SEOUL NATIONAL UNIVERSITY – SCHOOL OF PHYSICS

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SPRING SEMESTER 2004

Solid State Physics II

Chapter 8 Magnetism

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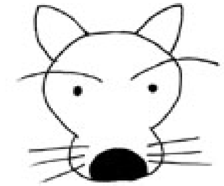

Theory of Magnetism

Reading Assignment:

1. Ashcroft/Mermin, Chap. 31, 32, and 33. [Basic]
2. Kittel, Chap. 14 and 15. [Basic]
3. R.M. White, Quantum Theory of Magnetism [Advanced]

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Magentism in Materials

Magnetic responses of materials are characterized by the magnetic susceptibility.

$$\mathbf{M} = \chi \mathbf{H}$$

- Pauli paramagnetism: [Good metals]

$$\chi_P(T) = \mu_B^2 D(\epsilon_F)$$

- Ferromagnetism: [Transition metals]

  Curie-Weiss law

$$\chi_F(T) = \frac{C}{T - T_c} \qquad (T > T_c)$$

  with the Curie constant

$$C = \frac{N}{V} \frac{(g\mu_B)^2}{3k_B} J(J+1)$$

- Anti-ferromagnetism: [Insulators, e.g., transition metal oxides]

$$\chi_{AF}(T) = \frac{C}{T + T_c} \qquad (T > T_c)$$

- Diamagnetism: [molecular insulators]

$$\chi_{VV} < 0$$

- Perfect diamagnetism: [superconductors]

$$\chi_L = -\frac{1}{4\pi}$$

Pauli Paramagnetism

Consider a metal under the external magnetic field $\mathbf{H}$:

$$\mathcal{H}_o = \sum_{k\sigma} \epsilon_k n_{k\sigma}$$

$$\mathcal{H}_1 = -\mu_B H m$$

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_1 = \sum_{k\sigma} (\epsilon_k - \sigma\mu_B H) n_{k\sigma}$$

where $n_{k\sigma} = c^+_{k\sigma} c_{k\sigma}$, $m = \sum_{k\sigma} \sigma n_{k\sigma} = \sum_k (n_{k+} - n_{k-})$ and $\sigma = \pm 1$.

Magnetization:

$$M = \langle\Phi|\mu_B \sum_{k\sigma} \sigma n_{k\sigma}|\Phi\rangle = \mu_B(N_+ - N_-)$$

$$|\Phi\rangle = \prod_{k_\sigma < k_{F\sigma}} c^+_{k\sigma}|O\rangle = \prod_{(\epsilon_k - \sigma\mu_B H) < \epsilon_F} c^+_{k\sigma}|O\rangle$$

$$N_\sigma = \langle\Phi|\sum_k n_{k\sigma}|\Phi\rangle = \sum_{\epsilon_k < \epsilon_F + \sigma\mu_B H} 1 = \int_{-\infty}^{\epsilon_F+\sigma\mu_B H} \frac{1}{2} D(\epsilon) d\epsilon$$

$$N_+ - N_- = \int_{-\infty}^{\epsilon_F+\mu_B H} \frac{1}{2} D(\epsilon) d\epsilon - \int_{-\infty}^{\epsilon_F-\mu_B H} \frac{1}{2} D(\epsilon) d\epsilon = \frac{1}{2} \int_{\epsilon_F-\mu_B H}^{\epsilon_F+\mu_B H} \frac{1}{2} D(\epsilon) d\epsilon = \mu_B D(\epsilon_F) H$$

Therefore, from the magnetization $M = \mu_B^2 D(\epsilon_F) H$, we can obtain the T-independent susceptibility χ_P

$$\chi_P = \mu_B^2 D(\epsilon_F)$$

Stoner Theory of Ferromagentic Metals

Interacting electron gas:

$$\begin{aligned}
\mathcal{H}_o &= \sum_k \epsilon_k n_{k\sigma} + U \sum_{kk'q\sigma} c^+_{k-q\sigma} c^+_{k'+q-\sigma} c_{k'-\sigma} c_{k\sigma} \\
&\approx \sum_k \epsilon_k n_{k\sigma} + U \sum_\sigma \left(\sum_k n_{k\sigma} \sum_{k'} n_{k'-\sigma} \right) \\
&= \sum_k \epsilon_k n_{k\sigma} + U(N_+N_- + N_-N_+) \\
&= \sum_k \epsilon_k n_{k\sigma} + U\frac{1}{2}(N^2 - m^2) \\
&= \sum_k \epsilon_k n_{k\sigma} + \frac{1}{2}UN^2 - \frac{1}{2}Um^2
\end{aligned}$$

