Basic Concepts in Magnetism; Many-electron atoms

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- I. Spin-orbit interaction
- 2. Magnetism of single-electron atom
- 3. Magnetism of many-electron atoms
- 4. Paramagnetism
- 5. Crystal field



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MAGNETISM AND MAGNETIC MATERIALS

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I. Spin-orbit interaction



Spin-Orbit Coupling



which produces a magnetic field $\mu_0 I/2r$ at the centre

$$B_{so} = \mu_0 Zev/4\pi r^2 \quad [\sim 10 \text{ T for B or C}]$$

$$E = -m.B \qquad E_{so} = -\mu_B B_{so}$$
Since $r \approx a_0/Z$ and $m_e vr \approx \hbar$

$$E_{so} \approx -\mu_0 \mu_B^2 Z^4/4\pi a_0^3$$
The spin – orbit Hamiltonian for a single electron is of the form:
in general $\mathcal{H}_{so} = (1/2m_e^2 c^2 r) dV/dr$

Here the two $\hbar s$ have been assimilated into λ , making it an energy (c.f. exchange)

I.s

2. Single-electron atom



Orbital angular momentum

The orbital angular momentum operators also satisfy the commutation rules:



Orbital angular momentum operators



 $\begin{bmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{bmatrix} \hbar, \begin{bmatrix} 0 & -i/\sqrt{2} & 0 \\ i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & i/\sqrt{2} & 0 \end{bmatrix} \hbar, \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \hbar$

where

$$\hat{\boldsymbol{l}}^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} 2\hbar^2$$

Solution of Schrodinger's equation

Schrodinger's equation:
$$\mathcal{H}\psi_i = \varepsilon_i\psi_i$$
: $\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2}\hat{l}^2\right) - \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi_i = \varepsilon_i\psi_i$. $\varepsilon_n = \frac{-Zme^4}{8\epsilon_0^2 h^2 n^2} = \frac{-ZR_0}{n^2}$ Satisfied by the wavefunctions: $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ Where: $R(r) = V_n^\ell(Zr/na_0)\exp[-(Zr/na_0)]$ $(V_n^{-1} \text{ are Laguerre polynomials } V_i^0=I)$ And the combined angular parts are $Y_\ell^{m_\ell}(\theta, \phi) \propto P_\ell^{m_\ell}(\theta)e^{im_{\ell\ell}\phi}$.(Legendre polynomials)

Normalized spherical harmonics:

$$\begin{array}{ll} s & Y_0^0 = \sqrt{1/4\pi} \\ p & Y_1^0 = \sqrt{3/4\pi} \cos\theta & Y_1^{\pm 1} = \pm \sqrt{3/8\pi} \sin\theta \exp(\pm i\phi) \\ d & Y_2^0 = \sqrt{5/16\pi} (3\cos^2\theta - 1) & Y_2^{\pm 1} = \pm \sqrt{15/8\pi} \sin\theta \cos\theta \exp(\pm i\phi) \\ f & Y_3^0 = \sqrt{7/16\pi} (5\cos^3\theta - 3\cos\theta) & Y_3^{\pm 1} = \pm \sqrt{21/64\pi} (5\cos^2\theta - 1) \sin\theta \exp(\pm i\phi) \\ s \\ p \\ d & Y_2^{\pm 2} = \sqrt{15/32\pi} \sin^2\theta \exp(\pm 2i\phi) \\ f & Y_3^{\pm 2} = \sqrt{105/32\pi} \sin^2\theta \cos\theta \exp(\pm 2i\phi) & Y_3^{\pm 3} = \pm \sqrt{35/64\pi} \sin^3\theta \exp(\pm 3i\phi) \end{array}$$

One-electron hydrogenic states

The three quantum number n, l, m_l denote an orbital.

Orbitals are denoted nx_{ml} , x = s, p, d, f... for l = 0, 1, 2, 3, ...

