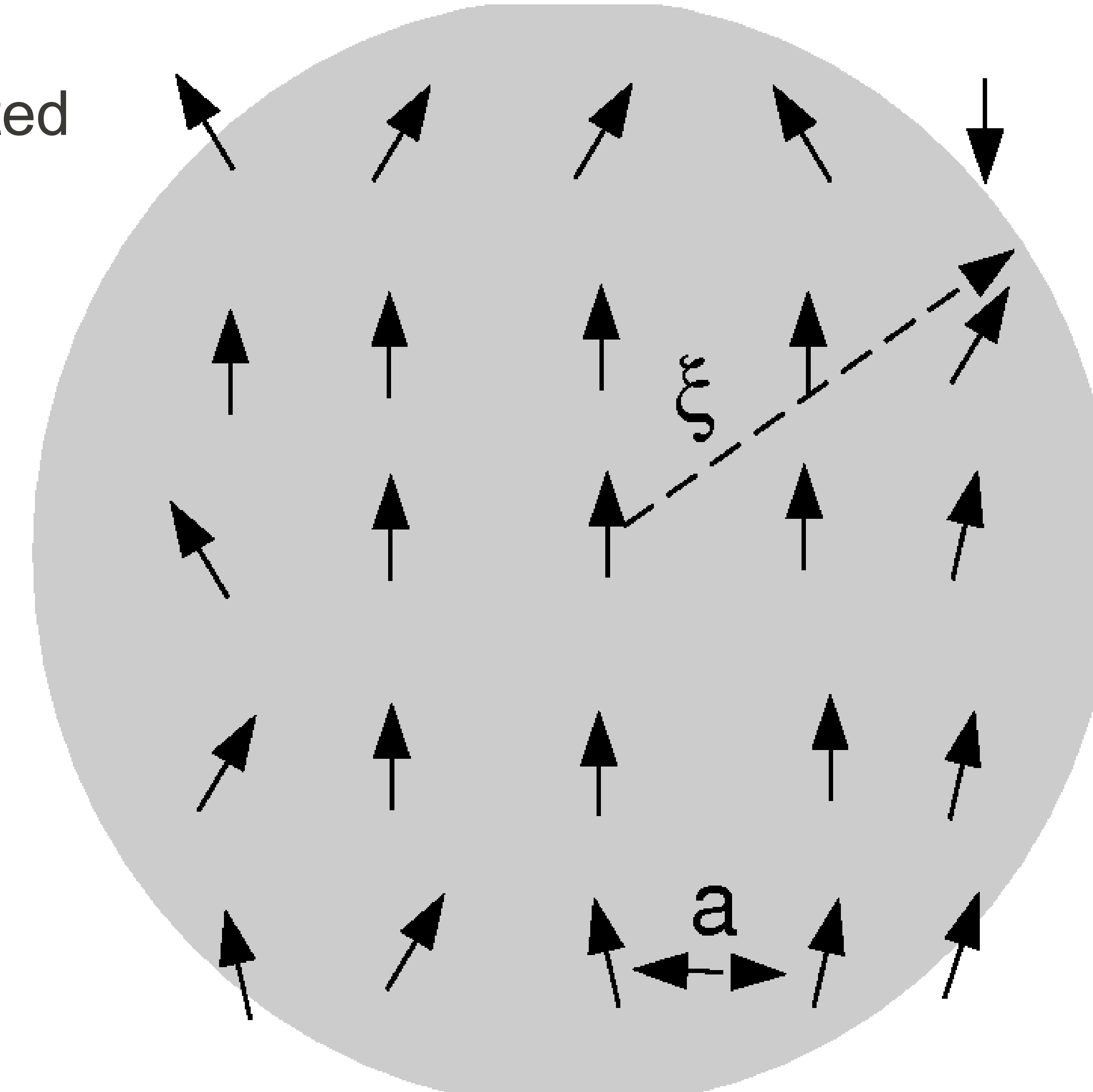
Magnetism and Intersite Correlations

Consider once again an isolated moment of magnitude *mμB* in an external field

$$\chi \approx \frac{(m\mu_B)^2}{k_B T}$$

$$E \approx \frac{(m\mu_B B)^2}{k_B T}$$



If we consider two s =1/2 spins, $\uparrow_1 \downarrow_2$, then the correlation is usually parameterized by the Heisenberg exchange Hamiltonian, or

$$H = -2J\sigma_1 \cdot \ \sigma_2$$

where J is the exchange splitting between the singlet and triplet energies.

$$\left\{ \begin{array}{ll} |\uparrow\uparrow\rangle & \\ |\uparrow\downarrow\rangle & +|\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle & \end{array} \right\} E_t$$

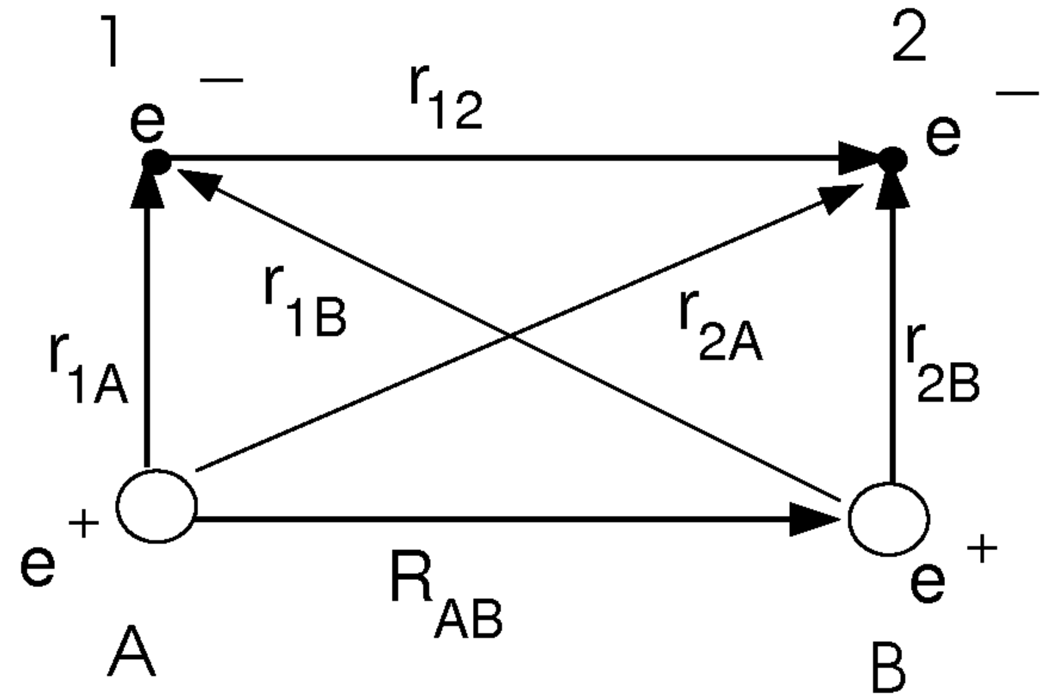
$$\{|\uparrow\downarrow\rangle \ - |\downarrow\uparrow\rangle\} \, E_s$$

