Fundamentals II
– Atomic Basis of Magnetism

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Outline

- Origin of magnetic moment
- Isolated magnetic moments
- Magnetic interactions
- Environments (ligand field)
- Magnetism in metals

reference:
Magnetism in Condensed Matter, S. Blundell
Magnetism from fundamentals to nanoscale dynamics, J. Stohr and H.C. Siegmann
The origin of magnetic moment

- orbital moment
- spin moment
- nuclear moment
Classical definition of magnetic moment

**Magnetic Dipole**

- $+p$
- $-p$
- $d$

**Magnetic Field**

$$H_D = \frac{p}{4\pi\mu_0 r_1^3} \mathbf{r}_1 - \frac{p}{4\pi\mu_0 r_2^3} \mathbf{r}_2$$

$r \ll d$

$$|H_D| = \frac{|m|}{4\pi\mu_0 r^3} \sqrt{1 + 3\cos^2 \varphi} \propto \frac{|m|}{r^3}$$

**quadrupoles, sextupoles, octopoles, …**

$H_D \propto r^{-5}, r^{-7}, r^{-9}$

**at large distance $H_D \propto r^{-3}$** Most important in magnetism
Magnetic moment (classical definition)

Current loop

\[ m = \mu_0 IS \]

\[ S = \pi r^2 \quad I = -e(\omega / 2\pi) \]

\[ m = \frac{-\mu_0 er^2}{2} \quad \omega = \frac{-\mu_0 e}{2} (r \times \nu) \]

Angular momentum

\[ l = m_e (r \times \nu) \]

Angular momentum \(\Rightarrow\) magnetic moment

\[ m = -\frac{e\mu_0}{2m_e} l \]
<table>
<thead>
<tr>
<th>Classical</th>
<th>Quantum</th>
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</table>
| \[ m = -\frac{e\mu_0}{2m_e} l \] | \[ m_l = -\frac{e\mu_0}{2m_e} g_l l = -\frac{\mu_B}{\hbar} g_l l \]  
  \[ g -- g \text{ factor} \]  
  \[ \text{orbital moment } g=1 \]  
| \[ m_s = -\frac{\mu_B}{\hbar} g_s s \] | \[ \text{spin moment } g=2.0023 \]  
| \[ m_{tot} = m_l + m_s \] |  

Bohr magneton

\[ \mu_B = \frac{e\mu_0\hbar}{2m_e} = 0.5788 \times 10^{-4} \text{ eV T}^{-1} \]

Magnetic moment ↔ Angular momentum
Quantum mechanics of moment

**moment**

\[ m_l = -g_l \mu_B \frac{l}{\hbar} \]

**the value of moment**

\[ m_l = -g_l \sqrt{l(l+1)} \frac{\mu_B}{\hbar} \]

**at \( z \)-direction**

\[ m_{l,z} = -g_l l_z \mu_B \frac{1}{\hbar} \]

\[ l_z = 0, \pm 1, \pm 2, \cdots \pm l \]

**magnetic moment is quantized along \( z \)-direction**
Magnetic moment of one atom

- Total spin and orbital angular moment: \[ J = L + S \]
- Total angular moment: \[ J = L + S \]

\( L \) and \( S \) are independent of each other without coupling. 
\( L \) and \( S \) are not conserved with coupling. \( J=L+S \) is conserved.

- Magnetic moment is quantized along \( J \)-direction

\[ m_J = m_L \cos(L,J) + m_S \cos(S,J) \]
\[ m_L = -\frac{\sqrt{L(L+1)~\mu_B}}{\hbar} \]
\[ m_S = -2\sqrt{S(S+1)~\mu_B} \]
\[ m_J = -g_J\sqrt{J(J+1)~\mu_B} \]

- Landé g-factor

\[ g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \]
Nuclear moment

Electron

\[ m_l = -\frac{e\mu_0 l}{2m_e} = -\frac{\mu_B l}{\hbar} \]

Proton or neutron

\[ m_z = -\frac{g_p l e\mu_0 l_z}{2m_p} = -\frac{\mu_N l_z}{\hbar} \]

\[ m_p = 1836m_e \]

Nuclear moment of proton and neutron is 3 orders smaller than moment of orbital and spin moment.
Isolated magnetic moments

