AD NUMBER
AD039108
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JUL 1954. Other requests shall be referred to Office of Naval Research, Washington, DC.**
AUTHORITY
onr ltr, 9 nov 1977

QUARTERLY PROGRESS REPORT

JULY 15, 1954

SOLID-STATE AND MOLECULAR THEORY GROUP
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

QUARTERLY PROGRESS REPORT NO. 13

SOLID-STATE AND MOLECULAR THEORY GROUP

Massachusetts Institute of Technology
Cambridge, Massachusetts

O. N. R. Contract N5ori-07856

July 15, 1954

PERSONNEL

Faculty

Professor J. C. Slater, Director

Staff Members, Research Assistants and Graduate Students

L. C. Allen

S. Bucksbaum

F. J. Corbató (in Professor Morse's group)

A. J. Freeman

D. J. Howarth

H. Kaplan

R. McWeeny

M. M. Saffren

T. D. Schultz

H. C. White

Staff Members, Lincoln Laboratory
(Air Force Contract No. AF 19(122)-458)

W. H. Kleiner

G. F. Koster

A. Meckler

Computers

Edith Moss

Evelyn Walker

I. Prakash

Secretary

Phyllis Fletcher

PUBLICATIONS

Quarterly Progress Reports Nos. 1 - 13, July 15, 1951 - July 15, 1954.

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

Technical Report No. 2, Determination of the Dielectric Constant and Conductivity of Germanium by Microwave Methods, Hsi-Teh Hsieh, May 1, 1952.

Technical Report No. 3, Electronic Structure of Atoms and Molecules, J. C. Slater, February 15, 1953.

Technical Report No. 4, Electronic Structure of Solids I: The Energy Band Method, J. C. Slater, July 15, 1953.

Technical Report No. 5, Electronic Structure of Solids II: The Perturbed Periodic Lattice, J. C. Slater, December 15, 1953.

Technical Report No. 6, Electronic Structure of Solids III: Configuration Interaction in Solids, J. C. Slater, April 15, 1954.

Journal Articles since June 1, 1953

A. J. Freeman, Effective Nuclear Charges for Atoms From Self-Consistent Field Calculations, Phys. Rev. 91, 1410 (1953).

G. F. Koster and J. C. Slater, Wave Functions for Impurity Levels (L), Phys. Rev. 94, 1392 (1954).

P. O. Löwdin, Studies of Atomic Self-Consistent Fields. II. Interpolation Problems, Phys. Rev. 94, 1600 (1954).

A. Meckler, Electronic Energy Levels of Molecular Oxygen, J. Chem. Phys. 21, 1750 (1953).

G. W. Pratt, Jr., Eigenfunctions of S^2 by a Spin Operator Method, Phys. Rev. 92, 278 (1953).

M. M. Saffren and J. C. Slater, Augmented Plane Wave Method for the Periodic Potential Problem II, Phys. Rev. 92, 1126 (1953).

J. C. Slater, A Generalized Self-Consistent Field Method, Phys. Rev. 91, 528 (1953).

J. C. Slater, H. Statz and G. F. Koster, A Two-Electron Example of Ferromagnetism, Phys. Rev. 91, 1323 (1953).

J. C. Slater, Augmented Plane Wave Method for the Periodic Potential Problem, Phys. Rev. 92, 603 (1953).

J. C. Slater and G. F. Koster, Simplified LCAO Method for the Periodic Potential Problem, Phys. Rev. 94, 1498 (1954).

TABLE OF CONTENTS

Quarterly Progress Report No. 13

on

Project N5ori-07856

SURVEY

The greatest effort of the group during the period described by this Progress Report has gone into the problem of configuration interaction in solids, and its relation to the correlation energy. My Technical Report No. 6, dealing with this problem, came out at the beginning of the period. Dr. Löwdin, though he has left the group after his profitable period here and has returned to Sweden, has now found time to write up the extensive work which he did while he was here on these subjects, and his contribution forms a major part of the present Progress Report. He hopes to elaborate some of this material in the form of later papers, and also probably will write a Technical Report for this group, dealing with some aspects of the many-electron problem. Dr. McWeeny too has been concerned with these problems. In the present Progress Report he presents valuable conclusions from his study of the π electrons in benzene, in which he has been able to compare the results of several different approaches. He delivered a series of lectures during May on the subject of configuration interaction in solids, which are being written up in the form of a Technical Report. In these lectures he presented the theory of molecular calculations from the point of view of the density matrix, a point of view which has been independently followed by Löwdin in his contribution to the present Progress Report.

Several conclusions emerge from this work. In the first place, there seems to be no simple way of avoiding the labor of a configuration interaction calculation. McWeeny's results on benzene show that in even as simple a problem as this, a rather extensive configuration interaction is required to get acceptable results, whether one starts with molecular orbitals, with the valence bond method using ordinary atomic orbitals, or with the valence bond method and orthogonalized atomic orbitals. It is true that in certain cases one can introduce rather extensive configuration interactions merely by considerations of symmetry, particularly in the problem of spin degeneracy, as has been discussed by Löwdin; but this will hardly go far enough, in the ordinary case, to make further configuration interaction unnecessary, though the simple case of the ordinary Heitler-London calculation for hydrogen is one in which it gives moderately acceptable results.

If one is to use configuration interaction methods, then for practical reasons it is essential to start with the best one-electron functions, in order that there will be the most rapid convergence of the configuration interaction; that is, in order that one can get an acceptable answer from a minimum number of determinantal functions formed from these one-electron functions. I suggested some time ago that this goal might well be reached if the one-electron functions were to be chosen as solutions of

a one-electron Schrödinger problem, with a potential determined by a certain self-consistent condition. This condition could be put in a form general enough to hold even in the presence of configuration interaction. Löwdin now appears to have proved that this suggestion of mine, which I arrived at intuitively, really has a rigorous basis. His proof, and the "natural spin-orbitals" which he discusses, deserve further study, and if they prove to be justified, they allow us to draw some conclusions about practicable methods of carrying out configuration interaction.

Let us ask what this procedure implies, if carried through completely. Suppose one starts with a set of one-electron orbitals, constructs determinantal wave functions from them, but decides to use only a limited number of such determinantal functions. One carries through a configuration interaction using this limited number of configurations. Then the implication of the theorems is that the configuration interaction will converge most rapidly if the one-electron functions are determined from the self-consistent field. That is, we conclude that the effect of the configurations which we have omitted will be a minimum, if we use the self-consistent field to determine the one-electron functions. Löwdin has not proved the theorem in precisely this form, but his proof is close enough so that this is probably what is implied.

In practice, one will probably never carry through this whole procedure; it is likely that after anyone has carried through a configuration interaction in any given problem, he will be so exhausted with his labors that he will not want to take any further steps to get self-consistency. Nevertheless the theorems point out the direction to work in, and suggest that if we could find a good approximation to the self-consistent field, and use solutions of this for the one-electron functions, we should get good convergence from the configuration interaction problem. For instance, the simplified Hartree-Fock method using a free-electron correction for exchange, which I proposed several years ago, might be close enough to the correct self-consistent field so that if we could solve a one-electron Schrödinger problem using this potential we should get good convergence from a configuration interaction.

Further progress has also been made during this period, in the solution of the one-electron problem. Dr. Koster presents further results on the problem of perturbed periodic lattices: he has considered the question of scattering of a wave by a perturbation, a problem whose applications to such phenomena as electrical resistance are obvious. He has also carried further the tight-binding approximation for energy bands, which he and I worked out some time ago. It seemed to us too bad that there was no calculation of density of states for the face-centered cubic structure, such as we recently carried out for the body-centered case. The calculations of Fletcher and Wohlfarth on nickel would give a suitable example, but they had not carried their work through, on account of the tedious mathematics involved. We had worked out methods of solving the necessary secular equations, using Whirlwind, in

connection with the body-centered case, and we have decided that it will be worth while to complete the work of Fletcher and Wohlfarth by computing the energy bands at many points in the Brillouin zone, and finding the density of states. The reason why this will be interesting is to compare with the calculations which Krutter and I made many years ago by the cellular method. From the work of Howarth on copper we know that this early cellular calculation agrees much more closely with the tight-binding method than with the older cellular work. The old calculations gave a dip in the density of states near the middle of the d-band, for copper; we wish to find if a similar dip is indicated by the tight-binding calculation.

In the meantime, Howarth is continuing his study of the augmented plane wave method for copper, to compare with his cellular calculations. The results, as of the moment, are encouraging: the convergence appears to be more rapid than by the cellular method, and the method seems to be practicable. Saffren has made some interesting studies of the behavior of the method at symmetry points in the Brillouin zone, and has suggested improvements in the method to be used at those points. Corbató continues his study of energy bands in graphite, by the tight-binding method. A number of the other pieces of research in the group are going on successfully. One investigation which has been carried to completion is Kleiner's work on the magnetic scattering of slow neutrons from oxygen gas, using Meckler's wave function. His calculated results agree within a few percent with the experimental determination at Brookhaven.

There have been several changes in personnel since the last Progress Report. Dr. Pratt, who was spending a number of months on leave of absence at the Raytheon Manufacturing Company, has returned to the Lincoln Laboratory, but in Group 35, where he will be less closely associated with the Solid-State and Molecular Theory Group. Dr. Kleiner is leaving shortly to join Dr. Pratt in Group 35. Dr. Schweinler is spending the summer on leave of absence at the Oak Ridge National Laboratory. One new graduate student, Mr. Schultz, appears in this Progress Report. There are several others who have been doing a little work with the group, and several new postdoctoral members will join the group next fall. Several of the present staff members will leave at the beginning of the fall, including Drs. Howarth, Kaplan, and McWeeny.

Our faithful secretary Phyllis Fletcher, who is responsible for the handsome appearance of these Progress Reports, had the misfortune to break her arm just as this Report was ready to be typed. We trust that the readers will pardon the delayed date of its appearance.

J. C. Slater

1. SOME REMARKS ON THE BASIS OF THE ONE-ELECTRON APPROXIMATION IN THE QUANTUM THEORY OF ATOMS, MOLECULES AND CRYSTALS

This contribution was originally meant for the April 15 Progress Report, but due to the author's traveling and other circumstances, it was delayed beyond the deadline and has therefore instead been prepared for this issue. It is here presented as a series of more or less independent short notes on the one-electron scheme, but the results will also be published in full length.

I would like to take this opportunity to express my sincere gratitude to Professor J. C. Slater for the great hospitality I have enjoyed during my stay with his Solid-State and Molecular Theory Group at M. I. T. I am also greatly indebted to him and to the members of the group for many inspiring and fruitful discussions.

Density Matrices, Natural Spin-Orbitals and the Extended Hartree-Fock Method

Let us consider a system of N antisymmetric particles described by the normalized wave function $\Psi = \Psi(x_1, x_2, \cdots x_N)$, where the coordinate x_i gives the situation of the particle i in ordinary space, spin space, and, in also considering nucleons, isotopic spin space. The basic Hamiltonian may have the form

$$H_{op} = W + \sum_i H_i + \frac{1}{2}\cdot\sum_{ij}{}' G_{ij}, \tag{1.1}$$

where the different terms contain zero-, one-, and two-particle operators, respectively. For the following discussion the explicit appearance of the Hamiltonian, which also may contain many-particle terms, is without importance, but we note that, for an electronic system (atom, molecule, or crystal) without external field at absolute zero, we have simply

$$W = \frac{e^2}{2} \sum_{gh} \frac{Z_g Z_h}{r_{gh}}, \qquad H_i = \frac{p_i^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{ig}}, \qquad G_{ij} = \frac{e^2}{r_{ij}}, \tag{1.2}$$

where we have neglected relativistic effects and the zero-point vibrations of the nuclei.

The wave function Ψ may describe a particular physical situation exactly or in an approximate way. If the first and second order density matrices, γ and Γ, are defined by

$$\begin{aligned}\gamma(x_1'|x_1) &= \binom{N}{1}\int \Psi^*(x_1' x_2 x_3 \cdots x_N)\,\Psi(x_1 x_2 x_3 \cdots x_N)\,dx_2 dx_3 \cdots dx_N,\\ \Gamma(x_1' x_2'|x_1 x_2) &= \binom{N}{2}\int \Psi^*(x_1' x_2' x_3 \cdots x_N)\,\Psi(x_1 x_2 x_3 \cdots x_N)\,dx_3 \cdots dx_N,\end{aligned} \tag{1.3}$$

with the usual probability interpretations of their diagonal elements, then the average energy of the situation may be expressed in the form

$$\langle H_{op} \rangle_{Av} = W + \int H_1 \, \gamma(x_1'|x_1) \, dx_1 + \int G_{12} \, \Gamma(x_1' x_2'|x_1 x_2) \, dx_1 dx_2, \qquad (1.4)$$

where, after the operations in the integrands have been carried out, we have to put $x_1' = x_1$, $x_2' = x_2$. If the Hamiltonian contains also many-particle terms, the higher densities are introduced analogously.

In order to analyze the situation, we shall introduce a complete orthonormal system of one-particle functions or spin-oribtals $\psi_k(x)$ $(k = 1, 2, 3 \ldots)$. The total wave function may then be expanded in a system of Slater determinants over all configurations K, i.e. over all selections of N indices $k_1 < k_2 < \ldots < k_N$:

$$\Psi = \sum_K C_K \Psi_K, \qquad (1.5)$$

where

$$\Psi_K = \frac{1}{\sqrt{N!}} \det \left\{ \psi_{k_1}, \psi_{k_2} \ldots \psi_{k_N} \right\} \qquad (1.6)$$

If K and L are two arbitrary configurations, one may derive the formula

$$\int \Psi_K^* \Psi_L \, dx_1 dx_2 \ldots dx_N = D_{KL} = \det \left\{ d_{k\ell} \right\}, \qquad d_{k\ell} = \int \psi_k^* \psi_\ell \, dx, \qquad (1.7)$$

where $d_{k\ell}$ are the "overlap integrals" between the basic functions belonging to K and L. We note that, due to the orthonormality, the only non-vanishing elements in the determinant D_{KL} appear for pairs (k, ℓ) referring to the same orbital occurring in both configurations K and L $(d_{k\ell} = 1)$. For the following discussion we need D_{KL} as well as its first and second order minors, $D_{KL;\, k\ell}$, $D_{KL;\, k_1 k_2,\ \ell_1 \ell_2}$, $\ldots$ etc.

The density matrices γ and Γ are Hermitian and may be expanded in the basic set ψ_k in the form

$$\gamma(x_1' \, x_1) = \sum_{k\ell} \psi_k^*(x_1') \, \psi_\ell(x_1) \, \gamma_{\ell k},$$

$$\Gamma(x_1' x_2' \, x_1 x_2) = \sum_{\substack{k_1 < k_2 \\ \ell_1 < \ell_2}} \begin{vmatrix} \psi_{k_1}^*(x_1') & \psi_{k_2}^*(x_1') \\ \psi_{k_1}^*(x_2') & \psi_{k_2}^*(x_2') \end{vmatrix} \begin{vmatrix} \psi_{\ell_1}(x_1) & \psi_{\ell_2}(x_1) \\ \psi_{\ell_1}(x_2) & \psi_{\ell_2}(x_2) \end{vmatrix} \Gamma_{\ell_1 \ell_2,\ k_1 k_2}, \qquad (1.8)$$

where we have used the fact that Γ is antisymmetric in each pair of its indices; the matrices of the coefficients are again Hermitian. Taking over a terminology from quantum chemistry, we may call γ_{kk} the "charge order" with respect to the spin-orbital ψ_k and $\gamma_{\ell k}$ the "bond order" with respect to the pair of spin-orbitals ψ_k and ψ_ℓ. By using (1.3), (1.5), (1.6), and (1.7), and expanding the Slater determinants Ψ_K in their first and second order minors, we may derive the relations

$$\gamma_{\ell k} = \sum_{K}^{(k)} \sum_{(L)}^{(\ell)} C_K^* D_{KL;k\ell} C_L \Big/ \sum_{KL} C_K^* D_{KL} C_L ,$$

$$\Gamma_{\ell_1\ell_2, k_1k_2} = \sum_{K}^{(k_1k_2)} \sum_{L}^{(\ell_1\ell_2)} C_K^* D_{KL;k_1k_2,\ell_1\ell_2} C_L \Big/ \sum_{KL} C_K^* D_{KL} C_L , \tag{1.9}$$

where the symbol $\sum_K^{(k)}$ means summation over all configurations K containing the index k, and the symbol $\sum_K^{(k_1,k_2)}$ means summation over all configurations containing the pair k_1, k_2), etc. For the diagonal elements we obtain in particular

$$\gamma_{kk} = \sum_{K}^{(k)} |C_K|^2 \Big/ \sum_{K} |C_K|^2 \leqslant 1$$

$$\Gamma_{k_1k_2, k_1k_2} = \sum_{K}^{(k_1k_2)} |C_K|^2 \Big/ \sum_{K} |C_K|^2 \leqslant 1. \tag{1.10}$$

showing that γ_{kk} measures the probability for the occurrence of the spin-orbital k. We note that the special case $\gamma_{kk} = 1$ occurs only if the spin-orbital k is present in <u>all</u> configurations in expansion (1.5), necessary for describing the situation.