$$E_t - E_s = -J$$

The trick then is to calculate J!

The Exchange Interaction Between Localized Spins

$$
\begin{aligned}
H &= H_1 + H_2 + H_{12} \\
H_1 &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} \\
H_{12} &= \frac{e^2}{r_{12}} + \frac{e^2}{R_{AB}}
\end{aligned}
$$



$$
\begin{aligned}
\psi_{12} &= (\phi_A(1) + \phi_B(1))\,(\phi_A(2) + \phi_B(2)) \otimes \text{spin part} \\
&= (\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2) + \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)) \\
&\quad \otimes \text{spin part}
\end{aligned}
$$

Heitler-London approximation:

For the anti-symmetric spin singlet states

$$\psi_{12} \simeq \ (\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)) \otimes \text{spin singlet}$$

For the symmetric spin triplet states

$$\psi_{12} = \phi_A(1)\phi_B(2) \pm \phi_B(1)\phi_A(2) \otimes \ \text{spin part}$$

The energy of these states may then be calculated by evaluating $\frac{\langle\psi_{12}|H|\psi_{12}\rangle}{\langle\psi_{12}|\psi_{12}\rangle}$

$$E = \frac{\langle\psi_{12}|H|\psi_{12}\rangle}{\langle\psi_{12}|\psi_{12}\rangle} = 2E_I + \frac{C \pm \ A}{1 \pm S}, \quad + \text{singlet} \ , - \ \text{triplet}$$

Where:

$$E_I = \int d^2 r_1 \phi_A^*(1) \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{1A}} \right\} \phi_A(1) < 0$$

The Coulomb integral

$$C = e^2 \int d^3 r_1 d^3 r_2 \left\{ \frac{1}{R_{AB}} + \frac{1}{r_{12}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} \right\} |\phi_A(1)|^2 \, |\phi_B(2)|^2 < 0$$

the exchange integral

$$A = e^2 \int d^3 r_1 d^3 r_2 \left\{ \frac{1}{R_{AB}} + \frac{1}{r_{12}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} \right\} \phi_A^*(1) \phi_A(2) \phi_B(1) \phi_B^*$$

the overlap integral

$$S = \int d^3 r_1 d^3 r_2 \phi_A^*(1) \phi_A(2) \phi_B(1) \phi_B^*(2) \quad (0 < S < 1)$$

All EI , C, A, S ∈ R. So

$$-J = E_t - E_s = 2E_I + \frac{C-A}{1-S} - \left\{ 2E_I + \frac{C+A}{1+S} \right\}$$

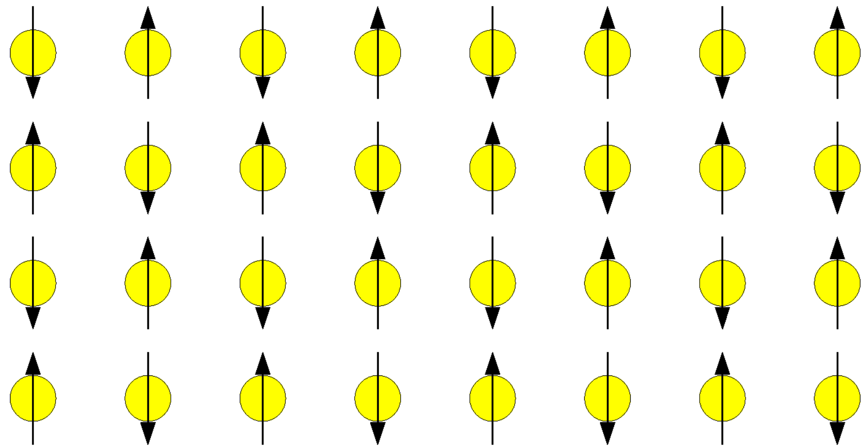
$$-J = \frac{C-A}{1-S} - \frac{C+A}{1+S} > 0$$

