

Lecture 27

We saw in previous lecture that magnetic dipole interaction between the ~~aligned~~ atomic moments can't lead to ferromagnetism, as it is observed, since the corresponding energy scale is too small.

What actually leads to ferromagnetism is a combination of Coulomb repulsion between the electrons and Pauli principle. This is best illustrated on the simplest example - two interacting electrons.

Consider two unspecified single-electron states with wavefunctions $\psi_1(\vec{r})$ and $\psi_2(\vec{r})$, which can be occupied by two electrons. Assume the electrons are interacting via Coulomb interactions:

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

The two-electron wavefunction has the following general form:

$$\psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2) = \underbrace{\psi(\vec{r}_1, \vec{r}_2)}_{\text{orbital wavefunction}} \underbrace{\chi(\sigma_1, \sigma_2)}_{\text{spin wavefunction}}$$

$\psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2)$ must be antisymmetric:

$$\psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2) = -\psi(\vec{r}_2\sigma_2, \vec{r}_1\sigma_1)$$

This leaves two possibilities:

1. $\Psi(\vec{r}_1, \vec{r}_2)$ is symmetric but $\chi(\sigma_1, \sigma_2)$ is antisymmetric
2. $\Psi(\vec{r}_1, \vec{r}_2)$ is antisymmetric but $\chi(\sigma_1, \sigma_2)$ is symmetric.

Since the total spin of the two electrons is conserved, we can choose S - the magnitude of the total spin and $S^z \equiv M$ - z -component of the total spin, as quantum numbers, labeling the spin states.

Using Dirac notation we will write the spin states as $|S, M\rangle$.

There are 4 possible states:

$$|0, 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$$|1, 1\rangle = |\uparrow\uparrow\rangle$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

$$|1, -1\rangle = |\downarrow\downarrow\rangle$$

Thus ~~antisymmetric~~ χ is antisymmetric for $S=0$ and symmetric for $S=1$.

Then we obtain:

$$\Psi_{1M}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) - \Psi_1(\vec{r}_2) \Psi_2(\vec{r}_1)] \quad |1, M\rangle$$

$$\Psi_{00}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) + \Psi_1(\vec{r}_2) \Psi_2(\vec{r}_1)] \quad |0, 0\rangle$$

These 4 states all have the same energy ~~if~~ if we neglect Coulomb interaction.

Coulomb interactions lift this degeneracy. To see this we need to do degenerate perturbation theory.

The first step is to calculate the matrix elements of $V(\vec{r}_1 - \vec{r}_2)$ between these 4 ~~degenerate~~ degenerate states.

Since $V(\vec{r}_1 - \vec{r}_2)$ is spin-independent, these matrix elements will obviously be proportional to the scalar products of spin wavefunctions:

$$\langle SM | S' M' \rangle = \delta_{SS'} \delta_{MM'}$$

Thus the matrix elements will have the form:

$$V_{SM, S' M'} = V_S \delta_{SS'} \delta_{MM'}$$

Here V_S is the matrix element of $V(\vec{r}_1 - \vec{r}_2)$ with respect to the orbital part of the wavefunction.

$$\begin{aligned}
 V_1 &= \int d\vec{r}_1 d\vec{r}_2 \frac{1}{r_{12}} \left[\psi_1^*(\vec{r}_1) \psi_2^*(\vec{r}_2) - \psi_1^*(\vec{r}_2) \psi_2^*(\vec{r}_1) \right] \\
 &\cdot V(\vec{r}_1 - \vec{r}_2) \frac{1}{r_{12}} \left[\psi_1(\vec{r}_1) \psi_2(\vec{r}_2) - \psi_1(\vec{r}_2) \psi_2(\vec{r}_1) \right] = \\
 &= \int d\vec{r}_1 d\vec{r}_2 |\psi_1(\vec{r}_1)|^2 |\psi_2(\vec{r}_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} - \\
 &- \int d\vec{r}_1 d\vec{r}_2 \psi_1^*(\vec{r}_1) \psi_2^*(\vec{r}_2) \psi_1(\vec{r}_2) \psi_2(\vec{r}_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}
 \end{aligned}$$

where I've used that $V(\vec{r}_1 - \vec{r}_2) = V(\vec{r}_2 - \vec{r}_1)$.