Each orbital can accommodate at most two electrons* $(m_s = \pm 1/2)$

	n	1	m _l	m _s	No of states
1s	1	0	0	±1/2	2
2s	2	0	0	±1/2	2
2p	2	1	0,±1	±1/2	6
3 s	3	0	0	±1/2	2
3 p	3	1	0,±1	±1/2	6
3d	3	2	0,±1,±2	±1/2	10
4 s	4	0	0	±1/2	2
4p	4	1	0,±1	±1/2	6
4 d	4	2	0,±1,±2	±1/2	10
4f	4	3	0,±1,±2,±3	±1/2	14

*The Pauli exclusion principle: No two electrons can have the same four quantum numbers. \Rightarrow Two electrons in the same orbital must have opposite spin.

Single-electron orbitals





3. Many-electron atom



The many-electron atom

$$\mathcal{H}_0 = \sum_i [-(\hbar^2/2m_e)\nabla_i^2 - Ze^2/4\pi\epsilon_0 r_i] + \sum_{i < j} e^2/4\pi\epsilon_0 r_{ij}.$$

Hartree-Fock approximation

- No longer a simple Coulomb potential.
- I degeneracy is lifted.
- Solution: Suppose that each electron experiences the potential of a different spherically-symmetric potential.





Addition of angular momenta



First add the orbital and spin momenta l_i and s_i to form L and S.Then couple them to give the total J

J = L + S

 $|L-S| \leq J \leq |L+S|$

Different J-states are termed multiplets, denoted by;

$$^{2S+1}X_{J}$$

$$X = S, P, D, F, ...$$
 for $L = 0, 1, 2, 3, ...$

Hund's rules

To determine the ground-state of a multi-electron atom/ion.

- 1) Maximize S
- 2) Maximize L consistent with S.
- 3) Couple *L* and S to form *J*.
 - Less than half full shell J = L-S
 - More than half full shell J = L + S

Hund's rules; examples



Note; Maximizing S is equivalent to maximizing M_s = Σm_{si} , since $M_s \leq S$



⁴F_{9/2}

Note; Maximizing L is equivalent to maximizing $M_L = \Sigma m_{li}$, since $M_L \leq L$



Ni²⁺ $3d^8$ S = I L = 3 J = 4

³F₄









4**|**_{9/2}

$$Dy^{3+} 4f^{9}$$

S = 5/2 L = 5 J = 15/2
 $^{6}H_{15/2}$

Hund's rules 3d and 4f



$$\mathcal{H}_{so}$$
=AL.S

 Λ is the spin-orbit coupling constant

 $\Lambda > 0$ for the 1st half of the 3d or 4f series. $\Lambda < 0$ for the 2nd half of the 3d or 4f series.

(for Hund's 3rd rule)

Compare single-electron atom case:	$\mathcal{H}_{so} = \lambda \mathbf{I}.\mathbf{s}$
	50

$$\Lambda = \pm \lambda/2S$$

	ion	Λ(K)
3d ¹	Ti ³⁺	124
3d ²	Ti ²⁺	88
3d ³	V ²⁺	82
3d4	Cr ²⁺	85
3d ⁶	Fe ²⁺	-164
3d ⁷	Co ²⁺	-272
3d ⁸	Ni ²⁺	-493

L.S = $(1/2)(J^2 - L^2 - S^2) = (\hbar^2/2)[J(J+1) - L(L+1) - S(S+1)]$

The magnetic moment of an ion is represented by the expression \mathcal{M} = - (\mathbf{L} + 2 \mathbf{S}) $\mu_{\rm B}/\hbar$

The Zeeman Hamiltonian for the magnetic moment in a field **B** along \mathbf{e}_z is $\mathcal{H}_{\text{Zeeman}} = -m\mathbf{B}$

$$\mathcal{H}_{\text{Zeeman}} = (\mu_{\text{B}}/\hbar)(\boldsymbol{L}_{z} + 2\boldsymbol{S}_{z})B_{z}$$

For a particular J-multiplet the matrix elements of L + 2S are proportional to those of J (Wigner Eckart theorem)



Landé g-factor

The vector model of the atom, including magnetic moments. First project \mathcal{M} onto J. J then precesses around z.

The g-factor for the atom or ion is the ratio of the component of magnetic moment along \mathbf{J} in units of $\mu_{\rm B}$ to the magnitude of the angular momentum in units of \hbar .

