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3. DIAMAGNETISM AND PARAMAGNETISM

The interaction of electrons with a uniform magnetic field. A uniform magnetic field couples to the electronic motion, and to the electron spin. The coupling with the spin adds to the Hamiltonian the *Zeeman interaction*

$$g_0\mu_B\mathbf{H}\cdot\mathbf{S}, \quad (3.1)$$

in which \mathbf{H} is the magnetic field. Here, \mathbf{S} is the total spin of the electrons, i.e.,

$$\mathbf{S} = \sum_i \mathbf{s}_i, \quad \text{and} \quad \mathbf{s}_i = \frac{1}{2}\boldsymbol{\sigma}, \quad (3.2)$$

where $\boldsymbol{\sigma}$ is the vector of Pauli matrices,

$$\boldsymbol{\sigma} = \hat{x}\sigma_x + \hat{y}\sigma_y + \hat{z}\sigma_z, \quad (3.3)$$
$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

In Eq. (3.1), μ_B is the Bohr magneton $\mu_B = e\hbar/2m = 0.927 \times 10^{-20}$ erg/G and g_0 is the g -factor (Landé factor), which is about 2. The coupling of the magnetic field to the *orbital* motion of the electron is described by the vector potential \mathbf{A} , such that

$$\mathbf{H} = \nabla \times \mathbf{A}. \quad (3.4)$$

We shall use the gauge in which $\nabla \cdot \mathbf{A} = 0$. (One can always shift the vector potential by an arbitrary function $\nabla\chi$ and make $\nabla \cdot \mathbf{A} = 0$ without changing the magnetic field, which is the physical quantity). We hence take the vector potential to be

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}\mathbf{r} \times \mathbf{H}. \quad (3.5)$$

(Note that the magnetic field is uniform.) The vector potential modifies the kinetic energy, making the momentum of the i -th electron, \mathbf{p}_i , to be $\mathbf{p}_i + (e/c)\mathbf{A}(\mathbf{r}_i)$. The kinetic energy part of the Hamiltonian becomes, in the presence of a uniform magnetic field,

$$\frac{1}{2m} \sum_i \mathbf{p}_i^2 \rightarrow \frac{1}{2m} \sum_i \left(\mathbf{p}_i + \frac{e}{c}\mathbf{A}(\mathbf{r}_i) \right)^2. \quad (3.6)$$

It follows from Eqs. (3.1) and (3.6) that the change in the Hamiltonian of the electrons due to the magnetic field is

$$\Delta\mathcal{H} = g_0\mu_B\mathbf{H} \cdot \mathbf{S} - \frac{e}{2mc} \sum_i \mathbf{p}_i \cdot \mathbf{r}_i \times \mathbf{H} + \frac{e^2}{8mc^2} \sum_i \left(\mathbf{r}_i^2 \mathbf{H}^2 - (\mathbf{r}_i \cdot \mathbf{H})^2 \right). \quad (3.7)$$

The terms *linear* in the magnetic field can be combined together. Since the total electronic angular momentum of the electrons, \mathbf{L} , is

$$\hbar\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i, \quad (3.8)$$

the linear terms give

$$\mu_B\mathbf{H}(\mathbf{L} + g_0\mathbf{S}). \quad (3.9)$$

We can therefore write the change in the Hamiltonian in the form

$$\Delta\mathcal{H} = \mu_B\mathbf{H}(\mathbf{L} + g_0\mathbf{S}) + \frac{e^2}{8mc^2} \mathbf{H}^2 \sum_i (x_i^2 + y_i^2). \quad (3.10)$$

In writing down the second term here we have assumed that the magnetic field is along the z -direction. Once we know the modifications of the Hamiltonian in the presence of a uniform magnetic field, we can find the change in the energy of the system (or the change in the free energy) and use them in order to compute the magnetic properties of our system.