- Larmor precession
- Diamagnetism
- Paramagnetism
**Larmor precession**

Toque \( T = \mathbf{m} \times \mathbf{B} \)

Torque causes angular momentum to move

\[
T = \frac{d\mathbf{L}}{dt} = -\frac{\hbar}{g\mu_B} \frac{d\mathbf{m}}{dt} \quad \iff \quad \mathbf{m} = -\frac{\mu_B}{\hbar} \mathbf{L}
\]

\[
\frac{d\mathbf{m}}{dt} = -\frac{g\mu_B}{\hbar} \mathbf{m} \times \mathbf{B} \equiv \gamma \mathbf{m} \times \mathbf{B} \quad (\gamma = -\frac{g\mu_B}{\hbar} \text{ gyromagnetic ratio})
\]

\( \mathbf{m} \) processes around \( \mathbf{B} \) with frequency:

\[
\omega = \gamma B \quad \text{(Larmor precession frequency)}
\]

\[
\frac{\omega}{B} = \frac{g\mu_B}{\hbar} = 1.759 \times 10^{11} \text{ rad T}^{-1}\text{s}^{-1}
\]

1T: one full precession is 36ps, 10ps/90°

**Time scale to switch moment**

\( \theta \) does not change during procession. M turns into \( \mathbf{B} \) direction?
Damping of the precession

\[ T = m \times B \quad \text{Time reversal} \]

\[ T_D = C [m \times \frac{dm}{dt}] \quad \text{Time irreversible} \]

\( T_D \) causes \( m \) to became irreversible

\[ \frac{dm}{dt} = \gamma [m \times H] + \alpha [m \times \frac{dm}{dt}] \]

\( \alpha \) damping parameter

\[ \frac{dm}{dt} = \gamma [m \times H] + \frac{\alpha \gamma}{m} [m \times m \times H] \]
Damping of the precession

- damping \(\Rightarrow\) change in angular momentum
- angle momentum conservation
- angular momentum transfer
- spin wave, lattice, spin pumping effect ...

\(\alpha\) positive

Require energy (switch \(M\))

Spin injection to provide energy

\(\alpha\) negative

Switch \(M\)
Magnetic resonance

H’ rotates in a plane perpendicular to H.
H’ supplies torque and energy to compensate for damping.

Resonance:
H’ rotates at Larmor frequency => θ is fixed

- Electron Paramagnetic Resonance (EPR) 10GHz
- Ferromagnetic Resonance (FMR) 10GHz
- Nuclear Magnetic Resonance (NMR) 10MHz

Spin-flip transition

\[ \Delta E = \hbar \omega = g \mu_B H \]
Larmor Precession

1. Ultrafast Spin Dynamics in Ferromagnetic Nickel
   [PRL 76, 4250 (1996)]
2. Ultrafast precessional magnetization reversal by picosecond magnetic field pulse shaping
   [Nature 418, 509 (2002)]
3. Ultrafast non-thermal control of magnetization by instantaneous photomagnetic pulses
   [Nature 435, 655 (2005)]
An atom in a magnetic field

Hamiltonian of a atom

\[ \hat{H}_0 = \sum_{i=1}^{Z} \left( \frac{p_i^2}{2m} + V_i \right) \]

- kinetic energy
- potential energy

Magnetic field \( \mathbf{B} = \nabla \times \mathbf{A} \)

Magnetic vector potential \( \mathbf{A}(\mathbf{r}) = \frac{\mathbf{B} \times \mathbf{r}}{2} \)

\[ \hat{H} = \sum_{i=1}^{Z} \left( \frac{[p_i + eA(\mathbf{r}_i)]^2}{2m_e} + V_i \right) + g\mu_B \mathbf{B} \cdot \mathbf{S} \]

\[ = \sum_{i=1}^{Z} \left( \frac{p_i^2}{2m_e} + V_i \right) + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_{i=1}^{Z} (\mathbf{B} \times \mathbf{r}_i)^2 \]

\[ = \hat{H}_0 + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_{i=1}^{Z} (\mathbf{B} \times \mathbf{r}_i)^2 \]

