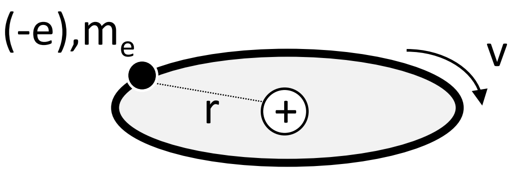
MAGNETISM IN MATERIALS

Lecture 2: Isolated Magnetic Moments

Ivica Zivkovic

ISOLATED MAGNETIC MOMENTS

- an atom in magnetic field
- diamagnetism
- paramagnetism
- Hund's rules
- spin-orbit coupling
- nuclear spins

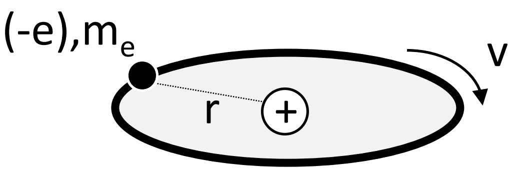


not one but several electrons

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

applying magnetic field

$$\mathcal{H}_0 = \sum_i \left(\frac{\boldsymbol{p}_i^2}{2m} + V_i \right) \rightarrow \sum_i \left(\frac{[\boldsymbol{p}_i + e\boldsymbol{A}]^2}{2m} + V_i \right) + g\mu_B \boldsymbol{BS}$$



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$$\boldsymbol{F} = m\frac{d\boldsymbol{v}}{dt} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}) \longrightarrow m\frac{d\boldsymbol{v}}{dt} + q\left(\frac{\partial \boldsymbol{A}}{\partial t} + (\boldsymbol{v}\cdot\nabla)\boldsymbol{A}\right) = -q\nabla(V - \boldsymbol{v}\cdot\boldsymbol{A})$$

$$\boldsymbol{B} = \nabla \times \boldsymbol{A}$$

because $\nabla \boldsymbol{B} = 0$

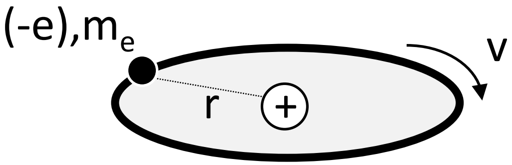
$$\boldsymbol{\mathcal{E}} = -\nabla V - \frac{\partial \boldsymbol{A}}{\partial t}$$

$$\boldsymbol{v} \times \boldsymbol{B} = \boldsymbol{v} \times (\nabla \times \boldsymbol{A}) = \nabla(\boldsymbol{v}\cdot\boldsymbol{A}) - (\boldsymbol{v}\cdot\nabla)\boldsymbol{A}$$

$$\left(\frac{\partial \boldsymbol{A}}{\partial t} + (\boldsymbol{v}\cdot\nabla)\boldsymbol{A}\right) = \frac{\partial \boldsymbol{A}}{\partial t} + \left(\frac{d\boldsymbol{r}}{dt}\cdot\frac{d}{d\boldsymbol{r}}\right)\boldsymbol{A} = \frac{d\boldsymbol{A}}{dt}$$

$$\frac{d}{dt}(m\boldsymbol{v} + q\boldsymbol{A}) = -q\nabla(V - \boldsymbol{v}\cdot\boldsymbol{A})$$

canonical momentum: $\boldsymbol{p} = m\boldsymbol{v} + q\boldsymbol{A}$



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applying magnetic field

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q = -e

choice of gauge: $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r}$

kinetic energy

$$E_k = \frac{1}{2} m\boldsymbol{v}^2 = \frac{1}{2m}\boldsymbol{p}^2$$

$$\overset{B>0}{=} \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2$$

$$\mathcal{H} = \mathcal{H}_0 + \mu_B(\boldsymbol{L} + g\boldsymbol{S})\boldsymbol{B} + \frac{e^2}{8m}\sum_i (\boldsymbol{B} \times \boldsymbol{r}_i)^2$$

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- field-induced response
- response is magnetization

$$\mathcal{H} = \mathcal{H}_0 + \mu_B(\boldsymbol{L} + g\boldsymbol{S})\boldsymbol{B} + \frac{e^2}{8m}\sum_i (\boldsymbol{B} \times \boldsymbol{r}_i)^2$$

- ❖ field-induced response
- ❖ response is magnetization

what is magnetic field?

$$\boldsymbol{F} = q\boldsymbol{E} + q\boldsymbol{v} \times \boldsymbol{B}$$

- magnetic field
- magnetic induction
- magnetic-flux density

$$\varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = \boldsymbol{D}$$

$$\frac{1}{\mu_0}\boldsymbol{B} - \boldsymbol{M} = \boldsymbol{H}$$

- magnetic field
- magnetizing field

$$\mathcal{H} = \mathcal{H}_0 + \mu_B(\boldsymbol{L} + g\boldsymbol{S})\boldsymbol{B} + \frac{e^2}{8m}\sum_i (\boldsymbol{B} \times \boldsymbol{r}_i)^2$$