When the external field H is applied,

$$\mathcal{H}_1 = -\mu_B H m$$

Redefining the energy offset,

$$\mathcal{H} = \mathcal{H}_o + \mathbf{H}_1 - \frac{1}{2} U N^2$$

we have

$$\mathcal{H} = \sum_k \epsilon_k n_{k\sigma} - \frac{U}{2} m^2 - \mu_B H m$$

Introducing the effective mean field H_{eff},

$$\mathcal{H} = \sum_k \epsilon_k n_{k\sigma} - \mu_B H_{\text{eff}} m$$

$$H_{\text{eff}} = H + \frac{U}{2\mu_B} m$$

$$m = N_+ - N_- = \frac{1}{2} \int_{\epsilon_F - \mu_B H_{\text{eff}}}^{\epsilon_F + \mu_B H_{\text{eff}}} D(\epsilon) d\epsilon \approx \mu_B D(\epsilon_F) H_{\text{eff}}$$

$$m = \mu_B D(\epsilon_F) H_{\text{eff}} = \mu_B D(\epsilon_F) \left(H + \frac{U}{2\mu_B} m \right)$$

$$\therefore m = \frac{\mu_B D(\epsilon_F)}{1 - UD(\epsilon_F)/2} H$$

Since $M = \mu_B m$, the Stoner susceptibility χ_S becomes

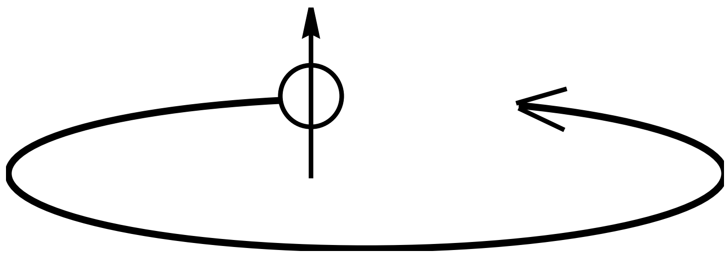
$$\chi_S = \frac{\mu_B^2 D(\epsilon_F)}{1 - UD(\epsilon_F)/2}$$

If $UD(\epsilon_F)/2 > 1$, then the paramagnetic state becomes unstable!

Stoner criterion for the ferromangetic instability

Local Magnetic Moment

- Magnetic moment: $\mathcal{M} = g\mu_B \mathbf{J}$
  proportional to the angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$
  - Spin moment $\mathbf{S}$
  - Orbital moment $\mathbf{L}$



Localized State

- Since the rotational symmetry is preserved, it has the quantum eigenstates $|jm\rangle$:

