Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XVII

To: Group 63 Staff

From: Arthur L. Loeb and Norman Menyuk

Date: December 11, 1952

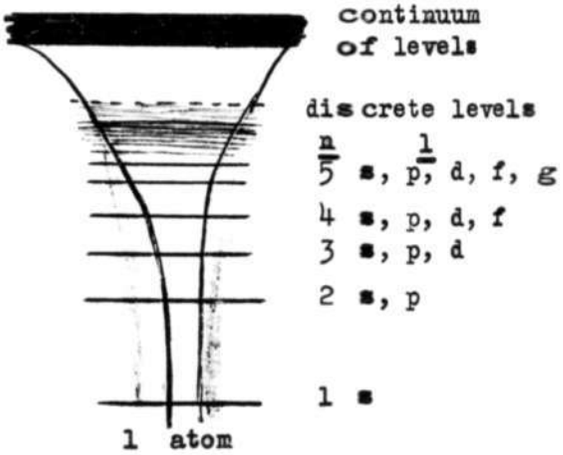


FIGURE 30

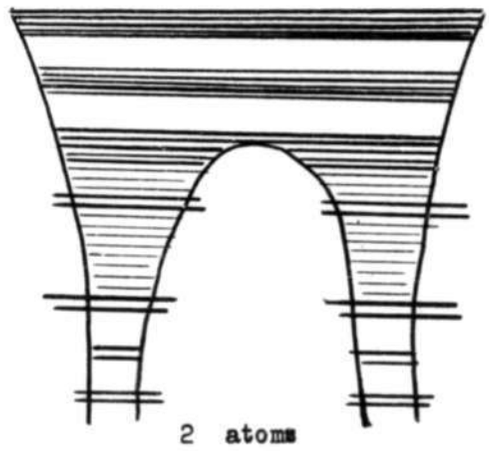


FIGURE 31

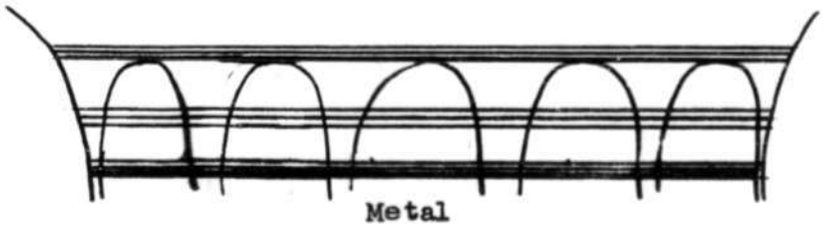
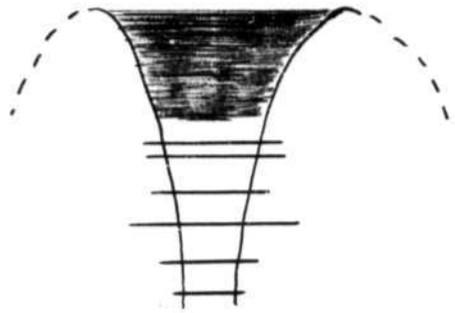


FIGURE 32

Field Free Electron Gas Approximation

FIGURE 33



WIGNER - SEITZ APPROXIMATION

FIGURE 34

BRILLOUIN - BLOCH APPROXIMATION

FIGURE 35

The explanations of the properties of metals we have discussed depended upon a knowledge of the allowed energy levels and the distribution of the electrons over these levels. These two factors will now be discussed in some detail.

The above figures represent exact potentials in which electrons move and several approximations thereto. The horizontal lines and regions for each figure represent the allowed energy levels of electrons.

The simplest picture is that of one atom (figure 30). For the hydrogen atom (one electron) an exact solution is possible, and it has been calculated. The energy is found to be quantized, as is shown in figure 30. The angular momentum and its component in the external field direction are also quantized. (See Appendix II)

An atom with more than one electron cannot be solved exactly, so the self-consistent field method may be employed to approximate the true solution. In helium each of the two electrons moves in the field of the other electron and the nucleus. It is assumed that this field is spherically symmetrical on the average, so the motion of the electron under consideration can be solved. In order that the result be consistent with the initial assumption, the electron motion thus found must give rise to a spherically symmetrical field distribution.

