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QUARTERLY PROGRESS REPORT NO. 7

SOLID -STATE AND MOLECULAR THEORY GROUP

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- Technical Report No. 1, Ferroelectricity in the Ilmenite Structure, H. C. Schweinler, October 15, 1951

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Quarterly Progress Report No. 7

on

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SURVEY

During the three months since the Quarterly Progress Report of October 15, 1952, the Group has moved into its new quarters, and the improvement in the general morale and rate of progress has been profound. Instead of being in cramped rooms, which encouraged most of the members of the Group to work elsewhere, there is plenty of space, and in particular a very fine conference room, which is often used several times a day for general conferences of the whole Group, as well as almost constantly for private conversations, work on the blackboard, and computing. With my own office adjacent to this conference room, the situation is ideal for real scientific work, and the rapid progress during the three months shows strikingly the value of adequate working space. The Administration of the Institute has been very farsighted and generous in making the space available.

Since the beginning of the term, I have been giving an advanced series of lectures, which a number of the members of the Group, as well as a good many other students, have been attending. My object in this course is to cover the whole application of the determinantal method, and the self-consistent field, to the problem of the electronic energy levels of atoms, molecules, and solids. During the first term I am handling atoms and molecules, and the solids will follow in the spring. I am using this course as an occasion for formulating the whole procedure which we are evolving in the Group for handling molecular and solid-state problems, and many things have become clarified in the process. I am writing a very complete set of notes for the lectures, which are being passed out in planographed form during the term. At the end of the first term the notes for this term will be collected into a Technical Report, dealing in a very broad way with the electronic structure of atoms and molecules, and this Technical Report will be circulated to the same mailing list which receives these Quarterly Progress Reports. Similarly the notes on the theory of solids, during the second term, will be circulated as another Technical Report. One feature of the first Technical Report will be a very complete bibliography which I have been preparing, on the electronic theory of molecular structure.

The point of view to which we are coming more and more all the time is one which I have outlined in several recent progress reports. This is to set up a considerable number of one-electron wave functions or orbitals, make all the possible determinantal wave functions from these by picking out different sets of orbitals, or different configurations, and finally to solve the problem of configuration interaction between these configurations. This is the method which has been used by Meckler in his study of oxygen. It is a method which, in its straightforward form, cannot be used for very complicated problems, for the number of configurations goes up almost astronomically. It then becomes of the greatest importance to know how to treat it so that we can pick out the configurations whose interaction is important,

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and disregard the rest. To get experience leading in this direction, we have been seeking examples sufficiently informing so that we can learn a great deal from them, but simple enough so that we can solve them. We have considered a number of problems, with surprising results. In methane, for instance, it seems that a straightforward application of the configuration interaction method would involve us in a secular equation with the order of magnitude of 150 rows and columns, a clearly impracticable task. However, we find that the water molecule involves only 18 combining configurations leading to the ground state, and this we feel to be practicable, so Drs. Koster and Schweinler have joined forces in a very intensive program of calculating this molecule by very complete and accurate methods. Though this molecule has been treated many times during the last twenty years, the results which they should obtain should have a much greater accuracy than any previous work.

Drs. Koster and Schweinler are not using the approximation which Meckler did, of using Gaussian atomic orbitals rather than the correct type of orbitals. Thus the three-center integrals, which are very simple with Gaussian orbitals, become a major undertaking to compute; many of the previous workers with such problems have merely estimated such three-center integrals. Koster and Schweinler, on the contrary, are calculating these integrals exactly, so that their work should involve no approximations. The standard method of computing these integrals involves the use of the spherical Bessel and Hankel functions of imaginary arguments. Complete tables of these functions do not exist, and while individual entries in the tables are not hard to compute, and are being computed by Koster and Schweinler, a complete set of tables would be extremely useful for all workers in this field. Accordingly, with the cooperation of Professor Morse, and of Mr. Corbato, a graduate student in Professor Morse's group, we are starting a program of preparing such tables, using the IBM equipment at the Institute. The tables, when ready, should be extremely useful in all our molecular and solid-state calculations. For instance, Parmenter's calculations on chromium have been almost brought to a halt by the difficulty of computing the necessary three-center integrals; his work will become much easier when the tables are ready.

A number of other molecular calculations are being made to test the method of configuration interaction. One of these is the calculation of Mr. Merrifield, graduate student in chemistry, on the $(FHF)^-$ ion. This is being carried out to investigate the nature of the hydrogen bond; his work so far deals with the preliminary problem of the HF molecule. The configuration interaction problem of the $(FHF)^-$ ion does not involve many configurations, and by getting a solution which reduces to the correct limiting behavior as the atoms get far apart, which we shall do, we believe that we can find a reliable curve for the energy of the hydrogen as a function of its position between the fluorines, for different fluorine-fluorine distances. This curve should of course show a single minimum for small enough F-F distance, and two minima as the F's get further apart, and the hydrogen becomes bound to one of the fluorines or the other. The present calculations deal only with the linear configuration of the ion.

Several other molecular calculations are under way. Mr. Callen's work on configura-

tion interaction in H_2 was mentioned in the preceding progress report; its object is simply to test the configuration interaction method in a case where we know the correct wave function. Mr. Allen is working on the molecule of KCl, with a view to understanding how to handle the polarization effects which are undoubtedly important in a molecule of that sort. This case is particularly interesting on account of its value to the workers in the field of nuclear resonance; nuclear data exist, from use of the nuclear quadrupole interaction, from which we can get information about the gradient of the electric field at the nucleus, and Mr. Allen will hope to calculate this, if the problem proves simple enough. Dr. Kaplan is looking at the problem of S_8 . This chain molecule is one of the simplest cases of a molecule held together by saturated covalent bonds. We feel that it would be a good one to study first by the molecular orbital method, and then to explore ways of approaching the configuration interaction problem. The number of interacting configurations is enormous, but there may well be ways of approaching the problem which can give us a usable approximation, and we should hope to explore these. The ion ClO_4^- , which Dr. Koster was working on, has been temporarily dropped in favor of the work on water; we felt that the configuration interaction in water was a more important problem than the ClO_4^- ion, in which we could not hope with our present means to do more than a molecular orbital treatment.

In addition to all these problems of molecular structure by the method of configuration interaction, which we are undertaking mostly to gain understanding of the method, we are beginning to make important progress with the magnetic problem, as handled by configuration interaction methods. In the Quarterly Progress Report of July 15, I indicated the sort of approach which we could hope to make. In particular, on Page 32 of that Report I pointed out that the naive energy-band theory, equivalent to the molecular orbital theory without configuration interaction, could show unequivocally that for substances with wide bands, ferromagnetism was impossible; but that for narrow bands it can only show that ferromagnetism is possible, but cannot distinguish without more accurate calculations than have been made so far whether ferromagnetism actually exists in these cases, or non-ferromagnetism, or anti-ferromagnetism. I also pointed out, on Page 34, that for a band almost filled, with only a few holes, these holes would tend to repel each other, and that this effect should lead to a correlation effect whose influence on ferromagnetism should be examined, and might throw light on such problems as nickel, with its almost filled d band.

Dr. Stutz, on his arrival, became interested in this problem, and he has proceeded with it, following a general line which I had investigated last spring, though I had not described it in these Reports. Two holes in an almost filled band are very similar to two electrons in an otherwise empty band, and we can properly ask the question, will these two electrons have a lower energy if their spins are parallel or antiparallel? I was able to show last spring that if we set up the equations of motion of these two electrons by means of Wannier functions, we can then separate variables, separating off the motion of the center of gravity of the two electrons rigorously from their relative motion. The wave function for their rela-

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tive motion shows distinctive symmetry properties: for the triplet states, the wave function is antisymmetric, and for the singlet it is symmetric. These states represent states of a continuum, not bound states, on account of the repulsive potential between the electrons. The lowest triplet wave function, being antisymmetric or having odd parity, corresponds to a p-like wave function, while the lowest singlet wave function corresponds to an s-like wave function. We should therefore think it plausible that the singlet, or s-like function, would have to have an energy below the triplet. Dr. Statz has examined this question, and has been able to show that this is indeed the case: two electrons in an otherwise empty band will always have their spins antiparallel in the lowest state, and it will always require energy to raise them to a state of parallel spins.

Dr. Koster has extended this proof to the case of two holes in an otherwise full band; and thus we conclude in a very straightforward way that the holes in an almost full band will always arrange themselves in a non-ferromagnetic manner. The theorem holds, however, only for a non-degenerate band; as Dr. Statz has shown, if each atom has two possible Wannier functions in which the electron or hole can be located, we have the possibility, provided the bands are not too broad, that a triplet state will lie lower, in which the two electrons, when they find themselves on the same atom, set themselves with parallel spins in different atomic orbitals, their energy being lower in the triplet state than in the singlet by Hund's rule as applied to atoms. We seem therefore to be coming to the straightforward conclusion that the origin of ferromagnetism is to be found in the effect which Van Vleck (in his contribution to the Washington conference on magnetism) has called the intra-atomic effect. Two electrons (or more often two holes) on a given atom want to set their spins parallel, on account of the same interaction which always tends to make an atomic state of maximum spin the most stable; and they carry their spins over to the neighboring atoms, influencing other electrons on the neighbors to set themselves parallel too.

This of course is similar to the idea which Zener has been recently propounding. Nevertheless we do not believe that Zener's interpretation is correct, that the electrons which carry the memory, so to speak, of the magnetic moment of one atom to the next atom must be 4s electrons in the iron group. We see every reason to believe that this function is fulfilled by the 3d electrons themselves, and believe that a 3d shell with a certain number of holes would be ferromagnetic, on account of the degeneracy or overlapping bands of the d shell itself. These arguments do not in any way supplant the earlier conclusion that ferromagnetism is impossible when we are dealing with broad bands; they merely supplement it by saying that under certain circumstances ferromagnetism is also impossible with narrow bands. The reason why we do not believe that the 4s electrons are as important as Zener thinks is simply that the 4s band is so broad that the Fermi energy involved in promoting 4s electrons to have parallel spin is almost certainly great enough to discourage such promotion on a large scale, whereas as has just been stated we do not agree with Zener's premise that the interaction of the d shells themselves is not ferromagnetic.

These important conclusions, which we are carrying further, should show the power of the energy band and configuration interaction method for handling magnetic problems, which I stressed in the July 15 Progress Report. Two other investigations are underway dealing with similar magnetic problems: Dr. Kikuchi is continuing the study of a one-dimensional chain of atoms each containing a single electron in a Gaussian orbital, and Dr. Pratt is studying the same problem from a different point of view. Dr. Kikuchi is starting with a band filled with electrons of one spin, empty of electrons of the other spin, and then is investigating the problem where one electron has its spin reversed, to see if the reversal lowers the energy (non-ferromagnetic interaction) or raises it (ferromagnetic interaction). Dr. Pratt is comparing the energies of three configurations: first that with all spins parallel, next that of an antiferromagnetic configuration with alternating spin, finally that with the lower half band filled equally with electrons of both spins, using the energy-band approximation to the latter configuration. These calculations are all being made properly, using orthogonalized atomic orbitals, and taking ionic states properly into account. Now that we know Stutz's result, we assume that both investigations will tell us that this model is non-ferromagnetic; but we feel that it will be informing to carry the calculations through, so as to check our results from several different points of view. It should be pointed out that these calculations of the one-dimensional chain are not being carried out by the Heisenberg method, and hence are not at all comparable to the well-known results of Hulthen, Bethe, and others; we regard the present calculations as having much closer relation to a correct treatment of the magnetic interaction problem.

These results of which I have spoken represent the most interesting and significant new results of the last three months, though several other pieces of work continue in an interesting way, as will be plain from the contributions to this Progress Report. In my own contribution to this Report, I have collected together some of my thoughts on the general subject of configuration interaction, amplifying some of the remarks that have been made recently in other reports. In this connection, I have arrived at a new formulation of the method of the self-consistent field, more general than the Hartree-Fock method in that it is not limited to a problem in which we deal with only a single determinantal function, but applies equally well to a problem with configuration interaction. It has the same advantage as the simplification of the Hartree-Fock method, which I recently proposed, resulting in a single potential energy function applicable for all molecular orbitals, and in fact reduces to that method for the special case where we use only a single determinantal function. When this method is once formulated, it seems so obvious and straightforward that one wonders why it was not thought of years ago. I believe that it is almost the uniquely right way to look at the self-consistent field method, and feel that it will replace the Hartree-Fock and other methods in the application of the self-consistent field method to molecular and solid-state problems.

J. C. Slater

1. A GENERALIZED SELF-CONSISTENT FIELD METHOD

The Hartree-Fock method, and the simplification of it recently suggested by the writer,⁽¹⁾ rest on the assumption that we are dealing with an n -electron wave function given by a single determinant, or antisymmetrized product, formed from n one-electron orbital functions of coordinate and spin. Often, however, we wish to deal with a more general case, in which the wave function is approximated by a linear combination of such determinantal wave functions. The process of combining such determinants to get a better approximation that can be secured by one alone is generally called configuration interaction. In this note we shall examine the more general self-consistent field method to be used in such cases of configuration interaction.

If we start with a complete orthogonal set of one-electron spin-orbital functions u_i , then the products $u_j(x_1) u_k(x_2) \dots u_p(x_n)$, where the indices j, k, \dots, p are to take on all combinations of values, obviously form a complete orthogonal set of n -electron functions of coordinates and spin, and the antisymmetrized products or determinants $(n!)^{-1/2} \det \{u_i(x_1) u_k(x_2) \dots u_p(x_n)\}$ form a complete orthogonal set of antisymmetric n -electron functions of coordinates and spin. Thus the exact wave function of an n -electron problem can be expanded as a linear combination of such determinantal functions, so that a proper treatment of configurational interaction can give an exactly correct solution, and can yield a function which takes full account of the correlation between the motion of electrons, though of course it is well known that a single determinantal function by itself does not correctly describe this correlation. The expansion of a given wave function in terms of determinantal wave functions may be slowly convergent; studies of the problem of the ground state of helium by Taylor and Parr,⁽²⁾ and by Green, Mulder, Ufford, Slaymaker, Krawitz, and Mertz,⁽³⁾ show that in this case the convergence is rather slow. On the other hand, the recent success of Meckler⁽⁴⁾ in studying the oxygen molecule suggests that in at least some important cases the method of configuration interaction may converge well enough to be of practical value. It is well known that the Heitler-London and valence-bond methods can be regarded as examples of configuration interaction between a number of different configurations set up in terms of antisymmetrized products of molecular orbitals. Thus any advantages lying in those methods can surely be secured by using configuration interaction, between a relatively limited number of configurations. The case of oxygen studied by Meckler included enough configurations so that his treatment is more general than a valence-bond method, and the same thing is true of various other investigations under way in this laboratory.

Let us then consider the problem of determining the one-electron orbitals u_j by a self-consistent method. It is at once obvious that no variation method, like the Hartree-Fock procedure, can be used in this case, for that depends on choosing those u_i 's which allow us to make the best single determinantal function. In the present case, no matter what orbitals we use, provided they form a complete orthogonal set, we can eventually get a precisely correct answer, by carrying the configuration interaction far enough. The only criterion which we can now use to determine the u_i 's is that we wish that set in terms of which the process of

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configuration interaction will give a series which converges most rapidly. This is not a criterion which is readily expressed analytically. Accordingly we turn in quite a different direction for the determination of the u_i 's, and go back to something much more like Hartree's original intuitive argument for setting up the self-consistent field. We shall demand very simply that the u_i 's be solutions of a Schrödinger equation representing the motion of an electron in the field of all nuclei, and in the field of all other electrons, averaged over the motions of these other electrons.