- paramagnetic term
- diamagnetic term
Diamagnetism

\[ \hat{H} = \hat{H}_0 + \mu_B (\mathbf{L} + g \mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_{i=1}^{Z} (\mathbf{B} \times \mathbf{r}_i)^2 \]

Consider \( \mathbf{B} \parallel z \)-direction \quad \( (\mathbf{B} \times \mathbf{r}_i)^2 = B^2 (x_i^2 + y_i^2) \)

\[ \Delta E_o = \frac{e^2 B^2}{8m_e} \sum_{i=1}^{Z} \langle 0 | (x_i^2 + y_i^2) | 0 \rangle \quad |0\rangle \text{ is ground state} \]

assume a spherically symmetric atom: \( \langle x_i^2 \rangle = \langle y_i^2 \rangle = \frac{1}{3} \langle r_i^2 \rangle \)

\[ \Delta E_o = \frac{e^2 B^2}{12m_e} \sum_{i=1}^{Z} \langle 0 | r_i^2 | 0 \rangle \]

\[ M = - \frac{\partial F}{\partial B} = - \frac{N}{V} \frac{\partial E_0}{\partial B} = - \frac{Ne^2 B}{6m_e V} \sum_{i=1}^{Z} \langle r_i^2 \rangle \]

susceptibility \( \chi_{\text{dia}} = \frac{M}{H} \approx \frac{\mu_0 M}{B} = - \frac{N}{V} \frac{e^2 \mu_0}{6m_e} \sum_{i=1}^{Z} \langle r_i^2 \rangle \quad (\chi \ll 1) \)

\[ \chi_{\text{dia}} \propto Z_{\text{eff}} r^2 \]
Diamagnetism

\[ \chi_{\text{dia}} \propto Z_{\text{eff}} r^2 \]

Lorentz force \( \Rightarrow \) electron motion
\( \Rightarrow \) additional angular momentum \( \Rightarrow \) additional moment

- all the electrons contribute diamagnetism.
- depends on the number of electrons.
- depends on the orbital radius of electrons.
- presents in all materials.

\[ \pi \text{ electrons run around the edge of the benzene} \Rightarrow \text{large } \chi \]

- anisotropic diamagnetism.
- large \( \chi \).
Paramagnetism

\[ \hat{H} = \hat{H}_0 + \mu_B (L + gS) \cdot B + \frac{e^2}{8m_e} \sum_{i=1}^{Z} (B \times r_i)^2 \]

associated with total angular momentum \( J = L + S \)

\[ \mu_B B \]

\[ \mu_B B \]

average moment

\[ \langle \mu_B m_J \rangle = \frac{-\mu_B e^{\mu_B B/k_BT} + \mu_B e^{-\mu_B B/k_BT}}{e^{\mu_B B/k_BT} + e^{-\mu_B B/k_BT}} = \mu_B \tanh\left(\frac{\mu_B B}{k_BT}\right) \]

\[ \frac{M}{M_s} = \tanh\left(\frac{\mu_B B}{k_BT}\right) \]

\[ \chi_{\text{para}} = \frac{n \mu_0 \mu_B^2}{k_B T} \quad (\mu_B B / k_B T \ll 1) \]

\[ \frac{M}{M_s} \]

\[ \mu_B B / k_B T \]
Paramagnetism \( (J \neq \frac{1}{2}) \)

**Partition function**

\[
Z = \sum_{m_j = -J}^{J} \exp(m_j g J \mu_B B / k_B T) = \sum_{m_j = -J}^{J} \exp(m_j x) = \frac{\sinh[(2J + 1)x / 2]}{\sinh[x / 2]} \\
\text{where} \quad x \equiv g J \mu_B B / k_B T
\]

**Average moment**

\[
\langle m_j \rangle = \frac{\sum_{m_j = -J}^{J} m_j e^{m_j x}}{\sum_{m_j = -J}^{J} e^{m_j x}} = \frac{1}{Z} \frac{\partial Z}{\partial x}
\]

\[
M = n g J \mu_B \langle m_j \rangle = n g J \mu_B \frac{\partial Z}{Z} \frac{\partial B}{\partial x} = n k_B T \frac{\partial Z}{\partial B} = M_S B_J(y)
\]

\[
M_s = n g J \mu_B J, \quad y = g J \mu_B B / k_B T
\]