For lithium, which has three electrons, we consider the third (outer) electron as travelling in the resultant field of the nucleus and the two inner electrons. The resultant energy levels are similar to those

of the hydrogen atom, and lithium is therefore known as a hydrogen-like atom.

The hydrogen atom energy levels are dependent on the principal quantum number n, but they are independent of the angular momentum. Thus a single energy level of figure 30 corresponds to a particular value of n, as shown; but the angular quantum number l may have any of the values 1, 2, 3 ---- n-1. Thus a single energy level may correspond to more than one set of quantum numbers, in which case the level is said to be degenerate.

In an atom of more than one electron, the magnetic moments due to the angular momentum of the electrons cause electron interaction. In this case the energy levels are dependent upon the angular momentum quantum state l as well as the principal quantum number n.

One may note in figure 30 that the values of l are given as s, p, d, f, g, etc. This is the nomenclature in use today, where s = 0, p = 1, d = 2, f = 3, g = 4, h = 5, and so on. When referring to the state of an electron, a number representing n is placed first, followed by a letter for l. Thus a 3d electron is one for which n = 3 (in the third "orbit") and l = 2.

A system of two atoms is shown in figure 31. It is analagous to two coupled oscillators and leads to two modes of oscillation, neither of which has the frequency of the individual oscillators. The analogue of the two frequencies are the split energy levels as shown.

A metal may be thought of as a lattice in which electrons move, or as atoms coming together to form a lattice. For an exact solution both models would be completely identical. However, since exact solution is impossible, approximate methods are employed, each of which corresponds to an exact solution for some extreme case. The models employed correspond to these extreme cases, and assist in determining which approximation would be most valid for the case in question.

The approximations for the true picture (figure 32) for metals are shown in figures 33, 34, and 35.

The simplest approximation was that of an electron gas in a force free field (figure 33). This picture proved inadequate for reasons discussed previously.

A better approximation was given by Wigner and Seitz. They split the lattice into quasi-spherical shells within which the atom at the center predominates. This was discussed at the preceding meeting (see figure 25). The lower energy levels obtained using this picture (figure 34) are not very different from those of the single atom.

The validity of this approximation for the interior electrons of an atom has been verified by a study of X-ray spectra. X-rays are a measure of the difference in energy between the energy levels of the "deep seated" electrons of an atom. They, therefore, give us an insight into the very levels for which the Wigner-Seitz approximations hold. It has been found that the X-ray spectrum of an element is relatively independent of the state

of aggregation of that element. Thus we find, in agreement with the Wigner-Seitz approximation, that the lowest energy levels of the gas atom and the atom in a metal are similar.

The Wigner-Seitz approximation is therefore useful for phenomena which must be explained in terms of the properties of the inner electrons. An example, which has been mentioned previously, is the problem of the paramagnetism of the rare earth metals.

At the higher energy levels the potential slopes off, whereas the potential curve for atoms is still very steep at the upper levels. In conduction problems it is precisely this region in which we are interested, so the Wigner-Seitz approximation is not valid here.

The Brillouin-Bloch approximation of a periodic potential gives rise to definite energy bands. This is useful in dealing with the properties of the conduction electrons, but it is not sufficient for a treatment of the interaction of lower levels with conduction zones.

Both these methods neglect surface characteristics. We may consider these characteristics in terms of the field free electron gas approximation (figure 33). In order for electrons to leave the metal, it must have an energy greater than $W + \phi$. The energy levels shown in the figure obtains at $0^{\circ}K$, but as the temperature increases some of the more energetic electrons will gain sufficient energy to overcome the surface barrier. The number of electrons escaping increases with temperature, leading to Richardson's equation for thermionic emission:

$$I = AT^2 e^{-\phi/kt}$$

where I = Current per unit area
ϕ = Work function of metal
A = Constant
T = Temperature in degrees Kelvin

This picture may also be used to explain contact potential. This will not be done here, but an explanation can be found in Eckl's article.*

Appendix IV deals with the theory of contact potential measurements.

Up to now we have used Maxwell-Boltzmann statistics whenever a statistical solution to a problem was required. This set of statistics applies in a system containing n distinguishable particles, and any interchange of particles leads to a new state for the system.