This very simple requirement leads to a perfectly unique Schrödinger equation. Let the wave function of all n electrons be $U(x_1, \dots, x_n)$. This is an antisymmetric function, which may well be expressed as a linear combination of determinantal functions of the type we have just been discussing. The quantity $U^*(x_1, \dots, x_n) U(x_1, \dots, x_n) dx_1 \dots dx_n$ measures the probability that simultaneously electron 1 be in dx_1, \dots electron n in dx_n (where we are including the spins with the coordinates). The electrostatic interaction energy between electron 1 and all other electrons is $\sum (j) e^2/r_{1j}$, where j goes from 2 to n , and r_{1j} is the distance from electron 1 to the j^{th} electron. Thus

$$dx_1 \int U^*(x_1, \dots, x_n) \sum (j) e^2/r_{1j} U(x_1, \dots, x_n) dx_2 \dots dx_n$$

can be considered as the probability that the electron 1 be in dx_1 , times the average value of the electrostatic interaction energy as averaged over all positions and spins of the electrons 2 . . . n . Since the probability that electron 1 be in dx_1 , irrespective of the positions of other electrons, is $dx_1 \int U^*(x_1, \dots, x_n) U(x_1, \dots, x_n) dx_2 \dots dx_n$, we see that the average potential energy of interaction between electron 1 and all other electrons, when electron 1 has coordinates and spin given by x_1 , is

$$V_e(x_1) = \frac{\int U^*(x_1, \dots, x_n) \sum (j) e^2/r_{1j} U(x_1, \dots, x_n) dx_2 \dots dx_n}{\int U^*(x_1, \dots, x_n) U(x_1, \dots, x_n) dx_2 \dots dx_n} \quad (1.1)$$

If we add this to $V_n(x_1)$, the potential energy of an electron of coordinate and spin x_1 in the field of the nuclei, to get $V(x_1)$, then we see that $V(x_1)$ represents the average potential energy of the electron of coordinates and spin x_1 , averaged over the motions and spins of all other electrons. We assume, then, that the correct generalization of the method of the self-consistent field is to set up a one-electron Schrödinger equation for an electron moving in this potential $V(x)$.

We have already mentioned (Ref. 1) the simplification of the Hartree-Fock method, by which a single Schrödinger equation was introduced in place of the Hartree-Fock equations, in the case where the wave function of the many-electron problem could be written as a single determinant. If we replace our function U by a single determinant, then it is easily shown that our Schrödinger equation reduces to that given in Eq. (7) of Ref. 1, so that the method of

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Ref. 1 is a special case of that which is now proposed. We can give the same interpretation to the potential V_e that was done in Ref. 1. That is, it is the potential energy of interaction of the electron with coordinates and spin x_1 , with an electronic distribution of density

$$\frac{(n - 1) \int U^*(x_1 \dots x_n) U(x_1 \dots x_n) dx_3 \dots dx_n}{\int U^*(x_1 \dots x_n) U(x_1 \dots x_n) dx_2 \dots dx_n} \quad (1.2)$$

with coordinates and spin given by x_2 . This electronic distribution consists of a total charge equal to $(n - 1)$ electrons, and its density goes to zero when x_2 equals x_1 ; that is, when electrons 1 and 2 have the same spin, and are at the same position of space. This is just as if the electronic distribution consisted of the whole charge of n electrons, diminished by an exchange charge whose properties are like those discussed in Ref. 1. In other words, the qualitative discussion given in Ref. 1 is more general than the assumption made there that the wave function could be represented by a single determinant or a single configuration. In particular, the simplification introduced in Section 5 of Ref. 1, replacing the exchange potential by a value calculated from a free-electron gas, is as plausible a simplification in the general case of configuration interaction as it is for the single determinantal function, and is not tied in any way to the Hartree-Fock case.

One way to appreciate the useful features of the expression (1.1) for the potential V_e is to ask how to calculate the electronic repulsive interaction energy of the whole system. The average values of each term e^2/r_{ij} over the wave function are the same, on account of the antisymmetry of the wave function, and since there are $n(n - 1)/2$ pairs, the total interaction energy will be just $n(n - 1)/2$ times the integral for one term. Now if we multiply $V_e(x_1)$, as given in Eq. (1.1), by the denominator $\int U^*(x_1 \dots x_n) U(x_1 \dots x_n) dx_2 \dots dx_n$, and integrate over dx_1 , the result will be just the value of $(n - 1)$ interaction terms like e^2/r_{ij} . Thus the total interaction energy will be $n/2$ times as great as this. But $n \int U^* U dx_2 \dots dx_n$ is just the total charge density, in units of the electronic charge. Thus we see that the total electronic interaction energy can be written as

$$\frac{1}{2} \int \rho(x_1) V_e(x_1) dx_1, \quad (1.3)$$

where $\rho(x_1)$ is the electronic charge density at the position and with the spin given by x_1 .

The expression (3.3) is formally just like the interaction energy of a charge distribution with itself in classical electrostatics; only in the classical case, V_e would be related to ρ by Poisson's equation, whereas here it is not. The possibility of writing the electrostatic energy in this form, in the quantum theory, has been discussed by the writer,⁽⁵⁾ using arguments closely related to those of the present note. The reader should realize clearly that, if the exact wave function of the problem is used in calculating the potential $V_e(x_1)$ of Eq. (1.1), and in calculating the charge density, then Eq. (1.3) represents an exact result, including all

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exchange terms. The total electrostatic energy of the system of course includes in addition to (1.3) the interactions between electrons and nuclei, which can be computed from the charge density $\rho(x_1)$ alone, and the interactions between pairs of nuclei.

We have now seen that there is a straightforward method in principle for setting up a self-consistent field calculation for any atomic or molecular system. We set up the potential $V_e(x) + V_n(x)$, using Eq. (1.1) for $V_e(x)$. We solve Schrödinger's equation for the one-electron orbitals in this potential field. By general properties of Schrödinger's equation, these orbitals form a complete orthogonal set. We form from them a complete set of antisymmetrized products of n one-electron functions, and set up and solve the secular problem involved in finding those linear combinations of antisymmetrized products which make the energy of the n -electron system stationary. One of the resulting solutions represents the state of the system in which we are particularly interested. We then take the antisymmetric wave function U representing this state, formed as a sum of the antisymmetrized products, and insert it in Eq. (1.1), to find a new V_e . Our condition of self-consistency implies that this final V_e should be identical with the original value.

The one-electron orbitals which we have obtained in this way are what are usually called molecular orbitals. Most writers, for instance Lennard-Jones⁽⁶⁾ and Roothaan,⁽⁷⁾ have derived molecular orbitals from the Hartree-Fock method. On account of the involved nature of this method, their discussions are necessarily somewhat complicated. In contrast, the present method, setting up a unique potential and Schrödinger equation of the usual sort, of which the molecular orbitals are eigenfunctions, makes a discussion much simpler. For instance, the potential V_e will usually have the same symmetry as the nuclear system, so that the application of the group theory to the discussion of the symmetry properties of the molecular orbitals follows very straightforwardly. Another advantage of the present method is that it gives us an infinite set of orbitals, in a much more direct way than the Hartree-Fock method, and the configuration interaction gives us (in principle) an infinite number of solutions, representing excited configurations. Since the one-electron orbitals are not chosen to make the problem self-consistent for these excited configurations, the process will presumably not converge as rapidly for these other configurations as for the ground state (if, as usual, it is the ground state which is made self-consistent), but the calculation of these excited configurations is on as firm a theoretical basis as that of the ground state.

The procedure which we have outlined is of course an idealized one which could never be carried through in practice, since we can neither solve the one-electron Schrödinger problem exactly to get the one-electron orbitals, nor carry out exactly the problem of configuration interaction. In an actual case, then, one must compromise, and our general discussion has been more with the aim of suggesting an ideal toward which one may aim in the calculation, than with the hope that it can represent a practicable program. We should ordinarily set up approximate solutions of the self-consistent problem in the form of linear combinations of atomic orbitals. We then note the following situation. If we are using a finite and very

(A GENERALIZED SELF-CONSISTENT FIELD METHOD)

limited set of orbitals, and are solving the configuration interaction problem between all configurations which can be set up from these orbitals, as Meckler did in the work referred to, then we can equally well set the problem up in terms of any linear combinations of the orbitals. As Meckler has pointed out, the final results will be independent of what linear combinations we use. In such a case, it is useless extra labor to find those combinations of our orbitals which best represent solutions of the self-consistent field problem. This is the special case, for a limited number of orbitals, of the general statement that if we are completely solving the problem of configuration interaction, it makes no difference what complete orthogonal set of one-electron orbitals we use.

The difficulty with Meckler's procedure, however, is that as the number of electrons and orbitals goes up, the number of interacting configurations increases enormously. In such a case we can obviously handle interaction only between a limited number of configurations, normally those of lowest diagonal energy, and with largest non-diagonal matrix components of energy connecting them with the ground state. We may expect that in such problems, if we are using all configurations arising from N orbitals, then our results will be the more accurate, the more accurately we can write the N lowest molecular orbitals of the self-consistent field problem as linear combinations of these N orbitals. Our aim in setting up linear combinations of atomic orbitals, or other methods of setting up one-electron orbitals, must then be to have a set of unperturbed one-electron functions capable of approximating the lowest N molecular orbitals as accurately as possible.

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J. C. Slater

2. THE WATER MOLECULE

Calculations have been started on the wave functions for the water molecule including configuration interaction. The nuclear framework of the water molecule has the symmetry C_{2v} . Using 1s wave functions for the hydrogen and 1s, 2s, and 2p wave functions for the oxygen, one is able to form 210 determinantal wave functions if the 1s and 2s orbitals of the oxygen are kept filled. They can be divided into systems as follows: 5 quintets, 45 triplets, and 50 singlets. The 50 singlets lead to 18 combinations of determinants that have A_1 symmetry, that is, are completely symmetric. Of these 1 can be described as $O^{--}(H_2)^{++}$, 2 as $O^-(H_2)^+$, 8 as $O(H_2)$, 4 as $O^+(H_2)^-$, and 3 as $O^{++}(H_2)^{-}$. These states, $\psi_1 \dots \psi_{18}$, are given in the form of the table below. The column headings represent one-electron wave functions. The α and β represent conventional spin functions. z is the oxygen $2p_z$ function, where the z axis bisects the H-O-H angle; x is the $2p_x$ -like function; and y is the $2p_y$ -like function, where the plane $y = 0$ contains the nuclei; and s and σ are the 1s and 2s oxygen functions. ϕ_o is the sum of hydrogen functions made orthogonal to s , σ , and z , and ϕ_x is the difference of the two hydrogen functions made orthogonal to x . This gives an orthonormalized set of one-electron functions. Each row in the table represents a determinant, i. e., the first row represents a determinant whose diagonal element is $y(1) \alpha(1) y(2) \beta(2) z(3) \alpha(3) z(4) \beta(4) x(5) \alpha(5) x(6) \beta(6) s(7) \alpha(7) s(8) \beta(8) \sigma(9) \alpha(9) \sigma(10) \beta(10)$, a state being represented by a sum of determinants, the coefficients in this sum preceding the row.

In terms of these states the valence bond wave function (non-normalized) is given by

$$\psi_{V.B.} = \sqrt{12} \cos(\theta_{12}/2) \sin(\theta_{12}/2) \psi_5 + \sin^2(\theta_{12}/2)(\psi_{11} - \psi_{10}) + \cos^2(\theta_{12}/2)(\psi_8 - \psi_9)$$

where θ_{12} is the H-O-H angle. It may be interesting to compare the energy of this state with the final solution to the problem.

Among these 18 states there are 114 non-vanishing matrix elements of the spin-free Hamiltonian operator. These matrix elements have been expressed in terms of the orbitals given above but will not be recorded here. They involve, besides one electron integrals, one-, two-, and three-center integrals of the interelectronic interaction. These integrals will be calculated by the method of Löwdin,⁽¹⁾ using the Hartree-Fock wave functions of oxygen⁽²⁾ for our one-electron orbitals. The convergence of this method for three-center integrals was tested on the typical integral $\iint s_A(1) s_B(1) 1/r_{12} [\sigma(2)]^2 d\tau_1 d\tau_2$ for $R(O-H) = 2$ atomic units. This integral can be expressed as an infinite series of which the first four terms are

$$c \left\{ .405 + .152 P_1(\cos \theta_{12}) + .0340 P_2(\cos \theta_{12}) + .0144 P_3(\cos \theta_{12}) \right\}.$$

The convergence appears to be rapid. For certain details of the expansions necessary for evaluating this integral, see the section of this Quarterly Progress Report by Corbato, Koster, and Schweinler.

Calculations on the energy of the water molecule will be carried out as a function of

(THE WATER MOLECULE)

Table 2-1

State	Coefficient	ya	yβ	za	zβ	φ _O ^a	φ _O ^β	xa	xβ	φ _X ^a	φ _X ^β	sa	sβ	σa	σβ
ψ ₁		1	2	3	4			5	6			7	8	9	10
ψ ₂	1/√2	1	2	3			4	5	6			7	8	9	10
	-1/√2	1	2		3	4		5	6			7	8	9	10
ψ ₃	1/√2	1	2	3	4			5			6	7	8	9	10
	-1/√2	1	2	3	4				5	6		7	8	9	10
ψ ₄	1/2	1	2	3		4			5		6	7	8	9	10
	1/2	1	2		3		4	5		6		7	8	9	10
	-1/2	1	2		3	4		5			6	7	8	9	10
	-1/2	1	2	3			4		5	6		7	8	9	10
ψ ₅	2/√12	1	2	3			4	5			6	7	8	9	10
	2/√12	1	2		3	4			5	6		7	8	9	10
	-1/√12	1	2	3		4			5		6	7	8	9	10
	-1/√12	1	2		3		4	5		6		7	8	9	10
	-1/√12	1	2		3	4		5			6	7	8	9	10
	-1/√12	1	2	3			4		5	6		7	8	9	10
ψ ₆				1	2			3	4	5	6	7	8	9	10
ψ ₇				1	2	3	4	5	6			7	8	9	10
ψ ₈		1	2	3	4					5	6	7	8	9	10
ψ ₉		1	2	3	4	5	6					7	8	9	10
ψ ₁₀		1	2					3	4	5	6	7	8	9	10
ψ ₁₁		1	2			3	4	5	6			7	8	9	10
ψ ₁₂	1/√2	1	2	3			4			5	6	7	8	9	10
	-1/√2	1	2		3	4				5	6	7	8	9	10
ψ ₁₃	1/√2	1	2			3	4	5			6	7	8	9	10
	-1/√2	1	2			3	4		5	6		7	8	9	10
ψ ₁₄	1/√2			1	2	3	4	5			6	7	8	9	10
	-1/√2			1	2	3	4		5	6		7	8	9	10
ψ ₁₅	1/√2			1			2	3	4	5	6	7	8	9	10
	-1/√2				1	2		3	4	5	6	7	8	9	10
ψ ₁₆		1	2			3	4			5	6	7	8	9	10
ψ ₁₇						1	2	3	4	5	6	7	8	9	10
ψ ₁₈				1	2	3	4			5	6	7	8	9	10

(THE WATER MOLECULE)

internuclear distance and bond angle. Since the integrals which appear are closely related to those in the OH molecule, we shall carry out a calculation of the energy of this molecule simultaneously.

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G. F. Koster, H. C. Schweinler

3. THEORY OF MOLECULAR OXYGEN

An article covering the work on molecular oxygen is being prepared for publication, to appear most likely in the Journal of Chemical Physics. The numerical material (integrals, matrix elements, eigenvectors) will be compiled into a Technical Report of this Group.