- ❖ field-induced response
- ❖ response is magnetization

$$\boldsymbol{M} = \bar{\bar{\chi}}\boldsymbol{H}$$

→ magnetic susceptibility (a tensor)

↓ isotropic, linear material

$$\boldsymbol{M} = \chi\boldsymbol{H} \qquad \boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M}) = \mu_0\mu_r\boldsymbol{H} \qquad \mu_r = 1 + \chi$$

<u>what is magnetic field?</u>

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small perturbation

dominant contribution

$$\mathcal{H}_0|\Psi_i\rangle = E_i|\Psi_i\rangle$$

$$\underset{\text{ground state}}{E_0} < \underbrace{E_1 < E_2 < E_3 \cdots}_{\text{excited states}}$$

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perturbation theory

1. order $\quad \Delta E_0 = \langle 0|\mathcal{H}_{pert}|0\rangle$

2. order $\quad \Delta E_0 = \sum_i \frac{\langle 0|\mathcal{H}_{pert}|i\rangle\langle i|\mathcal{H}_{pert}|0\rangle}{E_0 - E_i}$

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$$\Delta E^{dia} = \left\langle 0 \left| \frac{e^2}{8m}\sum_i (\boldsymbol{B} \times \boldsymbol{r}_i)^2 \right| 0 \right\rangle$$

$$B \parallel z \Rightarrow \boldsymbol{B} = \begin{pmatrix} 0 \\ 0 \\ B \end{pmatrix} \qquad \boldsymbol{r}_i = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} \qquad (\boldsymbol{B} \times \boldsymbol{r}_i) = B\begin{pmatrix} -y_i \\ x_i \\ 0 \end{pmatrix}$$

$$\Delta E^{dia} = \frac{e^2B^2}{8m}\sum_i \langle 0|x_i^2 + y_i^2|0\rangle = \frac{e^2B^2}{12m}\sum_i \langle 0|r_i^2|0\rangle$$

spherical symmetry

$$\langle 0|x_i^2|0\rangle = \langle 0|y_i^2|0\rangle = \langle 0|z_i^2|0\rangle = \frac{1}{3}\langle 0|r_i^2|0\rangle$$

$$\chi_{dia} = \frac{M}{H} \sim \frac{1}{H}\frac{\partial \Delta E^{dia}}{\partial B} \sim \sum_i \langle 0|r_i^2|0\rangle$$

$$\boxed{\chi_{dia} \sim Z_{out} r^2}$$

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NEUTRON STARS!!!

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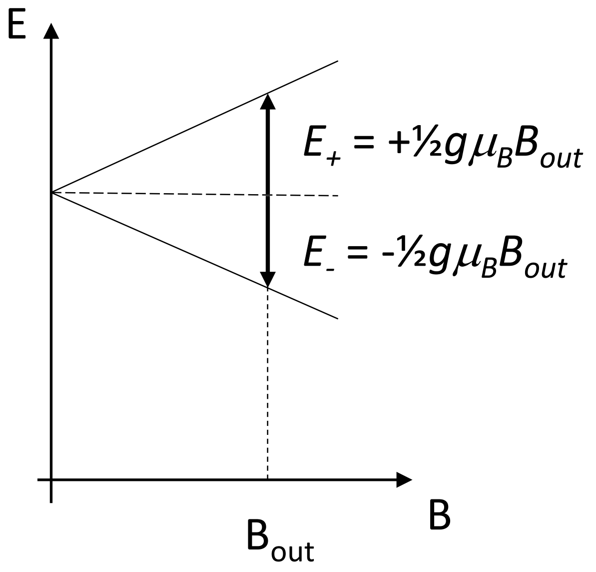
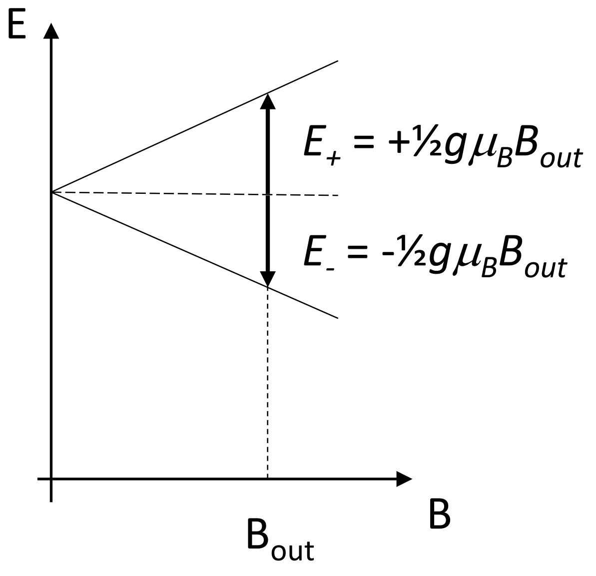
temperature and field independent



$$\Delta E = E_+ - E_- = g\mu_B B_{out}$$

the principle of ESR (EPR)