 $\begin{array}{l} g_{J} = (\boldsymbol{L} + 2\boldsymbol{S}) \mbox{ Take scalar product with } \boldsymbol{J} \\ g_{J} = -(\boldsymbol{\mathcal{M}}.\boldsymbol{J}/\mu_{B})/(\boldsymbol{J}^{2}/\hbar) \mbox{ = -}\boldsymbol{\mathcal{M}}.\boldsymbol{J}(\hbar/\mu_{B})/[(J(J+1))] \end{array}$

but $\mathcal{M}.J = -(\mu_{B}/\hbar)\{(L + 2S).(L + S)\} \qquad J^{2} = J(J + I)\hbar^{2}; \qquad J_{z} = M_{J}\hbar -(\mu_{B}/\hbar)\{(L^{2} + 3L.S + 2S^{2})\} -(\mu_{B}/\hbar)\{(L^{2} + 2S^{2} + (3/2)(J^{2} - L^{2} - S^{2})\} \text{ since } J^{2} = L^{2} + S^{2} + 2LS -(\mu_{B}/\hbar)\{((3/2)J^{2} - (1/2)L^{2} + (1/2)S^{2})\} -(\mu_{B}/\hbar)\{((3/2)J(J + I) - (1/2)L(L + I) + (1/2)S(S + I)\}$

hence

 $g = 3/2 + {S(S+1) - L(L+1)}/{2J(J+1)}$

Check; $g_S = 2$, $g_L = 1$

Ζ

m

S

Co²⁺ free ion

The energy levels for a free ion with electronic configuration $3d^7$: Co^{2+} $S = \frac{3}{2}, L = 3, J = \frac{9}{2}; g = \frac{5}{3}.$



4. Paramagnetism



Paramagnetic susceptibility - Brillouin theory

Curie law
$$\chi = C/T$$

Curie's constant.
Units: Kelvin, K.
Typical values ~ IK
The thermodynamic average of the moment: $\langle \mathfrak{m} \rangle = \frac{\sum_{i} \mathfrak{m}_{i} \exp(-\varepsilon_{i}/k_{B}T)}{\sum_{i} \exp(-\varepsilon_{i}/k_{B}T)}$
 $\mathbf{B} = B_{z}$
 $E = -m.B$ \Rightarrow $\langle \mathfrak{m}_{z} \rangle = \frac{\sum_{-J}^{J} -g\mu_{B}M_{J}(1 - \mu_{0}g\mu_{B}M_{J}H/k_{B}T)}{\sum_{-J}^{J}(1 - \mu_{0}g\mu_{B}M_{J}H/k_{B}T)}$
Using the identities:
 $\sum_{-J}^{J} 1 = 2J + 1;$ $\sum_{-J}^{J} M_{J} = 0$ $\sum_{-J}^{J} M_{J}^{2} = J(J + 1)(2J + 1)/3,$
and the fact that $X = n\langle m \rangle/H$ (*n* is the number density of atoms/ions)
we find $C = \frac{\mu_{0}ng^{2}\mu_{B}^{2}J(J + 1)}{3k_{B}}.$ $X = \mu_{0}nm_{eff}^{2}\mu_{B}^{2}/3k_{B}T$



Energy levels of an ion with J = 5/2 in an applied field

4f ions

	Table 4.6.	The sat	e 4 f turati	ions. on m	The p omen	aramagneti t m ₀ are in	ic moment \mathfrak{m}_{eff} and tunits of $\mu_{\mathcal{B}}$	he
4 <i>f</i>	n	S	L	J	8	$m_0 = gJ$	$m_{eff} = g\sqrt{J(J+1)}$	$m_{e\!f\!f}^{e\!c\!p}$
1	Ce ³⁺	$\frac{1}{2}$	3	52	67	2.14	2.54	2.5
2	Pr ³⁺	1	5	4	45	3.20	3.58	3.5
3	Nd ³⁺	<u>3</u> 2	6	<u>9</u> 2	<u>8</u> 11	3.27	3.52	3.4
4	Pm ³⁺	2	6	4	3 5	2.40	2.68	
5	Sm ³⁺	<u>5</u> 2	5	<u>5</u> 2	27	0.71	0.85	1.7
6	Eu ³⁺	3	3	0	0	0	0	3.4
7	Gd ³⁺	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	8.9
8	Tb ³⁺	3	3	6	$\frac{3}{2}$	9.0	9.72	9.8
9	Dy ³⁺	<u>5</u> 2	5	15 2	<u>4</u> 3	10.0	10.65	10.6
10	Ho ³⁺	2	6	8	54	10.0	10.61	10.4
11	Er ³⁺	$\frac{3}{2}$	6	15 2	<u>6</u> 5	9.0	9.58	9.5
12	Tm ³⁺	1	5	6	76	7.0	7.56	7.6
13	Yb ³⁺	$\frac{1}{2}$	3	$\frac{7}{2}$	87	4.0	4.53	4.5