$$\mathbf{J}^2|jm\rangle = j(j+1)|jm\rangle$$

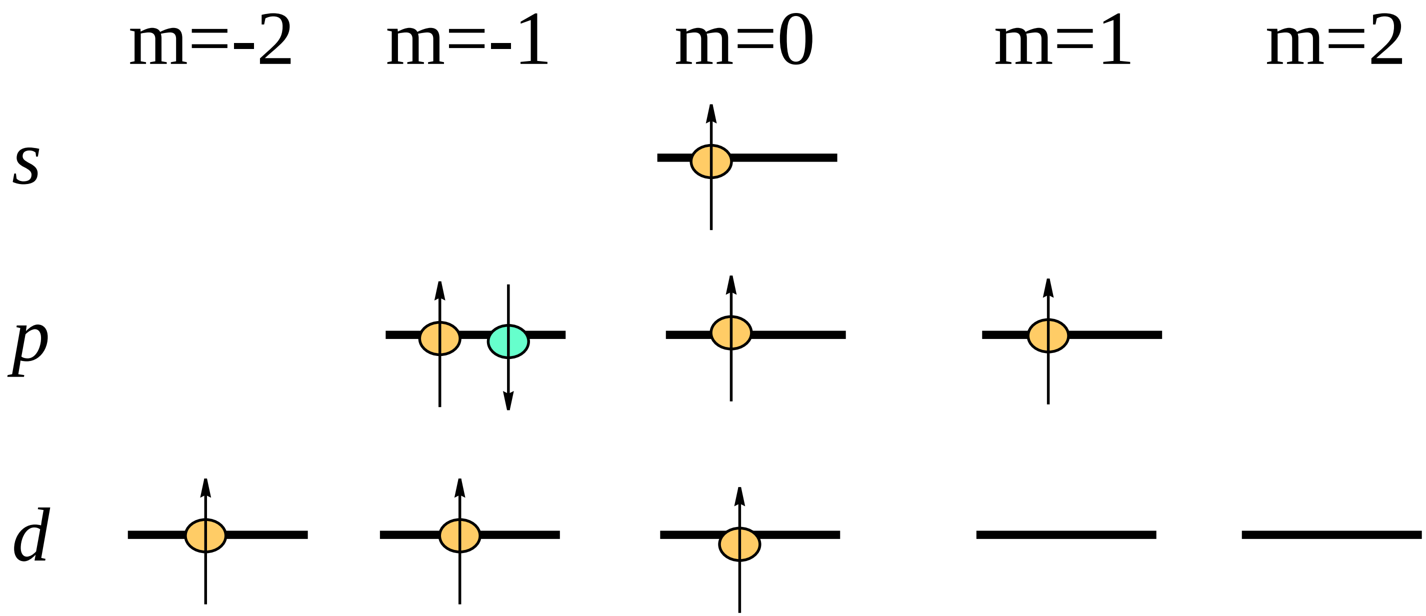
where

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

- If the spherical symmetry is broken, e.g., inside a lattice, the orbital moment can be quenched due to the lack of rotational symmetry, i.e.,

$$\langle \mathbf{L} \rangle = 0$$

Magnetic Moment of an Atom



Hund's Rule

1. Maximum total $S = \max S_z$ with $S_z = \sum_i m_{si}$
   Obeying the Pauli exclusion principle

2. Maximum total $L = \max L_z$ with $L_z = \sum_i m_{li}$
   Minimizing the Coulomb interaction energy

3. Spin-orbit interaction:

$$J = \begin{cases} |L+S| & \text{if less than half-filled} \\ |L-S| & \text{if more than half-filled} \end{cases}$$

Exchange Energy

- Pauli exclusion principle: anti-symmetric two-particle wavefunction

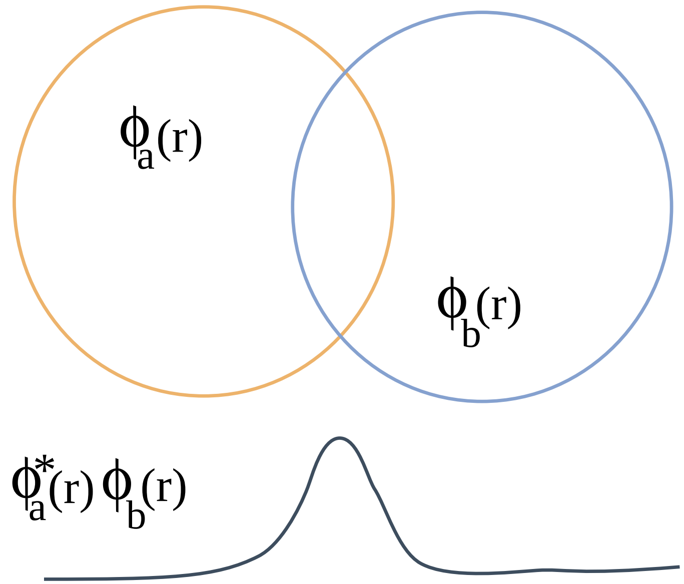
$$|\Psi(\mathbf{r}_1 \uparrow; \mathbf{r}_2 \uparrow)\rangle = \frac{1}{\sqrt{2}}\left[\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\right] | \uparrow\rangle | \uparrow\rangle$$

- Coulomb interaction

$$V_C(\mathbf{r}_1 - \mathbf{r}_2) = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\begin{aligned} E_{C2} &= \ < \Psi(1,2)|V_C|\Psi(1,2)\rangle \\ &= \int d\mathbf{r}_1 d\mathbf{r}_2 V_C(\mathbf{r}_1 - \mathbf{r}_2)|\phi_a(\mathbf{r}_1)|^2|\phi_b(\mathbf{r}_2)|^2 - \\ & \int d\mathbf{r}_1 d\mathbf{r}_2 V_C(\mathbf{r}_1 - \mathbf{r}_2)\phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_2)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \\ &= U_{ab} - J_{ab} \end{aligned}$$

