

III. SOLID STATE PHYSICS

Prof. J. C. Slater	C. F. Davis, Jr.	G. F. Koster	H. C. Schweinler
Prof. G. G. Harvey	E. M. Gyorgy	A. Meckler	M. Tinkham
Prof. A. F. Kip	R. H. Kingston	R. H. Parmenter	R. Weinstein
Prof. L. Tisza	W. H. Kleiner	G. W. Pratt, Jr.	H. C. White

A. EXTENSION OF THE ENERGY BAND THEORY

Application of the self-consistent field method to the problem of antiferromagnetism has been further considered. It seems clear that two different approaches to such a problem, both based on self-consistent methods, are possible. (1) We can start with the assumption that the Hartree-Fock potential is independent of spin. Then we are led to wave functions which are similar for electrons of both spins, and this leads to charge densities which are the same for both spins, and hence in a self-consistent way to potentials independent of spin. This is the basis of the usual Bloch theory. (2) We can start by assuming two different Hartree-Fock potentials, one for electrons of each spin. Each will have different wave functions and charge densities, and hence will lead to different self-consistent potentials, thereby again getting a solution of the Hartree-Fock equations. This is the scheme (described in the Quarterly Progress Report, January 15, 1951) in which, if we know that we are to describe a crystal with alternating spins on alternating atoms, the potential will show a double periodicity. As pointed out in that report, this second method can easily lead in the first approximation to the existence of antiferromagnetism, whereas, to explain it it would be necessary to carry out further higher-order approximations superposed on the first method.

The considerations just described lead to interesting consequences when we apply them to such a simple case as the H_2 molecule. There the first method leads to the usual molecular orbital solution for the molecule, which is known to be good for small internuclear distances but to fail completely at large distances. The second method would suggest that we could satisfy the Hartree-Fock equations for the molecule in an alternative way. We start by assuming that one of the atoms, say atom a, has an electron of positive spin, and the other, say atom b, has an electron of negative spin. We then find different Hartree-Fock potentials for electrons of the two spins. In particular, for an electron of positive spin, we find a Hartree-Fock potential arising from a bare nucleus on atom a, but a nucleus and electron, or neutral atom, on atom b. Thus the solution of the Hartree-Fock equation for the positive electron results in an atomic wave function around atom a. Similarly the Hartree-Fock equation for the negative electron results in an atomic wave function around atom b.

The existence of these two quite different types of solution of the Hartree-Fock equations for the H_2 problem has been checked by a simple calculation. If we symbolize the ordinary atomic function around atom a by a, that around b as b, we can set up

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one-electron wave functions of the form

$$c_{11}a + c_{12}b \quad , \quad c_{21}a + c_{22}b \quad ,$$

where the c 's are constants, and where these functions can be made into the limiting case of atomic functions by making $c_{12} = c_{21} = 0$, and into molecular orbitals by making $c_{11} = \pm c_{12}$, $c_{21} = \pm c_{22}$. We now make up a determinantal two-electron wave function, assuming that the first one-electron function is associated with an electron of positive spin, the second with an electron of negative spin. As a substitute for the Hartree-Fock procedure, we vary the c 's to make the energy integral stationary. When this is done a somewhat complicated algebraic problem results. The writer has examined this and finds that there are in fact solutions of two types, one of the molecular orbital type, the other of the atomic type. Mr. Pratt is carrying this problem further, to see just what is the nature of the atomic wave functions as a function of internuclear distance. At infinite internuclear separation these reduce to the ordinary atomic functions, but at finite distances the coefficients c_{12} , c_{21} are not zero. It has been surmised before (1) that two such solutions exist for the Hartree-Fock equations, but this example seems a particularly simple and direct one, in which it can be shown in an algebraic way.

There is an important difference between these two types of solution of the Hartree-Fock equation for the hydrogen molecule. The molecular orbital solution, in which both electrons are in the symmetric molecular orbital, is nondegenerate, and forms by itself a good solution for the molecule at small internuclear distances. It corresponds essentially to a closed shell, the symmetric molecular orbital being occupied by an electron of each spin. Thus this type of solution is equivalent to that which Mulliken, Roothaan, and their collaborators have been using for a wide variety of molecules. The atomic type of solution, however, is degenerate: the state with a positive spin associated with the wave function concentrated on atom a , and a negative spin on atom b , is degenerate with the state with spin negative on atom a , positive on atom b . It is this degeneracy which is removed in the Heitler-London solution for the molecule. The diagonal energy of one of the atomic states corresponds approximately to the Coulomb energy in the Heitler-London method, whereas the energy after carrying out the perturbation calculation includes the Heitler-London exchange energy as well, which is known to make the major contribution to the tightness of binding. At large distances of separation, even the unperturbed atomic functions lead to lower diagonal energies than the molecular orbital solution, which goes to much too high an energy at infinite separation, and in that sense we might be tempted to say that the Hartree-Fock method indicates that the molecular orbital type of solution has lower diagonal energy, and should be used, at small interatomic distances, whereas the atomic solution has lower diagonal energy, and should be used, at larger distances. This view is too superficial. We should rather conclude that at such large distances the molecular orbital method