$\Delta E = E_+ - E_- = g\mu_B B_{out}$

the principle of ESR (EPR)

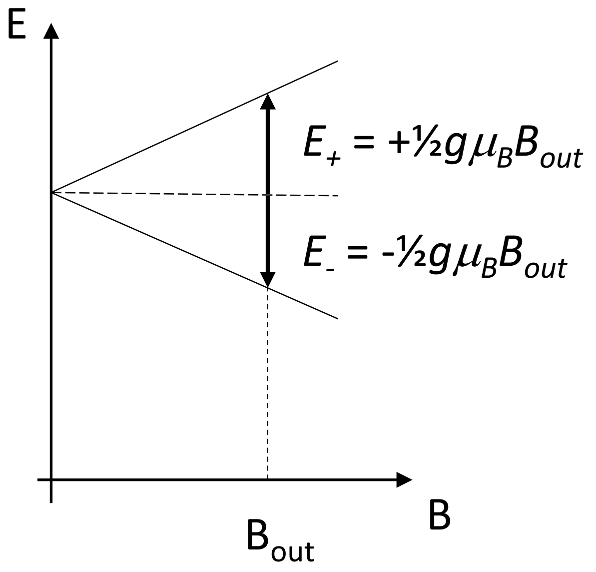
<u>thermodynamics through the partition function:</u>

$$Z = \sum_i e^{\frac{E_i}{k_B T}} = \sum_{m_J=-J}^{J} e^{\frac{m_J g_J \mu_B B}{k_B T}}$$

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

$$M = n g_J \mu_B \langle m_J \rangle = n g_J \mu_B \frac{\sum_{m_J=-J}^{J} m_J e^{m_J x}}{\sum_{m_J=-J}^{J} e^{m_J x}}$$

$$x = \frac{g_J \mu_B J B_{out}}{k_B T}$$



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$$M = n g_J \mu_B J B_J(x)$$

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

Brillouin function

$$M = \underbrace{n g_J \mu_B J}_{\text{saturation value}} B_J(x) \qquad x = \frac{g_J \mu_B J B_{out}}{k_B T}$$

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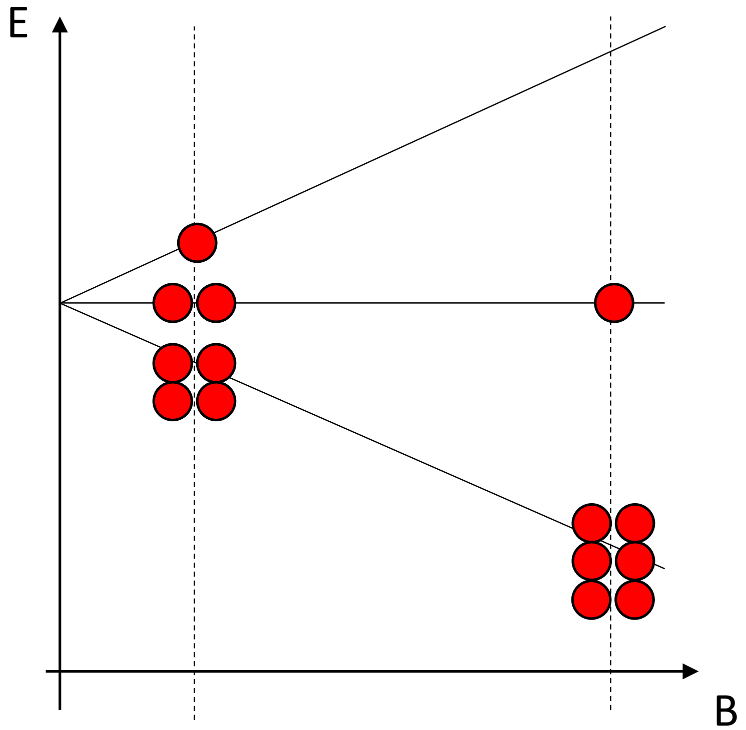

