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QUARTERLY PROGRESS REPORT

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SOLID-STATE AND MOLECULAR THEORY GROUP

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

CAMBRIDGE, MASSACHUSETTS

QUARTERLY PROGRESS REPORT NO. 14

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on

Project N5ori-07856

SURVEY

Even though this is a short Progress Report, there are a number of interest-
ing results which have appeared during the period which it covers. One of these is
the calculation of the density of states curve for nickel, which Koster has been carry-
ing out. Much use had been made in the past of the density of states curve for this
element which Krutter and I calculated many years ago. This curve showed a dip in
the middle of the 3d band, which was of considerable importance in the theory of ferro-
magnetism, electronic specific heat, and other properties of the transition elements.
More recent work, both by the cellular and the tight binding approximation, had shown
that the details of the old cellular calculation on which this work of Krutter's and mine
was based, were certainly not correct: the detailed curves of energy versus k, which
now appear to be fairly certain from newer calculations, are quite different from our
older ones, as a result of the small number of spherical harmonics which were used
in this older cellular calculation. As mentioned in the preceding Progress Report, it
seemed worthwhile to make a new calculation of density of states for nickel, on the
basis of the tight binding calculation of Fletcher and Wohlfarth, which seems to agree
qualitatively rather well with the new calculations on copper made by Howarth, by both
the improved cellular method and the augmented plane wave method. Fletcher and
Wohlfarth computed the density of states just at the top of the energy band, but the
mathematical problem was too severe for them to wish to carry out the complete cal-
culation.

The facilities of Whirlwind make this calculation rather easy, and consequently
Koster has carried through this work, and reports on it in the present Progress Re-
port. His result is very interesting, in that it shows a curve closely resembling the
old one which Krutter and I had found. The dip in the center, which was the basis of
most of the qualitative deductions from the curve, remains much as in the earlier cal-
culations. Hence we may consider these many deductions from the earlier curve to
be still valid, even though the details of the earlier calculations were not. What has
happened is that the errors in the earlier calculation become rather well ironed out
in the process of taking the density of states curve: we have about as many states as
before in each energy range, even though they are located in different parts of the
Brillouin zone.

I have just mentioned the calculations of Howarth. He left to return to Eng-
land before being able to finish completely his work on copper, but he obtained the
essential results required from Whirlwind, and will shortly be able to finish his cal-
culations. The net result was that he found that the augmented plane wave method

converges remarkably rapidly, more so than the cellular method, and it seems as of now to be the best method which we have for solving the periodic potential problem. The qualitative results on copper resemble those of Fletcher and Wohlfarth for nickel, as determined by the tight binding method. The agreement between the results for copper by the augmented plane wave method, and by the cellular method, is not perfect. This may be partly a result of the fact that the calculations were not made for exactly the same potential, for evidence is rapidly increasing that energy bands are remarkably sensitive to small changes in potential. To check this point, Howarth is preparing to repeat the cellular calculation, for exactly the same potential used for the augmented plane wave method, so as to get a precise comparison of the two methods; he finished the necessary calculations for this on Whirlwind before he left. We shall hope to learn more details of the results later.

Another calculation which has led to a definite result is that of Kaplan on the ammonia molecule. Just before he left to take a new post at the University of Buffalo, he obtained preliminary results, also by means of Whirlwind, for the LCAO SCF calculation for this molecule, on which he has been working for a long time; though there is still considerably more to be done before the work is completed. These preliminary results indicated a binding energy about 75 percent of the observed value. This represents one of the most complicated molecules which have been attacked by this method; the calculation was entirely non-empirical, and the values of the three- and four-center integrals were calculated, rather than being estimated.

McWeeny has also left, to return to England, and before leaving he finished up the calculations on the water molecule, which he describes in this Progress Report. His aim was to find whether a simple configuration interaction method, based on the $\overline{VB}$ method, could lead to results significantly better than the LCAO SCF method. The results are somewhat discouraging: he was not able to do nearly as well as the LCAO SCF method, as it was applied to this molecule by Ellison and Shull. Taken together with his earlier results on benzene, and with Kaplan's success with ammonia, it begins to be clearer than before that the LCAO SCF method is probably much better fitted to a discussion of molecular energies and wave functions than other easily usable methods. It is fortunate, in this connection, that Meckler's Whirlwind program for the LCAO SCF method is available. This program is proving to be remarkably flexible; and Meckler, in the present Progress Report, outlines its uses, and those of some of the other programs which are now being used on Whirlwind.