$$J = 2\frac{A-SC}{1-S^2} < 0$$

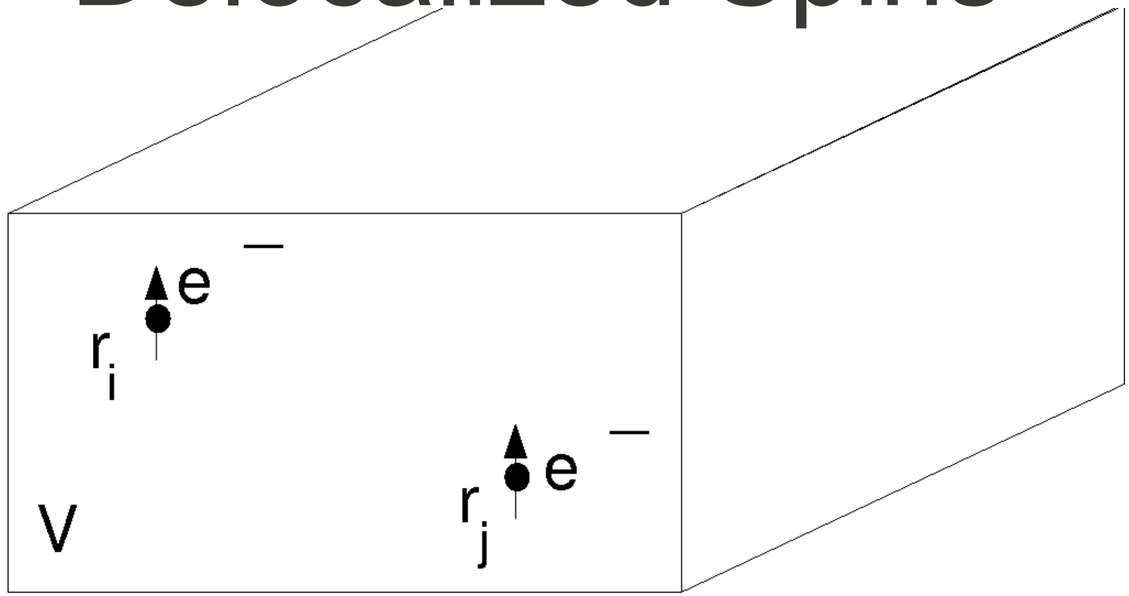
where the inequality follows since the last two terms in the {} dominate the integral for A and in the Heitler-London approximation S ≪ 1. Or, for the effective Hamiltonian

$$H = -2J \sum_{\langle ij \rangle} \sigma_i \cdot \sigma_j , \qquad J < 0$$

antiferromagnetic alignment of the spins



Exchange Interaction for Delocalized Spins

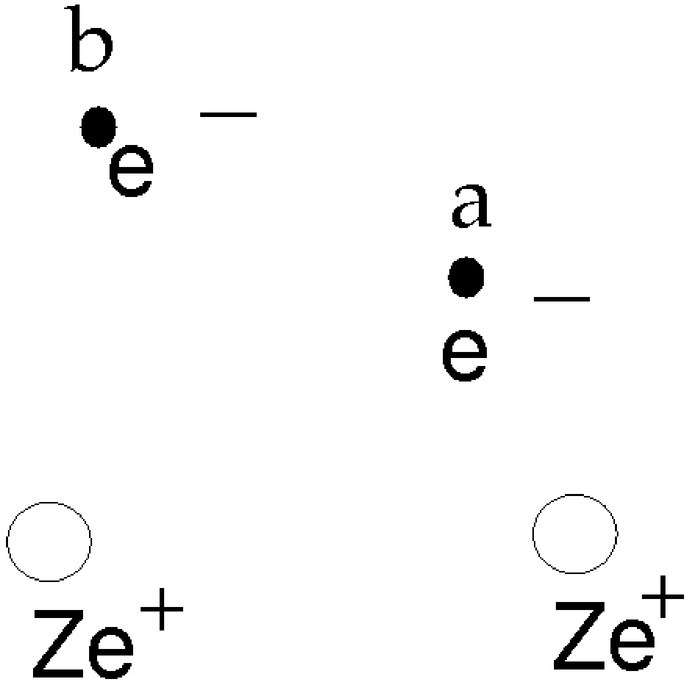


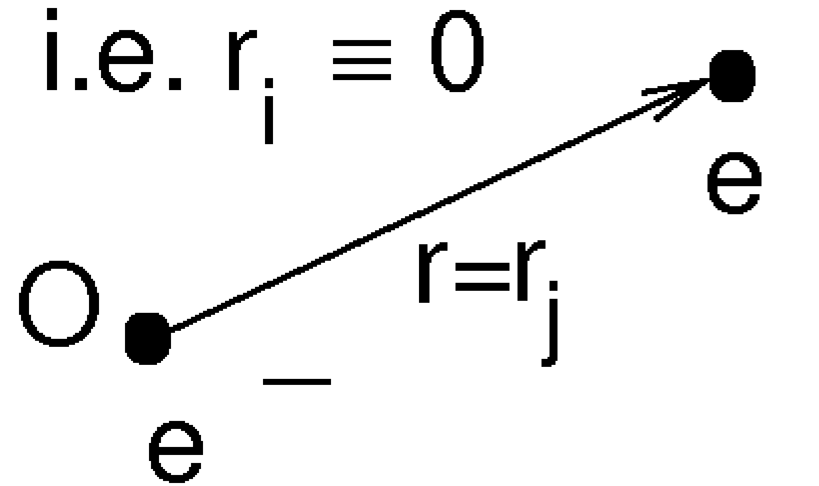
$$\psi_{ij} = \frac{1}{\sqrt{2}V}\left\{e^{ik_i\cdot r_i}e^{ik_j\cdot r_j} - e^{ik_i\cdot r_j}e^{ik_j\cdot r_i}\right\}$$

$$= \frac{1}{\sqrt{2}V}e^{ik_i\cdot r_i}e^{ik_j\cdot r_j}\left\{1 - e^{i(k_i-k_j)\cdot(r_i-r_j)}\right\}$$

The probability that the electrons are in volumes d^3r_i and d^3r_j is

$$|\psi_{ij}|^2 d^3r_i d^3r_j = \frac{1}{V^2}\left\{1 - \cos\left[(k_i - k_j)\cdot(r_i - r_j)\right]\right\} d^3r_i d^3r_j$$