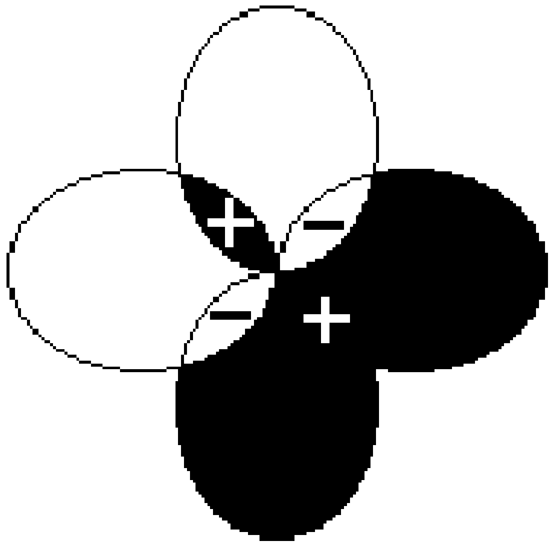
Exchange Density



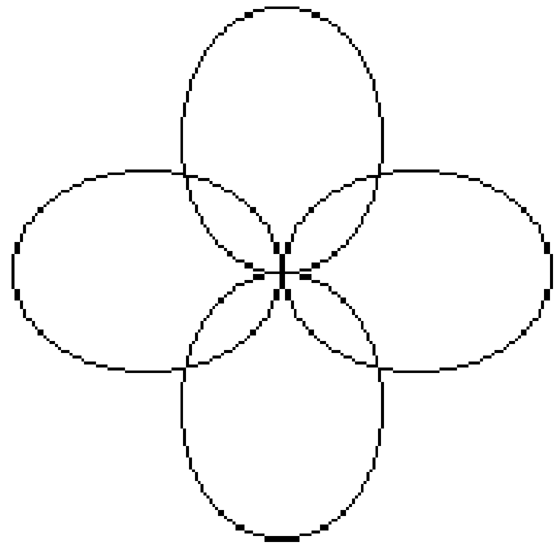
$\Rightarrow$ Gaining more (negative) exchange energy by aligning spins:

Hund's 1st rule

Overlap and Exchange Integrals of the atomic p-orbitals



$S_{ab} = 0$

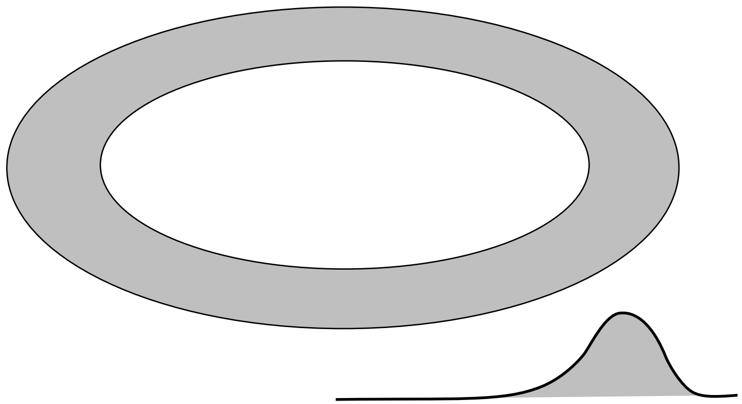


$K_{ab} > 0$

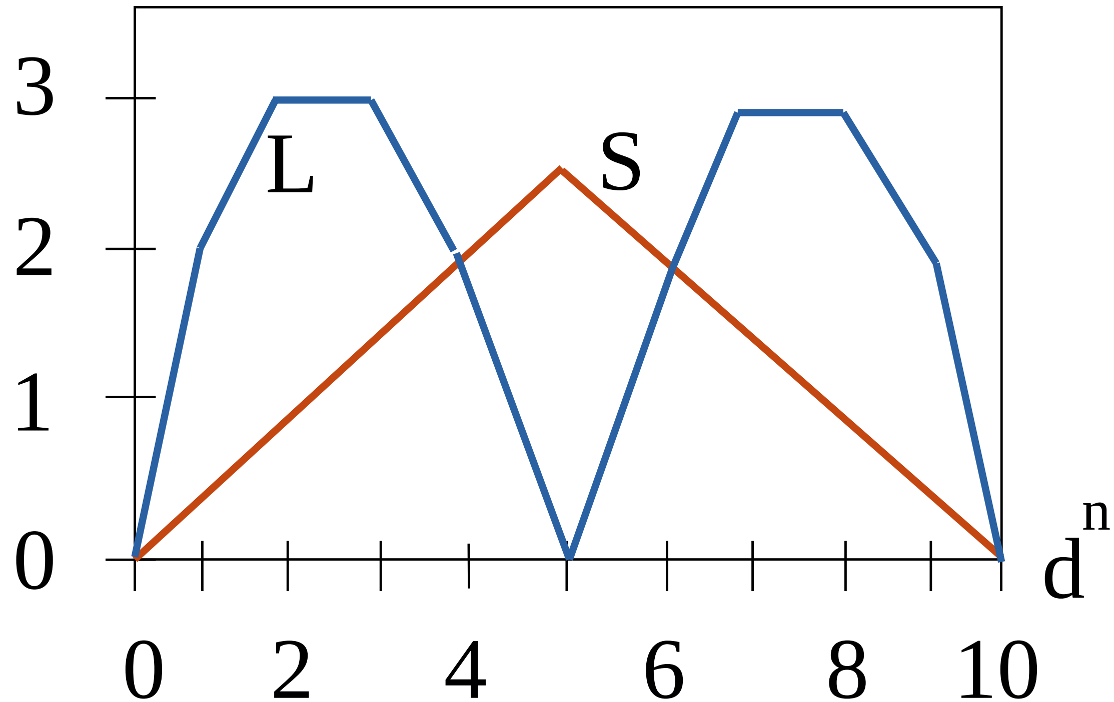
Minimization of Coulomb Energy Term U_{ab}

