III. SOLID STATE PHYSICS

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A. A SIMPLIFIED HARTREE METHOD FOR ENERGY BANDS

Since the early days of the quantum-mechanical treatment of molecules and solids, two types of approximate calculation of solutions of the Schrödinger equation have been used with varying success. The first of these is the Heitler-London method. It assumes that in a molecule or solid we can use the wave function which an electron would have in an isolated atom as a first approximation, proceeding from there by perturbation theory. It is at the basis of a good deal of the theory of molecular valence, of Heisenberg's theory of ferromagnetism, and of the theory of paramagnetism. The other theory is that of molecular orbitals, when applied to molecules, or of energy bands, when applied to metals. It starts by using wave functions which are solutions of a many-center problem (for molecules) or of a periodic potential problem (for metals and crystals). Both methods have their advantages and disadvantages.

Heitler-London Method

Advantages: It is easy to understand and describe; leads to exchange integrals concerned in interatomic forces and magnetic problems. Wave functions are easily set up; excessive charge fluctuations, the piling up of too much charge on an atom, are eliminated.

Disadvantages: Wave functions are not orthogonal; there is great complication when quantitative calculations are attempted. Exchange integrals for ferromagnetism are of wrong sign. No real explanation of ferromagnetism is possible. The method fails to account for energy bands in metals, energy gap theory.of semiconductors, properties of insulators.

Molecular Orbital Method

Advantages: Wave functions are orthogonal. Energy ban theory of metals and insulators follows directly. Application to ferromagnetism leads to correct results; predicts which elements should be ferromagnetic. Provides a wide application to study of chemical valence and band spectra.

Disadvantages: Leads to excessive charge fluctuations, and as usually used, leads to wrong limiting behavior at large internuclear distances.

Examination of these advantages and disadvantages will probably convince the reader that the molecular orbital, or energy band, method is the best approximation to use. The great advance in semiconductor theory since the war justifies this view, leading to very precise ways of measuring gap widths between energy bands. The writer therefore feels that the most important step toward further development of the electronic theory of solids depends on putting the energy band or molecular orbital method on the soundest basis possible, and then using it in a straightforward way for making all sorts of calculations. Many problems being worked on experimentally in the various laboratories at M.I.T. have theories which could be improved by better study of this method. We may enumerate the following:

1. Soft x-ray emission spectra of solids (solid-state group, Research Laboratory of Electronics), which depends very directly on calculation of energy bands.

2. Semiconductor work (physical electronics group, Research Laboratory of Electronics, and Insulation Laboratory), in which the width of the energy gap can be measured fairly accurately, but calculations so far fail completely to reproduce the experimental values. The Insulation Laboratory is interested not only in gap width, but also in its change with pressure, which should give particularly valuable information to check the theory.

3. Paramagnetism of iron group and rare earth salts (solid-state group, Research Laboratory of Electronics, low temperature group, Research Laboratory of Electronics, for application to adiabatic demagnetization, and Insulation Laboratory). These problems have generally been treated by the Heitler-London method; it is very desirable to fit them into the framework of the energy band theory, and also to tie in the ground state of the paramagnetic ions, which alone is concerned in paramagnetism, with the excited levels and spectroscopic behavior of the salts.

4. Ferromagnetism of metals and oxides (solid-state group, Research Laboratory of Electronics, and Insulation Laboratory). The ferromagnetic oxides, such as Fe_3O_4 and the ferrites, being studied by the Insulation Laboratory, are of particularly great interest here, for they combine ferromagnetic and antiferromagnetic behavior, and further have λ-point transitions below which the electrons are ordered (some of the ions are Fe^{++} and some Fe^{+++}) in a regular arrangement, while above the transition they are disordered. Below the transition the properties could be described alternatively by the Heitler-London or the energy band method, while above it the energy band method is practically necessary. Solution of this problem will almost certainly lead to increased insight into the relations of the two methods.

