Origin of magnetism

e-ESM, an online
higher-education Magnetism event

Stephen Blundell
University of Oxford

European School of Magnetism 2020

1

1

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

2

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

3

Lagrangian for a charged particle in a magnetic field

Lagrangian $\quad L = \underbrace{\text{kinetic energy}}_{\frac{1}{2}mv^2} - \underbrace{\text{potential energy}}_{qv^\mu A_\mu}$

$$v^\mu = (c, \vec{v}) \quad A^\mu = \left(\frac{V}{c}, \vec{A}\right) \quad A_\mu = \left(\frac{V}{c}, -\vec{A}\right)$$

$$\Rightarrow L = \frac{1}{2}mv^2 - qV + q\vec{v}\cdot\vec{A}$$

$\Rightarrow$ canonical momentum $\quad \vec{p} = \frac{\partial L}{\partial \vec{v}} = m\vec{v} + q\vec{A}$

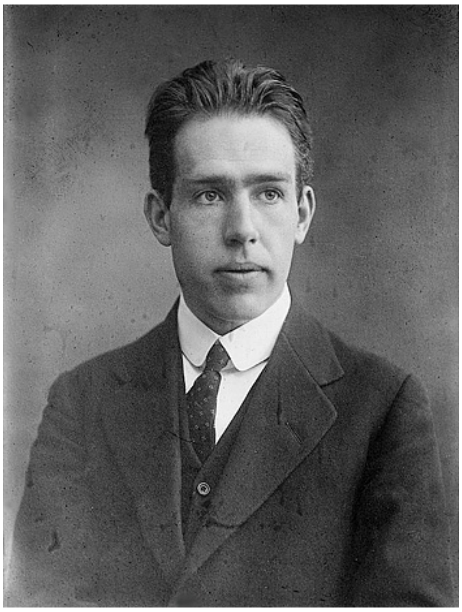
$$H = \vec{p}\cdot\vec{v} - L = \frac{1}{2}mv^2 + qV = \frac{(\vec{p} - q\vec{A})^2}{2m} + qV$$

$$m\dot{\vec{v}} = q(\underbrace{\vec{E}}_{-\nabla V - \dot{\vec{A}}} + \vec{v}\times\vec{B}) \qquad \nabla\times\vec{A}$$

Lagrangian for a charged particle in a magnetic field

Effect of magnetic field $\vec{B} = \nabla \times \vec{A}$
is $\vec{p} = m\vec{v} + q\vec{A}$
and so the kinetic energy $\frac{1}{2}mv^2$
becomes $\dfrac{(\vec{p} - q\vec{A})^2}{2m}$ gauge invariant

Bohr-van Leeuwen theorem



Niels Bohr
(1885-1962)

Hendrika Johanna van Leeuwen
(1887-1974)

Bohr-van Leeuwen theorem

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A}$$

$$\Longrightarrow Z = \int\int\cdots\int \exp(-\beta E(\{\mathbf{r}_i, \mathbf{p}_i\})\ \mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_N\ \mathrm{d}\mathbf{p}_1\cdots\mathrm{d}\mathbf{p}_N$$

In a magnetic field, we replace $\mathbf{p}_i$ by $\mathbf{p}_i - q\mathbf{A}$

Bohr-van Leeuwen theorem

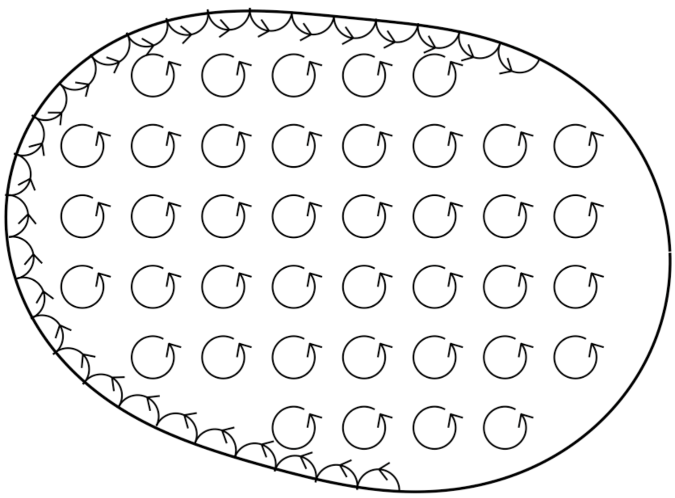
$$\mathbf{p} = m\mathbf{v} + q\mathbf{A}$$

$$\Longrightarrow Z = \int\int\cdots\int \exp(-\beta E(\{\mathbf{r}_i, \mathbf{p}_i\})\ \mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_N\ \mathrm{d}\mathbf{p}_1\cdots\mathrm{d}\mathbf{p}_N$$

In a magnetic field, we replace $\mathbf{p}_i$ by $\mathbf{p}_i - q\mathbf{A}$

$$F = -k_{\mathrm{B}}T\log Z$$

$$\mathbf{M} = -\left(\frac{\partial F}{\partial B}\right)_T$$

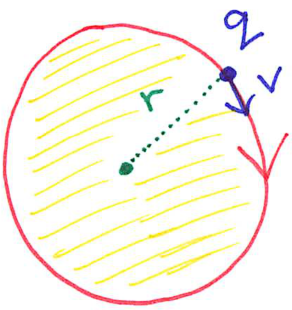


Outline

9

Orbtial magnetism – connection to angular momentum

ORBITAL ANGULAR MOMENTUM



$$I = \frac{q}{2\pi r / v}$$

Magnetic moment $\mu = I\pi r^2 = \frac{q}{2m}\underbrace{mvr}_{L}$

GYROMAGNETIC RATIO γ

Orbtial magnetism – connection to angular momentum

LINEAR MOMENTUM

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$$

e^{ikx} eigenfunction

$\hbar k$ eigenvalue

ANGULAR MOMENTUM

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$e^{im\phi}$ eigenfunction

$m\hbar$ eigenvalue

INTEGER $\because e^{im(\phi+2\pi)} = e^{im\phi}$

Orbtial magnetism – connection to angular momentum

LINEAR MOMENTUM

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$$

e^{ikx} eigenfunction

$\hbar k$ eigenvalue

ANGULAR MOMENTUM

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$e^{im\phi}$ eigenfunction

$m\hbar$ eigenvalue

INTEGER $\because e^{im(\phi+2\pi)} = e^{im\phi}$

$$\hat{\underline{L}} = \hat{\underline{r}} \times \hat{\underline{p}} = -i\hbar\, \underline{r} \times \nabla$$

$$\hat{L}_z = i\hbar \left[y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right] = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}_z |\ell, m\rangle = m\hbar |\ell, m\rangle \qquad \hat{L}^2 |\ell, m\rangle = \ell(\ell+1)\hbar^2 |\ell, m\rangle$$

$$\langle \theta, \phi | \ell, m\rangle = Y_\ell^m(\theta,\phi) \propto P_\ell^m(\cos\theta)\, e^{im\phi}$$

SPHERICAL HARMONICS

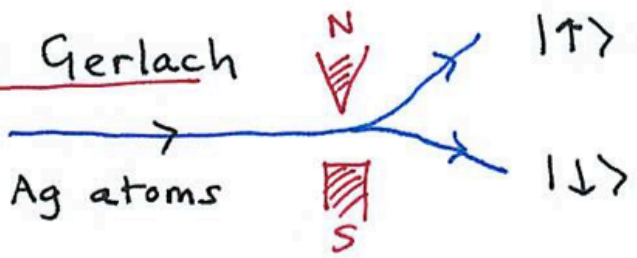
ASSOCIATED LEGENDRE POLYNOMIAL

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

Spin

Stern Gerlach



2-state system

look for Hermitian operator as 2×2 matrix

$$M = \begin{pmatrix} a & c-id \\ c+id & b \end{pmatrix} \qquad a, b, c, d \in \mathbb{R}$$

with eigenvalues ± 1.

$$\therefore \ \mathrm{Tr}\, M = \lambda_+ + \lambda_- = 0 \qquad \therefore \ b = -a$$

$$\det M = \lambda_+ \lambda_- = -1 \qquad a^2 + c^2 + d^2 = 1$$

$$M = \begin{pmatrix} a & c-id \\ c+id & -a \end{pmatrix}$$

Spin

Simplest $M = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. Call this σ_z.

Eigenvectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ eigenvalue $+1$

$\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ eigenvalue -1

General state: $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle \equiv \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$

spinor

Note $\langle\psi|\sigma_z|\psi\rangle = (\alpha^* \ \beta^*)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$

$= |\alpha|^2 - |\beta|^2$

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Spin

Look for σ_x and σ_y. To be $\perp z$, need

$$\left.\begin{aligned} \langle\uparrow_z|\sigma_\perp|\uparrow_z\rangle = 0 \\ \langle\downarrow_z|\sigma_\perp|\downarrow_z\rangle = 0 \end{aligned}\right\} \Rightarrow a = 0$$

$\therefore \ \sigma_\perp = \begin{pmatrix} 0 & c-id \\ c+id & 0 \end{pmatrix}$ with $c^2 + d^2 = 1$

i.e. $c + id = e^{i\phi}$

$$\sigma_\perp = \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix}.$$

eigenvectors

Choose $\phi = 0$ $\therefore$ $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$. $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Spin

Construct σ_y from $\langle \uparrow_x | \sigma_y | \uparrow_x \rangle = 0$

$$\therefore \quad \frac{1}{\sqrt{2}}(1 \;\; 1) \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = 0$$

$$\therefore \quad \cos\phi = 0 \qquad \therefore \quad \phi = \frac{\pi}{2} \qquad \underline{\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}$$

eigenvectors $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}, \; \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$.

$$\hat{\boldsymbol{S}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$$

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Spin

- Spin operators : $\vec{S} = \frac{1}{2}\hbar\,\vec{\sigma}$
- Raising and lowering operators : $\sigma_\pm = \sigma_x \pm i\sigma_y$

$$\sigma_+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}, \quad \sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}.$$

$$\hat{S}_z |S\; m_s\rangle = m_s\hbar\, |S\; m_s\rangle$$

$$\hat{S}_\pm |S\; m_s\rangle = \hbar\sqrt{S(S+1) - m_s(m_s\pm 1)}\; |S\; m_s \pm 1\rangle$$

$$\hat{S}^2 |S\; m_s\rangle = S(S+1)\hbar^2\, |S\; m_s\rangle$$

Spin

$$\vec{S}^a \cdot \vec{S}^b = \underbrace{S_x^a S_x^b + S_y^a S_y^b}_{\downarrow} + S_z^a S_z^b$$

re-express in terms of raising and lowering operators

$$\frac{1}{2}\left(S_+^a S_-^b + S_-^a S_+^b \right)$$

$\Rightarrow$ FLIP-FLOPS of antiparallel spins

$$\underset{a\ \ b}{\uparrow\downarrow} \longleftrightarrow \underset{a\ \ b}{\downarrow\uparrow}$$

Spin arrangements

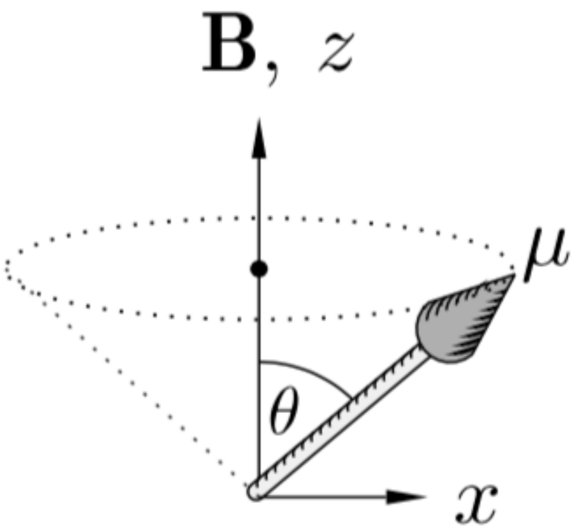
↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓
↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑
↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓ antiferromagnet
↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑
↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓↑↓

↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑
↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑
↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑ ferromagnet
↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑
↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

Spin precession



spin precession

E-fields don't do this to electric dipole moments

Spin precession

Classical treatment of spin precession

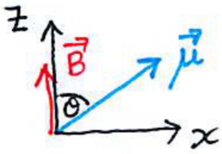
energy

$$E = -\vec{\mu}\cdot\vec{B}$$

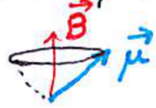
$$\vec{G} = \vec{\mu}\times\vec{B}$$

torque

$$\left.\begin{array}{l} E = -\vec{\mu}\cdot\vec{B} \\ \vec{G} = \vec{\mu}\times\vec{B} \end{array}\right\} \quad \frac{d\vec{\mu}}{dt} = \gamma\,\vec{\mu}\times\vec{B}$$



$$\begin{pmatrix}\dot{\mu}_x \\ \dot{\mu}_y \\ \dot{\mu}_z\end{pmatrix} = \begin{pmatrix}\gamma B\mu_y \\ -\gamma B\mu_x \\ 0\end{pmatrix} \Rightarrow \begin{array}{l} \mu_x(t) = |\vec{\mu}|\sin\theta\cos\omega t \\ \mu_y(t) = -|\vec{\mu}|\sin\theta\sin\omega t \\ \mu_z(t) = |\vec{\mu}|\cos\theta \end{array}$$



$\Rightarrow$ SPIN PRECESSION $\quad \omega = \gamma_\mu B$

Spin precession

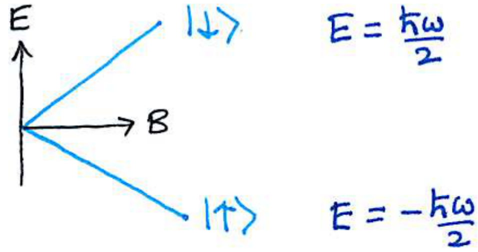
Quantum mechanics of spin-$\frac{1}{2}$

$$|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \begin{pmatrix}a \\ b\end{pmatrix} \leftarrow \text{SPINOR}$$

$$|\uparrow\rangle = \begin{pmatrix}1 \\ 0\end{pmatrix}, \qquad |\downarrow\rangle = \begin{pmatrix}0 \\ 1\end{pmatrix}$$

$$\hat{H} = -\vec{\mu}\cdot\vec{B} = -\frac{\hbar}{2}\gamma B\sigma_z = -\frac{\hbar\omega}{2}\begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}$$

$$\vec{S} = \frac{\hbar}{2}\vec{\sigma}$$



Zeeman splitting

Pauli spin matrices

$$\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

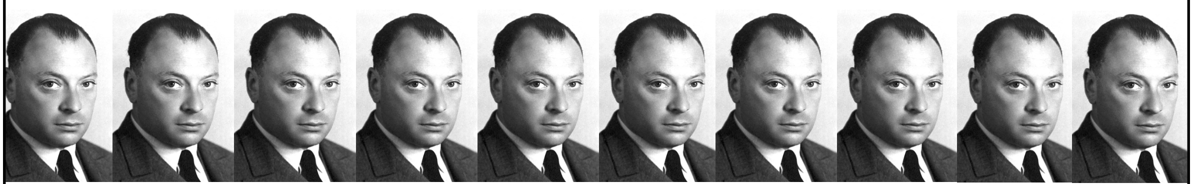
$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

