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The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals

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ABSTRACT. It is shown that the collective electron and London-Heitler models are not to be regarded as different approximations to the same exact wave function for solids in which, according to the former model, there is a partially filled zone of energy levels. It can thus be shown why nickel oxide in the pure state is a non-conductor, although it contains an incomplete zone. The properties of the metals nickel, palladium and platinum are discussed in the light of these results; platinum differs from nickel in that the orbital contribution to the moment of the elementary magnets is not quenched. A discussion is given of x-ray absorption edges, and it is shown why exciton lines are absent for metals.

§ 1. THE COLLECTIVE ELECTRON AND LONDON-HEITLER METHODS

IN discussing the cohesive forces in metals, or their electrical or magnetic properties, it is first necessary to set up an approximate electronic wave function. In doing this, all investigators have used one or other of two approximations; these are:

(a) The London-Heitler or Heisenberg approximation, in which one starts from atomic wave functions, such as that in which $\psi_a(\mathbf{r}_n)$ describes the space coordinate of the n th electron in the atom a . One then forms products of the type

$$\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\dots,$$

multiplied by appropriate spin functions, and from these an anti-symmetrical determinant or sum of anti-symmetrical determinants can be set up. This method, though convenient for insulators such as NaCl, where each atom or ion is in a singlet state, has not been applied with much success to metals, owing to the mathematical difficulties introduced by the spin degeneracy. The only exact result deduced by this method is that of Bloch (1930), who treated the case where the exchange integral between neighbours is positive, so that in the lowest state all spins are parallel (ferromagnetism); he showed that if I , I_0 are the values of the intrinsic magnetic intensity at temperatures T and zero,

$$I - I_0 = \text{const. } T^{3/2}. \quad \dots\dots(1)$$

The same argument shows that the electronic specific heat with this model varies as $T^{3/2}$. The case where the exchange integral is negative is much more difficult and has not been used to obtain successfully the electronic specific heat. For a discussion of the paramagnetism in this case, cf. Hulthén (1936).

(b) The collective electron treatment, also first used in a quantitative way by Bloch (1928). This is the same as the molecular orbital method of quantum chemistry. Wilson (1931) first showed how convenient the model was for explaining the sharp division of pure solids at low temperatures into metals and non-conductors; the former are those with a partially filled "zone" of electronic states, the latter those in which all zones are either quite full or quite empty.

Stoner * has recently applied the model to ferromagnetics, and obtained a form for $I_0 - I$ which, though surprisingly similar to the $T^{3/2}$ law mentioned above, is derived in quite a different way. The experimental results are certainly not good enough to decide between them.

The main purpose of this paper is to suggest that these two models are *not*, as is usually believed, different approximations to the same exact wave function. We believe, on the other hand, that crystalline solids, which in model (b) have incomplete zones, fall quite sharply into two classes: those for which model (b) is a good approximation (metals), and those for which model (a) is a good approximation.

Let us consider first the physical properties of a substance which we believe to belong to the class (a), namely NiO. This has the simple cubic structure, and may be thought of as being made up of nickel ions Ni^{++} and oxygen ions O^{--} . It is paramagnetic (Batnagar and Bal 1934), the nickel ions being the paramagnetic elements. The nickel ion has the electronic configuration $(3d)^8$; the 3d state should give rise to a zone containing 10 electrons which may be split by a cubic field into sub-zones containing 4 and 6; thus, using model (b), at least one of these sub-zones is partly empty. Thus, according to model (b), NiO should show metallic conductivity, increasing as the temperature is lowered. But this is not in accordance with the facts. Pure nickel oxide is an insulator, and is transparent to visible light, being pale greenish yellow. And this is what we should expect, starting from model (a). In order that NiO should conduct, there must be present some Ni^{+++} ions and some Ni^+ ions, which can move about by electron transfer. But a definite amount of energy, E_{say} , is required to remove an electron from one ion (leaving Ni^{+++}) and to put it on a *distant* ion, forming Ni^+ . Therefore, unless the crystal of NiO as a whole is in an excited electronic state (e.g. at a high temperature), no such pairs are present. Nickel oxide can actually be made to behave as a semiconductor by introducing Ni^{+++} ions into the lattice, e.g. by replacing some of the nickel ions by Li^+ ions, an electron being removed from another ion to secure electrical neutrality (Verwey, Haayman and Romeyn 1948); clearly, then, electrons are not impeded by the rather large interionic distance (c. 7 Å.) from jumping from ion to ion.