Löwdin, in the last preceding Progress Report, outlined several interesting aspects of the self-consistent field method; more extended papers on the same subject, which he has prepared for publication, have been accepted by The Physical Review. In connection with the "natural orbitals" which he introduced in those papers, Koster examines a simple special case in the present Progress Report, which throws some

doubt on the practical usefulness of these natural orbitals in obtaining rapid conver-
gence in a configuration interaction problem.

A number of other problems under consideration are coming along well.
Schultz is getting well into the problem of the interaction of electrons and lattice vibra-
tions, a very involved problem which will probably receive much more attention in the
future. White's work on the elastic vibrations and elastic constants of copper is near-
ing completion, and represents a very interesting piece of work. Wood's self-consist-
ent calculation of the iron atom, using two different potentials for the electrons of plus
and minus spin, is practically finished, and shows that the potentials and charge dis-
tributions for the two spins are not as different as one might have thought. Saffren is
coming along with extensions of the augmented plane wave method, and Howland is
starting consideration of the application of this method to a polar crystal, KCl. Other
work is also progressing, as the items in the Report will indicate.

I have already stated that Kaplan, Howarth, and McWeeny have recently left
the group, after profitable periods with it. White expects to leave shortly. Pratt and
Kleiner have taken up their duties with Group 35 at the Lincoln Laboratory, and while
we see them frequently, they no longer belong directly to this group. Schweinler,
after a very profitable summer at the Oak Ridge National Laboratory, has decided to
remain there permanently. We shall shortly add to the group R. K. Nesbet, who took
his bachelor's degree at Harvard, and is just finishing his work for the doctorate at
the University of Cambridge, where he has been working with Dr. S. F. Boys on prob-
lems very similar to those which have concerned this group. During the summer, we
have had two visitors: Dr. A. Delgano, of the University of Belfast, who has been at
the Institute in connection with the Foreign Students' Summer Program; and Dr. P.
Merryman, a member of Professor Mulliken's group at the University of Chicago,
who has been here studying the application of Whirlwind to the calculation of molecular
integrals. We expect a visit shortly from Dr. K. Ruedenberg, also of the University
of Chicago, also in connection with this same problem.

J. C. Slater

1. CALCULATION OF A DENSITY OF STATES CURVE FOR NICKEL

The calculation of the density of states curve for nickel which was described in the last Progress Report[1] has now been completed. The density of states curve is shown in Fig. 1-1. The curve has been normalized to have a total area of five cor-
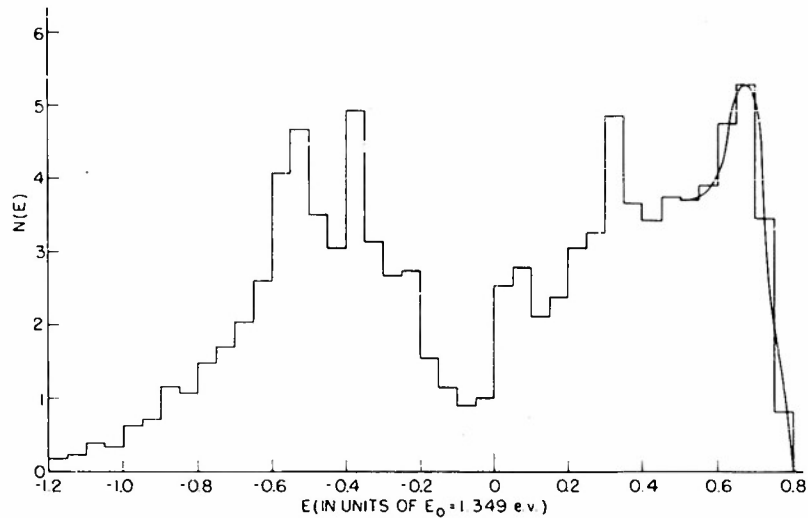
Fig. 1-1