let $C = \int d\vec{r}_1 d\vec{r}_2 |\psi_1(\vec{r}_1)|^2 |\psi_2(\vec{r}_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ -
 average Coulomb repulsion between the ~~two~~ electrons.

$$J = \int d\vec{r}_1 d\vec{r}_2 \psi_1^*(\vec{r}_1) \psi_2^*(\vec{r}_2) \psi_1(\vec{r}_2) \psi_2(\vec{r}_1) \cdot$$

$\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ - exchange interaction - this appears due to Pauli principle.

$$V_1 = C - J, \quad V_0 = C + J.$$

Thus Coulomb interaction makes $S=0$ and $S=1$ states have different energy.

Which state has lower energy depends on the sign of J .

$J > 0$ - $S=1$ state has lower energy.

$J < 0$ - $S=0$ state has lower energy.

We can express this in terms of spin operators:

$$\vec{S}^2 = (\vec{S}_1 + \vec{S}_2)^2 = S_1^2 + S_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$$

$$H = -J \vec{S}^2 = -2J \vec{S}_1 \cdot \vec{S}_2 + \text{const.}$$

when $J > 0$ \vec{S}_1 and \vec{S}_2 want to align with each other.

$J < 0$ - anti-align.

In ferromagnets $J > 0$ - this leads to alignment of atomic moments.

The physics behind this: the orbital wavefunction for $S=1$ (aligned spins) is antisymmetric:

$$\Psi(r_1^+, r_2^+) = \frac{1}{\sqrt{2}} [\psi_1(r_1^+) \psi_2(r_2^+) - \psi_1(r_2^+) \psi_2(r_1^+)]$$

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This means that $\psi(\vec{r}_i, \vec{r}_i^+) = 0$ - vanishes when two electrons bump into each other - this minimizes Coulomb repulsion energy (recall hydrogen wavefunction)

Generalization to many interacting spins:

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad \text{Heisenberg model.}$$

This model is very ~~too~~ oversimplified since it ignores the fact that the spin is carried by mobile d-electrons. But it does ~~capture~~ capture the basics of magnetism.

Typical size of $J \sim \frac{e^2}{r} \gg U_{\text{dir}}$.

Most often Heisenberg model is simplified even further by retaining only ~~nearest~~ the interactions between nearest-neighbor spins:

$$H = -\frac{J}{2} \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - g\mu_B \vec{B} \cdot \sum_i \vec{S}_i$$

I have also added external magnetic field \vec{B} .

\vec{S}_i are quantum-mechanical spin operators:

$$[S_{i\alpha}, S_{j\beta}] = i \epsilon_{\alpha\beta\gamma} S_{i\gamma}$$

In general, this is a hard quantum many-body problem to solve. As usual, we need approximations. The simplest is the 'mean-field' approximation.

We write spin operators as:

$$\begin{aligned}\vec{S}_i &= \langle \vec{S}_i \rangle + \vec{S}_i - \langle \vec{S}_i \rangle \\ \vec{S}_i \cdot \vec{S}_j &= (\vec{S}_i - \langle \vec{S}_i \rangle + \langle \vec{S}_i \rangle) \cdot (\vec{S}_j - \langle \vec{S}_j \rangle + \langle \vec{S}_j \rangle) \\ &= (\vec{S}_i - \langle \vec{S}_i \rangle) \cdot (\vec{S}_j - \langle \vec{S}_j \rangle) + \vec{S}_i \cdot \langle \vec{S}_j \rangle + \\ &+ \vec{S}_j \cdot \langle \vec{S}_i \rangle - \langle \vec{S}_i \rangle \cdot \langle \vec{S}_j \rangle\end{aligned}$$

Crucial assumption: assume fluctuations of the spins from their expectation values are small (not really ~~rigorously~~ justified in most cases).