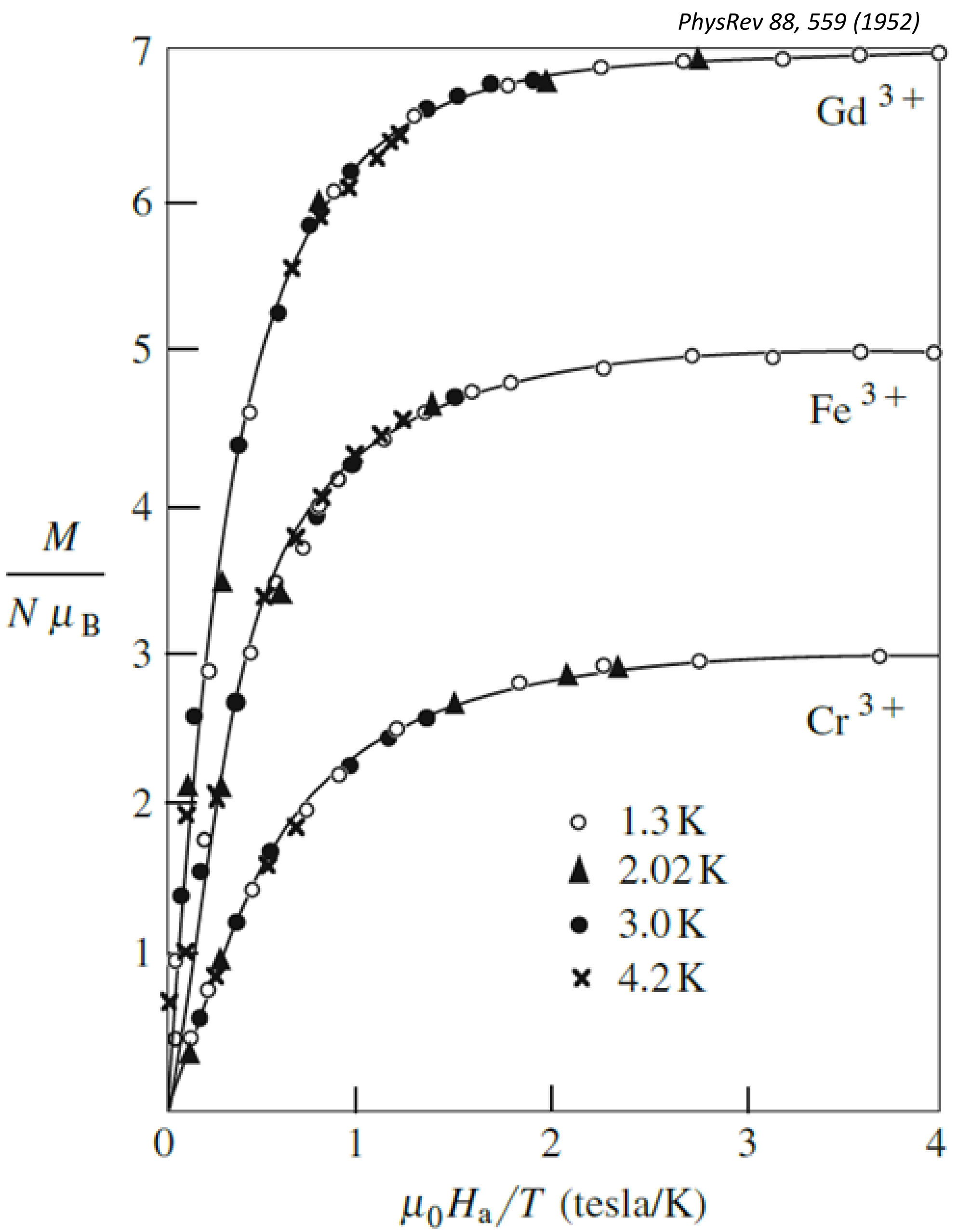

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$\underline{J \to \infty}$

$$B_\infty(x) \to L(x) = \coth x - \frac{1}{x}$$

Langevin function

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Langevin function

$\underline{x \ll 1}$

$$B_J(x) \approx \frac{J+1}{3J}x \to M = f(T)B$$

$$\chi = \frac{N_A \mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T}$$

Curie law