The magnetic susceptibility. The response of a system to a magnetic field is characterized by its magnetic *susceptibility*. This quantity is defined as follows. Let us consider a quantum-mechanical system at zero temperature, and calculate the change in the ground state energy, E_0 , under the application of a magnetic field. Then, the *magnetization* density is given by

$$M(\mathbf{H}) = -\frac{1}{V} \frac{\partial E_0(\mathbf{H})}{\partial \mathbf{H}}, \quad (3.11)$$

where V is the volume. The susceptibility, χ , is defined by

$$\chi = \frac{\partial M}{\partial \mathbf{H}}. \quad (3.12)$$

At finite temperatures, where the system is not in the ground state, we have to replace in the above definitions the ground state energy by the *free energy*.

Larmor diamagnetism. When a solid consists of ions whose all electronic shells are filled, the wave function of the ground state is characterized by zero angular momentum (since such ions are spherically symmetric) and zero spin. In such a case there is no contribution to the ground state energy from the term linear in H [see Eq. (3.10)], and we are left with

$$\Delta E_0 = \frac{e^2}{12mc^2} H^2 \langle \Psi_0 | \sum_i r_i^2 | \Psi_0 \rangle . \quad (3.13)$$

The magnetic susceptibility given in Eq. (3.12) is *negative*, and the material is diamagnetic. This is dubbed ‘Larmor diamagnetism’. Materials in which the magnetic susceptibility is negative are called ‘diamagnetic’ since in the presence of a magnetic field their energy increases, they try to avoid it by directing the induced magnetic moment opposite to the field.

*** **exercise:** Explain how Eq. (3.13) is obtained, find an explicit form for the diamagnetic Larmor susceptibility and estimate its magnitude.

Partially filled shells. A partially filled ion is an ion whose all shells are either completely filled or completely empty, except for one (the ‘outer’ shell). There are two questions to be asked: (a) what is the modification of the ground state energy caused by the magnetic field, and (b) how is the ground state specified.

The first question is somewhat easier. Going back to Eq. (3.10), we use *perturbation theory* to find the change in the energy caused by the extra term in the Hamiltonian, $\Delta\mathcal{H}$.

The calculation of the change in the energy in perturbation theory is carried out as follows. The full Hamiltonian is $\mathcal{H} + \Delta\mathcal{H}$, where $\Delta\mathcal{H}$ is assumed to be small. The eigen functions of the part \mathcal{H} of the Hamiltonian are denoted Ψ_n , and their corresponding energies are E_n . It is important to remember that the eigen functions form a complete orthonormal basis. In order to find the correction of the ground state energy, we write the (full) Schrödinger equation in the form

$$\begin{aligned} & \left(\mathcal{H} + \Delta\mathcal{H} \right) \left(\Psi_0 + \sum_n \left[a_n^{(1)} \Psi_n + a_n^{(2)} \Psi_n + \dots \right] \right) \\ & = \left(E_0 + E_0^{(1)} + E_0^{(2)} + \dots \right) \left(\Psi_0 + \sum_n \left[a_n^{(1)} \Psi_n + a_n^{(2)} \Psi_n + \dots \right] \right) . \end{aligned} \quad (3.14)$$

Here, n runs over all eigen values, the coefficients $a_n^{(i)}$ give the correction of order i ($i = 1, 2, \dots$) of the eigen functions, (namely, the corrections to the eigen functions are expanded

in the complete basis formed by the Ψ_n) and $E_0^{(i)}$ is the correction of order i of the ground state energy. The next step is to equate identical orders in Eq. (3.14).

At order zero, $\Delta\mathcal{H} = 0$, and all $a_n^{(i)}$ and $E_0^{(i)}$ are zero as well. Equation (3.14) is then

$$\mathcal{H}\Psi_0 = E_0\Psi_0 . \quad (3.15)$$

In first order in $\Delta\mathcal{H}$, Eq. (3.14) is

$$\mathcal{H} \sum_n a_n^{(1)} \Psi_n + \Delta\mathcal{H}\Psi_0 = E_0 \sum_n a_n^{(1)} \Psi_n + E_0^{(1)}\Psi_0 . \quad (3.16)$$

When his equation is multiplied on the left by Ψ_0 , it gives

$$E_0^{(1)} = \langle \Psi_0 | \Delta\mathcal{H} | \Psi_0 \rangle , \quad (3.17)$$

and when it is multiplied from the left by any other eigen function Ψ_ℓ , $\ell \neq 0$ it gives

$$a_\ell^{(1)} = \frac{\langle \Psi_\ell | \Delta\mathcal{H} | \Psi_0 \rangle}{E_0 - E_\ell} , \quad \ell \neq 0 . \quad (3.18)$$