Let us now consider the physical interpretation of results obtained in a one-electron scheme based on an arbitrarily chosen basic set ψ_k. The physical properties of the system are determined by the total wave function Ψ, i.e., by the coefficients C_K in (1.5), and, e.g. the eigenfunctions of the Hamiltonian (1.1), and may be derived from the variation principle

$$\delta \langle H_{op} \rangle_{Av} = 0, \tag{1.11}$$

which, applied to the expression (1.4), leads to a secular equation of infinite order. Even in approximate forms, the numerical calculations involved are a formidable size, but, as shown by Boys[1] and Meckler[2] in their treatments of atoms and mole-

cules, the numerical work can be carried out, at least by the aid of electronic computers. However, the preliminary result is then a rather complicated wave function in configuration space, and one is still looking for simple physical interpretations. In this connection, we would like to point out the importance of the first, second, and higher order density matrices (1. 3).

For the sake of simplicity, let us consider only the first order density $\gamma(x_1' x_1)$ having the Hermitian charge and bond order matrix $\gamma_{\ell k}$ with respect to the basic system ψ. We let U be the unitary matrix which transforms $\gamma_{\ell k}$ to diagonal form with the diagonal elements $n_{kk} = n_k$:

$$U^{\dagger}\gamma U = n = \text{diagonal matrix.} \tag{1.12}$$

We have further $\gamma = UnU^{\dagger}$, and, if we introduce a new set of spin-orbitals φ_k by $\varphi = \psi U$, or

$$\varphi_k = \sum_a \psi_a U_{ak}, \tag{1.13}$$

we may rewrite the density matrix in the form

$$\gamma(x_1' x_1) = \sum_k n_k \varphi_k^*(x_1') \varphi_k(x_1) \tag{1.14}$$

This form is characterized by the fact that all bond orders are vanishing, and the new spin-orbitals $\varphi_k(x)$ will therefore be called the natural spin-orbitals associated with the system and the corresponding "charge orders" n_k, which are the eigenvalues of $\gamma_{\ell k}$, will be interpreted as their occupation numbers. If two or more charge orders are the same, the corresponding orbitals form a degenerate group, and $\gamma(x_1'|x_1)$ is then invariant with respect to unitary transformations of the orbitals of the same spin type within such a group.

According to (1. 10) and the relation $\int \gamma(x_1|x_1)\, dx_1 = N$, the occupation numbers fulfill the conditions

$$0 \leqslant n_k \leqslant 1, \qquad \sum_k n_k = N, \tag{1.15}$$

and we can therefore conclude that the particles must be distributed over more than N natural spin-orbitals with a limiting case when they are occupying exactly N spin-orbitals. The condition for the limiting case may be expressed in the form

$$\gamma^2 = \gamma, \qquad \mathrm{Tr}(\gamma) = N \tag{1.16}$$

showing that the matrix γ_{lk} has exactly N eigenvalues equal to 1 and the remaining zero. If, in such a case, we choose the natural spin orbitals as our basic set, all configurations in expansion (1. 5) must contain the fully occupied spin-orbitals, i. e., this expansion is reduced to a single Slater determinant. This would mean that, if the necessary existence and convergency theorems for the solution Ψ are fulfilled, the relation (1. 16) would form a sufficient condition for the possibility of reducing the total wave function to a single determinant, i. e., for the strict validity of the Hartree-Fock approximation. The reverse theorem has previously been proved by Dirac.[3]

It is well known that, in a system where the particles show mutual interaction, the Hartree-Fock approximation is usually not strictly valid, and this means that the occupation numbers by the effect of this interaction are depressed below 1: $0 \leqslant n_k < 1$. The corresponding Cayley-Hamiltonian equation for the matrix is then more complicated than the first relation (1. 16).

We note that the antisymmetry condition on Ψ, which leads to the first condition (1. 15), is here much more general than Pauli's exclusion principle in its original form, which considers only the occupation numbers 0 or 1 and therefore explicitly must refer to the Hartree-Fock approximation. We note that, in the Hartree-Fock scheme, some changes of the system, as ionization[4] or excitation, may be described as resulting from entire particles jumping from occupied to unoccupied spin-orbitals (or to infinity), whereas the circumstances in an exact theory are more complicated with the occupation numbers changed by fractions of 1 (and possible changes also in the non-diagonal elements n_{kl}). The same complications occur, for instance, in an exact electron-positron theory, which is based on Dirac's idea of a fully occupied vacuum.

In the Hartree-Fock approximation the natural spin-orbitals are identical with the ordinary Hartree-Fock functions, being undetermined on a unitary transformation between functions of the same spin type. Already at this stage, the numerical computations involved are extremely laborious, but, by the aid of the modern electronic computing machines, it seems now possible to reach beyond this approximation. It will be interesting to see how much the natural spin-orbitals and the occupation numbers will be changed in the higher approximations; for "closed-shell" systems, where we know that the Hartree-Fock schemes already give good results, the changes will certainly be small, but, in other systems, they may be appreciable.

In the higher approximations, the natural spin-orbitals are of importance for obtaining as rapid convergence as possible in the expansion (1. 5) of the total wave function in Slater determinants over all configurations. It could happen that the arbitrarily chosen basic set ψ_k is inconvenient for its purpose, and the convergence of (1. 5) is then correspondingly slow. By using (1. 13) and carrying out the transformation $\psi = \varphi U^\dagger$ or

$$\psi_k = \sum_a \varphi_a U^\dagger_{ak}, \tag{1.17}$$

we obtain

$$\Psi_K = \sum_L \Phi_L A_{LK}, \qquad \Phi_L = \frac{1}{\sqrt{N!}} \det\left\{\varphi_{\ell_1}, \varphi_{\ell_2}, \ldots \varphi_{\ell_N}\right\}$$

$$A_{LK} = \begin{vmatrix} U^\dagger_{\ell_1 k_1}, U^\dagger_{\ell_1 k_2}, \ldots U^\dagger_{\ell_1 k_N} \\ \ldots\ldots\ldots\ldots\ldots \\ U^\dagger_{\ell_N k_1}, U^\dagger_{\ell_N k_2}, \ldots U^\dagger_{\ell_N k_N} \end{vmatrix}, \tag{1.18}$$

and, according to (1.5), the total wave function Ψ may then instead be expanded in configurations Φ_L of the natural spin-orbitals φ_ℓ:

$$\Psi = \sum_L \Phi_L \left(\sum_K A_{LK} C_K \right). \tag{1.19}$$

In the most favorable case (1.16), this expansion is reduced to a single determinant. If only a finite number of the occupation numbers n_k are different from zero, expansion (1.19) will be reduced to a sum of comparatively few determinants, and we see that, in this way, we shall obtain a solution of the convergency problem previously discussed by Slater.[5]

There is also a close connection between our natural spin-orbitals and the functions discussed by Slater[5] in his extension of the Hartree-Fock method. Let us assume that our basic set contains only M orthonormal functions ψ_k (k = 1, 2, ... M), and let us introduce their projection density matrix

$$\rho(x_1, x_2) = \sum_{k=1}^{M} \psi^*_k(x_1)\, \psi_k(x_2). \tag{1.20}$$

This matrix is a projection operator,[6] which fulfills the relation $\rho^2 = \rho$. For every function $g(x_1, x_2)$ which is expansible in the basic set $\psi_1, \psi_2, \ldots \psi_M$, i.e., which belongs to the subspace defined by this set, we have further

$$\rho g = g\rho = g \tag{1.21}$$

For the sake of simplicity, let us consider the special case when $G_{ij} = e^2/r_{ij}$. The variation principle (1.11) gives, as before, certain conditions for the coefficients C_K, but it gives now also a condition for choosing the set $\psi_1, \psi_2, \ldots \psi_M$ in the most

convenient way in the form of "extended Hartree-Fock equations". By multiplying the equations for each k by $\psi_k^*(\xi_1)$ and summing over k from 1 to M, this condition may be condensed in the form

$$H_1\,\gamma(\xi_1|x_1) + 2e^2\int\frac{\Gamma(\xi_1 x_2|x_1 x_2)}{r_{12}}\,dx_2 = f(\xi_1, x_2), \tag{1.22}$$

$$f(\xi_1, x_1) = \sum_{k,\ell=1}^{M}\psi_k^*(\xi_1)\,\psi_\ell(x_1)\,\lambda_{\ell k}. \tag{1.23}$$

Since the Lagrangian multipliers $\lambda_{\ell k}$ associated with the orthonormality conditions form a Hermitian matrix, the same is true for the right-hand member function $f(x_1, x_2)$, which may be considered as the "projection" of an arbitrary Hermitian function $F(x_1, x_2)$ on the subspace defined by the set $\psi_1, \psi_2, \ldots \psi_M$:

$$f = \rho F \rho. \tag{1.24}$$

We see that, when $M \to \infty$ and the system $\psi_k(x)$ becomes complete, we have

$$\lim_{M\to\infty}\rho(x_1, x_2) = \delta(x_1, x_2). \tag{1.25}$$

In this limiting case, the function $f(x_1, x_2)$ in (1.22) may be an arbitrary Hermitian function, and the extended Hartree-Fock equations (1.22) loose their meaning as a restraining condition on the basic set ψ_k, which may then be chosen arbitrarily.

Let us now keep M finite, and let us carry out the transformation (1.17) to natural spin-orbitals φ_k. By multiplying (1.22) by $\varphi_k^*(\xi_1)$, integrating over $d\xi_1$ and dividing by $n_k \neq 0$, we obtain

$$H_1\,\varphi_k(x_1) + \frac{2e^2}{n_k}\int\frac{\varphi_k^*(\xi_1)\,\Gamma(\xi_1 x_2|x_1 x_2)}{r_{12}}\,d\xi_1 dx_2 = \sum_{\ell=1}^{M}\varphi_\ell(x_1)\,\lambda'_{\ell k}\,n_k^{-1} \tag{1.26}$$

where $\lambda' = U^+\lambda U$. The second term in the left-hand member may be written in the form

$$V_{op}(1)\,\varphi_k(x_1) \tag{1.27}$$

where V_{op} is a complicated operator containing ordinary potentials as well as exchange operators. Eqs. (1.26) for k = 1, 2, ... M represent the exact integro-differential

equations or extended Hartree-Fock equations satisfied by the natural spin-orbitals having $n_k \neq 0$.

In order to obtain the connection with Slater's approach, we shall now replace V_{op} by its "best approximation" in x space:

$$V_{op}\,\varphi_k(x) \approx V(x)\,\varphi_k(x), \quad k = 1, 2, \ldots M \tag{1.28}$$

which may be defined by the condition that the sum

$$\sum_{k=1}^{M} \kappa_k \left| V_{op}\,\varphi_k(x) - V(x)\,\varphi_k(x) \right|^2 \tag{1.29}$$

should be as small as possible. The quantities κ_k are here appropriate weights, and for the natural spin-orbitals, it seems natural to choose them as being just the occupation numbers: $\kappa_k = n_k$. In this way, we obtain

$$V(x_1) = \frac{\sum_k n_k\,\varphi_k^*(x_1)\,V_{op}\,\varphi_k(x_1)}{\sum_k n_k\,\varphi_k^*(x_1)\,\varphi_k(x_1)} = 2e^2 \int \frac{\Gamma(x_1x_2|x_1x_2)}{r_{12}}\,dx_2 \Big/ \gamma(x_1|x_1), \tag{1.30}$$

where we have used the fact that Γ belongs to the subspace defined by our basic set and satisfies (1.21), i.e., $\rho\Gamma = \Gamma$. Our approximate form of (1.26) is then

$$\left\{H_1 + V(x_1)\right\}\varphi_k(x_1) = \sum_{\ell=1}^{M} \varphi_\ell(x_1)\,\lambda'_{\ell k}\,n_k^{-1}. \tag{1.31}$$

Since the operator $(H_1 + V_1)$ is Hermitian, the same must hold also for the matrix $\lambda'_{\ell k}\,n_k^{-1}$, which means that we can have λ' couplings only between natural spin-orbitals having the same occupation number. Within such a group we can then carry out a unitary transformation, bringing (1.31) to the final form

$$\left\{H_1 + V(x_1)\right\}\varphi_k(x_1) = \varepsilon_k\,\varphi_k(x_1), \tag{1.32}$$

which are just the equations intuitively proposed by Slater.[5] Our procedure gives also a new derivation of Slater's average exchange potential[7] in the ordinary Hartree-Fock scheme based on a single determinant.

Our investigation confirms Slater's assumption that the solutions to (1.32) would form a convenient basic set for obtaining rapid convergency of the expansion (1.5). However, we have also shown that, instead of forming the average potential (1.30) and solving (1.32), we may find the natural spin-orbitals simply by diagonalizing

the first order density matrix, $\gamma(x_1' \, x_1)$.

Treatment of Spin and Orbital Degeneracies by Projection Operators

In treating many-particle systems having a Hamiltonian (1. 1), there is always a certain complication if the system shows spin or orbital degeneracies. Let us assume that the degenerate states are classified by an operator Λ having a finite number of discrete eigenvalues $\lambda_0, \lambda_1, \ldots \lambda_n$, and let further Ψ be an arbitrary function associated with the space of degeneracy and having an expansion of the form

$$\Psi = \sum_{k=1}^{n} a_k \Psi_k , \tag{1.33}$$

where Ψ_k is an eigenfunction to Λ belonging to the eigenvalue λ_k. We note that, since the factor $(\Lambda - \lambda_p)$ annihilates the term for k = p in this expansion, the operator

$$O_\ell = \prod_{k=i,n}^{k \neq \ell} (\Lambda - \lambda_k)/(\lambda_\ell - \lambda_k) \tag{1.34}$$

takes out only the term for $k = \ell$, i. e., it gives the "projection" of Ψ on the eigenstate of Λ having the eigenvalue λ_ℓ:

$$O_\ell \Psi = a_\ell \Psi_\ell \tag{1.35}$$

The operator O_ℓ is therefore another projection operator,[6] which, in matrix representation, fulfills the Cayley-Hamilton equation $(\Lambda - \lambda_\ell) O_\ell = 0$, from which we easily derive the relation

$$O_\ell^2 = O_\ell \tag{1.36}$$

As an example, let us consider the projection operators associated with the spin degeneracy of N antisymmetric particles. Measuring the spin in units of $\hbar$, we know that S^2 has the eigenvalues $\ell(\ell + 1)$, where $\ell = N/2, (N/2) - 1, (N/2) - 2, \ldots 0$ or $1/2$, depending on whether N is even or odd. According to (1. 34), the operator for creating a state of multiplicity $(2\ell + 1)$ is then

$$(2\ell + 1)O = \prod^{k \neq \ell} \left\{S^2 - k(k + 1)\right\} / \left\{\ell(\ell + 1) - k(k + 1)\right\}, \tag{1.37}$$

where the product is taken over all $k \neq \ell$ from 0 to 1/2 or N/2. For S^2 we may here use one of the expressions

$$
\begin{aligned}
S^2 &= \sum_{ij} S_i \cdot S_j \\
&= S^+S^- + S_z^2 - S_z \\
&= -\left\{N(N-4)/4\right\} + \sum_{i<j} (1 + \sigma_i \cdot \sigma_j)/2 \\
&= -\left\{N(N-4)/4\right\} + \sum_{i<j} P_{ij}^{\sigma}
\end{aligned}
\tag{1.38}
$$

We shall now investigate the effect of our spin projection operators (1.37) on a single Slater determinant, built up from N spin-orbitals. Let us assume that N is even (N = 2n) and that we are interested in states with $S_z = 0$, i.e., having an equal number of α and β spins. Let us further assume that we have N space orbitals a_1, a_2, ... a_n, b_1, b_2, ... b_n at our disposal and that the first n orbitals are occupied by particles with plus spin and the last n orbitals are occupied by particles with minus spin. The corresponding Slater determinant

$$
\frac{1}{\sqrt{N!}} \det \left\{a_1\alpha, a_2\alpha, \ldots a_n\alpha; b_1\beta, b_2\beta, \ldots b_n\beta\right\} \tag{1.39}
$$

may then be denoted by the abbreviated symbol

$$
(\alpha\alpha \ldots \alpha|\beta\beta \ldots \beta) \tag{1.40}
$$

showing the spin distribution over the given orbitals in their given order. Let us further introduce the notations

$$
\begin{aligned}
T_0 &= (\alpha\alpha\alpha \ldots |\beta\beta\beta \ldots), \\
T_1 &= (|\beta\alpha\alpha \ldots | + |\alpha\beta\alpha \ldots | + \ldots ||\alpha\beta\beta \ldots | + |\beta\alpha\beta \ldots | + \ldots), \\
T_2 &= (|\beta\beta\alpha \ldots | + |\beta\alpha\beta \ldots | + \ldots ||\alpha\alpha\beta \ldots | + |\alpha\beta\alpha \ldots | + \ldots), \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
T_n &= (\beta\beta\beta \ldots |\alpha\alpha\alpha \ldots),
\end{aligned}
\tag{1.41}
$$

where T_k contains all different combinations obtained by k spin interchanges between the two originally given groups of orbitals; T_0 is identical with the given determinant (1.39). Following Pratt,[8] we have here used a symbolic form of "multiplying" determinants. T_k is the "product" of two factors, each containing $\binom{n}{k}$ terms, and T_k consists therefore of $\binom{n}{k}^2$ determinants.