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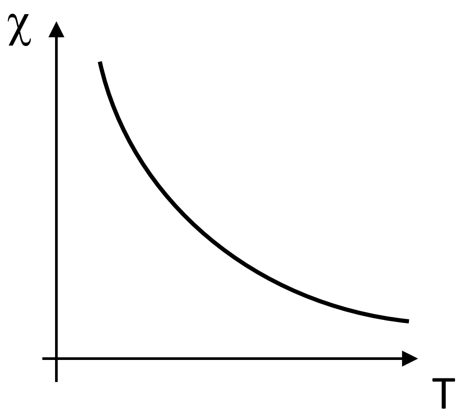
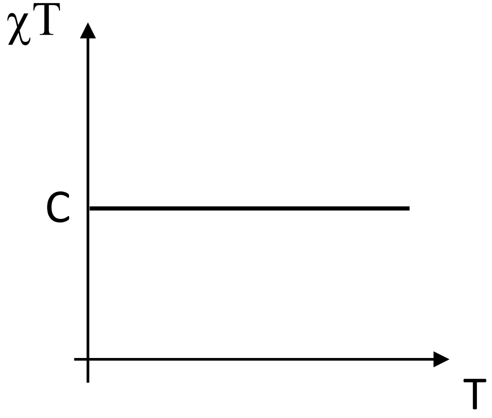
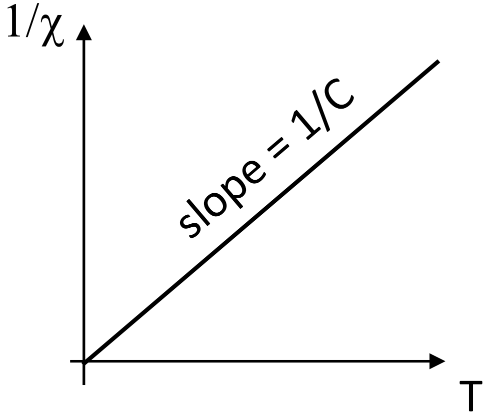
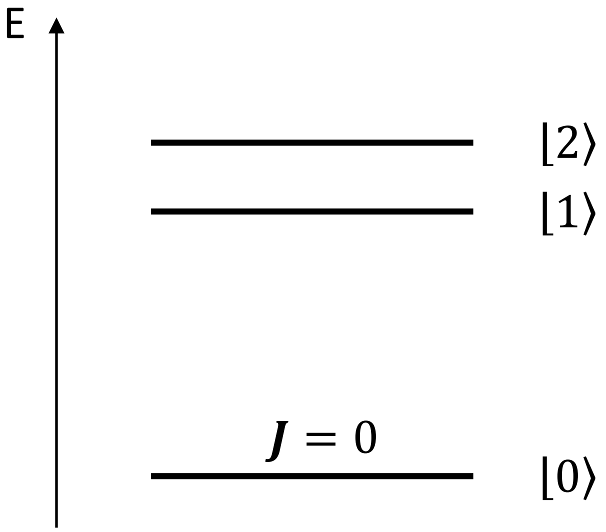








$$\Delta E^{(1)} = \langle 0|\boldsymbol{J}|0\rangle = 0$$

$$\Delta E^{(2)} \sim \sum_{i \geq 1} \frac{|\langle 0|(\boldsymbol{L} + g\boldsymbol{S})\boldsymbol{B}|i\rangle|^2}{E_i - E_0}$$

$$\boxed{\chi_{VV} \sim \sum_{i \geq 1} \frac{|\langle 0|(L_z + gS_z)|i\rangle|^2}{E_i - E_0} > 0}$$

