Ferromagnetism continued

last time: 1D Ising model
exact solution

$$M = \frac{\overbrace{\sinh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}^{\sinh(\beta h)\cosh(\beta h)}}{\cosh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}$$

for $h = 0$ $\cosh(\beta h) = 1$ but $\sinh(\beta h) = 0$

$\Rightarrow M = 0$ ↯ with experiment

- 2nd problem:

no ferromagnetic phase transition
at $h \neq 0$
unless $T = 0$ $\Rightarrow$ critical temp: $T_c = 0$

↯ with exp.

So, back to Heisenberg:

$$H^{\text{Heisenberg}} = -\sum_{ij} \frac{J_{ij}}{\mu_B^2} \vec{m}_i \vec{m}_j$$

for ferromagnetic ground state $\uparrow\uparrow\uparrow\uparrow\uparrow$

lowest excited state ? $\uparrow\downarrow\uparrow\uparrow\uparrow$ spin flip

instead

at large wave length

spin wave (magnon)

- not possible in Ising model
- not possible in mean field
- but in reality magnons are frequently observed

e.g. C_V

(2) mean-field limit:

$$H = -\sum_i \vec{m}_i \underbrace{\left(\sum_j \frac{J_{ij}}{(\mu_B)^2} \vec{m}_j \right)}_{\mu_0 \vec{H}} = -\sum_i \vec{m}_i \, \mu_0 \vec{H}$$

approximate $\vec{H}$ by thermal average:

$$\mu_0 \langle \vec{H} \rangle = \sum_j \frac{J_{ij}}{\mu_B^2} \langle m_j \rangle = \underbrace{\sum_j \frac{J_{ij}}{\mu_B^2} \left(\frac{N}{V}\right)}_{\lambda} \vec{M}_S(T) = \lambda \vec{M}_S(T)$$

linear as assumed by Weiss

cubic fcc crystal and nearest neighbors:

$$J = J_{ij} = \frac{\mu_B^2 \, \mu_0 H}{12 \, \overline{m}_S}$$

for $\bar{m}_s$ from table and $\mu_0 H \approx 10^3$ Tesla

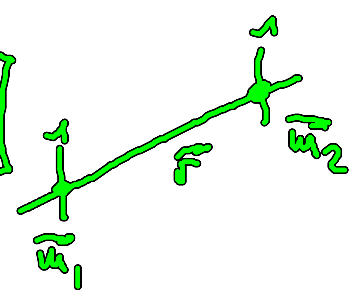
$$J \approx 10^{-2} \text{ eV for TM}$$
$$\approx 10^{-4} - 10^{-3} \text{ eV for RE}$$

Small interaction gives large fields ?!

Microscopic interaction

- Since it's a „magnetic" interaction maybe it arises from magnetic dipoles?

$$J^{\text{mag dipole}} = \frac{1}{r^3}\left[\vec{m}_1 \vec{m}_2 - 3(\vec{m}_1 \vec{r})(\vec{m}_2 \vec{r})\right]$$



$$\approx \frac{1}{r^3} m_1 m_2$$

$\approx 10^{-4}$ eV for typical mag moment and $r \approx 2$ Å

$\ll J_{ij}$ from Heisenberg model (at least T_C)

now try quantum mechanics:

Coulomb interaction $\leftrightarrow$ Pauli exclusion principle

$\uparrow \; \uparrow$

spatial separated

$\rightarrow$ reduces Coulomb

$\rightarrow$ increase kinetic energy

$\uparrow\!\downarrow$ —

- higher Coulomb
- lower kinetic

balance between kinetic and Coulomb energy determines which conf. is lower in energy