J is a good euantum number

3d ions

	Table	e 4.7	. Th	e 3 <i>d</i>	ions.	. m _{eff} is in units	s of μ_B	
3d ⁿ		s	L	J	g	$m_{eff} = g\sqrt{J(J+1)}$	$m_{eff} = g\sqrt{S(S+1)}$	$m_{e\!f\!f}^{e\!x\!p}$
1	Ti^{3+}, V^{4+}	$\frac{1}{2}$	2	$\frac{3}{2}$	45	1.55	1.73	1.7
2	Ti ²⁺ , V ³⁺	1	3	2	23	1.63	2.83	2.8
3	V ²⁺ , Cr ³⁺	<u>3</u> 2	3	<u>3</u> 2	25	0.78	3.87	3.8
4	Cr ²⁺ , Mn ³⁺	2	2	0			4.90	4.9
5	Mn ²⁺ , Fe ³⁺	<u>5</u> 2	0	52	2	5.92	5.92	5.9
6	Fe ²⁺ , Co ³⁺	2	2	4	32	6.71	4.90	5.4
7	Co ²⁺ , Ni ³⁺	$\frac{3}{2}$	3	<u>9</u> 2	43	6.63	3.87	4.8
8	Ni ³⁺	1	3	4	54	5.59	2.83	3.2
9	Cu ²⁺	$\frac{1}{2}$	2	<u>5</u> 2	<u>6</u> 5	3.55	1.73	1.9

S is a good quantum number L is 'quenched' ESM Cluj 2015

Magnetization curve - Brillouin theory

To calculate the complete magnetization curve, set $y = g\mu_B \mu_0 H/k_B T$, then

$$\langle m \rangle = g\mu_B \partial / \partial y[\ln\Sigma_J \exp\{M_J y\} [d(\ln z)/dy = (1/z) dz/dy]$$

The sum over the energy levels must be evaluated; it can be written as $exp(Jy) \{I + r + r^2 +r^{2J}\}$ where $r = exp\{-y\}$ The sum of a geometric progression $(I + r + r^2 + + r^n) = (r^{n+1} - I)/(r - I)$

:.
$$\Sigma_{J} \exp{\{M_{J}y\}} = (\exp{\{-(2J+1)y\}} - 1)\exp{\{Jy\}}/(\exp{\{-y\}}-1)$$

multiply top and bottom by $\exp\{y/2\}$ = $[\sinh(2J+1)y/2]/[\sinh y/2]$ $\langle m \rangle$ = $g\mu_B(\partial/\partial y)\ln\{[\sinh(2J+1)y/2]/[\sinh y/2]\}$ = $g\mu_B/2 \{(2J+1)\coth(2J+1)y/2 - \coth y/2\}$ setting x = Jy, we obtain

 $\langle \mathfrak{m}_z \rangle = \mathfrak{m}_0 \mathcal{B}_J(x)$

where $\mathcal{B}_{l}(x)$ is the Brillouin function { }

$$\langle \mathfrak{m}_{z} \rangle = \mathfrak{m}_{0} \left\{ \frac{2J+1}{2J} \operatorname{coth} \frac{2J+1}{2J} x - \frac{1}{2J} \operatorname{coth} \frac{x}{2J} \right\}$$

This reduces to $\langle m \rangle = \mu_B \tanh(x)$ in the limit $J = \frac{1}{2}$, g = 2. and $\langle m \rangle = \mathcal{L}(x)$ is the Langevin function {coth x - 1/x} in the large-J limit.