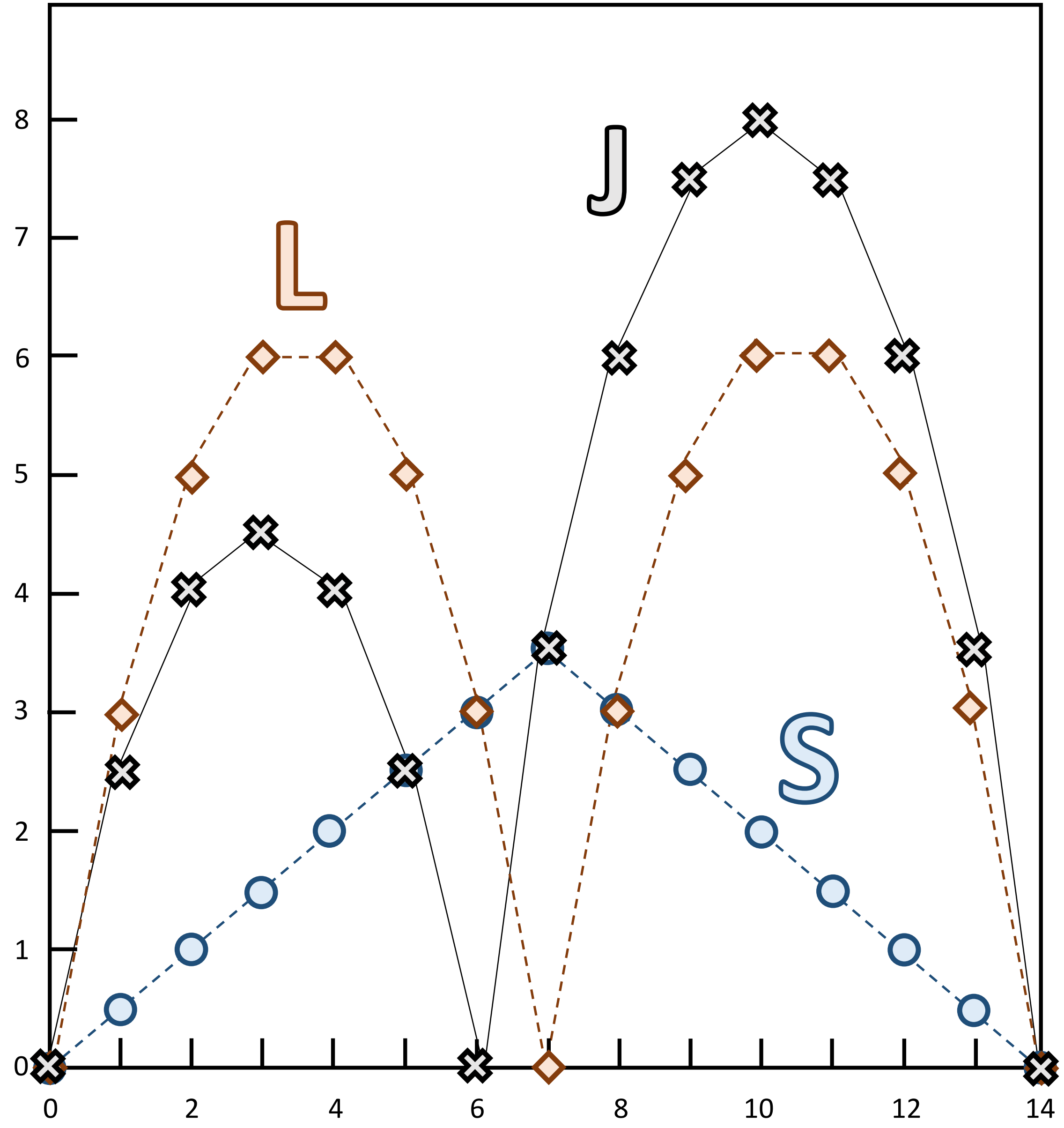
temperature and field independent

1 Maximize S

2 Maximize L

3 subtract/add

ion	N	S	L	J	3
La^{3+}	0	0	0	0	J = |L-S|
Ce^{3+}	1	1/2	3	5/2	
Pr^{3+}	2	1	5	4	
Nd^{3+}	3	3/2	6	9/2	
Pm^{3+}	4	2	6	4	
Sm^{3+}	5	5/2	5	5/2	
Eu^{3+}	6	3	3	0	
Gd^{3+}	7	7/2	0	7/2	
Tb^{3+}	8	3	3	6	J = |L+S|
Dy^{3+}	9	5/2	5	15/2	
Ho^{3+}	10	2	6	8	
Er^{3+}	11	3/2	6	15/2	
Tm^{3+}	12	1	5	6	
Yb^{3+}	13	1/2	3	7/2	
Lu^{3+}	14	0	0	0	



