



Keble College - Hilary 2012
Section VI: Condensed matter physics
Tutorial 5 - Magnetism

Please leave your work in the Clarendon laboratory's 'J' pigeon hole by 5pm on Monday of 8th week. Hook & Hall 7,8; Kittel 11,12; Ashcroft and Mermin 31-33.

Magnetism is about the behaviour of the magnetic moments of a solid, principally those associated with electrons, including their response to a magnetic field. So far we have worked within the independent electron approximation, in which single electron eigenstates are organised into bands. In tutorial 1 we looked at one type of magnetism which arises in this approximation; Pauli paramagnetism contributes $\chi_{\text{Pauli}} = \mu_0 \mu_B^2 g(\epsilon_F)$ to the susceptibility. Although this effect, and the related but off-syllabus Landau diamagnetism ($\chi_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}}$), are seen in simple metals, they represent only a very small part of the magnetic effects observed in solids. To describe other effects we must go beyond the independent electron approximation. This is the topic of this tutorial.

As a first attempt we might take a partially filled conduction band and ask what effects arise if we introduce some energy penalty U for having two electrons on the same site (representing the electron-electron Coulomb interaction). This is the Hubbard model. We will show that the model displays ferromagnetism for U above a critical value, while also predicting that if the conduction band is half-filled and U is very large then antiferromagnetism occurs.

The Hubbard model also shows that large interactions U can turn a metal into an insulator, with electrons fixed to their respective nuclei. In these cases the problem of magnetism divides quite nicely into finding the magnetic moments of individual atoms, modelling their interactions and then considering the collective response to a magnetic field. We will look at an idealised example of this, the Heisenberg model. This model predicts magnetic order, and so it is a good basis for discussing ferromagnetism and antiferromagnetism, though more consideration is needed to explain domains and hysteresis. At sufficiently high temperatures we will find the order due to inter-atom interactions is lost and we can consider each atom individually. In this regime, magnetism becomes quite simple and is just an exercise in atomic physics.

In what follows, we will work backwards through the above discussion, taking a route through the subject from what is most familiar to that which may be more unfamiliar. The array of models used to describe magnetism reflects the complexity and variety of magnetic properties in solids. Justifying which of the models we expect to describe any one solid from first principles is often not possible and so an input from experiment is often required.

1 General definitions

1. Before we go into depth on each, briefly explain the terms *susceptibility, paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism, ferrimagnetism* and *itinerant ferromagnetism*.

2 Atomic magnetism

The Hamiltonian describing an atom's fine structure, with no applied magnetic field, is

$$\mathcal{H}_0 = \sum_i \frac{p_i^2}{2\mu} + V(\{\mathbf{r}_i\}) + \xi \mathbf{L} \cdot \mathbf{S}.$$

When a magnetic field is applied, we must adjust the Hamiltonian and we do this in two ways:

- We replace the momentum of each electron \mathbf{p}_i in the kinetic energy term by $\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i)$, where \mathbf{A} is the magnetic vector potential and the magnetic field is given by $\mathbf{B} = \nabla \times \mathbf{A}$. This is called 'minimal coupling'.
- We include the terms $\sum_i g_s \mu_B \mathbf{S}_i \cdot \mathbf{B}$ to represent the interaction of the magnetic field with the spin-induced magnetic moment of electrons.

There are other effects of course, e.g., due to the magnetic moment of nucleons, but generally these are much smaller and we can safely neglect them. So the Hamiltonian is

$$\mathcal{H} = \sum_i \left[\frac{(\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i))^2}{2\mu} + g_s \mu_B \mathbf{S}_i \cdot \mathbf{B}(\mathbf{r}_i) \right] + V(\{\mathbf{r}_i\}) + \xi \mathbf{L} \cdot \mathbf{S}. \quad (1)$$

2. *Classical treatment* — Classically, without considering spin, atoms should always have zero magnetisation; this is the Bohr-van Leeuwen theorem. Consider the classical partition function

$$Z = \int \int d\mathbf{p}^{3n} d\mathbf{r}^{3n} \exp(-\beta\mathcal{H}).$$

Show, using Eq. 1, that in this classical picture, a simple substitution within the integrals demonstrates that Z does not depend on \mathbf{A} , and hence argue that magnetism is impossible.

