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# QUARTERLY PROGRESS REPORT

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SOLID-STATE AND MOLECULAR THEORY GROUP  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
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QUARTERLY PROGRESS REPORT NO. 11

SOLID-STATE AND MOLECULAR THEORY GROUP

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## PUBLICATIONS

- Quarterly Progress Report No. 1, July 15, 1951
- Quarterly Progress Report No. 2, October 15, 1951
- Quarterly Progress Report No. 3, January 15, 1952
- Quarterly Progress Report No. 4, April 15, 1952
- Quarterly Progress Report No. 5, July 15, 1952
- Quarterly Progress Report No. 6, October 15, 1952
- Quarterly Progress Report No. 7, January 15, 1953
- Quarterly Progress Report No. 8, April 15, 1953
- Quarterly Progress Report No. 9, July 15, 1953
- Quarterly Progress Report No. 10, October 15, 1953
- Quarterly Progress Report No. 11, January 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

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on

Project N5ori-07856

SURVEY

Since writing my Survey for the last Progress Report, I have spent a month in Japan, attending the International Conference on Theoretical Physics. This was a very interesting meeting, though strenuous. Its most interesting features, from the point of view of the Group, were the symposium on molecular theory, held at Nikko, in the mountains, before the main conference; and the opportunity to visit the research group in molecular theory headed by Professor Kotani of the University of Tokyo. These meetings brought together Coulson, Löwdin, Mulliken, and a number of other workers in the field, and gave an excellent opportunity to talk over many of the problems on which we are working with other workers in the field, particularly the Japanese. Their programs are very similar to ours; and in some problems, such as the oxygen molecule, they are extremely close. Thus, Ishiguro is carrying through a configuration interaction treatment of oxygen, using the same configurations which Meckler had used, but with much better atomic orbitals; his results so far, though very preliminary, look rather similar to Meckler's. It was extremely interesting to talk over such questions as the computation of molecular integrals, with representatives of most of the groups actively working on them.

Dr. Löwdin, who was in Japan, has now joined our Group, for several months, and has already been giving interesting seminar talks, both on the determination of analytic atomic wave functions, about which he writes in this Report, and on general methods of numerical integration of differential equations.

Perhaps the most interesting new development since the last Progress Report has been the discovery of the new method of handling the difference equations encountered in the theory of perturbed wave functions in crystals, which is reported in contributions Nos. 1 and 2 to this Report. This method, which was largely the work of Dr. Koster, is much more elegant and general than the method mentioned in the preceding Progress Report, and should open up the field of wave functions and energy levels of crystals containing impurity atoms in a way which may well lead to substantial progress. We must realize that these same difference equations will be met in other connections. Thus, the two-electron example of ferromagnetism, about which Drs. Koster and Statz and I wrote recently, encounters just such mathematical problems, and these new methods should help greatly in carrying that theory further. Then again, the exciton problem is another case where similar methods are applicable. Putting the matter a little more generally, the whole question of electron correlation is essentially a matter of the relative motion of electron pairs under the action of their Coulomb interactions, and of the periodic potential in which they move in a real

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crystal; and the separation of variables in such a problem into coordinates of the center of mass, and relative coordinates, will in every case lead to a problem of this type, so that we should be able to make real progress toward a theory of correlation energy in periodic potentials, rather than being limited to free electron gases as in most previous treatments.

The calculation of energy bands in solids is a problem in which we are always very interested, partly on account of treating perfect crystals, and partly because its results are necessary in order to handle the questions of impurity atoms, ferromagnetism, and correlation energy about which we have just been speaking. The augmented plane wave method, about which we wrote in the preceding Progress Report, still seems like a promising method of attack, and Dr. Howarth reports on the work which he is starting, to program this method for the Whirlwind digital computer. As soon as the difficulties (purely technical) of this programming are ironed out, we hope to give the method a real test, on copper, and see whether it is really any better than the other existing methods. In connection with this method, or any method of energy band computation, one needs information about the atomic wave functions and potentials, and for this reason the type of study which Dr. Löwdin is giving to interpolation methods of deriving atomic wave functions is of great promise.

In molecular problems, we continue to feel that the most pressing question is to investigate methods of simplifying configuration interactions, so that we can handle more complicated molecules by methods which are likely to be valid. The study which Dr. McWeeny is making of configuration interaction in simple molecules, proceeding by the use of orthogonal atomic orbitals, is likely to be very useful in this respect. His discovery that the exchange integrals in this method are almost negligibly small may prove to be a real key to the simplification of the calculation. The small size of these integrals was already known for the hydrogen molecule, but it now appears to be general enough so that perhaps it always holds. In addition to McWeeny's study, the work of Kaplan, and of Schweinler and Koster, continues; Callen's problem is practically completed. Meckler's mechanization of the molecular orbital method continues. Pratt's further study of antiferromagnetism demonstrates how really complicated that problem is. In the preceding Progress Report, I mentioned that something like the superexchange which has so often been postulated for this problem seemed to form the basis of the action of oxygen in antiferromagnetic crystals, and no reason has appeared to change this conclusion. However, when we try to extend Pratt's results to more complicated cases than the three-atom example which he discussed, we meet difficulties in the way of handling the required configuration interactions which are of the same sort which we encounter in any complicated molecular problem. It is clear that the simple sort of way out of these difficulties which is usually considered in the literature is by no means adequate; in fact, if the various calculations described

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qualitatively in the literature are carried out quantitatively, it seems clear that they result in ferromagnetic, rather than antiferromagnetic, interactions. We shall apparently have to go further in understanding configuration interaction before we find really adequate techniques for solving the problem of antiferromagnetism.

The various other subjects under study by members of the Group are progressing; and with the addition of the foreign visitors who are here at present, there is a lively atmosphere which should lead to rapid progress. As mentioned in the preceding Progress Report, I am lecturing this term on energy levels in perturbed crystals, and the notes of these lectures will appear as Technical Report No. 5, which we hope will appear at approximately the same time as this Progress Report.

J. C. Slater

## 1. WAVE FUNCTIONS FOR IMPURITY LEVELS

In the preceding Progress Report, <sup>(1)</sup> we outlined a general approach to the problem of setting up wave functions for a crystal perturbed by impurity atoms, writing the perturbed wave function as a superposition of Wannier functions in the well-known way. We proposed that instead of regarding the coefficients  $U_n(\vec{R}_i)$  of the Wannier functions of the  $n^{\text{th}}$  band on the atomic site at vector position  $\vec{R}_i$  as a continuous function of a vector position  $\vec{r}$ , taking on the values  $\vec{R}_i$  at the atomic sites, and using the approximate differential equation for the continuous function, we might better operate with the coefficients directly, setting up the difference equations which determine them. We mentioned that in some important cases these difference equations could be handled rigorously. Since writing that Report, we have found a much more powerful method of handling the difference equations, which is so useful that it indicates that this technique may become really usable for practical problems. This method will be outlined in the present note, and its application to a three-dimensional problem will be presented in the next section.

We start our procedure by expanding the perturbed function, not in terms of Wannier functions directly, but in terms of Bloch functions; though later we transform it into an expansion in terms of Wannier functions, which is physically more informing. We shall formulate it first for the simplest case, of a single non-overlapping band with a perturbation only at the atom at the origin, but then shall describe its extension to a general case. Let us use periodic boundary conditions, with  $N$  atoms in the repeating region. We have Wannier functions  $a(\vec{r} - \vec{R}_i)$  for the band in question. Then the corresponding Bloch functions are

$$B_{\vec{k}}(\vec{r}) = N^{-1/2} \sum(\vec{R}_i) e^{i\vec{k} \cdot \vec{R}_i} a(\vec{r} - \vec{R}_i). \quad (1.1)$$

These functions are normalized and orthogonal, and there are  $N$  of them corresponding to  $N\vec{k}$  values. The matrix component of the perturbative energy between two of these Bloch functions will be

$$N^{-1} \sum(\vec{R}_i, \vec{R}_j) e^{i(-\vec{k} \cdot \vec{R}_i + \vec{k}' \cdot \vec{R}_j)} V(\vec{R}_i, \vec{R}_j), \quad (1.2)$$

where  $V(\vec{R}_i, \vec{R}_j)$  is the matrix component of the perturbation between the corresponding Wannier functions. In our special case, we assume that  $V(\vec{R}_i, \vec{R}_j)$  is zero unless both  $\vec{R}_i$  and  $\vec{R}_j$  are zero, in which case it is  $V_0$ . Then the matrix component (1.2), between the Bloch functions corresponding to propagation constants  $\vec{k}$  and  $\vec{k}'$ , is merely  $V_0/N$ , the same for all pairs of propagation constants. It is this very simple form of the matrix component which leads to a very simple solution for this problem.

Let us now set up our solution as a series of Bloch functions,  $\sum(\vec{k}) f_{\vec{k}} B_{\vec{k}}(\vec{r})$ . Then, remembering that the periodic potential problem has a diagonal matrix with

(WAVE FUNCTIONS FOR IMPURITY LEVELS)

respect to the Bloch functions, with matrix components  $E_{\vec{k}}$ , the equations for the  $f_{\vec{k}}$ 's become

$$E_{\vec{k}} f_{\vec{k}} + \sum(\vec{k}') (V_0/N) f_{\vec{k}'} = E f_{\vec{k}}. \quad (1.3)$$

We can immediately solve these equations, in the form

$$f_{\vec{k}} = \frac{(V_0/N) \sum(\vec{k}') f_{\vec{k}'}}{E - E_{\vec{k}}}. \quad (1.4)$$

Since  $\sum(\vec{k}') f_{\vec{k}'}$  is a constant independent of  $\vec{k}$ , this at once tells us that  $f_{\vec{k}}$  is a constant divided by  $E - E_{\vec{k}}$ , which gives a complete solution of the problem of determining the wave function; the constant can be determined by the normalization condition. We can at once find an equation for the energy. Let  $(V_0/N) \sum(\vec{k}') f_{\vec{k}'} = A$ . Then from (1.4),  $f_{\vec{k}} = A/(E - E_{\vec{k}})$ . We substitute this in the definition of A above, and find that

$$(V_0/N) \sum(\vec{k}) \frac{1}{E - E_{\vec{k}}} = 1. \quad (1.5)$$

This is an equation for E, determining the energies of the perturbed states as a function of the perturbative potential  $V_0$ .

The general nature of Eq. (1.5) allows us to make some deductions about the energy levels. The function  $\sum(\vec{k}) 1/(E - E_{\vec{k}})$  becomes infinite when E equals any one of the  $E_{\vec{k}}$ 's. Its reciprocal, which according to (1.5) equals  $V_0/N$ , becomes zero at each of the  $E_{\vec{k}}$ 's, so that if  $V_0$  is zero, the solutions are just the  $E_{\vec{k}}$ 's. Between each pair of zeros of this reciprocal function, there will be a simple pole. Thus as  $V_0$  goes from zero to positive or negative infinity, each of the energy levels will be displaced, but not further than the next adjacent  $E_{\vec{k}}$ . There are exceptional cases, where the energy lies outside the unperturbed energy band. These are the discrete levels produced by impurity atoms. As the energy gets well outside the unperturbed band, we may approximate each term  $E - E_{\vec{k}}$  by  $E - E_0$ , where  $E_0$  is the average energy in the band. Thus the summation will be approximately  $N/(E - E_0)$ , so that (1.5) will become approximately  $E = E_0 + V_0$ . A discrete energy level, in other words, is pushed out of the band, which becomes linear in  $V_0$  for large perturbations.

We can find the wave functions, as well as the energy. We know that the wave function can be written as  $\sum(\vec{k}) f_{\vec{k}} B_{\vec{k}}(\vec{r})$ , where  $f_{\vec{k}} = A/(E - E_{\vec{k}})$ . We are more interested in the wave function as an expansion in Wannier functions, rather than in Bloch functions. We can find this at once, by substituting for the Bloch functions in terms of the Wannier functions, from Eq. (1.1). When we do this, we find that the coefficient  $U(\vec{R}_i)$  of the Wannier function  $a(\vec{r} - \vec{R}_i)$  is given by

## (WAVE FUNCTIONS FOR IMPURITY LEVELS)

$$U(\vec{R}_i) = AN^{-1/2} \sum(\vec{k}) \frac{e^{i\vec{k} \cdot \vec{R}_i}}{E - E_{\vec{k}}}. \quad (1.6)$$

This simple result is the complete solution of the problem of finding the wave function in the presence of an impurity producing a perturbation on only one atom. It is to be understood, of course, that the  $E$  which appears in (1.6) is that which results from the solution of (1.5).

We shall now state the results which hold in the more complicated case where the perturbative potential is felt over a number of atoms, and where a number of overlapping bands, with their corresponding Wannier functions, are concerned; though we shall not give the analytical treatment here. We find that the solution can be written as a linear combination of functions of the type we have just been considering, arising from perturbations on single atoms. One such function is to be centered on each atom on which there is a perturbative potential, and one is to be constructed from the Wannier function of each band concerned. The number of coefficients of these functions, then, will equal the number of atoms on which there is perturbative potential, multiplied by the number of Wannier functions concerned on each atom. These coefficients are determined by a set of simultaneous homogeneous linear equations, which are incompatible unless the determinant of coefficients vanishes. This furnishes a secular equation for the energy, though it is not of the usual type of secular equation. All the various functions which are superposed to find the final solution are to be computed for the energy determined from this secular equation. Consideration of symmetry properties of the resulting solution will ordinarily lead to relations between the coefficients, reducing greatly the order of the secular equation to be solved; in some cases it can remove entirely the requirement of solving a secular equation, and lead directly to the final wave function. This general method has not yet been used for the solution of any problems; it will be discussed in somewhat more detail in Technical Report No. 5, which is under preparation.

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1. J. C. Slater and G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., October 15, 1953, p. 6.

J. C. Slater and G. F. Koster

## 2 AN EXAMPLE OF IMPURITY LEVELS IN SOLIDS

The general method of treating impurity levels in solids mentioned in the preceding contribution to this Quarterly Progress Report can be carried quite far in the case of the simplified three-dimensional impurity problem. Let us imagine a simple cubic lattice whose primitive translations are

$$\vec{R}_{pqr} = p\vec{a}_1 + q\vec{a}_2 + r\vec{a}_3$$

where  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{a}_3$  form the sides of the unit cell and lie along the x, y, and z directions respectively. In this solid, we could discuss the effect of a perturbation on a single non-overlapping energy band. The Bloch functions of this band we shall denote by  $B_{\vec{k}}(\vec{r})$  and are eigenstates of a one-electron periodic Hamiltonian  $H$  with eigenvalues  $E_{\vec{k}}$

$$HB_{\vec{k}}(\vec{r}) = E_{\vec{k}} B_{\vec{k}}(\vec{r}) \quad (2.1)$$

This energy band is describable in terms of a Wannier function  $a(\vec{r} - \vec{R}_{pqr})$  which has cubic symmetry. For simplicity we shall assume that these Wannier functions have only nearest neighbor interactions. In this case, the energy band energies are given by

$$E_{\vec{k}} = 2\mathcal{E}(1) [\cos k_1 + \cos k_2 + \cos k_3] \quad (2.2)$$

Here

$$\begin{aligned} \mathcal{E}(1) &= \int a(\vec{r} - \vec{R}_{000}) H a(\vec{r} - \vec{R}_{100}) d\tau \\ &= \int a(\vec{r} - \vec{R}_{000}) H a(\vec{r} - \vec{R}_{010}) d\tau, \text{ etc.} \end{aligned} \quad (2.3)$$

$k_1$ ,  $k_2$ , and  $k_3$  are the x, y, and z components of the propagation vector  $\vec{k}$  times the interatomic distance. We now apply a perturbation  $V(\vec{r})$  to this problem which has the property that

$$\int a(\vec{r} - \vec{R}_{000}) H a(\vec{r} - \vec{R}_{000}) d\tau = V_0 \quad (2.4)$$

The matrix elements of this perturbation between the Wannier functions vanish unless both Wannier functions are centered about the atom at the origin.

From the preceding report, we see that if we try to expand our impurity wave function in terms of the Bloch functions for the unperturbed problem

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$$\sum(\vec{k}) f_{\vec{k}} B_{\vec{k}}(\vec{r}) \quad (2.5)$$

then for this case we have as the eigenvalue condition that

$$1 = \sum_{k_1 k_2 k_3} (V_0/N) \left\{ 1 / \left[ E - 2\mathcal{E}(1)(\cos k_1 + \cos k_2 + \cos k_3) \right] \right\} \quad (2.6)$$

If the wave functions of the perturbed problem are expressed in terms of the coefficients of the Wannier functions at the various atomic sites ( $U_{pqr}$ ), these are given by

$$U_{pqr} = \text{const.} \sum_{k_1 k_2 k_3} \exp(ik_1 p + ik_2 q + ik_3 r) / \left\{ E - 2\mathcal{E}(1) [\cos k_1 + \cos k_2 + \cos k_3] \right\} \quad (2.7)$$

If we allow the crystal to become infinite, we can convert the summations in (2.6) and (2.7) to integrations over continuous variables in the first Brillouin zone. In this case, the eigenvalue condition becomes

$$1 = V_0' / \pi^3 \int_0^\pi \int_0^\pi \int_0^\pi \left\{ E' - [\cos k_1 + \cos k_2 + \cos k_3] \right\}^{-1} dk_1 dk_2 dk_3 \quad (2.8)$$

The coefficients of the Wannier functions are given by

$$U_{pqr} = \text{const.} \int_0^\pi \int_0^\pi \int_0^\pi \frac{\cos k_1 p \cos k_2 q \cos k_3 r}{E' - [\cos k_1 + \cos k_2 + \cos k_3]} dk_1 dk_2 dk_3 \quad (2.9)$$

Here

$$E' = E/2\mathcal{E}(1) \quad V_0' = V_0/2\mathcal{E}(1) \quad (2.10)$$

In order to study the solutions of this problem all we need do is evaluate the integrals (2.8) and (2.9). We shall do this for the bound states in the case that  $V_0$  and  $\mathcal{E}(1)$  are both negative. (The bottom of the band is  $E' = 3$ .) The integrals (2.8) and (2.9) can be evaluated by doing two of the integrations directly, but this becomes involved with complete elliptic integrals and the final integration becomes a difficult numerical integration. Instead of this we shall digress on a different approach to this integral.