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

**Para-magnetic susceptibility**

\[
\chi_{\text{para}} = \frac{n \mu_0 \mu_{\text{eff}}^2}{3k_B T}
\]

\[
\mu_{\text{eff}} = g_J \mu_B \sqrt{J(J + 1)}
\]
Van Vleck paramagnetism (J=0)

\[ \chi = \frac{n \mu_0 \mu_{\text{eff}}^2}{3k_B T} \quad \text{J} = 0 \quad \chi = 0 \]

\[ \hat{H} = \hat{H}_0 + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_{i=1}^{Z} (\mathbf{B} \times \mathbf{r}_i)^2 \]

if J=0 is the ground state,

the first-order perturbation \( \langle 0 | m | 0 \rangle = g_J \mu_B \langle 0 | \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} | 0 \rangle = 0 \)

the second-order perturbation \( \Delta E_0 = \sum_n \frac{|\langle 0 | \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} | n \rangle|^2}{E_0 - E_n} \)

\[ \chi_{\text{para-VV}} = \frac{N}{V} 2\mu_B^2 \sum_n \frac{|\langle 0 | (L_z + gS_z) | n \rangle|^2}{E_n - E_0} > 0 \]
Summary

\[ \chi = \chi_{\text{dia}} + \chi_{\text{para}} + \chi_{\text{para-VV}} \]

1. \( \chi_{\text{dia}} \): magnetic field induced electron motion
   - small value
   - increases with atomic number and orbital radius
   - usually not depends on temperature

2. \( \chi_{\text{para}} \): originates from the atom or ion with non-zero moment
   - larger than \( \chi_{\text{dia}} \)
   - competition of magnetic field and temperature
   - strongly depends on temperature
   \[ \chi = \frac{C}{T} \]

3. \( \chi_{\text{para-VV}} \): originates from second-order perturbation
   - small value, comparable with \( \chi_{\text{dia}} \)
   - not depends on temperature
Magnetic Interactions

- Dipolar interaction
- Exchange interaction
  - Heisenberg interaction
  - superexchange
  - double exchange
- Spin-Orbit coupling
- Hund’s rules
- Zeeman energy
Dipolar interaction

Two magnetic dipoles \( m_1 \) and \( m_2 \)

\[
E = -\frac{\mu_0}{4\pi r^3} \left[ m_1 \vec{m}_2 - \frac{3}{r^2} (m_1 \vec{r}) (m_2 \vec{r}) \right]
\]

\( m = 1 \mu_B \quad r = 0.1 \text{nm} \implies E = 10^{-23} \text{J} \ll 1 \text{K} \)

weak interaction

AFM

FM
Exchange interaction

two indistinguishable electrons

\[ \Psi_s = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)] \chi_s \]
\[ \Psi_T = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)] \chi_T \]

\[ \chi_s = \frac{1}{\sqrt{2}} [\alpha\beta - \beta\alpha] \]
\[ \chi_T = \begin{cases} 
\alpha\alpha & \text{singlet state} \\
\beta\beta & \text{triplet state} 
\end{cases} \]

S=0, Ms=0 (spin antiparallel)
S=1, Ms=1.0.-1 (spin parallel)

The overall wave function is antisymmetric due to Pauli exclusion principle.
**Helium atom (two electrons)**

\[
H(r_1, r_2) = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} - \frac{2e^2}{4\pi \varepsilon_0 |r_1|} - \frac{2e^2}{4\pi \varepsilon_0 |r_2|} + \frac{e^2}{4\pi \varepsilon_0 |r_2 - r_1|}
\]

\[H_0\]

\[H_{e-e}\]

Ground state of \(H_0\): both electrons are in \(nlm=100\) state

Spin part has to be antisymmetric state

\[
\Psi_{gs} = \frac{1}{\sqrt{2}} \left[ \psi_{100}(r_1)\psi_{100}(r_2) + \psi_{100}(r_2)\psi_{100}(r_1) \right] \chi_S \Rightarrow E_0 = 2E_{100}
\]

perturbation theory

\[
E_1 = \left\langle \Psi_{gs} \left| H_{e-e} \right| \Psi_{gs} \right\rangle
\]

\[E_0 + E_1\]
Helium atom  one in ground state(100), one in excited state(nlm)

