FoP3B Part I Lecture 8: Exchange interaction and ferromagnetism

We now move onto solids that display long range ordering of magnetic moments. This is due to a unique quantum mechanical property called **exchange interaction**. After introducing the exchange interaction, we will discuss one type of long range order, known as **ferromagnetism**, which, unlike paramagnetism, results in strongly magnetic solids.

Particle Indistinguishability and the Exchange Interaction

Consider electrons in a small 'box' (e.g. an atom) such that their wavefunctions overlap. The electrons are therefore *indistinguishable.* This behaviour is very different to classical physics where point particles are distinguishable. For simplicity let us assume that there are only two electrons in the box, labelled as electrons '1' and '2', and that their wavefunctions are $\phi_\alpha(\mathbf{r}_1)$ and $\phi_\beta(\mathbf{r}_2)$. $\phi_\alpha(\mathbf{r}_1)$ simply means that electron '1' is in the quantum state α and similarly for $\phi_\beta(\mathbf{r}_2)$. If the two electrons are non-interacting then a possible solution for the total wavefunction $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ might be $\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)$. However, this does not satisfy the condition of indistinguishability, i.e. if $\mathbf{r}_1$ and $\mathbf{r}_2$ are swapped in $\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)$ we do not recover the same electron density ($|\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)|^2 \neq |\phi_\alpha(\mathbf{r}_2)\phi_\beta(\mathbf{r}_1)|^2$). To be consistent with the indistinguishability criterion we can instead propose the following solutions for Ψ:

$$\Psi_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) + \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2)\right]$$

$$\Psi_a(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) - \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2)\right]$$

The first solution Ψ_s is a **symmetric wavefunction** since $\Psi_s(\mathbf{r}_1,\mathbf{r}_2) = \Psi_s(\mathbf{r}_2,\mathbf{r}_1)$, while Ψ_a is **anti-symmetric** (i.e. $\Psi_a(\mathbf{r}_1,\mathbf{r}_2) = -\Psi_a(\mathbf{r}_2,\mathbf{r}_1)$). The $1/\sqrt{2}$ factor is a normalisation constant. The *strong form* of the **Pauli Exclusion principle** states that *the total wavefunction for indistinguishable electrons must be anti-symmetric*. This means that Ψ_a is a valid wavefunction for electrons, but not Ψ_s. A consequence of the Pauli Exclusion principle is that electrons cannot have the same quantum state. This is also known as the *weak form* of the Pauli Exclusion principle and follows from the fact that $\Psi_a(\mathbf{r}_1,\mathbf{r}_2) = 0$ for $\alpha = \beta$.

Let us introduce electron spin into the mix. The wavefunction can be broken down into a spatial (ψ) and spin-dependent (χ_{spin}) part, such that $\Psi(\mathbf{r}_1,\mathbf{r}_2) = \psi(\mathbf{r}_1,\mathbf{r}_2)\chi_{\text{spin}}$. Due to Ψ being anti-symmetric (Pauli Exclusion principle) if χ_{spin} is anti-symmetric, ψ must be symmetric and vice-versa. Consider an anti-symmetric χ_{spin} (i.e. electron spins anti-parallel), so that the spatial part is given by $\psi_s(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) + \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2)\right]$. The total spin angular momentum $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$ and the quantum number $S = \frac{1}{2} - \frac{1}{2} = 0$. Since $m_S = S, S-1,\ldots,-S$ there is only one quantum state corresponding to $m_S = 0$. A suitable wavefunction that satisfies the indistinguishability criterion is $\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$. This is known as the spin **singlet**, due to the fact that there is only one quantum state. For a singlet $\psi_s \neq 0$ for $\mathbf{r}_1 = \mathbf{r}_2$, i.e. the distance of separation of singlet electrons can be small and hence the average Coulomb interaction energy large.

For χ_{spin} symmetric (i.e. parallel electron spins), the anti-symmetric spatial part is $\psi_a(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) - \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2)\right]$. The total spin angular momentum quantum number $S = \frac{1}{2} + \frac{1}{2} = 1$ and consequently there are three degenerate sates corresponding to $m_S = 1,0,-1$.

Since there are three states this configuration is known as a spin **triplet**. The wavefunctions are $|\uparrow\uparrow\rangle$ ($m_S = 1$), $\frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}$ ($m_S = 0$) and $|\downarrow\downarrow\rangle$ ($m_S = -1$). For a triplet $\psi_a = 0$ for $\mathbf{r}_1 = \mathbf{r}_2$, i.e. parallel electrons are well separated, so that their Coulomb energy is also lowered.