Density of states curve for nickel

responding to five states of a given spin. The method of calculation of this density of states curve from the energies of the d bands calculated on the 10 degree mesh in the first Brillouin zone is given in a recent paper by J. C. Slater and the author on the tight binding method.[2]

The striking feature of this density of states curve is the dip in the middle. This curve can be compared with the density of states curve for the d bands in the body-centered structure recently calculated[2] using the same parameters for the nearest neighbor interactions used in this calculation. This curve also showed a pronounced dip in the center of the distribution. Thus it seems on the basis of this simplified tight binding calculation that both the body-centered and the face-centered structure show a minimum for the density of states curves at some point near the middle of the d bands. This dip in the density of states curve for a face-centered structure was predicted many years ago by Krutter[3] by using the cellular method and it is interesting to find that the calculation carried out by the tight binding method shows a similar dip.

The purpose of this calculation was to extend the calculation of the density of states curve given by Fletcher and Wohlfarth[4] over the entire range of energies for

the d bands. We can therefore compare only a small portion of the density of states curve with that calculated already. In the figure we show a smooth curve drawn through the step-like curve. This curve extends over the range of energies that Fletcher and Wohlfarth covered in their density of states curve. This compares quite well with the curve published by the aforementioned authors which tends to give us confidence in the method of calculating the density of states we have used.

References

1. G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 40.

2. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

3. H. M. Krutter, Phys. Rev. 48, 664 (1935); J. C. Slater, Phys. Rev. 49, 537, 931 (1936).

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

G. F. Koster

2. ENERGY BANDS IN COPPER

The calculation of the electronic eigenvalues of metallic copper by the augmented plane wave method has been completed and an account of it will shortly be submitted for publication. The rapid convergence reported previously[1] has been found in every state considered. In all cases, it has been found that combining two solutions inside a sphere, both joined to the same plane wave outside the sphere, is sufficient to give the "best" wave function possible using only one plane wave. In other words, two branches of the E versus E_o curves[2] are sufficient to give accurate eigenvalues for the lowest states. Inclusion of six such terms gives no change in the lowest eigenvalues, and yet does not produce satisfactory convergence in higher eigenvalues. The method would therefore appear to be limited at present to calculations of states in the valence and conduction bands, and to obtain accuracy in these, the numerical labor is not excessive.

In the case of copper, the inclusion of plane waves corresponding to wave vectors in the two innermost Brillouin zones is sufficient to produce convergence. This is not surprising since (1) the conduction electrons of copper deviate only slightly from the free electron behavior and (2) the wave functions of the d electrons are almost entirely confined inside the atomic sphere.

Some of the results obtained for copper are given in Tables 2-1 and 2-2 below; *

Table 2-1

Eigenvalues of conduction band of copper using (a) Hartree and (b) Hartree-Fock atomic potentials

State	Γ_s	L_s	L_p^1	X_s	X_p^1	K_s	K_p^1	A
A	-.558	-.0519	.0887	.080	.2409	-.147	-.136	.124
B	-.354	.2219	.3263	.375	.502	.0951	.086	.361

Table 2-2

Eigenvalues of 3d band of copper

State:	Γ_d^1	Γ_d^2	X_d^1	X_d^2	X_d^3	X_s	L_s
	-.155	-.0541	-.1062	-.0742	-.0660	-.335	-.2756

State:	L_p^2	L_d^1	K_s	K_p^1	K_p^2	K_d	A
	-.0652	-.1456	-.3448	-.1528	-.0688	-.1621	-.2693

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*The notation used is fully described in Ref. 3. Eigenvalues are quoted in Rydberg units.

others are being analyzed at the time of writing. As an example of the power of the method, a point of no symmetry in k-space has been considered, the point A, $(\frac{3\pi}{a}, \frac{2\pi}{a}, \frac{\pi}{a})$. Using two solutions inside the sphere for each plane wave, and using 7 plane waves (with wave vectors in the two innermost zones) a secular equation of order 14 was solved in this case, the highest order equation which has occurred in this work. The power of the method may be judged from the results; in all cases, the error due to truncation of the infinite series of augmented waves is estimated as less than 0.5 in the last figure quoted.

