Digital Computer Laboratory
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXXIII

To: Group 63 Staff

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If the quantum states of electrons in a condensed system
are represented graphically in two dimensions as in Figure 56, the
cells appear as squares, and the surfaces passing through states
of equal energy (ergodic surfaces) appear as lines. Two such lines
are shown, representing energies ϵ_j and $\epsilon_j + d\epsilon$. We are interested
in determining the number of cells which exist between ergodic
surfaces and the number of these cells which are filled. The dis-
tribution of electrons over the cells is determined by the total
energy of the system.
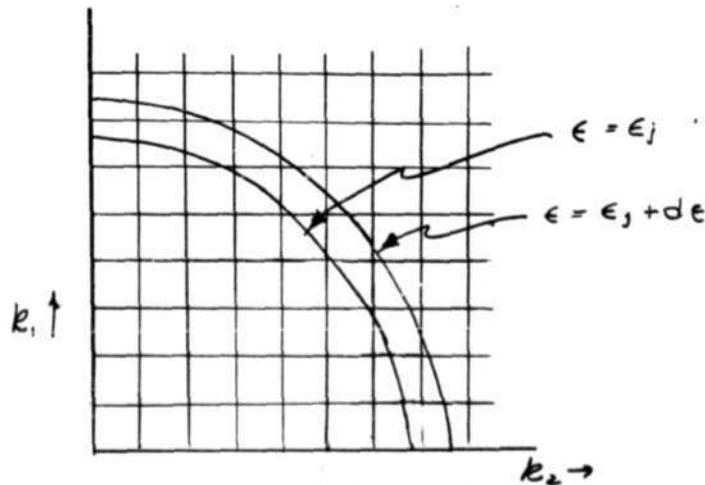
Each cell represents a quantum state

Figure 56

For Fermi-Dirac statistics it can be shown that the number of quantum states of one particle, $C(\epsilon)d\epsilon$, with energy between ϵ and $\epsilon + d\epsilon$ is given by

$$C(\epsilon)d\epsilon = 4\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} d\epsilon \qquad\qquad \text{XXXIII - 1}$$

Furthermore, for particles obeying Fermi-Dirac statistics, the number of particles per cell is

$$\frac{\text{No. particles}}{\text{state}} = \frac{1}{e^{\frac{\epsilon_j - \mu}{kt}} + 1} \qquad\qquad \text{XXXIII - 3}$$

where μ is a constant, as was defined at meeting XVII.

When $\epsilon_j > \mu$,

$$\frac{1}{e^{\frac{\epsilon_j - \mu}{kt}} + 1} < 1$$

Thus, for $\epsilon_j > \mu$ some states are filled and others are not. The electron distribution at temperature $T = 0°K$ and $T = T°k$ is shown in Figure 36, meeting XVII.

The number of states with energy equal to or less than μ can be found by integrating XXXIII - 1 over the energy range 0 to μ.

$$\int_0^\mu C(\epsilon)d\epsilon = 4\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\mu \epsilon^{\frac{1}{2}} d\epsilon$$

$$= \frac{8\pi V}{3}\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \mu^{\frac{3}{2}} \qquad\qquad \text{XXXIII - 4}$$

At absolute zero temperature, this must equal the total number of electrons per unit volume. Thus,

$$N = \frac{8\pi V}{3}\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \mu^{\frac{3}{2}}$$

$$\mu = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}} \qquad\qquad \text{XXXIII - 5}$$

$= $ maximum energy at $T = 0°K$.

The total energy at $T = 0°K$ is thus

$$E_o = \int_0^\mu \epsilon \, C(\epsilon) \, d\epsilon$$

$$= 4\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\mu \epsilon^{\frac{3}{2}} \, d\epsilon = \frac{8\pi V}{5} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \mu^{\frac{5}{2}}$$

$$= \frac{8\pi V}{5} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \left[\frac{h^5}{64\sqrt{8}\,m^{\frac{5}{2}}} \left(\frac{3N}{\pi V}\right)^{\frac{5}{3}}\right]$$

$$E_o = \frac{3h^2}{40m} N \left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}$$

XXXIII - 6

= zero point energy of free electron gas in a metal.
The average energy per electron is therefore

$$\frac{E_o}{N} = \frac{3h^2}{40m} \left(\frac{3N}{\pi V}\right)^{2/3}$$

Comparing this with equation XXXIII - 5 shows that the average energy per electron in a Fermi gas at $T = 0°K$ is 3/5 that of the Fermi energy μ.