3. *Quantum treatment* — Returning to the full quantum treatment, consider a uniform and constant magnetic field \mathbf{B} . You may wish to show that a valid choice of the vector potential in this case is $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$. Show using this choice that Eq. 1 can be rewritten as

$$\mathcal{H} = \mathcal{H}_0 + \mu_B (\mathbf{L} + g_s \mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8\mu} \sum_i (\mathbf{B} \times \mathbf{r}_i)^2.$$

Identify the terms that give rise to paramagnetic and diamagnetic behaviour. Why does magnetism arise in a quantum mechanical treatment when it was absent in the classical case?

To a good approximation, in the *LS* coupling regime, the eigenstates of \mathcal{H}_0 will have well defined quantum numbers J , M_J , L and S . For typical fields, the effects on energies are small, allowing us to use perturbation theory. Doing so, to second order in the field, the corrections to the eigenenergies are (a common approach from atomic physics is used to calculate the first term)

$$\begin{aligned} \Delta E(JM_JLS) = & g_J \mu_B B M_J + \sum_{J'M_J'L'S'} \frac{\mu_B^2 |\langle JM_JLS | (\mathbf{L} + g_s \mathbf{S}) \cdot \mathbf{B} | J'M_J'L'S' \rangle|^2}{E(JM_JLS) - E(J'M_J'L'S')} \\ & + \frac{e^2}{8\mu} \sum_i \langle JM_JLS | (\mathbf{B} \times \mathbf{r}_i)^2 | JM_JLS \rangle, \end{aligned} \quad (2)$$

If the first term, causing paramagnetism, is non-zero, i.e. $J \neq 0$, then it will be dominant, since it is the only linear term, and we can neglect the other two. If $J = 0$ then we should consider the other two, the first leads to Van Vleck diamagnetism and we do not discuss it here (it is just a footnote in the lecturer's notes), and the second leads to Larmor diamagnetism.

4. *Free spin (Curie or Langevin) paramagnetism* — Consider the ground state of \mathcal{H}_0 , defined by quantum numbers J , L and S (the actual values are determined by electron-electron interactions, and are normally found using Hund’s rules), with a degeneracy in M_J (due to spherical symmetry). So long as $J \neq 0$, we need only consider the term $g_J \mu_B B M_J$ above, which lifts the degeneracy in M_J . For typical temperatures, only states in this ground state Zeeman manifold will be occupied.

Find the partition function \mathcal{Z} and calculate the susceptibility of a density n of atoms with $J = 1$; this is an example of Curie’s law. [In other words, calculate the susceptibility of a so-called ‘free spins’ interacting with a magnetic field, represented by Hamiltonian $\mathcal{H} = g_J \mu_B \mathbf{J} \cdot \mathbf{B}$. Optional: do this for arbitrary J .]

5. *Larmor diamagnetism* — When the ground state has $J = 0$, the first order effects are zero and effects second order in the magnetic field become most important. Further, for $L = S = 0$ the Van Vleck term is zero, leaving only the third term in Eq. 2. Calculate the susceptibility arising from this, in terms of $\langle r^2 \rangle = \frac{1}{Z} \sum_i \langle r_i^2 \rangle$, where again the density of atoms is n .

Hydrogenic — Calculate this for a single electron in a wavefunction that you can take to be that of the ground state of hydrogen.

Diamagnetism of impurity bound states — An electron bound to an n-type impurity in a solid is often described like this where its effective mass is used and the relative permittivity of the material is accounted for. Therefore estimate the impurity contribution to the susceptibility of an Si crystal containing $n = 10^{20} \text{ m}^{-3}$ donors, given an electron effective mass of $0.4m$ and a relative permittivity of $\epsilon_r = 12$. This explains how doping can lead to large diamagnetic susceptibilities.