5. Superconductivity (solid-state group, Research Laboratory of Electronics). There is a close relation between the ordering of electrons below the λ-point in the ferromagnetic oxides, and in Tisza's theory of superconductivity. The same techniques of explaining the relations between energy band and Heitler-London methods which must be worked out for the ferromagnetic oxides would presumably be useful in that theory of

superconductivity as well, if it proves to be correct.

6. Order-disorder in alloys (x-ray group, physics department; metallurgy department). The energy band theory meets this problem in several aspects. First, the energy levels are distorted in an alloy, and a study of this distortion, which has not been made, should throw much light on the problems of solid solutions. In addition, new work at Oak Ridge with neutron diffraction shows that antiferromagnetic substances have an order-disorder situation for magnetic ions which bears close analogy to order-disorder in alloys, and which ties in closely with energy band theory.

7. Chemical valence (chemistry department). Physicists were active in the development of the quantum theory of valence, but have avoided it in recent years. It has developed far in a qualitative way, but the quantitative work has been mostly very crude, from the point of view of a physicist. A reliable quantitative theory of molecular orbitals is practically essential to a further development of valence theory.

With all of these problems in mind, the writer is starting a program of reexamining the molecular orbital method. The first step in this program is to find the best potential function to use for our one-electron problem. The molecular orbital method is an extension of Hartree's self-consistent field method. In that method we replace the actual force acting on an electron, which comes from the nucleus and all other electrons, and hence depends on the position of all other electrons, by an averaged potential of some sort, depending only on position. This is entirely analogous to the method of handling space charge in an electronic problem. The averaged potential is the electrostatic potential of the nuclei, and of the average charge density of all electrons except the one in question. If there are n electrons in the problem, we can consider the charge density of the electrons to be the density of all n electrons, minus a correction charge density for one electron, arising because the electron in question does not act on itself. Once we have set up this potential, we find solutions of Schrödinger's equation in it, get from these solutions the charge density of each electron, add these to get the total charge density, and demand that that agree with the charge density initially assumed. This is the requirement of self-consistency, which is characteristic of Hartree's method.

All this is clear and straightforward, and the only question comes in the formulation of the correction charge density. Two methods have been proposed for this, neither one wholly satisfactory. Hartree proposed that the correction charge density depend on which electron of the problem we were considering, and that it be just the charge density of that electron itself; that is, that the electron be acted on by all other electrons, each distributed according to its one-electron wave function. For an isolated atom, the method works fairly well. It seems at first sight intuitively obvious, until we remember that on account of the antisymmetry of the wave function we cannot distinguish between different electrons, so that it is hardly possible uniquely to say that an electron has a given one-electron function. We can see the difficulty more clearly if we consider the energy band problem. In an atom, the Hartree method removes the correction charge from the atom itself, so that the electron is acted on by the nucleus and (n - 1) other electrons. But in a crystal, the wave function of an electron is a wave corresponding to equal amplitudes on each of the N atoms of the crystal, so that the correction charge would be equally divided between N atoms, giving only 1/Nth of an electronic charge on each, which could be neglected for large N. Hence for a crystal the Hartree method is quite wrong. Another disadvantage of the Hartree method is that each electron moves in a different field, so that the wave functions of different electrons are not orthogonal.

The Hartree-Fock method avoids some of these difficulties. It starts by assuming an antisymmetric wave function, and hence automatically takes account of the identity of electrons. Like the Hartree method, its potential is different for each electron, and the correction charge density is determined in a complicated way involving exchange integrals between electrons. There are two great advantages over the Hartree method, particularly for molecular orbital and energy band work. First, the exchange terms are such that the correction charge is removed from the general neighborhood of the point where the electron is located. Thus in a crystal of N atoms, if the electron happens to be on one of the atoms, the correction charge is largely located on that atom; it moves around as the electron moves. Therefore the method has the qualitatively correct behavior. Second, the wave functions of the various electrons are orthogonal. Counterbalancing these advantages is the very serious practical disadvantage that the method is so hard to apply that it is almost impossible in practice to work it out for a molecule or solid; even for a single atom, it has been applied only to the lighter atoms (Cu^+ is the heaviest one), and it gets almost impossibly hard for a heavy atom.