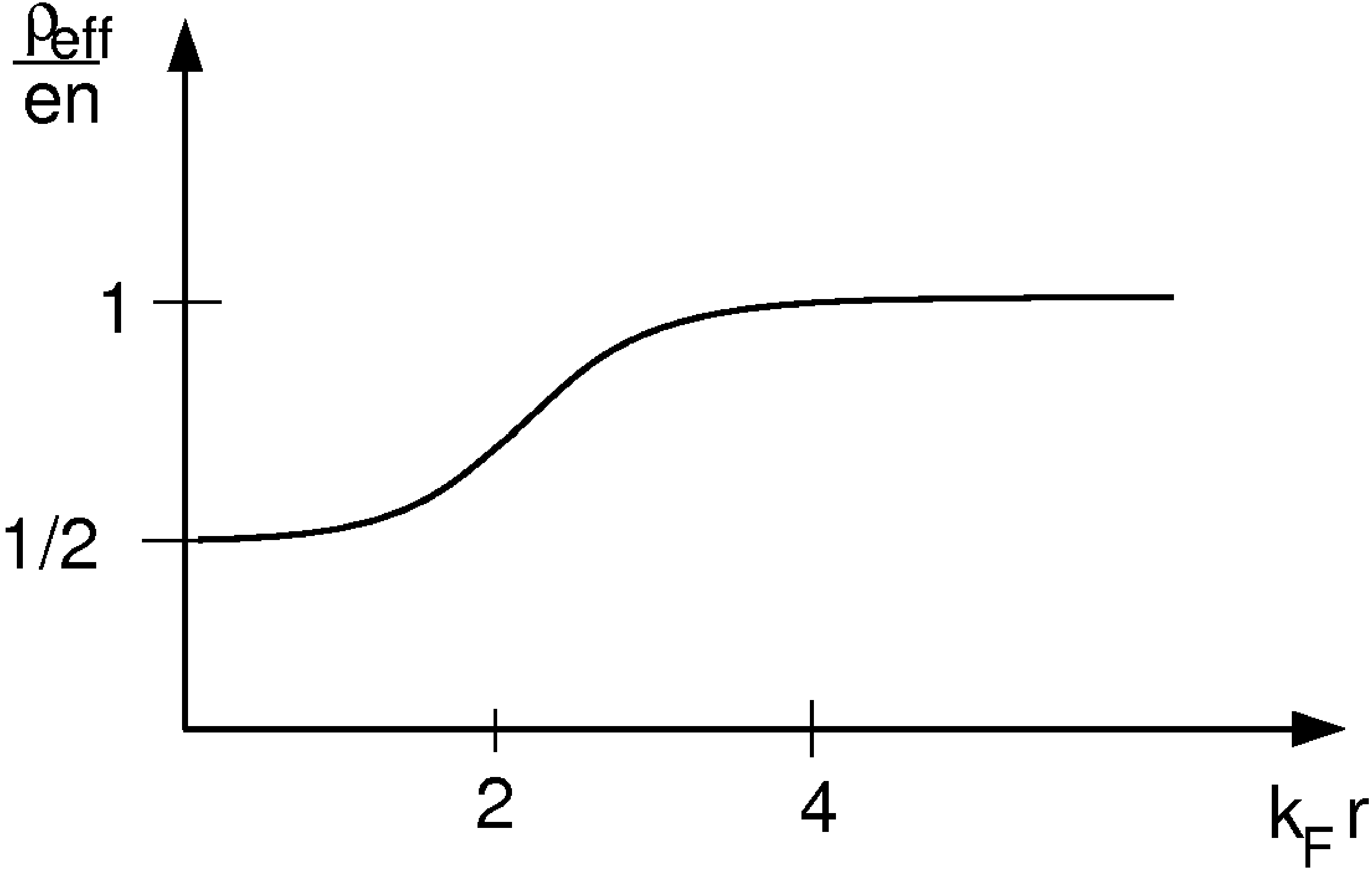




$$P_{\uparrow\uparrow}(r)d^3r = n_{\uparrow}d^3r \quad \underbrace{\overline{(1 - \cos\left[(k_i - k_j) \cdot r\right])}}_{\text{Fermi sea average}}$$

$$n_{\uparrow} = \frac{1}{2}n = \frac{1}{2} \; \frac{\text{\# electrons}}{\text{volume}}$$

$$
\begin{aligned}
\rho_{ex}(r) &= \frac{en}{2}\overline{(1-\cos\left[(k_i-k_j)\cdot r\right])} \\
&= \frac{en}{2}\left\{1-\frac{1}{(\frac{4}{3}k_F^3)^2}\int_o^{k_F} d^3k_i d^3k_j \frac{1}{2}\left(e^{\imath(k_i-k_j)\cdot r}+e^{-\imath(k_i-k_j)\cdot r}\right)\right\} \\
&= \frac{en}{2}\left\{1-(\frac{4}{3}k_F^3)^{-2}\int_0^{k_F} d^3k_i e^{\imath k_i\cdot r}\int_0^{k_F} d^3k_j e^{\imath k_j\cdot r}\right\} \\
&= \frac{en}{2}\left\{1-9\frac{(\sin k_F r - k_F r\cos k_F r)^2}{(k_F r)^6}\right\}
\end{aligned}
$$



$$\rho_{eff}(r) = en\left\{1 - \frac{9}{2}\frac{(\sin k_F r - k_F r\cos k_F r)^2}{(k_F r)^6}\right\}$$