By using the last form of (1.38) and counting terms, we may derive the formula

$$S^2 T_k = (n - k + 1)^2 T_{k-1} + \left\{n(2k + 1) - 2k^2\right\} T_k + (k + 1)^2 T_{k+1}, \qquad (1.42)$$

including the definition $T_{-1} = T_{n+1} = 0$. Since the projection operator (1.37) is a polynomial in S^2, we have then proved that there exists an expansion of the form

$$(2\ell + 1)O T_0 = \sum_{k=0}^{n} c_k T_k, \qquad (1.43)$$

The coefficients in this expansion may be determined by using (1.42) and the relation

$$S^2 \sum_k c_k T_k = \ell(\ell + 1) \sum_k c_k T_k, \qquad (1.44)$$

which leads to the recurrence formula

$$(n - k)^2 c_{k+1} + \left\{n(2k + 1) - 2k^2 - \ell(\ell + 1)\right\} c_k + k^2 c_{k-1} = 0 \qquad (1.45)$$

For the important cases of lowest and highest multiplicity ($\ell = 0$ and $\ell = n$), we obtain particularly

$${}^1O T_0 = c_0 \sum_{k=0}^{n} (-1)^k \binom{n}{k}^{-1} T_k, \qquad (1.46)$$

$$(2n + 1)O T_0 = c_0 \sum_{k=0}^{n} T_k. \qquad (1.47)$$

with the constants c_0 undetermined. The value of c_0 is usually unessential for the applications, but, by considering a system with doubly occupied orbitals, i.e., $a_k = b_k$, the value of c_0 for the singlet operator is determined: $c_0 = (n + 1)^{-1}$. The corresponding expansion for an arbitrary ℓ is somewhat more complicated.

It seems likely that, except for a constant factor, our projection operator for constructing singlets

$${}^1O = \left(1 - \frac{S^2}{1 \cdot 2}\right)\left(1 - \frac{S^2}{2 \cdot 3}\right) \cdots \left(1 - \frac{S^2}{n(n+1)}\right) \qquad (1.48)$$

is identical with the spin operator recently introduced by Pratt[8] in an entirely different way, and we note that (1.46) is just the Clebsch-Gordon expansion from which

Pratt started his investigations.

As an example, we shall calculate the energy of a spin state of multiplicity $(2\ell + 1)$ having a wave function obtained by projection of a single determinant

$$\Psi = {}^{(2\ell+1)}O\, T_0, \tag{1.49}$$

for a spin-free Hamiltonian. By using (1.36) and (1.43), we get

$$\int \Psi^* H_{op} \Psi(dx) = \sum_{k=0}^{n} c_k \int T_0^* H_{op} T_k(dx), \qquad \int \Psi^* \Psi(dx) = \sum_{k=0}^{n} c_k \int T_0^* T_k(dx). \tag{1.50}$$

In the simple case when all orbitals $a_1, a_2, \ldots a_n, b_1, b_2, \ldots b_n$ involved are strictly orthogonal (as for molecular orbitals), there will be contributions to the energy only for $k = 0$ and $k = 1$ and to the normalization integral only for $k = 0$. From (1.45) follows

$$c_1 = \frac{\ell(\ell+1) - n}{n^2}\, c_0, \tag{1.51}$$

and in this case, we obtain therefore

$$\langle H_{op} \rangle_{Av} = \int T_0^* H_{op} T_0(dx) + \frac{\ell(\ell+1) - n}{n^2} \int T_0^* H_{op} T_1 = W + \sum_{\mu} (\mu|H|\mu)$$
$$+ \frac{1}{2} \sum_{\mu\nu} (\mu\nu|G|\mu\nu) - \frac{1}{2} \sum_{\mu\nu}^{\parallel \text{ spins}} (\mu\nu|G|\nu\mu) - \frac{\ell(\ell+1) - n}{2n^2} \sum_{i,j=1}^{n} (a_i b_j|G|b_j a_i), \tag{1.52}$$

where the spin is eliminated in the matrix elements, and μ and ν are to be summed independently over all orbitals a_i, b_j.

Since the exchange integrals for Coulomb forces are always positive as "self-potentials", formula (1.52) shows that, under our specific assumption of orthogonality, the state with highest multiplicity will always have the lowest energy. This extension of Hund's rule was recently pointed out by Koster[9] by using Dirac's vector model.

Spin degeneracy problems have previously been treated by either Slater's determinant method or Dirac's vector model.[10] We note that, even if we have taken over some elements as the spin permutation operators in (1.38) from Dirac's theory, our approach is firmly based on Slater's determinant idea with the wave function (1.49) expressed as a sum of determinants. However, there is also a connection with the vector model, and if we form the mean value of the energy for all possible distributions of α- and β-electrons over the orbitals $a_1, a_2, \ldots a_n, b_1, b_2, \ldots b_n$, we obtain

$$\ll H_{op} \gg_{Av} \gg_{Av} = W + \sum_{\mu} (\mu|H|\mu) + \frac{1}{2} \sum_{\mu\nu} (\mu\nu|H|\mu\nu) - \left\{1 + \frac{4\ell(\ell+1) - 3N}{N(N-1)}\right\} \sum_{\mu\nu} (\mu\nu|G|\nu\mu), \tag{1.53}$$

which is just the average energy given by the vector model.

In the applications we shall sometimes free ourselves of the assumption of strict orthogonality and apply formula (1.50) to sets of orbitals having non-orthogonality or overlap integrals.

We note that the method described here is quite general and that degeneracies associated with the isotopic spin, the orbital angular momentum and other types of symmetry degeneracies may be treated analogously. A detailed report will be published.

An Extension of the Hartree-Fock Method to Degenerate Systems

The importance of the ordinary Hartree-Fock scheme depends partly on the fact that a single Slater determinant

$$\Psi_0 = \frac{1}{\sqrt{N!}} \det\left\{\psi_1, \psi_2, \cdots \psi_N\right\} \tag{1.54}$$

is the simplest wave function having the correct antisymmetry property which corresponds to the idea that the N particles are moving independently of each other in the N spin-orbitals $\psi_1, \psi_2, \psi_3, \cdots \psi_N$. Even if the antisymmetrization introduces a certain correlation between particles with parallel spins, the scheme has a visuality which is useful in the physical interpretations and in constructing ionized and excited states.

However, if the system has spin or orbital degeneracies, there is a difficulty connected with the fact that the total wave function must be expressed as a sum of Slater determinants, and part of the visuality seems then to be lost. We shall here show that this problem may be solved by treating the degeneracy by the projection operators introduced in the previous section.

Let Λ be the operator which is used for classifying the degenerate states (at least in a first approximation) and let O_ℓ be the projection operator (1.34) for selecting an eigenstate belonging to the eigenvalue λ_ℓ. The wave function

$$\Psi = O\,\Psi_0 \tag{1.55}$$

is then usually a sum of Slater determinants, but we note that it is still invariant with respect to unitary transformations of the spin-orbitals of the same spin type in Ψ_0.

It must therefore be possible to express the properties of the system in the invariant Dirac density matrix, [3]

$$\rho(x_1, x_2) = \sum_{k=1}^{N} \psi_k^*(x_1)\, \psi_k(x_2), \tag{1.56}$$

fulfilling the relation $\rho^2 = \rho$. In forming the average energy, we obtain

$$\int \Psi^* H_{op} \Psi(dx) = \int \Psi_0^* (O^+ H_{op} O)\, \Psi_0(dx), \qquad \int \Psi^* \Psi(dx) = \int \Psi_0^* O \Psi_0(dx), \tag{1.57}$$

i.e., the same expression as for a single determinant ψ_0 and a "composite" Hamiltonian of the form

$$\Omega_{op} = O^+ H_{op} O, \tag{1.58}$$

where one also has to take the normalization condition into account. Since the projection operator fulfills the relation (1.36), the composite Hamiltonian is reduced to $\Omega_{op} = H_{op} O$, if the operators H_{op} and Λ strictly commute.

The projection operators are symmetric with respect to the coordinates of the N particles involved, and, if their explicit form (1.34) is known, the composite Hamiltonian (1.58) may be expanded in the form

$$\Omega_{op} = \Omega + \sum_i \Omega_i + \frac{1}{2!} \sum_{ij}{}' \Omega_{ij} + \frac{1}{3!} \sum_{ijk}{}' \Omega_{ijk} + \dots, \tag{1.59}$$

containing also many-particle terms. Under specific assumptions about the basic spin-orbitals in (1.54), this expansion may sometimes be reduced to comparatively simple forms. As an example, we shall mention that if all the basic orbitals in (1.54) are strictly orthogonal, the combination of the equation $T_1 = (S^2 - n)\, T_0$ and the first relation in (1.52) leads to a composite Hamiltonian of the form

$$\Omega_{op} = W + \sum_i H_i + \frac{1}{2}\left\{1 + \frac{\ell(\ell+1) - n}{n^2} (S^2 - n)\right\} \sum_{ij}{}' G_{ij}, \tag{1.60}$$

containing also three- and four-particle operators, since S^2 is given by (1.38).

The question is now whether it is possible to extend the ordinary Hartree-Fock scheme to operators containing also many-particle terms. For a single determinant Ψ_0, all density matrices may be expressed as determinants of the invariant (1.56) and, in analogy to (1.4), we obtain therefore

$$\langle \Omega_{op} \rangle_{Av} = \int \Psi_0^* \, \Omega_{op} \, \Psi_0 (dx) = \Omega + \int \Omega_1 \, \rho(1', 1) \, dx_1 + \frac{1}{2!} \int \Omega_{12} \begin{vmatrix} \rho(1', 1) & \rho(1', 2) \\ \rho(2', 1) & \rho(2', 2) \end{vmatrix} dx_1 \, dx_2$$

$$+ \frac{1}{3!} \int \Omega_{123} \begin{vmatrix} \rho(1', 1) & \rho(1', 2) & \rho(1', 3) \\ \rho(2', 1) & \rho(2', 2) & \rho(2', 3) \\ \rho(3', 1) & \rho(3', 2) & \rho(3', 3) \end{vmatrix} dx_1 \, dx_2 \, dx_3 + \ldots , \tag{1.61}$$

where, after the operations in the integrands have been carried out, we have to put $x_i' = x_i$. The variation principle $\delta \langle \Omega_{op} \rangle_{Av} = 0$ leads then to extended Hartree-Fock equations of the form

$$\Omega_{eff}(1) \, \psi_k(x_1) = \sum_{\ell=1}^{N} \psi_\ell(x_1) \, \lambda_{\ell k} , \tag{1.62}$$

where the one-particle operator $\Omega_{eff}(1)$ is given by

$$\Omega_{eff}(1) = \Omega_1 + \int \Omega_{12} (1 - P_{12}) \, \rho(2', 2) \, dx_2$$

$$+ \frac{1}{2!} \int \Omega_{123} (1 - P_{12} - P_{13}) \begin{vmatrix} \rho(2', 2) & \rho(2', 3) \\ \rho(3', 2) & \rho(3', 3) \end{vmatrix} dx_2 \, dx_3 + \ldots , \tag{1.63}$$

and P_{ij} is the ordinary permutation operator for interchanging the coordinates x_i and x_j. Due to the invariance of (1.56), we may carry out a unitary transformation of the set ψ_k which brings the Hermitian matrix of the Lagrangian multipliers to diagonal form, and in this special case, we obtain

$$\Omega_{eff}(1) \, \psi_k(x_1) = \varepsilon_k \, \psi_k(x_1) \tag{1.64}$$

Since the operator Ω_{eff} is Hermitian, the eigenfunctions belonging to different "orbital energies" are automatically orthogonal.[11] The formal simplicity of our scheme depends partly on the fact that we are considering spin-orbitals without restraining conditions on the orbitals themselves; compare Ref. 11. Our results show that, even for a degenerate system, we may keep the idea of the existence of an "effective" Hamiltonian, but due to the degeneracy, all terms in (1.63) may now contain couplings between several spin-orbitals corresponding to the occurrence of many-particle forces.

In investigating the excited states, we shall now show that, in addition to its formal importance, the operator Ω_{eff} has also an essential physical meaning. Let us consider two states associated with the same eigenvalue of the classifying operator Λ and therefore having wave functions $\overline{\Psi}$ and Ψ, which are obtained from single determinants by the same projection operator:

$$\bar{\Psi} = O\,\bar{\Psi}_0, \qquad \Psi = O\,\Psi_0, \tag{1.65}$$

We characterize the determinants $\bar{\Psi}_0$ and Ψ_0 by their invariant density matrices (1.56), $\bar{\rho}$ and ρ. We have

$$\bar{\rho} = \rho + \Delta\rho = \rho + \Delta\rho_j - \Delta\rho_i, \tag{1.66}$$

and we shall assume that, in a first approximation, $\Delta\rho_i$ and $\Delta\rho_j$ are factorized in the following way:[12]

$$\Delta\rho_i(x_1, x_2) = \psi_i^*(x_1)\,\psi_i(x_2), \qquad \Delta\rho_j(x_1, x_2) = \psi_j^*(x_1)\,\psi_j(x_2). \tag{1.67}$$

This means that we are considering a single excitation $i \rightarrow j$, but the spin-orbitals ψ_i and ψ_j involved are still undetermined.