There is one case in which the Hartree-Fock method becomes very simple: the perfect gas of free electrons. If we have a volume filled with free electrons, with a uniform positive charge density just sufficient to balance the average negative charge of the electrons, the Hartree-Fock equations become simply the equations of a free particle, which can be immediately solved. The electrons obey the Fermi exclusion principle, and form a model for the Sommerfeld free-electron picture of a metal. The correction charge then proves to be a density, depending on the distance from the electron in question, and on its momentum, equal to the total density of electrons of the same spin as the electron in question at the location of the electron, and rapidly falling off with distance. If the charge density of electrons is ρ, we can say in a very crude way that the correction charge density is approximately ρ within a sphere of radius r, where $\frac{4}{3}\pi r^3 \rho$ equals the electronic charge, and is zero outside that sphere. We can readily find the correction to the potential on account of the correction charge: dimensionally it depends on the charge e, divided by the radius r of the sphere, or is proportional to $\rho^{1/3}$. This correction depends somewhat on whether the electron is at the bottom or top of the Fermi distribution. If it is at the bottom the correction is numerically greater, decreasing as we go to the top, and for an excited electron, well above the Fermi level, the correction goes to zero, since such an excited electron has a momentum quite different from any of the Fermi electrons, and the exclusion principle does not push the electrons out of its way very effectively, so that the correction charge is much more diffuse, and its potential correction is numerically smaller.

One can then set up a correction to the potential, using this free-electron calculation, which is proportional to $\rho^{1/3}$. This correction should depend on the energy or momentum of the electron; but we can average over the energy, and get a unique correction, proportional to $\rho^{1/3}$. The writer is now exploring the possibility of using this correction in the case where we have a potential varying with position, as in the Hartree method. It is well known that the Fermi-Thomas method of treating atomic structure handles the electrons at each point of a potential field as if they were free electrons. At a point where the potential is V, so that the potential energy of an electron is -eV, we assume that there are energy levels as for a free electron gas of Fermi energy E_F, in a region of uniform potential energy -eV, so that the energy levels are filled all the way from the value -eV up to E_F. This leads, according to Fermi statistics, to a definite charge density at each point of space, and we then apply Poisson's equation to derive a potential from this charge density, and make the self-consistent demand that this agree with the potential originally assumed. The Fermi-Thomas method neglects completely the wave nature of the electronic motion, and the electron shells; thus it does not lead to the periodic system of the elements. Nevertheless it leads to fairly accurate values for the potential at points inside an atom or molecule or crystal.

The Fermi-Thomas method as ordinarily used assumes that an electron acts on itself; it neglects the correction charge which we have been so far assuming. It has been modified, however, by using the correction to the potential proportional to $\rho^{1/3}$, which we have described in the preceding paragraphs. This improves the Fermi-Thomas method considerably, but it retains its fault of not considering properly the various electron shells. The present suggestion is then a simple one: to use the correction to the potential given by $\rho^{1/3}$, as described in the free-electron picture, along with the Hartree method. Here, in an atom with n electrons, we would be treating the potential of the n electrons properly; the free-electron correction would come in only in the correction charge, which is 1/nth of the total electronic charge. The wave functions of the electrons would be found in this corrected potential by Schrödinger's equation, so that we should take proper account of the shell structure. The result, then, would be close to that of the Hartree-Fock method, though not quite so accurate, and would be very much better than the Fermi-Thomas method, with or without exchange. There would be a unique potential function, and hence the wave functions would be orthogonal. Finally, the method would be very simple to apply, even simpler than the elementary Hartree method, since one potential would be used for all electrons, and the correction proportional to

$\rho^{1/3}$ is extremely easy to set up. The potential qualitatively is correct in the energy band problem of the crystal, as the Hartree-Fock method is; it avoids the shortcomings of the Hartree method.