Band Model of Ferromagnetism

$$E_\uparrow(k) = E(k) - \frac{IN_\uparrow}{N}; \qquad I < \ 1eV$$

$$E_\downarrow(k) = E(k) - \frac{IN_\downarrow}{N}.$$

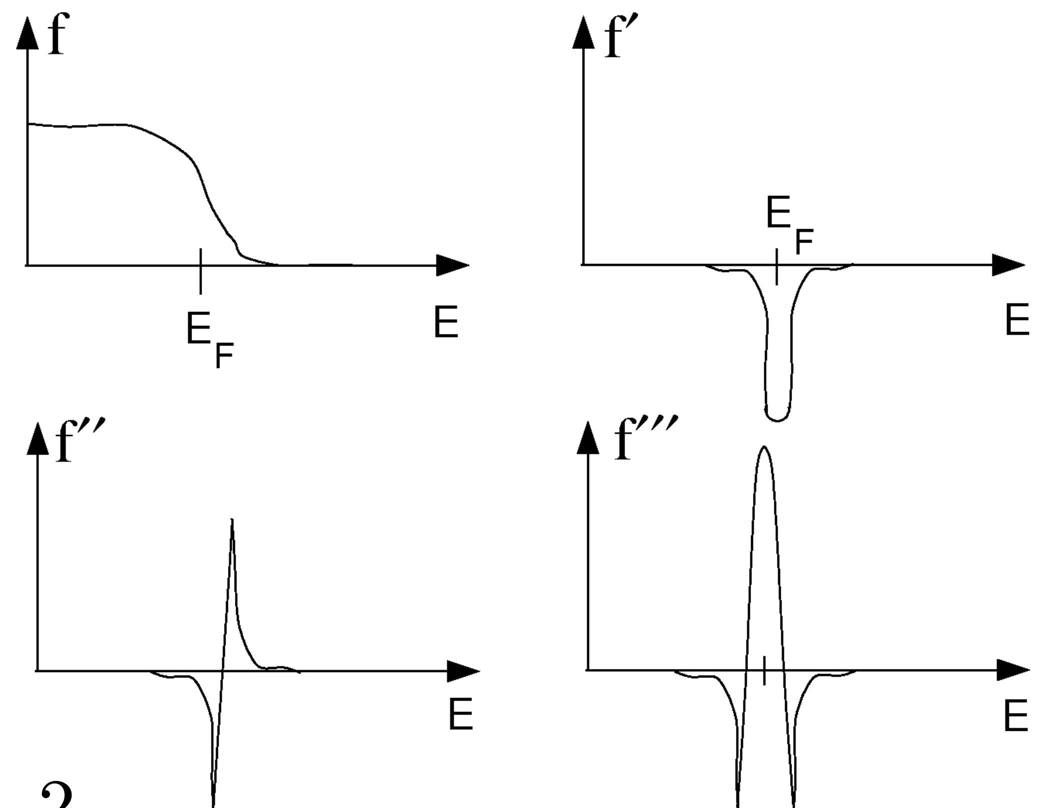
Where ***I***, the stoner parameter, quantifies the exchange hole energy. The relative spin occupation R is related to the bulk moment

$$R = \frac{(N_\uparrow - N_\downarrow)}{N}, \qquad M = \mu_B \left(\frac{N}{V}\right) R$$

$$\begin{aligned} E_\sigma(k) \quad &= E(k) - \tfrac{I(N_\uparrow + N_\downarrow)}{2N} - \tfrac{\sigma IR}{2}, \qquad (\sigma \ = \pm) \\ &\equiv \tilde{E}(k) - \tfrac{\sigma IR}{2}. \end{aligned}$$

If R is finite and real, then we have ferromagnetism.

$$R = \frac{1}{N}\sum_k \frac{1}{\exp\left\{(\tilde{E}(k) - IR/2 - E_F)/k_B T\right\} + 1} - \frac{1}{\exp\left\{(\tilde{E}(k) + IR/2 - E_F)/k_B T\right\} + 1}$$



For small R, we may expand around $E(k) = E_F$

$$f(x-a) - f(x+a) = -2af' - \frac{2}{3!}a^3 f'''$$

All derivatives will be evaluated at $E(k) = E_F$, so $f' < 0$ and $f''' > 0$. Thus,

$$R = -2\frac{IR}{2}\frac{1}{N}\sum_k \frac{\partial f}{\partial \tilde{E}(k)}\bigg|_{E_F} - \frac{2}{6}\left(\frac{IR}{2}\right)^3 \frac{1}{N}\sum_k \frac{\partial^3 f}{\partial \tilde{E}^3(k)}\bigg|_{E_F}$$

This is a quadratic equation in R

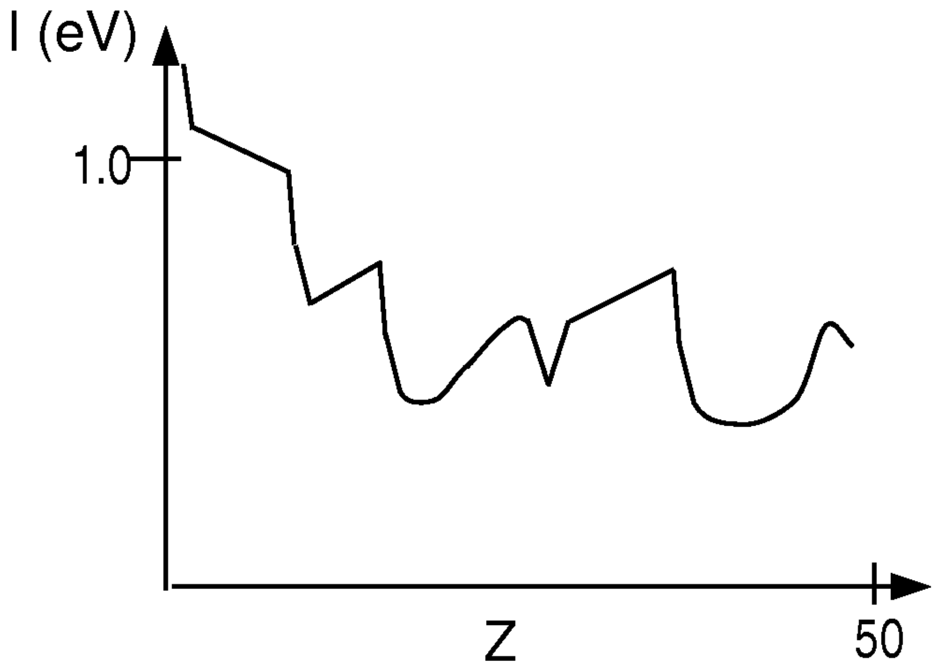
$$-1 - \frac{I}{N}\sum_k \frac{\partial f}{\partial E(k)}\bigg|_{E_F} = \frac{1}{24} I^3 R^2 \frac{1}{N}\sum_k \frac{\partial^3 f}{\partial E^3(k)}\bigg|_{E_F}$$