Comparison of these results with those obtained for copper by the cellular method[3] shows considerable discrepancies, particularly in the position of the states lying in the d-band. The total width of the d-band remains approximately the same (4.1 e.v. in the present work), but the top of the band lies at the center of the Brillouin zone, the base lying at the end of the (110) axis. The reason for the discrepancy in the two sets of results appears to lie in the different potentials used; a cellular calculation of the eigenvalues at the center of the zone in the d-band has been carried out using the exact potential used in the present work differing from that used in the original cellular calculation in that it is a constant outside the atomic sphere. The agreement between this calculation and the results of the augmented plane wave method is quite satisfactory. Hence, as has been observed in other work,[3,4] the excited energy levels in crystals appear to be extremely sensitive to the crystal potential used, and to obtain results of real physical significance, an attempt at self-consistency would seem necessary.

In concluding this series of reports, I would like to express my deepest gratitude to Professor J. C. Slater for making possible my stay with the Solid-State and Molecular Theory Group, and for his continued advice and encouragement throughout the year. My thanks are due to the whole group for many stimulating discussions and for much helpful advice. The entire numerical work involved in this project has been carried out on the Whirlwind I digital computer, and I am deeply indebted to all the staff there for their help and cooperation. Availability of the computer at this time was made possible by the Office of Naval Research, to whom thanks are due.

References

1. D. J. Howarth, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 42.

2. D. J. Howarth, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 10.

3. D. J. Howarth, Proc. Roy. Soc. (London) A220, 513 (1953).

4. F. Herman, private communication.

D. J. Howarth

3. AN AUGMENTED PLANE WAVE METHOD AS APPLIED TO SODIUM

Howarth's program for the augmented plane wave method having been applied to copper is now being applied to sodium. In the meantime I have been attempting to modify Howarth's program so that calculations on the energy bands in sodium can begin according to a modification of the APW method which I outlined in my last Report.[1] The modification requires only that the energy expression used by Howarth be replaced by the somewhat more complex expression which is given in my last Report.[1] I have also undertaken to build upon the part of Howarth's program which (in essence) makes properly symmetrized combinations of APW before the APW are allowed to interact in the secular equation; the plan is to simplify the coding of symmetry points in the Brillouin zone so as to make more complete the mechanization of the steps of the method which utilize the operations of the cubic point group.

The purpose of the present calculations is to examine the energy bands of sodium and also to compare the convergence of the APW scheme with the modified scheme.

Reference

1. M. M. Saffren, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 44.

M. M. Saffren

4. ENERGY BANDS IN POTASSIUM CHLORIDE

It is proposed to calculate the energy band structure of potassium chloride using the augmented plane wave (APW) method[1] to obtain the energies for certain high symmetry values of the propagation constant $\vec{k}$, and using the Slater-Koster tight binding scheme[2] for interpolation. A rigid lattice will be assumed, and on this assumption excited levels will be included. The works of S. R. Tibbs[3] and of W. Shockley[4] provide some preliminary information about alkali halide energy levels and functions, and the recent work of P. O. Löwdin[5] on cohesive energy provides tools which will be quite useful in the proposed band calculation. With the information resulting from such a calculation it is hoped that new light may be shed on such problems as the importance of lattice interactions in optical transitions and the effect of impurities (such as the F-center) on the energy band structure. There is no present work which attempts a complete quantum-mechanical calculation of the desired energy levels and functions.

The present attempt at a complete calculation is made possible by the rapid convergence of the new APW method of Slater and Saffren. The value of the method is illustrated by the work of D. J. Howarth[6] on the energy band structure of copper. Certain difficulties arise in adapting the method for an ionic crystal, however. First, the potential which is to be used must be spherical within a sphere about each lattice site and constant outside the spheres; in our case the real potential will probably be quite non-spherical and non-constant in these regions. Secondly, the computer program for Whirlwind developed by Howarth for the copper calculations must be sufficiently generalized to take account of the two types of centers in the alkali halide unit cell. As Howarth has already shown, the generalization of the first part of his program will not be difficult; that part consists of obtaining the E versus E_o curves of the APW method and the resultant single APW's. On the other hand, the second part, solving the secular equation between interacting APW's, will probably be quite difficult due to the fact that the linear combinations of APW's will not be real as they were for Howarth. This problem is presently being studied.