In the way of tying up loose ends: it will be remembered that the ground state energy curve showed a hump. This came about from the behavior of the Morse curve which was fitted to the calculated points at small internuclear distances. This Morse curve, although it yielded splendid values for the binding energy and the vibration frequency, rose to a value of 6.91 e. v. at infinite separation rather than zero. Our picture of the true energy curve, therefore, was one which started from the axis at infinite separation, moved above the axis to a maximum at about $R = 4.0$ a. u., and then descended along the Morse curve. (The $R = 4.0$ point was found by calculation to lie above the zero line.) We have tried to find experimental evidence of this hump but there doesn't seem to be any clear-cut way of exhibiting it -- or denying it. As we've said, the vibrational levels come in the right places but they haven't been observed high enough so that the hump would have any unique effect. However, it seems that other people have considered an energy curve which extrapolates to a positive height at infinite separation -- Pauling for one.

Pauling⁽¹⁾ has been led to the concept of the valence-state of an atom, a hypothetical state which is not "one of the stationary spectroscopic states of the isolated atoms, but . . . is defined as that state in which it (the atom) has the same electronic structure as it has in the molecule." In the paper referred to, Pauling deduces the value of the energy of this state by four different methods all of which agree reasonably well with one another. One of the methods is an extrapolation of the vibrational levels, the introduction of a Morse curve which goes to 6.69 e. v. at infinite separation. We have not been able to do more with this concept of the valence-state but the fact that it has been introduced lends credence to the hump, or vice versa.

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A. Meckler

4. SCATTERING OF NEUTRONS BY O_2^{16}

For use in interpreting diffraction experiments a calculation is under way to determine the differential scattering cross-section of slow neutrons on paramagnetic O_2^{16} gas in Born approximation. ^(1, 2, 3) The neutron- O_2 interaction Hamiltonian takes account of the nuclear-type interaction between the neutron and the two oxygen nuclei, and also the interaction between the neutron magnetic moment and both the magnetic moments and the charge motion ⁽⁴⁾ of the O_2 electrons. It is planned to use Meckler's ground state O_2 electronic wave function ⁽⁵⁾ in evaluating matrix elements.

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W. H. Kleiner

5. CONFIGURATION INTERACTION IN HYDROGEN FLUORIDE

The hydrogen fluoride molecule is being treated as a preliminary to a study of the bifluoride ion $(\text{FHF})^-$ which is the simplest system exhibiting the phenomenon of hydrogen bonding. The hydrogen bond occurs very widely in chemical systems, but very little is known of its fundamental nature.

The ground state wave functions for hydrogen fluoride are formed by assigning the ten electrons to the hydrogen $1s$ orbital and fluorine $1s$, $2s$, $2p_0$, $2p_+$, and $2p_-$ orbitals in such a manner that the resulting determinantal wave functions belong to the $^1\Sigma^+$ (totally symmetrical) representation of $C_{\infty v}$, and correspond to singlet states. In all of these configurations the fluorine $1s$ and $2s$ orbitals remain filled. These restrictions result in a total of four configurations for the ground state.

Hartree-Fock wave functions have been chosen for the fluorine atomic orbitals. ⁽¹⁾ The only atomic orbital which is not orthogonal to all others in the molecule is the hydrogen $1s$; this is orthogonalized by adding appropriate amounts of the fluorine $1s$, $2s$, and $2p_0$ functions. The required integrals are being evaluated numerically, and the two-center integrals are evaluated by expanding the hydrogen $1s$ orbital in spherical harmonics about the fluorine nucleus, a method due to Coulson. ⁽²⁾

The electronic energy is being calculated at internuclear separations of 1.50, 1.65, 1.75 (equilibrium value), 1.85, 2.00, 5.00, and 7.50 atomic units.

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R. E. Merrifield

6. THEORY OF THE S_8 MOLECULE

An investigation of the electronic structure of the S_8 molecule is in its initial stages. Interest in the problem stems from the resemblance of the S_8 molecule to a linear solid with periodic boundary conditions in which there also is valence bonding between neighboring atoms. It is hoped that the present study will reveal some of the characteristics of valence bonding in periodic structures and thus furnish some hints as to the treatment of diamond, germanium and other crystals in which valence bonding is dominant.

The eight sulfur atoms of the molecule are situated at the corners of two squares of side 3.4 \AA whose planes are parallel and separated by 1.15 \AA .⁽¹⁾ The centers of the squares lie on a line perpendicular to their planes and corresponding sides of the squares make angles of 45° with each other. Briefly, the sulfur atoms define a puckered octagon.

The initial plan of doing a configuration interaction between all states completely symmetric under the group of operations of the S_8 molecule and having total spin equal to zero, similar to the treatment of the H_2O molecule being carried out by Koster and Schweinler,⁽²⁾ was abandoned when a rough numerical estimate indicated that even if only 3p atomic states were considered partially occupied (3s states and all states having $n < 3$ were left completely filled), the resulting secular equation would have about 10^9 rows and columns. The further omission of all states in which any atoms are ionized would not improve the situation significantly.

The large number of states that must be taken into account in the straightforward solution of this relatively simple problem of 8 identical atoms makes it apparent that some further drastic approximation must be made in order that many-atom problems be tractable. The compromise with reality that has been accepted, at least for a first treatment of the ground state of the S_8 molecule, is a single determinant wave function using as one-electron functions the "equivalent orbitals" whose virtues have recently been expounded by Lennard-Jones and his co-workers.⁽³⁾ An advantage of this scheme is that the equivalent orbitals can be transformed into molecular orbitals without changing the value of the determinantal wave function. We will thus be able to see what molecular orbital combinations occur in a state based on the intuitive idea of localized bonds, an idea which has been used so successfully in the interpretation of the structure of many complex molecules.

The determination of the equivalent orbitals and molecular orbitals is now under way. The symmetry group of the S_8 molecule has been analyzed and its seven irreducible representations (four one-dimensional and three two-dimensional) have been found. The symmetry orbitals⁽³⁾ composed of atomic s and p functions have been constructed. From these the molecular orbitals will be determined by solving secular equations (one per representation) between sets of symmetry orbitals each of which forms a basis for the representation being considered. Equivalent orbitals will then be constructed by the methods indicated in the series of papers of Ref. 3.

(THEORY OF THE S₈ MOLECULE)

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H. Kaplan

7. CONFIGURATION INTERACTION APPLIED TO THE HYDROGEN MOLECULE

In the last Progress Report we discussed the solution of the hydrogen molecule problem using M. O. constructed of L. C. A. O. In this basis several main diagonal elements of the final fourteen-by-fourteen secular equation have been set up.

We are now following a procedure similar to that employed by Green, Ufford et al.⁽¹⁾ to test the speed of convergence of the finite sum of determinants to the correct wave function. Specifically, we are utilizing the very precise function found by James and Coolidge⁽²⁾ $\psi_{J.C.}$ and performing the integrations

$$c_i \equiv (D_i, \psi_{J.C.}) \quad i=1, 2 \dots 14$$

where D_i are the 2 x 2 determinants built up of our M. O. The completeness relation requires that

$$\sum_{c=1}^{\infty} c_i^2 = 1$$

By this method we can find not only the relative weights of the terms included, but the importance of all those ignored.

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E. Callen

8. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

Calculation of the electric quadrupole interaction in the KCl molecule is in progress. Recently, Fabricand, Carlson, Lee, and Rabi⁽¹⁾ have obtained the quadrupole coupling constants for K³⁹ and Cl³⁵ in the KCl molecule and the present calculation is directed at evaluation of that part of this constant which depends on the molecular charges outside the nucleus. It is further hoped that this determination will serve to test the hypothesis of Logan, Coté, and Kusch⁽²⁾ that this part is positive for both K and Cl in KCl.

The general theory for the interaction between a nuclear quadrupole moment and molecular electric fields has been given by Casimir.⁽³⁾ The appropriate term in the Hamiltonian is:

$$H(\bar{I}, \bar{J}) = 2eQ \left\{ \sum e(3 \cos^2 \theta - 1)/r^3 \right\}_{Av.} F(\bar{I}, \bar{J}) \quad (8.1)$$

where

$$F(\bar{I}, \bar{J}) = \frac{3(\bar{I} \cdot \bar{J})^2 + \frac{3}{2}(\bar{I} \cdot \bar{J}) - I(I+1)J(J+1)}{2J(2J-1)2I(2I-1)}$$

e = electronic charge

Q = quadrupole moment of nucleus

r = radius vector from nucleus to individual molecular charge

θ = angle between r and a space fixed axis

\bar{I} = nuclear spins in units of $h/2\pi$

\bar{J} = angular momentum caused by molecular rotation in units of $h/2\pi$.

The average in Eq. (8.1) is taken over the normal electronic state, the appropriate vibrational state, and the rotational state for which $M_J = J$. Nordsieck has shown⁽⁴⁾ that for a diatomic molecule Eq. (8.1) may be written:

$$H(\bar{I}, \bar{J}) = eqQ - \left(\frac{2J}{2J+3} \right) F(\bar{I}, \bar{J})^{(5)} \quad (8.2)$$

where

$$q = \frac{\partial^2 V}{\partial z^2} = \frac{2e}{R^3} - \left[\int \rho(r, \theta') \frac{3 \cos^2 \theta' - 1}{r^3} d\tau \right]_{Av.} \quad (8.3)$$

$$= 2e \left\{ \frac{1}{R^3} - \frac{1}{2} \sum_k \int |\psi(r_1 \theta'_1, r_2 \theta'_2, \dots, r_n \theta'_n)|^2 \left(\frac{3 \cos^2 \theta' - 1}{r^3} \right)_k d\tau_{1,2, \dots, n} \right\}$$

V = electrostatic potential produced by all charges except those inside a small sphere surrounding the nucleus

z = coordinate along the molecular axis

θ' = angle made by the radius vector r and the internuclear axis

(NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE)

R = internuclear distance

ρ = electron charge density

The average in Eq. (8.3) is to be taken over the zero-point vibration of the molecule. The coupling constant mentioned earlier is defined as eqQ and it is this quantity which is obtained from experimental results. Kellogg, Rabi, Ramsey, and Zacharias⁽⁶⁾ have pointed out that unlike the atomic case there is no empirical information like fine structure splitting from which the molecular q can be evaluated. The aim of the present investigation is the choice of an appropriate wave function, ψ , and the calculation of q using this ψ .

Since K^+ and Cl^- both have closed shells the wave function for KCl can be satisfactorily set up as a single determinant. This determinant is to be built up from Hartree-Fock atomic wave functions calculated by Hartree and Hartree for the $K^{+(7)}$ and $Cl^{-(8)}$ ions. Townes and Dailey have shown that, "Bonds of most of the alkali halides show less than three percent true covalent character and the molecules should be considered primarily ionic with a considerable amount of polarization of each ion."⁽⁹⁾ Thus aside from polarization effects this single determinant should be a good approximation to the ground state wave function. It is expected that later the polarization effect will be taken into account by parametric means within the framework of the single determinant.

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L. C. Allen

9. ENERGY BANDS IN CHROMIUM

As has been reported in the previous two Progress Reports, an attempt has been made to expand the crystal potential in terms of spherical harmonics. Completely independent of the question of the convergence of such an expansion, great difficulty has been met in attempting to evaluate the coefficients in the expansion. This difficulty results from the very great loss in number of significant figures, which occurs in the process of carrying out the numerical calculations involved in evaluating the coefficients.

At present, a different approach is being made to the problem of evaluating three-center potential energy integrals. As before, the crystal potential is taken as a spacial sum of atomic potentials, but the atomic potential is now represented by a function which vanishes for radial distances greater than one-half the nearest-neighbor distance in the crystal. Because of this approximation, three-center integrals (involving two atomic wave functions on two different lattice sites and an atomic potential on a third lattice site) will vanish unless both of the wave functions are 3d wave functions. (Here we are not considering integrals for the 4s electrons involving orthogonalized plane waves.) The assumption will also be made that a 3d wave function overlaps only nearest- and next-nearest-neighbor lattice sites. It can now easily be shown that the number of three-center integrals which need to be independently evaluated is less than 175.

The tail of a 3d wave function in chromium can be accurately represented by

$$r P_2^{lm}(\cos \theta) e^{im\phi} e^{-ar},$$

where $a = 1.3785$. In order to expand each 3d wave function in terms of spherical harmonics about the center containing the atomic potential, we will treat the wave function as a product of

$$r^2 P_2^{lm}(\cos \theta) e^{im\phi}$$

(which can be expanded in closed form about another center) multiplied by e^{-ar}/r (the expansion of which is given in Watson, Theory of Bessel Functions, p. 366). The expansion of e^{-ar}/r in spherical harmonics about another center is probably easier than is the case for any other simple function involving exponentials.

R. H. Parmenter

10. A SIMPLE MODEL OF FERROMAGNETISM⁽¹⁾

The theory of ferromagnetism has been essentially based on two approximations: the band model and the Heitler-London treatment. It is not the purpose of this report to compare these two approximations. There is a comprehensive treatment by J. C. Slater⁽²⁾ in which the advantages and disadvantages of the two methods are clearly pointed out. It seems obvious that the band treatment is superior in many respects to the Heitler-London approximation. But there is no question that both theories are incomplete. This results mainly from a lack of more detailed knowledge of the solutions of the Schrödinger equation in a ferromagnetic crystal.

In order to get more insight into this involved problem we try to look upon the interaction of only two electrons. We are especially interested in the conditions under which the two electrons set their spins parallel or antiparallel. Because of the simplicity of this case we may hope to get more accurate solutions than in the collective treatments of the many-body problem. Those more correct solutions may show the way to correct and integrate the already existing theories of ferromagnetism.

Our procedure is straightforward. We start with the problem of two electrons in free space and proceed to the case of two electrons moving in an otherwise empty energy band. Finally one can consider a doubly degenerate band instead of a single one. By this procedure we take into account the fact that there are always degenerate bands in ferromagnetic crystals.

G. F. Koster⁽³⁾ has pointed out, as one would expect, that the case of two holes is identical with our treatment in its substantial features.

Two Electrons in Free Space

In this section we are trying to get solutions of the Schrödinger equation for the motion of two electrons in their repulsive field. If the electrons move in the unbounded space they will repel each other and keep an infinite distance apart; the energy spectrum will be continuous. There will be no measurable correlation of spins of the two particles. In order to get a discrete spectrum one has to set up some kind of boundary condition. The most natural way is to put both electrons in a box. (We shall show below that there are mathematically more convenient boundary conditions, the physical interpretation of which is somewhat more involved.)

It is very instructive to consider first the one-dimensional case. The two electrons may move on the x-axis from $-\pi/2$ to $+\pi/2$. The Schrödinger equation of their motion

$$\frac{d^2 \psi}{dx_1^2} + \frac{d^2 \psi}{dx_2^2} + (E - V_{12}) \psi = 0 \quad (10.1)$$

may be interpreted as the vibration of a membrane with variable mass confined by a square-sided frame (see Fig. 10-1). Because of the antisymmetry principle we know that the wave

(A SIMPLE MODEL OF FERROMAGNETISM)

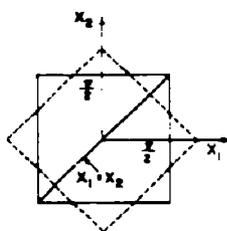


Fig. 10-1

functions of coordinates only will be symmetric with respect to interchange of x_1 and x_2 in the case of the singlet and antisymmetric in the case of the triplet. So the corresponding vibrations of the membrane must have a node along the line $x_1 = x_2$ for the case of the triplet and must not have one for the singlet. If one is considering the case without interaction, i. e. $V_{12} = 0$, then the solutions of the problem are well known. The lowest singlet and triplet states are

$$\begin{aligned} \psi_{\text{singlet}} &= \cos x_1 \cos x_2, \\ E_{\text{singlet}} &= 2; \\ \psi_{\text{triplet}} &= \cos x_1 \sin 2x_2 - \cos x_2 \sin 2x_1, \\ E_{\text{triplet}} &= 5. \end{aligned} \tag{10.2}$$

In this case the singlet state has lower energy. We must now ask whether the interaction V_{12} can produce an interchange in the order of the energies of the singlet and triplet state. With respect to such an interchange the most effective form of an interaction potential is a δ -function in the coordinates of $x_1 - x_2$. This potential raises the energy of the singlet state only and leaves the triplet function unchanged. One can show that the energies of the two states approach each other when the magnitude of the δ -function increases. In going to the limit of an infinite δ -function the two energies will coincide but never cross. One can find this by a simple geometric consideration.⁽⁴⁾ The increasing δ -function will make the amplitude of the symmetric vibration go to zero along the line $x_1 = x_2$. We therefore have the same solution in the singlet and triplet case except for the different sign of the amplitude in the two triangles separated by $x_1 = x_2$. From this one may conclude that for every form of the interaction potential the singlet will lie below the triplet.