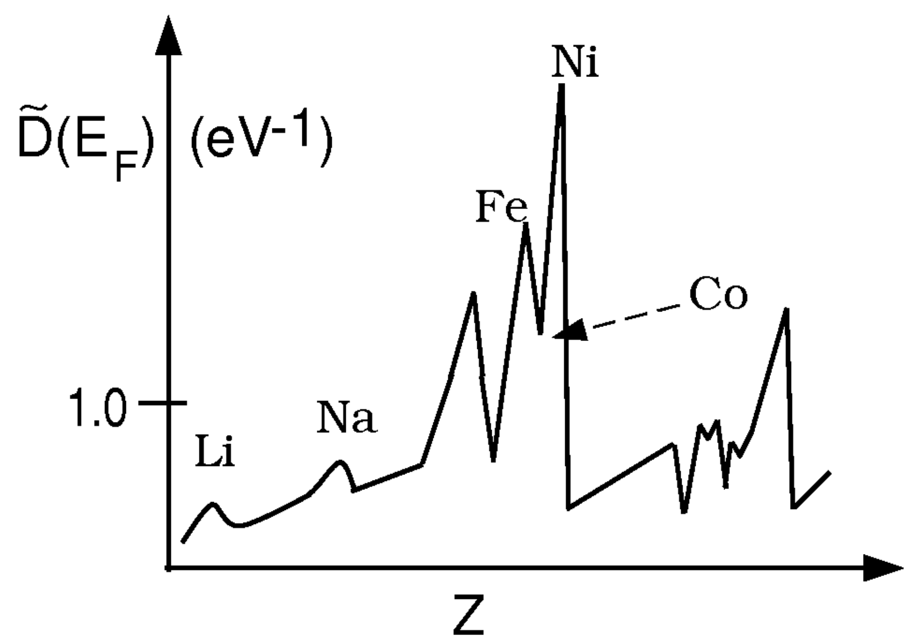
which has a real solution iff

$$-1 - \frac{I}{N}\sum_k \frac{\partial f}{\partial E(k)}\bigg|_{E_F} > 0$$

$$T = 0, \quad -\frac{1}{N}\sum_k \frac{\partial f}{\partial E_k} = \int d\tilde{E}\frac{V}{2N} D(\tilde{E})\delta(\tilde{E} - E_F) = \frac{V}{2N} D(E_F) = \tilde{D}(E_F)$$

So, the condition for FM at T = 0 is $ID(E_F) > 1$. This is known as the Stoner criterion. I is essentially flat as a function of the atomic number, thus materials such as Fe, Co, & Ni with a large $D(E_F)$ are favored to be FM.





Enhancement of χ

$$E_\sigma(k) = E(k) - \frac{I n_\sigma}{N} - \mu_B \sigma B$$

$$\begin{aligned} R &= -\tfrac{1}{N}\textstyle\sum_k \frac{\partial f}{\partial \tilde{E}_k}(IR + 2\mu_B B) \\ &= \tilde{D}(E_F)(IR + 2\mu_B B) \end{aligned}$$

or as M = μ_B(N/V) R, we get

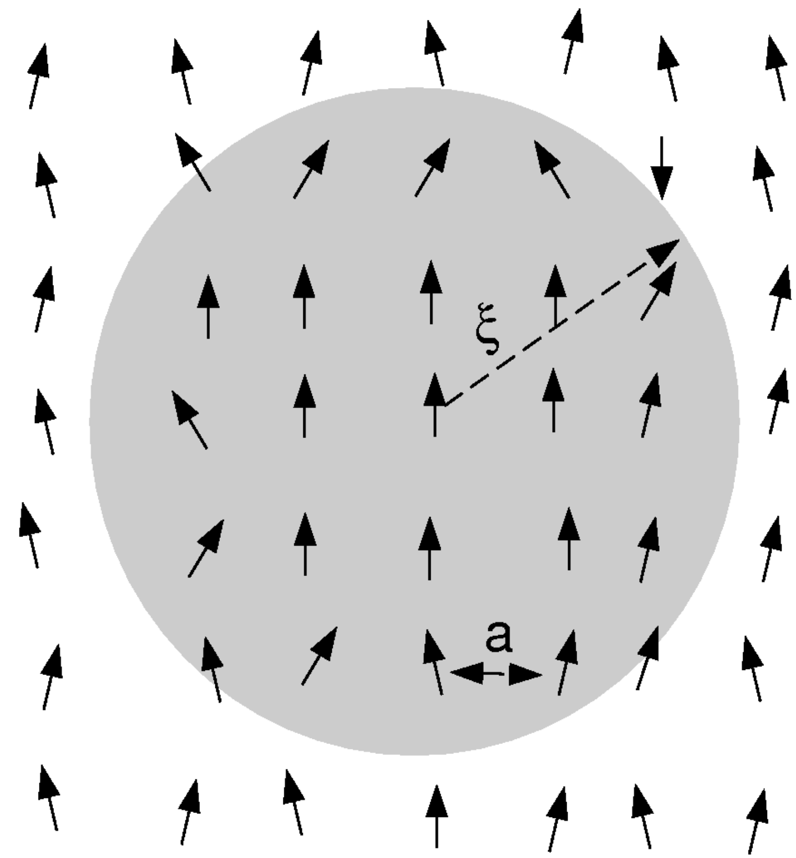
$$M = 2\mu_B^2 \frac{N}{V} \frac{\tilde{D}(E_F)}{1 - I\tilde{D}(E_F)} B$$