Then we can neglect the first term above, which is quadratic in fluctuations. The Hamiltonian becomes:

$$\begin{aligned}H &= -\frac{J}{2} \sum_{\langle ij \rangle} [\vec{S}_i \cdot \langle \vec{S}_j \rangle + \vec{S}_j \cdot \langle \vec{S}_i \rangle] - \\ &- g\mu_B \vec{B} \cdot \sum_i \vec{S}_i\end{aligned}$$

The constant term we neglected, proportional to $\langle \vec{S}_i \rangle \cdot \langle \vec{S}_j \rangle$, can be neglected here, but needs to be taken into account if, e.g. the free energy of the system is calculated!

Assume $J > 0 \Rightarrow$ we expect ferromagnetic ordering of the spins:



In this case we can expect $\langle \vec{S}_i \rangle$ to be independent of the site index i .

The Hamiltonian then becomes:

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \langle \vec{S} \rangle - g\mu_B \vec{B} \cdot \sum_i \vec{S}_i =$$

$$= -Jz \langle \vec{S} \rangle \cdot \sum_i \vec{S}_i - g\mu_B \vec{B} \cdot \sum_i \vec{S}_i$$

Here z is the coordination number - number of nearest neighbors of any lattice site in a given lattice.

E.g. $z=6$ for a cubic lattice.

Introduce $\vec{B}_m = \frac{Jz \langle \vec{S} \rangle}{g\mu_B}$ - molecular field.

~~Therefore~~ The Hamiltonian becomes:

$$H = -g\mu_B (\vec{B} + \vec{B}_m) \cdot \sum_i \vec{S}_i$$

Physical meaning of \vec{B}_m - effective mean magnetic

field, acting on a given spin in addition to the external field, due to its interaction with other spins.

Thus we have converted a many-interacting-spins problem into a single spin in a field problem - ultimately this is how many of the approximate methods in many-body theory work.

The molecular field B_m is of course unknown and has to be determined self-consistently.

Assume the external field \vec{B} is in the z -direction.

$\vec{B} = B \hat{z}$. Then the spins will also align in the z -direction since \vec{B} is the only thing that chooses a particular direction, the spin-spin interaction part of the Hamiltonian is rotationally invariant.

Then we have:

$$H = -g\mu_B (B + B_m) \sum_i S_i^z$$

Given this H , we can calculate $\langle S_i^z \rangle$ (assume spin- $\frac{1}{2}$ for simplicity):

$$\langle S^z \rangle = \frac{\sum_{S^z = \pm \frac{1}{2}} e^{\frac{g\mu_B (B+B_m) S^z}{k_B T}}}{\sum_{S^z = \pm \frac{1}{2}} e^{\frac{g\mu_B (B+B_m) S^z}{k_B T}}} =$$

$$= \frac{1}{2} \frac{e^{\frac{g\mu_B(B+B_M)}{2k_B T}} - e^{-\frac{g\mu_B(B+B_M)}{2k_B T}}}{e^{\frac{g\mu_B(B+B_M)}{2k_B T}} + e^{-\frac{g\mu_B(B+B_M)}{2k_B T}}} =$$

$$= \frac{1}{2} \tanh\left(\frac{g\mu_B(B+B_M)}{2k_B T}\right)$$

On the other hand,

$$B_M = \frac{Jz}{g\mu_B} \langle S^z \rangle$$

Thus we get a nonlinear equation for B_M :