Magnetization curves for paramagnetic ions



Experimental confirmation



Reduced magnetization curves of three paramagnetic salts, compared with Brillouin function predictions

5. Crystal field



Summary – so far

- Filled electronic shells are not magnetic (the spins are paired; $m_s = \pm I/2$)
- Only partly-filled shells may possess a magnetic moment
- The magnetic moment is given by $m = g_j \mu_B J$, where $\hbar J$ represents the total angular momentum. For a given configuration the values of J and g_j in the ground state are given by Hund's rules

—<u>**</u>**—

When the ion is embedded in a solid, the crystal field interaction is important. This is the electrostatic Coulomb interaction of an ion with its surroundings. The third point is modified:

• Orbital angular momentum for 3*d* ions is *quenched*. The spin only moment is $m \approx g\mu_B S$, with g = 2.

• Magnetocrystalline anisotropy appears, making certain crystallographic axes easy directions of magnetization.

Magnitudes of the interactions

The Hamiltonian is now

$$\mathcal{H} = \mathcal{H}_{0} + \mathcal{H}_{so} + \mathcal{H}_{cf} + \mathcal{H}_{Z}$$

Typical magnitudes of energy terms (in K)

	\mathcal{H}_{0}	$\mathcal{H}_{ m so}$	$\mathcal{H}_{ ext{cf}}$	\mathcal{H}_{Z} in 1 T
3 <i>d</i>	1 - 5 10 ⁴	$10^2 - 10^3$	104	1
4 <i>f</i>	1 - 6 10 ⁵	1 - 5 10 ³	≈3 10 ²	1

 \mathcal{H}_{so} must be considered before \mathcal{H}_{cf} for 4f ions, and the converse for 3d ions. Hence J is a good quantum number for 4f ions, but S is a good quantum number for 3d ions. The 4f electrons are generally localized, and 3d electrons are localized in oxides and other ionic compounds.

Magnitudes of the interactions

 $\mathcal{H}_i = \mathcal{H}_0 + \mathcal{H}_{so} +$ \mathcal{H}_{Z}

Coulomb interactions $|L,S\rangle$

spin-orbit interaction $\Lambda L.S |J\rangle$

	ion	Λ
3d ¹	Ti ³⁺	124
3d ²	Ti ²⁺	88
3d ³	V ²⁺	82
3d ⁴	Cr ²⁺	85
3d ⁶	Fe ²⁺	-164
3d ⁷	Co ²⁺	-272
3d ⁸	Ni ²⁺	-493

4f ¹	Ce ³⁺	920
4f ²	Pr ³⁺	540
4f ³	Nd ³⁺	430
4f ⁵	Sm ³⁺	350
4f ⁸	Tb ³⁺	-410
4f ⁹	Dy ³⁺	-550
4f ¹⁰	Ho ³⁺	-780
4f ¹¹	Er ³⁺	-1170
4f ¹²	Tm ³⁺	-1900
4f ¹³	Yb ³⁺	-4140

Zeeman interaction $g\mu_{\rm B}B.J\hbar$ $|M_{\rm J}\rangle$

Crystal field interaction $\int \rho_0(\mathbf{r}) \phi_{cf}(\mathbf{r}) d^3 \mathbf{r}$

	\mathcal{H}_{0}	$\mathcal{H}_{\mathrm{so}}$	\mathcal{H}_{cf}	\mathcal{H}_{Z} in 1 T
3d	1 - 5 10 ⁴	10 ² -10 ³	10 ⁴	1
4 <i>f</i>	1 - 6 10 ⁵	1 - 5 10 ³	≈3 10²	1

3d and 4f compared



As metallic atoms or ions the transition metals occupy one third of the volume of the rare earths.

Oxides

Oxides are usually insulating. Structures are based on densepacked O²⁻ arrays, with cations in interstitial sites.



Octahedral and tetrahedral sites are common in transition metal oxides and other compounds.

Both have *cubic* symmetry if undistorted

$$R_{oct} = (2^{1/2} - 1)r_0 = 58 \text{ pm}$$
 R_{te}

$$R_{tet} = ((3/2)^{1/2} - 1)r_0 = 32 \text{ pm}$$

Cation radii in oxides: low spin values are in parentheses.