For a general direction $\hat{\vec{n}}$

$$\hat{n}\cdot\vec{\sigma} = \begin{pmatrix} n_z & n_x - i n_y \\ n_x + i n_y & -n_z \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta\, e^{-i\phi} \\ \sin\theta\, e^{i\phi} & -\cos\theta \end{pmatrix}$$

Eigenstates are $|+\rangle = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2}\, e^{i\phi} \end{pmatrix}$ $\quad |-\rangle = \begin{pmatrix} \sin\frac{\theta}{2} \\ \cos\frac{\theta}{2}\, e^{i\phi} \end{pmatrix}$



Pauli spin matrices

σ_x	σ_y	σ_z
$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Eigenstates

$\lvert\uparrow_x\rangle$	$\lvert\downarrow_x\rangle$	$\lvert\uparrow_y\rangle$	$\lvert\downarrow_y\rangle$	$\lvert\uparrow_z\rangle$	$\lvert\downarrow_z\rangle$
$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \mathrm{i} \end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -\mathrm{i} \end{pmatrix}$	$\begin{pmatrix} 1 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Spin precession

Quantum mechanical treatment of spin precession (1)

$B \parallel z$ Initial muon polarization

$$|\psi(0)\rangle = \begin{pmatrix} \cos\theta/2 \\ \sin\theta/2 \end{pmatrix} = \cos\frac{\theta}{2}\,|\uparrow\rangle + \sin\frac{\theta}{2}\,|\downarrow\rangle$$

Time-dependence : $\hat{H}|\psi\rangle = i\hbar\frac{d}{dt}|\psi\rangle$

$$|\psi(t)\rangle = e^{i\omega t/2}\cos\frac{\theta}{2}\,|\uparrow\rangle + e^{-i\omega t/2}\sin\frac{\theta}{2}\,|\downarrow\rangle$$

$$\left.\begin{aligned} \langle\psi(t)|\sigma_x|\psi(t)\rangle &= \sin\theta\cos\omega t \\ \langle\psi(t)|\sigma_y|\psi(t)\rangle &= -\sin\theta\sin\omega t \\ \langle\psi(t)|\sigma_z|\psi(t)\rangle &= \cos\theta \end{aligned}\right\}$$ spin precession

Spin precession

Quantum mechanical treatment of spin precession (2)

Time-evolution operator $\hat{H} = -\frac{\hbar\omega}{2}\,\vec{n}\cdot\vec{\sigma}$

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar} = \cos\frac{\omega t}{2}\,I + i\sin\frac{\omega t}{2}\,\overbrace{\hat{n}\cdot\vec{\sigma}}^{\sigma_z}$$

$$|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle = \begin{pmatrix} \cos\frac{\omega t}{2} + i\sin\frac{\omega t}{2} & 0 \\ 0 & \cos\frac{\omega t}{2} - i\sin\frac{\omega t}{2} \end{pmatrix}\begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix}$$

$$= \begin{pmatrix} e^{i\omega t/2}\cos\frac{\theta}{2} \\ e^{-i\omega t/2}\sin\frac{\theta}{2} \end{pmatrix}$$ → same result

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

total angular momentum

orbital angular momentum

spin angular momentum

$$\hat{\vec{\mu}} = -\mu_B(\hat{\vec{L}} + g\hat{\vec{S}}) = -g_J \mu_B \hat{\vec{J}}$$

$$\hat{\vec{\mu}} \cdot \hat{\vec{J}} = g_J \mu_B \underbrace{\hat{\vec{J}}^2}_{J(J+1)}$$

$$= \mu_B(\underbrace{\hat{\vec{L}} \cdot \hat{\vec{J}}}_{\frac{1}{2}(\hat{J}^2 + \hat{L}^2 - \hat{S}^2)} + 2\underbrace{\hat{\vec{S}} \cdot \hat{\vec{J}}}_{\frac{1}{2}(\hat{J}^2 - \hat{L}^2 + \hat{S}^2)}) \quad (g = 2)$$

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

Hund's rules

- maximise S
- maximise L
- fix $J = \begin{cases} |L-S| & < \frac{1}{2} \text{ full} \\ L+S & > \frac{1}{2} \text{ full} \end{cases}$

e.g. Dy^{3+} $4f^9$ f electrons have $\ell = 3$

m_ℓ	↑	↓
3	•	•
2	•	•
1	•	
0	•	
−1	•	
−2	•	
−3	•	

$S = \frac{5}{2}$, $L = 5$

$> \frac{1}{2}$ full $\Rightarrow$ $J = \frac{15}{2}$

$\Rightarrow$ $\underbrace{{}^{6}}_{2S+1}\underbrace{H}_{L=5}\underbrace{{}_{15/2}}_{J}$

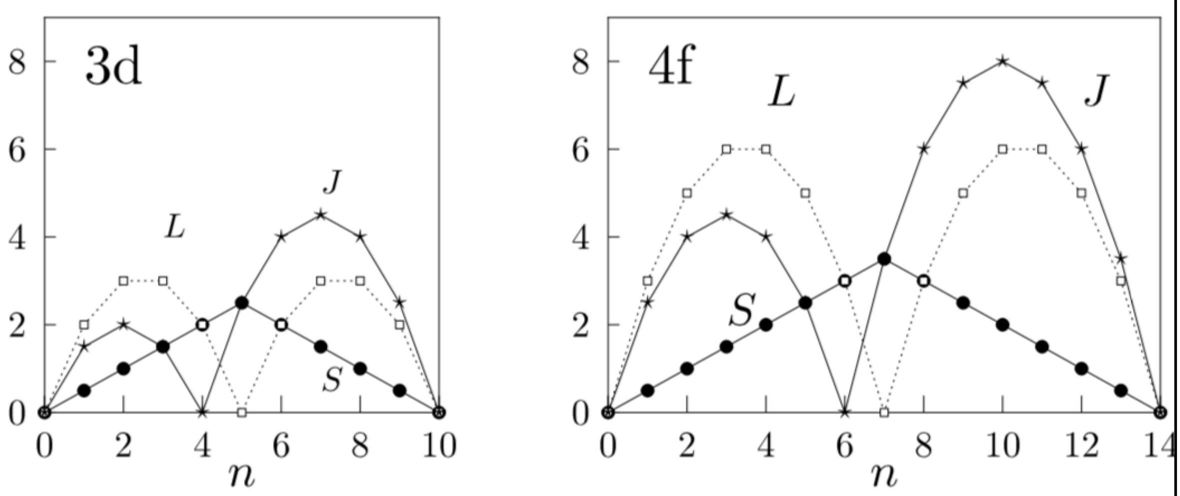
${}^{2S+1}L_J$

L	0	1	2	3	4	5	6	…
	S	P	D	F	G	H	I	…

31

Hund's rules

- maximise S
- maximise L
- fix $J = \begin{cases} |L-S| & < \frac{1}{2} \text{ full} \\ L+S & > \frac{1}{2} \text{ full} \end{cases}$