❖ informational

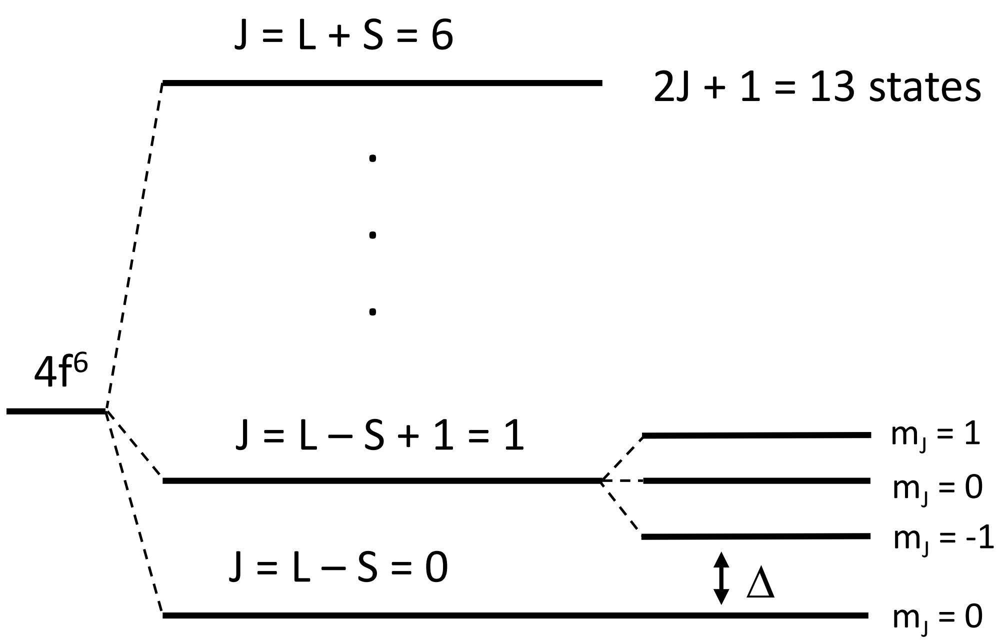
The ground state is written in the form

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

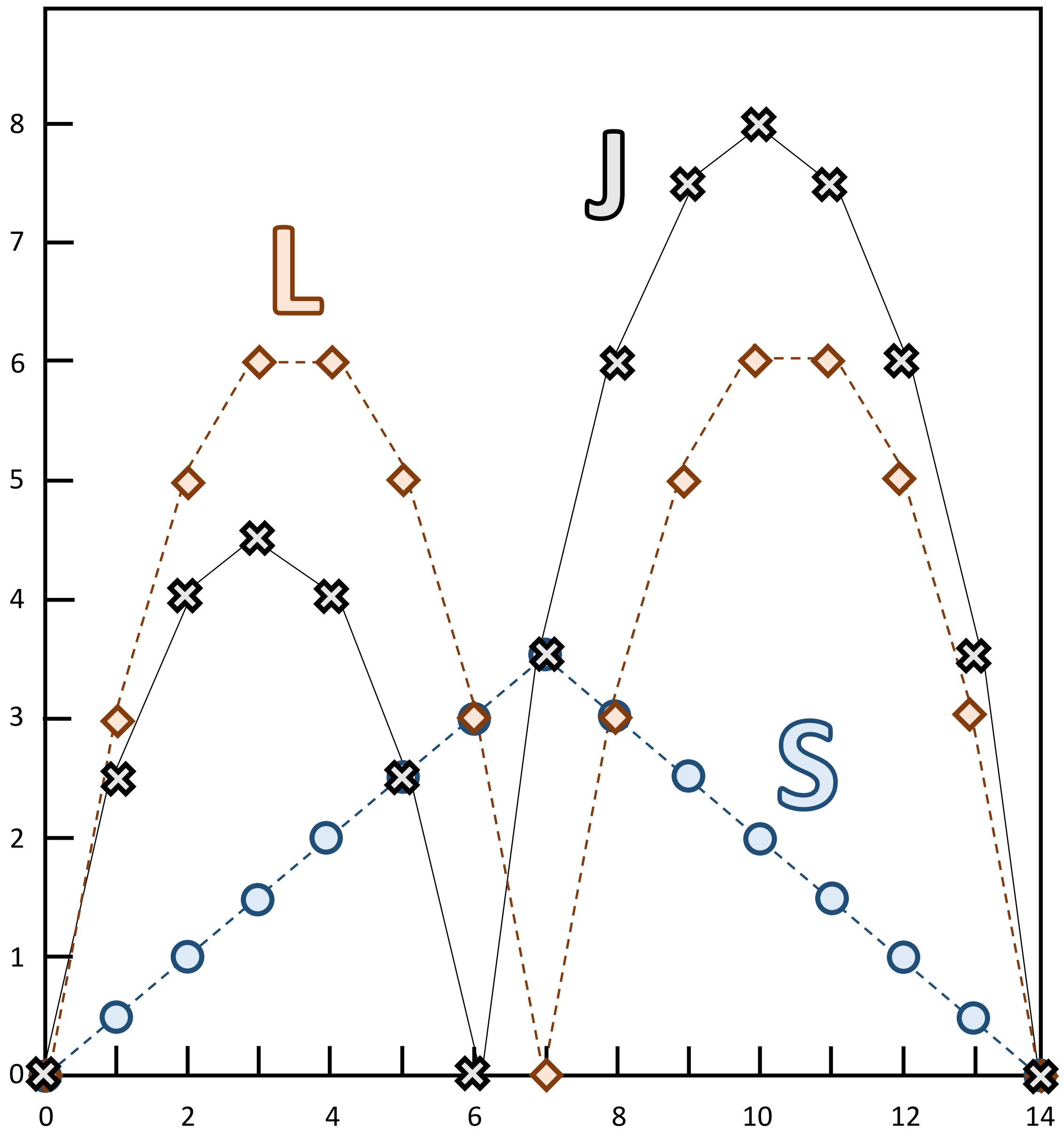
J and S are expressed in numbers. For L capital letter are used:

$$L = |\Sigma L_z| = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$
$$= S \quad P \quad D \quad F \quad G \quad H \quad I$$

deviations (Sm, Eu)



when $k_BT \sim \Delta$, $\mu > 0$



total (measured) moment

$$\hat{\boldsymbol{\mu}} = g_J \mu_B \hat{\boldsymbol{J}} = \mu_B (g_L \hat{\boldsymbol{L}} + g_S \hat{\boldsymbol{S}})$$

$$g_J \hat{\boldsymbol{J}}^2 = (g_L \hat{\boldsymbol{L}}\hat{\boldsymbol{J}} + g_S \hat{\boldsymbol{S}}\hat{\boldsymbol{J}})$$

total angular momentum

$\vec{\boldsymbol{J}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}$ $\rightarrow$ but also operators!