To second order in the perturbation $\Delta\mathcal{H}$, Eq. (3.14) gives

$$\mathcal{H} \sum_n a_n^{(2)} \Psi_n + \Delta\mathcal{H} \sum_n a_n^{(1)} \Psi_n = E_0 \sum_n a_n^{(2)} \Psi_n + E_0^{(1)} \sum_n a_n^{(1)} \Psi_n + E_0^{(2)} \Psi_0 . \quad (3.19)$$

Multiplying from the left by Ψ_0 , we obtain

$$\begin{aligned} E_0^{(2)} &= \sum_n a_n^{(1)} \langle \Psi_0 | \Delta\mathcal{H} | \Psi_n \rangle \\ &= \sum_{n \neq 0} \frac{\langle \Psi_n | \Delta\mathcal{H} | \Psi_0 \rangle \langle \Psi_0 | \Delta\mathcal{H} | \Psi_n \rangle}{E_0 - E_n} = \sum_{n \neq 0} \frac{|\langle \Psi_n | \Delta\mathcal{H} | \Psi_0 \rangle|^2}{E_0 - E_n} . \end{aligned} \quad (3.20)$$

We have used here Eq. (3.18). Obviously, we can use the second-order equation to find other coefficients in the expansion of the eigen functions, but those are not required for our purposes.

**** * exercise:** Does the second-order correction to the energy have a definite sign? what is this sign? what happens to the second-order corrections of energies which are not the ground state energy?

In our case, $\Delta\mathcal{H}$, Eq. (3.10), includes a term linear in the magnetic field, and a term which is quadratic in the magnetic field. Therefore, the correction to the ground state energy, valid

up to second order in the magnetic field is

$$\begin{aligned} \Delta E_0 = & \mu_B \mathbf{H} \cdot \langle \Psi_0 | \mathbf{L} + g_0 \mathbf{S} | \Psi_0 \rangle + \frac{e^2}{8mc^2} H^2 \langle \Psi_0 | \sum_i (x_i^2 + y_i^2) | \Psi_0 \rangle \\ & + \sum_{n \neq 0} \frac{|\langle \Psi_0 | \mu_B \mathbf{H} \cdot (\mathbf{L} + g_0 \mathbf{S}) | \Psi_n \rangle|^2}{E_0 - E_n}. \end{aligned} \quad (3.21)$$

Hund's rules. In order to find the magnetic nature of systems made of partially filled ions, we now need to (a) specify the ground state (in the absence of the magnetic field), (b) insert the result in Eq. (3.21) to find the change in the energy of the ground state, and (c) take the second derivative with respect to the magnetic field and find the magnetic susceptibility.

For example, in the case of *transition metals*, e.g., copper, the outer shell is the d -shell, of angular momentum $\ell = 2$. [This means that the orbital angular momentum squared of each electron—the expectation value of \mathbf{L}^2 , has the value $\ell(\ell + 1)$.] The projection of the angular momentum vector along the z -direction, ℓ_z , can take $2\ell + 1$ values,

$$\ell_z = -\ell, -\ell + 1, \dots, \ell - 1, \ell. \quad (3.22)$$

Hence the d -shell is five-fold degenerate, namely, there are five single-electron wave functions (or orbitals) corresponding to the d -shell. Each of these orbitals can accumulate two spin directions, namely it may have $s_z = \pm 1/2$, and therefore the full degeneracy of the d -shell is 10. In other words, we can put up to 10 electrons in the d -shell. Copper, for example, has 9 electrons in that shell.

In general, the number of electrons in the outer shell is n , such that $0 < n < 2(2\ell + 1)$. If these electrons do not interact with each other, then there are many ways to distribute n electrons on $2(2\ell + 1)$ levels. However, the electron-electron interactions, and the spin-orbit interaction, reduce significantly the number of these different possibilities. This is achieved according to famous rules (which are in fact only approximate), called the Hund rules. We shall state these rules without their derivation, assuming that the many-electron eigen states and eigen energies of the ion are characterized by the quantum numbers corresponding to the total spin of the electrons, S , their total orbital angular momentum, L , and their total angular momentum, J .