It has, of course, been noticed by many authors (e.g. Schubin and Wonsowski 1934) that the London-Heitler approximation does not allow for any electric current, and it has been suggested that, in the exact wave function, there will be present *ionised* states—i.e. some atoms having one extra electron and an equal number having one missing; these we may call positive holes. We suggest that this is not quite correct, and that, starting from the London-Heitler approximation, there will either be no pairs (electrons and holes) which have separated *many* atomic distances, or else, as one goes to higher approximations, the number of completely separated pairs will increase indefinitely, so that the whole approximation breaks down and one has to start with the collective electron treatment.

The evidence for this view is as follows:

(i) The facts about NiO quoted above and similar facts about oxides of other transition metals.

(ii) The difficulty in believing that a state with a *small* number of pairs can ever have lower energy than a state with no pairs. One will always have to do work to separate the electron and hole constituting the first pair to be formed,

* In a series of papers; for references cf. Stoner (1948).

because the electron and positive hole attract each other with a force derived from a potential energy $-e^2/\kappa r$, where κ is a dielectric constant. It is known from Schrödinger's equation that two particles which attract each other with a force of this type are capable of existing in a number of stationary states in which they are bound to each other. On the other hand, if some pairs already exist, it no longer follows that work must necessarily be done to form some more. This is because the material is now in a state where a current can be carried; therefore (Mott and Jones 1936, p. 87), the field between the electron and hole is now screened, and is of the form to be derived from a potential $-(e^2/\kappa r) \exp(-qr)$. The constant q increases with the number of electrons and holes present. In a field of this sort, if q is large enough, there are no bound stationary states. It no longer follows, then, that work must be done when the number of pairs is increased; it is possible that energy may be gained, owing to the negative energy of particles with collective electron orbitals.

We suggest tentatively, then, that the energy E of a crystalline array of N atoms—e.g. an array of Na atoms or Ni^{++} ions, may be as shown in Figure 1. E is here the energy corresponding to a wave function containing n pairs of electrons and holes and is plotted against n . E may be supposed to be the minimum (and hence most accurate) energy value obtainable from a wave function of London-Heitler type with ionized states. E , as we have shown, will always rise first as n increases. We suggest that it will then decrease. It may or may not drop below

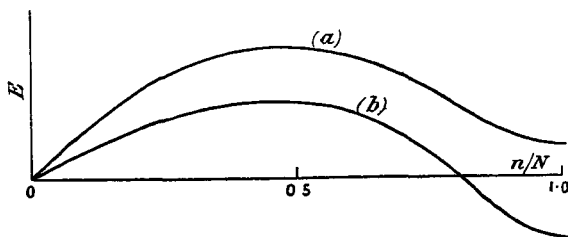


Figure 1. Hypothetical plot of energy E against number n of pairs, (a) for large separations between atoms as in NiO, (b) for small separations as in metals.

the value for $n=0$. Presumably it will not if the interatomic distance is large (case of NiO), but will otherwise (case of metals). If it does, the number of holes becomes large (comparable with N), the approximation breaks down, and we go over to the collective electron treatment.

Some further evidence that the view is correct may perhaps be provided by a recent theoretical paper on the wave functions of the hydrogen molecule (Coulson and Fischer 1949). These authors write the wave function in the unsymmetrical form

$$\{\psi_a(1) + \lambda\psi_b(2)\}\{\psi_b(1) + \lambda\psi_a(2)\},$$

where ψ_a, ψ_b are atomic wave functions for electrons in the atoms a, b , and λ is a parameter. By minimizing the energy calculated with this wave function, λ is determined as a function of the distance R between the nuclei of the two atoms. In H_2 this is actually 1.4 Å.; the calculations show that $\lambda=1$ gives the best approximation up to $R=2.3$ Å., but thereafter λ tends rapidly to zero. In our view the abrupt transition only occurs for infinite chains or lattices.

On the view explained above, therefore, if a substance such as NiO were subjected to very high pressure it should suddenly show metallic conduction for some value of the pressure, and the effective number of free electrons would suddenly jump to about one per atom. This view seems to be in accord with the observed fact that no metals show a very small effective number of free electrons except bismuth and similar elements (Mott and Jones 1936, p. 210). We believe that at the absolute zero of temperature a very small number of free electrons free to take part in a current is impossible, because the electrons and holes would attract each other and form bound pairs, i.e. electrons trapped in the field of holes. A metal substance is only a conductor at $T=0$ if there are enough electrons and holes to screen the field round any one of them sufficiently to prevent pair formation. Bismuth, of course, proves the rule because, although the number of free electrons is very small, their effective mass is also very small (Mott and Jones 1936, Chap. VI), and hence much less screening (smaller q) is necessary to prevent pair formation.

Experiments on the conductivity of cupric salts would be of great interest. One cannot say *a priori* whether or not they should show metallic conduction. According to Hilsch and Brunner (1947), CuS is a superconductor.