In the integral (2.9), we can carry out a power series expansion of the denominator (since  $E' > 3$ ) and get the result that

(AN EXAMPLE OF IMPURITY LEVELS IN SOLIDS)

$$U_{pqr} = (1/E') \int_0^\pi \int_0^\pi \int_0^\pi (dk) \cos pk_1 \cos qk_2 \cos rk_3 \sum_n (\cos k_1 + \cos k_2 + \cos k_3)^n / E'^n \quad (2.11)$$

( $p = q = r = 0$  gives the eigenvalue condition integral.) Introducing a parameter  $t$  we see that

$$U_{pqr} = (1/E') \sum_n \frac{1}{E'^n} \left[ \frac{d^n}{dt^n} \int_0^\pi \int_0^\pi \int_0^\pi \cos pk_1 \cos qk_2 \cos rk_3 e^{t(\cos k_1 + \cos k_2 + \cos k_3)} \right]_{t=0} \quad (2.12)$$

$$= \left( \frac{\pi^3}{E'} \right) \sum_n (1/E'^n) \left[ \frac{d^n}{dt^n} I_p(t) I_q(t) I_r(t) \right]_{t=0}$$

$I_p(t) = (1/\pi) \int_0^\pi e^{t \cos k} \cos pk \, dk$  is the Bessel function of pure imaginary argument.

We can formally write

$$U_{pqr} = (\pi^3/E') \left[ 1 / \left( 1 - \frac{1}{E'} \frac{d}{dt} \right) I_p(t) I_q(t) I_r(t) \right]_{t=0} \quad (2.13)$$

(We get Eq. (2.12) by expanding the denominator.) If we define

$$U_{pqr}(t) = (\pi^3/E') \left[ 1 / \left( 1 - \frac{1}{E'} \frac{d}{dt} \right) I_p(t) I_q(t) I_r(t) \right] \quad (2.14)$$

for all  $t$ , we can formally multiply both sides of this equation by  $(E' - \frac{d}{dt})$  and find that

$$(E' - \frac{d}{dt}) U_{pqr}(t) = \pi^3 [I_p(t) I_q(t) I_r(t)] \quad (2.15)$$

We can solve this first order differential equation and get the result that

$$e^{-E't} U_{pqr}(t) = \pi^3 \int_t^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt + \text{const.} \quad (2.16)$$

The constant of integration can be shown to be zero by studying the asymptotic forms of (2.12) and (2.16) for large  $t$ . Therefore the quantity we want,  $U_{pqr}(0) = U_{pqr}$ , is given by

$$\int_0^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt \quad (2.17)$$

The eigenvalue condition is given by

(AN EXAMPLE OF IMPURITY LEVELS IN SOLIDS)

$$V_0' \int_0^\infty e^{-E't} [I_0(t)]^3 dt = 1 \quad (2.18)$$

The wave function (2.17) is not normalized but the normalization can easily be found

$$\sum(\vec{k}) f_{\vec{k}}^* f_{\vec{k}} = \sum(\vec{k})(E - E_{\vec{k}})^{-2} = -\frac{d}{dE} \sum(\vec{k})(E - E_{\vec{k}})^{-1} = \int_0^\infty t e^{-E't} [I_0(t)]^3 dt \quad (2.19)$$

Therefore (2.17) can be normalized by multiplying by  $\left\{ \int_0^\infty t e^{-E't} [I_0(t)]^3 dt \right\}^{-1/2}$ .

After this digression on the evaluation of this integral, we can give the results on the values of the wave function and energy. The integral in (2.18) was carried out for a number of values of  $E'$  and the corresponding value of the perturbation  $V_0'$  was found. These results are given in Fig. 2-1. We notice that a finite value of the perturbation is necessary before the bound state pulls out of the bottom of the energy band. For  $V_0'$  slightly greater than this minimum perturbation the energy behaves quadratically as a function of  $V_0'$ . For large perturbations the energy  $E'$  approaches  $V_0'$  and becomes essentially linear as a function of  $V_0'$ .

The coefficients of the Wannier functions have also been computed for the energies in Fig. 2-1. These coefficients have been computed (unnormalized) in the (100) direction and are given in Table 2-1. The values in the expression (2.17)

$$U_{p00} = \int_0^\infty e^{-E't} [I_0(t)]^2 I_p(t) dt$$

Table 2-1

$$U_{p00} = \int_0^\infty e^{-E't} I_p(t) [I_0(t)]^2 dt \text{ as a function of energy and } p$$

| $E' \backslash P$ | 3.0   | 3.1    | 3.2    | 3.5     | 4.2     | 5.0      |
|-------------------|-------|--------|--------|---------|---------|----------|
| 0                 | .4990 | .4311  | .4001  | .3410   | .2646   | .2137    |
| 1                 | .1658 | .1123  | .0935  | .0645   | .0371   | .0238    |
| 2                 | .0778 | .0376  | .0270  | .0141   | .00564  | .00278   |
| 3                 | .0501 | .0154  | .00929 | .00350  | .000924 | .000343  |
| 4                 | .0411 | .00717 | .00365 | .000964 | .000162 | .0000439 |

It has already been pointed out<sup>(1)</sup> that if the difference equations for the Wannier function coefficients were replaced by an approximate differential equation we might expect the coefficients of the Wannier functions to fall off as  $e^{-\gamma r}/r$  ( $r \neq 0$ )

(AN EXAMPLE OF IMPURITY LEVELS IN SOLIDS)

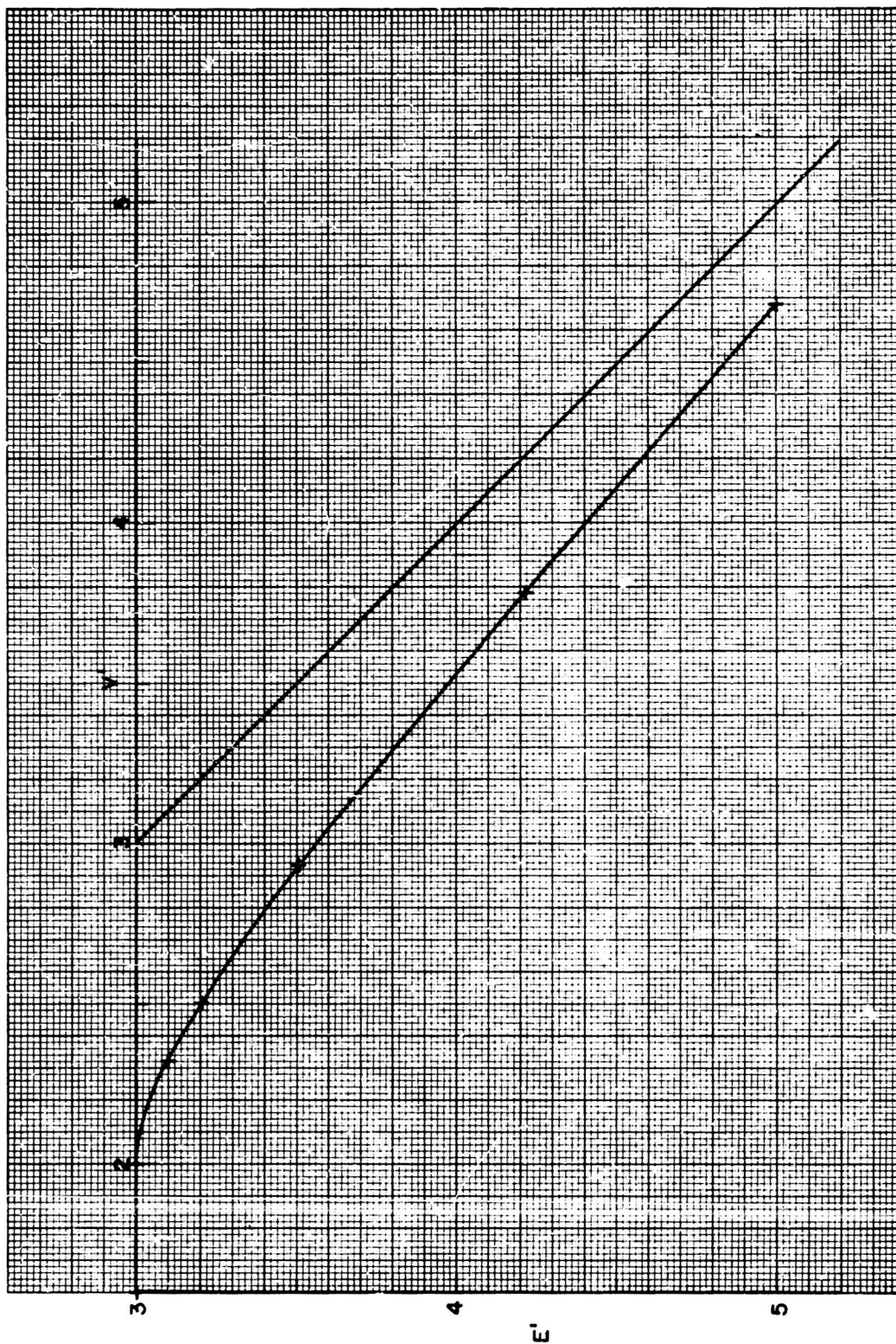


Fig. 2-1  
Energy ( $E'$ ) vs perturbation potential ( $V_0'$ )

(AN EXAMPLE OF IMPURITY LEVELS IN SOLIDS)

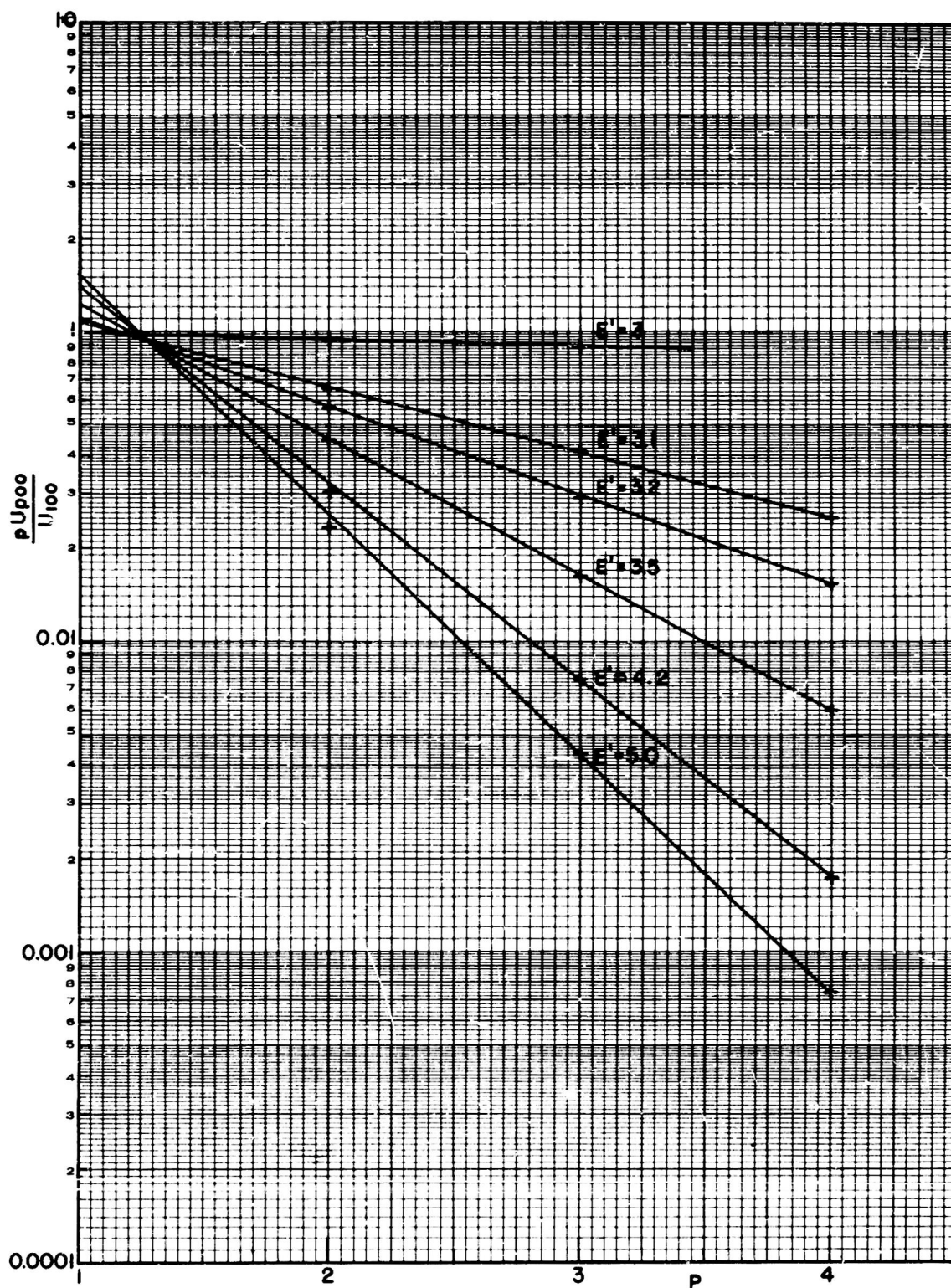


Fig. 2-2

Coefficients of the Wannier function in the (100) direction ( $p(U_{p00}/U_{100})$ ) as a function of  $p$  for various values of  $E'$ .

(AN EXAMPLE OF IMPURITY LEVELS IN SOLIDS)

where  $\gamma = 0$  when the bound state first comes out of the energy band ( $E' = 3$ ). This behavior is also predicted when we assume that  $E'$  is near to the bottom of the band and the principle contribution to the integral (2.9) comes from  $E_{\vec{k}}$  near the bottom of the band when the denominator of the integral is small. In this case,

$$U_{pqr} = \int \frac{e^{i(pk_1 + qk_2 + rk_3)}}{\Delta E' + \frac{1}{2}(k_1^2 + k_2^2 + k_3^2)} \quad (2.20)$$

where  $\Delta E' = E' - 3$  and the denominator is obtained by expansion of  $\cos k_1$ , etc. Carrying out the integral (2.20) gives the result that

$$U_{pqr} = (p^2 q^2 r^2)^{-1/2} e^{-\sqrt{2\Delta E'} \sqrt{p^2 + q^2 + r^2}} \quad (2.21)$$

which agrees with the result of the differential equation approach.

In Fig. 2-2 we plot  $p(U_{p00}/U_{100})$  on semi-log graph paper. The log of this function should be a linear function of  $p$  if the behavior predicted by the differential equation approach or the approximation to the integral (2.9) is valid. We have not plotted the points  $U_{000}$  since neither approximate approach is valid for this point. We notice that for  $E' = 3$  the graph is very nearly linear and horizontal. This is predicted by both approximations. For  $E' > 3$  the linearity becomes quite good for points removed from the impurity atom. (i. e.,  $p = 2, 3, 4$ , lie nearly on a straight line.) We can also compare the actual slopes of the curves in Fig. 2-2 with those predicted from approximation (2.21). Eq. (2.21) predicts a slope

$$(\text{Log}_{10} e) \sqrt{2\Delta E'}$$

For  $E' = 3.1$  this gives a value .193, for  $E' = 3.2$  the value is .275. The corresponding slopes calculated from the actual values of  $U_{p00}$  are .209 for  $E' = 3.1$  and .285 for  $E' = 3.2$ . We can see therefore that the approximation to the slope gives a value to within about 5% of the true value.

Work on this problem will continue to calculate the coefficients of the Wannier functions in other directions than the (100) direction, in order to check the spherical symmetry of the wave function.

#### Reference

1. J. C. Slater and G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1953, p. 7.

G. F. Koster

### 3. ENERGY BANDS IN COPPER

The use of the recently proposed augmented plane wave method<sup>(1)</sup> for calculating energy bands in crystals depends, for its practical use, upon the convergence of the secular equation which arises as an attempt to ensure continuity of slope of the wave function at the boundary of the matching sphere. It is hence of immediate importance to apply the method to a particular metal to study the convergence and value of the method. The case of copper has been selected as being of particular interest owing to the overlapping of the 4s conduction band with the narrow 3d band. Calculations of the 3d band structure of copper have been made previously by the tight binding method,<sup>(2)</sup> and of the 3d and 4s band by the cellular method.<sup>(3)</sup> There is close resemblance in the results for the d band in these two cases, and it is hoped that the present method will agree substantially with these calculations, and in addition may be used to investigate the higher excited electronic states.