A check of the method is at present being made by the writer and Mr. George W. Pratt, Jr., on the atomic problem of Cu^+, which has been handled by the Hartree and Hartree-Fock methods. Preliminary indications are that the results will lie intermediate between those of the Hartree and Hartree-Fock methods, or near the Hartree-Fock case, the deviations being somewhat different for the wave functions of the various electrons. The method gives promise of being so much simpler than the Hartree-Fock method that it should be practicable to handle even the heavy atoms by it. And it should provide a direct and straightforward approach to finding the self-consistent field for determining molecular orbitals and energy bands for molecules and solids.

J. C. Slater

B. HARTREE CALCULATIONS FOR ATOMS

The differential analyzer is being used for calculation of the wave functions of the Cr^+ ion, using the Hartree method without exchange. This ion was chosen as a simple one, near others which had already been computed, and of considerable interest on account of its position midway through the iron group; it was done largely for practice, to see how great the problem of calculation of atomic wave functions is if the differential analyzer is available. Calculations are almost completed. The differential analyzer is also being used for a check of the simplified treatment of exchange mentioned elsewhere in this report. This simplified Hartree method is being applied to the Cu^+ ion, the heaviest which has been solved by both the Hartree and Hartree-Fock methods, to compare the results of the three methods. This work is still in its early stages.

J. C. Slater, G. W. Pratt, Jr.

C. QUANTUM THEORY OF ANTIFERROMAGNETISM

The quantum-mechanical description of the lowest state of an antiferromagnetic substance reflects the non-classical nature of a spin system, which prevents attainment of simply ordered structures. The situation is analagous to the chemical problem and there exists the phenomenon of "resonance" among different bond structures such as occurs in certain molecules. Thus the concept of "bond order" which has been applied to the molecular case is also a useful concept to apply to antiferromagnetism since it is a measure of the correlation in direction of the spin magnetic moments of neighboring electrons.

The eigenfunction describing the spin state of the antiferromagnetic system may be expanded in terms of a set of independent spin functions. Two such sets have been used frequently. One of these we call the "spin product-functions." These functions are eigenfunctions of S_z but not of S^2. For this reason, the secular equation to which they lead is of higher order than that which results from use of the "valence bond functions" which are eigenfunctions of both S^2 and S_z.

A formal solution to the problem of a linear chain of spins has been given by Bethe. The energy in the limiting case of very large numbers of spins is given simply; but one cannot tell very much about the eigenfunction corresponding to this solution.

Another approach to the problem of the infinite linear chain is the approximation developed by Slater and by Hulthen, in which the eigenstate is expanded in terms of spin product-functions, with some simplified assumptions for the coefficients.

A different approximation, based on the valence bond functions, has been used in molecular problems. The assumption is made that all canonical structures having the same degree of excitation, i.e. same number of "double bonds," enter in the correct eigenfunction with the same coefficient. We have modified the Slater-Hulthen method to utilize this approximation. One would expect to obtain an improved result since the expansion is carried out in terms of functions having the same multiplicity as the correct eigenfunction; and we do in fact obtain a value for the energy which is closer to Bethe's "exact" value than are the values obtained by Slater and Hulthen. The canonical structures which are found to contribute appreciably to the eigenfunction are all within an extremely narrow range of the degree of excitation.

This work is described in more detail in a doctoral thesis in physics submitted by R. J. Harrison, "The Quantum Theory of Antiferromagnetism."

L. Tisza, R. J. Harrison

D. SOFT X-RAY VACUUM SPECTROGRAPH

An evaporating system has been designed and constructed. It consists of a small tantalum cup about 3/16 inch in diameter and 5/16 inch long, easily removable for refilling or replacement, placed inside a helical tungsten filament and heated by radiation, and electron bombardment with a power of 50 to 75 watts maximum. This makes it possible to attain temperatures up to about 2000°C. The unit has been tested with aluminium, in an auxiliary glass vacuum system in which the progress of the operation can be observed. A uniform coating covering an area greater than that needed for the x-ray target was easily attained, and the evaporation unit is now considered satisfactory.