The first difficulty inherent in the proposed calculation concerns the initial crystal potential which is to be used. The model we are employing is that of a rigid lattice with "free ions", Cl^- and K^+, located at alternate lattice sites. The electron charge density of the crystal is taken as that which would exist if all the electrons were located in Hartree-Hartree determined[7] free ion functions centered on the various lattice sites.

The ground state ψ of the crystal is written as a single determinant of electrons in free ion states; this is possible because the ions K^+ and Cl^- both have closed-shell electronic structures, with eighteen electrons apiece. The charge density $\rho(\vec{r})$ is obtained by integrating $-\psi^*\psi$ over the coordinates of all but one electron and summing over all spins. The usual periodic boundary conditions are used, the periodic

cell being a cube containing N Cl$^-$ ions and N K$^+$ ions. ψ is normalized so that the integral of $\rho(\vec{r})$ over this cube is $- 36$ Ne.

Written out to the first order in overlaps, the charge density is:

$$\rho(\vec{r}_1) = \rho_{free}(\vec{r}_1) + \rho_{overlap}(\vec{r}_1) . \tag{4.1}$$

Here $\rho_{free}(\vec{r}_1)$ is that charge density which is obtained by simply summing the charge densities $-eu^*u$ at $\vec{r}_i$ of the electrons in their free ion functions u, with an appropriate normalization factor; and $\rho_{overlap}(\vec{r}_1)$ is proportional to the following sum of products:

$$\sum_{\substack{qm \\ q'm'}}{}' \; s(qm|q'm') \left[\sum_{spin \; 1} u_m^{q*}(1) \, u_{m'}^{q'}(1) \right] .$$

Here $u_m^q(1)$ is the free ion function with quantum numbers m, centered on lattice site q, and containing electron 1, s is the overlap integral (including spin summation), and the prime on the summation symbol means $(qm) \neq (q'm')$. All the terms in $\rho_{overlap}$ involve just two sites and contain all functions u as sums of the form $\sum_m u_m^q(1) \times u_m^q(2)$. By a theorem of Löwdin[5] (which follows directly from the additional theorem for spherical harmonics) each such term may be evaluated by taking the vector between the two sites as a z-axis for the two ions affected. On this basis the overlap integrals calculated by Löwdin for KCl may be used directly, and the evaluation of ρ should not be too difficult.

The Hartree-Fock equation for the one-electron function $\phi(\vec{r})$ can be written in the following form:

$$\left[-\frac{\hbar^2}{2m} - e \, V_{coul}(\vec{r}) - e \, V_{exch}(\vec{r}) - E \right] \phi(\vec{r}) = 0 . \tag{4.2}$$

The potential which must be evaluated, then, is $V(\vec{r}) = V_{coul}(\vec{r}) + V_{exch}(\vec{r})$. The exchange potential V_{exch} may be approximated by use of Slater's $\rho^{1/3}$ equation,[8] where ρ is calculated as described in the preceding paragraph.

$V_{coul}(\vec{r})$ is made up of contributions from both the electron cloud and the nuclei. By various elementary operations $V_{coul}(\vec{r})$ can be written as follows (in the MKS system):

$$V_{coul}(\vec{r}) = \frac{e}{4\pi\epsilon_o a} \left[S(\vec{r}) + \omega T(\vec{r}) + \omega F(\vec{r}) \right] , \tag{4.3}$$

where a is the interionic distance, and $\vec{r}$ is measured in units of a. The terms on the

right of (4. 3) are defined as follows:

$$S(\vec{r}) = \sum_q \frac{-(-1)^q}{|\vec{r} - \vec{R}_q|} , \qquad (4.4)$$

where $\vec{R}_q$ is a vector to the lattice site q, q even being a Cl^- site, and q odd being a K^+ site;