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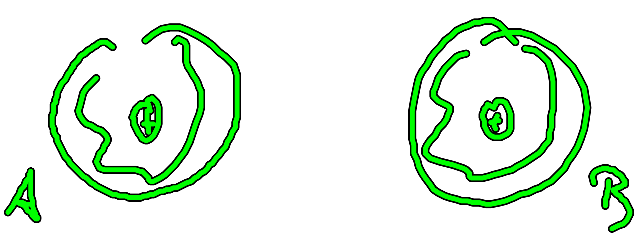
simple direct exchange picture: 2 electron H_2 (after Heitler-London)



one atom: $h_0 |\phi\rangle = \epsilon_0 |\phi\rangle \qquad \phi = \langle \underline{r}\, \sigma | \phi \rangle$

two atoms

$$H |\Phi\rangle = \left(h_0(A) + h_0(B) + h_{int} \right) |\Phi\rangle$$

2 e⁻ w/c

H does not depend on spin

=> separate w/c:

$$\Phi(\underline{r}_1, \sigma_1, \underline{r}_2, \sigma_2) = \Psi_{orb}(\underline{r}_1, \underline{r}_2)\, \chi_{spin}(\sigma_1, \sigma_2)$$

Spin 1/2: four possibilities:

$$|\uparrow\uparrow\rangle, \; |\uparrow\downarrow\rangle, \; |\downarrow\uparrow\rangle, \; |\downarrow\downarrow\rangle$$

take this as basis, choose eigenfc of S^2 and S_z

try: $\chi_{00} = \frac{1}{\sqrt{2}} \underbrace{\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)}_{\text{antisymmetric}}$

$S^2 \chi_{00} = 0$

$S_z \chi_{00} = 0$

singlet state

other choices:

$$\chi_{1\mu} \begin{cases} \chi_{11} = |\uparrow\uparrow\rangle & S=1 \quad S_z = 1 \\ \chi_{10} = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & S=1 \quad S_z = 0 \\ \chi_{1-1} = |\downarrow\downarrow\rangle & S=1 \quad S_z = -1 \end{cases}$$

symmetric   triplet

$$|\phi\rangle_{singlet} = |\Psi_{orb,sym}\rangle\,|\chi_0\rangle$$

$$|\phi\rangle_{triplet} = |\Psi_{orb,anti}\rangle\,|\chi_{1\mu}\rangle$$

- already here we see that although H is not spin dependent we get correlation between spatial and spin degrees of freedom

- start with infinitely separated atoms:

$$\langle \Phi | h_{int} | \Phi \rangle = 0$$

$$\Rightarrow \phi_A(\underline{r}) = \frac{1}{\sqrt{N}} e^{-\alpha(\underline{r}-\underline{R}_A)} \qquad \text{same for } \phi_B$$

$$\Rightarrow \Psi_{orb,sym} = \frac{1}{\sqrt{2}}\left[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)\right]$$

$$\psi_{orb,\,anti} = \frac{1}{\sqrt{2}}\left[\phi_A(1)\,\phi_B(2) - \phi_A(2)\,\phi_B(1)\right]$$

(left out ionic states $\phi_A(1)\,\phi_A(2)$, $\phi_B(1)\,\phi_B(2)$)

$\rightsquigarrow$ energy for both $E = 2\,\varepsilon_0$

- finite separation : electron densities become perturbed and start to overlap

Heitler-London approximation $\leftarrow$ distortion

$$\phi_A = \frac{1}{\sqrt{N}}\, e^{-\alpha \underline{r}\left(1+\beta \frac{\underline{r}\,\underline{R}_A}{r}\right)}$$

same for ϕ_B

$$|\psi_{orb,\,sym}\rangle = \frac{1}{\sqrt{2(1+S^2)}}\left[\phi_A(1)\,\phi_B(2) + \phi_A(2)\,\phi_B(1)\right]$$

$$|\psi_{orb,\,anti}\rangle = \frac{1}{\sqrt{2(1-S^2)}}\left[\;-\;\text{''}\;-\quad -\quad -\text{''}-\right]$$