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does not furnish a good approximation; we should really carry out the further perturbation calculation, of the Heitler-London type, superposed on the atomic Hartree-Fock solution. This can be easily done for hydrogen, but it is a somewhat dismal prospect for complicated molecules and solids, since the well-known nonorthogonality difficulties are still present; they are not avoided by having the starting points solutions of a Hartree-Fock problem.

These considerations regarding the hydrogen problem are of interest particularly as they affect the related problem of solids. Here the situation is somewhat different and more encouraging. Suppose we consider an antiferromagnetic linear chain of atoms (if such a thing can exist), in which we hope to show that the ground state has atoms with alternating spins, as $+ - + - + - + -$. Such a problem suggests using method 2 of solving the Hartree-Fock equation (described in the first paragraph and taken up in the Quarterly Progress Report, January 15, 1951). The one-electron wave functions in such a problem are not real atomic functions, but modulated functions corresponding to a crystal with a double period. By analogy with the hydrogen case, we should think that it was necessary to consider perturbations between this state and other states with spin interchanges. We easily convince ourselves, however, that the nondiagonal matrix component of energy will be negligibly small except between the original state and one in which a relatively small number of spins have been interchanged, such as a chain with only one interchange, as $+ - + - - + + -$. Such states are not identical with the original one, and hence are not degenerate with it, so that the effect of the perturbation may be much less important than in hydrogen. This problem of perturbation has been often considered (2) from the point of view of Heitler-London exchange integrals, and it has been shown that the ground state does not correspond to the regular alternating arrangement of spins, but that there is an appreciable mixture of states with spin interchanges. This result has been very puzzling to theorists confronted with the evidence of neutron diffraction which indicates that the real antiferromagnetic materials show a very regular spin alternation. The perturbation calculations quoted above are based directly on analogies with the Heitler-London hydrogen calculation, which imply certain relationships between the difference between the diagonal energies of states with interchanged spins and the related nondiagonal matrix components of energy. If the nondiagonal matrix components were smaller than this relation indicates, the admixture of states with interchanged spins would be less than shown in the calculations. The writer believes that the correct way to carry out such a calculation is to start with the energy band solution for the regular antiferromagnetic arrangement of atoms, of type 2 described in the first paragraph; to set up similar solutions for cases with spin interchanges; and to proceed from there by perturbation methods. Such a calculation is difficult, but it seems unlikely that the relation between diagonal and nondiagonal matrix components of energy will be as in the Heitler-London case, so there is a real

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chance that the difficulty will be removed.

The considerations outlined above are given in more detail in a paper which has been submitted to the Physical Review. Calculations of the type outlined in the preceding paragraph are under way. These involve approximate solution of the Hartree-Fock equations for an antiferromagnetic crystal involving a regular alternation of spins, except for one or a few spin interchanges. This latter problem is essentially one of a perturbed periodic lattice; and to make it possible to handle it in a usable way, the writer is looking into the adaptation to it of the method earlier described by him (3) for handling electrons in perturbed periodic lattices, by means of expansion of the wave function as a series of Wannier's orthogonal atomic orbitals.

This study of the Wannier functions has suggested a somewhat different approach to the general problem of solution of Schrödinger's equation for a periodic potential. Mr. Parmenter's study of this problem is making it seem more and more likely that any method based on Fourier expansion in plane waves will converge so slowly as to be impracticable for the conduction band and low energy levels. On the other hand, the Bloch method of expansion in terms of atomic functions, which is the adaptation to a crystal of the method which Mulliken calls Linear Combination of Atomic Orbitals in the molecular case, is rather good. The main objection to it has been the feeling that the atomic functions which are the solutions for free atoms certainly have no great significance when the atoms are pushed close together into a crystal. However, Wannier's results show that if we start with the orthogonal atomic orbitals, the Bloch-like wave function constructed from them will be an exact solution of the periodic potential problem. In other words, it is possible to set up atomic functions which will lead to an exact solution of Schrödinger's equation for a periodic potential, when they are combined as Bloch suggested. This suggests the following procedure for attempting a solution of this periodic potential problem: to set up an atomic function with a number of variable parameters in it, make a Bloch combination of such atomic functions, and then vary the parameters so as to make the one-electron energy of this wave function in the periodic potential stationary. This is a workable scheme, which was carried out in a somewhat simplified way by Jones, Mott, and Skinner (4). It seems sufficiently promising to warrant a study of its feasibility and accuracy which Mr. Parmenter is making.