If one rotates the frame with respect to the membrane by 45° then the differential equation (10.1) becomes separable in the center of gravity $x_1 + x_2$ and the relative coordinates $x_1 - x_2$. The singlet and triplet states are now connected with the symmetry properties of the solution of the equation in the relative coordinates. The symmetric and antisymmetric solutions with respect to the origin correspond now to the singlet and triplet states respectively. The solution of the whole problem is the product of the solutions of the two separated differential equations, the total energy is the sum of the two eigenvalues. For a fixed eigenstate of the movement of the center of gravity the whole problem reduces to finding the lowest eigenvalue of the solution in the relative coordinates. In the one-dimensional case we know from the oscillation theorem that the nodeless solution lies lowest. So in this modified problem we get the same result as above: the singlet state has the lowest energy.

The rotated frame no longer corresponds to the simple boundary condition of two electrons moving between $-\pi/2$ and $+\pi/2$ of the x axis. We have now independent boundary

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conditions for the movement of the center of gravity and the relative movement of the two electrons. This allows us to study separately the interaction of two electrons. By our modified boundary conditions we introduce a maximum distance between the two electrons which they cannot exceed but below which they can move unrestrictedly. If the two electrons move in a box, these idealistic boundary conditions become mixed up with the movement of the center of gravity. If, for example, the center of gravity is near the wall of the box the two electrons cannot get more than a relative small distance apart because they are hindered by the box. That is the geometrical reason for the complexity of the original solutions. Yet it seems obvious that the essential features of the interaction of two electrons are inherent in the simplified treatment.

The three-dimensional Schrödinger equation

$$\left(-\nabla_1^2 - \nabla_2^2 + \frac{2}{r_{12}} - E\right)\psi(\vec{r}_1, \vec{r}_2) = 0 \quad (10.3)$$

can correspondingly be separated in equations for the center of gravity and relative coordinates. Calling $\vec{r}_1 + \vec{r}_2 = \vec{u}$ and $\vec{r}_1 - \vec{r}_2 = \vec{v}$, we get

$$\begin{aligned} (-2\nabla_u^2 - E_u)\psi(\vec{u}) &= 0 \\ (-2\nabla_v^2 + \frac{2}{v} - E_v)\psi(\vec{v}) &= 0 \end{aligned} \quad (10.4)$$

with $\psi(\vec{v}_1, \vec{v}_2) = \psi(\vec{u})\psi(\vec{v})$ and $E = E_u + E_v$. By using the same kind of simplified boundary conditions in \vec{v} space we are led to the problem of solving the Schrödinger equation of a repulsive field in a spherical box. The potential in that problem as a function of v is shown in

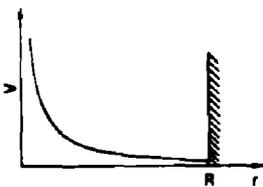


Fig. 10-2

Fig. 10-2. Because of the antisymmetry principle the wave function of coordinates only must again be symmetric or antisymmetric with respect to interchange of \vec{r}_1 and \vec{r}_2 for the singlet and triplet respectively. $\psi(\vec{u})$ is always symmetric and we can therefore conclude that $\psi(\vec{v})$ must be symmetric with respect to the origin for the singlet and antisymmetric for the triplet. Because of the spherical symmetry of the problem, the solutions $\psi(\vec{v})$ can be written as a product of a radial function and a spherical harmonic, characterized by a lower index l . All functions

belonging to even values of l correspond to singlets, those belonging to odd values of l to triplets. H. C. Schweinler has given a general proof that for every type of spherically symmetric field the lowest eigenvalue will belong to a solution with $l = 0$ (see Appendix). We find here again the result that the singlet state has the lowest energy.

Two Electrons in an Otherwise Empty Band

In this section we proceed in a similar manner as in the treatment in free space. The essential difference in the solution is that the wave function around each nucleus will

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have atomic-like character. So we make the assumption

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{i, j} U(\vec{R}_i, \vec{R}_j) \left\{ a(\vec{r}_1 - \vec{R}_i) a(\vec{r}_2 - \vec{R}_j) \pm a(\vec{r}_2 - \vec{R}_i) a(\vec{r}_1 - \vec{R}_j) \right\} \quad (10.5)$$

in which the symbol $a(\vec{r} - \vec{R})$ is used for a Wannier function⁽⁵⁾ around atom \vec{R} . The symmetry or antisymmetry with respect to interchange of coordinates is taken into account by a proper linear combination of Wannier functions. The plus sign in (10.5) belongs to the singlet and the minus sign to the triplet. One can show that $U(\vec{R}_i, \vec{R}_j)$ also has symmetry properties with respect to interchange of \vec{R}_i and \vec{R}_j : $U(\vec{R}_i, \vec{R}_j)$ is symmetric for the singlet and antisymmetric for the triplet. We shall prove this property for the triplet. Let us assume $U(\vec{R}_i, \vec{R}_j)$ to be symmetric. We rewrite the sum (10.5) by collecting together the terms multiplied by $U(\vec{R}_i, \vec{R}_j)$ and $U(\vec{R}_j, \vec{R}_i)$. Because the Wannier term in (10.5) is antisymmetric with respect to interchange of \vec{R}_i and \vec{R}_j these two terms cancel each other and the whole sum will vanish. From this one can conclude $U(\vec{R}_i, \vec{R}_j)$ must be antisymmetric for the triplet. A similar proof holds for the singlet.

The Hamiltonian of the problem has the form

$$H = H_1 + H_2 + \frac{2}{r_{12}} \quad (10.6)$$

where H_1 and H_2 are the one-electron Hamiltonians for the movement of one electron in the crystalline field.

We now insert the assumption (10.5) in the Schrödinger equation and multiply the whole expression by $a^*(\vec{r}_1 - \vec{R}_m) a^*(\vec{r}_2 - \vec{R}_n)$ and integrate over r_1 and r_2 . Using a theorem derived by G. F. Koster⁽⁶⁾ one gets after some algebraic manipulation the following expression.

$$\begin{aligned} & \sum_s U(\vec{R}_m - \vec{R}_s, \vec{R}_n) \mathcal{E}(\vec{R}_s) + \sum_{s'} U(\vec{R}_m, \vec{R}_n - \vec{R}_{s'}) \mathcal{E}(\vec{R}_{s'}) \\ & + \sum_{k, l} U(\vec{R}_m - \vec{R}_k, \vec{R}_n - \vec{R}_l) \int a^*(\vec{r}_1 - \vec{R}_m) a^*(\vec{r}_2 - \vec{R}_n) \frac{2}{r_{12}} \\ & a(\vec{r}_1 - \vec{R}_m + \vec{R}_k) a(\vec{r}_2 - \vec{R}_n + \vec{R}_l) d\tau_1 d\tau_2 - EU(\vec{R}_m, \vec{R}_n) = 0 \end{aligned} \quad (10.7)$$

In this equation $\mathcal{E}(\vec{R})$ are the Fourier components in the expansion of the energy as a function of momentum. The energy as a function of momentum is periodic in reciprocal space. The expansion coefficients can therefore be associated with lattice points in real space. E is the total energy. For each value of m and n there is such an equation. The mathematical problem of solving these equations is involved. By introducing differential operators one

can simplify the problem considerably. By proceeding in a similar way as in the paper by J. C. Slater⁽⁷⁾ on perturbed lattice functions we get

$$\begin{aligned} & (E(\vec{p}^{(1)}) + E(\vec{p}^{(2)})) U(\vec{R}_m^{(1)}, \vec{R}_n^{(2)}) \\ & + \sum_{k,l} U(\vec{R}_m - \vec{R}_k, \vec{R}_n - \vec{R}_l) \int a^*(\vec{r}_1 - \vec{R}_m) a^*(\vec{r}_2 - \vec{R}_n) \frac{2}{r_{12}} \\ & a(\vec{r}_1 - \vec{R}_m + \vec{R}_k) a(\vec{r}_2 - \vec{R}_n + \vec{R}_l) d\tau_1 d\tau_2 - EU(\vec{R}_m, \vec{R}_n) = 0 \end{aligned} \quad (10.8)$$

In our notation $E(\vec{p}^{(1)})$ and $E(\vec{p}^{(2)})$ are to be considered as operators. In the expression for the energy as a function of \vec{p} one has to replace \vec{p} by its operator $(\hbar/i)\nabla$. The superscripts indicate that $\vec{p}^{(1)}$ and $\vec{p}^{(2)}$ act on $\vec{R}^{(1)}$ and $\vec{R}^{(2)}$ respectively.

For the case of slightly overlapping Wannier functions we can replace the summation in (10.8) by its leading term characterized by $\vec{R}_k = \vec{R}_l = 0$. The summation has approximately the value $2/|\vec{R}_m - \vec{R}_n|$ (omitting a factor $U(\vec{R}_m, \vec{R}_n)$) except for the case $\vec{R}_m = \vec{R}_n$. This term gives the interaction energy of two electrons on the same atom. One can show that even for Wannier functions with greater overlap the summation in (10.8) defines a potential which is practically the same for the singlet and triplet type solution. (If we solved the problem of free electrons by using Wannier functions we would have maximum overlap. Yet we know from the direct solution that even this amount of overlap will not destroy the result derived below.) Thus we have the following differential equation for $U(\vec{R}^{(1)}, \vec{R}^{(2)})$:

$$\{E(\vec{p}^{(1)}) + E(\vec{p}^{(2)})\} U(\vec{R}^{(1)}, \vec{R}^{(2)}) + \{V(R^{(1)} - R^{(2)}) - E\} U(\vec{R}^{(1)}, \vec{R}^{(2)}) = 0 \quad (10.9)$$

Using now a quadratic approximation for the energy as a function of p the equation (10.9) is identical to (10.3). One can then use the same kind of argument to show that the singlet state has lower energy.

Two Electrons in a Doubly Degenerate Band

We assume here that one electron is moving in one band and the other one in the other band. There are now two types of Wannier functions $a(\vec{r} - \vec{R})$ and $b(\vec{r} - \vec{R})$, each belonging to one band. The expression (10.5) can easily be generalized to

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{i,j} U(\vec{R}_i, \vec{R}_j) \{a(\vec{r}_1 - \vec{R}_i) b(\vec{r}_2 - \vec{R}_j) \pm a(\vec{r}_2 - \vec{R}_i) b(\vec{r}_1 - \vec{R}_j)\} \quad (10.10)$$

The plus sign in (10.10) holds for the singlet, the minus sign for the triplet. Our proof of the last section concerning the symmetry or antisymmetry of $U(\vec{R}_i, \vec{R}_j)$ in the cases of the

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singlet and triplet respectively turns out to fail in (10.10). Singlets and triplets can be both symmetric and antisymmetric. The physical meaning of this result is obvious. In the last section we found $U(\vec{R}_l, \vec{R}_l)$ to be zero in the triplet case. Two electrons with the same spin could not stay on the same atom because of the exclusion principle. In this section there are two possible quantum states per atom so that now two electrons with the same spin can be found on a certain atom. By using the same kind of calculation as in the preceding section we finally arrive at the following equation

$$\begin{aligned}
 & \left\{ E_a(\vec{p}^{(1)}) + E_b(\vec{p}^{(2)}) \right\} U(\vec{R}_m^{(1)}, \vec{R}_n^{(2)}) \\
 & + \sum_{l, k} U(\vec{R}_m - \vec{R}_l, \vec{R}_n - \vec{R}_k) \int a^*(\vec{r}_1 - \vec{R}_m) b^*(\vec{r}_2 - \vec{R}_n) \\
 & \frac{2}{r_{12}} \left\{ a(\vec{r}_1 - \vec{R}_m + \vec{R}_l) b(\vec{r}_2 - \vec{R}_n + \vec{R}_k) \right. \\
 & \left. \pm a(\vec{r}_2 - \vec{R}_m + \vec{R}_l) b(\vec{r}_1 - \vec{R}_n + \vec{R}_k) \right\} d\tau_1 d\tau_2 \\
 & - EU(\vec{R}_m, \vec{R}_n) = 0
 \end{aligned} \tag{10.11}$$

The plus and minus sign in the summation holds for the singlet and triplet state respectively. The meaning of the summation is most easily seen by assuming that we have non-overlapping Wannier functions. The summation then reduces to $2/|\vec{R}_m - \vec{R}_n|$ (omitting a factor $U(\vec{R}_m, \vec{R}_n)$) except for the case $\vec{R}_m = \vec{R}_n$. This term gives for the minus and plus sign the interaction energy of two electrons on the same atom with or without exchange respectively. So we are left with a different interaction term $V(\vec{R}_m - \vec{R}_n)$ in the singlet and triplet case. The interaction energy is about the same for $\vec{R}_m \neq \vec{R}_n$ but is smaller for $\vec{R}_m = \vec{R}_n$ in the case of the singlet. Because both solutions can be either symmetric or antisymmetric with respect to interchange of \vec{R}_m and \vec{R}_n we can conclude that the state with the lower interaction energy, that is the triplet, must always lie lowest. In the case of two degenerate bands two electrons tend to align their spins.

Conclusions

By a straightforward calculation we found that two electrons in free space or in a single otherwise empty band will tend to set their spins antiparallel. If there are two degenerate bands of equal width then the two electrons will align their spins. The alignment of the spins results from the lowering of the energy when both electrons are on the same atom according to Hund's rule. For the single band there is in the triplet case no such ionic state. The wave function has a node for $\vec{R}^{(1)} = \vec{R}^{(2)}$. Yet it turns out that the gain in Coulombic energy is more than offset by the increase of kinetic energy associated with that node.

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The calculations concerning our model are not yet complete. There is, for example, the case of two degenerate bands of different width. This case may bear the general feature of a degenerate 4s and 3d band. There is some indication that this combination of two bands will not give ferromagnetism. There will be more detail about this question in the next Progress Report.

Appendix

The solution of the Schrödinger equation (10.4) in the relative coordinates v may be written as a product of a radial function $R_\ell(r)$ and a spherical harmonic with lower index ℓ . By assuming $P_\ell(r) = r R_\ell(r)$ we are led to the following differential equation for $P_\ell(r)$

$$P_\ell''(r) + \left\{ \frac{1}{2} E - \frac{1}{2} V_{12}(r) - \frac{\ell(\ell+1)}{r^2} \right\} P_\ell(r) = 0 \quad (\text{A10.1})$$

For $r = 0$, $P_\ell(r)$ has always zero value. Furthermore the solution must vanish for $r = R$ where R is the maximum distance of the two electrons. We wish to show that the solution with $\ell = 0$ has lowest energy. For the proof we assume that a certain state with $\ell \neq 0$ would have an energy E_ℓ which is lower than E_0 . In Fig. 10-3 we plot then the functions $P_0(r)$ and

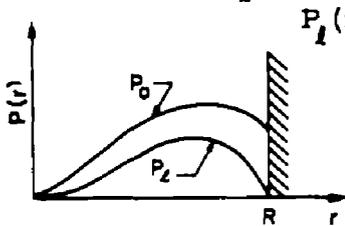


Fig. 10-3

Consider next the differential equations for $P_0(r)$ and $P_\ell(r)$

$$P_0''(r) + \left\{ \frac{1}{2} E_0 - \frac{1}{2} V_{12}(r) \right\} P_0(r) = 0 \quad (\text{A10.2})$$

$$P_\ell''(r) + \left\{ \frac{1}{2} E_\ell - \frac{1}{2} V_{12}(r) - \frac{\ell(\ell+1)}{r^2} \right\} P_\ell(r) = 0$$

We multiply the first by $P_\ell(r)$, the second by $-P_0(r)$ and add. This sum can be written in the form

$$\frac{d}{dr} (P_0'(r) P_\ell(r) - P_\ell'(r) P_0(r)) + \frac{\ell(\ell+1)}{r^2} P_0(r) P_\ell(r) = 0 \quad (\text{A10.3})$$

If we integrate this expression from $r = 0$ to $r = R$ we get

$$P_0(R) P_\ell'(R) = \int_0^R \frac{\ell(\ell+1)}{r^2} P_0(r) P_\ell(r) dr \quad (\text{A10.4})$$

One can see now that this equation is inconsistent with the assumptions in Fig. 10-3. There we have $P_0(R) > 0$, $P_\ell'(R) < 0$ and $\int_0^R \frac{\ell(\ell+1)}{r^2} P_0(r) P_\ell(r) dr > 0$. From this one must conclude that $P_0(r)$ has a node in between and therefore lies lowest.