$$B_M = \frac{Jz}{2g\mu_B} \tanh\left(\frac{g\mu_B(B+B_M)}{2k_B T}\right)$$

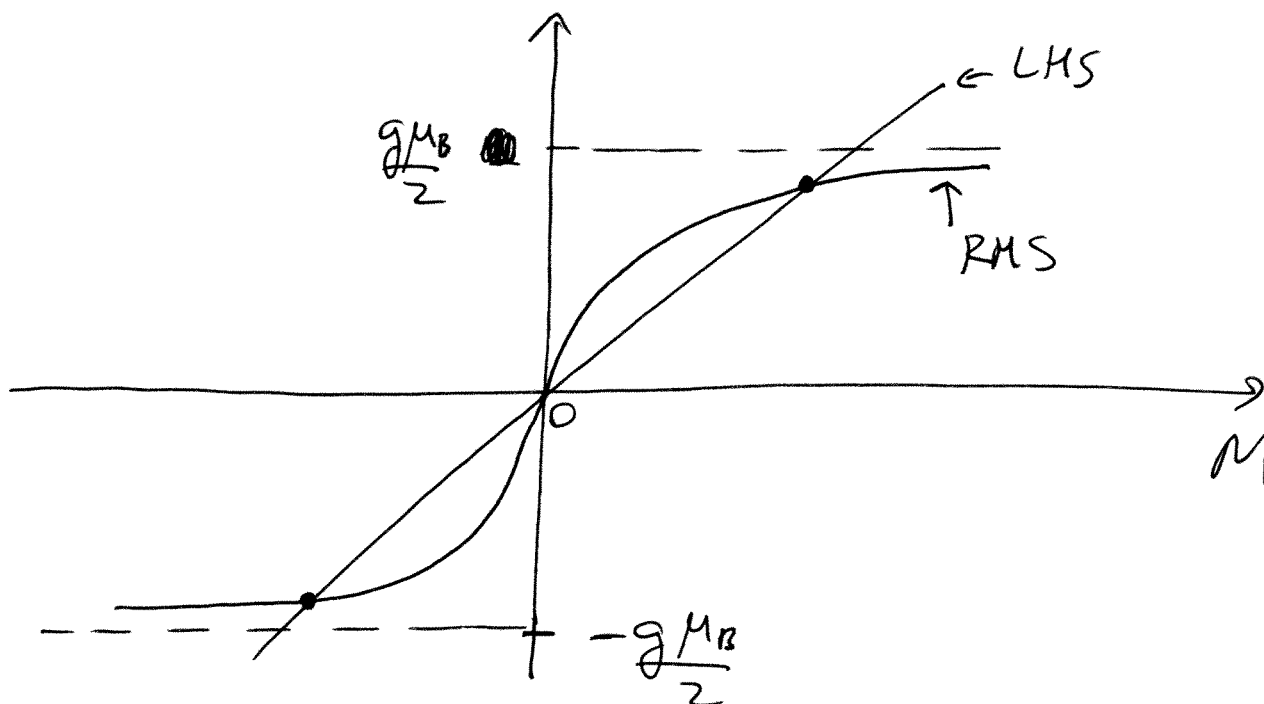
Can also write this as an equation for macroscopic magnetization (per spin):

$$M = g\mu_B \frac{1}{N} \sum_i \langle S_i^z \rangle = g\mu_B \langle S^z \rangle$$

$$M = \frac{g\mu_B}{2} \tanh\left(\frac{g\mu_B B + \frac{Jz}{g\mu_B} M}{2k_B T}\right)$$

Analyze this equation at zero external field: $B=0$.

$$M = \frac{g\mu_B}{2} \tanh\left(\frac{\gamma Z M}{2g\mu_B k_B T}\right)$$



The slope of the RHS ~~changes as a function of T~~ at $M=0$ changes as a function of T : it increases with decreasing T . Thus for low enough T a solution with nonzero M exists.

To determine the critical temperature T_c , at which a nontrivial solution appears, expand \tanh at small M :

$$\tanh\left(\frac{\gamma Z M}{2g\mu_B k_B T}\right) \approx \frac{\gamma Z M}{2g\mu_B k_B T}$$

$$\text{Thus } M = \frac{\gamma Z}{4k_B T_c} M \Rightarrow T_c = \frac{\gamma Z}{4k_B} - \text{Curie temperature.}$$