Singlet  \( \Psi_{es}^{S} = \frac{1}{\sqrt{2}} [\psi_{100}(r_1)\psi_{nlm}(r_2) + \psi_{100}(r_2)\psi_{nlm}(r_1)] \chi_{S} \)

Triplet  \( \Psi_{es}^{T} = \frac{1}{\sqrt{2}} [\psi_{100}(r_1)\psi_{nlm}(r_2) - \psi_{100}(r_2)\psi_{nlm}(r_1)] \chi_{T} \)

Energy  \( E_{es} = E_{100} + E_{nlm} \)

perturbation theory  \( E_{e-e}^{S} = \langle \Psi_{gs}^{S} | H_{e-e} | \Psi_{gs}^{S} \rangle = I + J \)

\( E_{e-e}^{T} = \langle \Psi_{gs}^{T} | H_{e-e} | \Psi_{gs}^{T} \rangle = I - J \)

\[ I = \int \int |\psi_{100}(r_1)|^2 \frac{e^2}{4\pi\varepsilon_0 |r_2 - r_1|} |\psi_{nlm}(r_2)|^2 dr_1dr_2 \]

\[ J = \int \int \psi_{100}(r_1)\psi_{nlm}(r_2) \frac{e^2}{4\pi\varepsilon_0 |r_2 - r_1|} \psi_{100}^*(r_2)\psi_{100}^*(r_1) dr_1dr_2 \]

Coulomb repulsion  exchange integral

- Coulomb interaction
  - symmetrization postulate  \( E_{e-e}^{S} - E_{e-e}^{T} = 2J \)  J positive => spin parallel  J negative => spin antiparallel
The spin alignment depends on the sign of the exchange integral.
Spin does not enter the Hamiltonian. The spin enters in the solution because of the symmetry of the wave function requirement.

J > 0, S = 0 is ground state. AFM coupling
J < 0, S = 1 is the ground state. FM coupling

Many-electron system

\[ H_{\text{exch}} = - \sum_{i \neq j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j \]

\[ J_{ij} = \iint \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \psi_i^*(\mathbf{r}_2)\psi_j^*(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \]
Heisenberg model

1. J is positive for FM coupling and negative for AFM coupling.
2. Coupling of individual spins, located on the same atom, is called intra-atomic exchange.
3. Coupling of atomic moments (sum of spins) on different atoms is called inter-atomic exchange.

One dimension => Ising model

Heisenberg model may be regarded as the first term in an expansion of the exchange energy. The next higher term would be of the form

\[ H_{\text{exch}} = - \sum_{i \neq j}^N J_{ij} (s_i \cdot s_j)^2 \]

Biquadratic exchange

\[ \cos^2(\theta) \]

Perpendicular coupling  JAP, 73, 5957(1993)
Superexchange

ground state

metal oxygen metal

high energy

indirect exchange
Double exchange

Metal O Metal

(\text{LaSr})\text{MnO}_3

Mn^{3+}(d^4) \quad Mn^{4+}(d^3)

FM

ground state

AFM

indirect exchange
Double exchange vs. Superexchange

Fe$^{3+}$ -- Fe$^{3+}$ (AFM)
Superexchange

Same-valence

Fe$^{2+}$ -- Fe$^{3+}$ (FM)
double exchange

Mixed-valence
RKKY interaction

A spin in an electron sea

coupling dependents on R

\[ H = -2 \sum J(R_{ij}) S_i \cdot S_j \]

RKKY exchange coefficient

\[ J(R_{ij}) = \frac{16A^2 m_e k_F^4}{(2\pi)^3 \hbar^2} \left[ \frac{\cos(2k_F R_{ij})}{(2k_F R_{ij})^3} - \frac{\sin(2k_F R_{ij})}{(2k_F R_{ij})^4} \right] \]

\[ J(R_{ij}) = \frac{2A^2 m_e k_F}{(2\pi)^3 \hbar^2} \cos(2k_F R_{ij}) \frac{R_{ij}^3}{R_{ij}} \quad k_F R \gg 0 \]
RKKY interaction