The initial step in the augmented plane wave method is to calculate the energy  $E$  of the augmented wave in terms of the energy  $E_0$  of the plane wave outside the matching sphere of radius  $R$ . The dependence of  $E$  upon  $E_0$  is given by

$$F(E) = \Omega(E - E_0) - 4\pi \sum_l (2l + 1) j_l^2(\sqrt{E_0} R) R^2 \frac{d}{dr} \ln u_l(E, r) \Big|_{r=R} = 0 \quad (3.1)$$

$\Omega$  is the volume of the unit cell outside the matching sphere, which, for a face-centered cubic structure such as copper is

$$\Omega = \frac{a^3}{4} - \frac{4}{3}\pi R^3$$

$a$  being the lattice constant.  $j_l(x)$  is the spherical Bessel function, and  $u_l(E, r)$  is the radial wave function. Both the numbers of parameters involved and the fact that  $u_l(E, r)$  is obtained by numerical integration have led to an attempt being made to compute (3.1) by use of the Whirlwind high speed digital computer.

The problem falls into three portions: the computation of  $P_l(E, r)$ , defined by

$$ru_l(E, r) = P_l(E, r);$$

the evaluation from this of

$$v_l(E, r) = r^2 \frac{d}{dr} \ln u_l(E, r)$$

and lastly, the computation of (3.1) as a function  $E$  for various values of  $E_0$ ,  $a$ ,  $R$ . The program devised will compute (3.1) and determine its roots for a given number of lattice parameters  $a$ , for a given number of matching radii  $R$  for each  $a$ , thus enabling

(ENERGY BANDS IN COPPER)

us to see the effect on the energy levels of choosing different matching radii, and for a given number of equally spaced energies  $E_0$ .

The function  $P_l(E, r)$  is a solution of the equation

$$\frac{d^2 P}{dr^2} = f(P, r) = P \left[ V - E + \frac{l(l+1)}{r^2} \right] \quad (3.2)$$

where  $V$  is the spherically symmetrical potential in which the electron is supposed to move inside the matching sphere. In order to forward integrate (3.2), use is made of the Gauss Jackson formula

$$P_n = \frac{h^2}{12} f_n + h^2 \delta^{-2} f_n \quad (3.3)$$

where  $\delta^{-2} f_n$  represents the second sum of  $f_n$  and  $h$  is the interval of  $r$ . The first correction term which has been omitted in (3.3) is  $-h^2/240 \delta^2 f_n$ , which can be made negligible by choice of sufficiently small intervals  $h$ . In order to use (3.3) to advance the integration from  $r_{n-1}$  to  $r_n$ , the second sum  $\delta^{-2} f_n$  is computed from previous knowledge, and is given as

$$\delta^{-2} f_n = 2\delta^{-2} f_{n-1} - \delta^{-2} f_{n-2} + f_{n-1}$$

In general, the resulting algebraic equation (3.3) must be solved for  $P_n$ , using (3.2), by iteration. In the case of the linear equation,  $P_n$  can be determined directly, the method reducing to the Noumerov method.

To preserve generality, the general solution of (3.2) involving iterations has been set up on Whirlwind. It is planned to increase the speed by taking into account the linearity of (3.2), to avoid the iterations.

The subroutine to advance the integration by one step is incorporated in a master routine which organizes the change of interval at given points, and the storage of the wave function. In order to carry out the rest of the computation, we require a table of the wave function for values of  $r$  greater than a prescribed value  $R_0$ . To use this program, the data to be specified, which is dependent upon the particular metal under consideration, consists of the potential  $V(r)$  tabulated at intervals of  $r$ ,  $h_i$ , in the range

$$r_{i-1} \leq r \leq r_i$$

## (ENERGY BANDS IN COPPER)

where  $r_0 = 0$ , and  $i \leq k$ , all of which parameters must also be specified. In the case of copper, we are using  $k = 2$ , and  $h_1 = .005$ ,  $h_2 = .04$ ,  $r_1 = .04$ ,  $r_2 = 4.0$ . In addition, two starting values  $P_l^{(0)}$ ,  $P_l^{(1)}$ , together with the initial value of  $r$ ,  $r^{(0)}$  are required to start the integration. The next section of the program computes  $v_l(E, R)$  for a given  $E$  and  $l$ , and for various  $R$ . A table of the derivatives of  $P$  is computed from the table of  $P$  by a forward difference formula. For a given  $R$ ,  $P$  and its derivative are interpolated from these tables by use of the Everett modified second difference formula, using three entries on either side of the argument; the truncation error is about  $0.0005 \delta^5 P$ . The function  $v_l(E, R)$  may thus be computed and stored for all  $R_i$ ; the preceding computation is repeated for all the  $l$  values required, and lastly, the parameter  $E$  is increased by equal amounts between two specified values. It is planned to use a sufficiently small range of  $E$  for each set of integrations carried out to enable the same starting solutions  $P_l^{(0)}$ ,  $P_l^{(1)}$  to be used for all  $E$ . The particular radii  $R$  and the number of parameters  $l$ ,  $E$ , are the only data required to carry through this part of the program.

Lastly, the use of  $v_l(E, R)$  to compute (3.1) in the form  $F_{\text{ar}E_0}(E)$  is a straightforward procedure. The only operation requiring comment is the calculation of the spherical Bessel functions  $j_l(\sqrt{E_0} R)$ . These are computed from the slowly varying function  $\Lambda_{l+1/2}$ , defined by

$$\Lambda_{l+1/2}(x) = \left(\frac{2}{x}\right)^l \sqrt{\frac{2}{\pi}} \Gamma\left(l + \frac{3}{2}\right) j_l(x).$$

For high  $l$ ,  $\Lambda_{l+1/2}$  can be calculated from a polynomial expansion, and use is then made of the backward recurrence formula

$$\Lambda_{l-1/2}(x) = \Lambda_{l+1/2}(x) - \frac{x^2}{(2l+1)(2l+3)} \Lambda_{l+3/2}(x)$$

This proceeds with negligible loss of accuracy for all  $l$  when  $x < 10$ , which is sufficient for the present purpose. The convergence of the sum in (3.1) is governed by the convergence of  $j_l(\sqrt{E_0} R)$ ; for values of  $E_0$  corresponding to wave vectors spanning the first Brillouin zone, terms for which  $l > 6$  are negligible, while for larger  $E_0$ , it is estimated that terms with  $l > 12$  may be neglected. The first two portions of this program have been tested and made error free. The last section, together with methods for determining the roots of (3.1) is at present being tested, preparatory to using the complete program to investigate the energy band structure of copper.

(ENERGY BANDS IN COPPER)

References

1. J. C. Slater and M. M. Saffren, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1953, p. 11.
2. G. C. Fletcher and E. P. Wohlfarth, *Phil. Mag.* 42, 106 (1951); G. C. Fletcher, *Proc. Phys. Soc. (London)* A65, 192 (1952).
3. D. J. Howarth, *Proc. Roy. Soc. (London)* (in the press).

D. J. Howarth

#### 4. THE AUGMENTED PLANE WAVE METHOD

I have begun work to apply the augmented plane wave method, described in the previous Progress Report, to sodium. An easy generalization of that method has been made which may or may not prove to be useful. The generalization is this: rather than choose our wave function to be continuous across the matching spheres, we choose the derivative of the wave function to be continuous across them. This condition along with the minimization of the expectation of the energy relative to the energy inside the spheres yields wave functions with properties analogous to the wave functions generated by the original procedure. All functions with different energy but with the same  $\vec{k}$  value are orthogonal and have no component of the energy between them.

The  $E$  vs  $\vec{k}^2$  curve for these functions has asymptotes for values of  $E$  for which  $u_l'(E; R_i)$  vanishes. The branches of these curves touch the asymptotes for  $\vec{k}$  values which cause the derivative of a spherical Bessel function  $j_l'(kR_i)$ , to vanish. Thus if we superimpose the  $E$  vs  $\vec{k}^2$  curves for the two cases (continuous slope method and continuous wave function method) we find that between every two old asymptotes we find a new one, and between every two old points of tangency to the asymptote we find a new one. Furthermore, the slope of each branch is everywhere decreasing. These comments are illustrated in Fig. 4-1.

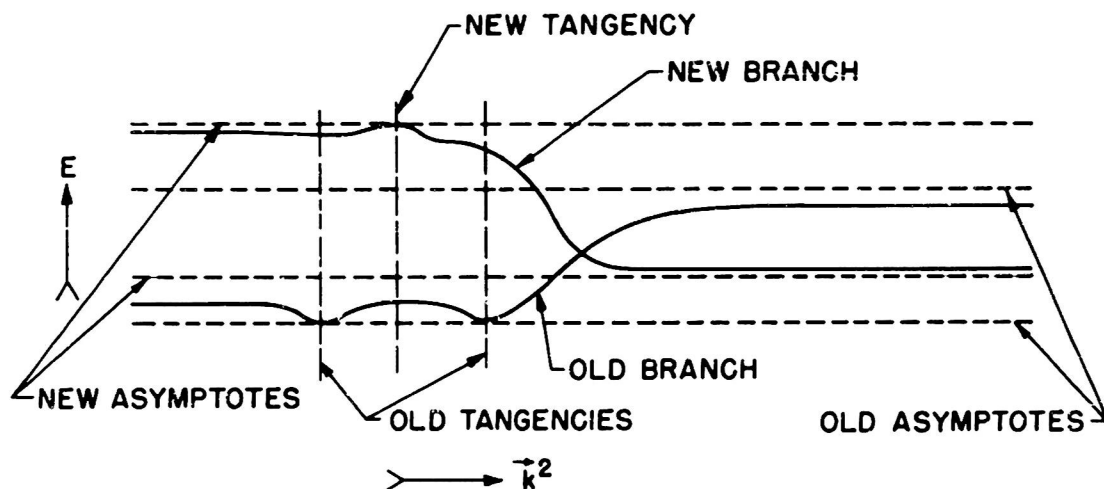


Fig. 4-1

A typical branch of  $E$  vs  $\vec{k}^2$  in the old and new schemes

These new functions may be useful in speeding up the convergence of the secular equation in that their spectrum combined with the old spectrum yields a denser spectrum than either alone. This affords us more functions for our secular equation which have energies close to the energy we wish to calculate. It may, however, not pay to make this combination but to use one scheme for one range of energies and

(THE AUGMENTED PLANE WAVE METHOD)

the other scheme for another range. These ideas will be investigated in the application of the method to sodium.

Because the asymptotes are suggestive of "gaps" it was thought that the scheme could be modified to place these "gaps" at more natural energies than those which cause  $u_l'(E;R_i)$  or  $u_l(E;R_i)$  to vanish. The modification was to make the combination,  $\alpha$ (wave function) +  $\beta$ (slope of wave function), (where  $\alpha$  and  $\beta$  are constants to be determined) continuous across the boundary spheres. The expectation of energy of such a wave function is then minimized with respect to the energy interior to the spheres and the parameter  $\beta/\alpha$ . This yields two equations. We can then solve for  $\beta/\alpha$  as a function of energy and then solve for energy as a function of  $\vec{k}^2$ . The "gaps" will then occur for values of energy which satisfy

$$\frac{u_l'(E;R_i)}{u_l(E;R_i)} = - \frac{\beta}{\alpha} = \gamma(E)$$

The "gaps" will no longer occur at the same energy for all  $\vec{k}$  but actually change with  $\vec{k}$ . Another attractive feature is that, since we have minimized the expectation of energy relative to two parameters, our approximation to the actual  $E$  vs  $\vec{k}^2$  curves should be better than in the two special cases in which we take either  $\alpha = 0$  or  $\beta = 0$  to start with. However, the mathematical difficulties in solving the energy equation for this scheme are so formidable that I do not consider its application worth while at the present time.

M. M. Saffren

## 5. ENERGY BANDS IN CHROMIUM

The calculation of matrix elements of the Hamiltonian between two Bloch waves (3d or ion-core) is in progress. The calculation of matrix elements of this type has been completed for the short-range portion of the crystal potential. (The short-range portion of the crystal potential is a spacial sum over the crystal lattice of non-overlapping atomic potentials; the remainder of the crystal potential, composed of a spacial sum of strongly overlapping atomic potentials, is called the long-range portion.) Work is continuing on the calculation of matrix elements of the kinetic energy and the long-range portion of the crystal potential.

R. H. Parmenter

## 6. STUDIES OF ATOMIC SELF-CONSISTENT FIELDS

The study of the properties of the atomic self-consistent fields, which was actually started some time ago at Uppsala, has been continued during my stay at the Solid-State and Molecular Theory Group. Of the main problems to be solved, we have treated the question of the analytic representation of the self-consistent field (SCF) wave functions, the interpolation (or extrapolation) of these wave functions to atoms or ions for which they have not yet been computed, and the problem of the connection between the SCF-functions and the simple hydrogen-like ones.

The question of the analytic representation has been solved in two steps. The numerically given SCF-functions were first expressed in a form, originally proposed by Slater,<sup>(1)</sup> as hydrogen-like functions having each exponential replaced by a sum of one, two, three, or more exponentials. The exponents and coefficients of these exponentials have been determined by a method of "quotient analysis" and successive approximations, and the details and the results of this first attack have already been published.<sup>(2)</sup> However, the method is tedious and rather time-consuming, since the time required for an almost perfect fit (0.001) is usually of the order 30-40 hours by using an ordinary desk machine.

The method for finding the analytic fit has now been modified. In the new approach, the SCF-function is expressed as the product of a polynomial, having the same nodes  $r_0'$ ,  $r_0''$ , ..., as the wave function itself, and a sum of exponentials. The essential problem is therefore to develop the function

$$g(r) = f_{nl}(\text{SCF } r)/r^{l+1}(r_0' - r)(r_0'' - r) \dots, \quad (6.1)$$

taken in equidistant points, into a sum of geometrical series, each one corresponding to an exponential term. In principle, such a problem can be exactly solved, but due to the vanishing of valid figures, this exact solution is without practical value. Instead we have used a method of successive approximation starting from the tail of the function, where, in addition to the previously mentioned quotient analysis, we have also used the theory for developing a series of equidistant entries into two geometrical progressions. The technique is so simple and straightforward that it now takes about 4-5 hours to get a perfect analytic fit even for a rather extensive SCF-function having several nodes.

The analytic SCF-functions have been utilized for a first attack on the interpolation problem. We have retained the rule given by Slater<sup>(1)</sup> that the exponents should be linear functions of the atomic numbers, but we have replaced his rule for the coefficients by a simpler law based on the analogy with the hydrogen-like case. Test interpolations<sup>(2)</sup> using these rules have shown an almost perfect accuracy (0.001 - 0.002).

We have, however, also attacked the interpolation problem in a more direct

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way by using only the numerical tables of the SCF-functions. We have used the basic principle that any quantity, which for a hydrogen-like function would equal the atomic number  $Z$ , for a SCF-function corresponds to an "effective nuclear charge"  $Z_{\text{eff}}$ , and practically, we have then found that this  $Z_{\text{eff}}$  is an almost linear function of the atomic number well suited for interpolation purposes. By considering the corresponding  $Z_{\text{eff}}$ , we have in this way treated the interpolation of the positions and magnitudes of the maxima and minima, the derivatives in origin, the eigenvalues, etc.

An important point is that the positions of the eventual nodes may be interpolated with almost perfect accuracy in this way. The nodes usually cause complications in the problem of interpolating the SCF-functions as a whole, and we have therefore found it convenient to divide them away and to consider simply the function  $g(r)$  given by (6.1). The logarithm of  $g(r)$  is for a hydrogen-like function a linear function of  $rZ$ , and, for a SCF-function, the corresponding quantity is therefore a linear function of  $rZ_{\text{eff}}(r)$  where, for a given  $r$ , the second factor is an almost linear function of the atomic number. The interpolation problem may therefore simply be solved by making a linear interpolation in the logarithm of  $g(r)$  for each  $r$ -value under consideration with an eventual renormalization of the interpolated wave function as a whole. Test interpolations have shown that this simple rule gives an accuracy of 0.001 for the inner wave functions and an accuracy of about 0.005 or better for the outermost one.

In this way it is also possible to compute an effective charge  $Z_{\text{eff}}(r)$  which is a continuously varying function of the radius. In addition to this function, we have studied the quotient

$$\omega(r) = Z_{\text{eff}}(r)/Z_{\text{eff}}(0). \quad (6.2)$$

which is monotonously decreasing from the value  $\omega(0) = 1$ . Practically we have found that this function is very slowly varying with the atomic number, and it may therefore be used for improving the accuracy of the interpolation of the outermost function. Another characteristic feature is that, for an isoelectronic series, the difference between the two  $\omega$ -functions for the fields with and without exchange seems to be approximately the same function of  $r$  for all elements of the series. This property may be used for estimating wave functions with exchange from those without exchange, when only one field with exchange is known in the series. For the moment, several fields with exchange have been determined up to  $\text{Cu}^+$  ( $Z = 29$ ) whereas various fields without exchange have been computed up to  $\text{Hg}$  ( $Z = 80$ ).

