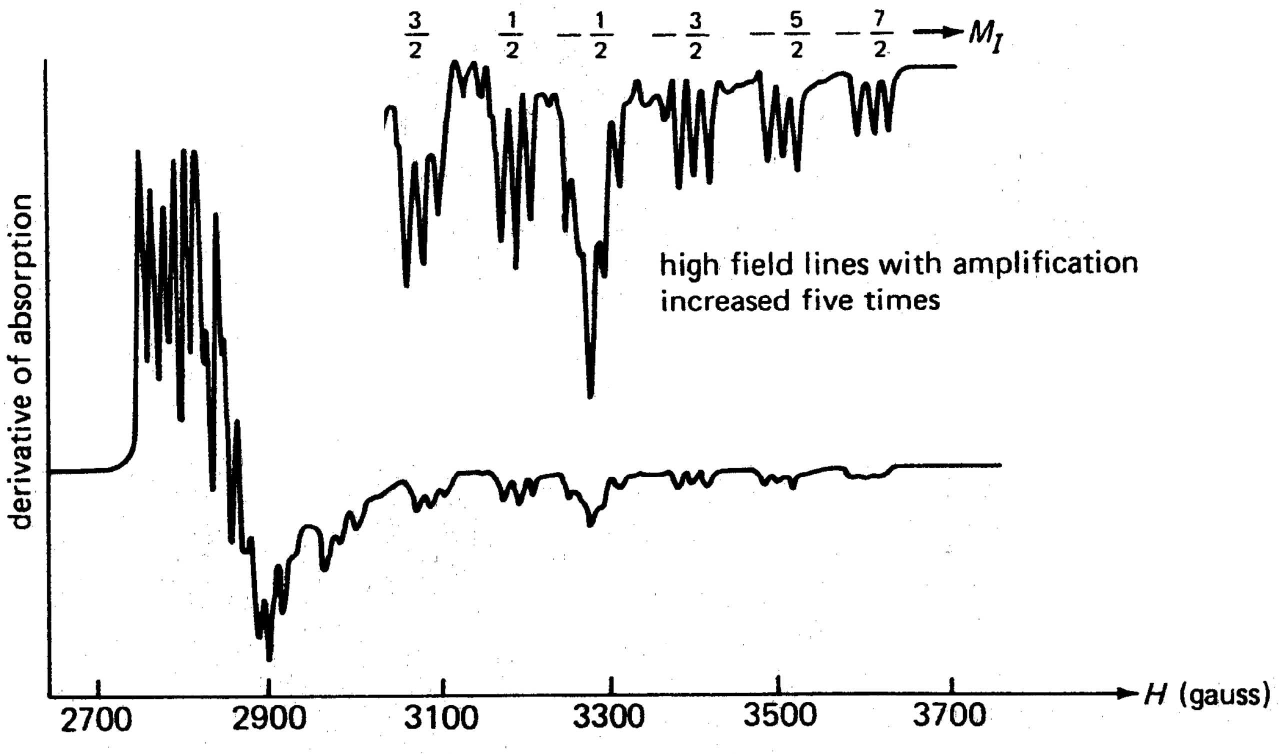


Example



- Shown is a spectrum of cobalt phthalocyanine (for Co, I = $^7/_2$), D_{4h} Co (II) porphyrin.
- (a) What are the values of $g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$? What is the origin of the observed hyperfine structure?

Example, cont.



(b) Dissolving cobalt phthalocyanine in 4-methyl pyridine produces a 1:1 adduct. The frozen solution spectrum at 77 K is shown here. Use a C_{4v} splitting for low-spin Co(II) to identify the orbital in which the unpaired electron resides. Why are each of the upfield components split into three lines?

(c) Why do you see super-hyperfine interaction from the pyridine nitrogen, but not from the four phthalocyanine nitrogen atoms?

Example

A solution of $[Rh(py)_4Cl_2]Cl$ in acetonitrile and 0.1 M (TBA)Cl was electrochemically reduced and the EPR spectrum measured (*Inorg. Chem.* **28**, 3905 (1989)) for the product is shown below (py = pyridine, TBA = tetrabutylammonium).

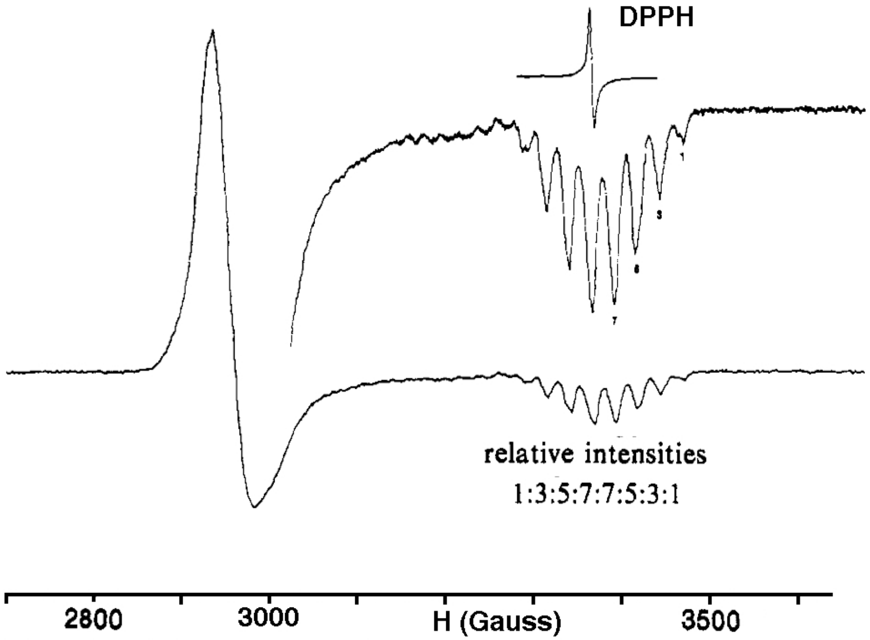


Figure 3. ESR spectrum of a frozen solution of a 2.2×10^{-3} M solution of $[Rh(py)_4Cl_2]Cl$ in 0.1 M (TBA)Cl, pyridine after electrolysis at −1.0 V vs SCE, −140 °C.

(a) The stereochemistry of the complex (*cis*- or *trans*-) is not explicitly indicated. What is it? (Why?) Has the symmetry changed in the reduced complex?

(b) What are the *g*-value(s)? ($g = 2.0037 \pm 0.0002$ for DPPH)

(c) How do the *g*-value(s) enable you to predict which orbital the unpaired resides in? (Give a concise, but *complete*, explanation.)

Example, cont.