Hund's first rule. The electronic states with the lowest energy are those with the largest value of the total spin, such that these states are still consistent with the exclusion principle.

This means that as long as the number of electrons, n , is such that $n \leq 2\ell + 1$, all their spins are parallel, and $S = n/2$. When $n > 2\ell + 1$, the total spin is reduced.

Hund's second rule. The electronic states with the lowest energy have the largest possible value of the angular momentum, $L = |\sum \ell_z|$, which is consistent with Hund's first rule and with the exclusion principle.

Hund's third rule. This rule has to do with the total angular momentum, J . The total angular momentum takes integral values in the range $|L - S|$ and $L + S$. Therefore, once S and L are given, there are still $(2L + 1)(2S + 1)$ many-electron possible states. (Remember that the degeneracy of a level with a certain J is $2J + 1$, since $J_z = -J, -J + 1, \dots, J$.) Hund's third rule uses the spin-orbit interaction to choose the ground state(s) among these states. The spin-orbit interaction reads $\lambda \mathbf{L} \cdot \mathbf{S}$, where λ is the spin-orbit coupling. It turns out that $\lambda > 0$ for shells that are less than half filled and is negative for shell which are more than half filled. Hund's third rule tells us that $J = |L - S|$ when $n \leq 2\ell + 1$, because then the spin-orbit interaction (with $\lambda > 0$) reduces the energy, and $J = L + S$, for $n \geq 2\ell + 1$, for the same reason (with negative λ).

The ground state of a d -shell ion.

n	2	1	0	-1	-2	S	L	J
1	↑					1/2	2	3/2
2	↑	↑				1	3	2
3	↑	↑	↑			3/2	3	3/2
4	↑	↑	↑	↑		2	2	0
5	↑	↑	↑	↑	↑	5/2	0	5/2
6	↑↓	↑	↑	↑	↑	2	2	4
7	↑↓	↑↓	↑	↑	↑	3/2	3	9/2
8	↑↓	↑↓	↑↓	↑	↑	1	3	4
9	↑↓	↑↓	↑↓	↑↓	↑	1/2	2	5/2
10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0

*** **exercise:** Prepare a similar table for the ions with partially filled f -shell ($L = 3$).

Hund's three rules determine the ground state(s) of the partially-filled ion. However, that ground state is still degenerate. Take for example, the case $n = 2$ in the Table. After applying Hund's first and second rules, it has total spin $S = 1$ and total orbital angular momentum $L = 3$. This means that the states with $J = 2, 3$, and 4 are all possible. This gives for the case of $n = 2$ electrons $5 + 7 + 9 = 21$ options. (Note that in this case, $(2L + 1)(2S + 1) = 21$.) However, Hund's third rule tells us that the lowest energy is obtained for $J = |L - S| = 2$, and therefore, the ground state of a partially-filled d -shell with two electrons has $J = 2$ and is 5-fold degenerate.

*** **exercise:** Repeat this argument and find the degeneracy of all ground states corresponding to the d and f shells.

Now that we have specified the ground state(s) of the ions, we turn to the calculation of the ground state energy. Here we distinguish between two possibilities: either the ground state is non degenerate, which happens when $J = 0$, or it is degenerate. If it is not degenerate, we may use Eq. (3.21) for the energy. It turns out that $\langle \Psi_0 | \mathbf{L} + g_0 \mathbf{S} | \Psi_0 \rangle = 0$ when $J = 0$, but $\langle \Psi_n | \mathbf{L} + g_0 \mathbf{S} | \Psi_0 \rangle \neq 0$ (this will be explained below). Therefore, only the two terms in Eq. (3.21) which are quadratic in H contribute to the energy. The first one leads to *diamagnetism*, as we have found above, and yields the Larmor diamagnetic susceptibility. The second term quadratic in H yields *positive* magnetization, which means that the material is *paramagnetic*. In a paramagnetic material, the application of a magnetic field reduces the energy, and therefore the material does not try to 'oppose' the effect of the magnetic field, as is the case with a diamagnetic material. We see that partially filled band with $J = 0$ can be either paramagnetic or diamagnetic, depending on the competition between the two H^2 -terms in Eq. (3.21). (Note that this is correct as long as one can deduce the magnetization from the ground state energy alone, namely, when the usual thermal energy is not enough to excite higher energy states.)

