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

To: Group 63 Staff

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Date: February 16, 1953

It has been shown that a system in which the spins are aligned parallel requires an anti-symmetric space function of the form (for the 2 electron system)

$$\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)$$

The probability of finding one electron in state a and the other in state b is then

$$\tfrac{1}{2}\left|\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)\right|^2$$

where the factor 1/2 is the normalization constant.

Expanding,

$$\text{Prob.} = \tfrac{1}{2}\left|\psi_a(1)\psi_b(2)\right|^2 + \tfrac{1}{2}\left|\psi_b(1)\psi_a(2)\right|^2 - \tfrac{1}{2}\left|\psi_a^*(1)\psi_b^*(2)\psi_b(1)\psi_a(2) + \psi_a(1)\psi_b(2)\psi_b^*(1)\psi_a^*(2)\right|$$

The first two terms represent the ordinary distribution function form which arises without considering exchange interaction. However, we see that there is an additional interaction term which changes the distribution function. The effect of this exchange interaction is the same as that of a repulsive force, tending to separate the electrons. If the first two terms of the above equation would give rise to the distribution indicated by the dashed lines of Figure 54, the total distribution is that indicated by the solid lines. For the case of anti-parallel spins, no exchange occurs. Thus when their spins are parallel the electrons spend less time near each other when exchange interaction is considered than they would if the Pauli exclusion principle did not hold. The average potential energy due to repulsion between electrons is therefore smaller for pairs of electrons of equal spin than between electrons of opposite spins. This decrease in potential energy is the exchange energy.

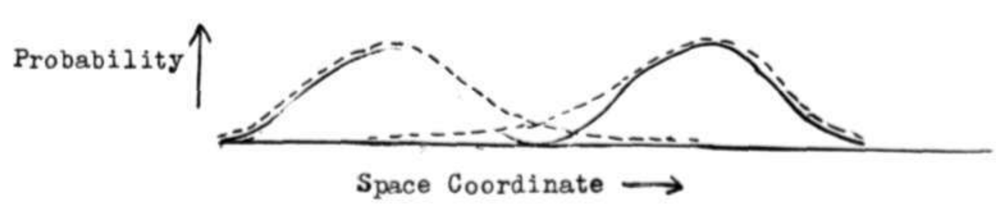

Figure 54

In the case of helium, we found that a large amount of energy was required to obtain parallel spin since the Pauli exclusion principle requires that the two electrons in the ground state ($n = 1$, $\ell = 0$) must have opposite spins. It is therefore necessary to raise one of the electrons to the $n = 2$ level so that parallel spin can be obtained. However, if sufficient energy is available to send an electron to the $n = 2$ level, and the spins are aligned parallel, the exchange effect causes a greater average separation of the electrons. This, in turn, lowers the energy below the value which would be required if the exclusion principle did not have to be taken into account.

The iron atom has all the $n = 1$ and $n = 2$ levels filled. The lowest shell in which the outer electrons can be found is therefore the $n = 3$ shell. There are 18 possible states in this shell, and all these states will interact, causing a splitting of energy levels. When dealing with a condensed system of iron atoms, the number of atoms close enough to interact is tremendous. In fact, a condensed system could be considered a molecule with $\sim 10^{23}$ atoms. Since an enormous amount of energy level splitting will occur within limited energy regions, the spectra within these regions will appear to be continuous, and are called bands. The condensed system must be treated statistically.

At meeting 18, we found that a statistical model involved two distinct energies: the Fermi energy and the exchange energy. The Fermi energy arises from the fact that the exclusion principle limits the number of electrons which can exist at the lowest energy levels, and the exchange energy arises from the tendency of electrons with parallel spins to be excluded from each other.

STATISTICAL MECHANICS

One could represent the space state of a single electron on a three-dimensional plot as shown in Figure 55. Each of the coordinates represents a spatial quantum number, and a cell as shown then represents a particular value of n, ℓ, m_ℓ.

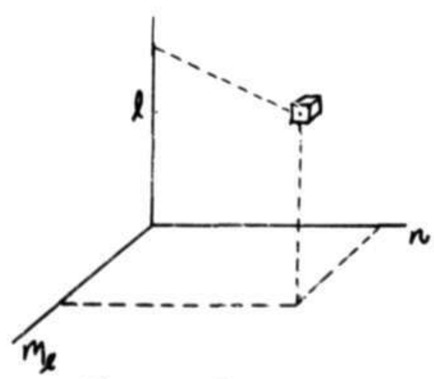

Figure 55

By expanding to a four-dimensional set of coordinates, one could then specify the total spin and space state of the atom by a four-dimensional cell. One can expand this concept for a system of N atoms by setting up a 4N-dimensional space. A single cell in this coordinate system is then a 4N-dimensional cell, <u>and this single cell describes one combination of all the quantum numbers of</u>

all N atoms of the system. Each cell therefore represents a different state of the entire system.

One may think of the 4N-dimensional space being filled with these cells each representing different states of the system. When the system is in a particular state, the corresponding cell may be thought of as filled while all the others are empty. Then, when the system changes its state another cell becomes filled. If one considers a single system over a finite time interval, a number of the cells will have been full at some time during that interval. Furthermore, it can be shown that there is an equal a priori probability of the system being in any one of the cells. This corresponds to the statement that the system spends an equal amount of time in each cell.

In statistical mechanics one can find the energy corresponding to each cell, and these equal energy cells can be joined by a surface known as an ergodic surface. One can then find the number of cells corresponding to each surface, and from this the probability of finding the system at a particular energy may be determined.

There are three types of statistics which one can apply to the statistical model. They are:

1. Maxwell-Boltzmann statistics
2. Bose-Einstein statistics
3. Fermi-Dirac statistics

It was stated at meeting 17 that Maxwell-Boltzmann statistics applied to systems in which the individual particles are distinguishible. This gives rise to many more states than we need consider for a system dealing with electrons, since the electrons are indistinguishible from one another.

If the particles are indistinguishible, there are two possible sets of statistics, depending upon whether the exclusion principle applies to the particles. If the principle does not apply, as is the case for photons, the Bose-Einstein statistics are applied. Such a system has a symmetric wave function.

For the system in which we are interested, which deals with electrons, the exclusion principle does apply. We therefore deal with a system describable by an anti-symmetric wave function with only one electron in a particular state. Fermi-Dirac statistics must therefore be used.

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Group 62 (20)

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