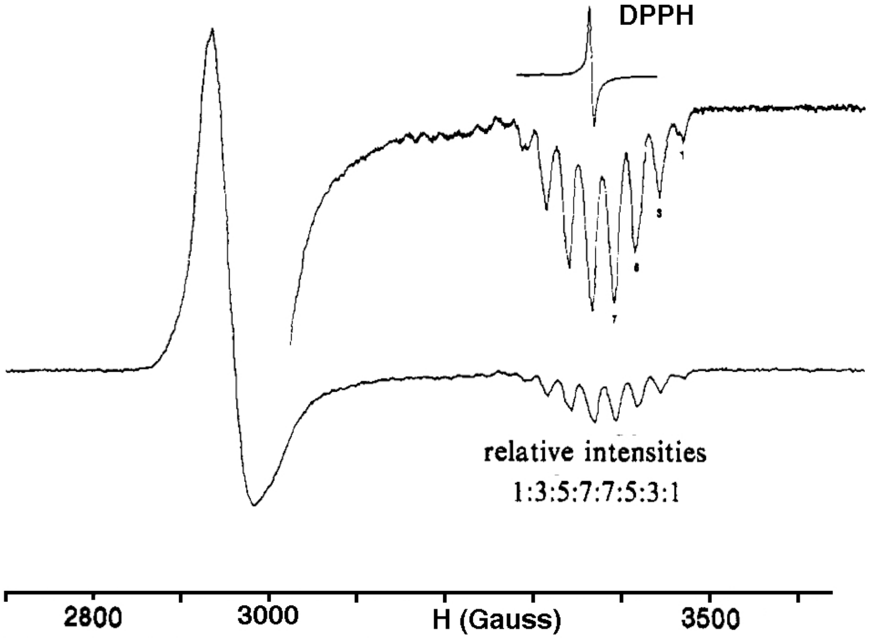


Figure 3. ESR spectrum of a frozen solution of a 2.2×10^{-3} M solution of $[Rh(py)_4Cl_2]Cl$ in 0.1 M (TBA)Cl, pyridine after electrolysis at −1.0 V vs SCE, −140 °C.

Isotope	Spin	Abundance (%)	A_0(MHz)
^{35}Cl	$^3/_2$	75.4	4664
^{37}Cl	$^3/_2$	24.6	3880
^{103}Rh	$^1/_2$	100	

(d) Draw a *d*-orbital splitting diagram and use the *g*-value information to determine as many of the *d*-orbital energy splittings as you can from the information given (for Rh^{2+}, $\zeta = 1220$ cm^{-1}). Indicate whether the value you calculate this way is likely to be correct – if not, is it likely to be too large or too small? (Why?)

(e) The hyperfine splitting pattern has unusual intensities. Explain what is likely to be responsible for this (Hints: Notice that the outer two lines might best be described as barely split into “doublets”.)

(f) Compute estimates for the relevant hyperfine coupling parameter(s) – properly label these – as you hopefully did for the *g*-values.

More than one unpaired electron

When there are more than one unpaired electrons, the spin Hamiltonian (ignoring hyperfine interactions) is written as

$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \hat{\mathbf{S}} + D\left(\hat{S}_z^2 - \frac{S(S+1)}{3}\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right)$$

Notes:

The new terms are due to *zero field splitting*; D is the *axial* splitting parameter, the *rhombic* E term disappears when the system is axially symmetric. The main origin of ZFS is different for organic triplets than for T.M. complexes. In the former it arises from dipole-dipole interactions between the electrons - in the latter, the dominant mechanism is spin-orbit coupling.

EPR usually easily observed in S = $^1/_2$ systems; often difficult for S = integer – this arises from two aspects of ZFS

- Relaxation times $\tau(T_1)$ can be very short due to mixing of ground state with excited states that are close in energy. Fluctuations in the environment modulate the mixing and yield rapidly relaxing states. It is often difficult to observe EPR in solution, usually need low-T in crystals.
- As we'll see below, ZFS may move the allowed ($\Delta M_S = \pm 1$) transitions too high in energy – out of the range accessible magnetic fields.

Group theory for half-integral J

$$\chi(C_{\alpha+2\pi}) = \frac{\sin(J+1/2)(\alpha+2\pi)}{\sin(\alpha+2\pi)/2} = \frac{\sin\left[(J+1/2)\alpha+(2J+1)\pi\right]}{-\sin\alpha/2}$$

If J is half-integral, then $2J+1$ is an even integer; if J is an integer, then $2J+1$ is an odd integer.

$$\therefore \quad \chi(C_{\alpha+2\pi}) = \chi(C_\alpha) \qquad \text{if } J \text{ is an integer}$$

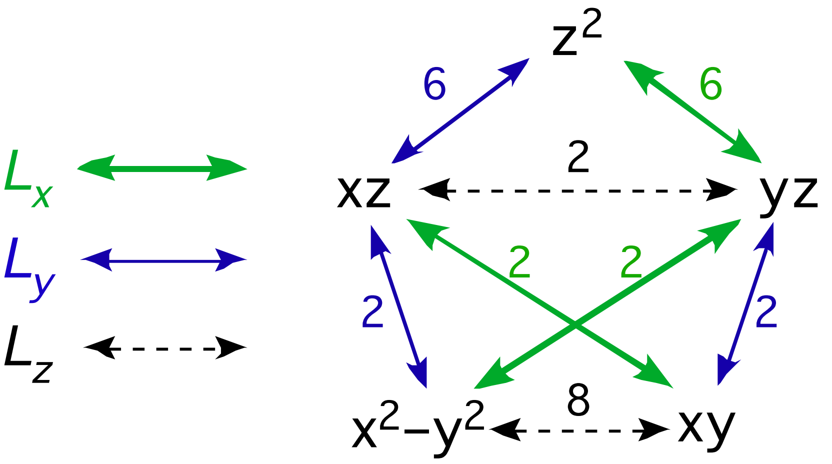
$$\text{and} \quad \chi(C_{\alpha+2\pi}) = -\chi(C_\alpha) \quad \text{if } J \text{ is half-integral}$$

- When J (or S) is half-integral, rotations by 2π are treated as if they are a new, distinct symmetry operation, since otherwise the the characters of the representations for which the J-states form a basis wouldn't be uniquely defined.
- This leads to the use of *double groups* (Cotton, Sec. 9.7) to handle these cases.