As applications of the interpolation methods here described we have estimated "initial" wave functions for two Ne-like configurations, namely  $\text{Ne}$  and  $\text{Al}^{+3}$ , and carried through the integrations of the Hartree-Fock equations for fields with exchange. The corrections to the "final" wave functions were extremely small.

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Finally, we have investigated the closer connection between the SCF-functions and the hydrogen-like functions by using a method with a varying scale factor. A function  $F(r)$  is here said to be obtained from another function  $f(r)$  by means of a constant scale factor  $\lambda$ , if

$$F(r) = \lambda^{1/2} f(\lambda r), \quad (6.3)$$

which transformation leaves the normalization integral invariant. An obvious generalization of this relation is to replace the linear function  $\lambda r$  by a more general function  $\psi = \psi(r)$  and to put

$$F(r) = \left[ \frac{d\psi}{dr} \right]^{1/2} f(\psi), \quad (6.4)$$

which transformation also leaves the normalization integral invariant. At the same time we obtain

$$\int_0^r F^2(\xi) d\xi = \int_0^{\psi(r)} f^2(\xi) d\xi, \quad (6.5)$$

which relation shows that we simply can get a table of the function  $\psi(r)$  by inverse interpolation from tables of the total spherical charges corresponding to the two radial distributions under consideration. The work is essentially simplified by preparing the table for the right-hand member of (6.5) with a particularly small interval, but this work may fortunately be done just once for all if we use the same set of standard functions  $f(r)$ , for instance the hydrogen functions.

According to this method we are able to express all SCF-functions with and without exchange as hydrogen-like functions having an effective charge given by

$$Z_{\text{eff}}(r) = \psi(r)/r. \quad (6.6)$$

All 1s-, 2s-, and 2p-functions available have been investigated in this way, and we have found that even the  $\psi$ -functions are very convenient for interpolation purposes. The method is simple and quite straightforward, but it shows a complication for the neighborhood of the nodes which appear to be slightly "out of scale". The method gives also a possibility of deriving the mutual scaling of two SCF-functions on each other.

The effective charge functions derived in this way may be useful for estimating molecular integrals for SCF-functions from the standard tables for hydrogen-like functions given by Kotani, Kopineck, and others. Let us consider a diatomic molecule

(STUDIES OF ATOMIC SELF-CONSISTENT FIELDS)

of two identical atoms with the internuclear distance equal to  $a$ . The molecular tables are then usually given in terms of an effective nuclear charge  $Z$ , and we have now attempted to get the SCF-value simply by replacing this  $Z$  by

$$Z = Z_{\text{eff}}(r_0 + a/2), \quad (6.7)$$

where  $r_0$  is a constant determined by the condition that the approximation should be valid for  $a = 0$ . For the  $2p\pi$ -functions of carbon, which are particularly important in the theory of conjugated organic compounds, we have carried out a comparison between these estimations and the actual integral values obtained by numerical integration: the accuracy of the estimations appeared to be surprisingly high, mostly around 95 - 100%. However, for  $\sigma$ -functions, the method must certainly be further developed before a similar accuracy can be obtained.

All the numerical computations are now essentially concluded and a series of articles is being prepared for publication.

References

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2. P. -O. Löwdin, Phys. Rev. 90, 120 (1953).

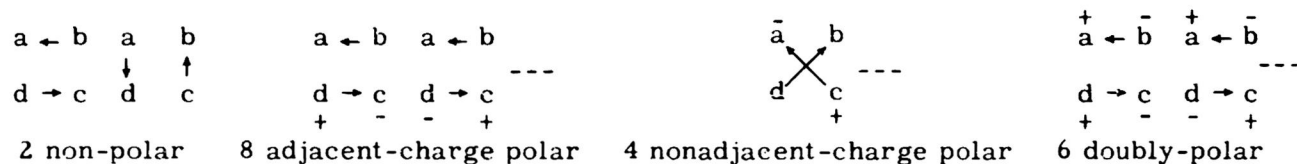
P. -O. Löwdin

## 7. A REVISED VALENCE BOND METHOD

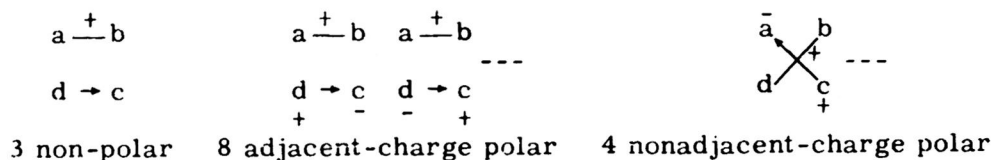
Work has proceeded along the lines indicated in the previous Report (to be referred to as I). Numerical calculations on the four-electron problem with the symmetry of the square (in fact, the  $\pi$ -electron system of the hypothetical molecule cyclobutadiene) have been completed and the results are sufficiently interesting to warrant inclusion in the present Report. More interesting will be the results from the six-electron problem (the hexagonal benzene molecule): calculations are already well-advanced and it therefore seems worth while reporting first on the general VB approach which is common to both problems.

In the four-electron case the following VB structures (i. e., spin-paired or valence bond structures defined over strictly orthogonal orbitals,  $\bar{AO}$ 's) are employed (see I for further details).

### Singlet States



### Triplet States



The structures not shown are obtained simply by rotation of the given pictures and in each case the basis of structures is complete subject to the limitation imposed by using a basic set of  $2p\pi$  orbitals alone. In the triplet case there are, at first sight, four non-polar structures; but only three are linearly independent, for a "vector rule" for the arrows shows that the fourth is (-1) times the sum of the other three. The number of linearly independent spin eigenfunctions of total spin  $S$  and given  $S_z$  which can arise from a given orbital configuration, and therefore the number of structures showing a given disposition of charges, follows of course from the Wigner formula as

$$\binom{N}{\frac{1}{2}N - S} - \binom{N}{\frac{1}{2}N - S - 1}$$

## (A REVISED VALENCE BOND METHOD)

where  $N$  is the number of singly occupied orbitals; this provides a simple and useful check on the number of structures set up by pictorial methods.

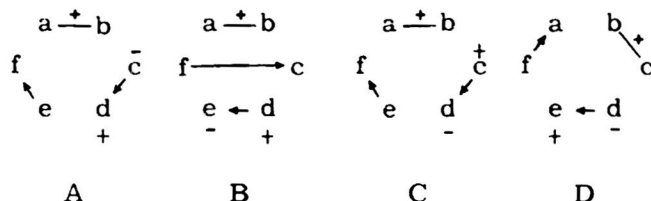
In the six-electron problem a little consideration shows that there are 175 independent singlet structures and 189 triplets; and, although the hexagonal symmetry permits a very substantial reduction of the problem, use of the full number of configurations would incur both the evaluation of many hundreds of matrix elements and the solution of secular equations of rather high order (e. g., 22 singlet combinations of  $A_{1g}$  symmetry can be formed). There are clearly two reasons for wishing to select, from the formidable array, just those structures of greatest potential value in the energy calculation: in the first place, extension of these methods to even slightly more difficult problems will be quite impossible unless a useful method of selection can be found; and secondly, our physical insight into the calculation is progressively weakened as more and more configurations are admitted. The methods now being developed provide a very natural and plausible way of making the necessary selection: for (see I) non-polar and singly-polar structures are expected to predominate in the description of a bonded system -- pictorially, they are sufficient to describe "charge hops" across all possible bonds and the inclusion of multiply-polar structures (which are in any case energetically less well favored) could only fulfil somewhat more freely this fundamental bonding requirement. First then we should look for the best approximation which can be built from non-polar and singly-polar structures; this would reduce the problem to one involving only 65 singlet and 99 triplet structures. We notice however that all bonds between nearest neighbors can be accounted for, pictorially, in terms of non-polar and adjacent-charge polar structures; in a preliminary calculation then we might tentatively admit this additional restriction -- working in terms of 29 singlet and 45 triplet structures. This last step in the selection becomes fairly convincing when it is realized that admission of nonadjacent-charge structures is tantamount to a recognition of considerable interactions between atoms which are known to be "non-bonded". At the same time the conventional VB structures, which arise by simple generalization of the Heitler-London type  $H_2$  function and which presumably do in some way describe the bond systems to which they are supposed to correspond, may be expanded in terms of  $\overline{VB}$  structures and the importance of a structure is then found to fall off as the separation of the charges increases.

The types of structure we shall first consider are shown below (together with the number of structures of each type -- formed by rotating the pictures)



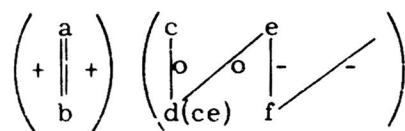
(A REVISED VALENCE BOND METHOD)

permuted under the group operations (a property not shared by, for instance, MO configurations). The matrix eigenvalue equation then breaks into "block form", each block involving structure-combinations of like symmetry and having elements which may be reduced, using the group properties, into expressions which contain a relatively small number of distinct elements of H between pairs of individual structures, and the latter may be evaluated without difficulty by the rule given in the last Report. The application of this rule (which was quite general) to VB structures will now be illustrated by reducing two typical matrix elements completely to one- and two-electron integrals. Take the pairs of structures below; they may be described as showing, respectively, a shift of negative charge and a shift of positive charge, and each is a triplet structure.



(1) (A|H|B)

The cycle diagram is (ignoring at first the arrow directions)



and, by direct application of the rule, gives a matrix element

$$2^2 \left[ Q_d(ce) - \frac{1}{2} (K_{da}(ce) + K_{db}(ce)) - (K_{df}(ce)) - (+1 K_{df}(ce)) \right]$$

where the modified Coulomb and exchange integrals are, more fully (see also I)  $Q_d(ce) = (c|h|e) + (ac|g|ae) + (bc|g|be) + \dots = \beta_{ce} + (aa, ce) + (bb, ce) + \dots$  and, for instance,  $K_{da}(ce) = (ca|g|ae) = (ca, ae)$ . Here  $\beta_{ce}$  is the "resonance" integral of an MO treatment and we use a common notation in which  $(ab, cd)$  is the mutual potential energy of charge distributions  $ab$  and  $cd$ . In the present case obvious symmetries exist, it is convenient to employ certain standard Coulomb integrals -- such as  $Q_a(ab)$ ,  $Q_a(ac)$ , and the simplest form of the result is

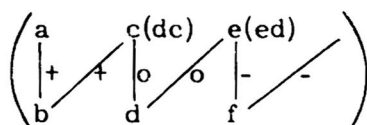
$$2^2 \left[ (Q_a(ac) + (aa, ac) - (bb, ac)) - \frac{1}{2} (ac, ae) - \frac{5}{2} (ab, ad) \right].$$

## (A REVISED VALENCE BOND METHOD)

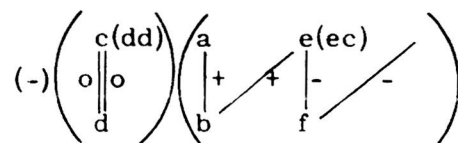
Since the original pictures are "matched" by an even number of arrow reversals, there is no need to affix a factor - 1 and this is the final result. In practice the reduction described is immediate.

## (2) (CIHID)

The cycle diagram is



but in this case only a one-orbital difference really occurs, for the columns containing orbitals d and c in the determinants of D may be interchanged, a factor - 1 being simultaneously added; and it is evident that this preliminary matching is precisely equivalent to making the interchange in the cycle diagram and breaking the cycle to give



(the (-) indicating that the matrix element is to be prefixed by a factor - 1). The rule is now directly applicable, giving the result

$$(CIHID) = -2^1 \left[ Q_{ce}(dd, ec) - \frac{1}{2}(2K_{ed}(ec)) + K_{ef}(ec) - K_{ea}(ec) - K_{eb}(ec) \right]$$

which again reduces on inspection to

$$-2 \left[ (Q_a(ac) + (ac, bb) - (ac, aa)) - (ab, bc) - (ac, ae) \right]$$

In working with valence bond structures a cycle change of this type is appropriate whenever a shift of positive charge is involved, but in no other case.

Although all the matrix elements involved may be written down with relatively little labor, by the above methods, it must not be forgotten that the integrals which occur are defined over the orthogonal  $\overline{AO}$ 's (though we shall now use the bar notation only when actually making comparisons between  $\overline{VB}$  and VB quantities). In fact, all the overlap and many-center integrals which the conventional theory omits are implicitly included (but in a more manageable way) in the simple types of  $\overline{AO}$  integrals which now appear. Thus the distinct AO integrals of the type (pq, rs), which may be set out as a matrix (A) with elements labeled by two double suffixes,  $A_{pq, rs}$  ( $p < q, r < s$ ),

(A REVISED VALENCE BOND METHOD)

transform into integrals  $(\overline{pq, rs})$  when the AO's are replaced by  $\overline{AO}$ 's. And if the orbital transformation be written  $(\overline{p}) = (p)(\lambda)$  then  $(\overline{A}) = (\lambda^2)_s (A)(\lambda^2)_s^\dagger$  where  $(\lambda^2)_s$  is the symmetrized Kronecker square of  $(\lambda)$ . This transformation (which in the six-electron case involves a product of three  $21 \times 21$  matrices can obviously be reduced when molecular symmetries exist -- but not in general. It may therefore ultimately be worth programming this transformation, which would also describe the calculation of integrals over MO's, for digital computation. Fortunately, however, when the new orbitals are strongly localized, an integral  $(\overline{pq, rs})$  is quite negligible unless the atom pairs  $pq, rs$  are very near (excluding  $p = q, r = s$ ) and then depends only on their immediate environment: thus, in practice, the  $\overline{AO}$  products such as  $\overline{pq}$  may be expanded directly, only a few neighboring orbitals occurring with significant weight, the important terms in the integrand of  $(\overline{pq, rs})$  then being picked out by inspection.

Certain features of the transformation to  $\overline{AO}$ 's have been noted in the previous Report. Broadly speaking, integrals of the form  $(\overline{pp, qq})$  do not differ greatly from their conventional counterparts  $(pp, qq)$  -- but all other integrals (of types  $(pq, rr)$  and  $(pq, rs)$ ) are almost completely "transformed away". This reduction in numerical values of all the exchange and hybrid integrals is so striking that it is worth giving figures (see Table 7-1): the AO values which follow are taken from Craig<sup>(2)</sup> in the first case and from Parr, Craig and Ross<sup>(3)</sup> in the second (all values are in e. v.). Most of the integrals not given are of the order 0.01 or less; and there is clearly a strong case for neglecting, in  $\overline{AO}$  calculations, most of the troublesome many-center terms which cannot be discarded in other formulations. There are, of course, reasons for expecting an effect of this kind -- for a charge distribution  $\overline{pq}$  contains zero net charge and interactions between differently located distributions should therefore be of "second order" -- but the results more than fulfill our expectations: indeed, it seems likely that the complete neglect of all non-Coulombic (or, more loosely, "exchange" -- including hybrid) integrals may have little effect upon our ultimate general conclusions. \* We shall therefore go on to examine the energy calculation, verifying previous conclusions<sup>(1)</sup> about the form of the secular problem (see I), and investigating the effect of the many small exchange integrals.

Below is given the H-matrix (which is symmetric), referred to the basis of

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\*It will be noticed that the assumptions made by Pariser and Parr<sup>(4)</sup> in a recent semi-empirical MO theory, which at first sight seem unreasonably drastic, may now be simply interpreted: indeed, if the  $\overline{AO}$ 's are used in constructing a MO theory, our observations on the numerical values of the integrals encountered suggest immediately the very assumptions made by Pariser and Parr. The success of our scheme of neglecting all exchange integrals would thus simultaneously justify, in a non-empirical way, the general sufficiency of the framework developed by those writers (essentially an MO theory), at the same time providing a more satisfactory theoretical interpretation of the basic parameters appearing in their formulation as integrals over AO's.

Table 7-1

|                            | Coulomb Integrals |          |          | Hybrid and Exchange Integrals |          |          |          |          |
|----------------------------|-------------------|----------|----------|-------------------------------|----------|----------|----------|----------|
|                            | (aa, aa)          | (aa, bb) | (aa, cc) | (aa, ab)                      | (aa, bc) | (aa, bd) | (aa, ac) | (ab, ab) |
| Defined over AO's          | 16.931            | 9.023    | 6.781    | 3.314                         | 2.151    | 1.067    | 1.073    | 0.952    |
| Defined over $\bar{A}O$ 's | 17.537            | 8.790    | 6.526    | -0.079                        | 0.066    | 0.145    | 0.056    | 0.122    |

|                            | Coulomb Integrals |          |          | Hybrid and Exchange Integrals |          |          |          |          |
|----------------------------|-------------------|----------|----------|-------------------------------|----------|----------|----------|----------|
|                            | (aa, aa)          | (aa, bb) | (aa, cc) | (aa, ab)                      | (aa, bc) | (aa, cd) | (ab, ab) | (ab, bc) |
| Defined over AO's          | 16.930            | 9.027    | 5.668    | 3.313                         | 1.870    | 1.421    | 0.923    | 0.677    |
| Defined over $\bar{A}O$ 's | 17.618            | 8.900    | 5.574    | -0.114                        | -0.047   | 0.037    | 0.088    | 0.017    |

Hexagon

(A REVISED VALENCE BOND METHOD)

5  $A_{1g}$  singlet functions. The types of structure from which these functions are constructed are indicated by the labels on the rows and columns: n and p signify non-polar and polar structures, affixes 1 or 2 meaning singly or doubly polar and suffixes a or na meaning adjacent or non-adjacent charges.