In order to determine the differences

$$\Delta E = \bar{E} - E, \qquad \Delta\Omega_{eff} = \bar{\Omega}_{eff} - \Omega_{eff}, \tag{1.68}$$

we shall put $\bar{\rho} = \rho + \Delta\rho$ into (1.61) and (1.63) and carry out the subtractions. The results may be expressed in terms of determinants of the elements ρ and $\Delta\rho$, and we note that all determinants of third or higher degree in $\Delta\rho$ will vanish identically independent of their order, since they may be expanded in determinants containing two or more columns of $\Delta\rho_i$ or $\Delta\rho_j$ which vanish due to the factorization in (1.67). Hence we obtain

$$\begin{aligned}\Delta E = {} & \int \Omega_{eff}(1, \Delta\rho(1', 1)\, dx_1 + \frac{1}{2}\int \Omega_{12} \begin{vmatrix} \Delta\rho(1', 1) & \Delta\rho(1', 2) \\ \Delta\rho(2', 1) & \Delta\rho(2', 2) \end{vmatrix} dx_1\, dx_2 \\ & + \frac{1}{2}\int \Omega_{123} \begin{vmatrix} \Delta\rho(1', 1) & \Delta\rho(1', 2) & \rho(1', 3) \\ \Delta\rho(2', 1) & \Delta\rho(2', 2) & \rho(2', 3) \\ \Delta\rho(3', 1) & \Delta\rho(3', 2) & \rho(3', 3) \end{vmatrix} dx_1\, dx_2\, dx_3 + \ldots,\end{aligned} \tag{1.69}$$

and

$$\begin{aligned}\Delta\Omega_{eff} = {} & \int \Omega_{12}(1 - P_{12})\, \Delta\rho(2', 2)\, dx_2 \\ & + \int \Omega_{123}(1 - P_{12} - P_{13}) \begin{vmatrix} \Delta\rho(2', 2) & \rho(2', 3) \\ \Delta\rho(3', 2) & \rho(3', 3) \end{vmatrix} dx_2\, dx_3 + \ldots.\end{aligned} \tag{1.70}$$

By putting $\rho = \bar{\rho} - \Delta\rho$ into (1.61) and repeating the subtraction, we obtain a new form for ΔE expressed in $\bar{\Omega}_{eff}$, $\bar{\rho}$, and $\Delta\rho$, which is analogous to (1.69) but has minus signs for all the determinants of the second degree in $\Delta\rho$. By adding the two expressions for ΔE, the determinants of second order cancel, and the higher order determinants combine to determinants of the third degree in $\Delta\rho$, which will then vanish identically due to (1.67). In this way, we obtain the simple formula

$$\Delta E = \frac{1}{2}\int\left\{\bar{\Omega}_{eff}(1) + \Omega_{eff}(1)\right\}\ \Delta\rho(1', 1)\, dx_1. \tag{1.71}$$

By using (1.70) and (1.67), we may derive the relation

$$\int\Delta\Omega_{eff}(1)\ \left\{\Delta\rho_i(1', 1) + \Delta\rho_j(1', 1)\right\}\ dx_1 = 0, \tag{1.72}$$

which, in combination with (1.71), gives

$$\Delta E = \int\bar{\Omega}_{eff}(1)\ \Delta\rho_j(1', 1)\, dx_1 - \int\Omega_{eff}(1)\ \Delta\rho_i(1', 1)\, dx_1, \tag{1.73}$$

or finally

$$\bar{E} = E + \int\psi_j^*(x_1)\,\bar{\Omega}_{eff}\,\psi_j(x_1)\, dx_1 - \int\psi_i^*(x_1)\,\Omega_{eff}\,\psi_i(x_1)\, dx_1, \tag{1.74}$$

According to the variation principle, the excited eigenstates of the Hamiltonian (1.1) are associated with the extreme values of $\bar{E}$, and since E is a constant, these occur simultaneously with the extreme values of the second and third terms in the right-hand member of (1.74), i.e., for functions ψ_j and ψ_i satisfying

$$\bar{\Omega}_{eff}\,\psi_j = \bar{\epsilon}_j\,\psi_j, \qquad \bar{\Omega}_{eff}\,\psi_i = \epsilon_i\,\psi_i. \tag{1.75}$$

For the excitation energy, we obtain

$$\bar{E} - E = \bar{\epsilon}_j - \epsilon_i. \tag{1.76}$$

The process may be described as an excitation $i \rightarrow j$ of an entire particle from an occupied spin-orbital ψ_i to an unoccupied spin-orbital ψ_j. We note that the orbital energy $\bar{\epsilon}_j$ refers to the "effective Hamiltonian" $\bar{\Omega}_{eff}$ for the excited state, which gives a correction of the naive form $\epsilon_j - \epsilon_i$ for the excitation energy.[13]

Let us now consider the corresponding wave functions $\bar{\Psi}$ and Ψ, which may be obtained from (1.65) and (1.66). By a suitable unitary transformation, the determinant Ψ_0 may be built up from eigenfunctions to the operator Ω_{eff}, and the determinant

Ψ_0 may be built up from eigenfunctions to the operator Ω_{eff}, and the determinant Ψ_0 may then be obtained by replacing the column containing the spin-orbital ψ_i in Ψ_0 with a new column containing the excited spin-orbital ψ_j. By using (1.70) and (1.67), we may derive the relation

$$\int \psi_j^* \, \Delta\Omega_{eff} \, \psi_i \, dx_1 = 0 , \tag{1.77}$$

which shows that the spin-orbitals ψ_j and ψ_i satisfying (1.75) are still orthogonal. The same is then true for the single determinants $\bar{\Psi}_0$ and Ψ_0, and one can further show that, for rather general forms of the projection operator O (as for the ordinary and isotopic spins), the total wave functions $\bar{\Psi}$ and Ψ also fulfill the necessary orthogonality condition.

The projection operator formalism renders also a simple way of calculating transition moments, for if $\vec{D} = e \sum_i \vec{r}_i$ is the moment operator, we have

$$\int \bar{\Psi}^* \, \vec{D} \, \Psi(dx) = \int \bar{\Psi}_0^* (O \, \vec{D} \, O) \, \Psi_0(dx) , \tag{1.78}$$

which may be expanded analogously to (1.61).

We have here treated the excited states before the ionized states, since, in the excitations, the total number of particles is kept constant, which is of importance for the form of the projection operator O in (1.65). However, since an ionization may be considered as the limiting case of an excitation to a spin-orbital ψ_j at infinity with $\bar{\epsilon}_j = 0$, we obtain from (1.76)

$$\bar{E} - E = -\epsilon_i , \tag{1.79}$$

showing that $(-\epsilon_i)$ is the ionization energy. This is an extension of Koopmans' theorem[4] to degenerate systems or to Hamiltonians containing many-particle interactions.

(REMARKS ON THE BASIS OF THE ONE-ELECTRON APPROXIMATION)

A Method of Alternant Molecular Orbitals*

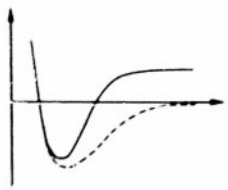

Fig. 1-1

In a theory of molecules and crystals, where the total wave function is approximated by a single determinant constructed from molecular spin-orbitals, there is a certain difficulty connected with the fact that the cohesive energy shows a wrong asymptotic behavior for separated atoms.[14] This depends on the fact that such a wave function permits electrons of different spins to accumulate on the same atom and give rise to negative and positive ions having higher energy together than the ordinary dissociation products. See Fig. 1-1. One way of removing this defect is by configurational interaction, but except for the simplest molecules, this approach leads usually to secular equations of such a high order that they are extremely hard to solve.

Fortunately, there seems to be also another approach to this problem. Slater[15] has many times pointed out that in an antiferromagnetic material there must be a tendency for a certain spin alignment with the crystal divided into two sublattices with the valence electrons having either plus or minus spin. Slater is accordingly looking for a crystal theory which would be similar to a valence bond method for separated atoms and similar to a molecular orbital method for small and intermediate distances between the atoms, but until now none has succeeded in finding a bridge between these two stages. The essential point is apparently to find a modification of the ordinary molecular orbital method which, for separated atoms, automatically would lead to a spin alignment of the type proposed by Slater, for then there would be no possibility for the excessive occurrence of ions.

Fig. 1-2
Semi-localized molecular orbitals for a diatomic molecule.

In investigating the hydrogen molecule, Coulson and Fischer[16] showed that by introducing an additional parameter they could continuously transform a molecular orbital over a semi-localized molecular orbital into an atomic orbital. See Fig. 1-2. The question is now whether one could generalize this idea to a polyatomic molecule or a crystal.

Let us say that by solving the Hartree-Fock equations by, e.g., the MO-LCAO method, we have found a set of MO's for the valence electrons[17] belonging to the system. In the naive MO theory, the orbitals for the valence electrons are only partly filled. By using all the MO's available, we may now

- - - - - - - - - - - - - - - -

*A preliminary report of the ideas in this section was first presented by the author at the Nikko symposium of the Japanese International Conference on Theoretical Physics, September, 1953, by using the conventional methods of construct-spin multiplets. The treatment is here essentially simplified by the introduction of the projection operators.

try to construct combinations which tend to be localized on two interpenetrating subsystems, I and II, for separated atoms. For the sake of simplicity, let us consider an alternant system, for instance, a crystal constituted of two equivalent sublattices I and II, as the body-centered cubic structure, or an alternant hydrocarbon[18] where the atoms, if one moves along a chain of unsaturated carbon atoms, belong alternately to set I and to set II.

We let ϕ_μ be the ordinary atomic orbitals associated with the system and having the overlap integrals

$$\phi_\mu \, \phi_\nu \, dx = \Delta_{\mu\nu} = \delta_{\mu\nu} + S_{\mu\nu} \tag{1.80}$$

and we introduce further the orthonormalized AO's φ_μ by the formula[19] $\varphi = \phi\Delta^{-1/2}$ or

$$\varphi_\mu = \sum_a \phi_a \, \Delta_{a\mu}^{-1/2} \tag{1.81}$$

It is a characteristic feature of the alternant systems that the MO's occur in pairs, j' and j'', with orbital energies $\varepsilon_{j'}$ and $\varepsilon_{j''}$ belonging to symmetric places in the lower and the upper half of the "energy band", respectively. The excited orbital $\psi_{j''}$ is obtained from the lower orbital $\psi_{j'}$ by changing the sign of the coefficients of the AO's of one of the subsystems, let us say II:

$$\begin{aligned} \psi_{j'} &= \sum_\mu^{\mathrm{I}} \varphi_\mu \, c_{\mu j} + \sum_\mu^{\mathrm{II}} \varphi_\mu \, c_{\mu j}, \\ \psi_{j''} &= \sum_\mu^{\mathrm{I}} \varphi_\mu \, c_{\mu j} - \sum_\mu^{\mathrm{II}} \varphi_\mu \, c_{\mu j}. \end{aligned} \tag{1.82}$$

Let us now form the combinations

$$\begin{aligned} \psi_{j\mathrm{I}} &= a\psi_{j'} + b\psi_{j''} = (a+b) \sum_\mu^{\mathrm{I}} \varphi_\mu \, c_{\mu j} + (a-b) \sum_\mu^{\mathrm{II}} \varphi_\mu \, c_{\mu j}, \\ \psi_{j\mathrm{II}} &= a\psi_{j'} - b\psi_{j''} = (a-b) \sum_\mu^{\mathrm{I}} \varphi_\mu \, c_{\mu j} + (a+b) \sum_\mu^{\mathrm{II}} \varphi_\mu \, c_{\mu j}. \end{aligned} \tag{1.83}$$

Since the normalization condition takes the form $a^2 + b^2 = 1$, we may put $a = \cos\theta$ and $b = \sin\theta$ and describe the mixing between the MO's by an angle θ. We note that the special cases:

$\theta = 0$, ordinary lower half MO's,

$\theta = 45^{\circ}$, purely alternant MO's

$\theta = 90^{\circ}$, ordinary upper half MO's.

For $0 < \theta < 90^{\circ}$, the orbitals ψ_{jI} are semi-localized on system I and the orbitals ψ_{jII} on system II, and we shall therefore call them alternant molecular orbitals. For $\theta = 45^{\circ}$ this localization may be complete. We note further that orbitals belonging to different indices j are orthogonal and that

$$\psi_{jI}\,\psi_{jII}\,dx = \cos 2\theta = \lambda . \tag{1.84}$$

As a simple example, we may consider the lowest orbitals for a linear chain. See Fig. 1-3.

Fig. 1-3

In order to construct a wave function for the system, which has the correct asymptotic behavior for separated atoms, we shall now consider a Slater determinant

$$T_0 = (\underset{I}{\alpha\alpha\alpha\ldots} \mid \underset{II}{\beta\beta\beta\ldots}) \tag{1.85}$$

where we have used the notation (1.40), and each orbital of type I is occupied by an electron with plus spin and each orbital of type II by an electron with minus spin. The various spin multiplets may then be obtained by using the projection operator (1.37):

$$\underset{\sim}{\Psi} = {}^{(2\ell+1)}O\,T_0 , \tag{1.86}$$

If, for separated atoms, we let θ tend to the value $\theta = 45^{\circ}$, there will be a spin alignment of the type proposed by Slater, and the wave function (1.85) will then have the correct asymptotic behavior. We shall now check that the various spin multiplets with the wave function (1.86) also have preserved this property. For $\theta = 45^{\circ}$, the discussion is simplified by the fact that all the alternant MO's become strictly orthogonal, cf (1.84), and the energy is then given by formula (1.52):

$$\langle H_{op}\rangle_{Av} = \int T_0^{*}\,H_{op}\,T_0(dx) - \frac{\ell(\ell+1) - n}{2n^2} \sum_{j,k=1}^{n} (jI, kII|G|kII, jI) . \tag{1.87}$$

Since the exchange integrals in the last term in the right-hand member tend to go to zero for $\theta = 45^{\circ}$ and separated atoms, our theorem is proved.

For $\theta = 0$ and $l = 0$, the function (1.86) reduces to the well known single determinant wave function of the ordinary MO theory. This means that, by varying θ, we may obtain a depression of the energy curve also for intermediate distances, and in particular cases, the improvement of the energy minimum may be appreciable. The physical interpretation of this procedure will be discussed in the next section. The energy expression in the general case ($\theta \neq 45^{\circ}$) is somewhat more involved than (1.87), due to the occurrence of the non orthogonality integral $\lambda = \cos 2\theta$ in (1.84), but there are no principal difficulties in its derivation. A full discussion of the energy at intermediate distances, including a comparison between the spin states of various multiplicity, is now being prepared for publication.

Some Aspects on Correlation Energy

The basic idea of the "independent-particle model" is that, in a first approximation, one can neglect the mutual interaction between the N particles in the system in constructing the total wave function, which then takes the simple product form

$$\psi_1(x_1)\psi_2(x_2) \cdots \psi_N(x_N), \tag{1.88}$$

where $\psi_1, \psi_2, \cdots \psi_N$ are a set of N spin-orbitals. However, between the particles i and j there is in a reality a potential G_{ij} which, particularly for small distances $r_{ij} \approx 0$, may be tremendously large. If this potential is repulsive, like the Coulomb potential $G_{ij} = e^2/r_{ij}$, it tries naturally to keep the particles apart, and since this "correlation" between the movements of the particles is entirely neglected in forming (1.88), the corresponding energy is affected by an error which is usually called the "correlation energy".

The situation is somewhat changed by the antisymmetrization procedure, which transforms the product function (1.88) into a single Slater determinant. For every antisymmetric wave function, the second order density matrix (1.3)

$$\Gamma(x'_1 x'_2 x_1 x_2) \tag{1.89}$$

is also antisymmetric in each pair of its indices, and this implies that, if two indices are the same ($x'_1 = x'_2$ or $x_1 = x_2$), the corresponding element will vanish identically. For the diagonal element we obtain in particular

$$\Gamma(x_1 x_2 x_1 x_2) = 0, \qquad \text{for } x_1 = x_2, \tag{1.90}$$

showing that the probability density for two particles with the same spin to be in the same place is zero (the "Fermi hole"). This means that the antisymmetry itself acts as if there would be a rather strong repulsion[20] between particles with the same spin at small distances, and this consequence of the Pauli principle automatically diminishes the error due to the neglect of the G_{ij} correlation. The exchange energy will therefore take care of a rather large part of the original correlation energy, referring to particles with parallel spins, and the corresponding effect of the antisymmetrization on the particle distribution has been investigated by Lennard-Jones.[21]

The main problem is apparently to take the correlation between particles having different spins into proper account, and a first estimate of this effect was given by Wigner.[22] Here we shall now use another approach to this problem and show that it is possible to treat the main part of this effect within our extension of the Hartree-Fock approximation.

Part of the importance of the ordinary Hartree-Fock scheme depends on its visuality, which is useful in the physical interpretations and in constructing the ionized and excited states, and in a previous section, we have shown that this visuality is also preserved in our extended scheme, where the wave function Ψ is a projection of a single determinant Ψ_0:

$$\Psi = O\Psi_0 , \tag{1.91}$$

cf. (1.55). We shall now take the correlation into account by utilizing the fact that we build up our basic determinant Ψ_0 from spin-orbitals of such a type that the orbitals for particles having different spins may be different in order to let the particles avoid each other. This extension of the ordinary picture is possible since we have become free of the idea of "doubly filled orbitals".[23]

As a first example, we may consider the two-electron problem and its applications to the helium atom and to the hydrogen molecule. By starting from two basic orbitals $u(\vec{r})$ and $v(\vec{r})$, we may construct a total wave function $\Psi = O(u\alpha, v\beta)$, which for the singlet state, is reduced to the form

$$\Psi = \text{const.} \left\{u(\vec{r}_1)\, v(\vec{r}_2) + u(\vec{r}_2)\, v(\vec{r}_1)\right\} \left\{\alpha(1)\, \beta(2) - \alpha(2)\, \beta(1)\right\} . \tag{1.92}$$

This is one of the exceptional cases, where it is possible to separate the orbital and spin parts of the total function into two factors. The orbitals u and v may be strongly overlapping, and their best form is found by solving the extended Hartree-Fock equations (1.64). However, due to the connection with other investigations, we may obtain some preliminary results without further calculations.