$\Rightarrow$ by letting $\rho(\mathbf{r})$ be separated: Hund's 2nd rule

$$Y_{lm}(\theta,\phi) = (-1)^m Y^*_{l-m}(\theta,\phi)$$



Configuration of 3d Transition Metal Ions



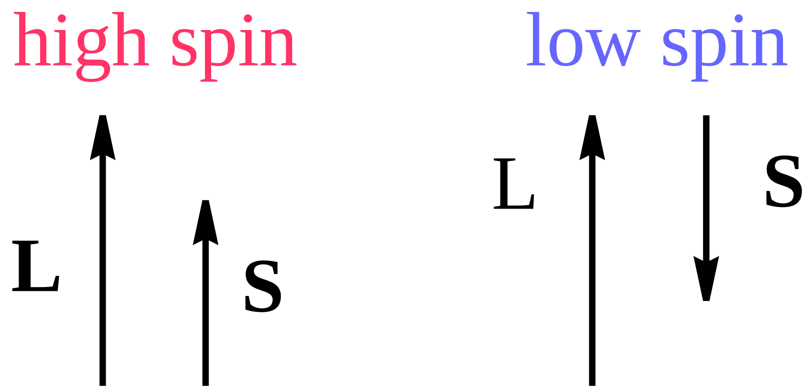
Spin-Orbit Coupling

$\Rightarrow$ determined by the sign of the coupling constant

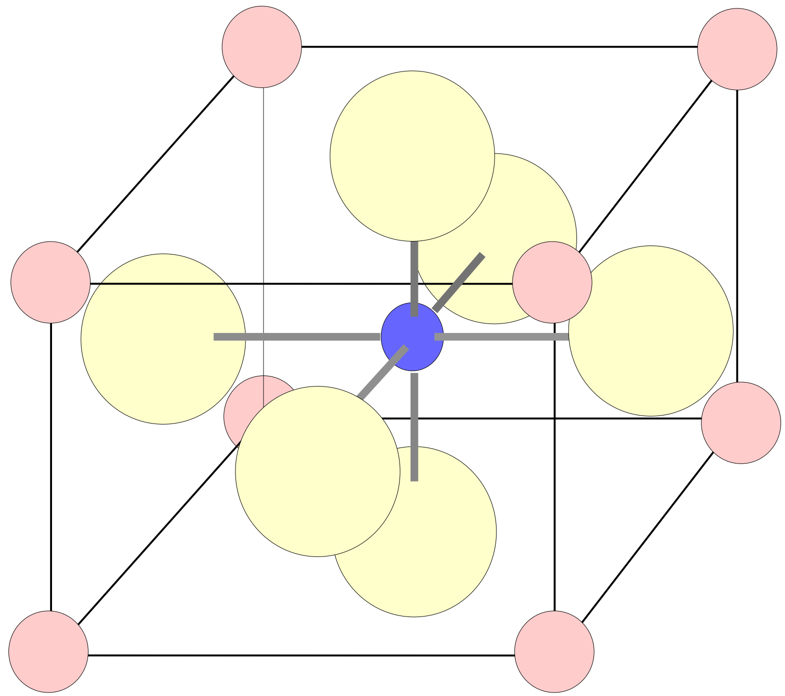
$$\lambda \mathbf{L} \cdot \mathbf{S}$$

where

$$\lambda \sim -\frac{dV(r)}{dr}$$

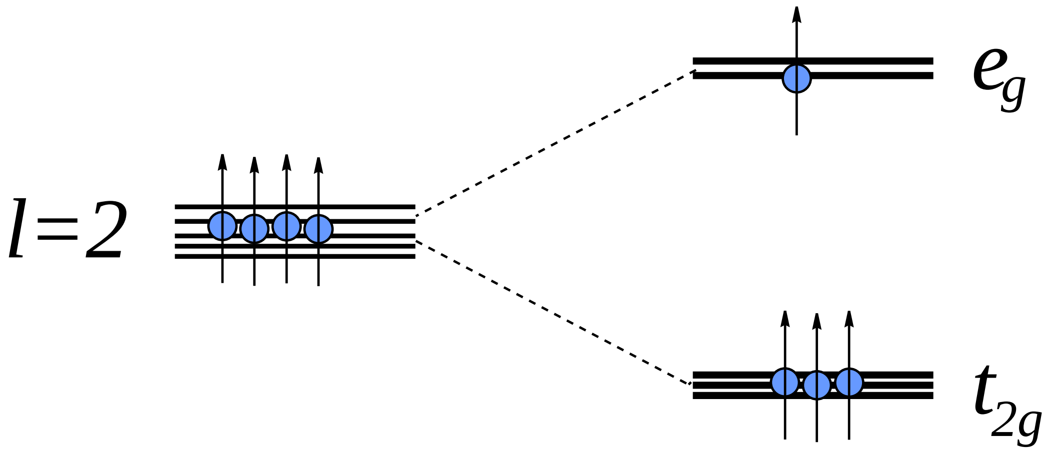


Orbital States in a Crystal Lattice



Cubic Lattice Symmetry: Broken Spherical Symmetry

$\Rightarrow$ Crystal Field Splitting:



$$|e_g\rangle = \{|x^2 - y^2\rangle, |z^2 - r^2/3\rangle\}$$

$$|t_{2g}\rangle = \{|xy\rangle, |yz\rangle, |zx\rangle\}$$

Curie's Law

Consider a set of identical atoms with spin J.

$$\vec{\mu} = -g\mu_B \mathbf{J}$$

Partition Function:

$$Z = e^{-\beta F} = \sum_{m=-J}^{J} e^{-\beta\gamma H m} = \frac{e^{\beta\gamma H(J+1/2)} - e^{-\beta\gamma H(J+1/2)}}{e^{\beta\gamma H/2} - e^{-\beta\gamma H/2}}$$

where $\gamma = g\mu_B$.

$$M = -\frac{N}{V}\frac{\partial F}{\partial H} = \frac{N}{V}\gamma J B_J(\beta\gamma J H)$$

where the Brillouin function:

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