As of February 1, 1951, the group in solid state theory, consisting of the writer, and Messrs. W. H. Kleiner, G. F. Koster, A. Meckler, R. H. Parmenter, G. W. Pratt, Jr., and H. C. Schweinler, has become a separate group, under a contract with the Office of Naval Research, rather than part of the Research Laboratory of Electronics. Further reports from the group will be issued separately.

References

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J. C. Slater

B. SELF-CONSISTENT FIELD CALCULATIONS

A final evaluation of methods of solving Schrödinger's equation has been completed. It was found that one can obtain good results from the integral equation method (Quarterly Progress Report, January 15, 1951) only for the lowest eigenstate for a given l value. If one attempts to determine a 2S wave function, for example, successive iterates converge to the 1S function unless extreme care is taken. Results have shown that although the method is basically sound, it is not practical to try to use the method for the higher states.

Attention has been turned on the problem of applying IBM machines to the problem. Investigations have been made as to the best method of numerical integration to use on these machines from the standpoint of time of solution and flexibility of directing the machine. At present a method has been devised for using the IBM machines which appears to be satisfactory.

In addition to the work on the Hartree self-consistent field calculations, work has been started on a new method of finding molecular wave functions. In brief, this method is an application of the variation method to the molecular orbital scheme. Work is still in progress on this problem and the final result should be forthcoming shortly.

G. W. Pratt, Jr.

C. ENERGY BANDS IN SOLIDS

The calculations mentioned in the Quarterly Progress Report, January 15, 1951, have been completed. These were calculations of the valence electronic energy band in the lithium crystal, using a method proposed by Slater (see Phys. Rev. 51, 846, 1937). As one might expect, the roots of the determinantal equation are rapidly convergent at the bottom of the band. At the top of the band convergence is so slow that the method is impractical for accurate numerical calculations. This result holds even when the wave vector has some of the symmetries of the reciprocal lattice, a condition which allows the secular determinant to be drastically reduced in size. This lack of convergence is probably a characteristic of the method, independent of the particular solid being studied.

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A study has been made of the difficulty in calculating the electronic band-structure (i. e. the energies of the tops and bottoms of the various bands), especially for the higher bands, when one expands the wave function everywhere in a three-dimensional Fourier series. The wave functions will have certain symmetries at the band edges, and the scheme mentioned previously may be used to reduce the size of the secular determinant. In general, for wave functions having the complete symmetry of the given crystal it is not difficult to calculate the corresponding energies accurately. For those wave functions not having the complete crystal symmetry the accurate calculation of the energies is considerably more difficult. This results from the fact that the secular determinant can be reduced less in the latter case than in the former.

R. H. Parmenter

D. THEORY OF MOLECULAR OXYGEN

Much progress has been made in the computation of integrals by the discovery of a rather complete set of tabulated values (H. J. Kopineck: Zeit. für Naturforschung 8, 420, 1950). Kopineck has gone even further than our plans by working out coulomb and exchange integrals involving 2s as well as 2p wave functions. The existence of these computations makes feasible the inclusion, in the multiplet calculation, of the configurations in which 2s electrons are excited into p orbitals.

A. Meckler

E. FERROELECTRICITY IN THE ILMENITE STRUCTURE

The general background of this problem was given in the Quarterly Progress Report, January 15, 1951. The dyadics relating local electric field strength F to the dipole moments at the lattice points p have all been checked and the results are given below. Since there are ten atoms per unit cell, one hundred dyadics are in principle required (relating the field at each of the ten atoms to each of the ten lattices of dipoles), but conditions of symmetry reduce this number to six. Only these six dyadics, and the rules for getting the others, are given here.