4-fold tetrahedral	pm	6-fold octahedral	pm	6-fold octahedral	pm	12-fold substitutional	pm
Mg ²⁺	53	Cr ⁴⁺ 3d ²	55	Ti ³⁺ 3d ¹	67	Ca ²⁺	134
Zn ²⁺	60	Mn ⁴⁺ 3d ³	53	V ³⁺ 3d ²	64	Sr ²⁺	144
Al ³⁺	42			Cr ³⁺ 3d ³	62	Ba ²⁺	161
Fe ³⁺ 3d ⁵	52	Mn ²⁺ 3d ⁵	83	Mn ³⁺ 3d ⁴	65	Pb ²⁺	149
		Fe ²⁺ 3d ⁶	78 (61)	Fe ³⁺ 3d ⁵	64	Y ³⁺	119
		Co ²⁺ 3d ⁷	75 (65)	Co ³⁺ 3d ⁶	61 (56)	La ³⁺	136
		Ni ²⁺ 3d ⁸	69	Ni ³⁺ 3d ⁷	60	Gd ³⁺	122

The radius of the O²⁻ anion is 140 pm

Orbital moment quenching is a cubic crystal field



To demonstrate quenching of orbital angular momentum, consider the 2p states ψ^0 , ψ^1 , ψ^{-1} corresponding to I = I, $m_l = 0, \pm 1$.

The functions are eigenstates in the central potential V (r) but they are not eigenstates of H_{cf} . Suppose the oxygens can be represented by point charges q at their centres, then for the octahedron,

$$\mathcal{H}_{cf} = V_{cf} = D(x^4 + y^4 + z^4 - 3y^2z^2 - 3z^2x^2 - 3x^2y^2)$$

where $D \approx eq/4\pi\epsilon_0 a^6$. But $\psi^{\pm 1}$ are *not* eigenfunctions of $V_{cf_i} e.g_i \oint \psi_i^* V_{cf} \psi_j dV \neq \delta_{ij}$, where i, j = -1, 0, 1. We seek linear combinations that are eigenfunctions, namely

$$\begin{split} \psi^0 &= R(r)\cos\theta &= zR(r) = p_z \\ (1/\sqrt{2})(\psi^1 + \psi^{-1}) &= R'(r)\sin\theta\cos\phi &= yR(r) = p_y \\ (1/\sqrt{2})(\psi^1 - \psi^{-1}) &= R'(r)\sin\theta\sin\phi &= xR(r) = p_x \end{split}$$



The 2p eigenfunctions are degenerate in an undistorted cubic environment

ψ^0 =	$R(r) \cos \theta$	$= zR(r) = p_z$
$(1/\sqrt{2})(\psi^1 + \psi^{-1}) =$	R' (r) $\sin\theta\cos\phi$	= yR(r) $=$ p _x
$(1/\sqrt{2})(\psi^1 - \psi^{-1}) =$	R' (r)sin	= xR(r) $=$ p _y

 $p_x \ p_y \ p_z$

Note that the z-component of angular momentum; $\mathbf{l}_{z} = i\hbar/\partial\phi$ is *zero* for these wavefunctions. Hence the orbital angular momentum is quenched.

The same is true of the 3d eigenfunctions, which are

The 3d eigenfunctions split into a set of three and a set of two in an undistorted cubic environment

Notation; a or b denote a nondegenerate single-electron orbital, e a twofold degenerate orbital and t a threefold degenerate orbital. Capital letters refer to multielectron states. a, A are nondegenerate and symmetric with respect to the principal axis of symmetry (the sign of the wavefunction is unchanged), b. B are antisymmetric with respect to the principal axis (the sign of the wavefunction changes). Subscripts g and u indicate whether the wavefunction is symmetric or

Orbitals in a cubic crystal field



Orbitals in the crystal field



Crystal-field theory regards the splitting of the 3*d* orbitals in octahedral oxygen, for example, as an electrostatic interaction with neighbouring point charges (oxygen anions). In reality the 3*d* and 2*p* orbitals of oxygen overlap to form a partially covalent bond. The oxygens bonding to the 3*d* metals are the *ligands*. The overlap is greater for the e_g than the t_{2g} orbitals in octahedral coordination.