Let us start by considering the normal state $(1s)^2$ of the helium atom. In the

literature are given the results obtained by approximating u = v by a single exponential function[24] or by a Hartree function.[25] (See Table 1-1.

Table 1-1

Approximation (u = v)	Energy
Single exponential function (Z = 1.6875)	2.8476
Hartree function	2.867
Experimental	2.9032

If we now try to include the correlation, we shall use two different orbitals ($u \neq v$) having a somewhat different radial distribution in order to permit the two electrons to avoid each other. If u and v are approximated by exponential functions associated with different effective nuclear charges Z_1 and Z_2, one obtains by using the variation principle:

Table 1-2

Approximation ($u \neq v$)	Energy
Exponential functions with $Z_1 = 1.19$ and $Z_2 = 2.184$	2.8756

a result first given by Eckart[26] by considering only the spatial part of the wave function (1.92); all energies are here expressed in the atomic units (e^2/a_o = 2 Ry). It is somewhat surprising to see that, already in this rather rough approximation, the energy comes out better than in the conventional Hartree-Fock scheme

Eckart's results have recently been improved by Taylor and Parr[27] by using a method of configurational interaction based on a series of determinants of exponential functions. Their results have been analyzed with respect to the electron distribution by Lennard-Jones[28] who has shown that the spatial correlation here may occur in two ways: as an "in-out" effect, with one electron tending to be outside the other, and as an "angular" effect with the two electrons tending to be on opposite sides of the nucleus. However, Taylor and Parr pointed out that, even if they obtained about 97 percent of the angular correction, their method showed a slow convergency with respect to the radial correlation and their best wave function contained only 64 percent of the radial correlation energy.

It will be interesting to see how good the wave function (1.92) can be, if the two orbitals u and v are determined as solutions to the Hartree-Fock equations (1.64) in their extended form. In contrast to Hylleraas' famous solution as well as to Taylor

and Parr's series of determinants, the function $\psi = O(u\alpha, v\beta)$ has a simplicity and visuality which is of advantage in the physical interpretations. Numerical calculations on the helium problem are now in progress.

The wave function (1. 92) could be applied also to the hydrogen molecule problem, and the question is how good an approximation of James and Coolidge's result one could obtain in this way. It would probably be very hard to solve the extended Hartree-Fock equations (1. 64) for such a problem, but significant results could be obtained by using the variation principle. In this connection we observe that the method of alternant molecular orbitals of the previous section is nothing but an approximate method for taking the correlation into account, since it is based on the use of orbitals (see Fig. 1-2 and 1-3) which permit electrons of different spins to avoid each other.

Our results are in close agreement with ideas of the correlation energy in crystals due to Slater,[29] who assumes that the main part of the difference between the two curves in Fig. 1-1 is just the correlation energy of the crystal in addition to the correlation energy of the constituents. As shown in the previous section, we can eliminate this difference by the method of alternant molecular orbitals which is just one of the ways of treating correlation effects in our extended Hartree-Fock scheme. In considering the atomic orbitals, we can say that our correlation correction is associated with the elimination of the excessive occurrence of negative ions with too closely condensed electrons. However, at intermediate distances and particularly at the energy minimum, there is a fraction of these negative ions left, and they are associated with Coulomb integrals which certainly are too large, since the electrons are too closely condensed. The same problem occurs in the theory of conjugated organic compounds (ethylene, benzene, etc.) and Moffitt and Pariser and Parr have proposed that one should solve this difficulty by replacing this atomic Coulomb integral by a lower value taken from experiments. We observe that a more strict approach is here possible, since we may construct our alternant molecular orbitals from atomic orbitals, which are slightly different for electrons having different spins.

In conclusion we note that, by using the idea of projection operators and wave functions of the form (1. 91), we have here given a generalization of the ordinary Hartree-Fock scheme to include the treatment of degeneracies as well as correlation effects. The extended Hartree-Fock equations (1. 64) are associated with a "composite" Hamiltonian (1. 58) containing also many-particle operators, but otherwise the scheme has preserved the simplicity and visuality characteristic for the theory based on a single Slater determinant. It seems to us therefore worth while to investigate the numerical applications of this scheme in greater detail, and in addition to the helium problem, we are now going to re-examine our previous treatment of the sodium crystal.

References

1. S. F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950); A201, 125 (1950); A206, 489 (1951); A207, 181, 197 (1951); etc.
2. A. Meckler, J. Chem. Phys. 21, 1750 (1953).
3. P. A. M. Dirac, Proc. Camb. Phil. Soc. 26, 376 (1930); 27, 240 (1931).
4. T. Koopmans, Physica 1, 104 (1933).
5. J. C. Slater, Technical Report No. 3, Solid-State and Molecular Theory Group, M. I. T., February 15, 1953, p. 39; Phys. Rev. 91, 528 (1953).
6. J. v. Neumann, Math. Grundlagen der Quantenmechanik, Dover Publications, New York, 1943, p. 41.
7. J. C. Slater, Phys. Rev. 81, 385 (1951).
8. G. W. Pratt, Phys. Rev. 92, 278 (1953).
9. G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., July 15, 1953, p. 37.
10. P. A. M. Dirac, Proc. Roy. Soc. (London) A123, 714 (1929); Principles of Quantum Mechanics, Oxford, 1935; see also references in E. M. Corson, Perturbation Methods in the Quantum Mechanics of n-Electron Systems, Glasgow, 1951.
11. Compare, e.g., D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A154, 588 (1936).
12. The condition for such a factorization may be expressed in the form that the three matrices $\rho - \Delta\rho_i$, ρ, $\rho + \Delta\rho_j$, should be idempotent ($\rho^2 = \rho$, etc.) and that the first should belong to the subspace defined by the third; see (1.24). The matrices $\Delta\rho_i$ and $\Delta\rho_j$ are then also idempotent with 0 and 1 as the only eigenvalues, and their traces are then integers. For a single excitation, their tracers are 1, and their coefficient matrices have then a single eigenvalue equal to 1 and the others equal to 0. By transformation to diagonal form, i.e., to natural spin-orbitals, $\Delta\rho_i$ and $\Delta\rho_j$ take then the form (1.67).
13. Compare, e.g., C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).
14. See, e.g., J. H. Van Vleck and A. Sherman, Revs. Modern Phys. 7, 167 (1930) and J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., January 15, 1952, p. 26.
15. J. C. Slater, Phys. Rev. 35, 509 (1930); Proc. Shelter Island Conf. on Quantum Mechanical Methods in Valence Theory, 121 (1951).
16. C. A. Coulson and I. Fischer (-Hjalmars), Phil. Mag. 40, 386 (1949).
17. The valence electrons may be of different types, corresponding to single bonds, double bonds, etc., and in a first approximation we shall assume that each type may be treated separately. The ion cores are completely filled and need not be discussed here.
18. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A192, 16 (1948).
19. P. O. Löwdin, Arkiv Mat. Astr. Fysik 35A, No. 9 (1947); J. Chem. Phys. 18, 365 (1950).
20. In analogy to (1.57) and (1.58), we may interpret the effect of the antisymmetrization as if we still considered simple product functions (1.88) but a "composite" Hamiltonian of the form

References (con'd)

20. (con'd)

$$\Omega_{op} = H_{op} A, \qquad A = \frac{1}{N!} \sum_{P} (-1)^{P} P,$$

where A is the antisymmetrization operator.

21. J. E. Lennard-Jones, J. Chem. Phys. 20, 1024 (1952).

22. E. P. Wigner, Phys. Rev. 46, 1002 (1934); Trans. Faraday Soc. 34, 678 (1938).

23. The possibility of having different orbitals for different spins was first pointed out by Hartree and Hartree (see Ref. 11) in their treatment of the excited states of beryllium, but was never used by them. The importance of this possibility for describing ferromagnetic and antiferromagnetic material has several times been emphasized by Slater.

24. G. Kellner, Z. Physik 44, 91 (1927).

25. D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 111 (1928); for the energy value, see H. Bethe, Handb. Physik XXIV:1, 370.

26. C. Eckart, Phys. Rev. 36, 878 (1930).

27. G. R. Taylor and R. G. Parr, Proc. Nat. Acad. Sci. 38, 154 (1952).

28. J. Lennard-Jones, Phil. Mag. 43, 581 (1952).

29. J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1952, p. 17.

P. O. Löwdin

2. MANY-CONFIGURATION CALCULATIONS ON BENZENE

The energy calculations on the π electron system of benzene have now been completed and an account will be published in due course as a third paper in the series, "The Valence Bond Theory of Molecular Structure".[1, 2] The calculations have already been outlined[3] and it now seems opportune, in the light of the final results, to attempt a comparative survey of the various many-configuration approaches.

In Fig. 2-1 we illustrate the results of three types of calculation of the benzene π electron levels. These comprise: (1) The MO method, with and without a limited amount of configuration interaction;[4] (2) The $\overline{\text{VB}}$ method, also in various stages of elaboration; (3) The conventional VB method, in which the five non-polar singlet and nine triplet VB structures were expanded into $\overline{\text{VB}}$ structures so that rigorous energy calculations could be made, using the existing $\overline{\text{VB}}$ techniques (see also Ref. 3). It will be remembered that in the parallel calculations on cyclobutadiene[3] both the principal methods (MO and $\overline{\text{VB}}$) could be carried through to completion (within the given basis of 2p AO's) and that they then yielded identical results as indeed they must from general theory. In the present case, however, there are too many configurations to make such a calculation at all attractive, and so the different incomplete approaches give "final" results which are still at variance. The most striking feature of the figure is probably the obvious importance of configuration interaction:

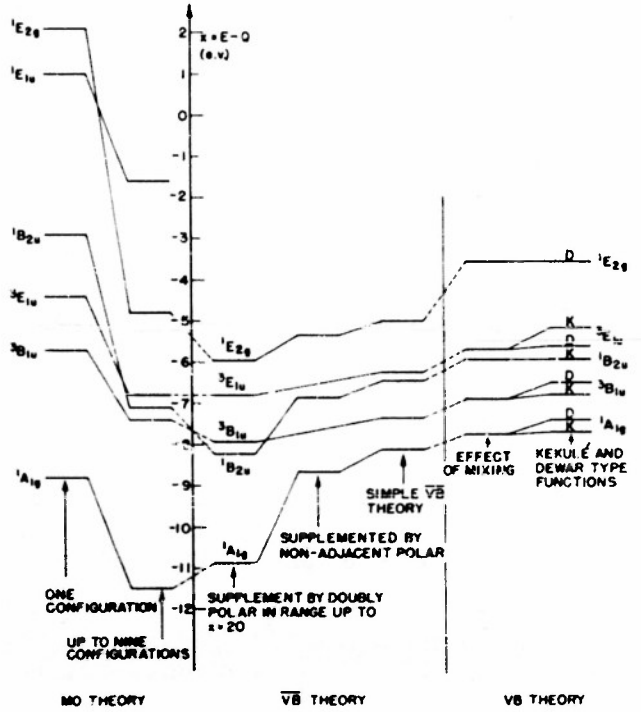

Fig. 2-1
Benzene π electron levels

its inclusion does not represent a refinement but leads rather to a complete reorganization of the energy level system, and taken at face value the results are almost equally discouraging by whichever method we proceed. But let us look at the various approaches individually.

The MO Method

The principal advantage of the MO theory is undoubtedly the simplicity of its first approximation to the ground state wave function; this simplicity is independent of molecular size and the approximation may, as the present calculations show, reach an accuracy which is not easily surpassed. But although these features of the MO method make it extremely attractive, they should not be overrated. In the first place, the one-configuration approximations to the excited states are obviously unreliable, while even the ground state predictions are not infallible (as, for instance, in the case of cyclobutadiene); and, in the second place, the conceptual and mathematical simplicity of the method is characteristic only of this first approximation.

On the other hand, the many-configuration method is inescapably clumsy and the absence (in general) of any guiding principles in selecting the appropriate configurations leads to considerable uncertainty. Parr, Craig and Ross, for instance, considered only excitation of one or two electrons from the lowest energy MO's: they confidently asserted, on the basis of previous calculations (where, however, many integrals were neglected), that their results should closely approach those of a complete calculation, but we now see that the configurations they omitted must have a considerable net effect, though individually they might appear unimportant. Both difficulties are clearly related to the non-localized character of the MO's. This means, firstly, that all the matrix elements involve orbitals which overlap strongly throughout the molecule and consequently that there is little scope for simplifying approximations in estimating the effect of the higher configurations (as there might be if the orbitals were tightly localized so that many of the component integrals in a matrix element were negligible). Secondly, that improvement of the wave function in particular regions, e.g., to keep two electrons off the same atom, or to describe the piling up of charge on an atom of high electron affinity, must demand the superposition of many configurations, since each one of them spreads every electron out fairly uniformly over the molecule. There is a rough parallel here with the exciton problem, where many configurations of Bloch orbitals must be superposed in order to describe the local correlation between electron and hole.[5]

The $\overline{\text{VB}}$ Method

From Fig. 2-1, we see that the $\overline{\text{VB}}$ method is perhaps better adapted to prediction of the general character of an energy level system, and particularly of the

excited states, which are so poorly approximated in the earlier stages of the MO approach. Even the simple theory (in which only the obvious structures are included) predicts levels which are probably in the correct order, * and it will be remembered that this was also true in the case of cyclobutadiene. And although, quantitatively, the ground state is slightly inferior to that of simple MO theory the excited states are very much better. The $\overline{VB}$ calculation is very easily systematized and owing to the strongly localized form of the basic orbitals the difficulties discussed in the last section do not arise. In fact, the smallness of most of the $\overline{AO}$ integrals allows us to approximate matrix elements between all pairs of structures, often in terms of just one integral, with remarkable accuracy -- precisely as in the cyclobutadine calculation,[3] and the results of the many-configuration calculation again were found to be scarcely affected by simplifications of this kind. At the same time, the pictorial interpretation of bonding, in terms of "charge hopping", suggests immediately which structures should be mixed to describe the lower energy states.

We must not lose sight, however, of the fact that large numbers of $\overline{VB}$ structures must be included in the calculation. The obvious way of accounting for nearest neighbor bonds, for example, is to include all non-polar and adjacent-charge singly-polar structures (e.g., 29 for the benzene singlet states) and, except in cases of high symmetry, this leads immediately to secular equations of high order; this is the penalty we pay for constructing functions which we can handle so easily. Moreover, to get good results we should certainly include a reasonable selection of doubly-polar structures, for in the present case the 36 doubly-polar structures which interact most strongly with those of the simple theory stabilize the ground state by no less than 2 ev. The corresponding figure for cyclobutadine was 1/2 ev and this suggests most strongly that the importance of the multiply-polar structures increases with their abundance, i.e., with increasing molecular size. The inference seems to be that the MO approach (which, in effect, puts the multiply-polar structures on the same footing as the non-polar) should become increasingly successful with increasing molecular size. It is well known that this is true of the naive MO theory of conjugated molecules and it is perhaps for similar reasons that the approximations of solid-state theory are so remarkably satisfactory. There are apparently two directions in which calculations of the present kind might be extended: (1) Simple saturated molecules, where the number of "reasonable" $\overline{VB}$ structures may be fairly small; (2) More complicated systems (e.g., larger conjugated molecules), with the assumption that similar structures may be grouped into "blocks" so as to artificially reduce the dimensions of the

*The final reversal of the $^1B_{2u}$ and $^3B_{1u}$ levels is probably spurious. Inclusion of non-adjacent charge triplet structures was not considered worth while in view of their small effect on the singlet states, but they would probably depress the $^3B_{1u}$ by as much as 1/2 ev.

secular problem (and in which the matrix elements would certainly be approximated throughout). First experiments along the lines of (2) have already been made in the case of cyclobutadiene,[3] and now in the case of benzene, by introducing the blocks of $\overline{VB}$ structures to which the orthodox VB structures are equivalent. This of course enables us at the same time to bring the old VB theory into the discussion.