The field at $x_1 a_1 + x_2 a_2 + x_3 a_3$ with respect to a dipole of the lattice is given by

$$\epsilon_0 F(x_1 x_2 x_3) = D(x_1 x_2 x_3) \cdot P$$

where $P = P_1 a_1 + P_2 a_2 + P_3 a_3$ is the polarization of the lattice of dipoles in question and $D(x_1 x_2 x_3)$ is a dyadic having as antecedents the unit cell displacement vectors a_1, a_2, a_3 and as consequents the reciprocal lattice vectors b_1, b_2, b_3 :

$$D(x_1 x_2 x_3) = \sum_{i,j} a_i C_{ij}(x_1 x_2 x_3) b_j \quad .$$

Writing the C_{ij} in matrix form, we have:

$$D(\mathbf{x} \times \mathbf{x}) = \begin{bmatrix} 0.333333 & C(x) & C(x) \\ C(x) & 0.333333 & C(x) \\ C(x) & C(x) & 0.333333 \end{bmatrix}$$

where $C(0) = -0.021317$; $C(1/6) = 0.668439$; $C(1/3) = -0.372748$; and $C(1/2) = 0.042006$.

$$D\left(\frac{1}{6} \frac{-1}{6} \frac{1}{2}\right) = \begin{bmatrix} -0.109429 & 0.031833 & 0.027067 \\ 0.031833 & -0.109429 & 0.027067 \\ 0.767171 & 0.767171 & 1.218858 \end{bmatrix}$$

$$D\left(\frac{5}{12} \frac{-1}{4} \frac{1}{12}\right) = \begin{bmatrix} 2.029088 & 0.179461 & 1.388216 \\ -1.517674 & -0.596318 & -0.718488 \\ 0.458462 & 0.048894 & -0.432770 \end{bmatrix}$$

The rules referred to above by the application of which all dyadics can be derived are:

$$(a) \quad D(x_1 x_2 x_3) = D(\bar{x}_1 \bar{x}_2 \bar{x}_3) \quad ,$$

where $\bar{x}_1 = -x_1$, etc.

$$(b) \quad C_{ij}(x_{P(1)} x_{P(2)} x_{P(3)}) = C_{P(i) P(j)}(x_1 x_2 x_3) \quad ,$$

where P is the permutation operator.

H. C. Schweinler

F. $\text{Cr} \cdot 6\text{H}_2\text{O}^{+++}$ COMPLEX IN CHROME ALUMS

The theory of the behavior of the chromium ion in chrome alums is of interest in interpreting optical and microwave absorption spectra, and low temperature specific heat and magnetic susceptibility data. Investigation of the $3d^3$ atomic configuration in a cubically symmetrical electric field as an approximation to the situation in the chrome alums has been continued (cf. Finkelstein, Van Vleck: J. Chem. Phys. 8, 790, 1940). Recently consideration has been given to the possibilities for a more rigorous treatment with the view to include at least the octahedron of water molecules surrounding the chromium ion as part of the system.

W. H. Kleiner

G. EFFECT OF CONFIGURATION INTERACTION ON THE MAGNETIC HYPERFINE INTERACTION

The theory of magnetic hyperfine interaction in atoms gives the positions of the energy levels

$$\frac{E}{h} = \frac{a}{2} [F(F+1) - I(I+1) - J(J+1)]$$

in units of sec^{-1} , where F is the total angular momentum (electrons plus nucleus), I is

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the spin of the nucleus, and J is the total angular momentum of the electron configuration. A simple theory, which assumes the separability of the wave functions into radial and angular parts, gives

$$ha = -\mu_o^2 g_I R \frac{2L(L+1)}{J(J+1)} \langle r^{-3} \rangle_{\text{average}} ,$$

($L \neq 0$), where L is the total orbital angular momentum of the electrons, R is a relativistic correction (~ 1), g_I is the nuclear g -factor, and μ_o is the Bohr magneton.

In Al, Ga, In, and Tl discrepancies have been noted (1) between the observed and predicted values of the ratio

$$\frac{a(^2P_{1/2})}{a(^2P_{3/2})}$$

for the ground configuration. From the formula above, this ratio should be 5, assuming that $\langle 1/r^3 \rangle_{\text{average}}$ is the same in the $^2P_{3/2}$ and $^2P_{1/2}$ states (neglecting the small relativistic correction). In Al this ratio is measured to be 5.1; in Ga, 6.5; and in In, 7.68 (corrected for R).

In order to explain these discrepancies a calculation is being carried out for Ga following a similar calculation for Tl by Fermi and Segre (2). The explanation is thought to lie in the approximation of atomic wave functions by those of a single configuration. Starting with the Hartree wave function for the ground state of Ga ($4s^2 4p$ configuration) one should, by the usual perturbation calculation, add to this wave function, wave functions of other configurations which give rise to the same terms. In this case the perturbation is the difference between the Hartree potential and the electrostatic interaction between the electrons and each other and the electrons and the nucleus. The perturbing configuration being considered is the $4s4p5s$. In order to carry out the perturbation calculation, integrals are necessary involving the $5s$ wave function for Ga. This wave function is being calculated with the Hartree method and the calculated ground state wave functions of Ga (3). It is hoped that the use of Hartree wave functions will give results of a more quantitative nature than those of Fermi and Segre.