The overlap leads to mixed wavefunctions, producing bonding and antibonding orbitals, whose splitting increases with overlap. The hybridized orbitals are

$$\phi = \alpha \psi_{2p} + \beta \psi_{3d}$$

where $\alpha^2 + \beta^2 = 1$.

For 3*d* ions the splitting is usually 1- 2eV, with the ionic and covalent contributions being of comparable magnitude

The spectrochemical series is the sequence of ligands in order of effectiveness at producing crystal/ligand field splitting.

Br⁻<Cl⁻<F⁻<OH⁻<CO²⁻₃<O²⁻<H₂O<NH₃<SO²⁻₃<NO⁻₂<S²⁻<CN⁻

The bond is mostly ionic at the beginning of the series and covalent at the end.

Covalency is stronger in tetrahedral coordination but the crystal field splitting is $\Delta_{tet} = (3/5)\Delta_{oct}$





Lower symmetry

As the site symmetry is reduced, the degeneracy of the one-electron energy levels is raised. For example, a tetragonal extension of the octahedron along the z-axis will lower p_z and raise p_x and p_y . The effect on the d-states is shown below. The degeneracy of the d-levels in different symmetry is shown in the table.





The effect of a tetragonal distortion of octahedral symmetry on the one-electron energy levels.

The splitting of the 1-electron levels in different symmetry

	1	Cubic	Tetragonal	Trigonal	Rhombohedral
S	1	1	1	1	1
p	2	3	1,2	1,2	1,1,1
d	3	2,3	1,1,1,2	1,2,2	1,1,1,1,1
f	4	1,3,3	1,1,1,2,2	1,1,1,2,2	1,1,1,1,1,1,1



The Jahn-Teller effect



•A system with a single electron (or hole) in a degenerate level will tend to distort spontaneously.

•The effect is particularly strong for *d*⁴ and *d*⁹ ions in octahedral symmetry (Mn³⁺, Cu²⁺) which can lower their energy by distorting the crystal environment- this is the *Jahn-Teller* effect.

•If the local strain is \mathcal{E} , the energy change is

 $\delta E = -A\mathcal{E} + B\mathcal{E}^2.$

where the first term is the crystal field stabilization energy and the second term is the increased elastic energy.

•The Jahn-Teller distortion may be static or dynamic.

High and low spin states

An ion is in a high spin state or a low spin state depending on whether the Coulomb interaction l leading to Hund's first rule (maximize S) is greater than or less than the crystal field splitting Δ_c

Consider a 3d⁶ ion such as Fe³⁺.



 $U_H > \Delta_{cf}$. gives a high-spin state, S = 2 e.g. FeCl₂ $U_H < \Delta_{cf}$. gives a low-spin state, S = 0 e.g. Pyrite FeS₂

Crystal Field Hamiltonian

$$\mathcal{H}_{cf} = \int \rho_0(r) \varphi_{cf}(r) \mathrm{d}^3 r.$$

Charge distribution of the ion

potential created by the crystal

$$\varphi_{cf}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \mathrm{d}^3 \mathbf{r}'.$$

Here 1/|r - r'| can be expanded spherical harmonics using spherical polar coordinates $r = (r, \theta, \phi)$ and $r' = (r', \theta', \phi')$:

$$\frac{1}{|r-r'|} = \frac{1}{r'} \sum_{n=0}^{\infty} \frac{4\pi}{(2n+1)} \left(\frac{r}{r'}\right)^n \sum_{m=-n}^n (-1)^m Y_n^{-m}(\theta',\phi') Y_n^m(\theta,\phi).$$

Hence

$$\varphi_{cf}(r,\theta,\phi) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} r^n \gamma_{nm} Y_n^m(\theta,\phi),$$

where

$$\gamma_{nm} = \frac{4\pi}{(2n+1)} \int \frac{\rho(r')(-1)^m Y_n^{-m}(\theta',\phi')}{r'^{n+1}} \mathrm{d}^3 r'.$$

structural parameters

The approximation made so far is *terrible*. It ignores the screening of the potential by the outer shells of the 4*f* ion for example, and also the covalent contribution. But it captures the symmetry of the problem. We proceed with it, but treat the crystal field coefficients as empirical parameters.