S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

32

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

Hamiltonian for electrons in an atom in a B field

Electrons in an atom

$$\hat{H} = \sum_{i=1}^{Z} \frac{\left(\vec{p}_i + e\vec{A}(\vec{r}_i)\right)^2}{2m_e} + V_i \quad + \underbrace{g\mu_B \vec{B}\cdot\vec{S}}_{\text{add Zeeman term for spin}}$$

choose gauge $\vec{A}(\vec{r}) = \frac{\vec{B}\times\vec{r}}{2}$

then a short calculation gives

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} \quad + \underbrace{\mu_B\underbrace{(\vec{L} + g\vec{S})\cdot\vec{B}}_{\text{Zeeman term}}}_{\text{paramagnetic}} \quad + \underbrace{\frac{e^2}{8m_e}\sum_i \left(\vec{B}\times\vec{r}_i\right)^2}_{\text{diamagnetic}}$$

dominant perturbation (if non-zero)

$$\hbar\vec{L} = \sum_i \vec{r}_i \times \vec{p}_i$$

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} \quad + \underbrace{\mu_B\underbrace{(\vec{L} + g\vec{S})\cdot\vec{B}}_{\text{Zeeman term}}}_{\text{paramagnetic}} \quad + \underbrace{\frac{e^2}{8m_e}\sum_i \left(\vec{B}\times\vec{r}_i\right)^2}_{\text{diamagnetic}}$$

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\mu_B(\vec{L} + g\vec{S})\cdot\vec{B}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e}\sum_i (\vec{B}\times\vec{r}_i)^2}_{\text{diamagnetic}}$$

Zeeman term

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\mu_B(\vec{L} + g\vec{S})\cdot\vec{B}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e}\sum_i (\vec{B}\times\vec{r}_i)^2}_{\text{diamagnetic}}$$

Zeeman term

$B // z$ $\quad \therefore \; \vec{B}\times\vec{r}_i = B(-y_i, x_i, 0)$

$\therefore \; (\vec{B}\times\vec{r}_i)^2 = B^2(x_i^2 + y_i^2)$

$$\Delta E_0 = \frac{e^2B^2}{8m_e}\sum_{i=1}^{Z}\langle 0 | x_i^2 + y_i^2 | 0\rangle$$

spherically symmetric atom $\quad \langle x_i^2\rangle = \langle y_i^2\rangle = \langle z_i^2\rangle$
$= \frac{1}{3}\langle r_i^2\rangle$

$$\Rightarrow \Delta E_0 = \frac{e^2B^2}{12m_e}\sum_{i=1}^{Z}\langle r_i^2\rangle$$

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\underset{\text{Zeeman term}}{\mu_B(\vec{L} + g\vec{S})\cdot\vec{B}}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e}\sum_i (\vec{B}\times\vec{r}_i)^2}_{\text{diamagnetic}}$$

$\chi \ll 1 \quad \therefore \quad \chi \equiv \frac{M}{H} \cong \frac{\mu_0 M}{B}$ and $M = -\frac{N}{V}\frac{\partial \Delta E_0}{\partial B}$

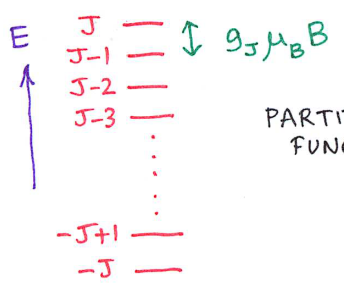
$$\Rightarrow \quad \chi = -\frac{N}{V}\frac{e^2\mu_0}{6m_e}\sum_{i=1}^{Z}\langle r_i^2\rangle$$

diamagnetism is

- weak
- negative
- T-independent

$$\sum_{i=1}^{Z}\langle r_i^2\rangle \approx Z_{eff}\, r^2$$

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\underset{\text{Zeeman term}}{\mu_B(\vec{L} + g\vec{S})\cdot\vec{B}}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e}\sum_i (\vec{B}\times\vec{r}_i)^2}_{\text{diamagnetic}}$$



PARTITION FUNCTION

$$Z = \sum_i e^{-\beta E_i} \qquad \beta = 1/k_B T$$

$$= \sum_{m_J=-J}^{J} e^{-\beta m_J g_J \mu_B B} \qquad x = g_J\mu_B B/k_B T$$

$$= \frac{\sinh\left[(2J+1)\frac{x}{2}\right]}{\sinh\frac{x}{2}}$$

$$M = \underset{N/V}{n} k_B T \frac{\partial \ln Z}{\partial B} = M_s\, B_J\left(g_J\mu_B J B/k_B T\right)$$

$M_s = n g_J \mu_B J$ SATURATION MAGNETIZATION

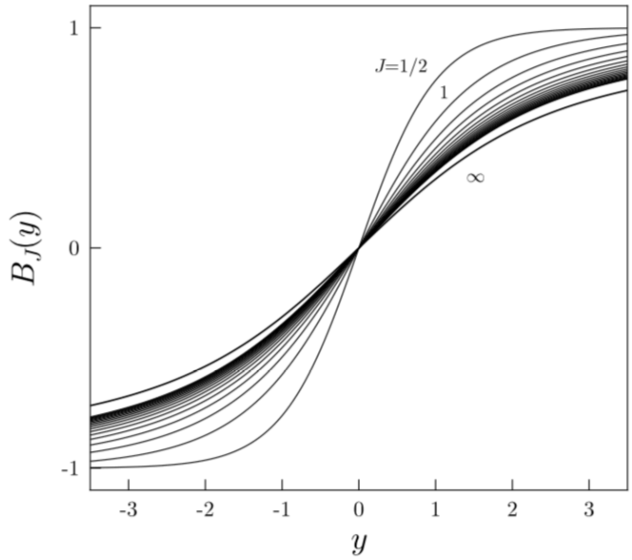
$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\frac{y}{2J}$$

BRILLOUIN FUNCTION

$y \ll 1 \qquad B_J(y) = \frac{J+1}{3J}y + O(y^3)$

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\underset{\text{Zeeman term}}{\mu_B (\vec{L} + g\vec{S}) \cdot \vec{B}}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2}_{\text{diamagnetic}}$$

$$M = M_s B_J (g_J \mu_B J B / k_B T)$$



S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\underset{\text{Zeeman term}}{\mu_B (\vec{L} + g\vec{S}) \cdot \vec{B}}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e} \sum_i (\vec{B} \times \vec{r}_i)^2}_{\text{diamagnetic}}$$

$$\chi = \frac{M}{H} \simeq \frac{\mu_0 M}{B} = \frac{n \mu_0 \mu_{eff}^2}{3 k_B T} \quad \text{(Curie)}$$