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References

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2. J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., July 15, 1952, p. 17.
3. G. F. Koster, see p. 31 of this Report.
4. This simple proof is due to J. C. Slater
5. G. H. Wannier, Phys. Rev. 52, 191 (1937).
6. G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., July 15, 1952, p. 41. (To appear in Phys. Rev. 89, January 1, 1953.)
7. J. C. Slater, Phys. Rev. 76, 1592 (1949).

H. Statz

11. THE EQUIVALENCE OF ELECTRONS AND HOLES

We wish to find out here if theorems of the type proved by Statz, in the present Progress Report are equally applicable to two holes in a full band.

Let us assume that we had a one-electron Hamiltonian H which was periodic with respect to translations through R_n and some one-electron wave functions, from a given band, u_i , which are multiplied by $e^{ik_i \cdot R_n}$ when translated through R_n . We could then define a one-electron energy

$$\epsilon(k_i) = \int u_i H u_i d\tau$$

which would describe a band as k_i went over reciprocal space.

Let us now try to solve the problem of two electrons using wave functions from this band. The Hamiltonian will now be

$$H_2 = H(1) + H(2) + \frac{2}{r_{12}}$$

and we shall try to find the singlet and triplet states of this two-electron system. As an approximation we shall seek solutions of the form

$$\Psi_K = \sum_{ij} U_{ij} \left\{ \det \left[u_i(1) \alpha(1) \quad u_j(2) \beta(2) \right] \pm \det \left[u_i(1) \beta(1) \quad u_j(2) \alpha(2) \right] \right\}$$

α and β are the conventional spin functions and the square bracket encloses the diagonal element in the determinant. The upper sign represents the triplet state and the lower sign the singlet. For any two terms in the summation

$$K = k_i + k_j = k_m + k_n,$$

since the two-electron function Ψ_K must multiply by $e^{iK \cdot R_n}$ when transplanted through R_n . From this we conclude that two terms appearing in the sum must differ in both one-electron wave functions in the determinant. The U_{ij} are determined by the condition

$$\int \Psi^* (H - E) \Psi = \min.$$

which yield, the set of simultaneous equations

$$U_{nm} \left[\epsilon(k_n) + \epsilon(k_m) + (mm|nn) \mp (mn|mn) - E \right] + \sum_{\substack{j \neq m \\ j \neq n}} U_{ij} \left[(mi|nj) \mp (mj|ni) \right] \\ m, n = 1 \dots N$$

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Here

$$(m_i | n_j) = 2 \int \frac{u_m^*(1) u_i(1) u_n^*(2) u_j(2)}{r_{12}} d\tau_1 d\tau_2$$

Let us now set up the secular equations for two holes in a band. Suppose we had some one-electron orbitals u_i^1 for this problem in analogy to u_i for the two-electron case. We can find an energy associated with one hole in a filled band. An approximate wave function for this case would be a $2N - 1$ by $2N - 1$ determinant with every orbital filled twice except for the orbital u_n^1 which is only filled with an electron of plus spin. We shall denote this by $\det [-u_n^1 \beta]$ just indicating the missing orbital in the determinant. The Hamiltonian is

$$H_{2N-1} = \sum_{i=1}^{2N-1} H(i) + \sum_{i,j}^{2N-1} \frac{2}{r_{ij}}$$

The energy of this state is

$$\int \det^* [-u_n^1 \beta] H_{2N-1} \det [-u_n^1 \beta] = \sum_{\substack{i>j \\ i,j \neq n}}^N [4(ii|jj) - 2(ij|ij)] + \sum_{i \neq n}^N [(ii|ii) + 2(i|i)] \\ + (n|n) + \sum_{i \neq n} [2(ii|nn) - (in|in)] = E_{2N} - \epsilon'(k_n)$$

where

$$(n|n) = \int u_n^{*1} H u_n^1 d\tau$$

and

$$E_{2N} = \sum_{i>j} 4(ii|nn) - 2(ij|ij) + \sum_{i=1}^N [(ii|ii) + 2(i|i)] \epsilon'(k_n) = \sum_{i=1}^N [2(ii|nn) - (in|in) + (n|n)]$$

The summation in $\epsilon'(k_n)$ represents the interaction of an electron with the entire filled band.

In complete analogy with the case of two electrons we could set up the wave functions for the two holes.

$$\Psi' = \sum_{i \neq j} U_{ij}^1 \left\{ \det [(-u_i \beta)(-u_j \alpha)] \pm \det [(-u_i \alpha)(-u_j \beta)] \right\}$$

where once again we only indicate the missing orbital in the determinant. The secular equa-

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tions involving the U'_{ij} will be

$$\begin{aligned}
 U'_{nm} & \left\{ \sum_{\substack{i \neq n \\ \neq m}} \left[2(i|i) + (ii|ii) \right] + (n|n) + (m|m) + \sum_{\substack{i > j \\ \neq m \neq n}} \left[4(ii|jj) - 2(ij|ij) \right] \right. \\
 & + \sum_{i \neq n} \left[2(nn|ii) - (ni|ni) + 2(mm|ii) - (mi|mi) \right] + (mm|nn) \mp (mn|mn) - E \left. \right\} \\
 & + \sum_{ij \neq m \neq n} U'_{ij} \left[(mi|nj) \mp (mj|ni) \right]
 \end{aligned}$$

Using the definitions of $\epsilon'(k_n)$ and E_{2n} this reduces to

$$U'_{nm} \left[E_{2N} - \epsilon'(k_n) - \epsilon'(k_m) + (mm|nn) - (mn|mn) - E \right] + \sum U'_{ij} \left[(mi|nj) \mp (mj|ni) \right]$$

The only formal difference between this and the case of two holes outside of the additive constant E_{2N} to the energy, is the fact that the one-electron energy appears with a negative sign. If we assume that the major contribution to the lowest wave function for two holes comes when the two holes are near the top of the band we can proceed as Stutz does in replacing $\epsilon'(k_n) = \text{constant} (-k_n^2)$. We see that the - sign in the one-electron energies is just what is needed to make the secular equation for two holes exactly analogous to the case for two electrons.

If there were other bands full of electrons in the crystal, there would be only one change in the foregoing argument. To the one-electron energy $\epsilon(k_n)$ and $\epsilon'(k_n)$ would be added the interaction of the electron and the closed shell. That is, to each $\epsilon(k_n)$ and $\epsilon'(k_n)$ would be added a term

$$\sum_{i=1}^N \left[2(ii|nn) - (in|in) \right]$$

where i runs over a band, for each filled band.

G. F. Koster

12. THEORY OF FERROMAGNETISM

The work on ferromagnetism has been continued following the general direction explained in the previous Progress Reports. ^(1, 2, 3) The simultaneous equations which determine the statistical properties of the system is now being solved, but the final conclusion has not been reached.

In a previous Progress Report ⁽³⁾ some properties of the density matrices were reported. The relations between them will be explained in the following as a preparation for minimizing the free energy with respect to parameters appearing in these density matrices.

We start with the wave functions for a pair of nearest neighbor points AB. As the ionized states are included, there can exist $\nu = 0, 1, 2, 3$ or 4 electrons on the pair AB. For $\nu = 4$ there is only one state, which is

$$\Phi_{AB}^{(4)}(\bar{x}_1 \bar{x}_2 \bar{x}_3 \bar{x}_4) = \frac{A}{\sqrt{6}} \Phi_4^{(2)}(\bar{x}_1 \bar{x}_2; AA) \Phi_4^{(2)}(\bar{x}_3 \bar{x}_4; BB) \quad (12.1)$$

where A is the antisymmetrizing operator, and $\Phi_4^{(2)}(\bar{x}_1 \bar{x}_2; AA)$ is the wave function for two electrons with antiparallel spins on the atom A, and is written as Eq. (3.3) of the Ref. 3. For $\nu = 3$, two electrons on the same atom have necessarily antiparallel spins, but the one on the other atom can have plus or minus spin. Out of the four possible functions, two are chosen gerade and the other two ungerade, and can be written as follows:

$$\Phi_{AB}^{(3)}(\bar{x}_1 \bar{x}_2 \bar{x}_3) = \frac{A}{\sqrt{6}} \left[\phi_A(x_1) \phi_A(x_2) \phi_B(x_3) \pm \phi_B(x_1) \phi_B(x_2) \phi_A(x_3) \right] \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \alpha(3), \quad (12.2)$$

where the upper and the lower signs correspond to $\Phi_1^{(3)}$ and $\Phi_2^{(3)}$ respectively. $\Phi_3^{(3)}$ and $\Phi_4^{(3)}$ are obtained when $\alpha(3)$ is changed to $\beta(3)$. For $\nu = 2$, we put

$$\Phi_i^{(2)}(\bar{x}_1 \bar{x}_2)_{AB} = \Phi_i^{(2)}(\bar{x}_1 \bar{x}_2; AB), \quad i = 1, 2, 3 \text{ and } 4 \quad (12.3)$$

where the functions on the right-hand side is listed in Eq. (3.2) of Ref. 3, $\Phi_i^{(2)}$ with $i = 1, 2$, and 3 being the triplet and $\Phi_4^{(2)}$ the singlet state. For the remaining two wave functions we choose the gerade and the ungerade combinations as follows:

$$\Phi_{AB}^{(2)}(\bar{x}_1 \bar{x}_2) = \frac{1}{2} \left[\phi_A(x_1) \phi_A(x_2) \pm \phi_B(x_1) \phi_B(x_2) \right] \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right], \quad (12.4)$$

$\Phi_5^{(2)}$ and $\Phi_6^{(2)}$ corresponding to the upper and the lower signs respectively. For $\nu = 1$, we have two gerade and two ungerade functions as follows:

$$\Phi_{AB}^{(1)}(\bar{x}_1) = \frac{1}{\sqrt{2}} \left[\phi_A(x_1) \pm \phi_B(x_1) \right] \alpha(1). \quad (12.5)$$

$\Phi_3^{(1)}$ and $\Phi_4^{(1)}$ are obtained when $\alpha(1)$ is changed into $\beta(1)$.

Using these wave functions, the reduced grand density matrix for a pair AB, Eq. (3.27) of Ref. 3, is written as follows:

$$\rho^{(M)}(\bar{x}_1 \dots \bar{x}_M; \bar{x}'_1 \dots \bar{x}'_M)_{AB} = \sum_{\nu=0}^4 \binom{M}{\nu}^{-1} \sum_{P(n_1 \dots n_\nu)} \rho^{(\nu)}(\bar{x}_{n_1} \dots \bar{x}_{n_\nu}; \bar{x}'_{n_1} \dots \bar{x}'_{n_\nu})_{AB}, \quad (12.6)$$

where $P(n_1 \dots n_\nu)$ indicates the permutation of electrons, ⁽⁴⁾ and

$$\rho^{(\nu)}(\bar{x}_{n_1} \dots \bar{x}_{n_\nu}; \bar{x}'_{n_1} \dots \bar{x}'_{n_\nu})_{AB} = \sum_k \sum_{k'} Z_{kk'}^{(\nu)} \Phi_k^{(\nu)}(\bar{x}_1 \dots \bar{x}_{n_\nu})_{AB} \Phi_{k'}^{(\nu)*}(\bar{x}'_1 \dots \bar{x}'_{n_\nu})_{AB}. \quad (12.7)$$

$\rho^{(\nu)}$'s can be written more explicitly as follows.

$$\rho_{AB}^{(0)} = Z_{AB}^{(0)} \Phi_{AB}^{(0)} \Phi_{AB}^{(0)*}, \quad (12.8)$$

where $\Phi_{AB}^{(0)}$ denotes the state with no electrons on the pair AB.

$$\rho^{(1)}(\bar{x}_1; \bar{x}'_1)_{AB} = \sum_{k=1}^4 Z_{kk}^{(1)} \Phi_k^{(1)}(\bar{x}_1)_{AB} \Phi_k^{(1)*}(\bar{x}'_1)_{AB} \quad (12.9)$$

In this and the following it is assumed that the cross term of wave functions with different parity or with different component of spin does not appear.

$$\begin{aligned} \rho^{(2)}(\bar{x}_1 \bar{x}_2; \bar{x}'_1 \bar{x}'_2)_{AB} &= \sum_{k=1}^6 Z_{kk}^{(2)} \Phi_k^{(2)}(\bar{x}_1 \bar{x}_2)_{AB} \Phi_k^{(2)*}(\bar{x}'_1 \bar{x}'_2)_{AB} \\ &+ Z_{26}^{(2)} \Phi_2^{(2)}(\bar{x}_1 \bar{x}_2)_{AB} \Phi_6^{(2)*}(\bar{x}'_1 \bar{x}'_2)_{AB} + Z_{62}^{(2)} \Phi_6^{(2)}(\bar{x}_1 \bar{x}_2)_{AB} \Phi_2^{(2)*}(\bar{x}'_1 \bar{x}'_2)_{AB} \\ &+ Z_{45}^{(2)} \Phi_4^{(2)}(\bar{x}_1 \bar{x}_2)_{AB} \Phi_5^{(2)*}(\bar{x}'_1 \bar{x}'_2)_{AB} + Z_{54}^{(2)} \Phi_5^{(2)}(\bar{x}_1 \bar{x}_2)_{AB} \Phi_4^{(2)*}(\bar{x}'_1 \bar{x}'_2)_{AB}, \end{aligned} \quad (12.10)$$

in which we have four cross terms, because $\Phi_2^{(2)}$ and $\Phi_6^{(2)}$ are both ungerade and $\Phi_4^{(2)}$ and $\Phi_5^{(2)}$ are both gerade, all of these four states having spin component zero.

$$\rho^{(3)}(\bar{x}_1 \bar{x}_2 \bar{x}_3; \bar{x}'_1 \bar{x}'_2 \bar{x}'_3)_{AB} = \sum_{i=1}^4 Z_{ii}^{(3)} \Phi_i^{(3)}(\bar{x}_1 \bar{x}_2 \bar{x}_3)_{AB} \Phi_i^{(3)*}(\bar{x}'_1 \bar{x}'_2 \bar{x}'_3)_{AB}, \quad (12.11)$$

$$\rho^{(4)}(\bar{x}_1 \bar{x}_2 \bar{x}_3 \bar{x}_4; \bar{x}'_1 \bar{x}'_2 \bar{x}'_3 \bar{x}'_4)_{AB} = Z_{AB}^{(4)} \Phi_{AB}^{(4)}(\bar{x}_1 \bar{x}_2 \bar{x}_3 \bar{x}_4)_{AB} \Phi_{AB}^{(4)*}(\bar{x}'_1 \bar{x}'_2 \bar{x}'_3 \bar{x}'_4)_{AB}. \quad (12.12)$$

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Eqs. (12.8) - (12.12) are to be inserted into Eq. (12.6) to compose the complete reduced density matrix. Coefficients z 's appearing in the above formulas have the meaning of or are connected closely with the probability of finding the corresponding state and are used as the parameters with respect to which the free energy is made minimum.