3 Magnetic order in the Heisenberg model

The results of the previous section are pertinent if we can think of electrons as being attached to individual ions, whence magnetism in a solid is simply the combination of magnetism in a number of independent ions. This is obviously not always the case, as it does not explain the ordering that we sometimes see in real solids. The typical approach of a theoretical physicist is to find the simplest model that still leads to the interesting physics, so that we may understand the mechanisms behind this physics; in this case we seek the simplest extension to the independent ions approach that predicts ferromagnetism and antiferromagnetism. In this simplest approach, we have identical atoms and each remains in its ground state Zeeman manifold (J , L and S the same as above), and so we are restricted to the subspace spanned by different M_J states. Each atom has a magnetic moment $\boldsymbol{\mu} = -g_J \mu_B \mathbf{J}$ which interacts with a magnetic field according to the Hamiltonian $-\boldsymbol{\mu} \cdot \mathbf{B}$, as above. Further, we consider a relatively simple interaction between nearest neighbour atoms, proportional to $\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j$. The combined Hamiltonian is called the Heisenberg spin Hamiltonian

$$\mathcal{H} = -\frac{J}{2} \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - g \mu_B \mathbf{B} \cdot \sum_i \mathbf{S}_i, \quad (3)$$

where the sum is over all nearest neighbours with each pair counted twice. \mathbf{S}_i , although called a spin, could represent any type of angular momentum. As well as being an interesting model to study for those looking generally at many-body correlations in quantum mechanics, it is a bonus that, in some limits, it is justified to represent magnetism in solids by the Heisenberg model, though exactly when and how is beyond the scope of this course.

The Heisenberg spin chains are tricky to solve exactly and so we will do so using a mean-field approximation. We find both ferromagnetism and antiferromagnetism at low temperatures, and recover Curie’s law at high temperatures. This ‘simple’ model has a lot of features!

6. *Ferromagnetism* — Consider the Hamiltonian of Eq. 3 where each \mathbf{S}_i represents a spin- $\frac{1}{2}$ and $J > 0$. This is called the spin- $\frac{1}{2}$ ferromagnetic Heisenberg Hamiltonian.
- Mean field* — Derive the effective mean-field Hamiltonian, where each spin has z nearest-neighbours.
 - Self-consistency* — Assuming $\langle \mathbf{S} \rangle$ is parallel to \mathbf{B} , find a self-consistency equation for the expected component of spin along \mathbf{B} , written $\langle S \rangle$.
 - Curie-Weiss law* — Use this to find the high temperature susceptibility. Compare this to Curie's law.
 - Ferromagnetism below T_c* — At low temperature, analytic solutions of the self-consistency equation are not possible. Show graphically that below a critical temperature T_c (which you should calculate), there are solutions with $\langle S \rangle \neq 0$ for $\mathbf{B} = 0$.
7. *Antiferromagnetism* — Consider the spin- $\frac{1}{2}$ Hamiltonian of Eq. 3 on a cubic lattice with $J < 0$. This is called the spin- $\frac{1}{2}$ antiferromagnetic Heisenberg Hamiltonian.
- Mean-field* — By splitting the lattice into two sub-lattices, derive the effective mean-field Hamiltonian.
 - Self-consistency* — Assuming that the net magnetisations of both sub-lattices are parallel to \mathbf{B} , show that the two self-consistency relations for the expectation values of spin-components along \mathbf{B} for the two sub-lattices, $\langle S \rangle_A$ and $\langle S \rangle_B$, are given by

$$\begin{aligned}\langle S \rangle_A &= \frac{1}{2} \tanh(\beta[Jz\langle S \rangle_B + g\mu_B B]/2), \\ \langle S \rangle_B &= \frac{1}{2} \tanh(\beta[Jz\langle S \rangle_A + g\mu_B B]/2).\end{aligned}$$

- High temperature susceptibility* — Derive the high temperature susceptibility, and compare your result with that for $J > 0$ and Curie's law.
- Antiferromagnetism below T_c* — Again, at low temperature, analytic solutions of the self-consistency equation are not possible. Argue that below a critical temperature T_c (which you should calculate), there are solutions with $\langle S \rangle_A = -\langle S \rangle_B \neq 0$ for $\mathbf{B} = 0$.
- Observing antiferromagnetism* — How would you detect antiferromagnetism experimentally?