Interaction 4f -> 5d -> 4f

Super exchange: indirect exchange through a third atom
RKKY: indirect exchange between two atoms through electrons;
long range interaction;
strongly dependent on the distance of atoms.
Spin-orbit interaction (semiclassical model)

SO 10-100 smaller than exchange interaction

Orbital momentum $\Rightarrow$ current loop $\Rightarrow$ field

Orbital field $H_{orb} = \frac{I}{2r} = -\frac{eL}{4\pi m_e r^3}$

Spin moment $m_S = -2\mu_B s / \hbar = -e\mu_0 S / m_e$

Energy $E = -m_S H_{orb} = -\frac{e^2}{4\pi \mu_0 m_e^2 r^3} L \cdot S$

H and He, SO splitting is $\sim 5 \times 10^{-5}\text{eV}$. $H_{orb} = 1\text{T}$

3d atom, SO splitting is $\sim 5 \times 10^{-2}\text{eV}$. $H_{orb} = 1000\text{T}$
Spin-orbit interaction

Fe Co Ni

Exchange interaction \(~1\text{eV}\)
Ligand field interaction: a few eV

\[\Rightarrow\] Small orbital moment

Rare earths, small ligand field
Large orbital moment

In solids, the SO interaction determines the magnetocrystalline anisotropy, spin scattering….

Tuning SO?

Strong dependent on Z, atomic shell (n)
Hund’s rules

1. The lowest electronic term has maximum spin $S$.
2. The lowest term has maximum angular momentum $L$.
3. The lowest term has the largest total angular momentum $J$ if the shell is more than half full, and the smallest $J$ if the shell is less than half full.

1. Spin-spin coupling: To minimize the Coulomb repulsion, the wave function is antisymmetric in space and symmetric in the spin. $\Rightarrow$ maximum $S$
2. Orbit-orbit coupling. Electrons orbiting in the same direction meet less often than electrons orbiting in opposite directions. $\Rightarrow$ maximum $L$
3. Spin-orbit coupling. The shell is more than half full, $S$ and $L$ point in the same direction. Highest $J$ gives lowest energy. For less than half filled shells, $S$ and $L$ are antiparallel and the energy is positive. Lowest $J$ has the lowest energy.

1. prediction of the ground state.
2. estimate the magnetic moment of an ion of ground state.
Hund’s rules

1. The lowest electronic term has maximum spin \( S \).
2. The lowest term has maximum angular momentum \( L \).
3. The lowest term has the largest total angular momentum \( J \) if the shell is more than half full, and the smallest \( J \) if the shell is less than half full.

\[
\text{Dy}^{3+} \text{ outer shell } 4f^9
\]

1. maximum \( S \) \( \Rightarrow S = (7-2) \times \frac{1}{2} = 5/2 \)
2. maximum \( L \) \( \Rightarrow L = 3+2 = 5 \)
3. largest \( J \) \( \Rightarrow J = |L+S| = |5+5/2| = 15/2 \)

a symbol of the ground state \( 2S+1L_J \)

\[
L=0, 1, 2, 3, 4, 5, 6, ... \\
S, P, D, F, G, H, I, ...
\]
Hund’s rules

d^2 and d^8

max. S is lowest
S=0

max. L is lowest
S=1, L=1

min. J is lowest
S=1, L=3, J=2

max. J is lowest
S=1, L=3, J=4

S=1

S=1, L=1

m_l 2 1
S=1, L=3

3F_2
J=|3-1|=2
S=1, L=3, J=2

3F_4
J=|3+1|=4
S=1, L=3, J=4

energy
Zeeman interaction

\[ H_{\text{zee}} = -m \mathbf{H} \]

without SO coupling

\[ m^\text{tot}_z = -\frac{\mu_B}{\hbar}(2s + 1) \]

with SO coupling

\[ m^\text{tot}_z = -\frac{\mu_B}{\hbar} g_J J \]

\[ H_{\text{zee}} = -\frac{\mu_B}{\hbar} \mathbf{H} \cdot (2s + 1) \]

\[ H_{\text{zee}} = -\frac{\mu_B}{\hbar} \mathbf{H} \cdot \mathbf{J} \]

Na: B=1T, \( E_{\text{zee}} \approx 0.1 \text{meV}, E_{\text{SO}} = 2.1 \text{meV} \)

Zeeman vs Exchange

Field: “real” field, from current flow and magnet.
Acting on spin and orbital moment

Exchange: effective field, molecular field, Weiss field
  Only acts on spin. \( H_{\text{ex}} = \frac{2\mu_B}{\hbar} s \mathbf{H}_W \)

Application: read and write bits
Summary

• **dipolar interaction** is too weak to account for the ordering of magnetic materials.