In order to derive the formula of entropy we need the reduced grand density matrix for a point A, which has the form

$$\rho^{(M)}(\bar{x}_1 \dots \bar{x}_M; \bar{x}'_1 \dots \bar{x}'_M)_A = \sum_{\nu=0}^2 \binom{M}{\nu}^{-1} \sum_S y_S^{(\nu)} \sum_{P(n_1 \dots n_\nu)} \psi_S^{(\nu)}(\bar{x}_{n_1} \dots \bar{x}_{n_\nu})_A \psi_S^{(\nu)*}(\bar{x}'_{n_1} \dots \bar{x}'_{n_\nu})_A \quad (12.13)$$

where $\psi_s^{(\nu)}$ is the s^{th} ν -electron wave function at a lattice point A and has the form as

$$\begin{aligned} \psi_1^{(1)}(\bar{x}_1)_A &= \phi_A(x_1) \alpha(1) \\ \psi_2^{(1)}(\bar{x}_1)_A &= \phi_A(x_1) \beta(1) \\ \psi^{(2)}(\bar{x}_1 \bar{x}_2)_A &= \frac{1}{\sqrt{2}} \phi_A(x_1) \phi_A(x_2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \end{aligned} \quad (12.14)$$

It should be noted that there is no cross term appearing in the above density matrix, because $\psi_1^{(1)}$ and $\psi_2^{(1)}$ have different spin components. The coefficients y 's are derived from z 's in Eqs. (12.8) - (12.12) by the reduction procedure explained in the following. For example, writing Eq. (12.9) explicitly,

$$\begin{aligned} \rho^{(1)}(\bar{x}_1; \bar{x}'_1)_{AB} &= \sum_{i=1}^4 Z_{ii}^{(1)} \psi_i^{(1)}(\bar{x}_1)_{AB} \psi_i^{(1)*}(\bar{x}'_1)_{AB} \\ &= Z_{11}^{(1)} \frac{1}{2} \left[\psi_1^{(1)}(\bar{x}_1)_A \psi_B^{(0)} + \psi_A^{(0)} \psi_1^{(1)}(\bar{x}_1)_B \right] \left[\psi_1^{(1)*}(\bar{x}'_1)_A \psi_B^{(0)*} + \psi_A^{(0)*} \psi_1^{(1)*}(\bar{x}'_1)_B \right] \\ &+ Z_{22}^{(1)} \frac{1}{2} \left[\psi_1^{(1)}(\bar{x}_1)_A \psi_B^{(0)} - \psi_A^{(0)} \psi_1^{(1)}(\bar{x}_1)_B \right] \left[\psi_1^{(1)*}(\bar{x}'_1)_A \psi_B^{(0)*} - \psi_A^{(0)*} \psi_1^{(1)*}(\bar{x}'_1)_B \right] \\ &+ Z_{33}^{(1)} \frac{1}{2} \left[\psi_2^{(1)}(\bar{x}_1)_A \psi_B^{(0)} + \psi_A^{(0)} \psi_2^{(1)}(\bar{x}_1)_B \right] \left[\psi_2^{(1)*}(\bar{x}'_1)_A \psi_B^{(0)*} + \psi_A^{(0)*} \psi_2^{(1)*}(\bar{x}'_1)_B \right] \\ &+ Z_{44}^{(1)} \frac{1}{2} \left[\psi_2^{(1)}(\bar{x}_1)_A \psi_B^{(0)} - \psi_A^{(0)} \psi_2^{(1)}(\bar{x}_1)_B \right] \left[\psi_2^{(1)*}(\bar{x}'_1)_A \psi_B^{(0)*} - \psi_A^{(0)*} \psi_2^{(1)*}(\bar{x}'_1)_B \right] \end{aligned} \quad (12.15)$$

The first term becomes

$$\begin{aligned} \frac{1}{2} Z_{11}^{(1)} \left[\psi_1^{(1)}(\bar{x}_1)_A \psi_1^{(1)*}(\bar{x}'_1)_A \psi_B^{(0)} \psi_B^{(0)*} + \psi_A^{(0)} \psi_A^{(0)*} \psi_1^{(1)}(\bar{x}_1)_B \psi_1^{(1)*}(\bar{x}'_1)_B \right. \\ \left. + \psi_1^{(1)}(\bar{x}_1)_A \psi_A^{(0)*} \psi_B^{(0)} \psi_1^{(1)*}(\bar{x}'_1)_B + \psi_A^{(0)} \psi_1^{(1)*}(\bar{x}'_1)_A \psi_1^{(1)}(\bar{x}_1)_B \psi_B^{(0)*} \right] \end{aligned} \quad (12.16)$$

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By the reduction procedure we mean the following: (1) Wave functions for the point A are untouched. (2) A product of two wave functions for B point is replaced by unity or zero depending on whether these two functions are the same or not. Applying these rules to Eq. (12.16), it can be reduced into

$$\frac{1}{2} Z_{11}^{(1)} \left[\bar{\psi}_1^{(1)}(\bar{x}_1)_A \bar{\psi}_1^{(1)*}(\bar{x}'_1)_A + \bar{\psi}_A^{(0)} \bar{\psi}_A^{(0)*} \right]. \quad (12.17)$$

Using the similar procedure, $\rho^{(1)}(\bar{x}_1; \bar{x}'_1)_{AB}$ of Eq. (12.15) can be reduced into

$$\begin{aligned} & \frac{1}{2} (Z_{11}^{(1)} + Z_{22}^{(1)}) \left[\bar{\psi}_1^{(1)}(\bar{x}_1)_A \bar{\psi}_1^{(1)*}(\bar{x}'_1)_A + \bar{\psi}_A^{(0)} \bar{\psi}_A^{(0)*} \right] \\ & + \frac{1}{2} (Z_{33}^{(1)} + Z_{44}^{(1)}) \left[\bar{\psi}_2^{(1)}(\bar{x}_1)_A \bar{\psi}_2^{(1)*}(\bar{x}'_1)_A + \bar{\psi}_A^{(0)} \bar{\psi}_A^{(0)*} \right] \end{aligned} \quad (12.18)$$

This makes a part of the reduced grand density matrix. Reducing completely and comparing with Eq. (12.13), we obtain the following relations between y's and z's:

$$\begin{aligned} y^{(0)} &= Z^{(0)} + \frac{1}{2} \sum_{i=1}^4 Z_{ii}^{(1)} + \frac{1}{2} (Z_{55}^{(2)} + Z_{66}^{(2)}) \\ y_{11}^{(1)} &= \frac{1}{2} (Z_{11}^{(1)} + Z_{22}^{(1)}) + Z_{11}^{(2)} + \frac{1}{2} (Z_{22}^{(2)} + Z_{44}^{(2)}) + \frac{1}{2} (Z_{11}^{(3)} + Z_{22}^{(3)}) \\ y_{22}^{(1)} &= \frac{1}{2} (Z_{33}^{(1)} + Z_{44}^{(1)}) + Z_{33}^{(2)} + \frac{1}{2} (Z_{22}^{(2)} + Z_{44}^{(2)}) + \frac{1}{2} (Z_{33}^{(3)} + Z_{44}^{(3)}) \\ y^{(2)} &= \frac{1}{2} (Z_{55}^{(2)} + Z_{66}^{(2)}) + \frac{1}{2} \sum_{i=1}^4 Z_{ii}^{(3)} + Z^{(4)}. \end{aligned} \quad (12.19)$$

The normalization conditions of y's is

$$\text{Trace} \left[\rho^{(M)}(\bar{x}_1 \dots \bar{x}_M; \bar{x}'_1 \dots \bar{x}'_M)_A \right] = 1 \quad (12.20)$$

which is written as

$$y^{(0)} + y_{11}^{(1)} + y_{22}^{(1)} + y^{(2)} = 1. \quad (12.21)$$

Using these reduced density matrices the entropy S of the system can be written following Eqs. (3.29), (3.31) and (3.32) of Ref. 3. Writing explicitly,

$$S = N \left[\omega S^{(2)} - (2\omega - 1) S^{(1)} \right]$$

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with

$$\begin{aligned}
 S^{(1)} &= -k \left[y^{(0)} \ln y^{(0)} + \sum_{i=1}^2 y_{ii}^{(1)} \ln y_{ii}^{(1)} + y^{(2)} \ln y^{(2)} \right] \\
 S^{(2)} &= -k \left[Z^{(0)} \ln Z^{(0)} + \sum_{i=1}^4 Z_{ii}^{(1)} \ln Z_{ii}^{(1)} + \sum_{i=1}^4 Z_{ii}^{(2)} \ln Z_{ii}^{(2)} \right. \\
 &\quad \left. + \lambda_4^{(2)} \ln \lambda_4^{(2)} + \lambda_5^{(2)} \ln \lambda_5^{(2)} + \sum_{i=1}^4 Z_{ii}^{(3)} \ln Z_{ii}^{(3)} + Z^{(4)} \ln Z^{(4)} \right]
 \end{aligned} \tag{12.22}$$

where $Z\omega$ is the coordination number. We need to say a work for $S^{(2)}$. Among the coefficients $Z^{(2)}$'s of Eq. (12.10), we can show $Z_{26}^{(2)}$ and $Z_{62}^{(2)}$ are zero, because these do not contribute to the energy. But $Z_{45}^{(2)}$ and $Z_{54}^{(2)}$ are different from zero. $\lambda_4^{(2)}$ and $\lambda_5^{(2)}$ in the above formula are the solutions of the following secular equation

$$\begin{vmatrix} Z_{44}^{(2)} - \lambda & Z_{45}^{(2)} \\ Z_{54}^{(2)} & Z_{55}^{(2)} - \lambda \end{vmatrix} = 0 \tag{12.23}$$

so that $\begin{pmatrix} \lambda_4^{(2)} & 0 \\ 0 & \lambda_5^{(2)} \end{pmatrix}$ is the diagonalized form of the matrix $\begin{pmatrix} Z_{44}^{(2)} & Z_{45}^{(2)} \\ Z_{54}^{(2)} & Z_{55}^{(2)} \end{pmatrix}$.

Next let us consider the energy. When we restrict ourselves to the nearest neighbor interaction, the parameters appearing in the energy formulas (3.12) and (3.18) of Ref. 3 are of the following type: $Z_{44}^{(AA; AA)}$, $Z_{44}^{(BB; AA)}$, $Z_{44}^{(AB; AA)}$, $Z_{kk}^{(AB; AB)}$, $y_i^{(A; A)}$, $y_i^{(A; B)}$ with $k = 1, 2, 3, 4$, and $i = 1, 2$. These are derived from Z 's by the following procedure. From Eq. (3.1) of Ref. 3,

$$\begin{aligned}
 &\binom{M}{2}^{1/2} \int \mathfrak{z}^{(M)}(\bar{x}_1 \dots \bar{x}_M)_{a_1 \dots a_N} \mathfrak{z}_k^{(2)*}(\bar{x}_1 \bar{x}_2; AB) d\bar{x}_1 d\bar{x}_2 \\
 &= \sum_{(a_3 \dots a_M)} \sum_l p_{kl}^{(AB; a_3 \dots a_M)} \mathfrak{z}_l^{(M-2)}(\bar{x}_3 \dots \bar{x}_M; a_3 \dots a_M)
 \end{aligned} \tag{12.24}$$

using which

$$\begin{aligned}
 &\binom{M}{2} \int d\bar{x}_3 \dots d\bar{x}_M \int d\bar{x}_1 d\bar{x}_2 \mathfrak{z}^{(M)}(\bar{x}_1 \bar{x}_2 \dots \bar{x}_M)_{a_1 \dots a_N} \mathfrak{z}_k^{(2)*}(\bar{x}_1 \bar{x}_2; AB) \\
 &\quad \int d\bar{x}_1' d\bar{x}_2' \mathfrak{z}^{(M)*}(\bar{x}_1' \bar{x}_2' \bar{x}_3 \dots \bar{x}_M)_{a_1 \dots a_N} \mathfrak{z}_m^{(2)*}(\bar{x}_1' \bar{x}_2'; AB) \\
 &= \sum_{(a_3 \dots a_M)} \sum_l p_{kl}^{(AB; a_3 \dots a_M)} p_{ml}^{(AB; a_3 \dots a_M)*} = Z_{km}^{(AB; AB)}
 \end{aligned} \tag{12.25}$$

In order to express $Z_{km}^{(AB; AB)}$ as a function of $Z^{(\nu)}$'s, we use Eq. (3.24) of Ref. 3 for the expansion of $\Phi^{(M)}(\bar{x}_1 \dots \bar{x}_M)_{a_1 \dots a_N}$. After mathematical manipulation, we obtain

$$Z_{km}^{(AB; AB)} = Z_{km}^{(2)} + 3 \sum_t Z_{tt}^{(3)} \sum_s q_{tks}^{(3)} q_{tms}^{(3)*} + 6 Z^{(4)} \sum_s q_{ks}^{(4)} q_{ms}^{(4)*}, \quad (12.26)$$

where q 's are the expansion coefficient in the following

$$\begin{aligned} \Phi_t^{(3)}(\bar{x}_1 \bar{x}_2 \bar{x}_3)_{AB} &= \sum_k \sum_s q_{tks}^{(3)} \Phi_s^{(1)}(\bar{x}_3)_{AB} \Phi_k^{(2)}(\bar{x}_1 \bar{x}_2; AB) \\ \Phi_t^{(4)}(\bar{x}_1 \bar{x}_2 \bar{x}_3 \bar{x}_4)_{AB} &= \sum_k \sum_s q_{kts}^{(4)} \Phi_s^{(2)}(\bar{x}_3 \bar{x}_4)_{AB} \Phi_k^{(2)}(\bar{x}_1 \bar{x}_2; AB). \end{aligned} \quad (12.27)$$

Similarly,

$$\begin{aligned} y_s^{(A; B)} &= Z_{ss}^{(1)} + 2 \sum_k \sum_{k'} Z_{kk'}^{(2)} \sum_t q_{kst}^{(2)} q_{k'st}^{(2)*} \\ &+ 3 \sum_k Z_{kk}^{(3)} \sum_t q_{kst}^{(3)} q_{k'st}^{(3)*} + 4 Z^{(4)} \sum_t q_{st}^{(4)} q_{st}^{(4)*}, \end{aligned} \quad (12.28)$$

where $q^{(\nu)}$'s are the expansion coefficients when $\Phi^{(\nu)}$ is expanded with respect to $\Phi_k^{(1)}(\bar{x}_1)_A$. Calculating q 's explicitly, we obtain the following relations:

$$\begin{aligned} Z_{11}^{(AB; AB)} &= Z^{(4)} + Z_{11}^{(3)} + Z_{22}^{(3)} + Z_{11}^{(2)} \\ Z_{22}^{(AB; AB)} &= Z^{(4)} + \frac{1}{2} \sum_{i=1}^4 Z_{ii}^{(3)} + Z_{22}^{(2)} \\ Z_{33}^{(AB; AB)} &= Z^{(4)} + Z_{33}^{(3)} + Z_{44}^{(3)} + Z_{33}^{(2)} \\ Z_{44}^{(AB; AB)} &= Z^{(4)} + \frac{1}{2} \sum_{i=1}^4 Z_{ii}^{(3)} + \frac{1}{2} (Z_{55}^{(2)} + Z_{66}^{(2)}) \\ Z_{44}^{(AB; AA)} &= \frac{1}{2\sqrt{2}} (-Z_{11}^{(3)} + Z_{22}^{(3)} - Z_{33}^{(3)} + Z_{44}^{(3)}) + \frac{1}{\sqrt{2}} Z_{45}^{(2)} \\ Z_{44}^{(AA; BB)} &= \frac{1}{2} (Z_{55}^{(2)} - Z_{66}^{(2)}) \\ y_1^{(A; A)} &= \frac{1}{2} (Z_{11}^{(1)} + Z_{22}^{(1)}) + Z_{11}^{(2)} + \frac{1}{2} (Z_{22}^{(2)} + Z_{44}^{(2)} + Z_{55}^{(2)} + Z_{66}^{(2)}) \\ &+ Z_{11}^{(3)} + Z_{22}^{(3)} + \frac{1}{2} (Z_{33}^{(3)} + Z_{44}^{(3)}) + Z^{(4)} \end{aligned} \quad (12.29)$$

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$$\begin{aligned}
 y_1^{(A; B)} &= \frac{1}{2}(Z_{11}^{(1)} - Z_{22}^{(1)}) - \frac{1}{2}(Z_{26}^{(2)} + Z_{62}^{(2)}) \\
 &\quad + \frac{1}{2}(Z_{45}^{(2)} + Z_{54}^{(2)}) + \frac{1}{2}(-Z_{33}^{(3)} + Z_{44}^{(3)}) \\
 y_1^{(A; A)} &= \frac{1}{2}(Z_{33}^{(1)} - Z_{44}^{(1)}) + \frac{1}{2}(Z_{26}^{(2)} + Z_{62}^{(2)}) \\
 &\quad + \frac{1}{2}(Z_{45}^{(2)} + Z_{54}^{(2)}) + \frac{1}{2}(-Z_{11}^{(3)} + Z_{22}^{(3)}).
 \end{aligned}$$

$y_2^{(A; A)}$ is obtained by interchanging 1 and 3, 2 and 4 in the subscripts of the right hand side of $y_1^{(A; A)}$.