The VB Method

The benzene states which we have considered (and no more) can all be built up out of 5 singlet VB structures (2 "Kekulé", 3 "Dewar") or 9 triplet structures (6 Kekulé type, 3 Dewar type, each with one (+) link). Expansion into $\overline{VB}$ structures (see Ref. 2) then yields 5 singlet combinations and 9 triplet, and the dimensions of the secular equations are then 5 and 9, ignoring for the moment symmetry reductions, instead of the corresponding 29 and 45 of simple VB theory. In practice of course the Kekulé and Dewar structures give independent symmetry combinations and the secular determinants never exceed 2 x 2. If the results are good we shall have good reason for saying that the molecule is well described by a mixture of "bonded structures"; if they are very bad we shall be tempted to say that, in this case, chemical intuition finds no support at all in the wave mechanics of the problem. The matrix elements are easily evaluted by $\overline{VB}$ methods. The diagonal energies of the combinations of various symmetry, labeled K or D according as they are built from Kekule or Dewar VB structures, are shown on the extreme right of Fig. 2-1, and these are mixed to get the best VB theory results in the next column. It is clear of course that the expansion of a VB structure should strictly include all kinds of $\overline{VB}$ structures, but the non-adjacent charge and multiply-polar structures are found to be so grossly underweighted that their inclusion does not materially affect the results and they are therefore best omitted. Inclusion, for example, of 36 of the doubly-polar terms improved the VB ground state by only about 1/2 ev, out of the 4 ev required. The energy levels we have given, then, are substantially representative of a rigorous energy calculation on the orthodox VB theory. It is now seen that in the ground state this theory is about as successful as simple MO theory (or only slightly inferior) but that it is considerably more reliable in its predictions of the excited states. This is encouraging, in spite of the fact that the results are still not very good quantitatively, and shows that the VB method, in whichever way it is developed, is worthy of further attention. The principal defect of VB wave functions is their failure to give sufficient weight to their polar $\overline{VB}$ constituents. Unfortunately, this failure cannot be corrected within the framework of simple (i.e., non-polar) VB theory; in order to get really good wave functions it would be necessary to add at least singly-polar VB structures (which have a correspondingly higher content of polar $\overline{VB}$ structures). It is evident then that the mixing of a few obvious "bonded structures" can give a rough account of the first few

electronic states, but that this procedure is not sufficiently flexible to be really adequate. In the circumstances it would seem better to keep to the straightforward $\overline{VB}$ formulation, which is inherently so flexible, rather than reverting to a wholehearted attack on the problems of orthodox VB theory, we might for instance expand intuitively satisfactory VB structures and subsequently improve them by increasing the weights of their polar constituents, either parametrically or simply in accordance with experience -- the idea simply being to get a better starting point before proceeding to the secular problem.

Conclusion

Convergent calculations by at least three many-configuration methods are certainly feasible for simple molecules. If attention is confined to the ground state, and if each theory is used in its simplest approximation, there seems to be little to choose between the three approaches. But in calculations of excited states, and in the systematic elaboration of each theory, the valence bond approach appears to offer distinct advantages. These conclusions can only be fully substantiated by detailed calculations on a number of molecules. In particular, we should consider simple saturated molecules: here all electrons can be treated explicitly and there is no need for the "framework" assumption which characterizes π electron calculations, and there are reasons for believing that the VB approximation of perfect pairing (one VB structure) may prove particularly satisfactory. Preliminary work along these lines is now in progress.

References

1. R. McWeeny, Proc. Roy. Soc. (London) A223, 63 (1954).
2. R. McWeeny, ibid., A223, 306 (1954).
3. R. McWeeny, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1954, p. 25.
4. R. G. Parr, D. P. Craig and I. G. Ross, J. Chem. Phys. 18, 1561 (1950).
5. J. C. Slater, Technical Report No. 6, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 15.

R. McWeeny

3. LIMITED CONFIGURATION INTERACTION TREATMENT OF THE NH_3 MOLECULE

All necessary one-electron integrals have been evaluated and progress has been made with the remaining two-electron integrals. In connection with integrals of the form (NH|HH) it has been found necessary to extend Schweinler's work on the decomposition of direct products of spherical harmonics[1] to include products of the forms $e_{\ell m} e_{4t}$ and $e_{\ell m} e_{5v}$ where t = 0, - 1, . . . , - 4 and v = 0, - 1, . . . , - 5. The results are available but were deemed too cumbersome to be worth reproducing here.

Reference

1. H. C. Schweinler, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1954, p. 51.

H. Kaplan and S. Bucksbaum

4. A THEORY OF SCATTERING IN SOLIDS

In a paper entitled, "Wave Functions for Impurity Levels" which the author and J. C. Slater have submitted to The Physical Review for publication, we have considered the effect on the wave functions of a crystal of a perturbation of some sort in it which destroys the perfect periodicity. This work was summarized in the recent Progress Reports of this group as well as in Technical Report No. 5. In this work, we set up the problem of this perturbation in a crystal in terms of a set of difference equations which the coefficients of the Wannier functions satisfy when the wave function of the impurity level is expanded in the complete set of Wannier functions. The method used to satisfy this set of difference equations was essentially a Green's function method applied to difference equations. This method was particularly useful in studying the bound states associated with an impurity. For the unbound states, those states whose energies lie in the band, the method turns out to be somewhat ambiguous. What we are interested in for the unbound states is essentially a scattering problem. The difficulty with the method described in the aforementioned paper was that it did not guarantee that the scattered wave corresponded to an outgoing wave. This difficulty has been overcome by modifying the formalism which is useful for the bound states. The results of this new treatment have been submitted to The Physical Review by the author under the same title as the title of this contribution to the Progress Report. We shall not reproduce the contents of this paper in this Progress Report but instead merely sketch the method. For further details, the reader is referred to the paper.

The way the impurity problem was treated consisted of expanding the perturbed wave function in terms of the complete set of Wannier functions. If we call $\psi(r)$ the perturbed wave function it is expanded as follows:

$$\psi(\vec{r}) = \sum(n) \sum(\vec{R}_j) U_n(\vec{R}_j)\, a_n(\vec{r} - \vec{R}_j) \tag{4.1}$$

In this equation, n denotes the band and $\vec{R}_j$ are the primitive translations in the crystal. $a_n(\vec{r} - \vec{R}_j)$ is the Wannier function associated with the n^{th} band and the $\vec{R}_j^{\,th}$ lattice site. $U_n(\vec{R}_j)$ are the unknown coefficients which are to be determined by a variation procedure. We assume that our Hamiltonian is split into two parts: an unperturbed part H_0 with which the Wannier functions are associated and the perturbation to this Hamiltonian H_1. If the variation is carried out, the unknown coefficients must satisfy a set of difference equations

$$\sum(m, \vec{R}_j)\left[\mathscr{E}_m(\vec{R}_i - \vec{R}_j)\,\delta_{nm} + V_{nm}(\vec{R}_i, \vec{R}_j)\right] U_m(\vec{R}_j) = EU_n(\vec{R}_i). \tag{4.2}$$

In this relation the quantity $\mathscr{E}_m(\vec{R}_i - \vec{R}_j)$ are the coefficients of the expansion of the energies in the m^{th} band in a Fourier series.

$$E_m(\vec{k}) = \sum(\vec{R}_s)\, \mathcal{E}(\vec{R}_s)\, e^{-i\vec{k}\cdot\vec{R}_s} \tag{4.3}$$

The quantity $V_{nm}(\vec{R}_i, \vec{R}_j)$ is a matrix element of the perturbation between a Wannier function associated with the n^{th} band located at the lattice site $\vec{R}_i$ and another Wannier function associated with the m^{th} band and situated at the lattice site $\vec{R}_j$. E is the energy of the perturbed state.

These equations (4.2) are the same whether we are doing the case of a bound state, E not in any band, or the scattering problem, E in one of the bands. For the scattering problem we wish the solution to the difference equations to consist of an incident Bloch wave at large distances plus an additional outgoing scattered wave. We do this by letting the unknown coefficients $U_n(\vec{R}_j)$ have the form

$$U_m(\vec{R}_j) = \delta_{q,m}\, e^{i\vec{k}\cdot\vec{R}_j} + \sum(\vec{R}_\ell)\, c_m(\vec{R}_\ell)\, K_{E,m}(\vec{R}_j - \vec{R}_\ell) \tag{4.4}$$

The first term on the right-hand side of this equation denotes the solution to the unperturbed difference equations which represents a Bloch wave. This Bloch wave is assumed to have an energy, E, lying in the q^{th} band. The second term on the right-hand side of (4.4) contains unknown coefficients $c_m(\vec{R}_\ell)$ multiplied by a kernel of Green's function $K_{E,m}(\vec{R}_j - \vec{R}_\ell)$.

In the treatment of the bound states arising from a perturbation this Green's function was taken in the form

$$K_{E,m}(\vec{R}_j - \vec{R}_\ell) = \sum(\vec{k})\, \frac{e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_\ell)}}{E - E_m(\vec{k})} \tag{4.5}$$

The solution to the bound state problem was obtained by eliminating the first term in (4.4) (since there are no propagating Bloch waves for energies not in one of the bands) and then substituting the Eq. (4.4) into the difference equations to obtain a set of simultaneous homogeneous equations for the c's. If we substitute (4.4) into (4.2) for the case of scattering it can be shown that the c's must satisfy the equations

$$\begin{aligned}\sum(m, \vec{R}_j, \vec{R}_\ell)\left[-N\delta(\vec{R}_i - \vec{R}_\ell)\,\delta_{nm} + V_{nm}(\vec{R}_i, \vec{R}_j)\, K_{E,m}(\vec{R}_j - \vec{R}_\ell)\right] c_m(\vec{R}_\ell) \\ = -\sum(\vec{R}_j)\, V_{nq}(\vec{R}_i, \vec{R}_j)\, e^{i\vec{k}\cdot\vec{R}_j}\end{aligned} \tag{4.6}$$

N is the number of lattice sites in the macrocrystal over which the periodic boundary conditions are applied. This equation was derived using the form of the kernel function given in Eq. (4.5). The summations extend only over those lattice sites over which

the impurity has matrix elements and for only those bands between which the perturbation has non-vanishing matrix elements. Thus we see that our scattering problem will be solved if we solve this set of simultaneous linear inhomogeneous equations whose order is determined by the extent of the perturbation. The only trouble with this formulation of the problem is that there is no clear way of ensuring that our Green's function consists only of outgoing waves for large distances from the perturbing center. We notice that the summation in (4.5) for the q^{th} band will contain a zero denominator of the fraction for some values of $\vec{k}$. It turns out that it is the manner in which we integrate around this singularity which determines the nature of the scattered wave.

In order to avoid this difficulty it is more convenient to use a Green's function of the form

$$K_{E,m}(\vec{R}_j - \vec{R}_\ell) = (1/i) \sum(\vec{k}) \int_0^\infty dt\, e^{i\left[E - E_m(\vec{k})\right]t}\, e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_\ell)} \qquad (4.7)$$

If this form of the Green's function is substituted into (4.4), the equations that the c's will satisfy can be shown to again be (4.6). This form of the Green's function has the great advantage of contributing to only outgoing waves for large distances from the perturbation. Actually the asymptotic form of this Green's function can be calculated by the method of stationary phases and an explicit form for the asymptotic behavior of this kernel function has been derived. We shall not reproduce this asymptotic form here since the derivation is rather involved.

In the paper to appear a simple one-dimensional example is worked out as well as the case of spherical energy surfaces in three dimensions.

G. F. Koster

5. CALCULATION OF A DENSITY OF STATES CURVE FOR NICKEL

In the Quarterly Progress Report of April 15, 1954, a calculation of the density of states for the 3d band in a body-centered structure was described. This density of states showed a pronounced dip in the middle. Since many of the transition elements display the face-centered structure instead of the body-centered structure, it was decided to do a density of states calculation for a face-centered transition element.

In the calculation of the density of states for the body-centered structure mentioned above, the nearest neighbor interactions of the d electrons were taken from the calculation of the band structure of nickel done by Fletcher and Wohlfarth.[1] (The method by which this was done is described in Technical Report No. 4 of this group and in a paper by J. C. Slater and G. F. Koster to appear in The Physical Review.) In the calculation of the band structure of nickel done by Fletcher and Wohlfarth, they also calculate part of the density of states for this element. Unfortunately their calculation only gives the density of states for about half the range in energy over which the bands extend. What we are doing is to extend just the calculation that they have made over the additional part of the energy range in order to get the complete density of states curve. We wish to see if the density of states curve shows a dip as appeared in the body-centered structure.

In order to calculate the density of states for nickel, we first calculate the band structure throughout the first Brillouin zone. This is done by using the matrix of the interaction between the five Bloch sums formed from d atomic orbitals as given by Fletcher and Wohlfarth. Because of the symmetry of the energy bands in reciprocal space all we need do is solve the secular equation associated with this interaction in one fourty eighth of the first Brillouin zone. We have chosen a mesh of 10^{o} in the three directions of reciprocal space. This gives us a total of 680 points in one-fourty eighth of the first Brillouin zone at which the five by five secular secular matrix must be diagonalized. The writing down of the matrix elements for this number of secular equations became such a chore that it was decided to program the calculation of the matrix elements on the Whirlwind computer as well as using the machine to diagonalize the matrix by a routine programmed by Dr. Meckler. This program was written and at this time we have the energies of the d bands at all of the 680 points in the segment of the first Brillouin zone mentioned.

We are now in the process of computing the density of states by the same method used in the body-centered calculation. Inderjit Prakash, who recently joined the group as a computer, is carrying out the major portion of these calculations and we hope to have them completed in the near future.

(CALCULATION OF A DENSITY OF STATES CURVE FOR NICKEL)

Reference

1. G. C. Fletcher and E. P. Wohlfarth, Phil. Mag. 42, 106 (1951); G. C. Fletcher, Proc. Phys. Soc. (London) A65, 192 (1952).

G. F. Koster

6. ENERGY BANDS IN COPPER

A previous report[1] outlined the methods used to determine the best linear combination of augmented plane waves to represent the wave function associated with a given point in k space. The formation and solution of the resulting secular equation has been programmed for the Whirlwind digital computer on the lines laid down previously.

A large number of states have been calculated for the three potentials used to represent copper; a detailed account of the results will be submitted on the conclusion of the work, but meanwhile several noteworthy features have emerged.

It will be recalled that in the linear combination we may make two choices of functions: those with the same reduced wave vector but with different values of E inside the sphere; and those with differing wave vectors. The work carried out has shown conclusively that, for copper, inclusion of terms including two values of E for each wave vector, and two wave vectors (the reduced wave vector and the smallest vector of the reciprocal lattice) is sufficient to produce at least three figure convergence in the lowest lying eigenvalues for s, p and d-like states. Several cases have been investigated using up to six different E's per k vector, and in such cases, four to five figure convergence is obtained.

As an example, the following table shows the lowest eigenvalue of the secular equation taken to various degrees of approximation. The example chosen is the state x_s (symmetric state at $\underline{k} = (0, 0, 2\pi/a)$ using the Hartree-Fock atomic potential for Cu^+. This is a state which caused particular trouble in the cellular calculation of the band structure of copper.[2] This is a typical result on all the state of high symmetry, and the extremely rapid convergence of the method is immediately apparent.

Table 6-1

State x_s	No. of E per k					
No. of wave vectors	1	2	3	4	5	6
1	.3760	.3752	.3747	.3747	.3746	.3746
2	.3754	.3746	.3746	.3746	.3746	.3746

So rapid is the convergence that it has been possible to extend the calculation to points of lower symmetry in the Brillouin zone. When the work underway is completed the following points in the Brillouin zone will have been considered, and it can be claimed that results for the lowest eigenvalue converge in every case to three figures, and often beyond this: (The notation for the points in momentum space is that of Bouckaert, Smoluchowski and Wigner.[3])

$$\Gamma : (0 \quad 0 \quad 0)$$

$$X : (0 \quad 0 \quad \frac{2\pi}{a})$$

$$L : (\frac{\pi}{a} \quad \frac{\pi}{a} \quad \frac{\pi}{a})$$

$$W : (\frac{\pi}{a} \quad 0 \quad \frac{2\pi}{a})$$

$$K : (\frac{3\pi}{2a} \quad \frac{3\pi}{2a} \quad 0)$$

$$\Sigma : (\frac{3\pi}{4a} \quad \frac{3\pi}{4a} \quad 0)$$

$$\Delta : (0 \quad 0 \quad \frac{\pi}{a})$$

$$\Lambda : (\frac{\pi}{2a} \quad \frac{\pi}{2a} \quad \frac{\pi}{2a})$$

$$A : (\frac{3\pi}{2a} \quad \frac{\pi}{a} \quad \frac{\pi}{2a})$$

The latter point is one of no symmetry, and accurate results can be obtained as a result of one hour's computation.