$$T(\vec{r}) = \sum_q \int_{|\vec{r} - \vec{R}_q|}^{\infty} \left[\frac{1}{|\vec{r} - \vec{R}_q|} - \frac{1}{x} \right] U_q(x) \, dx , \qquad (4.5)$$

where $U_q(x)$ is the total radial charge density at a radius x in a closed shell ion of the type which is located at lattice site q;

$$F(\vec{r}) = \frac{1}{2} \sum_{\text{spin } 1} \int_R \left[\sum_{q \text{ even}} \left(\frac{1}{|\vec{r} - \vec{R}_q - \vec{r}_1|} - \frac{1}{|\vec{r} - \vec{R}_q|} \right) \right.$$

$$+ \sum_{q \text{ odd}} \left(\frac{1}{|\vec{r} - \vec{R}_q - a\vec{i} - \vec{r}_1|} - \frac{1}{|\vec{r} - \vec{R}_q|} \right) \Bigg] \times$$

$$\left[\sum_{q' \neq 0} \sum_{mm'} s(0m|q'm') u_m^{0*}(\vec{r}_1, s_1) u_{m'}^{q'}(\vec{r}_1 - \vec{R}_{q'}, s_1) \right. \qquad (4.6)$$

$$+ \left. \sum_{q' \neq 1} \sum_{mm'} s(1m|q'm') u_m^{1*}(\vec{r}_1 + a\vec{i}, s_1) u_{m'}^{q'}(\vec{r}_1 - \vec{R}_{q'}, s_1) \right] dv_1 ,$$

where q = 0 is the origin (a Cl^- site) and q = 1 is the nearest K^+ site in the - x direction; and

$$\omega = \left[1 - \frac{1}{36N} \sum_{\substack{qm \\ q'm'}}' s^2(qm|q'm') \right]^{-1} . \qquad (4.7)$$

Physically, $S(\vec{r})$ (Eq. 4. 4) is the potential at a point $\vec{r}$ in a cubic lattice of unit point charges with alternating sign if one of the negative unit charges is taken as an origin. From symmetry it can be shown that $S(x, y, z) = -S(1 - x, y, z)$. $S(\vec{r})$ is presently being evaluated in the central unit cell by expanding $S(\vec{r}) - \frac{1}{r}$ in a Taylor series about $\vec{r} = 0$; the coefficients of the products $x^a y^b z^c$ take the form of combinations of lattice sums. The latter are being calculated by Evjen's method.[9] This method is not sufficiently accurate for all the sums involved, however; hence a few of the sums will be calculated by an extension of the Ewald method. $S(\vec{r})$ may also be checked by direct use of the Ewald method[10] at specific points in the lattice.

For $(a + b + c)$ odd, the coefficients of $x^a y^b z^c$ are of course zero; it appears that satisfactory accuracy is obtained when the expansion is extended to include the tenth order terms. The worst point in the unit cell is $(x, y, z) = (1/2, 1/2, 1/2)$, but this point is not included in either of the touching ionic spheres; the larger sphere (Cl^-) intersects the $(1, 1, 1)$ direction at $(1/3, 1/3, 1/3)$.

$T(\vec{r})$ (Eq. 4.5) represents the correction to the potential which arises from the spatial extension of the electronic charge. The contributions of nearest neighbors are large, but those of the further neighbors fall off rapidly with distance from the origin.

$F(\vec{r})$ (Eq. 4.6) mostly represents the potential contribution arising from the overlap charge density (Eq. 4.1). Several approximations for this term are presently being studied, but the term has not yet been evaluated. The terms in $F(\vec{r})$ are all such that the Lowdin theorem is applicable, and the Lowdin overlap integrals can again be used directly.

ω (Eq. 4.7) is the charge normalization factor; it is easily evaluated from Lowdin's overlap integrals. Of the four terms contributing to the potential, only $S(\vec{r})$ appears without a factor ω.