Further trial runs of the spectrograph with x-rays have been postponed in order to improve the optical alignment, and investigate the source of extraneous scattering giving rise to a high background intensity. Since the ultimate test of proper alignment is sharp focusing of a line spectrum, modifications were made toward this end. A high vacuum spark source operating at about 50 kv was built into the x-ray chamber, with the electrodes located where the x-ray target is normally. Either solid aluminium electrodes, or hollow aluminium charged with sodium hydroxide were used. Ilford Q2 plates were used and since they cannot be readily bent to a radius as small as one meter (the radius of the Rowland circle) without breaking, only a small region of the spectrum could be explored at one time. Two tentatively identified lines on one plate and one on another are about as sharp as the slit width would permit and indicate a reasonably good alignment of the grating system.

Electrical interference caused by the 50-kv spark was so excessive, even with extensive shielding, that it was not possible to use the photomultiplier circuits with the spark source.

We have recently secured some 35-mm Eastman Type SWR film which has properties similar to the Ilford plates in the extreme ultraviolet, and intend to study the line spectrum further with it. The extraneous scattering has been reduced somewhat by means of guard slits and baffles, but is still too high.

G. G. Harvey, E. M. Gyorgy, R. H. Kingston, A. Meckler

E. PARAMAGNETIC RESONANCE EXPERIMENTS

During the past four months primary emphasis has been given to improvement of measuring techniques and apparatus. A number of improvements have been made in the sensitivity and stability of our apparatus, and in addition we are now able to make routine measurements down to temperatures of 2°K. We are just starting to take advantage of our improved equipment and have already found a number of extremely interesting results in the several kinds of single crystals which we have had under observation. Since the improvement in our technique has played a major role in our ability to obtain our interesting results, we shall discuss briefly the important details of our present equipment. And we shall describe the most interesting of our preliminary results on the several salts tested.

The low temperature helium cryostat is of simple and conventional design. The outer glass dewar which holds liquid nitrogen is evacuated, and the inner dewar, containing the liquid helium and microwave cavity, is sealed off with 1-mm pressure of nitrogen at room temperature. This is the usual technique for allowing precooling before filling with helium. The inside of the inner dewar is made just large enough to allow insertion of standard 1-inch by 1/2-inch 3-cm wave guide. The thickness of the brass wave guide has been reduced from its original 0.050 inch to about 0.015 inch to reduce heat losses and heat capacity. The cavity is a one-wave-length piece of guide. Small holes are drilled in both guide and cavity to allow liquid helium inside. This increases the helium capacity of the cryostat and in no way interferes with the microwave resonance measurements. The coupling between cavity and guide can be changed by inserting irises with various hole sizes between cavity and guide.

It is interesting to note that 4°-temperatures can be maintained in the cryostat for as long as four hours with a single filling of about 3 liters of liquid helium, much of which is used up in the initial cooling. In common with others using pyrex glass cryostats, we find that after about six runs with liquid helium the heat leak through the inner dewar increases markedly and it is necessary to re-pump the inner dewar, presumably to remove helium gas which has leaked in. It is possible to evacuate the entire contents of the inner dewar, including the cavity and wave guide. Before precooling, the system is evacuated and filled with helium gas to allow heat transfer. The cryostat is 53 cm long, and narrows down to 6.4-cm diameter at the bottom to allow insertion between the poles of an electromagnet.

The method of measurement is similar to that described in previous Progress Reports (see also Research Laboratory of Electronics Technical Reports No. 91 and No. 61). Variations in the power absorbed by the crystal as a function of the externally applied magnetic field is measured by means of the change in the power reflected by the cavity. This change is a consequence of the change in the Q of the cavity containing the crystal. The modifications which have been made are primarily in the direction of improving stability and sensitivity. A major improvement in stability has been obtained by changing the method of amplitude modulation of the microwave power. We now run the klystron at a constant frequency, and obtain amplitude modulation by inserting a crystal in a tee in the transmission wave guide. Modulating voltage placed across the crystal changes its impedance and hence modulates the amplitude of the signal to the cavity. This rather standard modulation technique has a tremendous advantage, since it allows the klystron to be operated with batteries and hence eliminates the rather serious noise on the a-c lines and the frequency drift due to a-c line variation. A Pound stabilizer would give the necessary frequency stability without batteries but it is not certain that all of the line noise could be eliminated. In any case, power requirements are small and therefore battery operation presents no difficulties. With the increased stability of the power source, it became useful to improve the stability of the amplifier used on the audio frequency signal resulting from rectifying the microwave signal. At present we are operating this amplifier with batteries also, and have considerably improved the signal-to-noise ratio. We have not reached the ultimate possible sensitivity, but much further increase will bring us to the point where slight mechanical instability of the wave guide will begin to limit us. An increase of a factor of 2 to 4 is probably available to us by improving the Q of our cavity, and our frequency stability would justify such an improvement. However, our present sensitivity has opened up a considerable field of investigation, and we will pursue this for the present, making improvements as convenient.