When $J \neq 0$ the ground state energy is $2J + 1$ -fold degenerate, and Eq. (3.21) for the ground state energy cannot be used. The application of the magnetic field removes this degeneracy, but then we need to diagonalize an $(2J + 1) \times (2J + 1)$ matrix, made of the matrix elements $\langle JLSJ_z | (\mathbf{L}_z + g_0 \mathbf{S}_z) | JLSJ'_z \rangle$. Luckily enough, there is a theorem, called the

Eckart-Wigner theorem, which states that within the $2J + 1$ manifold,

$$\langle JLSJ_z | (\mathbf{L}_z + g_0 \mathbf{S}_z) | JLSJ'_z \rangle = g(JLS) J_z \delta_{J_z J'_z} , \quad (3.23)$$

where $g(JLS)$ is a number which depends on the values of J , L , and S . Therefore, (to first order in the magnetic field H), the ground state energy splits into a ladder-like spectrum of $2J+1$ levels. However, since in the absence of the field the ground state energy is degenerate, we must take into account the entropy in calculating the magnetic susceptibility, in addition to the energy. In other words, we need to find the *free energy*.

Curie's law. The free energy, F , of an ion, whose relevant possible energies are given by

$$E(J_z) \equiv \gamma H J_z , \quad \gamma = g(JLS) \mu_B , \quad (3.24)$$

is given by

$$e^{-\beta F} \equiv \sum_{J_z=-J}^J e^{-\beta \gamma H J_z} = \frac{e^{\beta \gamma H (J+1/2)} - e^{-\beta \gamma H (J+1/2)}}{e^{\beta \gamma H / 2} - e^{-\beta \gamma H / 2}} . \quad (3.25)$$

The magnetization of such an ion is given by [cf. Eq. (3.11)]

$$M \equiv - \frac{\partial F}{\partial H} = \gamma J B_J(\beta \gamma J H) ,$$

where $B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$ is the Brillouin function . (3.26)

Note that the Brillouin function approaches 1 as $x \rightarrow \infty$ (since then the coth approaches 1). This means that when the Zeeman energy $\gamma J H$ is much larger than the thermal energy, the magnetization of the ion attains its maximal value, γJ . At temperatures such that the thermal energy is larger than the Zeeman energy, we use the fact that $\coth(x) \simeq \frac{1}{x} + \frac{x}{3}$, to find

$$B_J(x) \simeq \frac{(J+1)x}{3J} . \quad (3.27)$$

It therefore follows that

$$\chi \Big|_{\text{single ion}} = \frac{(g\mu_B)^2 J(J+1)}{3 k_B T} , \quad k_B T \gg g\mu_B H . \quad (3.28)$$

To obtain the susceptibility of the entire solid, we multiply this susceptibility by the density of ions in the solid.

Equation (3.28) is the Curie's law. It tells us that partially-filled ions with $J \neq 0$ are, generally, paramagnetic, and that their inverse susceptibility is proportional to the temperature, at temperatures which are not too low.

**** exercise:** Derive in detail Eqs. (3.25), (3.26), (3.27), and (3.28). Give explicit expressions for the case $J = 1/2$, and compare with Eq. (3.30) below. Plot the magnetization and the susceptibility for this specific case, as function of the temperature.

***** exercise:** Consider an ion with a partially filled shell of total angular momentum J , and Z additional electrons in filled shells. Show that the ratio of the paramagnetic susceptibility to the Larmor diamagnetic susceptibility is

$$\frac{\chi_{\text{par}}}{\chi_{\text{dia}}} = -\frac{2J(J+1)}{Zk_{\text{B}}T} \frac{\hbar^2}{m\langle r^2 \rangle}, \quad (3.29)$$

and estimate its magnitude.