§ 2. THE TRANSITION METALS Ni, Pd AND Pt

Turning now to a metal such as nickel, we see that it can be represented as follows. Suppose that a London-Heitler type of wave function were set up representing nickel atoms in the singlet state $(3d)^{10}$; if a few electrons are removed and put into the 4s conduction band, leaving mobile holes in the 3d band, the energy will at first rise. But it seems very plausible that it will fall again, as in Figure 1, as the number is increased, owing to the bonding effect of the 4s conduction electrons—described of course by wave functions of the collective electron type. All the experimental evidence from the magnetic properties of these metals and their alloys goes to show that a minimum in the energy is reached when 0.6 holes per atom have been formed, giving 0.6 conduction electrons.

We thus consider that nickel contains 0.6 conduction electrons described by periodic wave functions and 0.6 holes; these must also be described by periodic wave functions extending through the lattice, quite independently of how big the interatomic distance may be. This is because the number of holes is non-integral; one could not set up a London-Heitler wave function with no ionized states for this case, and it seems certain that these holes can move through the lattice and contribute to a current. The model is essentially the same as the overlapping band model first introduced by Mott (1935), though we would now stress the applicability of the collective electron treatment for the holes rather than for the electrons of the d band.

The large electronic specific heats shown by Ni, Pd and Pt at liquid helium temperatures is known to be due to the holes, which can be treated in the usual way as a degenerate gas of particles with large effective mass. It is at first sight surprising that these metals do not all show an electronic specific heat at high temperatures given by

$$(C_v)_{el} = 0.6 \times \frac{3}{2} R = 1.8 \text{ cal/gm. atom.}$$

For nickel the position is complicated by the transition at the Curie point, though some 30° above it the effect dies out and the specific heat seems in good agreement with theory (Wohlfarth 1949); but Pd and Pt certainly do not show so large a term. For Pd a careful analysis has been given by Clusius and Schachinger

(1947), showing at $1,000^\circ\text{K}$. an electronic term of about 0.9 cal/gm. atom . The probable reason is the form of the d band, shown by Jones and Mott (1937) for small overlap between the wave functions to be as seen in Figure 2 (see also Slater 1936); the calculations of Jones and Mott were for a simple cubic lattice). If, as is quite possible, the d zone in Pd is full up to near the top of the first maximum,

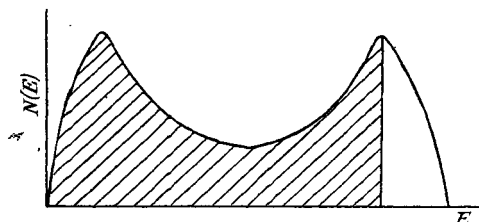


Figure 2. Plot of $N(E)$ as a function of E for a d band.

it is clear that the specific heat of the holes will not tend to the classical value but to a lower one. Calculations of the electronic specific heat with various band forms could easily be carried out and would be of interest. The reason for the difference between Ni and Pd is not known.

It has been suggested (Mott and Jones 1936, p. 222, Pauling 1949) that the magnetic carriers in nickel are not single holes, as stated here, but double holes, that is to say, ions in the triplet state of configuration $(3d)^8$. This suggestion was made in order to account for the paramagnetic behaviour of nickel above the Curie point, the slope of the line $(1/\chi \text{ versus } T)$ agreeing with the hypothesis that the elementary magnets have $j=1$ instead of $j=\frac{1}{2}$, g of course remaining equal to 2. But it is clear now that this hypothesis is inadmissible, because coupled spins would obey Einstein-Bose rather than Fermi-Dirac statistics, and thus would give an electronic specific heat proportional to $T^{3/2}$ instead of the observed T . Wohlfarth (1949) has shown that the observed paramagnetic behaviour can be explained in terms of the collective electron treatment without making any assumptions about coupled spins; one would have to go to higher temperatures than are actually possible to obtain a true paramagnetic magneton number.

In nickel, of course, the g -value for the holes is 2, there being no orbital contribution. Probably this is not the case for platinum, the orbital motion and spin remaining coupled to give $j=5/2$ and $g=6/5$; spectroscopic data for the free atom shows that the interval between the terms of the spin doublet of the ion in the state $5d^9$ is of the order 1 ev. for Pt, while the corresponding interval for Ni is 0.25 ev . There is no difficulty whatever in describing mathematically, through periodic wave functions of the collective electron type, the motion through the lattice of the configuration $5d^9$ with coupled spin and orbit.