Table 7-2

|            | n             | $p_a^1$                 | $p_{na}^1$                      | $p_a^2$                          | $p_a^2$                         |
|------------|---------------|-------------------------|---------------------------------|----------------------------------|---------------------------------|
| n          | $(Q - 0.244)$ | $2(\beta_{ab} + 0.058)$ | $2\sqrt{2}(\beta_{ac} + 0.284)$ | $2(0.039)$                       | $2\sqrt{2}(0.026)$              |
| $p_a^1$    |               | $(Q + 9.063)$           | $-\sqrt{2}(0.280)$              | $2(\beta_{ab} + 0.058)$          | $2\sqrt{2}(\beta_{ab} + 0.058)$ |
| $p_{na}^1$ |               |                         | $(Q + 10.895)$                  | $-2\sqrt{2}(\beta_{ac} + 0.284)$ | 0                               |
| $p_a^2$    |               |                         |                                 | $(Q + 21.842)$                   | $2\sqrt{2}(0.122)$              |
| $p_a^2$    |               |                         |                                 |                                  | $(Q + 15.166)$                  |

The  $Q$  appearing along the diagonal is appropriate to a non-polar configuration, the much higher energy  $Q$ -terms for the polar structures being expressed as  $Q$  plus the increase in Coulomb repulsion energy accompanying the charge transfer; thus, for an adjacent charge structure the  $Q$ -term is  $Q_a(bb) = Q + (aa, aa) - (aa, bb) = Q + 17.537 - 8.790$ . The difference between this value and the diagonal element shown arises from the small exchange terms which come along with  $Q_a(bb)$ . The only other large elements are those containing the  $\beta$ 's (Craig uses  $\beta_{ab} = -2.857$ ,  $\beta_{ac} = -0.355$ ) these arising between those structure-combinations which contain members differing by a shift of one charge. It is convenient to refer all energies to  $Q$  as zero, writing  $x = E - Q$ , and with this notation the eigenvalue equation is  $(H)(c) = x(S)(c)$ , where, in this instance (with normalized orthogonal combinations),  $(S)$  is the unit matrix. Numerical values of the elements of  $(H)$  are given below with and without the exchange terms; and it is obvious that the general pattern of the secular problem is not dependent on their inclusion.

Table 7-3

|     |         |         |         |         |          |          |          |          |          |
|-----|---------|---------|---------|---------|----------|----------|----------|----------|----------|
| $0$ | $-5.72$ | $-1.02$ | $0$     | $0$     | $-0.244$ | $-5.598$ | $-0.201$ | $0.078$  | $0.074$  |
|     | $8.75$  | $0$     | $-5.72$ | $-8.09$ |          | $9.063$  | $-0.396$ | $-5.598$ | $-7.917$ |
|     |         | $11.01$ | $1.02$  | $0$     |          |          | $10.895$ | $0.201$  | $0$      |
|     |         |         | $21.98$ | $0$     |          |          |          | $21.842$ | $0.345$  |
|     |         |         |         | $15.24$ |          |          |          |          | $15.166$ |

Approximate

Accurate

## (A REVISED VALENCE BOND METHOD)

Calculations have been carried out for the lowest singlet states of symmetry  $A_{1g}$  and  $B_{2g}$  and for the lowest triplet of symmetry  $A_{2g}$ . The approximate eigenvectors and energies (relative to Q) are shown below.

Table 7-4

| $^1A_{1g}$  |  | n     | $p_a^1$ | $p_{na}^1$ | $p_a^2$ | $p_a^2$ |              |
|-------------|--|-------|---------|------------|---------|---------|--------------|
| Accurate    |  | 0.806 | 0.537   | 0.051      | 0.111   | 0.219   | $x = -3.871$ |
| Approximate |  | 0.802 | 0.538   | 0.051      | 0.120   | 0.224   | $x = -4.06$  |

| $^1B_{2g}$  |  | n     | $p_a^1$ | $p_a^2$ |              |
|-------------|--|-------|---------|---------|--------------|
| Accurate    |  | 0.821 | 0.563   | 0.099   | $x = -6.426$ |
| Approximate |  | 0.822 | 0.557   | 0.118   | $x = -6.72$  |

| $^3A_{2g}$  |  | n     | $p_a^1$ | $p_{na}^1$ |              |
|-------------|--|-------|---------|------------|--------------|
| Accurate    |  | 0.776 | 0.576   | 0.274      | $x = -5.915$ |
| Approximate |  | 0.773 | 0.574   | 0.273      | $x = -6.00$  |

The most striking conclusion to be drawn from these results is that the exchange integrals do, indeed, have no very great effect on our predictions. If this is generally valid (and calculations on benzene so far provide no evidence to the contrary) an immediate simplification of the whole problem can be effected: for, ignoring from the start the many small exchange terms, matrix elements vanish for all pairs of structures which correspond to more than one charge shift. And, for normalized structures, the non-vanishing elements are given by the extremely simple rules

Table 7-5

| $\psi_1, \psi_2$        | Non-polars    | Similarly charged polars, $a^+ b^-$ | Non-polar with polar $a^+ b^-$        | Polar $a^+ b^-$ with $a^+ c^-$ | Polar $a^- b^+$ with $a^- c^+$  |
|-------------------------|---------------|-------------------------------------|---------------------------------------|--------------------------------|---------------------------------|
| $(\psi_1   H   \psi_2)$ | $2^{n-n_0} Q$ | $2^{n-n_0} Q_a (bb)$                | $\sqrt{2} \cdot 2^{n-n_0} \beta_{ab}$ | $2 \cdot 2^{n-n_0} \beta_{bc}$ | $-2 \cdot 2^{n-n_0} \beta_{bc}$ |

(A REVISED VALENCE BOND METHOD)

where  $n$  is the number of cycles in the diagram for  $\psi_1$  and  $\psi_2$  (and is easily visualized as the number of "islands" arising from superposition of their link patterns) and  $n_0$  is the total number of links in any structure ( $= N/2$ ); these results are, as usual, to be prefixed by  $-1$  if spin-matching involves an odd number of arrow reversals. Thus, in this approximation, all the matrix elements can be written down immediately, with no formal analysis whatever.

There is only one disconcerting feature in the results so far: the doubly-polar structures -- which lie between 20 and 30 e. v. above the ground state -- are clearly of considerable importance, and even if they are dealt with by the approximate method (i. e., exchange integrals neglected) the dimensions of the problem become, more generally, depressingly large. First, however, we shall ask how good an approximation can be constructed from non-polar and adjacent-charge singly-polar structures alone; and we shall see how successful a function is provided by the conventional VB structures -- which can be expanded in terms of  $\overline{\text{VB}}$  structures<sup>(1)</sup> to give an approximate eigenvector in the  $\overline{\text{VB}}$  basis. These results are summarized below.

Table 7-6

|                       |   |        |       |        | Accurate     | One configuration MO |       |
|-----------------------|---|--------|-------|--------|--------------|----------------------|-------|
| <u>A<sub>1g</sub></u> |   |        |       |        |              |                      |       |
|                       | Best $\overline{\text{VB}}$ combination | (0.905 | 0.424 | 0 0 0) | $x = -2.870$ | -3.871               | -0.77 |
|                       | Expanded VB function                    | (0.968 | 0.257 | 0 0 0) | $x = -2.380$ |                      |       |
| <u>B<sub>2g</sub></u> |   |        |       |        |              |                      |       |
|                       | Best $\overline{\text{VB}}$ combination | (0.837 | 0.547 | 0)     | $x = -6.134$ | -6.426               | -4.20 |
|                       | Expanded VB function                    | (0.912 | 0.410 | 0)     | $x = -5.621$ |                      |       |
| <u>A<sub>2g</sub></u> |   |        |       |        |              |                      |       |
|                       | Best $\overline{\text{VB}}$ combination | (0.862 | 0.508 | 0)     | $x = -4.773$ | -5.915               | -4.25 |
|                       | Expanded VB function                    | (0.932 | 0.363 | 0)     | $x = -4.312$ |                      |       |

The energy estimates given in the last two columns are included for comparison. These results prompt two concluding remarks: (1) The VB structures of conventional theory (i. e., defined over the overlapping AO's) may be useful in constructing quite good approximate wave functions by direct expansion into the more convenient  $\overline{\text{VB}}$  structures. In the present case there is only one VB combination of each symmetry, so no variational calculation is required: more generally the permissible VB combinations define a subspace in the space of  $\overline{\text{VB}}$  structures and best weights may be

(A REVISED VALENCE BOND METHOD)

found by a relatively trivial eigenvalue calculation. In any event, the approximate VB function may then be refined by an eigenvalue calculation in the full basis, when this is practicable. (2) Even the crude VB approximation may be considerably more accurate than the one-configuration MO approximation, particularly for the strongly bound states. Bearing in mind the example of the hydrogen molecule, this is not altogether unexpected; it appears that the gross overweighting of the multiply polar structures, in MO calculations, is more damaging to the wave function than their complete neglect (which is a feature of the present method in its most abbreviated form).

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R. McWeeny

## 8. LIMITED CONFIGURATION INTERACTION TREATMENT OF THE NH<sub>3</sub> MOLECULE

The numerical evaluation of all necessary integrals for the observed internuclear separations (OIS) and for the planar model is still underway. In the latter case it is assumed that as the nitrogen atom oscillates from one side of the hydrogen plane to the other the N-H distance remains constant. Experimental results indicate that this assumption is quite near the truth. Computationally this assumption leads to desirable duplication of many radial integrals with the OIS case.

H. Kaplan

## 9. CONFIGURATION INTERACTION APPLIED TO THE HYDROGEN MOLECULE

Calculations on this problem are being completed. The work is now being written up as a thesis.

E. Callen

## 10. THE WATER MOLECULE

Since the last Quarterly Progress Report, we have obtained and checked the expansion for the charge density of the hydrogen  $1s$  wave function (orthogonalized to the oxygen wave functions) about the oxygen nucleus. The integrals which had already been computed were extensively checked upon discovery of small errors in some of the basic functions. These errors either proved to have negligible effect on the final result or have now been corrected. Work on the remaining integrals is continuing as fast as our allotted time on the I. B. M. machines permits.

G. F. Koster and H. C. Schweinler

## 11. MECHANIZATION OF MOLECULAR ORBITAL DETERMINATION

The machine is almost ready for production runs on the self-consistent determination of linear combinations of orbitals. There remains only the problem of convergence which will be investigated empirically. The way the program is now set up, the machine begins with a first guess to the density matrix, forms the one-electron effective Hamiltonian matrix, diagonalizes it, constructs a new density matrix from the eigenvectors, computes the total energy of the system. The new density matrix is then fed back in, unmodified, to begin a new cycle if the new and old total energies do not agree to sufficient accuracy. In the case of the Hartree-Fock differential equations straight feeding back of the newly computed potential often leads to a divergent calculation. There is a good possibility that our situation is more stable. Differential equations correspond to infinite matricial equations, infinite and continuous; we deal with discrete, finite matrices. Explicitly, all the density matrices of the iteration scheme, those before and after, differ only by unitary transformations; the same Hamilton-Cayley equation is satisfied by all. There is therefore a certain boundedness to our region of computation. With the high-speed machine we need not worry too much about slow convergence but only about out-and-out divergence. Suspecting that divergence is impossible we will nevertheless try to force it. If there is no divergence we will learn about the rate of convergence.

We will take Löwdin's<sup>(1)</sup> exponential fit to the self-consistent Helium 1s function, concoct some 1s-like function orthogonal to it, and attempt to mix the two. The initial density matrix should be diagonal -- to the accuracy of Hartree and Löwdin. Insertion of outlandishly wrong first guesses will yield an empirical study of convergence.

### Reference

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A. Meckler

## 12. ANTIFERROMAGNETISM

In the previous Progress Report the details of the solution to a three-center spin coupling problem were given. An attempt has been made to generalize the results of this problem to a larger system of alternating magnetic and non-magnetic atoms in a chain or ring. If such a system is investigated by the methods of configuration interaction, the number of excited configurations becomes very large even for the simplest model and this would lead to unmanageable secular equations. Therefore, it was hoped that the complications inherent in the rigorous treatment might be avoided by using the results of the three-center problem and treating each magnetic center in the chain in the same way and each non-magnetic center in the same way.

The following procedure was used with these ideas in mind. The superexchange configurations of Kramers are the basis of the spin coupling in the three-center problem. Let this system be taken as  $A_1-B-A_2$  where the A centers represent paramagnetic ions and have one electron associated with each center in the ground configuration, and the B center represents a non-magnetic ion having two electrons associated with it in the same orbital in the ground state. Then the superexchange configurations are those in which one and finally both electrons are transferred from the non-magnetic ion to the magnetic ions. The superexchange treatment might be approximated by a single configuration if a compound orbital

$$B = b + C(A_1 + A_2)$$

is set up to describe the electrons on the non-magnetic center, this orbital being kept doubly filled. The orbitals  $b$ ,  $A_1$ , and  $A_2$  are orthonormal and associated with the various centers as indicated. The constant  $C$  is to be determined by minimizing the energy. The singlet and triplet states of the three-center system are given as

$$\psi = \text{const.} \left\{ A_1\alpha B\alpha B\beta A_2\beta \pm A_1\beta B\alpha B\beta A_2\alpha \right\} \quad (12.1)$$

If one expands out the B orbitals, a certain amount of cancellation comes about due to the Pauli principle. The net result is that the B functions reduce to polarized orbitals of the type  $b + CA_1$  and  $b + CA_2$  directed towards the  $A_1$  and  $A_2$  centers respectively. The singlet state given above is essentially the result of forming a covalent bond between  $A_1$  and the polarized function  $b + CA_1$ , and a covalent bond between  $A_2$  and the polarized orbital directed toward that center. This type of approach could easily be extended to a chain or ring and would lead to just one configuration, that in which each A orbital is singly occupied and each B function doubly filled.

Although this type of approach is appealing it has a serious fault which is of interest. If the singlet and triplet states given in (12.1) are expanded, we obtain

(ANTIFERROMAGNETISM)

$$\psi(S=0) = \text{const.} \{ \phi_0 + C\phi_1 + 2C^2\phi_2 \} \quad (12.2a)$$

$$\psi(S=1) = \text{const.} \{ \psi_0 + C\phi_1 \} \quad (12.2b)$$

where in (12.2a)  $\phi_0$ ,  $\phi_1$ , and  $\phi_2$  represent the singlets corresponding to the initial, singly excited, and doubly excited configurations respectively. In 12.2b)  $\psi_0$  and  $\phi_1$  represent the triplet states for the initial and singly excited configurations.

In the configuration interaction calculation using orthogonal orbitals and handled in the usual way, there would be two independent constants in the final singlet and one independent constant in the triplet. This approximate treatment, which has only one independent constant as shown in (12.2a) and (12.2b), can handle the triplet case exactly but not the singlet case. If the constant C turned out to be small and if the singlet energy were not very sensitive to the amount of the doubly excited configuration admixed, within reasonable limits, then the approximate method might be expected to work. Unfortunately, however, the energy difference between the singlet and triplet states depends critically on the weight given the doubly excited configuration. This can be shown graphically as follows. Let the triplet state as found by configuration interaction be

$$\psi(S=1) = \text{const.} \{ \phi_0 + d_1\phi_1 \} \quad (12.3)$$

and let the singlet state be

$$\psi(S=0) = \text{const.} \{ \phi_0 + c_1\phi_1 + c_2\phi_2 \} \quad (12.4)$$

Now we can plot the singlet energy as a function of  $|c_2|^2$  meaning that for a given value of  $|c_2|^2$  we find the best singlet energy or best value of  $c_1$  by the variation method. This is shown in Fig. 12-1 where the triplet energy, which is independent of the weight given the doubly excited configuration, is also plotted. The fact that the singlet must lie above the triplet for  $|c_2|^2 = 0$  was discussed in the last Progress Report. It is assumed that we are trying to describe a system in which the singlet does lie below the triplet for some value of  $|c_2|^2$ .