In order to clarify the use of the free energy [see Eq. (3.25) above], let us consider the magnetization of a single spin $1/2$, as function of the temperature. A spin half, in the presence of a magnetic field H , can be either aligned with the field, in which case its energy is *enhanced* by $\mu_{\text{B}}g_0H/2$, or it can be anti parallel to the field, in which case its energy is *reduced* by $\mu_{\text{B}}g_0H/2$. It is hence clear that at zero temperature, the spin will be anti parallel to the field, namely, it will be *magnetized*. However, at very high temperatures, that spin has equal probabilities to be aligned or anti aligned with the field, in which case its average magnetic approaches zero.

At temperature T , the average magnetization of the spin is

$$M = \mu_{\text{B}}g_0 \frac{0.5e^{\beta\mu_{\text{B}}g_0H/2} - 0.5e^{-\beta\mu_{\text{B}}g_0H/2}}{e^{\beta\mu_{\text{B}}g_0H/2} + e^{-\beta\mu_{\text{B}}g_0H/2}} = \frac{\mu_{\text{B}}g_0}{2} \tanh \frac{\beta\mu_{\text{B}}g_0H}{2}. \quad (3.30)$$

We can re-derive this formula using the definition of the free energy, Eq. (3.25), which in this case is simply

$$F = -k_{\text{B}}T \ln \left(e^{\beta\mu_{\text{B}}g_0H/2} + e^{-\beta\mu_{\text{B}}g_0H/2} \right). \quad (3.31)$$

It is easy to verify that using this free energy in Eq. (3.11) gives the result (3.30).

Pauli paramagnetism. Here we consider the contribution of the *conduction* electrons to the magnetic moment of the crystal. Stated in other words, we consider the (para)magnetism of metals, whose conduction electrons can be considered as free electron gas.

The magnetic moment of the free electron gas can be obtained as follows. Each electron has spin half, and therefore its energy is enhanced when it is aligned with the field, and is reduced when its spin is anti-parallel to the field. All we have to do is to find how many of the electrons at a temperature T are aligned with the field, and how many of them are anti-parallel to the field, and take the difference. For simplicity, we assume in this calculation that the Landé factor g_0 is 2.

The number of electrons having a certain energy E at temperature T is given by the Fermi distribution, $f(E) = (e^{\beta E} + 1)^{-1}$ (energies are measured with respect to the chemical potential). The number of energy levels of about the same energy E is given by the density of states (per unit volume), $\mathcal{N}(E)$. The chemical potential of the electrons with their spin aligned with the field is decreased by $\mu_B H$, and the chemical potential of those which are anti-parallel to the field is increased by the same amount. Hence, the density of electrons aligned with the field is

$$n_+ = \int dE \mathcal{N}(E) \frac{1}{e^{\beta(E+\mu_B H)} + 1}, \quad (3.32)$$

and the density of those which are anti-parallel to the field is

$$n_- = \int dE \mathcal{N}(E) \frac{1}{e^{\beta(E-\mu_B H)} + 1}. \quad (3.33)$$

The magnetic moment of the electron gas is

$$M = \mu_B(n_- - n_+) = \mu_B \int dE \mathcal{N}(E) \left(\frac{1}{e^{\beta(E-\mu_B H)} + 1} - \frac{1}{e^{\beta(E+\mu_B H)} + 1} \right). \quad (3.34)$$

Expanding in $\mu_B H \ll E_F$ (where E_F is the Fermi energy), we find

$$M \simeq 2\mu_B^2 H \int dE \mathcal{N}(E) \left(-\frac{\partial f}{\partial E} \right). \quad (3.35)$$

Since minus the derivative of the Fermi energy is very close to a delta-function confining the energy to be about the Fermi energy, we see that magnetization is simply given by the density of states at the Fermi energy,

$$M \simeq 2\mu_B^2 H \mathcal{N}(E_F). \quad (3.36)$$

It also follows that the *paramagnetic* susceptibility of the free electron gas, which is called Pauli paramagnetism, is essentially independent of the temperature.

*** **exercise:** Compare Eqs. (3.30) and (3.36), and discuss the similarity and the difference between the two cases.