The strongest evidence that in metallic platinum the spin-orbit coupling is not broken down comes from the measurements of Cauchois and Manescu (1940) and Coster and de Lang (1949) on the L absorption edges of the x-ray spectra. For the L_1 edge one neither expects, nor finds, any sharp line at the edge due to transitions into the empty d states, because the initial L state is s. For L_2 and L_3 , on the other hand, the initial state is p. For the free atom the empty state in the 5d shell has the j value $5/2$; one would therefore expect a transition from L_3 ($j=3/2$) but not from L_2 ($j=1/2$). This is in fact what one finds in the

metal, showing that the spin-orbit coupling is not broken down. If it were broken down, the empty d states in the metal would be a mixture of the atomic states with $j=3/2$ and $j=5/2$, and both edges would give lines of comparable strength at the edge. If it is possible to observe the lines for nickel, they should appear both for the L_2 and L_3 absorption edges.

A further application of these ideas to x-ray absorption spectra may be made. One expects that the x-ray absorption edge of an insulator will consist of a series of lines, more or less broadened by lattice vibrations, leading up to a series limit. This is because the ejection of an electron from an inner shell leaves behind a positive charge; there is thus in the insulator a field of potential $-e^2/\kappa r$, and for the excited electron a series of stationary states must exist in this field below the conduction band. If κ is large, these states will be close together and difficult to observe; they seem however to have been observed in manganate ions (Sunner 1941) for the K absorption edge of manganese.

In metals no such "exciton" lines have been observed. The reason seems to us to be the following: the field round the positive charge left when the electron is ejected is screened, and of the form $-(e^2/r) \exp(-qr)$. Now if q were not big enough to prevent the formation of bound states in this field, then, according to the argument given above, the atoms from which an electron is missing and those with an extra electron would join together to form pairs, and the material could no longer be a conductor.

Turning now to Bloch's law (1) for $I_0 - I$ in ferromagnetics, we see that the original derivation is valid only for non-conducting materials (e.g. ferrites). Döring (1949) has, however, shown that for low temperatures it can be derived more generally, from the assumption that the energy E of a small volume containing a large number of elementary magnets depends on the three components of magnetization I_x, I_y, I_z through a formula of the type

$$E = A[(\text{grad } I_x)^2 + (\text{grad } I_y)^2 + (\text{grad } I_z)^2],$$

giving its local dependence on the direction of magnetization. The derivation does not, therefore, depend on the use of one model or the other. Thus the $T^{3/2}$ must be regarded as correct at low temperatures, regardless of any special model; it is analogous to the Debye T^3 law for the specific heat. Stoner's treatment is analogous rather to the Einstein treatment, and should be a good approximation only for higher temperatures, where the "spin waves" have short wavelength.

For non-conducting paramagnetics we have no theoretical or experimental information about the electronic specific heat as T tends to zero. A theoretical treatment, owing to the difficulty of handling the spin degeneracy, has not been given (cf. Bethe 1931).

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The Experimental Basis of Electromagnetism— Part III: The Magnetic Field

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ABSTRACT. The principles outlined in previous parts, published in the *Proceedings of the Physical Society* in 1946 and 1948 respectively, which dealt with the direct current circuit and with electrostatics, are here applied to magnetism, with the object of showing how the basic concepts are defined in terms of the operations actually performed in measuring them. This part is confined to a discussion of the vector **B**, which is shown to be measurable independently of a knowledge of any other magnitude. It is solenoidal, and can therefore be determined at all points, even those within solid bodies.

§ 1. INTRODUCTION

THE general purpose of this work, as stated in the abstract of Part I (Campbell and Hartshorn 1946) *, was "to show to what extent the working principles of electromagnetism can be soundly based on real experimental facts, as distinct from the imaginary experiments which are common to most expositions of the subject". The general principles by which magnitudes are established in terms of experimental operations were described in § 2 of that paper, and at the outset we were optimistic enough to believe that by systematically applying these principles to operations that would be generally admitted as established practice, we should be able to derive the working laws of the experimentalist and a coherent outline of the whole subject in a form free from "mathematical fictions", that is to say, concepts like point charges that are so remote from real experiment that they must be classed as auxiliary devices invented by the human mind rather than anything encountered in nature.

We had some success in treating in this way the direct current circuit (Part I, 1946) and electrostatics (Part II, 1948), though it must be confessed that in Part II the jump from experiment to general law was not always so obvious as to leave no doubt in the mind of the reader about the wisdom of dispensing with the auxiliary devices. We have in the present part applied the same treatment to magnetism, and we have to admit that our early optimism has not been altogether justified. The laws that we have been able to base directly on real experiments can scarcely be regarded as forming a coherent structure, and it therefore seems

* For references seen end of Part IV, p. 000.