The importance of highly excited configurations, when a system is described in terms of orthogonal orbitals, was first shown by Slater in his analysis of the hydrogen molecule.<sup>(1)</sup> The same sort of situation is encountered here in that the type of spin coupling predicted is directly connected to the role played by the highest excited state of this system as shown in Fig. 1. The singlet obtained from the approximate approach in (12.2a) is of the form that the weight given the doubly excited configuration is directly dependent on the weight given the singly excited state. Therefore, the best

(ANTIFERROMAGNETISM)

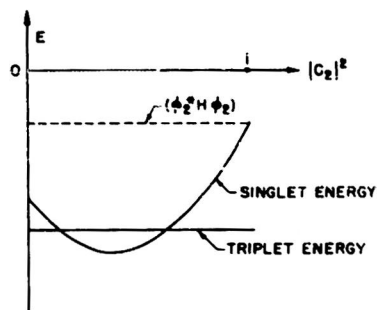


Fig. 12-1

value of  $C$  obtained from the variational method may weight the doubly excited configuration in such a manner that the best singlet will lie above the triplet. The calculation was carried out for the problem described in the last Progress Report and the singlet was found to be of higher energy than the triplet contrary to the actual state of affairs. In view of the generally unfavorable nature of the above approximate method it seems of no value to carry it further.

Kramers<sup>(2)</sup> devised a method of handling the configuration interaction problem in which the excited configurations of the system are treated as a perturbation on the ground configuration. The unperturbed ground states consist of the  $2^N$  single determinants which differ in the spin assignments to the  $N$  singly occupied orbitals of the ground configuration. The eigenstates of the system are found by diagonalizing an effective Hamiltonian but only with respect to the unperturbed ground states. The secular problem can be written<sup>(3)</sup>

$$\sum_{n=1}^{2N} (U_{mn} - E\delta_{mn}) C_n = 0, \quad (12.5)$$

and where  $U_{mn}$  is the effective Hamiltonian

$$U_{mn} = H_{mn} + \sum_a \frac{H_{ma} H_{an}}{E - H_{aa}} + \sum_{a \neq \beta} \frac{H_{ma} H_{a\beta} H_{\beta n}}{(E - H_{aa})(E - H_{\beta\beta})} + \dots \quad (12.6)$$

and  $\alpha, \beta$ , etc. refer to the excited states of the system. The spin coupling between the non-overlapping magnetic atoms first appears in the third order term.

As pointed out above it appears to be a rather general property of orthogonal orbitals that when they are used to describe a system one must take into consideration highly excited states in order that the results have any meaning at all. The third order term in the effective Hamiltonian

$$\sum_{a \neq \beta} \frac{H_{ma} H_{a\beta} H_{\beta n}}{(E - H_{aa})(E - H_{\beta\beta})} \quad (12.7)$$

can only connect the ground configuration with a doubly excited configuration at most. Therefore, it seems unlikely that one can obtain reliable results if the higher order terms in the effective Hamiltonian are neglected.

This method is easily applied to the three-center system  $A_1 - B - A_2$ . The

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two unperturbed ground states are

$$t_1 = |A_1\alpha\ b\alpha\ b\beta\ A_2\beta|, \quad t_2 = |A_1\beta\ b\alpha\ b\beta\ A_2\alpha| \quad (12.8)$$

and  $U_{t_1 t_2}$  is

$$U_{t_1 t_2} = -\frac{2d^2(J+g)}{(E-E_1)^2} - \frac{4dhg}{(E-E_1)(E-E_2)} \quad (12.9)$$

where

$$\begin{aligned} d &= (A_1|b) + (A_1b|A_1A_1) + (bb|bA_1) + (bA_2|A_1A_2) \\ J &= (bA_1|A_1b) > 0 \\ g &= (bA_1|A_2b) \\ h &= (b|A_1) + 2(A_1b|A_1A_2) + (bA_2|A_2A_2) \end{aligned} \quad (12.10)$$

the orbitals  $A_1$ ,  $b$ , and  $A_2$  being orthonormal.  $E_1$  and  $E_2$  are the energies of the states where one and two electrons respectively have been transferred to a magnetic atom from a non-magnetic center. The first term in  $U_{t_1 t_2}$  is  $< 0$ , then the triplet lies below the singlet. Considering only the first term we see that it is negative definite since  $J$  is always greater than  $g$ . This is in accord with the fact that in a treatment of the three-center system which excludes the doubly excited configuration the singlet cannot lie below the triplet regardless of what orthogonal orbitals are used.

The second term in (12.9) must be large enough to reverse the sign of  $U_{t_1 t_2}$  if the third order theory is to be adequate to describe a three-center problem where the singlet does lie below the triplet. In order for the second term to make this change the following inequality must be satisfied

$$|h| > \left| d \left( \frac{J+g}{2g} \right) \left( \frac{E-E_2}{E-E_1} \right) \right| \quad (12.11)$$

Since  $g$  is often quite small the inequality may not hold and one would be forced to carry higher terms in the effective Hamiltonian even for this three-center problem.

The perturbation treatment of superexchange has been applied by Shimizu<sup>(4)</sup> to a 3N electron system but restricted to singly excited configurations only. When one uses the fact that exchange integrals are never negative when expressed in terms of orthogonal orbitals (upon which this whole approach is based), and if it is assumed

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that intra-atomic exchange integrals are in general greater than inter-atomic exchange integrals, then Shimizu's results show a ferromagnetic spin coupling. This result also seems to show the need for including more highly excited states in the theory. Once these states are admitted the spin coupling will not only be of nearest neighbor type but will include next and even more distant neighbor interactions. Also there will be terms connecting the unperturbed states which differ by more than the interchange of a single pair of spins. If the perturbation method is not rapidly convergent, these new terms may well play an important role.

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G. W. Pratt, Jr.

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### 13. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

Further investigation into the suitability of the one-electron function,

$$\psi = \psi_0(1 + Cr^\nu \cos \theta) \quad (13.1)$$

for describing polarization effects has been made. As indicated in a previous Progress Report, <sup>(1)</sup> Slater and Kirkwood <sup>(2)</sup> have used  $\psi$

$$\psi = e^{-r} \left[ 1 + C \left( r + \frac{r^2}{r} \right) \cos \theta \right]$$

for the ground state of the hydrogen atom in a uniform field and (13.1) was shown to be equivalent to this in that they both gave the correct value for the polarizability. Hasse <sup>(3)</sup> also made very accurate calculations of the polarizability with the function

$$\psi = \psi_0 \left[ 1 + (C_1 r + C_2 r^2) \cos \theta \right]$$

for the lowest states of H and He. The problem of the H atom in a uniform field has been solved exactly by Epstein <sup>(4)</sup> in parabolic coordinates. Writing his first order functions in spherical coordinates yields a dependence

$$\psi = \psi_0 \left[ 1 + CR(r) \cos \theta \right]$$

for the excited states as well as the ground state. (R(r) is a polynomial in r for which the highest power is 2 for states through 2p.) Buckingham <sup>(5)</sup> has obtained good results for several closed shell atoms using the form (13.1) with  $\nu = 1$  for all one-electron functions.

For our  $\bar{F}^-$  calculation mentioned in the previous Progress Report we are thus led to the following ten orthonormal one-electron functions:

$$\psi_1 = N_1 e^{-8.75r} (1 + A_1 r^\nu \cos \theta) \alpha$$

$$\psi_2 = N_1 e^{-8.75r} (1 + A_1 r^\nu \cos \theta) \beta$$

$$\psi_3 = N_2 (r e^{-2.50r} - C_1 e^{-7.48r}) (1 + A_2 r^\nu \cos \theta) \alpha$$

$$\psi_4 = N_2 (r e^{-2.50r} - C_1 e^{-7.48r}) (1 + A_2 r^\nu \cos \theta) \beta$$

$$\psi_5 = N_3 (r e^{-2.35r} \sin \theta e^{i\phi}) (1 + A_3 r^\nu \cos \theta) \alpha$$

$$\psi_6 = N_3 (r e^{-2.35r} \sin \theta e^{i\phi}) (1 + A_3 r^\nu \cos \theta) \beta$$

(NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE)

$$\psi_7 = N_3(re^{-2.35r} \sin \theta e^{-i\phi})(1 + A_3 r^{\nu 3} \cos \theta) \alpha$$

$$\psi_8 = N_3(re^{-2.35r} \sin \theta e^{-i\phi})(1 + A_3 r^{\nu 3} \cos \theta) \beta$$

$$\psi_9 = N_4(re^{-2.35r} - C_2 re^{-2.50r} - C_3 e^{-8.75r}) \cos \theta (1 + A_4 r^{\nu 4} \cos \theta) \alpha$$

$$\psi_{10} = N_4(re^{-2.35r} - C_2 re^{-2.50r} - C_3 e^{-8.75r}) \cos \theta (1 + A_4 r^{\nu 4} \cos \theta) \beta$$

where the N's represent normalization factors. For the  $\psi_0$ 's we have used the functions given by Morse, Young, and Haurwitz<sup>(6)</sup> which have slightly better values for the constants appearing in the exponents than those given by Slater's shielding constants.<sup>(7)</sup> The above functions have been formed into a single determinant and an energy and polarizability calculation is being made using the following Hamiltonian:

$$H = - \sum_i \nabla_i^2 - \sum_i \frac{2z}{r_i} + \sum_{i>j} \frac{2}{r_{ij}} + \mathcal{O} \sum_i r_i \cos \theta_i$$

The A's and  $\nu$ 's are treated as variation parameters and orthogonality is maintained with  $C_1$ ,  $C_2$ , and  $C_3$ . The integrals for the angular parts are obtained using Condon and Shortley's  $C^k(l m_l, l' m_l')$ .<sup>(8)</sup> The integrals involving functions of  $r$  are being calculated by methods applied in a previous Progress Report<sup>(1)</sup> and by use of the  $k L^{n_i n_j}$  functions developed by Schrieffer.<sup>(9)</sup>

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L. C. Allen

#### 14. SCATTERING OF SLOW NEUTRONS BY O<sub>2</sub>

The calculation mentioned in the last Report is still in progress. We present here an outline of some of the results so far obtained.

We are concerned here only with a neutron's spin-spin magnetic interaction with the molecule, so that effectively the neutron interacts only with the electrons of unpaired spin. There are two of these, since the ground electronic level of O<sub>2</sub> is a triplet. The charge distribution of the electrons of unpaired spin has the same symmetry as the total electronic charge, and may be regarded as cylindrically symmetrical and fixed relative to the internuclear axis, since for slow neutron scattering the molecule remains in its ground electronic level.

Of particular interest is the effect on the cross section of the molecular rotation. It is instructive to view the problem classically, although the calculation is quantum mechanical. If there were no rotation, the scattering cross section would be given (in appropriate units) by the magnitude squared of

$$f(\vec{k}) = \int e^{i\vec{k} \cdot \vec{r}} \rho(\vec{r}) d\tau$$

where the integration is over all space;  $\vec{k}$  is the scattering vector, the difference between the wave vectors of the incident and scattered neutrons.  $\rho(\vec{r})$ , the density of electrons of unpaired spin<sup>(1)</sup> of the molecule, depends on the orientation of the molecule. We consider now two limiting cases of the scattering from a rotating molecule depending on the ratio  $\alpha$  of the time of transit of the neutron across the molecule to the period of molecular rotation. For  $\alpha \ll 1$ <sup>(2)</sup> each neutron sees an instantaneous picture of the molecule, so that the cross section is given by averaging  $|f|^2$  over all orientations of the molecule. This limiting case corresponds to neutrons of high energy. For  $\alpha \gg 1$ , corresponding to very slow neutrons, each neutron sees the same smeared out charge distribution given by averaging  $\rho$  over all orientations, and the cross section is given by squaring the corresponding  $f$ . In brief, the cross sections are given in the two limiting cases  $\alpha \ll 1$  and  $\alpha \gg 1$  by  $\langle |f|^2 \rangle$  and  $|\langle f \rangle|^2$ , respectively. The general quantum mechanical expression for the cross section reduces to the above expressions for molecules initially in  $J = 0$  rotational levels.

Under experimental conditions  $\alpha$  does not approach closely either limiting case, so that an investigation of the scattering for the intermediate range of  $\alpha$  is in order. An estimate of the rotational period may be obtained by equating the mean rotational energy of O<sub>2</sub> to  $kT$ . For molecules at room temperature and incident neutrons of wave length 5 A.,  $\alpha$  is about 1/4.

A general quantum mechanical expression for the cross section which takes account of the rotational effects has been obtained in terms of a number of integrals over angle involving  $f$ . The evaluation of these integrals is continuing.

(SCATTERING OF SLOW NEUTRONS BY O<sub>2</sub>)

References

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W. H. Kleiner

## 15. TRANSITION PROBABILITIES FOR X-RAY EMISSION IN THE TRANSITION METALS

In the previous Progress Report we set up the 4s wave function as an orthogonalized plane wave, which is by definition a plane wave made orthogonal to the ion-core Bloch wave functions by the Schmidt orthogonalization method. The OPW corresponding to the 4s crystal wave function is

$$x(\vec{r}) = e^{i\vec{k}_i \cdot \vec{r}} - \sum_j \mu_j \psi_j(\vec{r})$$

$$\mu_j = \frac{\int e^{i\vec{k}_i \cdot \vec{r}} \phi_j^*(\vec{r}) d\tau}{\int \phi_j^*(\vec{r}) \phi_j(\vec{r}) d\tau}$$

The coefficients  $\mu_j$  involve the Fourier transform of the Hartree atomic wave functions  $\phi_j(\vec{r})$ . These are now being calculated by expanding the plane wave in terms of spherical waves and carrying through the integrations.

A. J. Freeman

## 16. DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS

Most problems involving one or more centers of force, as for example molecular or crystal problems, are simplified by the introduction of spherical harmonics. These functions form a complete set for the surface of a sphere, and so any function of the type likely to be met in physics can be expanded in terms of them. In particular, the product of two or more spherical harmonics is so expansible. The expansion coefficients are certain integrals which are simple in principle but exceedingly tedious to perform. In practice, operator methods can be devised which depend on the "upward shift" and "downward shift" operators  $L^+$  and  $L^-$ , to be defined below, together with the decomposition of simple products. Strictly speaking, the only product which needs to be defined is that of the general harmonic with the three harmonics of degree unity, for all higher products can be built on these as a basis, but it is sometimes convenient to have explicit expressions for some of the higher products. In the work below we give general expressions for all products involving harmonics of degree zero through three inclusive, and specific form to all products of combined degree not exceeding six.

It will be convenient to use functions of norm  $4\pi$ , i. e. ,

$$\int e_{lm} \overline{e_{l'm}}, d\Omega = 4\pi \delta_{ll'} \delta_{mm'}$$

The relationship between partners of the same degree is given with the Dirac phase convention

$$L^+ e_{lm} = (L_x + iL_y) e_{lm} = e^{i\phi} \left\{ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right\} e_{lm} = \sqrt{(l-m)(l+m+1)} e_{l, m+1}$$

$$L^- e_{lm} = (L_x - iL_y) e_{lm} = e^{-i\phi} \left\{ -\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right\} e_{lm} = \sqrt{(l+m)(l-m+1)} e_{l, m-1}$$

These lead to the general relationship  $e_{l, -m} = (-1)^m \overline{e_{lm}}$ , which can be used to eliminate about half of all possible products. It is easy to show that an explicit form for these functions is

$$e_{lm} = \sqrt{\frac{(2l+1)(l-m)!}{(l+m)!}} P_l^{(m)}(\mu) \cdot (-\sin \theta e^{i\phi})^m \quad m \geq 0$$

$$e_{l-m} = \sqrt{\frac{(2l+1)(l-m)!}{(l+m)!}} P_l^{(m)}(\mu) \cdot (\sin \theta e^{-i\phi})^m \quad m \geq 0$$

where  $P_l^{(m)}(\mu)$  is the  $m^{\text{th}}$  derivative of the  $l^{\text{th}}$  Legendre function  $P_l(\mu)$  with respect to its argument  $\mu = \cos \theta$ . As special cases we have

(DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

$$e_{00} = 1$$

$$e_{l0} = \sqrt{2l+1} P_l(\cos \theta)$$

$$e_{ll} = \frac{\sqrt{(2l+1)!}}{2^l l!} (-\sin \theta e^{i\phi})^l$$

The expressions which follow were derived in at least two of the following ways:

(1) successive synthetic division of

$$e_{lm} e_{l'm'} = \sum_{p=0}^{\min(l, l')} c_p e_{l+l'-2p, m+m'}$$

by  $e_{l+l'-2p, m+m'}$  to determine the coefficients  $c_p$ .

(2) expansion of  $e_{ll} e_{l'l'}$  as above, followed by successive application of  $L^-$  to produce  $e_{lm} e_{l'm'}$  and then of  $L^+$  to produce simple algebraic equations easily solvable chainwise for  $e_{lm} e_{l'm'}$ ,  $e_{lm} e_{l'm'+1}$ ,  $e_{lm} e_{l'm'+2}$ , ...

(3) repeated multiplication by the harmonics of low degree, as illustrated by the following example (for degree unity): from  $e_{l'l'} = \mathcal{C}_{l'} (e_{11})^{l'}$  we get upon operation with  $(L^-)^{l'-m'}$  a homogeneous polynomial of degree  $l'$  in  $e_{11}$ ,  $e_{10}$ ,  $e_{1-1}$  for  $e_{l'm'}$ . The product  $e_{lm} e_{l'm'}$  can then be formed by successive application of the associative law of multiplication in such a way that one factor is always a harmonic of degree one.