Double Group Example: Cu(phthalocyanine)

D_4'	E	R	$2(C_4+RC_4^3)$	$2(C_4^3+RC_4)$	$2(C_2+RC_2)$ $(C_4^2+RC_4^2)$	$4(2C_2'+2RC_2')$	$4(2C_2''+2RC_2'')$		
A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	-1	-1	z, R_z	
B_1	1	1	-1	-1	1	1	-1		x^2-y^2
B_2	1	1	-1	-1	1	-1	1		xy
E	2	2	0	0	-2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)
Γ_6	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	$=\Gamma_{1/2}$	
Γ_7	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0		

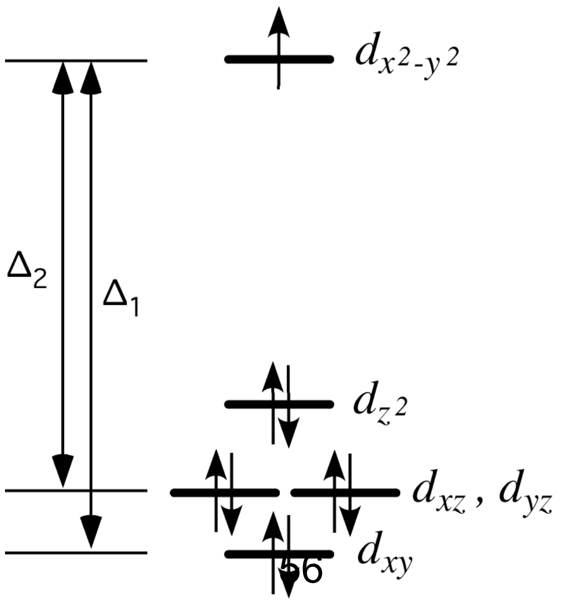
$$A_{1,2}\otimes\Gamma_6=\Gamma_6 \quad ; \quad B_{1,2}\otimes\Gamma_6=\Gamma_7 \quad ; \quad E\otimes\Gamma_6=\Gamma_6\oplus\Gamma_7 \quad ; \quad \Gamma_{3/2}=\Gamma_6\oplus\Gamma_7$$



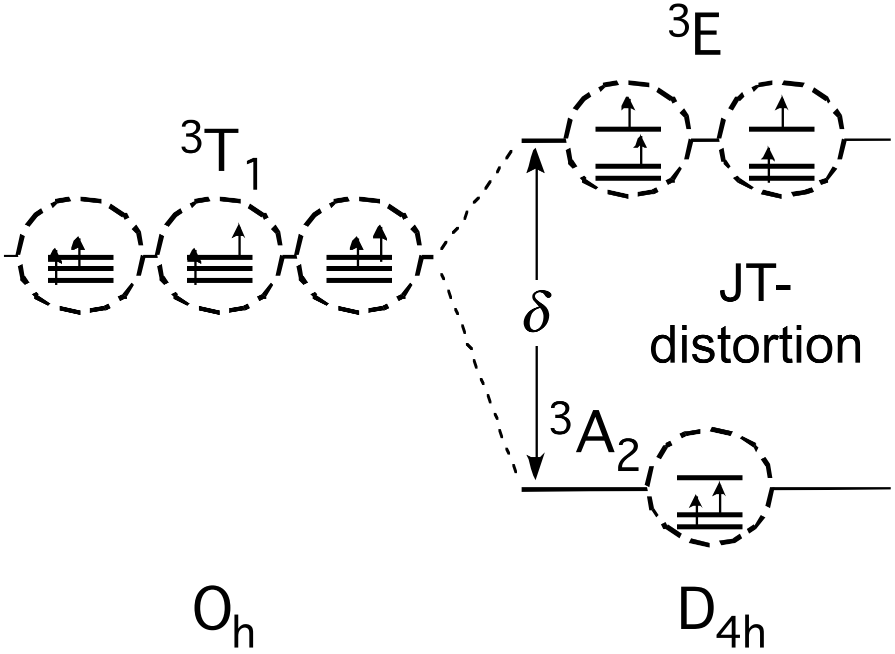
$^2A_1(\Gamma_6)$

$^2E(\Gamma_6+\Gamma_7)$

$^2B_2, {}^2B_1(\Gamma_7)$



V^{III} in a distorted octahedral complex; symmetry aspects of S-O Coupling



Q: How are the states split in the presence of Spin-Orbit Coupling?

Any angular momentum states with a value J (i.e., $2J+1$ states with $M_J = J, J-1, \ldots, -J$) that are subject to the influence by the symmetry of the environment, the character of a rotation is given by:

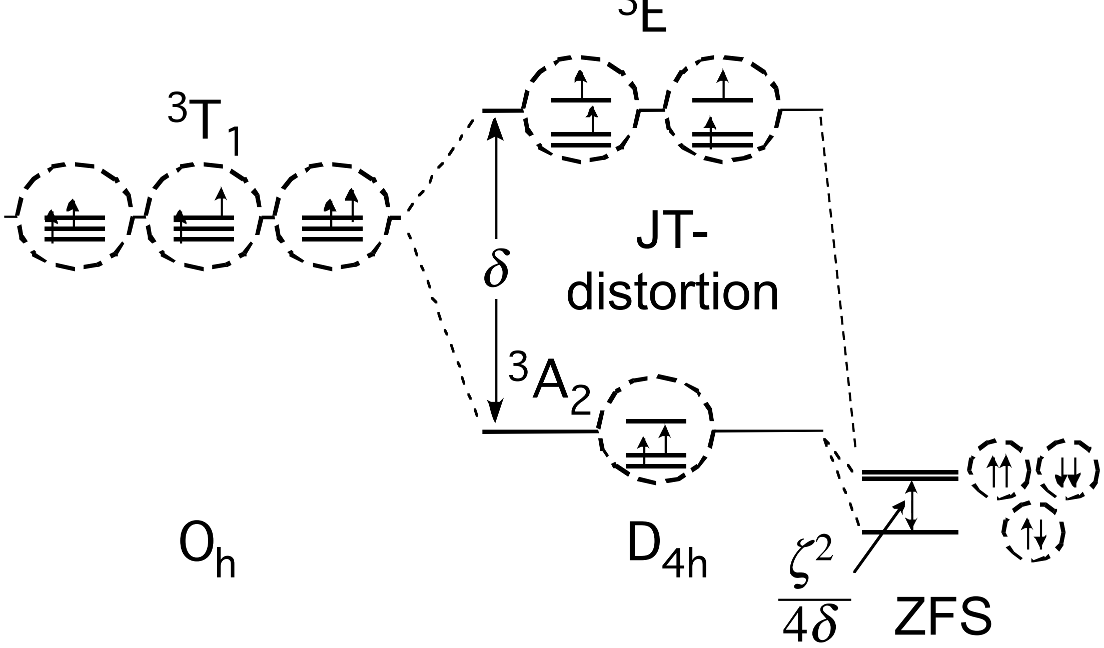
$$\chi(C_\alpha) = \frac{\sin(J+1/2)\alpha}{\sin \alpha/2}$$

D_4	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2	1	1	1	–1	–1	$z,\ R$	
B_1	1	–1	1	1	–1		x^2-y^2
B_2	1	–1	1	–1	1		xy
E	2	0	–2	0	0	$(x,\ y),\ (R_x, R_y)$	(xz, yz)
$\Gamma_{S=1}$	3	1	–1	–1	–1		

$$\Gamma_{S=1} \Rightarrow E \oplus A_2 \quad \therefore \quad \Gamma(^3A_2) = A_2 \otimes (E \oplus A_2) = E \oplus A_1$$

$$\Gamma(^3E) = E \otimes (E \oplus A_2) = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus E$$