It is clear that the Pauli Exclusion Principle gives rise to different Coulomb energies depending on the symmetry of the spin wavefunction. This is known as the **exchange interaction energy** and in the **Heisenberg exchange model** takes the form $-A\mathbf{s}_1\cdot\mathbf{s}_2$, where A is a constant. We have:

$$|\mathbf{S}|^2 = (\mathbf{s}_1 + \mathbf{s}_2)^2 = |\mathbf{s}_1|^2 + |\mathbf{s}_2|^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2$$

But $|\mathbf{s}_1|^2 = |\mathbf{s}_2|^2 = s(s+1)\hbar^2 = 3\hbar^2/4$ ($\because s = \frac{1}{2}$) . Similarly, $|\mathbf{S}|^2 = S(S+1)\hbar^2$, and is 0 for a singlet ($S = 0$) and $2\hbar^2$ for a triplet ($S = 1$). $-A\mathbf{s}_1\cdot\mathbf{s}_2 = 3A\hbar^2/4$ for a singlet and $-A\hbar^2/4$ for a triplet. Hence the lowest energy state is determined by the sign of A. For an atom obeying Hund's rules $A>0$ and the triplet with parallel spins is the ground state (Figure 1a). However, for a molecule with covalent bonding the lower energy bonding orbital is symmetric, since electrons must be shared between the two atoms in the molecule. χ_{spin} for the bonding orbital is therefore anti-symmetric and the ground state is a singlet with $A<0$ (Figure 1b).
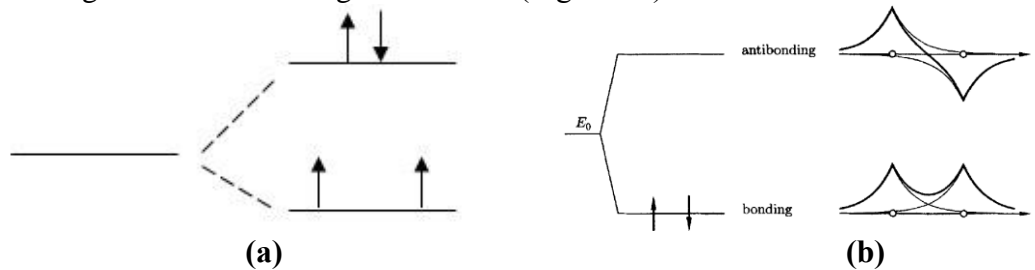
(a)   **(b)**
Figure 1: energy levels for (a) a single atom and (b) a diatomic molecule.

Ferromagnetism

If we include exchange the magnetic part of the Hamiltonian becomes:

$$\widehat{H}_{\mathrm{mag}} = \sum_{i,j} -J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i} \gamma g_J \mathbf{B} \cdot \mathbf{J}_i + \sum_{i} \frac{e^2}{8m}(\mathbf{B} \times \mathbf{r}_i)^2$$

J_{ij} is the **exchange integral** or **exchange constant** between two atom pairs i and j; it is effectively the constant A in the previous section. For a ferromagnet $J_{ij} > 0$, so that the triplet is the ground state and there is long range *parallel* alignment of spins. Define a molecular field $\mathbf{B}_{mf}$ due to neighbouring spins as (the molecular field is not real but instead represents the effects of the exchange interaction):

$$\boldsymbol{B}_{mf} = \frac{1}{\gamma g_J}\sum_{j\neq i} -J_{ij}\boldsymbol{S}_j$$

The molecular field is assumed to be constant at each atom site 'i'. Substituting in the Hamiltonian and assuming identical atoms/ions with $\mathbf{L} = 0$ and $\mathbf{J} = \mathbf{S}$ gives:

$$\widehat{H}_{\mathrm{mag}} = \sum_{i} \gamma g_J(\mathbf{B} + \mathbf{B}_{\mathrm{mf}}) \cdot \mathbf{J}$$