The expressions were checked with the aid of certain summation formulas such as

$$\sum_{m=-l}^l e_{lm} \overline{e_{lm}} = 2l+1.$$

General Formulas

$$e_{lm} e_{00} = e_{lm}$$

$$e_{lm} e_{1-1} = \sqrt{\frac{3}{2(2l+1)(2l+3)} \frac{(l-m+2)!}{(l-m)!}} e_{l+1, m-1} - \sqrt{\frac{3}{2(2l-1)(2l+1)} \frac{(l+m)!}{(l+m-2)!}} e_{l-1, m-1}$$

$$e_{lm} e_{10} = \sqrt{\frac{3}{(2l+1)(2l+3)} \frac{(l+m+1)(l-m+1)}{1}} e_{l+1, m} + \sqrt{\frac{3}{(2l-1)(2l+1)} \frac{(l+m)(l-m)}{1}} e_{l-1, m}$$

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$$e_{lm}e_{2-2} = \frac{1}{2(2l+3)} \sqrt{\frac{3 \cdot 5}{2(2l+1)(2l+5)} \frac{(l-m+4)!}{(l-m)!}} e_{l+2, m-2}$$

$$- \frac{1}{(2l-1)(2l+3)} \sqrt{\frac{3 \cdot 5 (l+m)! (l-m+2)!}{2(l+m-2)! (l-m)!}} e_{l, m-2}$$

$$+ \frac{1}{2(2l-1)} \sqrt{\frac{3 \cdot 5}{2(2l-3)(2l+1)} \frac{(l+m)!}{(l+m-4)!}} e_{l-2, m-2}$$

$$e_{lm}e_{2-1} = \frac{1}{2l+3} \sqrt{\frac{3 \cdot 5}{2(2l+1)(2l+5)} \frac{(l+m+1) (l-m+3)!}{1 (l-m)!}} e_{l+2, m-1}$$

$$- \frac{2m-1}{(2l-1)(2l+3)} \sqrt{\frac{3 \cdot 5}{2} \frac{(l+m)(l-m+1)}{1}} e_{l, m-1}$$

$$- \frac{1}{(2l-1)} \sqrt{\frac{3 \cdot 5}{2(2l-3)(2l+1)} \frac{(l+m)! (l-m)}{(l+m-3)! 1}} e_{l-2, m-1}$$

$$e_{lm}e_{20} = \frac{3}{2(2l+3)} \sqrt{\frac{5}{(2l+1)(2l+5)} \frac{(l+m+2)! (l-m+2)!}{(l+m)! (l-m)!}} e_{l+2, m}$$

$$+ \frac{l(l+1) - 3m^2}{(2l-1)(2l+3)} \sqrt{5} e_{lm}$$

$$+ \frac{3}{2(2l-1)} \sqrt{\frac{5}{(2l-3)(2l+1)} \frac{(l+m)! (l-m)!}{(l+m-2)! (l-m-2)!}} e_{l-2, m}$$

$$e_{lm}e_{3-3} = \frac{1}{4(2l+3)(2l+5)} \sqrt{\frac{5 \cdot 7}{(2l+1)(2l+7)} \frac{(l-m+6)!}{(l-m)!}} e_{l+3, m-3}$$

$$- \frac{3}{4(2l-1)(2l+5)} \sqrt{\frac{5 \cdot 7}{(2l+1)(2l+3)} \frac{(l+m)! (l-m+4)!}{(l+m-2)! (l-m)!}} e_{l+1, m-3}$$

$$+ \frac{3}{4(2l-3)(2l+3)} \sqrt{\frac{5 \cdot 7}{(2l-1)(2l+1)} \frac{(l+m)! (l-m+2)!}{(l+m-4)! (l-m)!}} e_{l-1, m-3}$$

$$- \frac{1}{4(2l-3)(2l-1)} \sqrt{\frac{5 \cdot 7}{(2l-5)(2l+1)} \frac{(l+m)!}{(l+m-6)!}} e_{l-3, m-3}$$

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$$\begin{aligned}
 e_{lm} e_{3-2} &= \frac{1}{4(2l+3)(2l+5)} \sqrt{\frac{2 \cdot 3 \cdot 5 \cdot 7}{(2l+1)(2l+7)} \frac{(l+m+1)(l-m+5)!}{1(l-m)!}} e_{l+3, m-2} \\
 &- \frac{l+3m-2}{4(2l-1)(2l+5)} \sqrt{\frac{2 \cdot 3 \cdot 5 \cdot 7}{(2l+1)(2l+3)} \frac{(l+m)(l-m+3)!}{1(l-m)!}} e_{l+1, m-2} \\
 &- \frac{l-3m+3}{4(2l-3)(2l+3)} \sqrt{\frac{2 \cdot 3 \cdot 5 \cdot 7}{(2l-1)(2l+1)} \frac{(l+m)!(l-m+1)}{1(l+m-3)!}} e_{l-1, m-2} \\
 &+ \frac{1}{4(2l-3)(2l-1)} \sqrt{\frac{2 \cdot 3 \cdot 5 \cdot 7}{(2l-5)(2l+1)} \frac{(l+m)!(l-m)}{1(l+m-5)!}} e_{l-3, m-2}
 \end{aligned}$$

$$\begin{aligned}
 e_{lm} e_{3-1} &= \frac{5}{4(2l+3)(2l+5)} \sqrt{\frac{3 \cdot 7}{(2l+1)(2l+7)} \frac{(l+m+2)!(l-m+4)!}{(l+m)!(l-m)!}} e_{l+3, m-1} \\
 &+ \frac{l^2 - 10lm - 15m^2 + 7l + 5m}{4(2l-1)(2l+5)} \sqrt{\frac{3 \cdot 7}{(2l+1)(2l+3)} \frac{(l-m+2)!}{(l-m)!}} e_{l+1, m-1} \\
 &- \frac{l^2 + 10lm - 15m^2 - 5l + 15m - 6}{4(2l-3)(2l+3)} \sqrt{\frac{3 \cdot 7}{(2l-1)(2l+1)} \frac{(l+m)!}{(l+m-2)!}} e_{l-1, m-1} \\
 &- \frac{5}{4(2l-3)(2l-1)} \sqrt{\frac{3 \cdot 7}{(2l-5)(2l+1)} \frac{(l+m)!(l-m)!}{(l+m-4)!(l-m-2)!}} e_{l-3, m-1}
 \end{aligned}$$

$$\begin{aligned}
 e_{lm} e_{30} &= \frac{5}{2(2l+3)(2l+5)} \sqrt{\frac{7}{(2l+1)(2l+7)} \frac{(l+m+3)!(l-m+3)!}{(l+m)!(l-m)!}} e_{l+3, m} \\
 &+ \frac{3[l(l+2) - 5m^2]}{2(2l-1)(2l+5)} \sqrt{\frac{7}{(2l+1)(2l+3)} \frac{(l+m+1)(l-m+1)}{1 \cdot 1}} e_{l+1, m} \\
 &+ \frac{3[(l+1)(l-1) - 5m^2]}{2(2l-3)(2l+3)} \sqrt{\frac{7}{(2l-1)(2l+1)} \frac{(l+m)(l-m)}{1 \cdot 1}} e_{l-1, m} \\
 &+ \frac{5}{2(2l-3)(2l-1)} \sqrt{\frac{7}{(2l-5)(2l+1)} \frac{(l+m)!(l-m)!}{(l+m-3)!(l-m-3)!}} e_{l-3, m}
 \end{aligned}$$

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Specific Formulas

$l + l' = 2$

$$e_{11}e_{11} = \sqrt{2 \cdot 3/5} e_{22}$$

$$e_{11}e_{10} = \sqrt{3/5} e_{21}$$

$$e_{11}e_{1-1} = \sqrt{1/5} e_{20} - e_{00}$$

$$e_{10}e_{10} = 2\sqrt{1/5} e_{20} + e_{00}$$

$l + l' = 3$

$$e_{22}e_{11} = 3\sqrt{1/7} e_{33}$$

$$e_{22}e_{10} = \sqrt{3/7} e_{32}$$

$$e_{22}e_{1-1} = \sqrt{3/5 \cdot 7} e_{30} - \sqrt{2 \cdot 3/5} e_{10}$$

$$e_{21}e_{11} = \sqrt{2 \cdot 3/7} e_{32}$$

$$e_{21}e_{10} = 2\sqrt{2 \cdot 3/5 \cdot 7} e_{31} + \sqrt{3/5} e_{11}$$

$$e_{21}e_{1-1} = 3\sqrt{1/5 \cdot 7} e_{30} - \sqrt{3/5} e_{10}$$

$$e_{20}e_{11} = 3\sqrt{2/5 \cdot 7} e_{31} - \sqrt{1/5} e_{11}$$

$$e_{20}e_{10} = 3\sqrt{3/5 \cdot 7} e_{30} + 2\sqrt{1/5} e_{10}$$

$l + l' = 4$

$$e_{33}e_{11} = 2\sqrt{1/3} e_{44}$$

$$e_{33}e_{10} = \sqrt{1/3} e_{43}$$

$$e_{33}e_{1-1} = \sqrt{1/3 \cdot 7} e_{42} - 3\sqrt{1/7} e_{22}$$

(DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

$l + l' = 4$  (con'd)

$$e_{32}e_{11} = 1 \cdot e_{43}$$

$$e_{32}e_{10} = 2\sqrt{1/7} e_{42} + \sqrt{3/7} e_{22}$$

$$e_{32}e_{1-1} = \sqrt{1/7} e_{41} - \sqrt{2 \cdot 3/7} e_{21}$$

$$e_{31}e_{11} = \sqrt{5/7} e_{42} - \sqrt{3/5 \cdot 7} e_{22}$$

$$e_{31}e_{10} = \sqrt{5/7} e_{41} + 2\sqrt{2 \cdot 3/5 \cdot 7} e_{21}$$

$$e_{31}e_{1-1} = \sqrt{2/7} e_{40} - 3\sqrt{2/5 \cdot 7} e_{20}$$

$$e_{30}e_{11} = \sqrt{2 \cdot 5/3 \cdot 7} e_{41} - 3\sqrt{1/5 \cdot 7} e_{21}$$

$$e_{30}e_{10} = 4\sqrt{1/3 \cdot 7} e_{40} + 3\sqrt{3/5 \cdot 7} e_{20}$$

$$e_{22}e_{22} = \sqrt{2 \cdot 5/7} e_{44}$$

$$e_{22}e_{21} = \sqrt{5/7} e_{43}$$

$$e_{22}e_{20} = (1/7)\sqrt{3 \cdot 5} e_{42} - (2/7)\sqrt{5} e_{22}$$

$$e_{22}e_{2-1} = (i/7)\sqrt{5} e_{41} - (1/7)\sqrt{2 \cdot 3 \cdot 5} e_{21}$$

$$e_{22}e_{2-2} = (1/7) e_{40} - (2/7)\sqrt{5} e_{20} + 1 e_{00}$$

$$e_{21}e_{21} = (2/7)\sqrt{2 \cdot 5} e_{42} + (1/7)\sqrt{2 \cdot 3 \cdot 5} e_{22}$$

$$e_{21}e_{20} = (1/7)\sqrt{2 \cdot 3 \cdot 5} e_{41} + (1/7)\sqrt{5} e_{21}$$

$$e_{21}e_{2-1} = (4/7) e_{40} - (1/7)\sqrt{5} e_{20} - 1 e_{00}$$

$$e_{20}e_{20} = (6/7) e_{40} + (2/7)\sqrt{5} e_{20} + 1 e_{00}$$

$l + l' = 5$

$$e_{44}e_{11} = \sqrt{3 \cdot 5/11} e_{55}$$

$$e_{44}e_{10} = \sqrt{3/11} e_{54}$$

$$e_{44}e_{1-1} = \sqrt{1/3 \cdot 11} e_{53} - 2\sqrt{1/3} e_{33}$$

(DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

$l + l' = 5$  (con'd)

$$e_{43}e_{11} = 2\sqrt{3/11} e_{54}$$

$$e_{43}e_{10} = 4\sqrt{1/3 \cdot 11} e_{53} + \sqrt{1/3} e_{33}$$

$$e_{43}e_{1-1} = \sqrt{1/11} e_{52} - 1 e_{32}$$

$$e_{42}e_{11} = 2\sqrt{7/3 \cdot 11} e_{53} - \sqrt{1/3 \cdot 7} e_{33}$$

$$e_{42}e_{10} = \sqrt{7/11} e_{52} + 2\sqrt{1/7} e_{32}$$

$$e_{42}e_{1-1} = \sqrt{2/11} e_{51} - \sqrt{5/7} e_{31}$$

$$e_{41}e_{11} = \sqrt{7/11} e_{52} - \sqrt{1/7} e_{32}$$

$$e_{41}e_{10} = 2\sqrt{2/11} e_{51} + \sqrt{5/7} e_{31}$$

$$e_{41}e_{1-1} = \sqrt{2 \cdot 5/3 \cdot 11} e_{50} - \sqrt{2 \cdot 5/3 \cdot 7} e_{30}$$

$$e_{40}e_{11} = \sqrt{5/11} e_{51} - \sqrt{2/7} e_{31}$$

$$e_{40}e_{10} = 5\sqrt{1/3 \cdot 11} e_{50} + 4\sqrt{1/3 \cdot 7} e_{30}$$

$$e_{33}e_{22} = 5\sqrt{2/3 \cdot 11} e_{55}$$

$$e_{33}e_{21} = 2\sqrt{5/3 \cdot 11} e_{54}$$

$$e_{33}e_{20} = (2/3)\sqrt{5/11} e_{53} - (1/3)\sqrt{5} e_{33}$$

$$e_{33}e_{2-1} = (1/3)\sqrt{5/11} e_{52} - (1/3)\sqrt{5} e_{32}$$

$$e_{33}e_{2-2} = (1/3)\sqrt{5/7 \cdot 11} e_{51} - (1/3)\sqrt{2} e_{31} + 3\sqrt{1/7} e_{11}$$

$$e_{32}e_{22} = \sqrt{2 \cdot 5/11} e_{54}$$

$$e_{32}e_{21} = (4/3)\sqrt{5/11} e_{53} + (1/3)\sqrt{5} e_{33}$$

$$e_{32}e_{20} = \sqrt{5/11} e_{52} + 0$$

$$e_{32}e_{2-1} = 2\sqrt{2 \cdot 5/3 \cdot 7 \cdot 11} e_{51} - \sqrt{1/3} e_{31} - \sqrt{2 \cdot 3/7} e_{11}$$

$$e_{32}e_{2-2} = (5/3)\sqrt{1/7 \cdot 11} e_{50} - (2/3) e_{30} + \sqrt{3/7} e_{10}$$

(DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

$l + l' = 5$  (con'd)

$$\begin{aligned}e_{31}e_{22} &= (5/3)\sqrt{2/11} e_{53} - (1/3)\sqrt{2} e_{33} \\e_{31}e_{21} &= (5/3)\sqrt{3/11} e_{52} + \sqrt{1/3} e_{32} \\e_{31}e_{20} &= 5\sqrt{2/7 \cdot 11} e_{51} + \sqrt{1/5} e_{31} + 3\sqrt{2/5 \cdot 7} e_{11} \\e_{31}e_{2-1} &= (5/3)\sqrt{2 \cdot 5/7 \cdot 11} e_{50} - (1/3)\sqrt{2/5} e_{30} - 2\sqrt{2 \cdot 3/5 \cdot 7} e_{10} \\e_{31}e_{2-2} &= 5\sqrt{1/3 \cdot 7 \cdot 11} e_{5-1} - 2\sqrt{2/3 \cdot 5} e_{3-1} + \sqrt{3/5 \cdot 7} e_{1-1} \\e_{30}e_{22} &= (5/3)\sqrt{1/11} e_{52} - (2/3) e_{32} \\e_{30}e_{21} &= (20/3)\sqrt{1/7 \cdot 11} e_{51} + (1/3)\sqrt{2/5} e_{31} - 3\sqrt{1/5 \cdot 7} e_{11} \\e_{30}e_{20} &= (10/3)\sqrt{5/7 \cdot 11} e_{50} + (4/3)\sqrt{1/5} e_{30} + 3\sqrt{3/5 \cdot 7} e_{10}\end{aligned}$$

$l + l' = 6$

$$\begin{aligned}e_{55}e_{11} &= 3\sqrt{2/13} e_{66} \\e_{55}e_{10} &= \sqrt{3/13} e_{65} \\e_{55}e_{1-1} &= \sqrt{3/11 \cdot 13} e_{64} - \sqrt{3 \cdot 5/11} e_{44} \\e_{54}e_{11} &= \sqrt{3 \cdot 5/13} e_{65} \\e_{54}e_{10} &= 2\sqrt{3 \cdot 5/11 \cdot 13} e_{64} + \sqrt{3/11} e_{44} \\e_{54}e_{1-1} &= 3\sqrt{1/11 \cdot 13} e_{63} - 2\sqrt{3/11} e_{43} \\e_{53}e_{11} &= 3\sqrt{3 \cdot 5/11 \cdot 13} e_{64} - \sqrt{1/3 \cdot 11} e_{44} \\e_{53}e_{10} &= 9\sqrt{1/11 \cdot 13} e_{63} + 4\sqrt{1/3 \cdot 11} e_{43} \\e_{53}e_{1-1} &= 3\sqrt{2/11 \cdot 13} e_{62} - 2\sqrt{7/3 \cdot 11} e_{42} \\e_{52}e_{11} &= 6\sqrt{3/11 \cdot 13} e_{63} - \sqrt{1/11} e_{43} \\e_{52}e_{10} &= 4\sqrt{2 \cdot 3/11 \cdot 13} e_{62} + \sqrt{7/11} e_{42}\end{aligned}$$