Zero Field Splitting: V^{III}



$$\mathcal{H}_{LS} = \zeta\left(\mathbf{L}_1 \bullet \mathbf{S}_1 + \mathbf{L}_2 \bullet \mathbf{S}_2\right) =$$

$$\zeta\begin{pmatrix} L_{1x}S_{1x} + L_{1y}S_{1y} + L_{1z}S_{1z} \\ +L_{2x}S_{2x} + L_{2y}S_{2y} + L_{2z}S_{2z} \end{pmatrix} =$$

$$\zeta\begin{pmatrix} \frac{1}{2}\left(L_{1+}S_{1-} + L_{1-}S_{1+}\right) + L_{1z}S_{1z} \\ +\frac{1}{2}\left(L_{2+}S_{2-} + L_{2-}S_{2+}\right) + L_{2z}S_{2z} \end{pmatrix}$$

$^3A_2$:

$$\psi_1 = \left\|(xz)^\alpha (yz)^\alpha\right\|$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left\{\left\|(xz)^\alpha (yz)^\beta\right\| + \left\|(xz)^\beta (yz)^\alpha\right\|\right\}$$

$$\psi_3 = \left\|(xz)^\beta (yz)^\beta\right\|$$

^3E:

$$\psi_4 = \left\|(xy)^\alpha (xz)^\alpha\right\|$$

$$\psi_5 = \frac{1}{\sqrt{2}}\left\{\left\|(xy)^\alpha (xz)^\beta\right\| + \left\|(xy)^\beta (xz)^\alpha\right\|\right\}$$

$$\psi_6 = \left\|(xy)^\beta (xz)^\beta\right\|$$

$$\psi_7 = \left\|(xy)^\alpha (yz)^\alpha\right\|$$

$$\psi_8 = \frac{1}{\sqrt{2}}\left\{\left\|(xy)^\alpha (yz)^\beta\right\| + \left\|(xy)^\beta (yz)^\alpha\right\|\right\}$$

$$\psi_9 = \left\|(xy)^\beta (yz)^\beta\right\|$$

Gory Detail: Typical Matrix Element

If we expand out the determinants, we can evaluate the a typical matrix element,

$$\psi_5 = \tfrac{1}{2}\left[xy(1)xz(2) - xz(1)xy(2)\right]\left(\alpha_1\beta_2 + \beta_1\alpha_2\right) \qquad ; \qquad \psi_1 = \tfrac{1}{\sqrt{2}}\left[xz(1)yz(2) - yz(1)xz(2)\right]\alpha_1\alpha_2$$

$$\left\langle\psi_5\middle|\mathcal{H}_{LS}\middle|\psi_1\right\rangle =$$

$$\frac{\zeta}{2\sqrt{2}}\left[\begin{array}{l} \left\langle\left[xy(1)xz(2) - xz(1)xy(2)\right]\left(\alpha_1\beta_2 + \beta_1\alpha_2\right)\right| \\ \tfrac{1}{2}\left(L_{1+}S_{1-} + L_{1-}S_{1+}\right) + L_{1z}S_{1z} + \tfrac{1}{2}\left(L_{2+}S_{2-} + L_{2-}S_{2+}\right) + L_{2z}S_{2z}\left|\left[xz(1)yz(2) - yz(1)xz(2)\right]\alpha_1\alpha_2\right\rangle \end{array}\right]$$

All the terms involving $L_{1z}S_{1z}$ and $L_{2z}S_{2z}$ drop out because of spin orthogonality. Also, the terms involving S_{1+} and S_{2+} drop out because they kill the α spin states they operate on.

So we have (so far),

$$\frac{\zeta}{4\sqrt{2}}\left[\left\langle\left[xy(1)xz(2) - xz(1)xy(2)\right]\left(\alpha_1\beta_2 + \beta_1\alpha_2\right)\middle|\left(L_{1+}S_{1-} + L_{2+}S_{2-}\right)\middle|\left[xz(1)yz(2) - yz(1)xz(2)\right]\alpha_1\alpha_2\right\rangle\right]$$

Carrying out the spin lowering operations, and doing the trivial spin integrals yields

$$\frac{\zeta}{4\sqrt{2}}\left[\left\langle\left[xy(1)xz(2) - xz(1)xy(2)\right]\middle|L_{1+}\middle|\left[xz(1)yz(2) - yz(1)xz(2)\right]\right\rangle\right] +$$

$$\frac{\zeta}{4\sqrt{2}}\left[\left\langle\left[xy(1)xz(2) - xz(1)xy(2)\right]\middle|L_{2+}\middle|\left[xz(1)yz(2) - yz(1)xz(2)\right]\right\rangle\right]$$

In the top integral we can trivially carry out the integrals over electron 2 coordinates, and in the bottom integral we can do the same for electron 1 coordinates, and things simplify!

$$\frac{-\zeta}{4\sqrt{2}}\left[\left\langle xy(1)\middle|L_{1+}\middle|yz(1)\right\rangle\right] - \frac{\zeta}{4\sqrt{2}}\left[\left\langle xy(2)\middle|L_{2+}\middle|yz(2)\right\rangle\right] = \qquad \text{(identical integrals!)}$$

$$= \frac{-\zeta}{2\sqrt{2}}\left\langle xy\middle|L_+\middle|yz\right\rangle = \frac{-\zeta}{2\sqrt{2}}\left\langle xy\middle|L_x + iL_y\middle|yz\right\rangle \quad \Rightarrow \quad \boxed{\left\langle\psi_5\middle|\mathcal{H}_{LS}\middle|\psi_1\right\rangle = \frac{\zeta}{2\sqrt{2}}}$$

Where we used the table for operations on d orbitals given earlier (only the L_y term survived).

More Detail

The spin-orbit energy matrices involving the mixing of ψ_5 and ψ_8 into ψ_1 and ψ_3 are:

