Digital Computer Laboratory
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM XVIII

To: Group 63

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Pauli Exclusion Principle

The Pauli exclusion principle states that two electrons in the same atom cannot be described by the same set of four quantum numbers n, ℓ, m_l, m_s. The principal quantum number n may be considered a measure of the energy region in which the electron remains. It describes the "shell" of the electron. The value $n = 1$ corresponds to the K shell, $n = 2$ to the L shell etc. The energy levels of electrons in different states, but with the same value of n, are not very far apart. However, it does not necessarily follow that electrons with different principal quantum numbers have widely different energy levels. One sometimes finds an overlapping of energy levels of states with different values of n.

The azimuthal quantum number ℓ is a measure of the orbital quantum number, and has been discussed previously. (See appendix II). It divides the n values in sub-levels. The quantum number ℓ is either 0 or a positive integer, and may have any value up to $n - 1$.

The component of ℓ in the direction of an external field is m_l, and it can take any of the values

$$\ell, \ell - 1, \ldots\ldots\ldots\ldots -\ell + 1, -\ell.$$

The component of s is $m_s = + 1/2$ or $- 1/2$.

On the basis of the Pauli exclusion principle we can build up the quantum states corresponding to the ground state of various atoms. For hydrogen $n = 1$; therefore $\ell = 0$, $m_l = 0$ and m_s can be $+ 1/2$ or $- 1/2$. In the absence of an external field, neither direction is preferred.

The helium atom has two electrons, and again $n = 1$, $\ell = 0$, $m_l = 0$ for both electrons, while for one of them $m_s = + 1/2$ and for the other $m_s = - 1/2$. This represents a closed shell since these are the only possible states for $n = 1$.

For lithium, atomic number 3, the two inner electrons will be in the n = 1 states, and the outer electron will have the quantum numbers $n = 2$, $\ell = 0$, $m_1 = 0$, $m_s = 1/2$ (+ or -).

A more complete picture may be found in Herzberg's book.* A short table, showing the possible states of electrons with n = 1 and n = 2, is given in table 1. The succeeding atoms are built up by "taking on" the succeeding electron in the table.

n	l	m_1	m_s
1	0	0	+ 1/2
			- 1/2
2	0	0	+ 1/2
			- 1/2
	1	1	+ 1/2
		0	+ 1/2
		-1	+ 1/2
		1	- 1/2
		0	- 1/2
		-1	- 1/2

Table 1

When a sub-shell is being filled, there is a tendency for the electrons to align their spins parallel to each other (Hund's rule). This is shown in Table 1, where we see that the atom of atomic number 7 (Nitrogen) has three unpaired electrons. (Two electrons, with their spins anti-parallel to each other, are referred to as an electron pair). The succeeding atom (oxygen) must have the additional electron with its spin in the opposite direction since there are no more states in the $n = 2$, $\ell = 1$ sublevel which can have $m_s = + 1/2$.

* Herzberg, G., Atomic Spectra and Atomic Structure, Dover Publications, New York, 1944, 138 ff.

On reaching atomic number 10 (neon), all electrons have been paired and the L shell is complete. Since a closed shell has no net orbital angular momentum ($\sum M_l = 0$) and no net spin angular momentum ($\sum M_s = 0$); and since it cannot take another electron or readily yield electrons, it is magnetically and chemically inactive. This is the condition of the inert gases.

Atomic number 11 (sodium) has a single electron in the state $n = 3$, $\ell = m_l = 0$, $m_s = 1/2$ travelling in a field due to the nucleus and complete K and L shells. Sodium, therefore, is a hydrogen-like atom.

As mentioned previously, we can find cases where the energy levels of states with different values of n overlap. A very important overlapping of this type occurs between the 3d and 4s levels, as shown in figure 37.