## (DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

 $l + l' = 6$  (cont'd)

$$e_{52}e_{1-1} = \sqrt{2 \cdot 3 \cdot 5/11 \cdot 13} e_{61} - \sqrt{7/11} e_{41}$$

$$e_{51}e_{11} = 2\sqrt{3 \cdot 7/11 \cdot 13} e_{62} - \sqrt{2/11} e_{42}$$

$$e_{51}e_{10} = \sqrt{3 \cdot 5 \cdot 7/11 \cdot 13} e_{61} + 2\sqrt{2/11} e_{41}$$

$$e_{51}e_{1-1} = 3\sqrt{5/11 \cdot 13} e_{60} - \sqrt{5/11} e_{40}$$

$$e_{50}e_{11} = 3\sqrt{7/11 \cdot 13} e_{61} - \sqrt{2 \cdot 5/3 \cdot 11} e_{41}$$

$$e_{50}e_{10} = 6\sqrt{3/11 \cdot 13} e_{60} + 5\sqrt{1/3 \cdot 11} e_{40}$$

$$e_{44}e_{22} = 3 \cdot 5\sqrt{1/11 \cdot 13} e_{66}$$

$$e_{44}e_{21} = 5\sqrt{3/11 \cdot 13} e_{65}$$

$$e_{44}e_{20} = 3 \cdot 5/11\sqrt{1/13} e_{64} - 4/11\sqrt{5} e_{44}$$

$$e_{44}e_{2-1} = 3/11\sqrt{5/13} e_{63} - 2/11\sqrt{3 \cdot 5} e_{43}$$

$$e_{44}e_{2-2} = 1/11\sqrt{5/13} e_{62} - 2/11\sqrt{2 \cdot 3 \cdot 5/7} e_{42} + \sqrt{2 \cdot 5/7} e_{22}$$

$$e_{43}e_{22} = 5\sqrt{2 \cdot 3/11 \cdot 13} e_{65}$$

$$e_{43}e_{21} = 4 \cdot 5/11\sqrt{3/13} e_{64} + 2/11\sqrt{3 \cdot 5} e_{44}$$

$$e_{43}e_{20} = 2 \cdot 3/11\sqrt{3 \cdot 5/13} e_{63} - 1/11\sqrt{5} e_{43}$$

$$e_{43}e_{2-1} = 4/11\sqrt{2 \cdot 5/13} e_{62} - 5/11\sqrt{3 \cdot 5/7} e_{42} - \sqrt{5/7} e_{22}$$

$$e_{43}e_{2-2} = 5/11\sqrt{1/13} e_{61} - 3/11\sqrt{2 \cdot 3 \cdot 5/7} e_{41} + \sqrt{5/7} e_{21}$$

$$e_{42}e_{22} = 5/11\sqrt{2 \cdot 3 \cdot 7/13} e_{64} - 2/11\sqrt{2 \cdot 3 \cdot 5/7} e_{44}$$

$$e_{42}e_{21} = 2 \cdot 3/11\sqrt{5 \cdot 7/13} e_{63} + 5/11\sqrt{3 \cdot 5/7} e_{43}$$

$$e_{42}e_{20} = 2/11\sqrt{2 \cdot 3 \cdot 5 \cdot 7/13} e_{62} + 8/7 \cdot 11\sqrt{5} e_{42} + 1/7\sqrt{3 \cdot 5} e_{22}$$

$$e_{42}e_{2-1} = 5/11\sqrt{2 \cdot 7/13} e_{61} - 9/7 \cdot 11\sqrt{3 \cdot 5} e_{41} - 2/7\sqrt{2 \cdot 5} e_{21}$$

$$e_{42}e_{2-2} = 5/11\sqrt{3/13} e_{60} - 2 \cdot 3 \cdot 5/7 \cdot 11\sqrt{3} e_{40} + 1/7\sqrt{3 \cdot 5} e_{20}$$

(DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

$l + l' = 6$  (con'd)

$$e_{41}e_{22} = 3/11\sqrt{2 \cdot 5 \cdot 7/13} e_{63} - 3/11\sqrt{2 \cdot 3 \cdot 5/7} e_{43}$$

$$e_{41}e_{21} = 4/11\sqrt{2 \cdot 5 \cdot 7/13} e_{62} + 9/7 \cdot 11\sqrt{3 \cdot 5} e_{42} - 1/7\sqrt{5} e_{22}$$

$$e_{41}e_{20} = 5/11\sqrt{2 \cdot 3 \cdot 7/13} e_{61} + 17/7 \cdot 11\sqrt{5} e_{41} + 1/7\sqrt{2 \cdot 3 \cdot 5} e_{21}$$

$$e_{41}e_{2-1} = 2 \cdot 5/11\sqrt{2 \cdot 3/13} e_{60} - 5/7 \cdot 11\sqrt{2 \cdot 3} e_{40} - 1/7\sqrt{2 \cdot 3 \cdot 5} e_{20}$$

$$e_{41}e_{2-2} = 5/11\sqrt{7/13} e_{6-1} - 2 \cdot 5/7 \cdot 11\sqrt{2 \cdot 3 \cdot 5} e_{4-1} + 1/7\sqrt{5} e_{2-1}$$

$$e_{40}e_{22} = 5/11\sqrt{2 \cdot 7/13} e_{62} - 2 \cdot 3 \cdot 5/7 \cdot 11\sqrt{3} e_{42} + 1/7 e_{22}$$

$$e_{40}e_{21} = 5/11\sqrt{5 \cdot 7/13} e_{61} + 5/7 \cdot 11\sqrt{2 \cdot 3} e_{41} - 4/7 e_{21}$$

$$e_{40}e_{20} = 3 \cdot 5/11\sqrt{5/13} e_{60} + 20/7 \cdot 11\sqrt{5} e_{40} + 2 \cdot 3/7 e_{20}$$

$$e_{33}e_{33} = 2 \cdot 5\sqrt{7/3 \cdot 11 \cdot 13} e_{66}$$

$$e_{33}e_{32} = 5\sqrt{2 \cdot 7/3 \cdot 11 \cdot 13} e_{65}$$

$$e_{33}e_{31} = 5/11\sqrt{2 \cdot 5 \cdot 7/3 \cdot 13} e_{64} - 1/11\sqrt{2 \cdot 3 \cdot 7} e_{44}$$

$$e_{33}e_{30} = 2 \cdot 5/11\sqrt{7/3 \cdot 13} e_{63} - 3/11\sqrt{7} e_{43}$$

$$e_{33}e_{3-1} = 2 \cdot 5/3 \cdot 11\sqrt{7/13} e_{62} - 3/11\sqrt{2 \cdot 3} e_{42} + 1/3\sqrt{2} e_{22}$$

$$e_{33}e_{3-2} = 5/3 \cdot 11\sqrt{7/13} e_{61} - 1/11\sqrt{2 \cdot 3 \cdot 5} e_{41} + 1/3\sqrt{5} e_{21}$$

$$e_{33}e_{3-3} = 5/3 \cdot 11\sqrt{1/13} e_{60} - 3/11 e_{40} + 1/3\sqrt{5} e_{20} - 1 e_{00}$$

$$e_{32}e_{32} = 2 \cdot 5/11\sqrt{2 \cdot 7/13} e_{64} + 1/11\sqrt{2 \cdot 5 \cdot 7} e_{44}$$

$$e_{32}e_{31} = 5/11\sqrt{2 \cdot 3 \cdot 7/13} e_{63} + 1/11\sqrt{2 \cdot 7} e_{43}$$

$$e_{32}e_{30} = 4 \cdot 5/3 \cdot 11\sqrt{2 \cdot 7/13} e_{62} - 1/11\sqrt{3} e_{42} - 2/3 e_{22}$$

$$e_{32}e_{3-1} = 5/11\sqrt{5 \cdot 7/3 \cdot 13} e_{61} - 4/11\sqrt{2} e_{41} - \sqrt{1/3} e_{21}$$

$$e_{32}e_{3-2} = 2 \cdot 5/11\sqrt{1/13} e_{60} - 7/11 e_{40} + 0 e_{20} + 1 e_{00}$$

(DECOMPOSITION OF DIRECT PRODUCTS OF SPHERICAL HARMONICS)

$l + l' = 6$  (con'd)

$$e_{31}e_{31} = 2 \cdot 5/11 \sqrt{5 \cdot 7/3 \cdot 13} e_{62} + 2/11 \sqrt{2 \cdot 5} e_{42} + 2 \sqrt{2/3 \cdot 5} e_{22}$$

$$e_{31}e_{30} = 5 \cdot 5/3 \cdot 11 \sqrt{2 \cdot 7/13} e_{61} + 1/11 \sqrt{3 \cdot 5} e_{41} + 1/3 \sqrt{2/5} e_{21}$$

$$e_{31}e_{3-1} = 5 \cdot 5/11 \sqrt{1/13} e_{60} - 1/11 e_{40} - \sqrt{1/5} e_{20} - 1 e_{00}$$

$$e_{30}e_{30} = 4 \cdot 5 \cdot 5/3 \cdot 11 \sqrt{1/13} e_{60} + 2 \cdot 3/11 e_{40} + 4/3 \sqrt{1/5} e_{20} + 1 e_{00}$$

H. C. Schweinler

## 17. THERMAL VIBRATIONS OF Cu-Zn SYSTEM CRYSTALS

Work on this topic continues to be focused almost entirely on the determination of the force constants between the various pairs of atoms in each crystal.<sup>(1)</sup> Workers in Professor B. E. Warren's x-ray laboratory at M. I. T. have succeeded in working backward from their thermal-diffuse-scattering isodiffusion contours in reciprocal lattice space to obtain values for the interatomic constants by finding the best match possible between the theoretical and experimental intensity curves along certain simple directions.<sup>(2)</sup> This technique furnishes the only experimental values available at present for atomic force constants. However, the experimental measurements are quite difficult because of the low intensities and possible surface effects involved. Likewise, higher-order scattering terms and higher than, say, third-nearest-neighbor interactions cannot be accurately taken into account by the theory used because of the involved nature of the calculations; nor can the Compton background scattering be corrected accurately everywhere. It is important to have theoretical atomic constant values for comparison with the x-ray values because of these weaknesses as well as for their own intrinsic interest.

Only elastic constant calculations have so far been published, and they are quite different from atomic constant calculations in that elastic deformations are homogeneous, while the atomic displacements to be considered are localized ones, much as in typical impurity problems. The procedure (analogous to that in the elastic case) of taking the second mixed partial derivatives with respect to two nuclear coordinates of the crystal cohesive energy to obtain the atomic force constants would consequently be a difficult task. Fortunately, Feynman's theorem tells us that the force on one nucleus at its lattice site resulting from the displacement of another in an otherwise perfect lattice is the classical Coulomb force produced by the change in total charge distribution of all the electrons in the crystal, bound and free, from the equilibrium distribution which produces no net forces.<sup>(3)</sup> Since the limiting value of such a force as the displacement goes to zero is in fact just the atomic force constant, the calculation of the perturbation in electronic wave functions resulting from a small nuclear displacement is the only difficult step in computing an atomic constant by this Feynman approach, which was suggested by Professor Slater. Moreover, the force constants for all orders of neighbors can be easily obtained by classical Coulomb potential integrations from this one expression for the change in charge density.

The difference between the perturbed and original nuclear frameworks of charge, which is the perturbation acting on the electron cloud, is clearly a dipole at the site of the displaced nucleus. Three lines of attack have been followed out. Treating the conduction electrons as a Thomas-Fermi gas spread out through the whole crystal, one obtains by a standard approximation the result that the ion-core dipole as screened by the electron cloud has a charge distribution and a potential which are both proportional to

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$$\left(\frac{p \cos \theta}{r^2}\right)(1 + qr) e^{-qr}$$

This potential gives considerably more anisotropic force constant values than a pure dipole. Furthermore, for a typical metal the parameter  $q$  is such that the screening takes place within a short distance, and in fact is about 90% complete within a radius equal to that of the actual ionic core. It would follow that the screened dipole force at a first-neighbor nucleus would only be a few percent of that produced by the unshielded ion-core displacement. Clearly these results cannot be relied upon quantitatively, since the conduction electrons are actually not free to move in the ion-core volumes in which the model of Thomas-Fermi has them doing most of the screening. Next an attempt was made to take the second step in a proper self-consistent field procedure by using the Thomas-Fermi screened-dipole potential as the perturbation term in a quantum-mechanical treatment. However, even using the simplest free-electron model of a metal and the equivalent of the Born scattering approximation in solving the one-electron Schrödinger equation, the integral for the perturbed wave function was quite difficult. Since further integrations over all occupied free-electron states and then over all space with the Coulomb factor  $1/r$  would have been required to get the new screened potential, it was not worthwhile to carry out the calculation in view of the crudeness even of a free electron model which excludes the conduction electrons from the central ion core.

A number of general statements can be made regarding the atomic force constants. From the equations of motion of the thermal vibrations and the symmetry properties of the lattice one can easily derive symmetry relations for the force constants, and this has been done for the first three orders of neighbors in the fcc and bcc lattices. Three-by-three matrices contain all the force constants between a given pair of atoms, and the symmetry restricts the internal structure of these matrices as well as relating the matrices for equivalent pairs of atoms. For example, there turn out to be but four independent parameters in the twenty-four three-by-three force constant matrices relating the (arbitrary) origin atom to the twenty-four third nearest neighbors in the fcc lattice. Elastic constants for the CuZn system crystals have been quite accurately measured experimentally, although the theoretical values are not very reliable. Thermal vibrations include the long wavelength elastic vibrations as a special case, and, as one would expect, the elastic constants can be expressed as sums of combinations of the atomic constants for each order of neighbors. Born has proved this general result by comparing the leading terms in a perturbation-theory expansion of the normal coordinate equations of motion for thermal vibrations (with the wave vector as perturbation parameter) with the terms of the elastic wave equation. <sup>(4)</sup> These relations have been established explicitly through third neighbors

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in the bcc and fcc lattices in the course of our work. They are useful as a completely unambiguous partial check of the atomic constants with reliable experimental results, although of course there are many more independent force constants than elastic constants even in the first few rings of neighbor atoms. Born has further proved by a thermodynamic argument that a lattice satisfying the usual elastic or long wavelength criteria for stability also automatically is stable to all the thermal vibrations: i. e., that  $\omega^2 > 0$  for all the  $10^{23}$  or so normal vibrations if only the few elastic stability criteria are satisfied. <sup>(5)</sup> Thus agreement of the appropriate sums of atomic constants with the experimental elastic constants guarantees that all stability criteria are satisfied as well, although there are still a few microscopic criteria which it proves instructive to evaluate. It should further be mentioned that the order of magnitude of the observed elastic constants shows that the actual atomic constants are of the same general magnitude as those which would result from an unscreened ion-core displacement, contrary to the Thomas-Fermi model prediction.

At present a general semi-empirical study of the force constants is being carried out. From the Thomas-Fermi model results one feels fairly confident that most of the perturbation in electronic charge distribution takes place within the sphere through the nearest neighbor atoms. Hence this  $\Delta\rho$  can be approximated in the usual way by a multipole expansion valid at all neighboring atoms. The force constant matrices produced by each multipole for the first through third orders of neighbors have been computed for fcc and bcc lattices in terms of the multiple moments as parameters. These multipole moments are then chosen so that the sum of the contributions they make to the force constants relating various orders of neighbors agree with the values which give the best fit with the x-ray data. Finally the  $\Delta\rho$  can be built up from these multipole moments. Since the multipole potentials each have a different radial dependence, the force constants produced by each multipole at all orders of neighbors must separately satisfy the symmetry requirements. In the fcc and bcc structures symmetry thus rules out monopole, quadrupole, etc. terms. Various other more qualitative restrictions on and relations among the force constants have been found and can be applied in determining a satisfactory match. In bcc  $\alpha$ -Fe fairly good matching with x-ray <sup>(6)</sup> and elastic values has been obtained for first and second neighbors using dipole plus octopole terms. The x-ray atomic force constant values for fcc Cu and hcp Zn being obtained by Warren's group are not yet well enough established to permit a reliable multipole fitting; however, from the stability criteria it is clear that dipole and octopole terms alone cannot be enough. At distant neighbors only dipole terms will be appreciable, and it therefore may prove feasible to include the effect on the vibration frequency spectrum of all the further neighbor lattice interactions, using the techniques applied in ionic lattices and the dipole moment which best fits the x-ray constants for the first few rings of neighbors. However, it is anticipated that the

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primary application of these semi-empirical results will be in forming a clear physical picture of the charge distortion resulting from a nuclear displacement as a guide in the fundamental task of developing an accurate quantum-mechanical calculation of this charge distortion, and thence the force constants, from first principles: several possible approaches to this task are under consideration.

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