We have another type of equipment which is an improved version of equipment built by Malvano (1) and used by him in Italy prior to his visit here. In this apparatus the external magnetic field can be modulated at 60 cps and the resulting absorption curve can be presented directly on a CRO. This method is exceedingly useful, especially as a supplement to our original method.

Actually the methods we are using are fairly conventional microwave techniques which have been applied in many allied fields. It is rather surprising, when there is so much to be gained, that they have not been used before in the paramagnetic resonance field.

We will now report briefly on the results we have so far obtained. During the process of improving our equipment and testing the operation of the cryostat we used a single crystal of $(NH_4)\,Cr(SO_4)_2 \cdot 12\,H_2O$, which has been measured by several others (1, 2, 3, 4), for testing our apparatus. Actually we had a special motive for using this salt, since Malvano had found the faint suggestion of an extra absorption peak at low magnetic fields. We hoped that our new apparatus would have sufficient sensitivity to determine whether this peak was real or whether it had to do with instrumental effects. Operation with both of our types of equipment have shown the peak to be real, and we have now made runs at five temperatures from room temperature down to 4°K. Complete results will be published soon; we can say this much at present: The presence of the extra peak indicates the existence of a double Stark splitting of the ground level of the paramagnetic Cr^{+++} ion at all temperatures. Data of previous workers (4, 5) indicated double splitting only below 90°K. We have further shown that the double splitting cannot be explained by assuming that one or more of the ions in the unit cell is different from the others.

In order to clarify some of the discordant experimental data on some paramagnetic rare earth salts we have undertaken to measure a number of them at the low temperatures required. In this work we are collaborating with Prof. F. H. Spedding and Mr. Buell Ayers who have provided the single crystals which we are using. So far, preliminary measurements have been made on three crystals, and the most interesting results will be briefly described.

$Pr\,Cl_3 \cdot 6\,H_2O$ gives a narrow resonance at 4°K at about 2300 gauss for a particular orientation of the crystal with respect to the external magnetic field. The width of the resonance is about 50 gauss at the half-power point. There is evidence of resolved hyperfine structure in this peak.

The most interesting of the rare earth salts which we have tested is $Nd_2(SO_4)_3 \cdot 8H_2O$. As has been previously pointed out, this crystal presents large anisotropy at low temperatures. In the easy direction of magnetization we find an anomalous dispersion curve. The frequency of the resonant cavity containing the single crystal changes rapidly (and possibly discontinuously) at a certain applied magnetic field. The magnetic field necessary to cause this transition decreases with temperature. Further work on this interesting effect is now in progress and will be reported in detail later.

A. F. Kip, R. Malvano, C. F. Davis, L. Jennings, D. Reiner

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F. THE INFLUENCE OF A TRANSVERSE MAGNETIC FIELD ON THE CONDUCTIVITY OF THIN METALLIC FILMS (1)

The numerical evaluation of the theory for the case of partially elastic surface scattering has now been completed by the Joint Computing Group. Complete details of the theory will be published as Technical Report No. 161 by this Laboratory.

E. H. Sondheimer

Reference

1. See Proceedings of the M.I.T. International Conference on the Physics of Very Low Temperatures, p. 105; Quarterly Progress Report, Research Laboratory of Electronics, M.I.T. January 15, 1950, p. 23; Nature 164, 920 (1949).