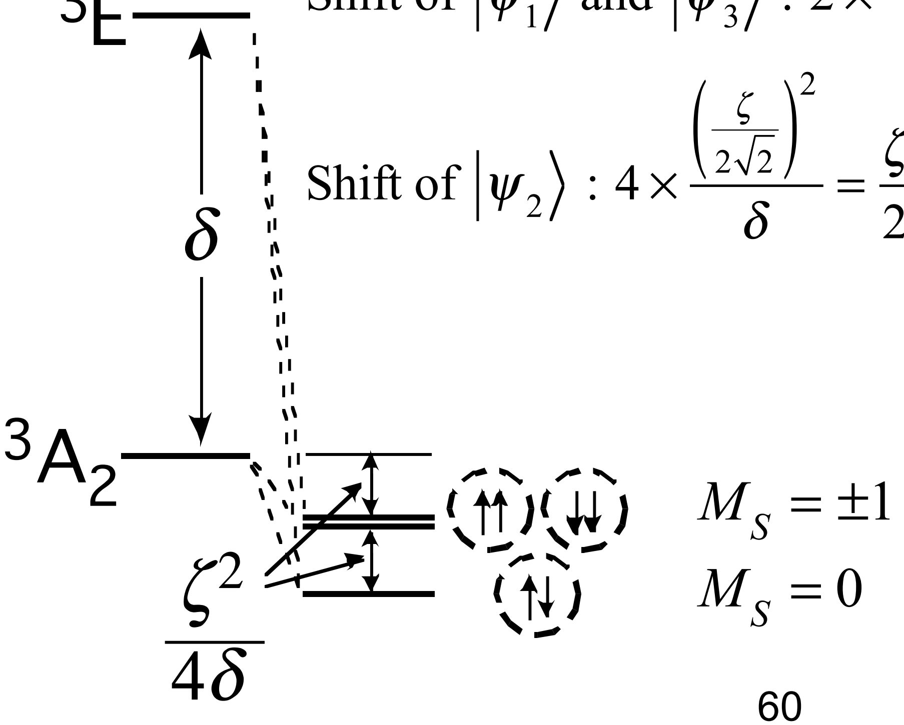
$$\begin{array}{c|ccc} & |\psi_1\rangle & |\psi_5\rangle & |\psi_8\rangle \\ \hline \langle\psi_1| & 0 & \frac{\zeta}{2\sqrt{2}} & \frac{i\zeta}{2\sqrt{2}} \\ \langle\psi_5| & \frac{\zeta}{2\sqrt{2}} & \delta & 0 \\ \langle\psi_8| & \frac{-i\zeta}{2\sqrt{2}} & 0 & \delta \end{array} \qquad \begin{array}{c|ccc} & |\psi_3\rangle & |\psi_5\rangle & |\psi_8\rangle \\ \hline \langle\psi_3| & 0 & \frac{\zeta}{2\sqrt{2}} & \frac{i\zeta}{2\sqrt{2}} \\ \langle\psi_5| & \frac{\zeta}{2\sqrt{2}} & \delta & 0 \\ \langle\psi_8| & \frac{-i\zeta}{2\sqrt{2}} & 0 & \delta \end{array}$$

The spin-orbit energy matrix involving the mixing of ψ_4, ψ_6, ψ_7, ψ_9 into ψ_2 is:

$$\begin{array}{c|ccccc} & |\psi_2\rangle & |\psi_4\rangle & |\psi_6\rangle & |\psi_7\rangle & |\psi_9\rangle \\ \hline \langle\psi_2| & 0 & \frac{-\zeta}{2\sqrt{2}} & \frac{\zeta}{2\sqrt{2}} & \frac{i\zeta}{2\sqrt{2}} & \frac{i\zeta}{2\sqrt{2}} \\ \langle\psi_4| & \frac{-\zeta}{2\sqrt{2}} & \delta & 0 & \frac{-i\zeta}{2} & 0 \\ \langle\psi_6| & \frac{\zeta}{2\sqrt{2}} & 0 & \delta & 0 & \frac{i\zeta}{2} \\ \langle\psi_7| & \frac{-i\zeta}{2\sqrt{2}} & \frac{i\zeta}{2} & 0 & \delta & 0 \\ \langle\psi_9| & \frac{-i\zeta}{2\sqrt{2}} & 0 & \frac{-i\zeta}{2} & 0 & \delta \end{array}$$

Shift of $|\psi_1\rangle$ and $|\psi_3\rangle$: $2\times\frac{\left(\frac{\zeta}{2\sqrt{2}}\right)^2}{\delta}=\frac{\zeta^2}{4\delta}$

Shift of $|\psi_2\rangle$: $4\times\frac{\left(\frac{\zeta}{2\sqrt{2}}\right)^2}{\delta}=\frac{\zeta^2}{2\delta}$



Spin Hamiltonian and EPR spectrum with ZFS.

Now that we've shown the physical origin of zero-field splitting, let's see how it fits together with the spin Hamiltonian ($E = 0$):

$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \hat{\mathbf{S}} + D\left(\hat{S}_z^2 - \frac{S(S+1)}{3}\right) = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \hat{\mathbf{S}} + D\left(\hat{S}_z^2 - \frac{2}{3}\right)$$

since $S = 1$. The states on which this operates have and are

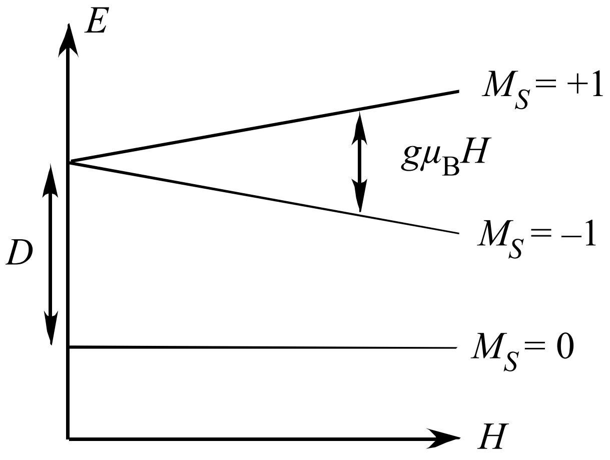
$\left|+\right\rangle, \left|-\right\rangle \quad M_S = \pm 1$

$\left|0\right\rangle \quad M_S = 0$

$\mathcal{H}_{eff}\left|+\right\rangle = +\mu_B g H + \tfrac{1}{3} D$;

$\mathcal{H}_{eff}\left|-\right\rangle = -\mu_B g H + \tfrac{1}{3} D$

$\mathcal{H}_{eff}\left|0\right\rangle = -\tfrac{2}{3} D$



When D > 0, the ground state is diamagnetic. If D is too large, no EPR signal is observed!

When D < 0, the ground state is paramagnetic, but transitions with $\Delta M_S = \pm 2$ are forbidden (allowed in second-order only).