or

$$\chi = \frac{\partial M}{\partial B} = \frac{\chi_0}{1 - I\tilde{D}(E_F)}$$

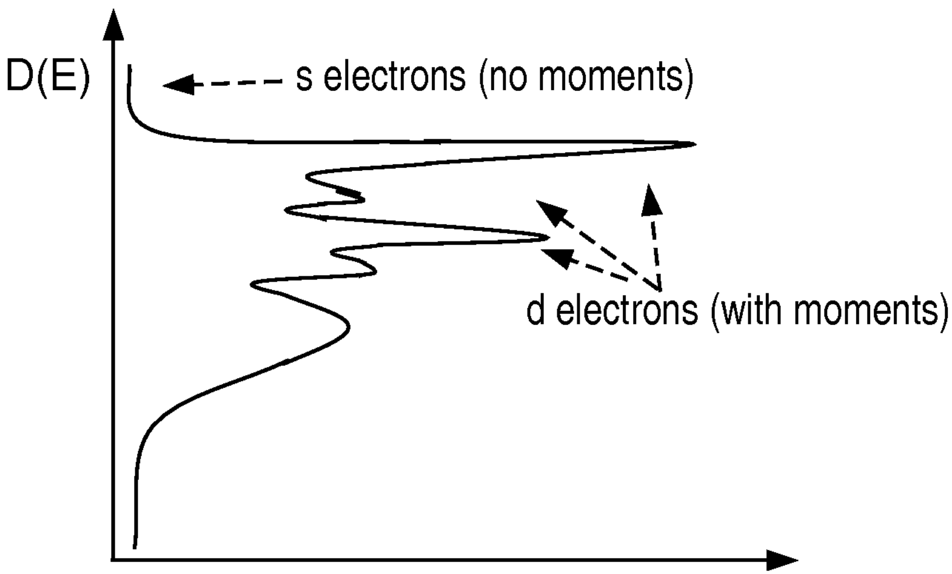
$$\chi_0 = 2\mu_B^2 \frac{N}{V} \tilde{D}(E_F)$$
$$= \mu_B^2 D(E_F)$$

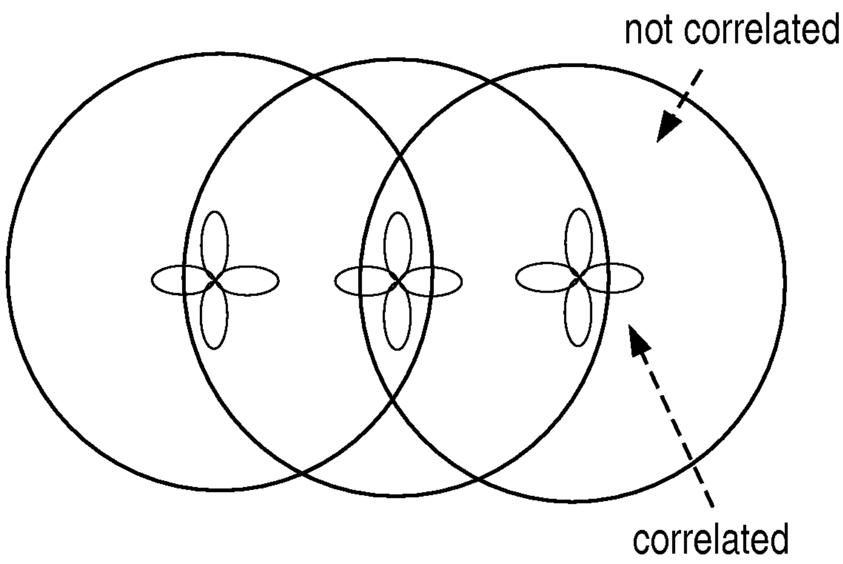
Thus, when I $D(E_F)\sim 1$, the susceptibility can be considerably enhanced over the non-interacting result χ0.



Spin fluctuations can reduce the total moment within the correlated region, and even reduce ξ itself.

Finite T Behavior of a Band Ferromagnet





$$R = \frac{1}{N}\sum_k f(\tilde{E}_k - \frac{IR}{2} - \mu_B B_0 - E_F) - f(\tilde{E}_k + \frac{IR}{2} + \mu_B B_0 - E_F)$$

However, only the d-electrons have a strong exchange splitting I and hence only they will tend to contribute to the magnetization.

➡ *Thus our D(E) should reflect only the d-electron contribution*

$$\tilde{D}(E) \approx C\delta(E - E_F), \qquad (C < 1)$$

C, an unknown constant, will be determined by the T = 0 behavior. Then

$$R = C\left\{f(-\frac{IR}{2} - \mu_B B_0) - f(\frac{IR}{2} + \mu_B B_0)\right\}$$

$$\Rightarrow \quad \tilde{R} = \frac{1}{\exp\left(\frac{-2\tilde{R}T_c}{T}\right)+1} - \frac{1}{\exp\left(\frac{2\tilde{R}T_c}{T}\right)+1} = \tanh\frac{\tilde{R}T_c}{T}$$