$$S = \int d\underline{r}^3\, \phi_A(\underline{r})\,\phi_B(\underline{r})$$

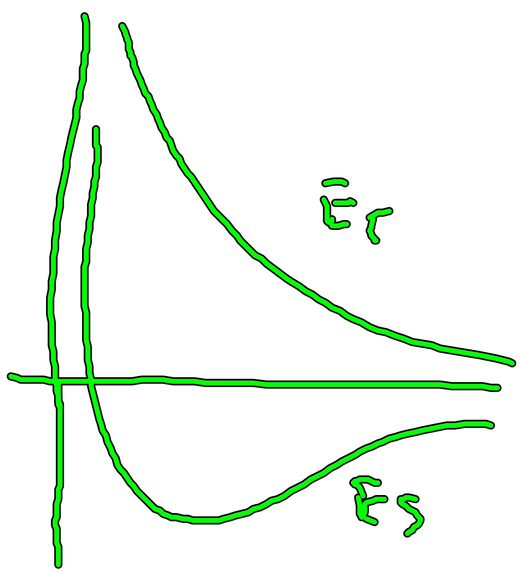
$\rightsquigarrow$ SE and apply variational principle to determine α, β

$$E_S = \frac{1}{1+S^2}\left(\langle 12|\,H\,|12\rangle + \langle 12|\,H\,|21\rangle\right)$$

$$E_T = \frac{1}{1-S^2}\left(\quad - \text{"} - \quad - \quad - \text{"} - \quad \right)$$

$$J := E_S - E_T$$

$$\approx \frac{2}{1-S^4}\Big(\underbrace{\langle 12 | \frac{1}{|\underline{r}-\underline{r}'|} | 21 \rangle}_{\text{exchange}} - S^2 \underbrace{\langle 12 | \frac{1}{|\underline{r}-\underline{r}'|} | 12 \rangle}_{\text{Coulomb}}$$



for H_2 $E_S < E_T$

but not in general

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how to get Heisenberg Hamiltonian?

$$H = \sum_i -\frac{\nabla^2}{2} - \sum_{ia} \frac{Z}{|\underline{r}_i - \underline{R}_a|} + \frac{1}{2}\sum_{ij} \frac{1}{|\underline{r}_i - \underline{r}_j|}$$

use 2nd quantization:

field operators: $\psi(\underline{r}) = \sum_{\alpha, n, \lambda} \phi_{n\lambda}(\underline{r} - \underline{r}_\alpha)\, a_{n\lambda}(\underline{r}_\alpha)$

annihilation operator

orbital site — state — spin

$\Rightarrow$ interacting part of H:

$$\frac{1}{2} \sum_{\substack{\{\alpha\} \\ \{n\} \\ \lambda_1 \lambda_2}} \langle \alpha_1 n_1 \alpha_2 n_2 | \underbrace{\frac{1}{|\underline{r} - \underline{r}'|}}_{V} | \alpha_3 n_3 \alpha_4 n_4 \rangle\, a^\dagger_{n_1 \lambda_1}(\underline{r}_{\alpha_1})\, a^\dagger_{n_2 \lambda_2}(\underline{r}_{\alpha_2})\, a_{n_3 \lambda_2}(\underline{r}_{\alpha_3})\, a_{n_4 \lambda_1}(\underline{r}_{\alpha_4})$$

this is still exact

now restrict to $\alpha_3 = \alpha_1$ and $\alpha_4 = \alpha_2$ or $\alpha_3 = \alpha_2$ and $\alpha_4 = \alpha_1$

$n_3 = n_1$ $\quad n_4 = n_2$ $\quad n_3 = n_2$ $\quad n_4 = n_1$

and omit orbital transfer terms in which e^- interchange orbital states

$\Rightarrow$

$$\frac{1}{2} \sum_{\substack{\alpha \alpha' \\ n n' \\ \lambda \lambda'}} \Big[\langle \alpha n \alpha' n' | V | \alpha n \alpha' n' \rangle\, a^\dagger_{n\lambda}(r_\alpha)\, a^\dagger_{n'\lambda}(r_{\alpha'})\, a_{n'\lambda'}(r_{\alpha'})\, a_{n\lambda}(r_\alpha)$$