ZFS: quartet state (axial symmetry)

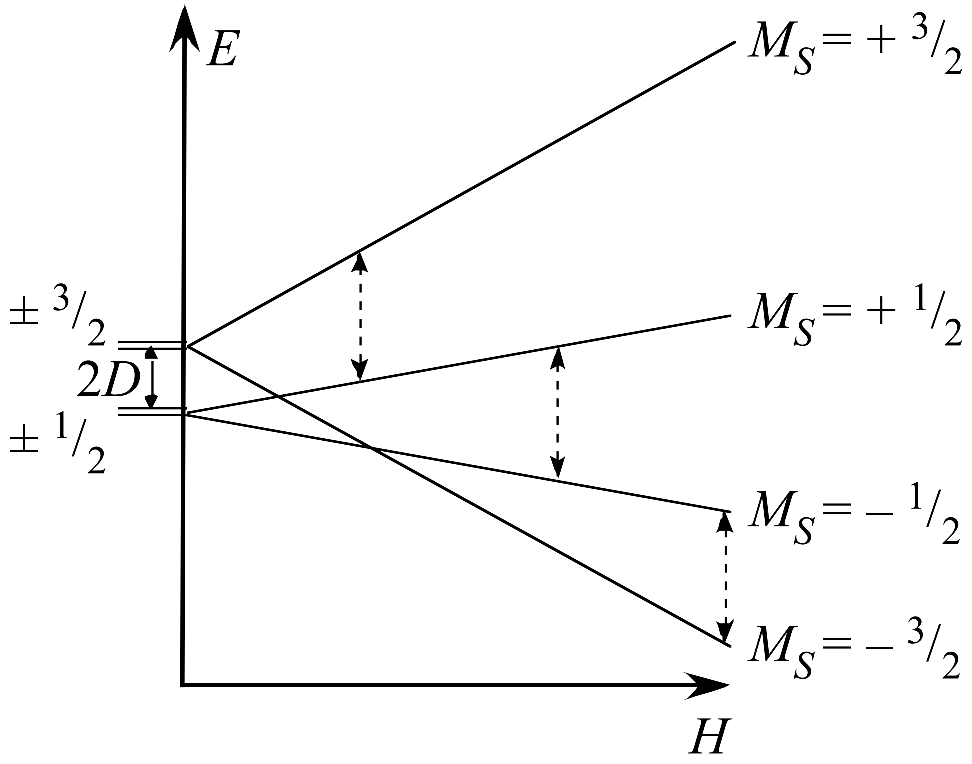
For an axially symmetric quartet state ($E = 0$) the spin Hamiltonian is

$$\mathcal{H}_{eff} = \mu_B \mathbf{H}\bullet\mathbf{g}\bullet\hat{\mathbf{S}} + D\left(\hat{S}_z^2 - \frac{S(S+1)}{3}\right) = \mu_B \mathbf{H}\bullet\mathbf{g}\bullet\hat{\mathbf{S}} + D\left(\hat{S}_z^2 - \frac{5}{4}\right)$$

since $S = \tfrac{3}{2}$. The states on which this operates are $\left|+\tfrac{3}{2}\right\rangle, \left|+\tfrac{1}{2}\right\rangle, \left|-\tfrac{1}{2}\right\rangle, \left|-\tfrac{3}{2}\right\rangle$.

$$\mathcal{H}_{eff}\left|+\tfrac{3}{2}\right\rangle = \tfrac{3}{2}\mu_B gH + D \quad ; \quad \mathcal{H}_{eff}\left|-\tfrac{3}{2}\right\rangle = -\tfrac{3}{2}\mu_B gH + D$$

$$\mathcal{H}_{eff}\left|+\tfrac{1}{2}\right\rangle = \tfrac{1}{2}\mu_B gH - D \quad ; \quad \mathcal{H}_{eff}\left|-\tfrac{1}{2}\right\rangle = -\tfrac{1}{2}\mu_B gH - D$$

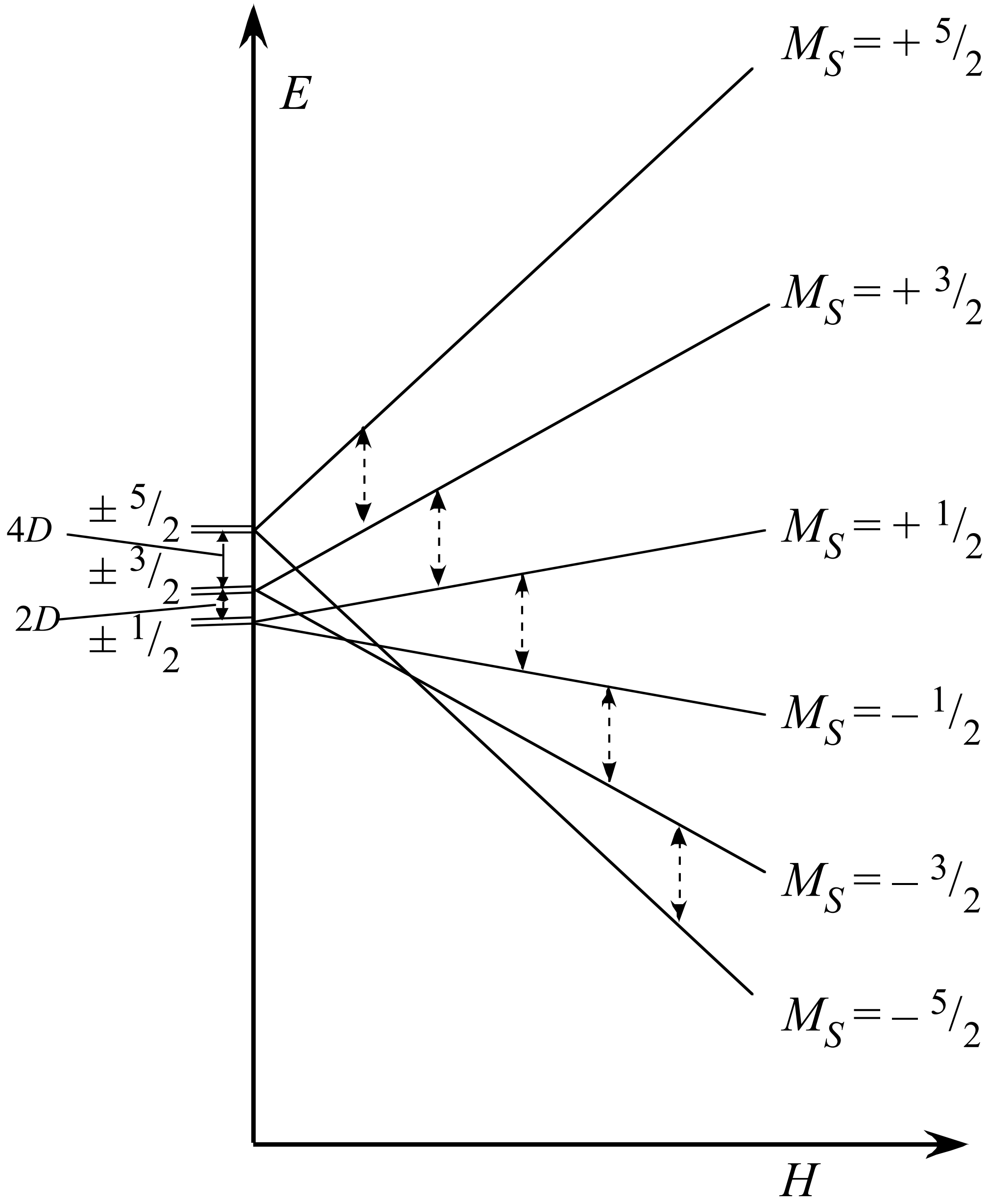


$$\Gamma_{3/2} = \Gamma_6 \oplus \Gamma_7 \quad \text{in } D_4'$$

When D > 0 and too large, the $+{}^1/_2 \leftrightarrow +{}^3/_2$ transition will not be observable in EPR. The $-{}^1/_2 \leftrightarrow -{}^3/_2$ transition would only be observable at high fields.