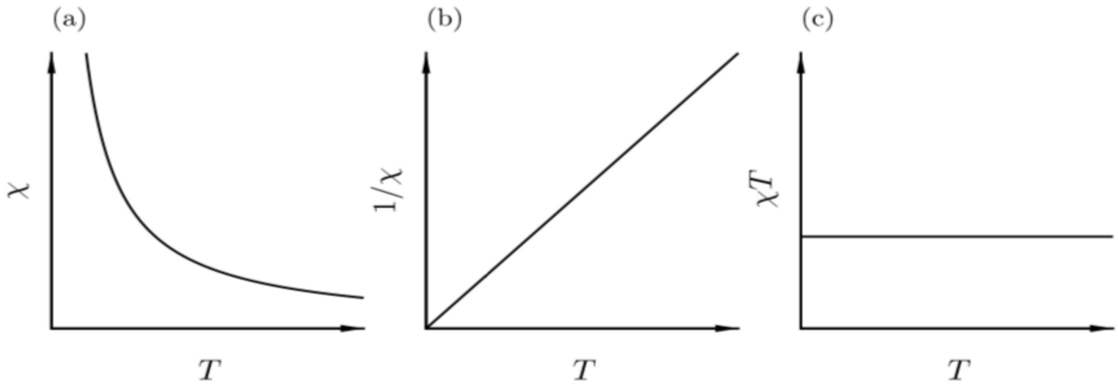
$$\chi << 1, \; B = \mu_0 (H + M) \simeq \mu_0 H$$

$$\mu_{eff} = g_J \mu_B \sqrt{J(J+1)}$$

paramagnetism is
- weak
- stronger than diamagnetism
- positive
- temperature-dependent $\propto 1/T$

$$\hat{H} = \underbrace{\sum_{i=1}^{Z} \frac{p_i^2}{2m_e} + V_i}_{\hat{H}_0} + \underbrace{\underbrace{\mu_B(\vec{L} + g\vec{S})\cdot\vec{B}}_{\text{Zeeman term}}}_{\text{paramagnetic}} + \underbrace{\frac{e^2}{8m_e}\sum_i \left(\vec{B}\times\vec{r}_i\right)^2}_{\text{diamagnetic}}$$

$$\chi = \frac{M}{H} \simeq \frac{\mu_0 M}{B} = \frac{n\mu_0 \mu_{eff}^2}{3k_B T} \quad \text{(Curie)}$$



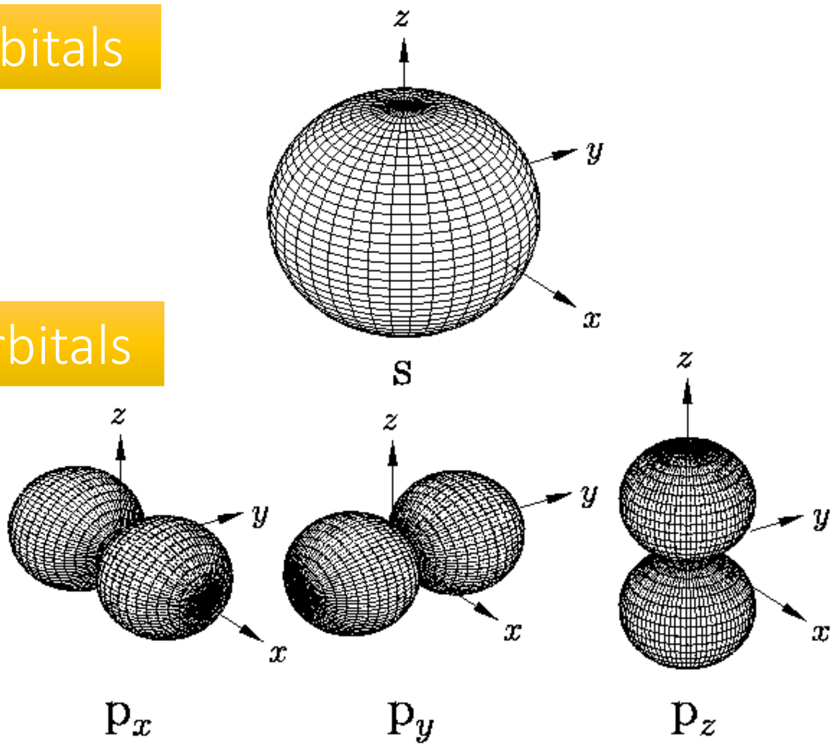
Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field