From Eq. (3.22) of Ref. 3, the normalization of $y_k^{(a_1; a_1)}$ becomes

$$1 = \text{Trace} \left[\rho^{(1)}(\bar{x}_1; \bar{x}_1)_{a_1 \dots a_N} \right] = M^{-1} \sum_{a_1} \sum_{k=1}^2 y_k^{(a_1; a_1)} = \frac{N}{M} \sum_{k=1}^2 y_k^{(A; A)} \quad (12.30)$$

or

$$\sum_{k=1}^2 y_k^{(A; A)} = \frac{M}{N} \equiv \rho,$$

which gives the density or the number of electrons per lattice point, because M is the number of electrons and N is the number of lattice points. It has simple interpretation when one inserts Eq. (12.29) into (12.30);

$$\frac{M}{N} = \frac{1}{2} \left[\sum_{i=1}^4 Z_{ii}^{(1)} + 2 \sum_{i=1}^6 Z_{ii}^{(2)} + 3 \sum_{i=1}^4 Z_{ii}^{(3)} + 4 Z^{(4)} \right] = y_{11}^{(1)} + y_{22}^{(1)} + 2y^{(2)}, \quad (12.31)$$

in which, for instance, $y^{(2)}$ is the probability of finding two electrons at a lattice point, and $\sum_{i=1}^4 Z_{ii}^{(3)}$ is the probability of finding three electrons at two lattice points.

For the case of nearest neighbor interaction, the energy formula of Eqs. (3.12) and (3.18) of Ref. 3 can be reduced to

$$\begin{aligned}
 \frac{E}{N} &= \frac{E_1}{N} + \frac{E_2}{N} = 2\omega Q \sum_{k=1}^2 y_k^{(A; B)} + \omega(K - J) \sum_{k=1}^4 Z_k^{(AB; AB)} + 2\omega J \left[Z_4^{(AA; BB)} + Z_4^{(AB; AB)} \right] \\
 &\quad + K_{55} Z_4^{(AA; AA)} + 2\sqrt{2} \omega K_{54} \left[Z_4^{(AA; AB)} + Z_4^{(AB; AA)} \right] + \text{const.}
 \end{aligned} \quad (12.32)$$

where

$$\begin{aligned}
 Q &= \int \phi_A(x_1) \left(-\frac{1}{2} \nabla^2 - \frac{q}{r_A} - \frac{q}{r_B} \right) \phi_B(x_1) dx_1 \\
 K &= \int \phi_A(x_1) \phi_B(x_2) \frac{1}{r_{12}} \phi_A(x_1) \phi_B(x_2) dx_1 dx_2 \\
 J &= \int \phi_A(x_1) \phi_B(x_2) \frac{1}{r_{12}} \phi_B(x_1) \phi_A(x_2) dx_1 dx_2 \\
 K_{55} &= \int \phi_A(x_1) \phi_A(x_2) \frac{1}{r_{12}} \phi_A(x_1) \phi_A(x_2) dx_1 dx_2 \\
 K_{54} &= \int \phi_A(x_1) \phi_A(x_2) \frac{1}{r_{12}} \phi_A(x_1) \phi_B(x_2) dx_1 dx_2
 \end{aligned} \tag{12.33}$$

The density of electrons ρ is inserted in Q indicating plus electric charge of amount ρ is located at each lattice point. Using the relation (12.29), Eq. (12.32) is written as

$$\begin{aligned}
 \frac{E}{N} &= \omega Q \left[Z_{11}^{(1)} - Z_{22}^{(1)} + Z_{33}^{(1)} - Z_{44}^{(1)} + 2Z_{45}^{(2)} + 2Z_{54}^{(2)} - Z_{11}^{(3)} + Z_{22}^{(3)} - Z_{33}^{(3)} + Z_{44}^{(3)} \right] \\
 &+ \omega(K - J) \left[\sum_{i=1}^4 Z_{ii}^{(2)} + 2 \sum_{i=1}^4 Z_{ii}^{(3)} + 4Z^{(4)} \right] + \omega J \left[2Z_{44}^{(2)} + Z_{55}^{(2)} - Z_{66}^{(2)} + \sum_{i=1}^4 Z_{ii}^{(3)} + 2Z^{(4)} \right] \\
 &+ K_{55} \left[\frac{1}{2} (Z_{55}^{(2)} + Z_{66}^{(2)} + \sum_{i=1}^4 Z_{ii}^{(3)}) + Z^{(4)} \right] + 2\omega K_{54} \left[Z_{45}^{(2)} + Z_{54}^{(2)} - Z_{11}^{(3)} + Z_{22}^{(3)} \right. \\
 &\left. - Z_{33}^{(3)} + Z_{44}^{(3)} \right].
 \end{aligned} \tag{12.34}$$

The free energy is composed of this E/N and the entropy (12.22). The next step is to minimize the free energy with respect to fifteen independent variables and to solve these simultaneous equations, but it will be explained in the next Progress Report together with some of the results derived from these equations.

References

1. J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., July 15, 1952, p. 17.
2. R. Kikuchi, *ibid.*, p. 36.
3. R. Kikuchi, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., October 15, 1952, p. 9.
4. $(-1)^P$ in Eqs. (3.24), (3.27) and (3.30) of Ref. 3 above are not necessary.

R. Kikuchi

13. ANTI-FERROMAGNETISM

An investigation of the quantum mechanical aspects of anti-ferromagnetism is being carried out. The object of this work is to develop an adequate and reasonable formalism and eventually to apply such results to a specific case such as MnO.

In order to gain insight into the problem, calculations are now being made on the linear chain, a subject which has received considerable attention in the past. The bulk of the previous work has been based on the Dirac vector model, and the nature of the approximations made using this method have been such as to warrant a re-examination of the problem. Slater has made extensive remarks on this subject in the July 15 Quarterly Progress Report.

A model of the linear chain has been assumed in which there are a large number of centers, say $2N$, and associated with each center is a single electron. One can set up orthogonal one-electron orbitals such that the orbital associated with any center is orthogonal to the orbital corresponding to any other center. Following Löwdin's method for finding these OAO's, ⁽¹⁾ we obtain

$$\phi_\mu = \phi_\mu - \frac{1}{2} \sum_a S_{a\mu} \phi_a + \frac{3}{8} \sum_a \sum_\beta \phi_a S_{a\beta} S_{\beta\mu} - \frac{5}{16} \sum_a \sum_\beta \sum_\gamma \phi_a S_{a\beta} S_{\beta\gamma} S_{\gamma\mu} + \dots$$

where ϕ_μ is the OAO corresponding to the μ^{th} center and ϕ_a is the non-orthogonal atomic orbital associated with the a^{th} center. $S_{\alpha\beta}$ is

$$S_{\alpha\beta} = \int \phi_\alpha^* \phi_\beta d\tau - \delta_{\alpha\beta}$$

The atomic functions used here are functions of both space and spin and this means that $S_{\alpha\beta}$ vanishes unless the spin of ϕ_α is the same as that of ϕ_β .

Two states of the linear chain were considered, the first in which all electrons have an equal z component of spin, corresponding to the ferromagnetic case, and the second state in which all even numbered centers are associated with electrons of α spin and all odd numbered centers are associated with electrons having β spin. One need not be concerned with the state degenerate with the second state obtained by reversing the spin assignment because there are no matrix components of the energy between them. The orthogonalized orbitals corresponding to these two states are given by

$$\begin{aligned} \text{First State: } \phi_j = & \phi_j \left(1 + \frac{3\delta_1^2}{4} \right) + (\phi_{j+1} + \phi_{j-1}) \left(\frac{3\delta_1\delta_2}{4} - \frac{\delta_1}{2} \right) + (\phi_{j+2} + \phi_{j-2}) \left(\frac{3}{8}\delta_1^2 - \frac{\delta_2}{2} \right) \\ & + (\phi_{j+3} + \phi_{j-3}) \frac{3\delta_1\delta_2}{4}, \end{aligned}$$

$$\text{Second State: } \phi_j = \phi_j - (\phi_{j+2} + \phi_{j-2}) \frac{\delta_2}{2}.$$

δ_1 is the overlap integral between nearest neighbors and δ_2 is the overlap integral between second nearest neighbors. Terms of the order $\delta_3, \delta_2^2, \delta_1^2 \delta_2, \delta_1^3$ and higher order have been neglected.

The total wave functions for the above two states were expressed as single determinants of the appropriate one-electron Löwdin space-spin orbitals, although the second state so expressed is not an eigenfunction of total S^2 . The expectation value of the Hamiltonian for the linear chain was set up using these states and the difference between the two results formulated in terms of the original atomic functions. It is clear that if one had not used different Löwdin functions for the first and second states, that the first, or ferromagnetic, state would necessarily be the one of lower energy due to the decrease in energy arising from exchange interactions. The state corresponding to the alternating spin assignment gives exchange integrals only between second nearest neighbors. It was hoped that the use of different OAO's might make the second state lower in energy under certain circumstances due to a decrease in other terms contributing to the total energy.

In order to get an idea of the actual numbers involved, hydrogen 1s functions written as a single Gaussian Ae^{-ar^2} , with the parameter a determined by a variational calculation on the hydrogen atom, were used for the atomic functions. The interatomic distance in the linear chain (now of hydrogen atoms) was taken so that overlap integrals regarded above as small could be neglected. If the Hamiltonian is written as

$$\mathcal{H} = H + G$$

where H depends only on the coordinates of a single electron and G depends on the coordinates of two electrons, the difference in total energy between our two states is given as

$$\begin{aligned} & \sum_j [\phi_j | H | \phi_j]_1 - \sum_j [\phi_j | H | \phi_j]_2 \\ & + \sum_{jk} \left\{ [\phi_j \phi_k | G | \phi_j \phi_k]_1 - [\phi_j \phi_k | G | \phi_j \phi_k]_2 \right\} \\ & - \sum_{jk} \left\{ [\phi_j \phi_k | G | \phi_k \phi_j]_1 - [\phi_j \phi_k | G | \phi_k \phi_j]_2 \right\} \end{aligned}$$

Using an interatomic distance, denoted by b , of four atomic units, the following results were obtained

$$\begin{aligned} \sum_j [\phi_j | H | \phi_j]_1 - 2 &= -0.054 (2N) \\ \sum_{jk} [\phi_j \phi_k | G | \phi_j \phi_k]_1 - 2 &= +0.049 (2N) \end{aligned}$$

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$$- \sum_{jk} [\phi_j \phi_k | G | \phi_k \phi_j]_{1-2} = - 0.039 (2N)$$

where in the above expressions $2N$ is the number of electrons. Therefore, in this case the ferromagnetic case still is of lower energy. In the case of a chain of hydrogen atoms, the ferromagnetic state lies lower than the alternating spin state for all b greater than four. The mathematics will allow the alternating spin state to be of lower energy if the parameter a is greater than about 1.5, as compared to the hydrogen value of about 0.283, and if b becomes large.

A further calculation is being carried out at present on the linear chain. In this work a comparison is to be made between the ferromagnetic state and a non-magnetic state. This calculation is based on the formulation of the one-electron orbitals as Bloch functions, where the Bloch functions are given by

$$\psi_k(r) = \frac{1}{\sqrt{2N}} \sum_u \phi_u(r) e^{2\pi i \vec{k} \cdot \vec{R}_u}$$

The magnetic state corresponds to the assignment of one electron to each Bloch function and assuming that all electrons have equal z component of spin. The expectation value of the Hamiltonian in this case is of course identical with that obtained above. The non-magnetic case is represented by assigning two electrons to each Bloch function, one of each spin, and filling up the bottom half of the energy band. The total wave function for both cases is expressed as a single determinant. Also the Bloch functions for the non-magnetic case are expressed in terms of the same OAO's as for the magnetic case. It is clear that the average energy of this non-magnetic state will differ from the average energy of the alternating spin state mentioned above. These preliminary calculations should furnish useful information for a more rigorous treatment of the linear chain problem.

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G. W. Pratt, Jr.

14. THE LOCAL FIELD IN A CRYSTAL LATTICE

For the present time this study will be confined to lattices of cubic symmetry. To find the local fields within arrays of dipoles arranged on body-centered cubic, face-centered cubic, perovskite, or more complex cubic lattices, it is only necessary to calculate the local field for a simple cubic array of dipoles. The more complicated arrays mentioned above can be formed by superimposing the proper number of simple cubic arrays. (1, 2)

The basic technique for investigating the local field in a lattice is due to Ewald. (3) His method gives the field in an infinite array of dipoles. Consider a simple cubic lattice whose lattice points are given by a set of vectors \vec{r}_n . Suppose there is a dipole moment \vec{P}_0 at each lattice point. The resulting field at any point $\vec{r} \neq \vec{r}_n$ is

$$\vec{E}(\vec{r}) = -\frac{1}{\epsilon_0 v} \sum'_h \frac{\vec{b}_h (\vec{b}_h \cdot \vec{P}_0)}{b_h^2} e^{i\vec{b}_h \cdot \vec{r}} \quad (14.1)$$

where the \vec{b}_h 's are the reciprocal lattice vectors and v is the volume of the unit cell. The prime on the summation indicates omission of the term corresponding to $\vec{b}_h = 0$. The expression for the field in Eq. (14.1) has a singularity at each point $\vec{r} = \vec{r}_n$ because of the dipole at that lattice point. When the field due to any given dipole is subtracted from the expression in Eq. (14.1), the remaining field is finite and well behaved at that lattice point.