where the weaker diamagnetic term has been ignored. The **Weiss model of ferromagnetism** further assumes that $\mathbf{B}_{mf} = \lambda\mathbf{M}$, where $\mathbf{M}$ is the magnetisation and λ is a constant. The Hamiltonian is similar to a paramagnetic material, but with $\mathbf{B}$ replaced by $(\mathbf{B} + \mathbf{B}_{mf})$ or equivalently $(\mathbf{B} + \lambda\mathbf{M})$.
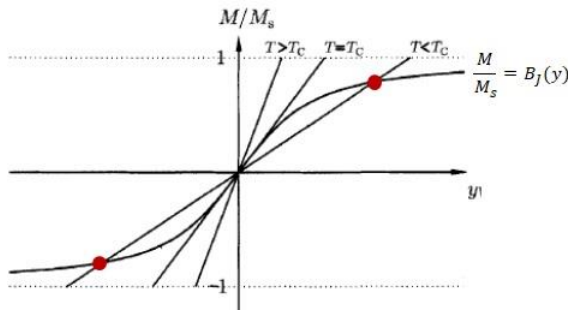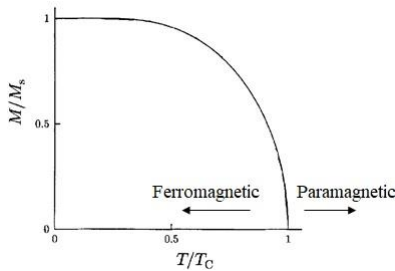

Figure 2

Using results derived previously for a paramagnetic solid (Lecture 7):

$$\frac{M}{M_s} = B_J(y)$$

$$\ldots (1)$$

$$y = \frac{g_J \mu_B J(B + B_{mf})}{kT} = \frac{g_J \mu_B J(B + \lambda M)}{kT}$$

$$\ldots (2)$$

where the Brillouin function $B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{y}{2J}\right)$. Note the inclusion of the molecular field in Equation 2. The magnetisation M must satisfy Equations 1 and 2 simultaneously. The situation for a zero applied $\mathbf{B}$-field is shown in Figure 2. At low temperatures Equation 2 (the straight line in the figure) intersects $B_J(y)$ at non-zero values of M (red points), meaning the material has *spontaneous magnetisation* even in the absence of an external magnetic field. The spontaneous magnetisation is due to the internal molecular field.

Figure 3

The gradient of the M vs. y straight line is proportional to temperature (Equation 2). Therefore, at a critical temperature T_c, called the **Curie temperature**, the spontaneous magnetisation will drop to zero, and the material will be paramagnetic at $T > T_c$ (Figure 2). The change in magnetisation as a function of temperature is shown in Figure 3; note the *continuous* decrease of M to zero at $T=T_c$.

We can calculate the magnetic susceptibility χ of the paramagnetic phase above T_c. To do this we have to solve Equations 1 and 2 for weak external $\mathbf{B}$-fields. The graphical solutions are shown in Figure 4. Note the straight lines representing Equation 2 are now shifted along the horizontal axis due to the applied field; this results in non-zero magnetisation even for $T > T_c$.
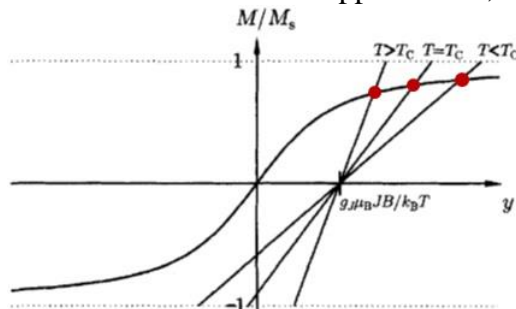
Figure 4

For a $J = \frac{1}{2}$ solid Equations 1 and 2 give (see also Lecture 7):

$$\frac{M}{M_s} = \frac{\mu_B(B+\lambda M)}{kT} \text{ or } \frac{M}{M_s}\left(1 - \frac{\lambda \mu_B M_s}{kT}\right) = \frac{\mu_B B}{kT}$$

For small magnetisations $\chi = \mu_0 M/B$ so that:

$$\chi = \frac{\mu_0 \mu_B M_s}{k\left[T - \frac{\lambda \mu_B M_s}{k}\right]} \propto \frac{1}{T - T_c}$$

For a ferromagnet above T_c the susceptibility varies as $\chi \propto 1/(T-T_c)$; this is known as the **Curie-Weiss law**. From the expression for χ it follows that $T_c = \frac{\lambda \mu_B M_s}{k}$. Since T_c can be measured experimentally we can use this equation to estimate the molecular field at saturation magnetisation $B_{mf} = \lambda M_s$. For ferromagnetic Fe, $T_c = 1043$ K and the maximum molecular field

is greater than 1,000 Tesla! This is an unimaginably large magnetic field (for reference a field of 1 Tesla is considered to be large). However, we have to bear in mind that B_{mf} is not an actual magnetic field and has such a large value because it represents the Coulomb forces between electrons resulting from the exchange interaction.