Orbitals

s-orbitals

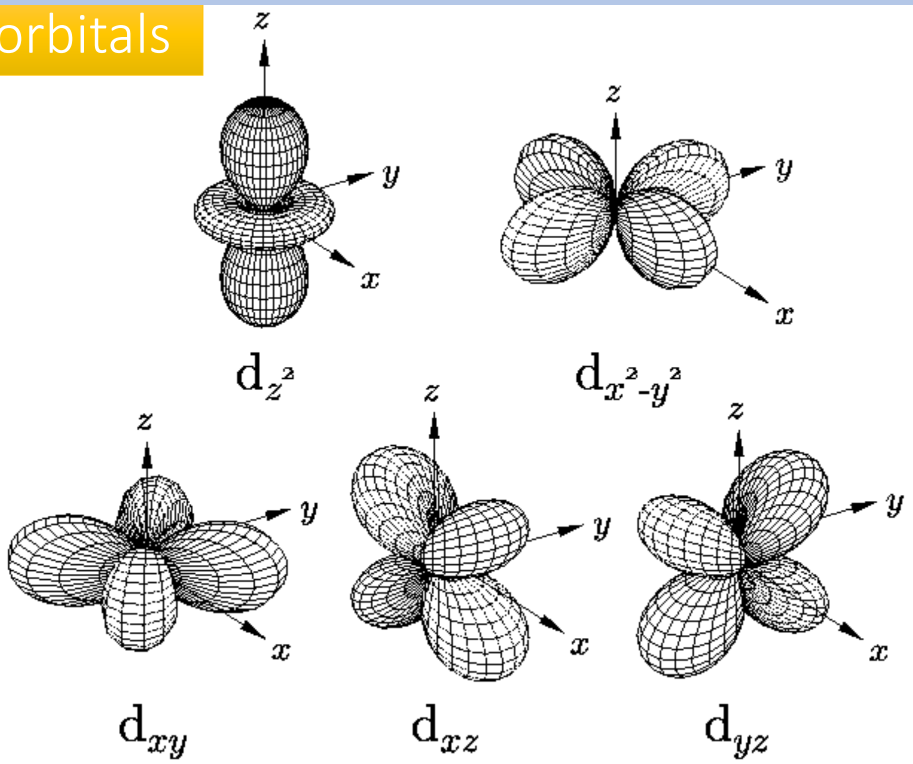
p-orbitals



S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

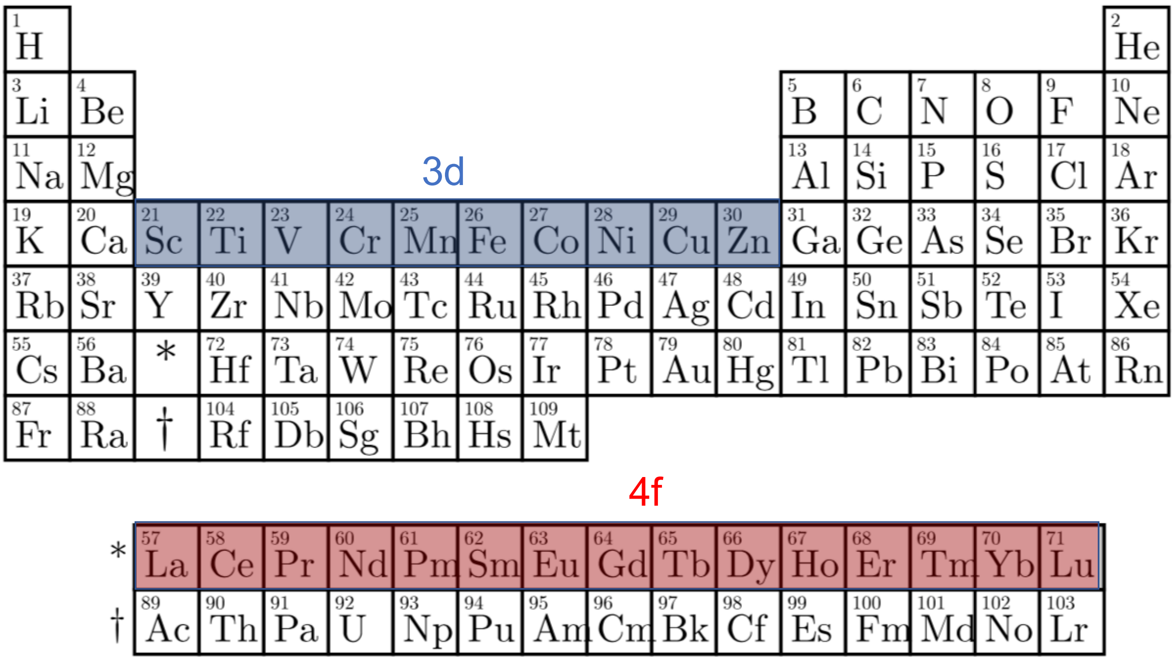
Orbitals

d-orbitals



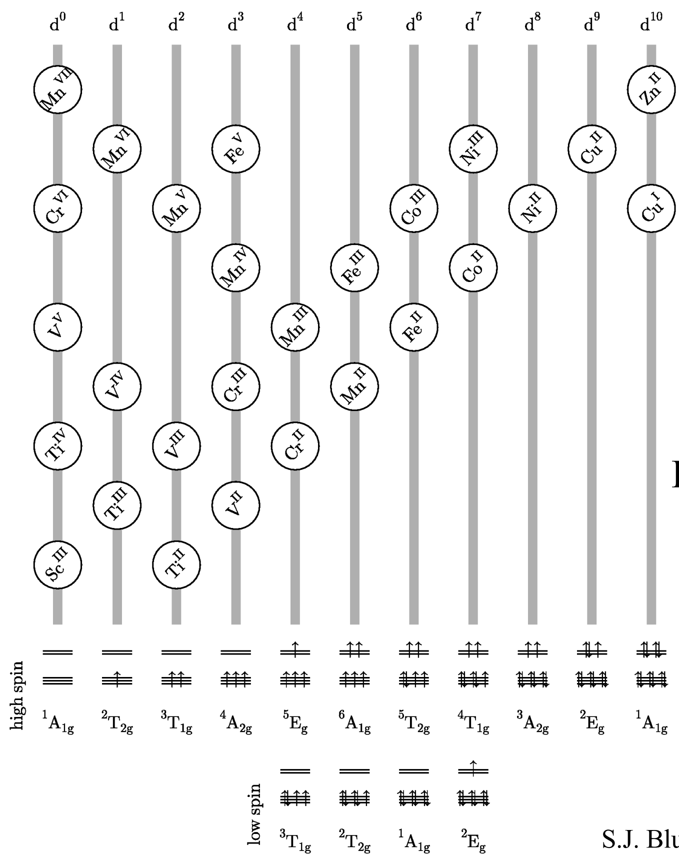
S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

Magnetic atoms and ions



S. J. Blundell, Magnetism in Condensed Matter (OUP, 2001)

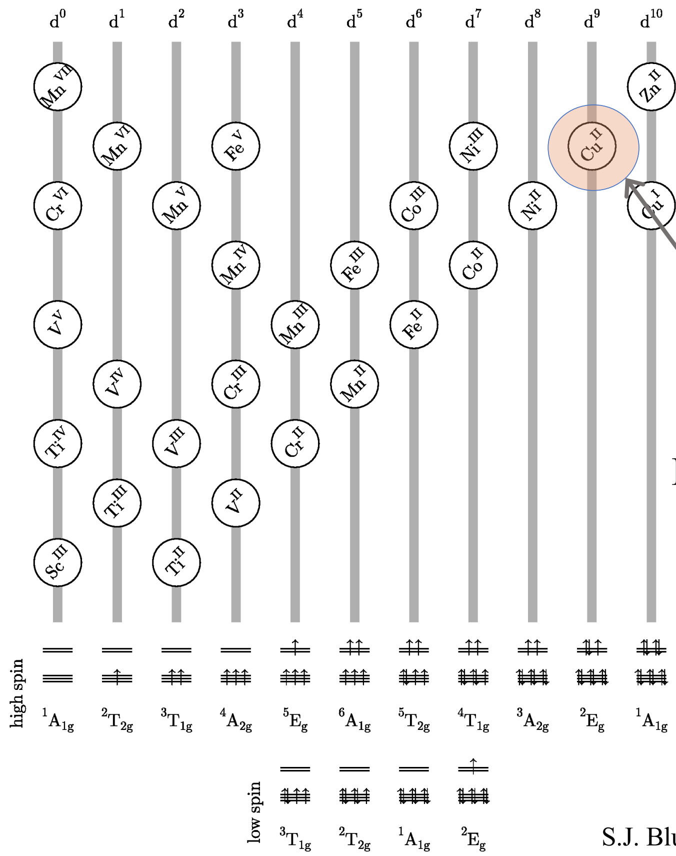
Transition metal (3d) ions



Partially filled 3d shell gives rise to a magnetic moment

S.J. Blundell, Contemp. Phys. **48,** 275 (2007)

Transition metal (3d) ions



$Cu^{II} = 3d^9$

Partially filled 3d shell gives rise to a magnetic moment

S.J. Blundell, Contemp. Phys. **48,** 275 (2007)

49

Spin-orbit and L_z eigenstates

Spin-orbit interaction

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

acts on $\psi(\vec{r})$

acts on spin

If states are $\approx$ atomic states, and s.o. acts as a perturbation, can focus on

$$\lambda\, S^z L^z$$

note $L_z = -i\hbar \dfrac{\partial}{\partial \phi}$ which has eigenfunctions $e^{im\phi}$

$$\hat{L}_z\, e^{im\phi} = m\hbar\, e^{im\phi}$$

Crystal field

The crystal field is a real potential due to electrostatic fields from neighbouring ions. The eigenfunctions cannot be $e^{im\phi}$ because require real solutions.

Recall: particle in a box

Solutions are real: $\cos kx$ and $\sin kx$

but not e^{ikx}.