In the light of further results, a more detailed summary of the work and of the results themselves will appear in the next report.

References

1. D. J. Howarth, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 10.
2. D. J. Howarth, Proc. Roy. Soc. (London) A220, 513 (1953).
3. L. P. Bouckaert, R. Smoluchowski and E. Wigner, Phys. Rev. 35, 52 (1935).

D. J. Howarth

7. SYMMETRY POINTS IN THE AUGMENTED PLANE WAVE METHOD

Since my last report I have sought methods by which the convergence of the augmented plane wave (APW) method[1] could possibly be improved. In this report I suggest a way of speeding convergence at the symmetry points in reciprocal space.

It is well known that if a solution, or an approximate solution, is to satisfy the symmetry requirements of the Hamiltonian of a periodic potential problem it must first satisfy Bloch's theorem and second belong to an irreducible representation of the operations which leave its reduced wave vector invariant.

The various augmented plane waves certainly satisfy Bloch's theorem. For the general APW the only operation which leaves its reduced wave vector invariant is the identity; so that the general APW has the proper symmetry as it stands. For any APW with a larger wave vector group the symmetry problem is still simple if the wave vector lies in or on the central Brillouin zone. Such an APW is invariant, as may readily be verified, under its wave vector group. Only for an APW with wave vector outside the central zone are degenerate symmetries possible. Such an APW must be replaced by a linear combination of APW all of which are generated by application to the initial APW the operations of the group of its reduced wave vector. (I denote such a symmetrized combination of APW as SCAPW.) The coefficients of the APW in this combination are obtained from the irreducible representations of the group. The resulting SCAPW will then transform properly under the operations of its wave vector group. Because the Hamiltonian is non-diagonal in the set of the APW in the SCAPW the expectation of energy of the SCAPW will differ from that of any of the APW. The SCAPW though it represents a better first approximation to a solution is not derived directly from a variational procedure even if the APW are.

In the augmented plane wave method as described elsewhere[3] there are two variational procedures. The first is applied to an APW to minimize its expectation of energy relative to the energy parameter. The second is applied to a combination of these APW and leads to, of course, the secular equation. If solutions are desired at symmetry points the SCAPW do not enter the problem until the secular equation is to be solved, the combination of the APW being taken to simplify the elements in the secular determinant. Howarth in his application of the augmented plane wave method to copper has proceeded in this way[2] and has found that the lowest root of the secular equation converges encouragingly well (his report appears elsewhere in this Progress Report). I now propose, even so, that rather than form SCAPW after the first variational procedure that they be formed before it. Once this is done it is found that the resulting energy expression is no longer independent of the direction of the reduced wave vector of the plane wave parts of the SCAPW and does indeed depend on the symmetry of the SCAPW and the particular set of Brillouin zones from which its wave vectors were chosen. I believe that this is not a complication. It is evidence that a part of the burden of the secular problem is placed on the energy expression. On the

face of it, were this true, it would indicate that a first approximation SCAPW obtained by this method is closer to a solution than the first approximation SCAPW obtained in the previous method. I shall try to make this more plausible after I have described the modified method. Furthermore, if the proposed modification is successful, a different energy expression for every different symmetry should be more welcome than a slowly converging secular equation, which even on a computing machine like Whirlwind, is no small job to compute compared to a simple matter of forming an energy expression and finding its roots. The new energy expressions not only resemble very closely the old energy expression[4] but, of course, include it as a special case when the SCAPW contains but one APW. Happily, though it is not surprising, all the other pleasant features of the previous augmented plane wave method are retained: the expectation of energy of a SCAPW is equal to the energy of its non plane wave portion; two SCAPW of the same wave vector magnitude but of different energy are orthogonal and have no component of the energy between them; the overlap and matrix component of energy between different SCAPW is relatively simple.

A SCAPW $\Psi_{\vec{k}+\vec{K},E}$ is written in terms of the unnormalized APW $\psi_{\vec{k}+\vec{K},E}$:

$$\Psi^{(n)}_{|\vec{k}+\vec{K}|,E} = \sum_i a_i^{(n)} \psi_{\vec{k}+\vec{K}_i,E} \tag{7.1}$$

In the above equation the subscript i refers to the i^{th} symmetry operation and the summation is to be taken over all operations which leave the reduced wave vector $\vec{k}$ invariant. The $a_i^{(n)}$ are given by the theory of group representations. The superscript in a SCAPW refers to the manner in which it transforms under the group of its wave vector. As pointed out before (in different language), $\Psi^{(n)}_{\vec{k}+\vec{K},E}$, will vanish except for particular n and $\vec{K}$. In the equation below, Eq. (7.2) is given the new energy expression and the notation is that of Ref. (2) and (3).

$$\Omega^{(n)}_{\vec{k}+\vec{K}} (E - |\vec{k}+\vec{K}|^2) = f^{(n)}_{\vec{k}+\vec{K}} \tag{7.2}$$

and

$$\Omega^{(n)}_{\vec{k}+\vec{K}} = \Omega p - 4\pi R^3 \sum_{\substack{i,j \\ i\neq j}} \frac{j_1(|\vec{K}_i - \vec{K}_j|R)}{|\vec{K}_i - \vec{K}_j|R} a_i^{(n)*} a_j^{(n)}$$

where p is the integer which is the quotient of the number of operations in the group of the wave vector by the degeneracy of the representation

$$f^{(n)}_{\vec{k}+\vec{K}} = 4\pi R^2 \sum_{\ell} S^{(n)}_{\vec{k}+\vec{K},\,\ell} \frac{u_\ell'}{u_\ell}(E;R)\, j_\ell^{\,2}(|\vec{k}+\vec{K}|R)(2\ell+1) + F^{(n)}_{\vec{K}}$$

and

$$F^{(n)}_{\vec{K}} = \sum_{ij} \frac{j_1(R|\vec{K}_i - \vec{K}_j|)}{R|\vec{K}_i - \vec{K}_j|} \frac{|\vec{K}_i - \vec{K}_j|^2}{2} a_i^{(n)*} a_j^{(n)}$$

and where

$$S^{(n)}_{\vec{k}+\vec{K},\,\ell} = \sum_{ij} a_i^{(n)*} a_j^{(n)} P_\ell \left(\frac{\{\vec{k}+\vec{K}_i\} \cdot \{\vec{k}+\vec{K}_j\}}{|\vec{k}+\vec{K}_i|\;|\vec{k}+\vec{K}_j|} \right)$$

where P_ℓ is the Legendre polynomial of order ℓ.

It is interesting to compare the modified energy expression with the unmodified. For the old energy expression it was possible to show that the analogue of the right member of Eq. (2) resembled a cotangent curve. The energy vs plane wave energy curve was generated by the intersections in the right member, plotted as a function of energy, by the left member which was a line of fixed slope whose position along the abscissas changed as the plane wave energy changed. In the modified expression the right member need not be cotangent-like, it could be tangent-like as well, or even change from one behavior to the other as the plane wave energy changed. There is an additional modification due to the term $F^{(n)}_{\vec{k}+\vec{K}}$ in the right member which shifts the point of inflection of the right member. There is the additional complication in that the left member, although a straight line, certainly does not have constant slope, indeed, the slope could possibly change sign. These features make a detailed exposition of the structure of the energy curves difficult. Yet a few things can be said about the new energy curves.

To each reduced wave vector direction will correspond a triply infinite set of energy vs reduced wave vector curves. If a curve is characterized first by the symmetry of the wave function which belongs to it and second by the set of Brillouin zones from which its wave vectors are taken and last by the order of the root of the energy expression which it solves. (At isolated symmetry points each such curve degenerates to a point.) From a glance at the energy expression (7.2) it will be seen that asymptotes[4] will appear which the energy curves cannot cross. However, since for certain symmetries particular angular momenta will appear neither in the SCAPW or the energy expression the spacing of asymptotes, and so the separation of energy

curves is greater in the modified method than in the unmodified. This suggests that the interaction in the secular equation between branches is smaller in the present method than in the previous method. Thus as a function of its energy parameter alone, a SCAPW would appear to be an improved first approximation as compared to a corresponding APW. I do not pretend this argument to be rigorous. I shall try to state it more precisely and in a different way.

Suppose the APW of the previous method to be expanded in exact solutions of the problem. For an arbitrary wave vector the APW will be a combination of solutions having the same reduced wave vector as the APW; but in this combination will appear many different symmetries. The coefficients of the exact solutions will depend on the energy parameter. When the value energy parameter is inserted which makes the expectation of energy a minimum the expanded APW will still contain a variety of symmetries, and because the APW is a function with discontinuous slope the expansion will converge quite slowly. Now suppose the functions which enter with the larger coefficients are of a particular symmetry. If when the APW is symmetrized it is symmetrized with that particular symmetry, then the expectation of energy is not a bad approximation. If, however, this is not the case, then on symmetrization the dominant terms disappear from the wave function and the resulting function is composed of many terms of comparable magnitude. This argument is not favored when the energy of the APW is low since at low energies terms of the same symmetry are widely separated in energy and the coefficients should fall off quite rapidly with energy. However, if it is hoped to examine higher bands with the augmented plane wave method the argument could very well be important.

By an argument similar to the above it would seem profitable to try to form combinations of wave functions which were "smoothed" in slope before varying the energy parameter. I have tried to do this by the following procedure. A definite number, say n, SCAPW are chosen which have the same symmetry and whose wave vector magnitudes are the n lowest for the reduced wave vector which characterizes the SCAPW linear combination is formed such that the first n radial parts which appear in the non plane portion of the SCAPW join with continuous slope the corresponding plane wave parts. The coefficients are then fixed by the condition that the resulting function be normalized. The expectation of energy is obtained and minimized with respect to the energy parameter. However, the resulting energy expression is quite intractable so far and I hold little hope for the success of this idea.

(SYMMETRY POINTS IN THE AUGMENTED PLANE WAVE METHOD)

References

1. J. C. Slater, Phys. Rev. 92, 603 (1953).
2. D. J. Howarth, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 10.
3. M. M. Saffren and J. C. Slater, Phys. Rev. 92, 1126 (1953).
4. M. M. Saffren, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1953, p. 16.

M. M. Saffren

8. ENERGY BANDS IN GRAPHITE

In a previous report,[1] there was described the basic outline of the tight-binding method applied to a single graphite layer. Since that time effort has been devoted to the evaluation of the integrals involved. For this purpose, the following assumptions have been made: (1) The carbon atomic potential can be approximated by $\frac{Z_p(r)}{r}$ and the crystal potential by a superposition of atomic potentials. (2) The one-electron atomic wave functions can be taken to be HF SCF AO's and the one-electron crystal wave functions to be Bloch sums of these AO's. (3) Two-center integrals (and estimates of three-center integrals) can be used to obtain the necessary integral values.

To carry out the calculations, considerable programming has been done on the M. I. T. high speed digital computer Whirlwind I. This machine work can be divided into three categories:

(1) Fitting of HF SCF AO's and the Z_p function with exponentials: The $Z_p(r)$ or the tabulated HF radial probability functions, $P_{tab}(r)$ (when divided by appropriate powers of r or node factor $r_o - r$) are "exponential-like". Each of these functions was fitted with a sum of exponentials by a machine iteration technique developed for the purpose. To apply the scheme, for an n exponential fit, 2n representative points of the "exponential-like" function are chosen, and fed into the machine program. The program then iterates until the fitting function agrees sufficiently with the 2n representative points, at which time the error curve, $P_{fit} - P_{tab}$, is generated, projected on an oscilloscope and automatically photographed. By trial and error variation of the 2n representative points, and subsequent re-runs, it is possible to optimize the fit. The functions which have been fitted in this manner are the 1s, 2s, 2p, and Z_p of the carbon ^3P configuration.[2, 3] It was found that two exponential fits of the radial probability functions were accurate to about one percent of the maximum values of the functions, and that three exponential fits were very nearly accurate to the round-off error of the tabulated functions; this is in substantial agreement with the accuracy attained by Löwdin.[4] The Z_p function was more difficult to fit and required three and four exponential fits, respectively, for corresponding accuracy. Although the most accurate fits are probably not warranted by the approximations of the problem, they can be used to estimate the effect of errors in the wave functions and in the potential upon the final energy levels.

(2) Evaluation of one-electron, two-center integrals between Slater AO's: The theory of two-center integrals between Slater AO's (normalized single exponential wave functions), has been comprehensively studied by Roothaan,[5] Rüdenberg,[6] and Mulliken, Rieke, Orloff and Orloff.[7] Although Ref. 7 gives short tables of overlap integrals, these were not sufficient for all the integrals required in the present problem. Ref. 5 gives formulas for the necessary integrals, but because of their complexity, it was felt worth while to use machine techniques to evaluate the expressions

desired. The following computer programs have been developed.

A "basic" subroutine which evaluates overlap integrals arising among the 0s, 1s, 2s, 1p, 2p Slater AO's, (the 14 integrals of Eq. 25 in Ref. 5), for arbitrary values of the parameters. The machine time is about 1.7 seconds per integral. The program is based upon the ability to rapidly generate the functions (7 significant figure accuracy):

$$A_n(\rho) = \int_1^\infty \xi^n e^{-\xi\rho}\, d\xi, \quad B_n(\sigma) = \int_{-1}^{1} \eta^n e^{-\eta\sigma}\, d\eta$$

A "combination" subroutine which, using the above program, automatically computes two-center integrals between wave functions, (1s, 2s, 2p), expressed as arbitrary sums of Slater AO's. This routine can be used with any of four operators, which are symmetric in the interchange of the two wave functions. If the integral between centers a and b, separated by a distance R, is defined as:

$$O_{ij}(R) = \int \psi_i(r_a)\, O_{op}\, \psi_j(r_b)\, d\tau$$

where

$$\psi_i(r_a) = \sum_{k=1}^{n_i} c_k\, \phi_k(r_a), \qquad \psi_j(r_b) = \sum_{\ell=1}^{n_j} c_\ell \phi_\ell(r_b)$$

and the c_k, c_ℓ are arbitrary coefficients of the one parameter Slater AO's, $\phi_n(r)$, then these operators can be written as:

$$O_a = 1 \text{ (overlap)}$$

$$O_b = -\frac{1}{2}\nabla^2 \text{ (kinetic energy)}$$

$$\left.\begin{aligned} O_c\, \psi_j(r_b) &= \psi_j(-r_a)\, \frac{Z_p(r_b)}{r_b} \\ O_d &= \frac{Z_p(r_a)}{r_a} + \frac{Z_p(r_b)}{r_b} \end{aligned}\right\} \quad Z_p(r) = \sum_{m=1}^{n_z} c_m\, e^{-Z_{rn} r}$$

Thus this subroutine evaluates the integrals of a particular operator, at several values of R, from the specification of: n_R, and the values of R; n_i, and the values of c_k and the ϕ_k parameters; n_j, and the values of c_ℓ and the ϕ_ℓ parameters. The foregoing scheme thereby allows one to calculate integrals involving wave functions fitted by several exponentials without serious extra effort. It should be noted however that the machine time required for a given integral is equal to $(n_R n_i n_j \lambda)$ x

(1.7 sec.) where λ varies with the operators a, b, c, d as 1, 1, n_z, $2n_z$, respectively.

(3) The secular equation between the one-electron states: The secular equation, which arises, is of the form $\det|H_{ij} - ES_{ij}| = 0$, where the matrix elements H_{ij} and S_{ij} are functions of the reciprocal lattice vector $\vec{k}$. Dr. Howarth,[8] presently with this group, has adapted Dr. Meckler's subroutine for solving the usual secular equation to handle this more difficult equation. In order to simplify the use of Dr. Howarth's program, an auxiliary program has been devised which, for a given $\vec{k}$, generates the required matrix elements from the basic two-center integrals of the first, second and third nearest neighbors of the graphite layer. With this procedure it will be possible to readily calculate the one-electron energy levels as a function of $\vec{k}$.