4 Domains and hysteresis

The Heisenberg spin Hamiltonians don't capture all of the features of magnetism. For example we must include long-range magnetic dipole interactions, anisotropies in the environment of each moment, and impurities if we are to explain ferromagnetic domains and hysteresis.

- Interactions in the Heisenberg model* — Estimate the strength of interactions between adjacent magnetic dipoles in a typical crystal. Could these give rise to nearest-neighbour interactions in the Heisenberg model? What is the real cause?
 - Long-range dipole interactions and domains* — Magnetic dipole interactions do, however, play another important role in magnetism. Explain how long range dipole interactions cause a lump of iron to be unmagnetised at room temperature, forming domains. Which two effects compete to determine the thickness of domain walls?
 - Hysteresis and impurities* — Discuss hysteresis and the role of impurities in permanent magnets.

5 Magnetic order in the Hubbard model

The derivation of magnetic properties in terms of contributions from individual ions contrasts with the description of delocalised Bloch electrons used to explain conduction properties of solids in the previous tutorial. More congruent with this description is the Hubbard model, an idealised approach to magnetic order starting from the tight-binding model and including on-site electron-electron Coulomb interactions. Here we look at the simplest case, where there is only a single band.

9. *Itinerant ferromagnetism* — In this question, we wish to see whether, at zero temperature $T = 0$ and magnetic field $B = 0$, ferromagnetic order is energetically preferable. We find that an on-site interaction strength U above a critical value U_c is needed for this to be the case.

- (a) *Tight-binding spectrum* — Ignoring on-site interactions for now $U = 0$, consider a 3D tight-binding band on a cubic lattice in which the density of electrons n is low, so that only states near the bottom of the band are occupied. What is the low energy eigenvalue spectrum $\epsilon(k)$ in terms of the hopping energy t ?
- (b) *Spin-polarised energy* — Show that at $T = 0$ the total energy per unit volume of the electrons, if they are constrained to have the same spin (spin-polarised), is given by

$$E/V = n\epsilon(0) + Cn^{5/3},$$

and calculate C .

- (c) *Unpolarised energy* — Write the density of spin up electrons be $n_\uparrow = (n/2)(1 + \alpha)$, and the density of spin down electrons be $n_\downarrow = (n/2)(1 - \alpha)$. Thus the total magnetization in the system is $M = \mu_B n \alpha$. Using part (b), calculate the total energy per unit volume of the electrons at $T = 0$ as a function of α , expanding your result to $\mathcal{O}(\alpha^4)$.
- (d) *No order without on-site interactions* — Show that $M = 0$ gives the lowest energy, and argue that this remains true to all orders of M .
- (e) *Mean-field Hubbard contribution* — Now consider an on-site interaction, which due to the Pauli exclusion principle must involve only electrons of different spins. We can account for the energy due to this interaction in a mean-field way by adding an energy $U \sum_i N_\uparrow^i N_\downarrow^i$ to the system, with N_σ^i being the mean number of electrons on site i with spin σ . Calculate the value of this term for electrons in part (c).
- (f) *Stoner criterion* — For which values of U is a non-zero M favourable? For values of U slightly above the critical value U_c , calculate M .
- (g) *Two dimensions* — How does this result change for a two-dimensional system?
10. *Antiferromagnetic Mott insulator* — The mean-field approach of the last question only alludes to a few of the phenomena captured by the Hubbard model. This question explores one extreme to which the mean-field approach is not applicable.
- (a) *Mott insulator* — Consider a tight binding model with hopping t and a strong Hubbard interaction U . If there is exactly one electron per site, why would you expect the system to be an insulator? [Note: For $U = 0$ it would be a metal.]
- (b) *1D Antiferromagnetic ground state* — For one dimension, consider a site and its two neighbours. Argue that a state with a spin in opposite alignment to its neighbours has a lower energy than a spin aligned with its neighbours. Use second order perturbation theory to formally show that this energy difference is $-2t^2/U$ (you should satisfy yourself that the first order of perturbation theory gives zero energy change). Therefore argue that the ground state of the Hubbard model with this density of electrons is antiferromagnetic.