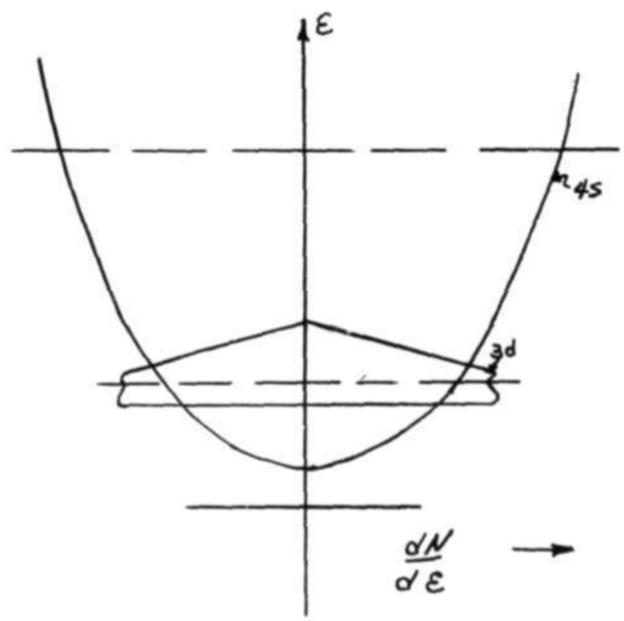

Figure 37

Suppose electrons fill the energy levels to the lower dashed line of figure 37. There will be some 3d electrons and some 4s electrons, with a certain probability of each. On a statistical basis, this can give rise to a fractional number of 3d electrons. Therefore, there is a fractional number of unpaired electrons left in the 3d shell, which gives rise to the fractional number of Bohr magnetons observed.

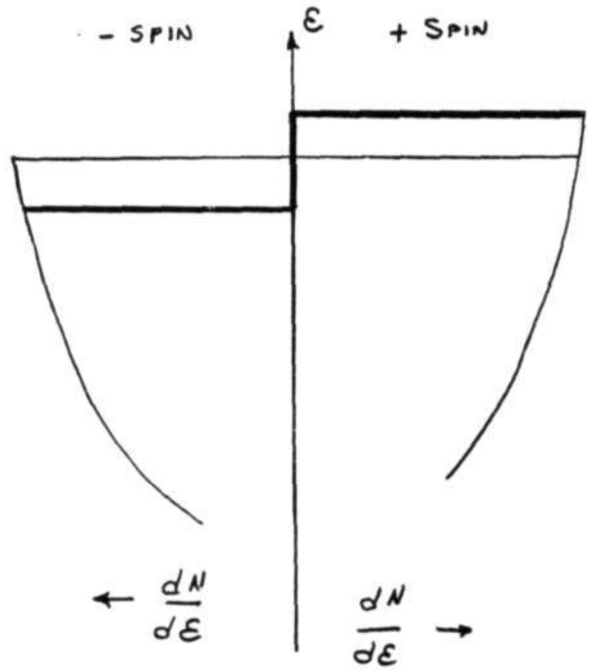

Figure 38

Magnetism

Figure 38 shows the top of a band; that is, the electrons of the system with the highest energy. For the system to be magnetic, there must be a number of unpaired electron spins. In order to determine the feasibility of having an excess of spin in one direction, let us investigate the energy considerations involved.

We define:

N_+ = total number of electrons with + spin in system
N_- = total number of electrons with - spin in system
n = excess of electrons with one spin direction

When $n = 0$, $N_+ = N_- = N_0$

Then assuming an equal number of electrons with each spin direction at the start, n/2 electrons have been transferred from one spin direction to the other. Let us perform this process in two main steps:

I - Remove $\frac{n}{2}$ electrons from the negative spin system.

II - Add these $\frac{n}{2}$ electrons to the positive spin system.

Step one is carried out by gradually stripping the negative spin system of electrons from the top Fermi level down, until n/2 electrons have been removed. In any energy region dE there are, by definition, dN electrons of average energy E; removing these dN electrons means a loss of energy equal to E dN.