The $-{}^1/_2 \leftrightarrow +{}^1/_2$ transition is always observable since it is independent of ZFS.

${}^6A_1$ states: HS-Mn^{II} and Fe^{III}



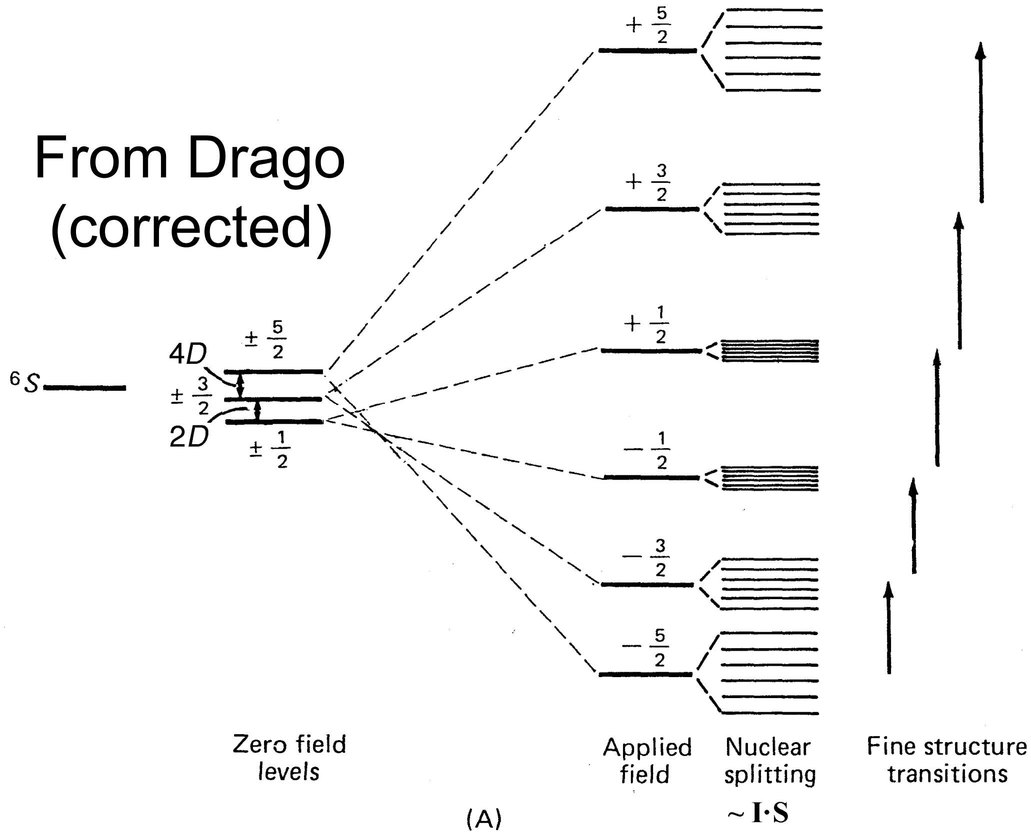
small D ~ 10^{-2} cm^{-1}

- Because ground state has no orbital angular momentum, only higher-order spin-orbit and/or direct dipole-dipole spin-spin couplings give ZFS.

∴ ZFS parameters are small, though measurable.

^{55}Mn (100%)

From Drago (corrected)



(A)

Mn^{2+} doped into MgV$_2$O$_6$

g_x = 2.0042 ± 0.0005

g_y = 2.0092 ± 0.001

g_z = 2.0005 ± 0.0005

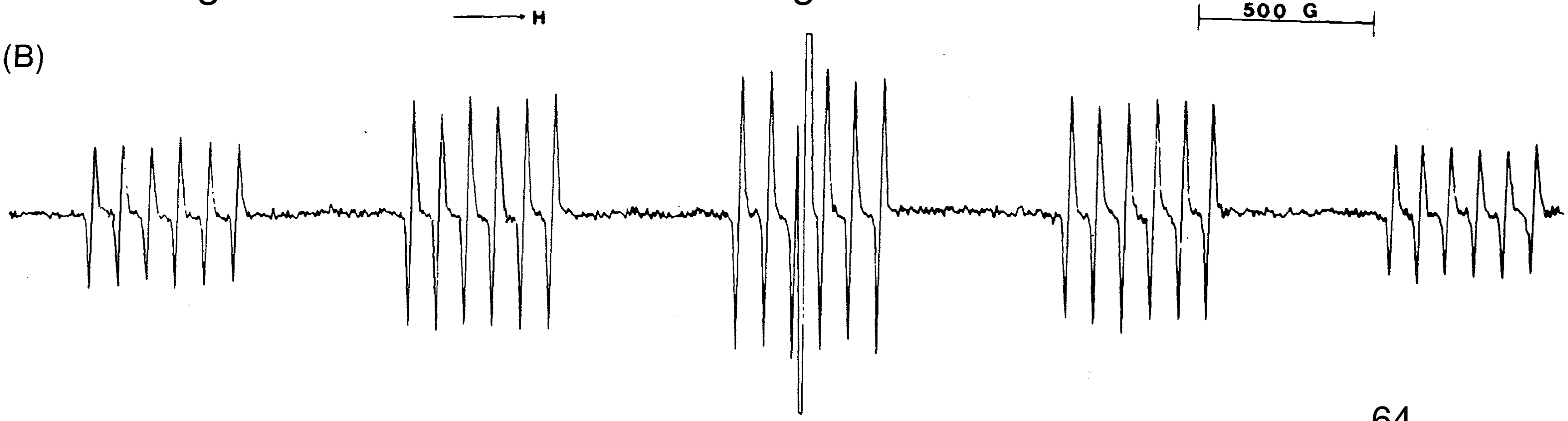
D_x = 218±5 G; D_y = -87±5 G;

D_z = -306±20 G;

from H. N. Ng and C. Calvo, Can. J. Chem. *50*, 3619 (1972).

Excited $^4T_{2g}$ state mixes into $^6A_{1g}$

(B)



Assign all the transitions with initial and final values of M$_S$ and m$_I$!