It is useful to expand the charge distribution of a central 4f ion in terms of the 2^n -pole moments of the charge distribution, n = 2, 4, 6

The quadrupole moment

$$Q_2 = \int \rho_{4f}(r) (3\cos^2\theta - 1)r^2 d^3r.$$

The hexadecapole moment

$$Q_4 = \int \rho_{4f}(r) (35\cos^4\theta - 30\cos^2\theta + 3)r^4 d^3r,$$

The 64-pole moment

$$Q_6 = \int \rho_{4f}(r)(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)r^6 d^3r.$$

Rare earth quadrupole moments



Single-ion anisotropy

Single-ion anisotropy is due to the electrostatic crystal field interaction + spin-orbit interaction. The 4f charge distribution $\rho_0(\mathbf{r})$ interacts with the crystal field potential $\varphi_{cf}(\mathbf{r})$ to stabilizes some particular orbitals; spin-orbit interaction - $\Lambda L.S$ then leads to magnetic moment alignment along some specific directions in the crystal.

The leading term in the crystal field interaction is

$$\varepsilon_a = (1/2)Q_2 A_2^0 (3\cos^2\theta - 1),$$

where A_2^0 is the uniaxial second-order crystal field parameter, which described the electric field gradient created by the crystal which interacts with the 4*f* quadrupole moment. Compare $\varepsilon_a = K_1 \sin^2 \theta$

The crystal field interaction can be expressed in terms of angular momentum operators, using the Wigner-Eckart theorem



Here $B_n^m = \theta_n \langle r_{4f}^n \rangle A_n^m$ and θ_n is different for each 4f ion, proportional to the 2ⁿ-pole moment

$$Q_2 = 2 \theta_2 \langle r_{4f}^2 \rangle \qquad \qquad Q_4 = 8 \theta_4 \langle r_{4f}^4 \rangle \qquad \qquad Q_6 = 16 \theta_6 \langle r_{4f}^6 \rangle$$

 $A_n^m \sim \gamma_{nm}$ parameterises the crystal field produced by the lattice.

NB.
$$Q_2 \neq 0$$
 for J (or L) ≥ 1
 $Q_4 \neq 0$ for J (or L) ≥ 2
 $Q_6 \neq 0$ for J (or L) ≥ 3

The Stevens operators are tabulated, as well as which ones feature in each point symmetry

e.g. The leading term in any uniaxial site is the one in O_2^0

$$\hat{\mathbf{O}}_2^0 = [3\,\hat{J}_z^2 - J(J+1)].$$

The complete second order (uniaxial) cf Hamiltonian is

$$\mathcal{H}_{cf} = \theta_2 \left< r_{\text{ESM}}^2 \left< A_2^0 \hat{\mathbf{O}}_3^0 + A_2^2 \hat{\mathbf{O}}_2^{2(c)} \right]$$



Charge distributions of the rare-earth ions. Those with a positive quadrupole moment ($\theta_2 > 0$), italic type distinguished from those with a negative quadrupole moment ($\theta_2 < 0$) bold type. Note the quarter-shell changes,



The cf Hamiltonian for a site with cubic symmetry is

$$\mathcal{H}_{cf} = \theta_4 \langle r_{4f}^4 \rangle \Big[A_4^0 \hat{\mathbf{O}}_4^0 + 5A_4^{4(c)} \hat{\mathbf{O}}_2^{2(c)} \Big] + \theta_6 \langle r_{4f}^6 \rangle \Big[A_6^0 \hat{\mathbf{O}}_6^0 - 21A_6^0 \hat{\mathbf{O}}_2^{2(c)} \Big]$$

For 3*d* ions only the fourth-order terms exist; (I = 2)

Kramer's theorem

It follows from time-reversal symmetry that the cf energy levels of any ion with an odd number of electrons, and therefore half-integral angular momentum, must be at least 2-fold degenerate. These are the $|\pm M_{\rm I}\rangle$ Kramers doublets.

When J is integral, ther will be a $|0\rangle$ singlet (with no magnetic moment) and a series of doublets.