Thus the total change of energy due to the removal of $\frac{n}{2}$ electrons is given by:

$$\Delta E_- = \int_{N_o}^{N_o - \frac{n}{2}} E \, dN_- \qquad \text{XVIII - 1}$$

Similarly, step two involves an energy change

$$\Delta E_+ = \int_{N_o}^{N_o + \frac{n}{2}} E \, dN_+ \qquad \text{XVIII-2}$$

Now the energy in the region $N_o < N_+ < N_o + \frac{n}{2}$ is greater than that for the region $N_o - \frac{n}{2} < N_- < N_o$, so that the magnitude of ΔE_+ is expected to exceed that of ΔE_-.

Since $\frac{n}{2} \ll N_o$, we can expand $E(N_-)$ and $E(N_+)$ in a Taylor series about $E(N_o)$.

Thus:

$$E(N_+) = E(N_o) + \left(\frac{dE}{dN}\right)_{N_+ = N_o} (N_+ - N_o) + \ldots\ldots\ldots\ldots \qquad \text{XVIII-3}$$

$$E(N_-) = E(N_o) + \left(\frac{dE}{dN}\right)_{N_- = N_o} (N_- - N_o) + \ldots\ldots\ldots\ldots \qquad \text{XVIII-4}$$

Then, from XVIII-3 and XVIII-2

$$\Delta E_+ = E(N_o) \int_{N_o}^{N_o + \frac{n}{2}} dN + \left(\frac{dE}{dN}\right)_{N_+ = N_o} \int_{N_o}^{N_o + \frac{n}{2}} (N_+ - N_o)\, dN_+ + \ldots\ldots$$

$$= E(N_o)\, \frac{n}{2} + \left(\frac{dE}{dN}\right)_{N_+ = N_o} \left[\frac{N_+^2}{2} - N_o N_+ \right]_{N_o}^{N_o + \frac{n}{2}} + \ldots\ldots$$

$$= E(N_o)\, \frac{n}{2} + \left(\frac{dE}{dN}\right)_{N_+ = N_o} \left[\frac{(N_o + \frac{n}{2})^2 - N_o^2}{2} - N_o \frac{n}{2} \right] + \ldots.$$

$$\Delta E_+ = E(N_o)\, \frac{n}{2} + \frac{1}{2} \left(\frac{dE}{dN}\right)_{N_+ = N_o} \left(\frac{n}{2}\right)^2 \qquad \text{XVIII-5}$$

Similarly, from XVIII-1 and XVIII-4, one obtains

$$\Delta E_- = -E(N_o)\, \frac{n}{2} + \frac{1}{2} \left(\frac{dE}{dN}\right)_{N_- = N_o} \left(\frac{n}{2}\right)^2$$

The total increase in Fermi energy,

$$\Delta E_f = \Delta E_+ + \Delta E_- = \left(\frac{n}{2}\right)^2 \frac{dE}{dN} \qquad \text{XVIII-6}$$

Thus we see that transferring $\frac{n}{2}$ electrons always results in an increase of the Fermi energy.

Thus, on the basis of Fermi energy considerations alone, one would never expect ferromagnetism. However, we have not considered exchange energies.

Slater obtained results which showed that exchange energy changed sign for ferromagnetic materials. However, Zener has since shown that this change of sign need not be assumed for a consistent theory of ferromagnetism.

Only electrons with their spins aligned have exchange energy. We will assume for simplicity that the exchange energy for any pair is equal to -I, where I is a positive quantity.