• **Exchange interaction** is the largest magnetic interaction and is the origin of the alignment of the spin system.

• The **spin-orbit interaction** creates orbital magnetism, couples the spin system to the lattice, and gives rise to the magnetocrystalline anisotropy.

• The **Zeeman interaction** allows the macroscopic alignment of spin and orbital magnetic moments, and therefore allows the creation of useful magnetic devices.
Environments

- Ligand field theory
- Jahn-Teller effect
Angular distribution of s, p, d orbitals

s

p_x

p_y

p_z

d_{z^2}

d_{xz}

d_{yz}

d_{xy}

d_{x^2-y^2}

positive

negative
Ligand field

Ligand: an atom or molecule or radical or ion that forms a complex around a central atom

\[ E_{d_{x^2-y^2}} > E_{d_{xy}} \]

ligand field originates from an electrostatic interaction (correlation).
Ligand field theory (one electron model)

SO is small. Ligand field acts on orbital only.

Single d electron in the negatively charged ligands

- $d_{xz}$
- $d_{yz}$
- $d_{xy}$
- $d_{x^2-y^2}$
- $d_{z^2}$

In tetrahedral geometry:
- $d_{xz}$
- $d_{yz}$
- $d_{xy}$

In octahedral geometry:
- $d_{xz}$
- $d_{yz}$
- $d_{xy}$
- $d_{x^2-y^2}$
- $d_{z^2}$
Spin state of multi-electrons

Octahedral

\[ \text{Ecoul} > \text{Et}_{2g} - \text{Ee}_g \]
\[ \text{Ecoul} < \text{Et}_{2g} - \text{Ee}_g \]

\( d^6(\text{Fe}^{2+}) \)

\( d_{z^2} \)
\( d_{x^2-y^2} \)
\( d_{xz} \)
\( d_{yz} \)
\( d_{xy} \)

S=2
S=0

coulomb energy is high => high spin
coulomb energy is low => low spin
John-Teller effect

Mn$^{3+}$ (d$^4$)

octahedral

distortion

tetragonal

\[ d_{x^2-y^2}, \ d_{z^2}, \ ? \ Mn^{4+} (d^3) \]

\[ d_{xy}, d_{xz}, d_{yz} \]
Magnetism in metals

- Pauli paramagnetism
- Landau diamagnetism
- Spontaneous Ferromagnetism
- Anisotropy
Pauli paramagnetism

\[ n_{\uparrow} = \frac{1}{2} N_{E_F} \mu_B B \quad n_{\downarrow} = \frac{1}{2} N_{E_F} \mu_B B \]

\[ M = \mu_B (n_{\uparrow} - n_{\downarrow}) = N_{E_F} \mu_B^2 B \]

\[ \chi_P = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \mu_0 N_{E_F} \mu_B^2 \]

\[ \chi = \frac{1}{2\pi^2} \mu_0 \mu_B^2 \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E_F} \]

• 2 or 3 orders smaller paramagnetism in insulator
  only electrons around Fermi surface contribute \( \chi_P \).
• weak T dependent
Landau diamagnetism

electrons in magnetic field $\Rightarrow$ orbital perpendicular to field is quantized

**Energy**

$$E = (l + \frac{1}{2}) \hbar \omega_c + \frac{\hbar k_z^2}{2m_e} \quad \omega_c = \frac{eB}{m_e}$$
cyclotron frequency

**difference in total energy**

$$\Delta U = U(B \neq 0) - U(B = 0) = \frac{V_k_Ε e^2 B^2}{24\pi^2 m_e}$$

$$\chi_L = -\frac{\mu_0}{V} \frac{\partial^2 \Delta U}{\partial B^2} = -\frac{V_k_Ε e^2}{12\pi^2 m_e} = -\frac{1}{3} \mu_0 \mu_B^2 N_{E_F}$$

if the mass of electron is effective $m^*$

$$\chi_L = -\frac{V_k_Ε e^2}{12\pi^2 m_e} = -\frac{1}{3} \left(\frac{m_e}{m^*}\right)^2 \mu_0 \mu_B^2 N_{E_F}$$