where $\frac{R}{C} \equiv \tilde{R}$ and $T_c = \frac{IC}{4k_B}$, for $B_0 = 0$

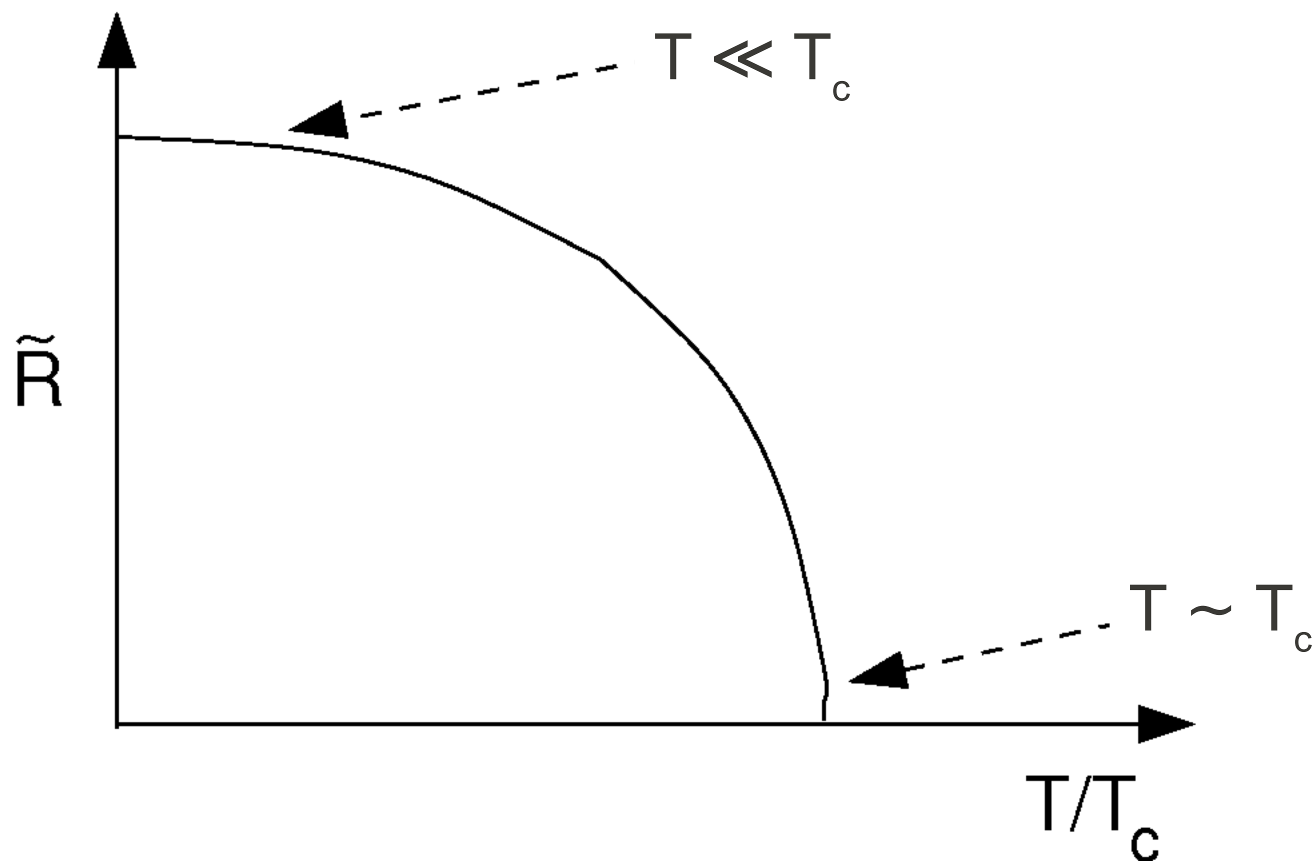
If $T = 0$, then $\tilde{R} = 1 = \frac{R}{C} = \frac{1}{C}\frac{n_\uparrow - n_\downarrow}{N}$.
For Ni, the measured ground state magnetization per Ni atom is $\frac{\mu eff}{\mu_B} = 0.54 = \frac{n_\uparrow - n_\downarrow}{N}$. Therefore, $C = 0.54 = \frac{\mu_{eff}}{\mu_B}$.

For small x, tanh x ≃ x − 1/3 x[3], and for large x

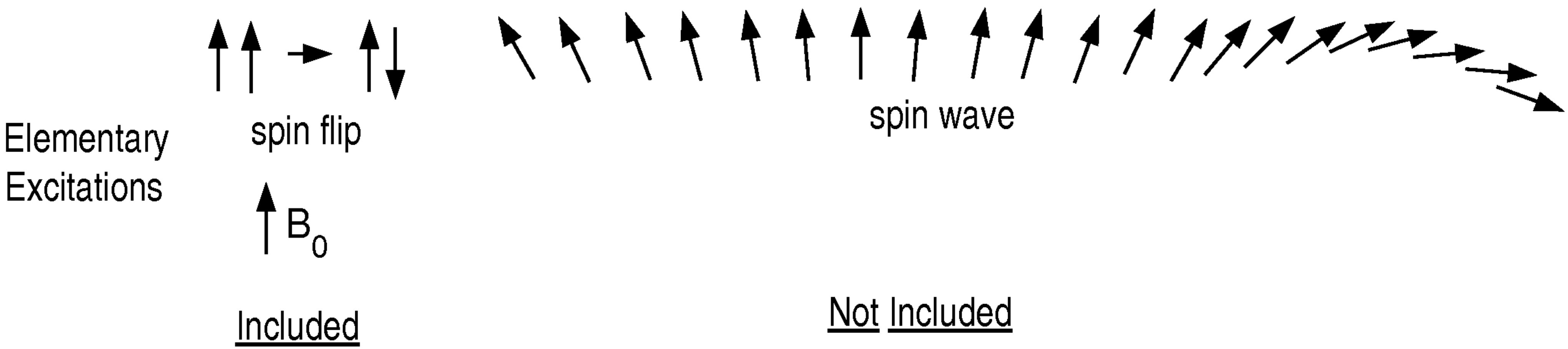
$$\begin{aligned}\tanh x &= \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{1 - e^{-2x}}{1 + e^{-2x}} \\ &= (1 - e^{-2x})(1 - e^{-2x}) \simeq 1 - 2e^{-2x}\end{aligned}$$

$$\tilde{R} = 1 - 2e^{-\frac{2T_c}{T}}, \qquad \text{for } T \ll T_c$$

$$\tilde{R} = \sqrt{3}(1 - \frac{T}{T_C})^{\frac{1}{2}}, \qquad \text{for small } \tilde{R} \text{ or } T < T_c$$



Clearly something fundamental is missing from this model - spin waves !!



Effect of B

If there is an external field $B_0 = 0$, then

$$\tilde{R} = \tanh\left\{\frac{\tilde{R}T_c + \mu_B B_0/2k_B}{T}\right\}$$

Or for small R and B_0, (or rather, large $T \gg T_c$)

$$\tilde{R} = \frac{\mu_B}{2kT}B_0 + \frac{T_c}{T}\tilde{R} \Rightarrow \ \tilde{R} = \frac{\mu_B}{2k}\frac{1}{T - T_c}B_0$$

$$\text{Thus since } M = \tfrac{\mu_B N}{V}R = \tfrac{C\mu_B N}{V}\tilde{R} \Rightarrow \ \chi = \tfrac{\partial M}{\partial B_0} = \tfrac{C\mu_B^2}{2kV}\tfrac{N}{T - T_c}.$$

$$\chi = \frac{\text{Const}}{T - T_c}$$

Curie-Weiss form