$\therefore$ make linear combinations: $e^{ikx} \pm e^{-ikx}$

Similarly, crystal field states can be $e^{im\phi} \pm e^{-im\phi}$

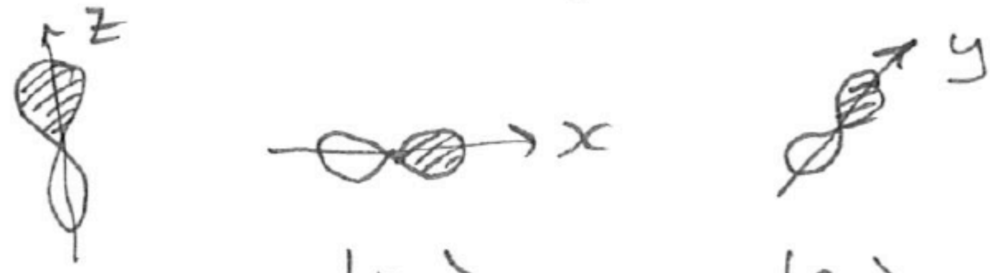
This is the origin of ORBITAL QUENCHING

$\because$ relevant states are of the form $|m\rangle \pm |-m\rangle$, and hence $\langle \psi | \vec{L} | \psi \rangle = 0$.

Notice this in 3d transition metal ions (where $L=0$, $J=S$ and $g=2$), but NOT in 4f lanthanide ions. Why?

ion	shell	S	L	J	term	p_1	p_{exp}	p_2
Ti^{3+}, V^{4+}	$3d^1$	$\frac{1}{2}$	2	$\frac{3}{2}$	$^2D_{3/2}$	1.55	1.70	1.73
V^{3+}	$3d^2$	1	3	2	$^3F_2$	1.63	2.61	2.83
Cr^{3+}, V^{2+}	$3d^3$	$\frac{3}{2}$	3	$\frac{3}{2}$	$^4F_{3/2}$	0.77	3.85	3.87
Mn^{3+}, Cr^{2+}	$3d^4$	2	2	0	$^5D_0$	0	4.82	4.90
Fe^{3+}, Mn^{2+}	$3d^5$	$\frac{5}{2}$	0	$\frac{5}{2}$	$^6S_{5/2}$	5.92	5.82	5.92
Fe^{2+}	$3d^6$	2	2	4	$^5D_4$	6.70	5.36	4.90
Co^{2+}	$3d^7$	$\frac{3}{2}$	3	$\frac{9}{2}$	$^4F_{9/2}$	6.63	4.90	3.87
Ni^{2+}	$3d^8$	1	3	4	$^3F_4$	5.59	3.12	2.83

A parable: p-orbitals



$|p_z\rangle$ $\quad$ $|p_x\rangle$ $\quad$ $|p_y\rangle$

$\cos\theta$ $\quad$ $\sin\theta\cos\phi$ $\quad$ $\sin\theta\sin\phi$

real eigenfunctions, for V(r) which is real

A parable: p-orbitals

$$Y_{lm}(\theta,\phi) \qquad l=1 \qquad \begin{array}{ll} m=0 & \cos\theta \\ m=1 & \sin\theta\,\mathrm{e}^{i\phi} \\ m=-1 & \sin\theta\,\mathrm{e}^{-i\phi} \end{array}$$

$\hat{L}_z = -i\hbar\dfrac{\partial}{\partial\phi}$ imaginary, $\quad|m\rangle$ eigenfunctions

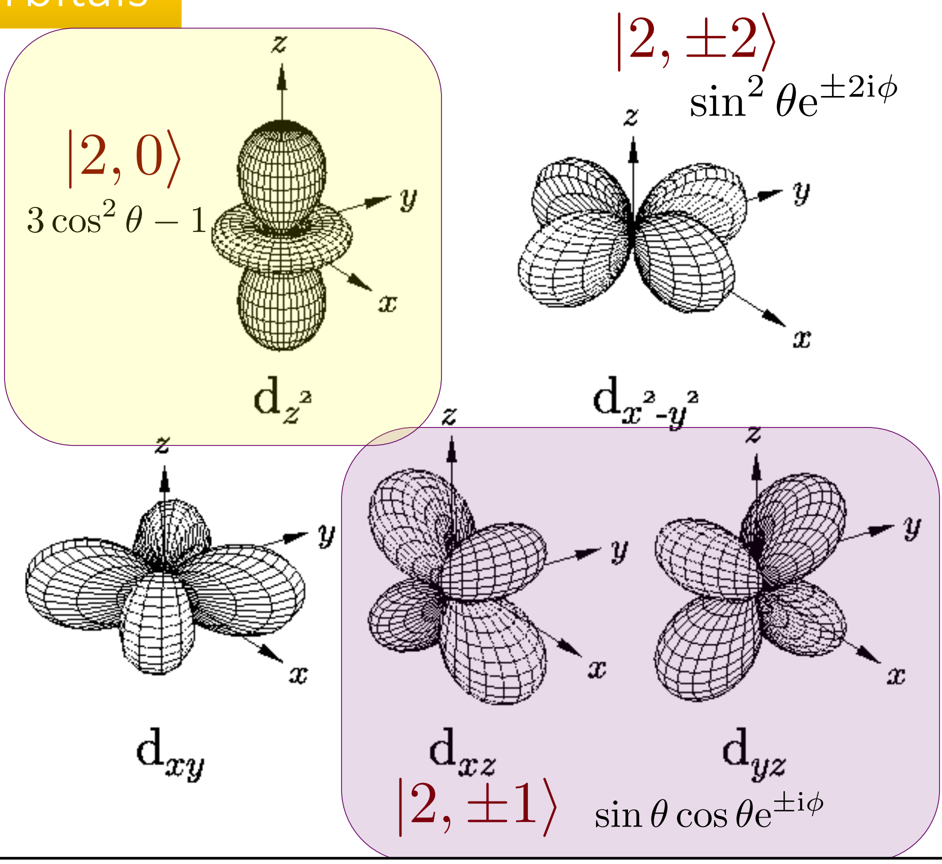
$$|p_z\rangle = |0\rangle$$

$$|p_x\rangle = \frac{|1\rangle + |-1\rangle}{\sqrt{2}}$$

$$|p_y\rangle = \frac{|1\rangle - |-1\rangle}{\sqrt{2}i}$$

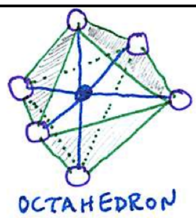
note that these contain the eigenfunctions $|m\rangle$ and $|-m\rangle$ in equal mixtures