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G. F. Koster

H. THEORY OF SUPERCONDUCTIVITY

In a recent paper (1) the superconducting state was described quantum mechanically in terms of many-electron wave functions providing an adequate description for most experimental facts. An important exception was the recently discovered isotope effect. Consequently the question has been reopened from the point of view of the systematic procedure of Born-Oppenheimer (adiabatic approximation). In its present form, the theory corresponds to the first step in this procedure whereby the electronic wave functions are determined at fixed nuclear positions. A more careful consideration shows that in the case of superconductors this approximation may not be consistently separated from the next, involving the nuclear dynamics. Preliminary results lead to perturbation terms similar to those obtained by Bardeen (2). The difference is that Bardeen's theory is expressed in terms of free electron wave functions. Whereas these have the advantage of easier handling, it seems likely that the many-electron wave functions are necessary to account for the phase transition aspects of superconductivity.

The work is being continued.

References

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L. Tisza

I. SOFT X-RAY VACUUM SPECTROGRAPH

We have succeeded in recording the band emission curves of Mg and Na; the results are in excellent agreement with work of previous investigators. (See Quarterly Progress Report, January 15, 1951, for references.)

We have redesigned the electron bombardment system so that the cathode of the electron-gun is operated at ground potential and the target is thus at high voltage with respect to the x-ray can. This was found necessary to eliminate stray photon emission from the spectrograph slit caused by secondary electrons from the target. In this way we have reduced the background considerably, e. g. latest curves for aluminum indicate a ratio of approximately 15 to 1 for the intensity of the high energy edge to the background, as compared to 3 to 1 for the curve published in the previous report. We have also mounted the target assembly on a bellows joint, which allows horizontal motion in any direction while the system is evacuated. In this way we can adjust the target position for optimum intensity directly.

In a recent communication from Prof. Skinner of Bristol we received a copy of the curves he had taken on the elements Ti through Zn in 1939. As he points out, the results obtainable for these metals are rather unsatisfactory since there is severe broadening of the emission edges, probably a result of satellite and Auger effects. Although we had

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hoped that our lower bombarding potentials would alleviate this problem, tentative curves on manganese indicate that the broadening effect is still observed. Before making further investigations of these transition metals we have decided to study K and Ca since soft x-ray data on them are missing from the literature, and they lie between the transition metals, which show the diffuse emission edges, and aluminum, which has a very sharp edge.

Correction: Figure III-1, the recorded curve for aluminum in the Quarterly Progress Report, January 15, 1951, is mislabeled. The caption should read "Energy in electron-volts" not "Wavelength in A".

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

J. PARAMAGNETIC RESONANCE EXPERIMENTS

We have finally resolved the problem regarding the anomalous characteristics of the microwave magnetic absorption spectrum of single crystals of ammonium chrome alum at low temperatures. As stated earlier, at temperatures below the transition which occurs at about 80°K, the positions of resonance peaks in the magnetic spectrum of this alum no longer appear to fit the simple theory which holds very well at room temperature. This fact can now be explained on the basis that there is a shift in the direction of the axis of symmetry of the paramagnetic chromium ions. (This axis is the result of the slight axial distortion of the octahedron of six water molecules of crystallization which surround the chromium ion and are the primary contributors to the crystalline electric field in the region of the chromium ion.)

Careful measurements of the magnetic spectrum as a function of the orientation of the crystal in the external magnetic field have been made. Comparison of these results with theory shows that the axis of symmetry of the ions shifts away from the (111) direction (as at room temperature) to a new direction approximately 20° away. Since the crystal gives the same spectrum for all (111) directions of orientation (i. e. with the external field parallel to any of the (111) directions) it must be that the shift is from the (111) direction to one of three possible directions, each making the same angle with the (111) direction.

A further problem still exists in the crystal; it has to do with the second Stark splitting which has been found, as described in previous progress reports. It is expected that we will be able to determine if the change in the axis of symmetry for these ions in which this smaller splitting occurs is the same or different from the change occurring in the case of the ions having the larger splitting.

Several other problems have been started recently. Since they are not very far advanced, they will be mentioned only briefly. The first is a study of resonance absorption by paramagnetic ions dissolved in liquids and the second is an attempt to investigate some characteristics of crystals containing F-centers by means of our

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resonance techniques. Other short-range plans involve measurements of various substances in order to clarify various aspects of their resonance spectra. This work will not be described until it is completed.

A. F. Kip, C. F. Davis, Jr., M. Tinkham, R. Weinstein, H. C. White