In the limit of $k_B T \gg \gamma H$,

$$\coth x \approx \frac{1}{x} + \frac{x}{3} + ...$$

$$B_J(x) \approx \frac{J+1}{3J} x + o(x^3)$$

Curie's law: ($k_B T \gg g\mu_B H$)

$$\chi_C = \frac{N}{V} \frac{(g\mu_B)^3}{3} \frac{J(J+1)}{k_B T}$$

Spin Hamiltonian: A Simple Model for the Exchange Interactions

When $U \gg W$, the localized states of $|\Psi_o\rangle$ becomes stable relative to the band (molecular) state $|\Psi_2\rangle$:

$$|\Psi_o\rangle = \frac{1}{\sqrt{2}} \left[|\phi_\alpha, s_1\rangle |\phi_\beta, s_2\rangle - |\phi_\beta, s_2\rangle |\phi_\alpha, s_1\rangle \right]$$

which is a combination of the localized orbitals $|\phi_{A,B}\rangle$ instead of the molecular states $|\psi_\pm\rangle$.

Here the starting Hamiltonian $\mathcal{H}_o$ include the interaction term of $\hat{U}$:

$$\mathcal{H}_o = h_A + h_B + \hat{U}$$

and the hopping term V_{AB} should be considered as a perturbation.

Many-Particle Excited States

Two-particle excited states:

$$|\Psi_o(s_1, s_2)\rangle = |\phi_A, s_1\rangle|\phi_B, s_2\rangle$$

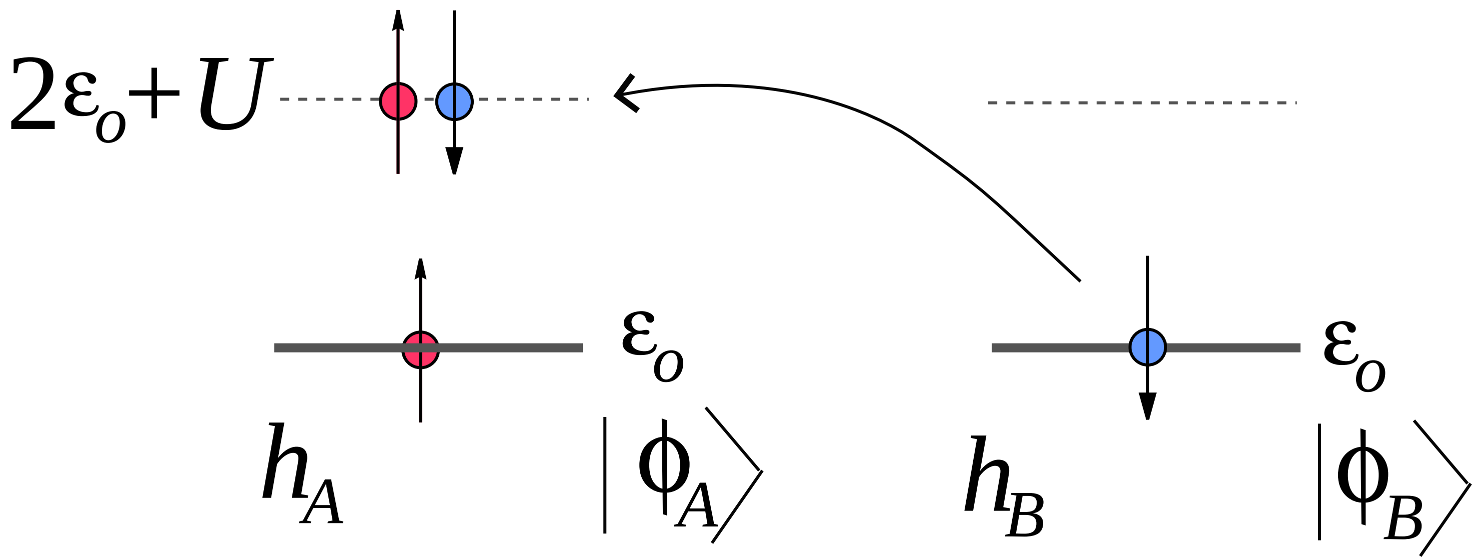
$$|\Psi_A(\uparrow,\downarrow)\rangle = |\phi_A,\uparrow\rangle|\phi_A,\downarrow\rangle$$