d-orbitals



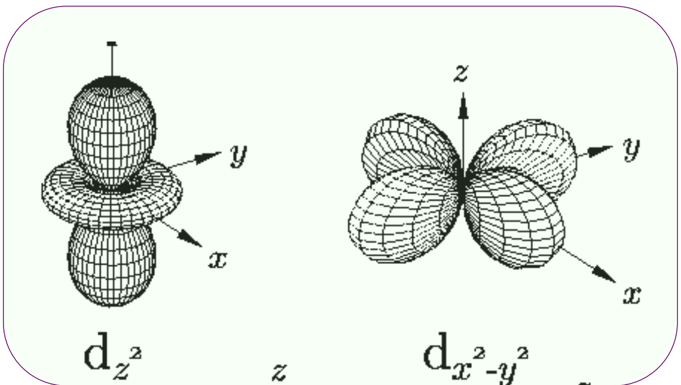
55

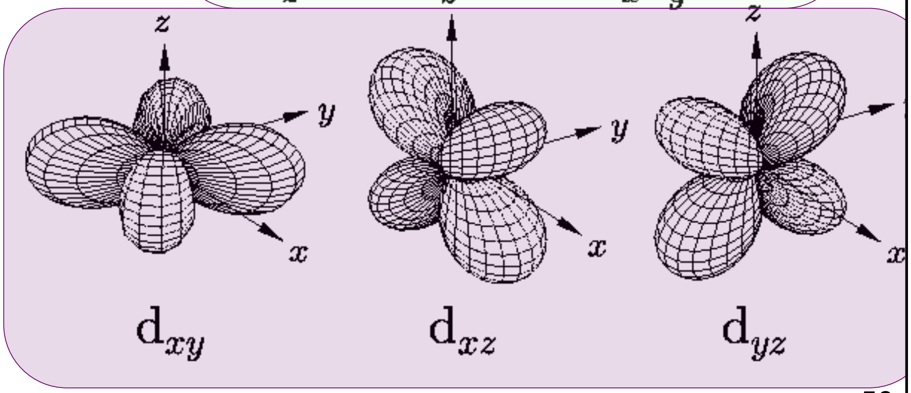
d-orbitals



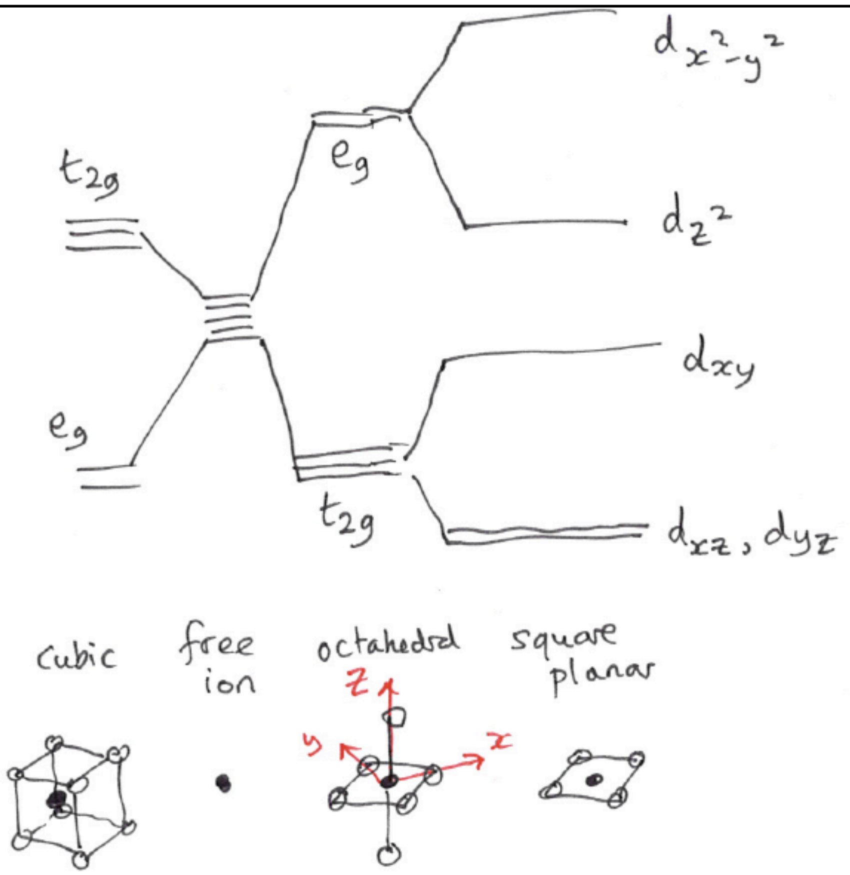
e_g
POINT ALONG BONDS

t_{2g}
POINT BETWEEN BONDS

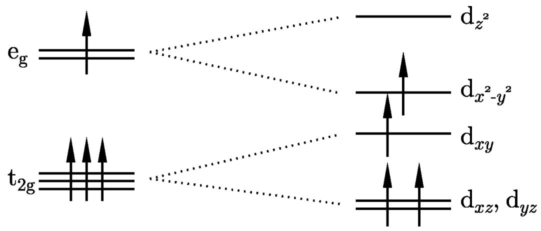


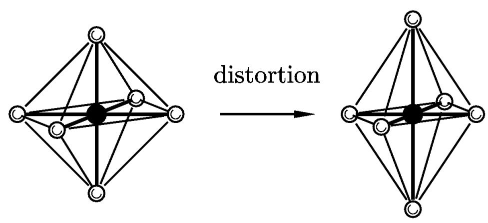


56



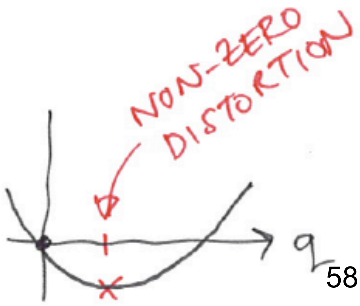
Jahn-Teller distortion in a $3d^4$ ion





distortion parameter = q

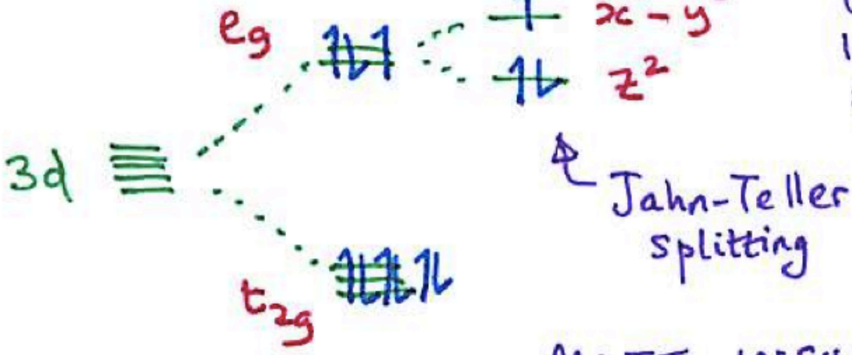
energy = $aq^2 - bq$
(elastic) (electronic)



Example (1)

La_2CuO_4 Cu^{2+} $3d^9$

ONE HOLE IN THE x^2-y^2 ORBITAL

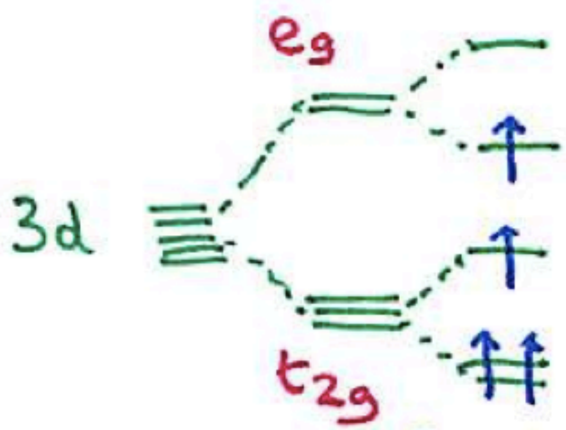


MOTT INSULATOR

(antiferromagnetically ordered insulator)

Example (2)

$LaMnO_3$ Mn^{3+} $3d^4$



note Mn^{4+} $(3d^3)$ has NO Jahn-Teller distortion $\Rightarrow$ CMR

Outline

1. Bohr-van Leeuwen theorem
2. Orbital magnetism
3. Spin magnetism
4. Spin precession
5. Hund's rules
6. Diamagnetism and paramagnetism
7. Orbitals and the crystal field