However, it is impossible to distinguish between electrons, and any permutation of electrons would lead to a state indistinguishable from the first. Hence all permutations of electrons should statistically be considered the same state.

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* Eckl, D. J. - "Introduction to the Theory of Semiconductors III, Conduction in Metals; the Field Free Case." Digital Computer Laboratory, Engineering Note E-474.

Furthermore, Maxwell-Boltzmann statistics do not limit the population of any state, whereas the electrons are known to obey the Pauli exclusion principle. This principle says that only one electron in a system may be described by the same set of four quantum numbers (n, l, m_l, s). In terms of our discussion, this means that only one electron may occupy any particular quantum state at a time. Thus a state can only be occupied (one electron in this state) or unoccupied (no electrons in this state).

Because of these factors the electrons do not obey Maxwell-Boltzmann statistics. Taking these conditions into account, Fermi and Dirac derived the following distribution function:

$$\frac{dN(\mathcal{E})}{d\mathcal{E}}\,\Delta\mathcal{E} = \text{No. of electrons in energy range between } \mathcal{E} \text{ and } \mathcal{E}+\Delta\mathcal{E}$$

$$\frac{dN(\mathcal{E})}{d\mathcal{E}} = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2} \frac{\sqrt{\mathcal{E}}}{e^{\frac{\mathcal{E}-u}{kt}}+1}$$

where

V = Volume
m = Mass
h = Planck's Constant
k = Boltzmann Constant
$\mathcal{E}$ = Energy
$N(\mathcal{E}$ = Number of electrons having energy $\leq \mathcal{E}$
u = A constant

The value of u can be found by integrating $\frac{dN(\mathcal{E})}{d\mathcal{E}}$ over all values of $\mathcal{E}$ since this integration gives the total number of electrons, $N(\infty)$.

At absolute zero temperature,

$$e^{\frac{\mathcal{E}-u}{kt}} = \infty \quad \text{when } \mathcal{E} > u$$
$$= 0 \quad \text{when } \mathcal{E} < u$$

Therefore, at absolute zero temperature,

$$\frac{dN(\mathcal{E})}{d\mathcal{E}} = 0 \quad \text{when } \mathcal{E} > u$$
$$= 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\mathcal{E}} \quad \text{when } \mathcal{E} < u$$

Thus the Fermi distribution function increases parabolically with $\mathcal{E}$ up to the level $\mathcal{E} = u$, and then drops abruptly to zero. The level $\mathcal{E} = u$ is called the (top) Fermi level.

The distribution for temperature $T = 0^{\circ}K$ is shown in figure 36 by the solid line. The change in this distribution as the temperature is increased is indicated by the broken line.

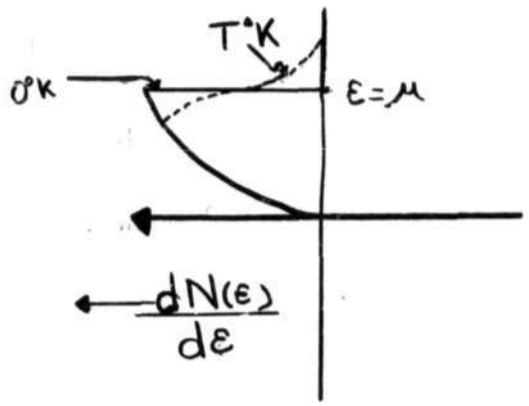

FIGURE 36

We see from figure 36 that the electron density is small at low energy values and increases according to a parabolic relationship as the energy is increased. It should be noted that raising the temperature affects only the most energetic electrons. Those at the lower levels are completely unaffected. This is not surprising since the amount of energy required to raise the energy level of an inner electron is of the order of X-ray energies. This is considerably higher than the energy produced by purely thermal effects.

The upper electrons require much less energy before being able to jump to an unoccupied energy level. Therefore these upper electrons are the only ones which can be raised to an excited level. So few electrons are effected by a temperature rise that electrons contribute little to the specific heat of a material.

Signed Norman Menyuk

Signed Arthur L. Loeb

Approved DRB

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