$$|\Psi_B(\uparrow,\downarrow)\rangle = |\phi_B,\uparrow\rangle|\phi_B,\downarrow\rangle$$

$$\mathcal{H}_o|\Phi_o\rangle = 2\varepsilon_o|\Psi_o\rangle$$

$$\mathcal{H}_o|\Phi_A\rangle = (2\varepsilon_o + U)|\Psi_A\rangle$$

$$\mathcal{H}_o|\Phi_B\rangle = (2\varepsilon_o + U)|\Psi_B\rangle$$



$2\varepsilon_o+U$
ε_o
ε_o
h_A
$|\phi_A\rangle$
h_B
$|\phi_B\rangle$

Only remaining degrees of freedom of the ground state $|\Psi_o\rangle$ are

spins!

$$|\Psi_p(s_1, s_2)\rangle = |s_1, s_2\rangle$$

Energy Correction via the Perturbation Theory with $\mathcal{H}_1 = V_{AB}$

- First-order correction:

$$\langle s_1, s_2|\mathcal{H}_1|s_1, s_2\rangle = 0$$

Pauli exclusion prohibits the double occupancy at the same site:

$$|\phi_A, \uparrow\rangle|\phi_A, \uparrow\rangle = 0$$

That is,

$$|\phi_A, s_1\rangle|\phi_A, s_1\rangle = 0$$

- Second-order correction:

$$\langle\uparrow,\downarrow|\mathcal{H}_1|\Phi_A\rangle = \langle\uparrow,\downarrow|\mathcal{H}_1|\Phi_B\rangle = t$$

$$\langle\uparrow,\uparrow|\mathcal{H}_1|\Phi_A\rangle = \langle\uparrow,\uparrow|\mathcal{H}_1|\Phi_B\rangle = 0$$

$$E^{(2)}_{\uparrow,\uparrow} = -{\sum_n}' \frac{|\langle\uparrow,\uparrow|\mathcal{H}_1|\Phi_n\rangle|^2}{E_n - E_o} = 0$$

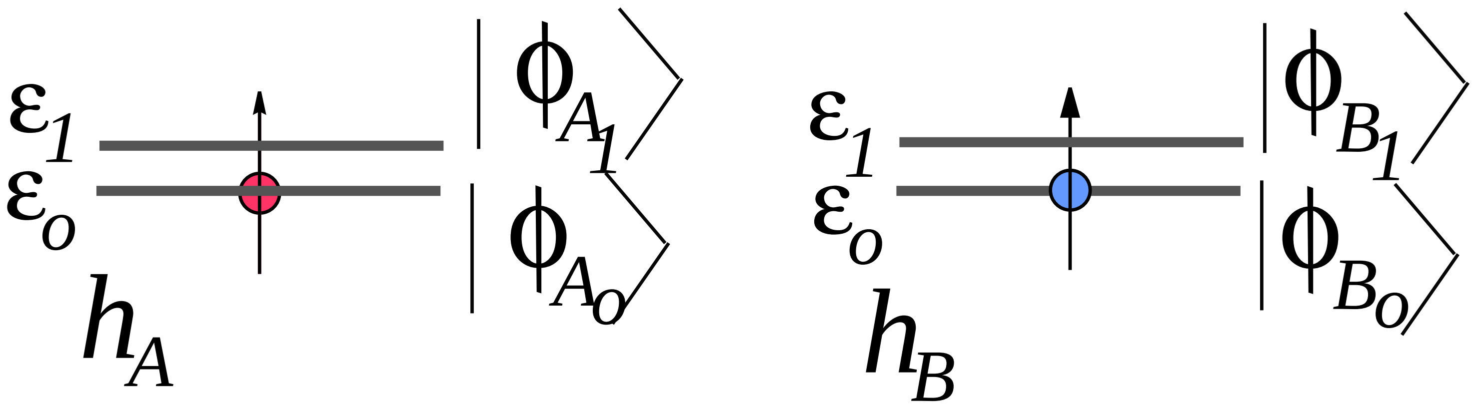
$$E^{(2)}_{\uparrow,\downarrow} = -{\sum_n}' \frac{|\langle\uparrow,\downarrow|\mathcal{H}_1|\Phi_n\rangle|^2}{E_n - E_o} = -\frac{2t^2}{U} = -J_{\mathrm{AF}}$$