Typical Spectra? Pitfalls

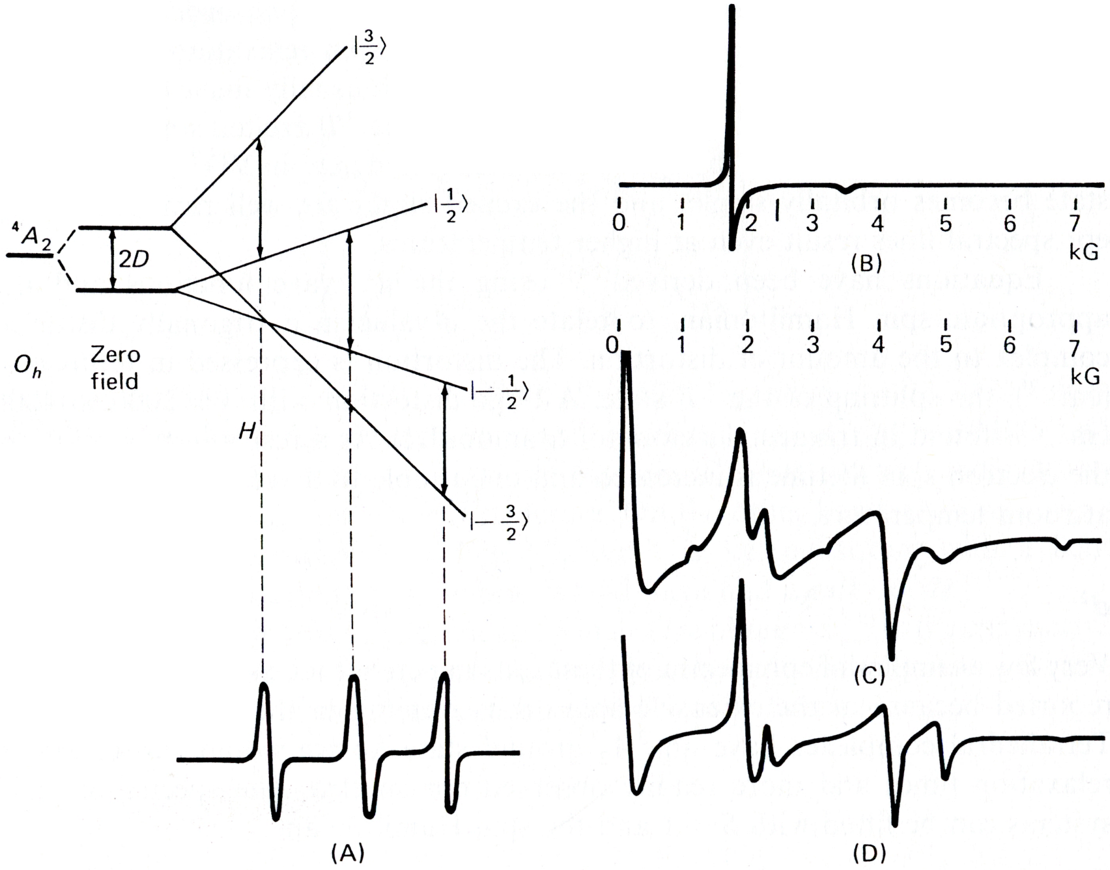


FIGURE 13–13 (A) Small zero-field and magnetic field splitting of the $^4A_2$ ground state (field along z) for a d^3 case and the resulting spectrum.
(B) *Trans*-$[Cr(C_5H_5N)_4I_2]^+$ in DMF, H_2O, CH_2O, CH_3OH glass[(33)] at 9.3 GHz. $D > 0.4$ cm^{-1}, $E < 0.01$.
(C) *Trans*-$[Cr(C_5H_5N)_4Cl_2]^+$ in DMF, H_2O, CH_3OH glass[(33)] at 9.211 GHz.
(D) Computer simulation[(33)] of (C) with $g_\parallel = g_\perp = 1.99$, $D = 0.164$ cm^{-1}, $E = 0$.
[Reprinted with permission from E. Pedersen and H. Toftlund, Inorg. Chem., *13*, 1603 (1974). Copyright by the American Chemical Society.]

Even reasonably straightforward systems can fail to give “typical” spectra.
Modern EPR interpretation is almost always accompanied by computer simulation.

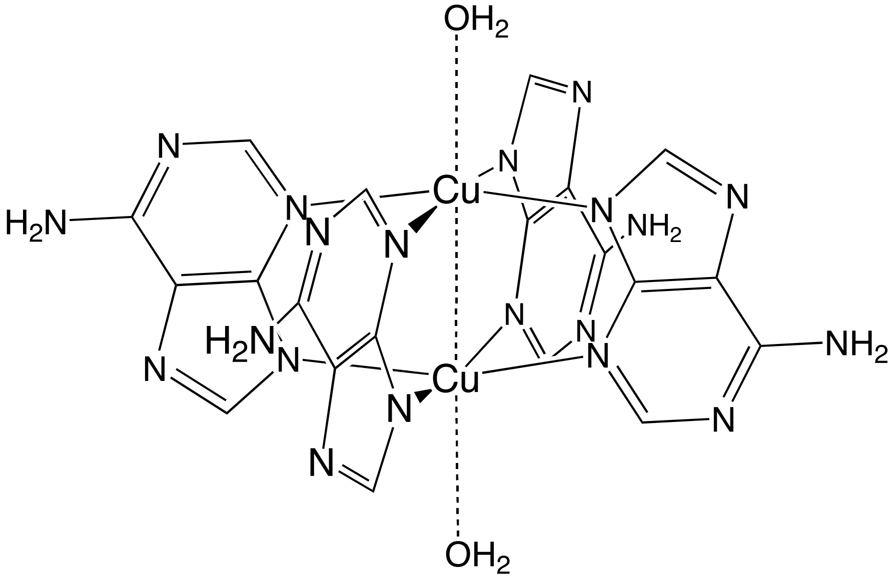
$$\mathcal{H}_{\text{Spin}} =$$

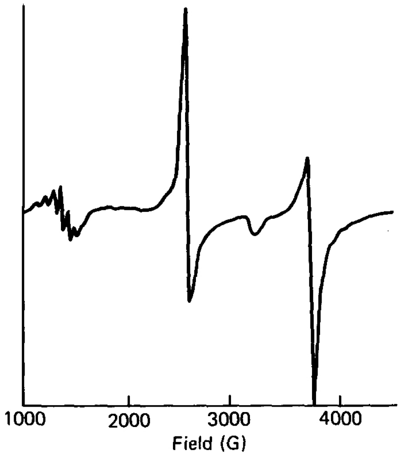
$$g_z \mu_B H_z \hat{S}_z + g_x \mu_B H_x \hat{S}_x + g_y \mu_B H_y \hat{S}_y +$$

$$D\left[\hat{S}_z^2 - \frac{5}{4}\right] + E\left[\hat{S}_x^2 - \hat{S}_y^2\right] +$$

$$A_\parallel \hat{S}_z \hat{I}_z + A_\perp\left[\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y\right]$$

Exchange Coupling





- Exchange-coupled dimers (usually antiferromagnetic) are usually EPR-silent at low temperatures.
- If the coupling is very weak, transitions from the S = 0 ground state can be observed (next slide), but it is unusual.

Exchange-coupled dimers