We may think of our Fermi gas as consisting of two systems of electrons with opposite spin orientations. Throughout the material the charge distribution of the electrons would be found to be uniform. However, we found as a consequence of the Pauli exclusion principle that electrons of the same spins tend to be spaced further apart than those of opposite spins. This effect is taken into account in the statistical model in the following way:

If, instead of examining the system over a long continuous period, we limit our observations to those moments when a certain small volume element of the crystal contains an electron of a given spin, we shall find that, on the average, the region near this small volume element contains more electrons of spin anti-parallel to that of the electron in the volume element than electrons of spin parallel to that of the electron in the volume element. The anti-parallel electrons would be distributed uniformly, but parallel electrons would be excluded from the vicinity of the central electron. This exclusion of electrons of parallel spin lowers the potential energy of the system because the average distance between the two electrons is greater for parallel spins than for anti-parallel spins.

We may think of this absence of electrons as a distribution of "holes," where the hole concentration is the same as the original electron concentration. This hole distribution is spherically symmetrical about the small volume, and the volume per hole is thus

$$\frac{V}{N} = \frac{4}{3} \pi r^3.$$

Therefore,

$$r = \left(\frac{3V}{4\pi N}\right)^{\frac{1}{3}}$$

and, since potential energy $\propto \frac{1}{r}$,

potential energy due to holes $\propto \left(\frac{N}{V}\right)^{\frac{1}{3}}$.

This represents the potential energy decrease in a statistical model due to the exchange energy.

It might seem artificial to limit our observations to those times when an electron of a given spin is in the critical volume element. However, at other times the system of opposite spin would be subject to an identical analysis, so that at all times when the volume element contains an electron, the exclusion principle leads to a lowering of the potential energy.

A classical analogy might be found in the energy of a dipole (see Figure 57).

$t = t_1$ $\overset{\bullet}{+}$ $\overset{\bullet}{-}$

$t = t_2$ $\overset{\bullet}{-}$ $\overset{\bullet}{+}$

Figure 57

Variable dipole at times $t = t_1$ and $t = t_2$

Over a large period of time the average charge at both ends of the dipole is zero. This might lead one to conclude that the average energy of the dipole is zero. However, at time $t = t_1$ the energy of the dipole is negative because of the attraction between the charges. At time $t = t_2$, when both charges have reversed, the energy is still negative. In fact, if both charges are always opposite in sign, the energy is always negative. Thus, while the time average of charge anywhere on the dipole is zero, the average energy is negative.

As we saw earlier (equation XXXIII - 6), the Fermi energy is proportional to $\left(\frac{N}{V}\right)^{\frac{2}{3}}$, hence the total energy may be expressed as:

$$E = A\left(\frac{N}{V}\right)^{\frac{2}{3}} - B\left(\frac{N}{V}\right)^{\frac{1}{3}}$$

where A and B are proportionality constants. It should be noted that the total energy represented here only involves those terms which are dependent on the distribution of the number of electrons in the two possible spin states. The numerous other terms, such as the electrostatic interaction of the electronics with each other and with the field of the nuclei, are lumped into the zero point energy. It is the exchange term which gives a connection to the electrostatic interaction energy of electrons with parallel spin which favors a parallel alignment of spin. It is the Fermi energy term which favors an even distribution of spin so that the lower energy states will be completely filled and the higher energy states will be empty. In order that there be a parallel alignment of spins, the distance between energy states in a band should be small and the exchange connection should be large. This is accomplished in the d- and f-bands in solids where, since the shells are predominantly influenced by their own nuclei, the bands are narrow, or the density of the states is large.
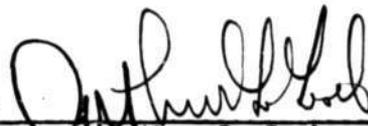
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Arthur L. Loeb
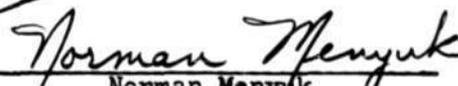
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