Anti-Ferromagnetic Superexchange Interactions

$$\mathcal{H}_{\mathrm{eff}} = +J_{\mathrm{AF}}\vec{\sigma}_A \cdot \vec{\sigma}_B$$

Ferromagnetic Exchange Interactions

What happens if additional degenerate (or almost degenerate) states exist at each atom while $U \gg W$?



Now additional excited states become available:

$$|\Phi_A(\uparrow,\uparrow)\rangle = |\phi_{A_o},\uparrow\rangle|\phi_{A_1},\uparrow\rangle$$

and

$$\langle\Phi_o(\uparrow,\uparrow)|\mathcal{H}_1|\Phi_A(\uparrow,\uparrow)\rangle \neq 0$$

$$\mathcal{H}_o|\Phi_A(\uparrow,\uparrow)\rangle = (\varepsilon_o+\varepsilon_1+U-J)|\Phi_A(\uparrow,\uparrow)\rangle = E_A(\uparrow,\uparrow)|\Phi_A(\uparrow,\uparrow)\rangle$$

If the exchange energy is larger than the difference $|\varepsilon_o-\varepsilon_1|$, i.e.,

$$J > |\varepsilon_o - \varepsilon_1|$$

we have

$$E_A(\uparrow,\uparrow) < E_A(\uparrow,\downarrow)$$

Therefore,

$$E^{(2)}_{\uparrow,\uparrow} = -\sum_n{}' \frac{|\langle\uparrow,\uparrow|\mathcal{H}_1|\Phi_n\rangle|^2}{E_n - E_o} \approx -\frac{2t^2}{U-J} < E^{(2)}_{\uparrow,\downarrow} = -\frac{2t^2}{U}$$

Ferromagnetic Exchange Interaction

$$\mathcal{H}_{\mathrm{eff}} = -|J_{FM}|\vec{\sigma}_A \cdot \vec{\sigma}_B$$

Spin Hamiltonian: Heisenberg Model

$$\mathcal{H} = -\sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i$$

Mean field solution:

Introducing an effective field $\mathbf{H}_{\text{eff}}$,

$$\mathcal{H} = -\sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i = g\mu_B \sum_i \mathbf{S}_i \cdot \mathbf{H}_{\text{eff}}$$

where the effective mean field

$$\mathbf{H}_{\text{eff}} = \mathbf{H} - \frac{1}{g\mu_B} \sum_j J_{ij} \mathbf{S}_j$$

and the average magnetization

$$\langle \mathbf{S}_i \rangle = \frac{V}{N} \frac{\mathbf{M}}{g\mu_B}$$

$$\mathbf{H}_{\text{eff}} = \mathbf{H} + \lambda \mathbf{M}$$

$$\lambda = \frac{V}{N} \frac{J_o}{(g\mu_B)^2}$$

$$M = -\frac{N}{V}\frac{\partial F}{\partial H} = M_o(\frac{H_{\text{eff}}}{T})$$

- For the case of $H = 0$,

  one can fine the magnetization M by solving the equation:

$$M(T) = M_o(\frac{\lambda M}{T})$$

$$\chi_o(T) = \left(\frac{\partial M_o}{\partial H}\right)_{H=0} = \frac{M_o'(0)}{T}$$

where the Curie's constant is determined to be $C_o = M_o'(0)$.

- For the case of $H \neq 0$,

$$\chi = \frac{\partial M}{\partial H} = \frac{\partial M_o}{\partial H_{\text{eff}}} \frac{\partial H_{\text{eff}}}{\partial H} = \chi_o(1 + \lambda\chi)$$

$$\chi = \frac{\chi_o}{1 - \lambda\chi_o} = \frac{C_o}{T - T_c}$$

where the critical temperature T_c becomes

$$T_c = \frac{N}{V} \frac{(g\mu_B)^2}{3k_B} S(S+1)\lambda = \frac{S(S+1)}{3k_B} J_o$$