For N electrons with spins aligned, the total number of pairs which can have exchange energies is

$$\frac{N(N-1)}{2}$$

Therefore the total exchange energy before transferring spin orientations will be

$$2x(-I) \quad \frac{N(N-1)}{2}$$

$$= \left(-\frac{I}{2}\right) (2N^2 - 2N) \qquad \text{XVIII-7}$$

However, after the spin directions of $\frac{n}{2}$ electrons have been changed, the exchange energies of the two directions will be

$$1) \quad (-I) \left[\frac{(N + \frac{n}{2})(N + \frac{n}{2} - 1)}{2} \right]$$

$$2) \quad (-I) \left[\frac{(N - \frac{n}{2})(N - \frac{n}{2} - 1)}{2} \right]$$

The total exchange energy is therefore

$$\left(-\frac{I}{2}\right) \left[(N + \tfrac{n}{2})^2 - 2N + (N - \tfrac{n}{2})^2 \right]$$

$$= \left(-\frac{I}{2}\right) \left[2N^2 - 2N + \frac{n^2}{2} \right] \qquad \text{XVIII-8}$$

Comparing this and XVIII-7, we see that reversing $\frac{n}{2}$ electron spins results in a change of energy equal to

$$\left(-\frac{I}{2}\right)\frac{n^2}{2} \qquad \text{XVIII-9}$$

Therefore,

$$\Delta \text{ Exchange energy} = -\frac{In^2}{4}$$

$$\Delta \text{ Fermi energy} = \frac{n^2}{4\,\frac{dN}{dE}}$$

The total energy change will therefore be

$$\Delta E = \frac{n^2}{4}\left[\frac{1}{dN/dE} - I\right]$$

and the decrease in exchange energy will, in some cases, overcome the increase in Fermi energy.

Depending on the relative values of these terms, the energy may either increase or decrease as n is increased. This is shown in Figure 39 (a) and (b).

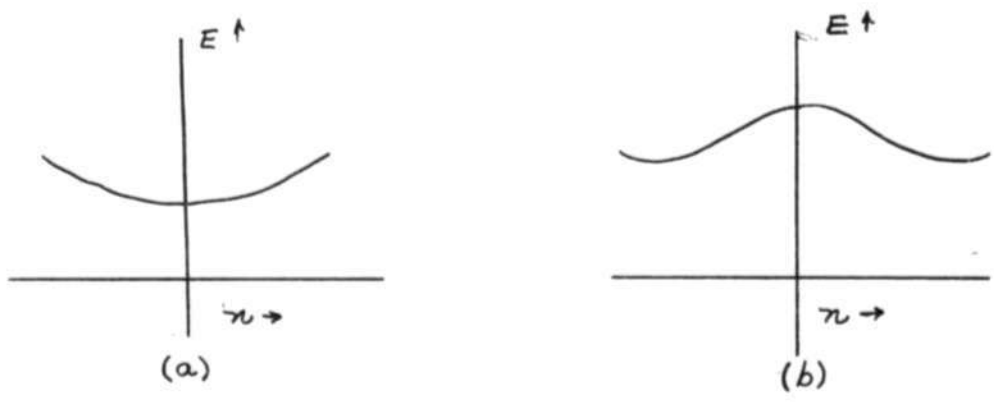

Figure 39

For a material to be magnetic, the energy must decrease as n increases from 0, as shown in Figure 39(b). Figure 39(a) indicates a non-magnetic material.

On reversing the magnetization of a ferromagnetic substance, the energy must be sufficiently great to overcome the peak energy shown on the curve of Figure 39(b). If the slope is such as to lead to a high peak value, one might expect the material to have a high coercive force. It should be easier to overcome this boundary as the temperature of the material is increased. The results obtained by C. Morrison* tend to agree with this hypothesis. He found that the coercive force of MF-1118 decreases with increasing temperature. A. Loeb has given this subject additional study.†

We are not yet equipped to deal with the exchange energy problem quantitatively. We will return to the subject after we are able to solve problems involving quantum mechanics.

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*Morrison, C., "Hysteresis Loop Characteristics of MF-1118 for Different Temperatures". Digital Computer Laboratory, Engineering Note E-491, October 1952, figure 4.

†Loeb, A. L., "A Statistical Model for Ferromagnetism", Digital Computer Laboratory, Memorandum M-1744, December 1952