Now consider the case in which the dipole moment at each lattice point is

$$\vec{P}_n = \vec{P}_0 e^{i(\vec{k} \cdot \vec{r}_n - \omega t)} \quad (14.2)$$

The complex exponential form is being used here because it is easy to manipulate mathematically, but it is to be understood that the real or imaginary parts of Eq. (14.2) and succeeding expressions are the significant quantities. Ewald's method gives

$$\vec{E}(\vec{r}) = -\frac{1}{\epsilon_0 v} e^{i(\vec{k} \cdot \vec{r} - \omega t)} \sum_h \frac{(\vec{b}_h + \vec{k}) [(\vec{b}_h + \vec{k}) \cdot \vec{P}_0] - k_0^2 \vec{P}_0}{(\vec{b}_h + \vec{k})^2 - k_0^2} e^{i\vec{b}_h \cdot \vec{r}} \quad (14.3)$$

for $k \neq k_0$, where $k_0 = \frac{\omega}{c}$ and c is the velocity of light. If this theory is being applied to lattice vibrations, k_0 is small enough so that it can be neglected in Eq. (14.3) except in the term with $b_h = 0$. Then Eq. (14.3) may be rewritten as

$$\vec{E}(\vec{r}) = \vec{F}_1(\vec{r}; \vec{P}_0, \vec{k}, k_0) + \vec{F}_2(\vec{r}; \vec{P}_0, \vec{k}, k_0) \quad (14.4)$$

where

$$\vec{F}_1(\vec{r}; \vec{P}_0, \vec{k}, k_0) = -\frac{1}{\epsilon_0 v} e^{i(\vec{k} \cdot \vec{r} - \omega t)} \sum_h \frac{(\vec{b}_h + \vec{k}) [(\vec{b}_h + \vec{k}) \cdot \vec{P}_0]}{(\vec{b}_h + \vec{k})^2} e^{i\vec{b}_h \cdot \vec{r}}$$

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$$\vec{F}_2(\vec{r}; \vec{P}_0, \vec{k}, k_0) = -\frac{1}{\epsilon_0 v} \frac{\vec{k}(\vec{k} \cdot \vec{P}_0) - k_0^2 \vec{P}_0}{k^2 - k_0^2} e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

In the functions \vec{F}_1 and \vec{F}_2 , the quantities \vec{P}_0 , \vec{k} , and k_0 are to be regarded as parameters.

Now it can be seen that Eq. (14.1) can be rewritten as

$$\vec{E}(\vec{r}) = \vec{F}_1(\vec{r}; \vec{P}_0, 0, 0) \quad (14.5)$$

As \vec{k} and k_0 approach zero, $\vec{F}_1(\vec{r}; \vec{P}_0, \vec{k}, k_0)$ will approach $\vec{F}_1(\vec{r}; \vec{P}_0, 0, 0)$. The difference between the field given in Eq. (14.4) as \vec{k} and k_0 approach zero and the field given in (14.5) will be the limit of $\vec{F}_2(\vec{r}; \vec{P}_0, \vec{k}, k_0)$ as \vec{k} and k_0 approach zero. The value of this last limit will depend on the exact manner in which \vec{k} and k_0 approach zero, and it will not in general be zero.

The singularity of the results at the point $k = k_0 = 0$ is a fault of the Ewald method only insofar as it must be applied to an infinite lattice. This can be illustrated by considering a continuum of polarization. If one wishes to find the field associated with a specified distribution of polarization, the field is given by potentials which must satisfy the equations

$$\nabla^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = \frac{1}{\epsilon_0} \nabla \cdot \vec{P} \quad (14.6)$$

$$\nabla^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} = \mu_0 \frac{\partial \vec{P}}{\partial t} \quad (14.7)$$

The electric field is then

$$\vec{E} = -\nabla \phi - \frac{\partial \vec{A}}{\partial t} \quad (14.8)$$

If the polarization is given by

$$\vec{P} = \frac{1}{v} \vec{P}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (14.9)$$

and $k^2 - k_0^2 \neq 0$, the result is

$$\vec{E} = -\frac{1}{\epsilon_0 v} \frac{\vec{k}(\vec{k} \cdot \vec{P}_0) - k_0^2 \vec{P}_0}{k^2 - k_0^2} e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

or

$$\vec{E} = \vec{F}_2(\vec{r}; \vec{P}_0, \vec{k}, k_0) \quad (14.10)$$

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If $k = k_0 = 0$, the result is just $\vec{E} = 0$. So there is the same discontinuity in treating a continuum of polarization as there is in treating a lattice of point dipoles by Ewald's method.

The essential points of this paradox are still contained in this problem if the polarization given in Eq. (14.9) is specialized to the case of $\omega = 0$ and \vec{k} parallel to \vec{P}_0 . So let us now consider a problem in which the polarization only extends over a finite region of space. Suppose that the polarization is

$$\vec{P} = \frac{1}{v} \vec{P}_0 e^{i\vec{k} \cdot \vec{r}} \quad (14.11)$$

inside of a sphere of radius a located at the origin and is zero outside of this sphere. Eq. (14.6) and the boundary conditions of the problem can be satisfied by the potential

$$\phi_i = -\frac{1}{\epsilon_0 v} \frac{P_0}{k} e^{i\vec{k} \cdot \vec{r}} + \sum_{n=0}^{\infty} i^{n+1} \frac{P_0 (n+1)}{\epsilon_0 v k a^n} j_n(ka) r^n P_n(\cos \theta)$$

in the interior of the sphere and

$$\phi_e = -\sum_{n=0}^{\infty} i^{n+1} \frac{P_0 n a^{n+1}}{\epsilon_0 v k} j_n(ka) \frac{1}{r^{n+1}} P_n(\cos \theta)$$

in the exterior of the sphere. The z-axis or polar axis of the spherical coordinate system is assumed here to be in the direction of \vec{k} and \vec{P}_0 . The $j_n(u)$'s are spherical Bessel functions $(\pi/2u)^{1/2} J_{n+1/2}(u)$. The electric field in the neighborhood of the center of the sphere will have only a z-component which will be

$$E_z = -\frac{P_0}{\epsilon_0 v} e^{i\vec{k} \cdot \vec{r}} + \frac{P_0}{\epsilon_0 v} \frac{2}{ka} j_1(ka) \quad (14.12)$$

As k approaches zero, the field approaches

$$E_z = -\frac{P_0}{3\epsilon_0 v} \quad (14.13)$$

which is just the answer for a uniformly polarized sphere. As k approaches infinity, the field approaches

$$E_z = -\frac{P_0}{\epsilon_0 v} e^{i\vec{k} \cdot \vec{r}} \quad (14.14)$$

which agrees with the result for an infinite medium of polarization.

The results for this sphere problem can be summarized in the following way. For

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For wavelengths long compared with the dimensions of the sphere, the field is essentially the same as for an infinite medium with $k = 0$. For wavelengths short compared with the dimensions of the sphere, the field is essentially the same as for an infinite medium with $k \neq 0$. The discontinuity at $k = 0$ in the case of an infinite medium might be explained by the fact that if $k \neq 0$, the wavelength is always small compared to the dimensions of the medium. But when $k = 0$, the wavelength is then of the same order of magnitude as the dimensions of the medium; then the result is indeterminate.

The results of the Ewald method and this simple electrostatic sphere problem seem to suggest that the internal field is composed of two parts. The first is the effect of the discreteness of the dipoles and is given by $\vec{F}_1(\vec{r}; \vec{P}_0, \vec{k}, k_0)$. The second is due to the similarity of dipoles to a continuum of polarization. This second part would be computed by considering the body as a polarized continuum and computing the field. This idea will be investigated further.

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J. H. Barrett

15. CONNECTION BETWEEN THE MANY-ELECTRON INTERACTION AND THE ONE-ELECTRON PERIODIC POTENTIAL PROBLEMS

The central approximation in the energy-band treatment of solids is the assumption that the effect of all the other electrons on a given electron can be represented by a periodic potential modifying the periodic nuclear potential, reducing the problem to a one-body from a many-body one. As in the case of molecular problems, where essentially the same assumption is introduced, the effect of the correlation of the positions of the electrons due to the inter-electron force can be taken into account by "configuration interaction" -- the inclusion in the total wave function of an indefinitely large number of the many-electron, antisymmetrized determinantal wave functions formed out of products of the one-electron wave functions derived from the approximate Schrödinger equation separable because of the one-electron periodic potential approximation.

Recently two authors have worked on the simpler treatment of the interactions in Fermi-Dirac assemblies of electrons in terms of the excitations of a Bose-Einstein assembly of phonons representing the Fourier components of the electron density. ^(1, 2, 3) Correct dispersion relations and other results are obtained, although no full solution of the quantum-mechanical problem has yet been published. It seemed of interest to include in the problem they consider the effect of a periodic potential with a view toward studying the transition between the two limiting cases of the periodic potential and electron plasma problems. In particular, insight might be gained in this respect into the type of configuration interaction which is of greatest importance as a correction to the one-electron problem, as well as into several other problems.

The extension is being made on Tomonaga's paper, which is a precise, mathematically-closed formulation of the problem in the second quantization formalism, although it applies only to the one-dimensional case. The central problem is to find a modified canonical transformation, and hence dispersion relation, from a Hamiltonian including the periodic potential term to the Hamiltonian of a system of uncoupled simple harmonic oscillators representing "sound" quanta.

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H. C. White

16. A STUDY OF $2Z_p$ IN ATOMS

The calculation of $2Z_p$, the effective nuclear charge for the potential in an atom, has been continued following the method stated in the previous Progress Report. So far, $2Z_p$ for 10 neutral, 5 singly ionized, 6 doubly ionized, 4 triply ionized and 2 quadruply ionized atoms has been calculated. These have been included on our graph of $2Z_p$ vs. the atomic number for constant values of r . Although still incomplete the graph tells us much more than did our original plot using published values of $2Z_p$.

A. J. Freeman

17. SPHERICAL BESSEL FUNCTIONS OF HALF INTEGRAL ORDER AND IMAGINARY ARGUMENT

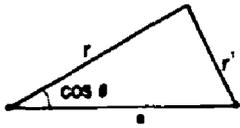


Fig. 17-1

Spherical Bessel functions of imaginary argument arise in molecular problems from the expansion of an exponential wave function about some displaced center. (Fig. 17-1). This expansion has the following form, ⁽¹⁾

$$\frac{e^{-kr'}}{r'} = \sum_n (2n+1) P_n(\cos \theta) \frac{I_{n+1/2}(kr)}{\sqrt{a}} \frac{K_{n+1/2}(ka)}{\sqrt{a}}$$

$$r < a$$

and a corresponding one with r and a interchanged for $r > a$. The expansion of $e^{-kr'}$ and $r'e^{-kr'}$, etc., can be derived from this by differentiation with respect to k . I and K are the usual Modified Bessel functions of imaginary argument. ⁽²⁾ Tables of these functions exist but are incomplete. ⁽³⁾ We have decided to tabulate functions closely related to these, namely

$$i_n(x) = \sqrt{\frac{\pi}{2x}} I_{n+1/2}(x)$$

$$k_n(x) = \sqrt{\frac{2}{\pi x}} K_{n+1/2}(x)$$

which arise in spherical problems.

This work is expected to be carried out on the M. I. T. Statistical Service's I. B. M. machines.

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F. J. Corbató, G. F. Koster, H. C. Schweinler

18. ELECTRIC FIELD GRADIENT AT NUCLEI OF MOLECULES

To determine the electric quadrupole moment of a nucleus from measurements of the electrostatic energy of interaction between the quadrupole moment and charges in the molecule outside of the nucleus of interest requires knowledge of the electric field gradient at that nucleus. For diatomic molecules the interaction energy is commonly written⁽¹⁾ eqQ where e is the proton charge, q the electric field gradient, and Q the electric quadrupole moment. In general it is difficult to calculate an accurate value of q in the usual way using a molecular wave function. Professor Rabi of Columbia University has found that for certain diatomic molecules the experimentally determined q is, except for a known constant factor, closely equal to the second derivative of the experimental Morse curve, which leads one to suspect the existence of an important theoretical relation. In fact, by using methods similar to those used by Feynman,⁽²⁾ we find the relation described below.

One is led to write the quadrupole interaction Hamiltonian for the a^{th} nucleus of a molecule in the form

$$H^{Q_a} = \left(\frac{1}{2q_a}\right) \sum_{\mu, \nu=1}^3 H_{\mu\nu}^a Q_{\mu\nu}^a \quad (18.1)$$

In (18.1) q_a is the charge of the a^{th} nucleus; μ, ν range from 1 to 3 corresponding to $x, y,$ and z . The nuclear quadrupole moment interaction tensor is

$$Q_{\mu\nu} = \int \rho(\vec{r})(x_\mu x_\nu - \frac{1}{3} \delta_{\mu\nu} r^2) d\tau$$

where $\rho(\vec{r})$ is the nuclear charge density and the x_μ denote rectangular components of the position vector in a frame of reference fixed in the molecule;

$$\sum_{\lambda=1}^3 x_\lambda^2 = r^2.$$

H is the adiabatic Hamiltonian for the electronic motion of the molecule. $H_{\mu\nu}^a$ is an abbreviation for $\partial/\partial x_\mu^a \partial/\partial x_\nu^a H$.

The expectation value of (18.1) with respect to the electronic wave function ψ , which satisfies $H\psi = U\psi$, where both ψ and U depend on the configuration of the nuclei of the molecule as parameters, may be written

$$(\psi, H^{Q_a}\psi) = \left(\frac{1}{2q_a}\right) \sum_{\mu, \nu=1}^3 (\psi, H_{\mu\nu}^a \psi) Q_{\mu\nu}^a \quad (18.2)$$

With such aspects as vibrational and rotational effects neglected, (18.2) evaluated at the equilibrium nuclear configuration represents the quadrupole interaction energy and

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$$\frac{(\psi, H_{\mu\nu}^a \psi)}{q_a} = -(\psi, \left[\frac{\partial}{\partial x_\mu^a} \frac{\partial}{\partial x_\nu^a} \frac{1}{q_a} \left\{ \sum_i V_{i_a} + \sum_{\beta \neq a} V_{\beta a} \right\} \right] \psi) \quad (18.3)$$

the electric field gradient, where $V_{i_a} = -eq_a/r_{i_a}$ and $V_{\beta a} = q_\beta q_a/r_{\beta a}$; r_{i_a} is the distance between the i^{th} electron and the a^{th} nucleus.

By simply differentiating U one finds that $(\psi, H_{\mu\nu}^a \psi)$ is related to U by

$$\frac{\partial}{\partial x_\mu^a} \frac{\partial}{\partial x_\nu^a} U = (\psi, H_{\mu\nu}^a \psi) + \Delta_{\mu\nu}^a \quad (18.4)$$

where

$$\Delta_{\mu\nu}^a = \Delta_{\nu\mu}^a = \int \left\{ \frac{\partial}{\partial x_\mu^a} (\psi^* \psi) \right\} \frac{\partial H}{\partial x_\nu^a} d\tau \quad (18.4')$$

in which the integration is over electronic coordinates.

For a diatomic molecule, with the z axis chosen along the internuclear axis, $(\psi, H_{\mu\nu}^a \psi)$ reduces to

$$(\psi, H_{\mu\nu}^a \psi) = (Q_{zz}^a / 2q_a) (\psi, H_{zz}^a \psi) \quad (18.5)$$

because of the cylindrical symmetry of $\psi^* \psi$. Only the components

$$\left(\frac{\partial}{\partial Z^a} \right)^2 U = (\psi, H_{zz}^a \psi) + \Delta_{zz}^a \quad (18.6)$$

of (18.4) and

$$\Delta_{zz}^a = eq_a \int \left\{ \frac{\partial}{\partial Z^a} (\psi^* \psi) \right\} \frac{\partial}{\partial Z^a} \sum_i r_{i_a}^{-1} d\tau \quad (18.6')$$

of (18.4') are of interest. The left member of (18.6) may be approximated from experimental data by the second derivative of the Morse curve, so that if (18.6') is known, one has a semi-empirical procedure for finding the electric field gradient. (18.6') does not vanish identically, for at the equilibrium internuclear distance $(\partial/\partial Z^a)^2 U$ is always positive, but the electric field gradient may be of either sign.

The evaluation of (18.6') is under investigation.

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