direct (Coulomb) term

$$+ \langle \alpha n \alpha' n' | V | \alpha' n' \alpha n \rangle \, a^\dagger_{n\lambda}(r_\alpha) a^\dagger_{n'\lambda'}(r_{\alpha'}) \, a_{n\lambda'}(r_\alpha) a_{n'\lambda}(r_{\alpha'}) \Big]$$

exchange term

using anti commutator:

$$\{ a^\dagger_{n\lambda}(r_\alpha), a_{n'\lambda'}(r_{\alpha'}) \} = \delta_{\alpha\alpha'} \delta_{nn'} \delta_{\lambda\lambda'}$$

$$\Rightarrow -\frac{1}{2} \sum_{\substack{\alpha\alpha' \\ nn' \\ \lambda\lambda'}} J_{nn'}(r_\alpha, r_{\alpha'}) \, a^\dagger_{n\lambda}(r_\alpha) a_{n\lambda'}(r_\alpha) \, a^\dagger_{n'\lambda'}(r_{\alpha'}) a_{n'\lambda}(r_{\alpha'})$$

expand spin sum:

$$= \sum_{\substack{\alpha\alpha' \\ nn'}} J_{nn'}(r_\alpha, r_{\alpha'}) \left[\overline{\frac{1}{4}} + \frac{1}{4} \underline{S}(\underline{r}_\alpha) \underline{S}(\underline{r}_{\alpha'}) \right]$$

spin on ion

restrict to lattice $r_\alpha \to i \quad r_{\alpha'} \to j$

$$H^{spin} = \sum_{ij} \tilde{J}_{ij} \underline{S}_i \underline{S}_j$$

we have shown that magnetism:

- does not arise from spin dependent term in H
- but from Pauli exclusion principle in many-body wave function

Homogeneous electron gas: exchange interaction

in Section 8.3.3. we considered HEG already

↳ weak paramagnet

↳ but, only considered non-interacting case

↳ so what about exchange?

Hartree-Fock for HEG

$$\frac{E}{N} = T_S + E_{xc} \approx \frac{30.1\,\text{eV}}{\left(\frac{r_s}{a_B}\right)^2} - \frac{12.5\,\text{eV}}{\left(\frac{r_s}{a_B}\right)}$$

exchange only

exchange is attractive

recall: $r_s = \frac{3}{4\pi}\left(\frac{V}{N}\right)^{1/3}$

$$\frac{E^{HF}_{HEG}}{V} = \left[78.2\,\text{eV}\left(\frac{N}{V}\right)^{5/3} - 20.1\,\text{eV}\left(\frac{N}{V}\right)^{4/3} \right]$$

kinetic

exchange

add spin dependence through $N_\uparrow \neq N_\downarrow$

$$E^{HF}_{HEG} = C_1 \left[\left(\frac{N_\uparrow}{V}\right)^{5/3} + \left(\frac{N_\downarrow}{V}\right)^{5/3} \right] - C_2 \left[\left(\frac{N_\uparrow}{V}\right)^{4/3} + \left(\frac{N_\downarrow}{V}\right)^{4/3} \right]$$

$$n = N_\uparrow - N_\downarrow \qquad = \frac{C_1}{2^{5/3}} \left[\left(\frac{N+n}{V}\right)^{5/3} + \left(\frac{N-n}{V}\right)^{5/3} \right] - \frac{C_2}{2^{4/3}} \left[\left(\frac{N+n}{V}\right)^{4/3} + \left(\frac{N-n}{V}\right)^{4/3} \right]$$

now minimize with respect to n:

- two solutions (Bloch 1929): $n = 0$ not polarized

  $n = N$ fully polarized

  phase transition at $\frac{r_s}{a_B} = 5.45$ (only Cs would be ferromagnetic)

- more modern results including correlation (Quantum Monte Carlo by D. Ceperley)

  transition at $\frac{r_s}{a_B} \approx 50 \pm 2$

  $\Rightarrow$ essentially no metal would be ferromagnetic

  $\hookrightarrow$ ↯ Fe, Ni, Co are ferromagnetic

  $\Rightarrow$ bandstructure effects are important!