- **quantum effect**
- **weak T dependent**

$$\chi_P = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \mu_0 N_{E_F} \mu_B^2$$

$$\chi = \chi_P + \chi_L = \chi_P \left[1 - \frac{1}{3} \left(\frac{m_e}{m^*}\right)^2\right] \Rightarrow \begin{cases} m^* > m / \sqrt{3} & \chi > 0 \text{ PM} \\ m^* < m / \sqrt{3} & \chi < 0 \text{ DM} \end{cases}$$
Spontaneously spin-split bands

move some electrons from spin down band to spin up band
the number of electrons moved is \( N_{Ef} \delta E / 2 \)

the energy change is
\[
\Delta E_K = N_{Ef} \delta E / 2 \times \delta E = \frac{1}{2} N_{Ef} \delta E^2
\]

Magnetization \( M = N_{Ef} \mu_B (n_\uparrow - n_\downarrow) = N_{Ef} \delta E \)
in molecular field theory, all spins ‘feel’ an field \( \lambda M \) produced by all their neighbors

molecular field energy
\[
\Delta E_{MF} = -\int_0^M \mu_0 (\lambda M')dM' = -\frac{1}{2} \mu_0 \lambda M^2 = -\frac{1}{2} \mu_0 \lambda (N_{Ef} \delta E)^2
\]

the total energy change is
\[
\Delta E = \Delta E_K + \Delta E_{MF} = \frac{1}{2} N_{Ef} \delta E^2 (1 - \mu_0 \lambda N_{Ef})
\]
if \( \Delta E < 0 \), spontaneous FM is possible.

\[ \mu_0 \lambda N_{Ef} \geq 1 \] 
stoner criterion
Spin-Orbit Interaction $\Rightarrow$ Anisotropy

$H_{SO} = \xi(r)L\cdot S$

Magneto-crystalline anisotropy (MCA)

$\Delta E_{SO} = \langle H_{SO} \rangle_{hard} - \langle H_{SO} \rangle_{easy} = \xi[\langle L\cdot S \rangle_{hard} - \langle L\cdot S \rangle_{easy}] > 0$

SO in 3d is small $\Rightarrow$ small MCA

Bruno Model

$\Delta E_{SO} = \xi[\langle L\cdot S \rangle_{hard} - \langle L\cdot S \rangle_{easy}] = \xi \frac{4\mu_B}{S} (m_o^{easy} - m_o^{hard}) > 0$

Orbital moment is larger along the easy axis.
MCA $\propto$ difference between the orbital moment along easy and hard directions.
Experiment

(a) (0001) Co
(111) Au

(b) Orbital moment

(c) Spin moment

**Origin of Band Structure**

In reality, the DOS is more complex than Stoner Model

\[
\phi_j(k) = \sum_n d_j^{(n)} e^{i n k a}
\]

\[
\phi_j(0) = \sum_n d_j^{(n)}
\]

\[
\phi_j(\pi/a) = \sum_n d_j^{(n)} e^{i n \pi} = \sum_n (-1)^n d_j^{(n)}
\]

\[
E = E_F
\]

\[
\Delta
\]

\[
d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}
\]

\[
k=0, k=\pi/a
\]
Anisotropy Bonding ⇔ Band

- **d_{xy}**, **d_{x^2-y^2}** — "in-plane" d-orbitals
- **d_{xz}**, **d_{yz}**, **d_{z^2}** — "out-of-plane" d-orbitals

**Bulk fcc**

**(001) surface**

**(001) interface**

- **2V_//**
- **2V_⊥**

Energy (E) vs. momentum plot:

- **E_{eg}**, **E_{t_{2g}}**, **E_{d_{xy}}**, **E_{d_{z^2}}**, **E_{d_{x^2-y^2}}**
Microscopic Origin of Magnetic Anisotropy in Au/Co/Au Probed with X-Ray Magnetic Circular Dichroism (Yang)  
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PRL 100, 076401 (2008)

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Thank You!