$$\vec{\boldsymbol{L}} = \vec{\boldsymbol{J}} - \vec{\boldsymbol{S}} \qquad \vec{\boldsymbol{S}} = \vec{\boldsymbol{J}} - \vec{\boldsymbol{L}}$$

$$\vec{\boldsymbol{S}}^2 = (\vec{\boldsymbol{J}} - \vec{\boldsymbol{L}})^2 = \vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 - 2\vec{\boldsymbol{J}}\vec{\boldsymbol{L}}$$

total (measured) moment

$$\hat{\boldsymbol{\mu}} = g_J \mu_B \hat{\boldsymbol{J}} = \mu_B (g_L \hat{\boldsymbol{L}} + g_S \hat{\boldsymbol{S}})$$

total angular momentum

$$\vec{\boldsymbol{J}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}$$ $\rightarrow$ but also operators!

$$g_J \hat{\boldsymbol{J}}^2 = (g_L \hat{\boldsymbol{L}}\hat{\boldsymbol{J}} + g_S \hat{\boldsymbol{S}}\hat{\boldsymbol{J}})$$

$$\vec{\boldsymbol{L}} = \vec{\boldsymbol{J}} - \vec{\boldsymbol{S}} \qquad \vec{\boldsymbol{S}} = \vec{\boldsymbol{J}} - \vec{\boldsymbol{L}}$$

$$\vec{\boldsymbol{S}}^2 = (\vec{\boldsymbol{J}} - \vec{\boldsymbol{L}})^2 = \vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 - 2\vec{\boldsymbol{J}}\vec{\boldsymbol{L}}$$

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

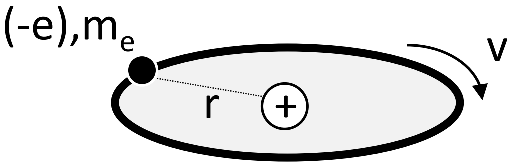
for $g_L = 1, g_S = 2$

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

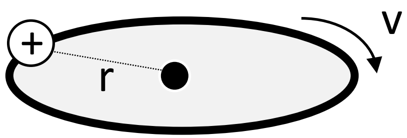
Landé g-factor

- triplet and singlet oxygen
- chemical reactivity
- biology

image source: wikimedia.org



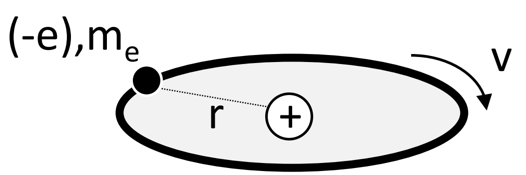
<u>nucleus orbiting electron produces magnetic field</u>



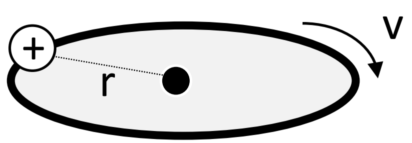
$$\vec{B} = \frac{\vec{\mathcal{E}} \times \vec{v}}{c^2}$$

$$\vec{\mathcal{E}} = -\nabla V(\boldsymbol{r}) = -\frac{\boldsymbol{r}}{r}\frac{dV(r)}{dr}$$

$$V(r) = \frac{Ze}{4\pi\epsilon_0 r}$$



nucleus orbiting electron produces magnetic field



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$$V(r) = \frac{Ze}{4\pi\epsilon_0 r}$$

relativistic correction

$$\Delta H_{SO} = -\frac{1}{2}\boldsymbol{\mu}\boldsymbol{B} \sim \frac{Z}{r^3}\boldsymbol{SL}$$

not too strict due to the screening

$$\Delta E^{(1)} \sim \left\langle 0 \left| \frac{Z}{r^3}\boldsymbol{SL} \right| 0 \right\rangle \sim Z^4 \langle 0|\boldsymbol{SL}|0\rangle$$

(2S+1)(2L+1) splitting → fine structure

$$\left\langle 0 \left| \frac{1}{r^3} \right| 0 \right\rangle \sim Z^3$$

(hyper-fine structure due to the coupling with nucleus)

$$\mu_N = \frac{e\hbar}{2m_P} = 5.0508 \times 10^{-27}\,\mathrm{Am^2}$$

$$\mu = g_I \mu_N I$$

$$I_p = I_n = \frac{1}{2}$$

$$g_p = 5.586$$

$$g_n = -3.826$$

hyperfine interaction

$$\Delta H = A\boldsymbol{I}\boldsymbol{J}$$

atomic magnetometer
(NMR/MRI)