References

1. F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954. p. 21.
2. A. Jucys, Proc. Roy. Soc. (London) A173, 59 (1939).
3. A. J. Freeman, Phys. Rev. 91, 1410 (1953).
4. P. O. Löwdin, Phys. Rev. 90, 120 (1953).
5. C. C. J. Roothaan, J. Chem. Phys. 19, 1445 (1951).
6. K. Rüdenberg, J. Chem. Phys. 19, 1459 (1951).
7. R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys. 17, 1248 (1949).
8. D. J. Howarth, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 16.

F. J. Corbató

9. SOFT X-RAY EMISSION SPECTRA

In order to better understand the observed soft x-ray emission spectra for the transition metals, and consequently the apparent band structure, it seems necessary to study the effect of spin-orbit[1] coupling on the crystal wave functions. For this reason I am setting up the secular equation for the d bands in nickel, making full use of the results of Fletcher's[2] calculation, and especially his analytic potential and one-electron atomic wave functions, including the added spin-orbit coupling terms in much the same way as Brooks.[3] Since the calculation is made according to the approximation of the tight binding method, the spin-orbit matrix elements are the same as for the free atom. Keeping within the approximations of the method, the spin-other-orbit terms are excluded as being negligible.

References

1. J. C. Slater, Technical Report No. 6, Solid-State and Molecular Theory Group, M. I. T., April 15, 1954.
2. G. C. Fletcher, Proc. Phys. Soc. (London) A65, 192 (1952).
3. H. Brooks, Phys. Rev. 58, 909 (1940).

A. J. Freeman

10. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

The calculation of polarizability effects for the F^- ion in both uniform and point charge perturbing fields is continuing along the lines given in the previous Progress Report.

L. C. Allen

11. MAGNETIC SCATTERING OF SLOW NEUTRONS FROM OXYGEN GAS

Some aspects of the calculation of the magnetic scattering of slow neutrons from O_2 gas have been discussed in previous reports. The calculation has been completed, and the results will be submitted for publication in the near future. Here we present a summary.

The original motivation for considering neutron magnetic scattering was to examine in detail the possibilities for deriving from experiment a distribution for the electrons of unpaired spin in a magnetic material. Neutron magnetic scattering has an advantage over x-ray scattering in which only the total electron distribution can be measured. There are several reasons why scattering by oxygen gas was considered. One of the simplest magnetic systems to treat theoretically with reasonable rigor is the oxygen molecule. The electronic structure of O_2 has been given considerable theoretical study by Meckler[1] in this group. Interest in the magnetic scattering experiment had already been stimulated several years ago by Halpern.[2] The experimental magnetic scattering is obtained by subtracting the nuclear scattering, which has been calculated by Halpern and Appleton,[3] from the measured scattering. Very recently the integrated cross section for the scattering of slow neutrons of a variety of wave lengths has been measured by Palevsky and Eisberg at Brookhaven National Laboratory.[4]

The gas was assumed to be in thermal equilibrium at room temperature and at low enough density so that double scattering and the correlation among molecules is negligible. The scattering is then given in terms of the cross section for one molecule. A major difficulty in extracting useful information from the experiment is associated with the variety of velocities, angular velocities, and orientations of the molecules of the gas. From the viewpoint of deriving the distribution of electrons of unpaired spin from a scattering experiment it is unfortunate that the gas does not consist of a number of stationary molecules all with the same orientation. In the scattering of x-rays from a gas the situation is similar, but, because the speed of light is greater than that of neutrons of appropriate wave length by a factor of 10^5, only the random distribution of orientations causes appreciable difficulty. The added difficulty which one may expect in the neutron case, associated with the low neutron velocities leading to a ratio a(of the transit time for the neutron across a molecule to the period of molecular rotation) which is of the order unity, was pointed out in a previous report.[5] A detailed analysis shows that the two limiting cases $a \ll 1$ and $a \gg 1$ yield cross sections which would be difficult to distinguish experimentally, even if each molecule were to have the same linear velocity. This suggests that for neutron magnetic diffraction as well as for x-ray diffraction from molecules the scattering will be rather insensitive to the distribution of angular velocities. For a more detailed discussion consider the general expression for the scattering.

The O_2 molecule partial magnetic cross section for unpolarized neutrons

corresponding to a molecular transition during scattering from the rotational level J to the rotational level J' is

$$\sigma_{J'J}(K) = (2J' + 1)(k'/k) \sum_{\ell=0}^{\infty} \left\{(2\ell + 1) \int_{-1}^{1} P_{J'}(\mu)\, P_J(\mu)\, P_\ell(\mu)\, d\mu/2\right\} A_\ell^2(K) \qquad (11.1)$$

in units of 0.3650×10^{-24} cm^2. The cross section (11.1) is in center-of-mass coordinates as a function of K ($\hbar\vec{K} = \hbar(\vec{k} - \vec{k}')$ is the momentum transfer), and is per initial state of the molecule; $\vec{k}$ and $\vec{k}'$ are the initial and final neutron wave vectors; $P_\ell(\mu)$ is a Legendre polynomial. The $A_\ell(K)$ are coefficients in the Legendre polynomial expansion of a "magnetic scattering amplitude":

$$f(\vec{K}) = \int e^{i\vec{K}\cdot\vec{r}} \rho(\vec{r})\, d\tau = \sum_{\ell=0}^{\infty} (2\ell + 1)\, i^\ell A_\ell(K)\, P_\ell(\mu)\,, \qquad (11.2)$$

the Fourier transform of the spin density $\rho(\vec{r})$, which gives the spatial distribution of electrons of unpaired spin;[5] μ is the cosine of the angle between the molecular axis and the radius vector from the molecular midpoint. Eq. (11.2) is derived in Born approximation and is associated with the classical dipole-dipole interaction between the neutron and electron-spin magnetic moments. It can be shown on the basis of time reflection symmetry that interaction between the neutron magnetic moment and the orbital electron motion contributes no scattering when the O_2 molecule is in its ground $\sum$ electronic level.

In the limiting cases $a \ll 1$ and $a \gg 1$ the cross section reduces to

$$\sum_{J'} \sigma_{J'J}(K) = \langle |f(\vec{K})|^2 \rangle \qquad (11.3)$$

independent of the initial level J, and

$$\sigma_{00}(K) = |\langle f(\vec{K}) \rangle|^2 = A_0^2(K) \qquad (11.4)$$

$\langle\rangle$ denotes a uniform average over all orientations of $\vec{K}$. The derivation of (11.3) depends on the static (or semi-classical) approximation in which the relative change of the neutron momentum by the scattering is neglected.

If the spin density $\rho(\vec{r})$ were spherically symmetrical, one can see from (11.2) that $A_\ell(K) = 0$, $\ell \neq 0$, and hence, from the selection rules on $\int_{-1}^{1} P_{J'} P_J P_\ell\, d\mu$, that only elastic transitions ($J' = J$) are allowed. In this circumstance (11.3) is rigorous in the sense that the static approximation is not required, and, in fact, Eq. (11.3) reduces to Eq. (11.4). One may in general associate the difference between (11.3)

and (11.4) with the non-vanishing of the A_ℓ, $\ell \neq 0$.

The $A_\ell(K)$ were computed for $\ell \leq 8$ from the spin density $\rho(\vec{r})$ derived from Meckler's[1] O_2 ground electronic wave function, and were found to have very roughly the form of spherical Bessel functions $(1/2)(1 + (-)^\ell)\, j_\ell(KR/2)$, but with considerable damping with increasing K. (R is the normal internuclear distance.) The overall magnitudes of the A_ℓ were also found to decrease rapidly with increasing ℓ. The result is that (11.3), based on the static approximation, gives the cross section to quite satisfactory accuracy.

Of basic interest is the sensitivity of the scattering to the form of the electronic wave function assumed in the calculation. It turns out that Meckler's approximate many-electron wave function leads to a spin density in which the only atomic orbital involved is the oxygen 2p. An alteration in Meckler's wave function which might be expected to cause a significant change in the calculated values of molecular parameters, e.g., the energy, is the replacement of Meckler's Gaussian atomic orbitals by Hartree-Fock orbitals, or other reasonable orbitals. To examine the effect of such a change on the magnetic scattering, the $A_\ell(K)$ were computed from a spin density which differed from that derived from Meckler's wave function only in that Meckler's 2p Gaussian orbital was replaced by a hydrogenic 2p with effective nuclear charge $Z = 4.44$. The difference in the A_ℓ's for the two orbitals is so small that the associated scattering in the two cases would be indistinguishable experimentally. Unfortunately, one must give up the hope that neutron magnetic scattering might provide a sensitive method of experimentally determining the distribution of magnetic electrons, at least in the case of gas scattering.

The integrated magnetic cross section was computed from (11.3) based on Meckler's wave function. This was then transformed to the laboratory frame of reference and averaged with respect to the thermal distribution of molecular velocities. The resulting integrated magnetic cross section per molecule σ is given in the table below as a function of the incident neutron wave length λ.

Table 11-1

λ(angstroms)	1	2	3	4	5	7.5	10	15	20	30
σ(barns)	.130	.490	.981	1.516	2.015	3.054	3.96	5.76	7.52	11.09

Preliminary analysis of the scattering data of Palevsky and Eisberg[4] of Brookhaven National Laboratory indicates agreement between theory and experiment to within experimental error.

I would like to express my thanks to Miss Edith Moss for performing a large part of the numerical computation involved in this work.

References

1. A. Meckler, J. Chem. Phys. 21, 1750 (1953).
2. O. Halpern, Phys. Rev. 72, 746 (1947).
3. O. Halpern and G. L. Appleton, Phys. Rev. 90, 869 (1953).
4. H. Palevsky and R. M. Eisberg, Bul. Amer. Phys. Soc. 29, No. 4 (1954).
5. W. H. Kleiner, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1954, p. 48.

W. H. Kleiner

12. THERMAL VIBRATIONS IN Cu-Zn SYSTEM CRYSTALS

Our principal task is to find the localized change in conduction electron charge density produced when one ion core is displaced in an otherwise perfectly regular metal lattice of ion cores. From this $\Delta\rho$ we can by Feynman's theorem[1] find the conduction electron contribution to the force produced by the displacement on all the other ion cores, and thence, by taking the derivative, to the 3 x 3 matrices of interatomic force constants between each pair of atoms. It is felt that the careful determination of these force constants is the crucial step in obtaining meaningful results for the frequency distribution spectra of thermal vibrations: from the experimental values of E. Jacobsen of Professor Warren's x-ray group[2] for the force constants of Cu one can see that the usual assumptions made -- such as that vibrations perpendicular to the interatomic radius are associated with a negligible force constant -- are definitely not justified.

Our approach to the calculation of $\Delta\rho$ using the perturbation theory expansion of wave functions in terms of displaced Bloch waves, following the Slater-Koster developments,[3] has proved successful. The method is feasible only for the solution of small size lattices, and considerable care must be paid to the mesh of allowed points in k-space inside the first Brillouin zone used in the perturbation theory expansion, which mesh depends of course on the size and shape of the lattice used, given the application of Born-von Karman boundary conditions. The dipole symmetry of the problem tells us that the matrix component of the perturbation potential between two Wannier functions on the central site vanishes, while the eight non-vanishing matrix components in a fcc lattice between the central and first neighbor atoms are all of the same magnitude, although half are positive and half negative. As our first step in a self-consistent procedure we neglect all other matrix components.

Our success in solving the unusual Slater-Koster secular determinant rests entirely on the fact that first order perturbation theory results are rigorously correct for our purposes, since the atomic force constants are derivatives at the equilibrium position of the expressions we obtain with respect to the perturbation parameter itself. The results of our explicit solution of the secular equation for a fcc lattice with the above matrix elements are that each group of degenerate levels has one level split off upward and one level downward in energy by equal amounts which increase from zero for the upper and lowermost levels to a maximum for the middle group of degenerate levels. Explicit expressions were obtained for the sets of perturbation coefficients corresponding to each of the split-off levels -- the levels which remain degenerate do not of course contribute to $\Delta\rho$. From these coefficients there can be set up expressions for the $\Delta\rho$ for the given finite lattice which take a quite simple general form, once certain well-justified expurgations are made. Since the approximation is introduced that the unperturbed Bloch waves used in the perturbation expansion are simply plane waves, one sees after elementary manipulation of the ex-

pression that it is essentially a three-dimensional Fourier expansion of $\Delta\rho$.

The expression for $\Delta\rho$ exhibits a symmetry consistent with that from which the perturbation matrix elements were obtained. Just as important, the imposition of self-consistency in magnitude is rendered relatively easy by the fact that the one independent matrix element magnitude can be factored out of the $\Delta\rho$ expression. Also this factorization means that this magnitude can be treated as a parameter to be fixed from the experimental force constants or elastic constants, relying on the difficult independent numerical calculation of Wannier function matrix elements only to check the order of magnitude. Calculations have been made for 32 and 500 atom cubic crystals, and are being extended to 2048 cubic and 512 Bravais-fcc cell-shaped crystals to check that the results are substantially independent of the size and shape of the finite lattice used, as we would expect from their Fourier expansion nature. From the analytic expression for $\Delta\rho$ it can be shown that $\Delta\rho$ is indeed not a function of the size of the crystal for very large crystals. Furthermore, the sum of the magnitudes of all the energy splittings (two to each degenerate initial set of levels) is independent of the size of the lattice for very large crystals.

The numerical results obtained so far indicate that $\Delta\rho$ is sufficiently localized about the displacement site so that it is a good approximation to have neglected all perturbation matrix elements but the eight ones connecting the central site to the eight nearest neighbors in the fcc structure which do not lie on the plane bisecting the direction of displacement along one of the cubic axes. A crude self-consistency calculation gives the result that the dipole moment roughly equivalent to $\Delta\rho$ cancels from one-half to three-quarters of the dipole moment produced by the displacement of the unshielded ion core.

The approximations made in our model are such that it applies with equal validity to Cu, Ag, and Au, the difference in the $\Delta\rho$ expressions coming only in the multiplicative factor. According to our model, therefore, the conduction electron contribution to the atomic force constants and hence to the elastic constants of any two of these metals should be proportional to each other, and we can exhibit the proportionality factors. Unfortunately, no accurate predictions are available of the contribution of closed shell repulsion terms to the elastic constants of Au and Ag, so this predicted proportionality cannot be tested, although crude estimates indicate it to be borne out. However, we observe the analysis we describe here can easily be extended to the bcc structure, leading to a similar prediction of proportionality among the elastic constants of Na, K, and the other bcc metals with a single S conduction electron outside a closed shell. After using the results of Fuchs[4] on the core-core repulsion effects to adjust the experimental elastic constants, we found that the predicted proportionalities between the conduction electron contributions for Na, K, and Li did exist, and that the constants of proportionality agreed with the very simple

expressions derived from our model to within a few percent.

The primary specific goal of our work is to predict numerical values for the atomic force constants relating the first three orders of neighbor atoms in Cu and compare them with the values found by Jacobsen[2] from thermal diffuse x-ray scattering data. In finding the conduction electron contribution from our $\Delta\rho$ results it is planned to use a numerical integration scheme to carry out the Coulomb integrations involved. It should be mentioned that the nature of our approach through calculation of $\Delta\rho$ is such that the accuracy of the predicted force constants is about the same for all orders of neighbors, no matter how far removed. We must also find the contribution of closed-shell repulsion terms to the force constants to make comparison with experimental results possible. Approximate results are easily obtained from the results given by Fuchs[4] for the interaction energy of the closed shells of two Cu ions on the basis of a Thomas-Fermi approximate calculation by Lenz. The important point is that the closed-shell effect contributes appreciably to only two of the three first neighbor constants, and to none of the further neighbor constants.

References

1. R. P. Feynman, Phys. Rev. 56, 340 (1939).
2. E. Jacobsen, Ph. D Thesis, M. I. T. Physics Department (1954).
3. J. C. Slater, Technical Report No. 5, Solid-State and Molecular Theory Group, M. I. T., October 15, 1953, p. 52.
4. K. Fuchs, Proc. Roy. Soc. (London) A151, 592 (1935); A153, 630 (1936).

H. C. White

13. ELECTRON-LATTICE INTERACTION

A study of the electron-lattice interaction problem has been initiated with particular emphasis on cases where the interaction is too large to be treated by perturbation theory. Treatments for slow electrons based on methods developed for meson theory by Tamm and Dancoff and by Tomonaga have been reviewed. Attempts at treating stronger coupling, higher energies, and the effects of the periodic potential are being made.

T. D. Schultz