Treating the component terms as indicated above, $V(\vec{r})$ will be evaluated on the surfaces of spheres centered on lattice sites with radii equal to the empirical ionic radii. The deviation from sphericity will be studied. If it does not seem too unreasonable, the potential $V(\vec{r})$ will be replaced by its spherical averages within the spheres and by an effective constant value outside them. The APW method will be applied using this as an initial potential, and approximations to E and ϕ (Eq. 4.2) will be sought.

KCl has been chosen as the particular alkali halide to be studied because for it the free ion functions[7] and the overlap integrals[5] have already been calculated, and because the ions Cl^- and K^+ are of comparable size, thus putting less strain on the accuracy of the expansion of $S(\vec{r})$. More overlap integrals are required than for NaCl, for instance, but the overlaps are also smaller. These reasons do not prohibit calculation for the other alkali halides, however, and future developments may even show that calculations for one of them might be preferable.

Finally, in anticipation of the results from the APW method, the tight binding interpolation formulas have been developed. 3s, 3p, and 4s orthogonal, localized functions were assumed for each type of ion. The 4s functions were included to allow consideration of excited levels. The matrix components of the Hamiltonian between Bloch functions were written out with the matrix components between localized functions appearing as disposable constants. With second-nearest-neighbor interactions considered, there are thirty-four such constants, while with only nearest neighbors, there are eighteen. Some of these may be neglected, however, on the assumption

that the orthogonalized functions are about the same as the free ion functions they re-place. The secular equation has been factored at many symmetry points in momentum space, and the roots have been extracted. When the APW energies are available at these points, the disposable constants will be determined. The exact numbers of points and constants actually used will of course depend on how much difficulty is encountered in carrying out the APW method for KCl.

References

1. J. C. Slater, Phys. Rev. 92, 603 (1953); M. M. Saffren and J. C. Slater, Phys. Rev. 92, 1126 (1953).

2. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

3. S. R. Tibbs, Trans. Faraday Soc. 35, 1471-1484 (1939).

4. W. Shockley, Phys. Rev. 50, 754 (1936).

5. P. O. Löwdin, "A Theoretical Investigation into Some Properties of Ionic Crystals", Thesis, University of Uppsala, 1948.

6. D. J. Howarth, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1954, p. 14; April 15, 1954, p. 10; July 15, 1954, p. 42.

7. D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A156, 45 (1936); A166, 450 (1938).

8. J. C. Slater, Phys. Rev. 81, 385 (1951).

9. H. M. Evjen, Phys. Rev. 39, 675 (1932); see also Ref. 5.

10. P. P. Ewald, Ann. Physik 64, 253 (1921).

L. P. Howland

5. ENERGY BANDS IN GRAPHITE

A tight binding calculation has been made on Graphite (described in the previous Report), but the results were unsatisfactory. Specifically, for certain values of the reciprocal lattice vector $\vec{k}$, the overlap matrix, which should be positive definite, was found to have negative eigenvalues. It is believed that this contradiction arose because of the following situation. In constructing the matrix elements S_{ij}, the terms arising from overlap integrals beyond the third nearest neighbor distance were neglected; however, the overlap integrals used were found by integrating analytically over all space. Thus, failure to include enough neighbors in the evaluation of the overlap matrix elements allows the possibility of negative overlap eigenvalues, an effect analogous to an insufficient number of terms in the Fourier series of a positive definite quantity.

At present, the calculations are being re-examined with the view of increasing the number of neighbors considered.

F. J. Corbató

6. A REVIEW OF THE USE OF WHIRLWIND BY THE SOLID-STATE AND MOLECULAR THEORY GROUP

This report will summarize the use of Whirlwind, the computing machine, by members of this group. Although special programs have been written for the machine, programs which perform a particular, formulized set of operations specific to one problem, the emphasis here will be on the description of more general programs: either basic mathematical routines which are called for naturally in the calculus of a class of physical theories, or programmed physical theories which are standards ready to compute on any structure, needing only the specification of an atomic number, potential, or a table of integrals. Whirlwind does have features that other machines do not, but no program has been written for Whirlwind only; except that with the machine's high speed and great capacity, we may be singularly adjusted to such things as large order matrices, highly iterative schemes, and wide gamuts of parameters.

The Computer

Whirlwind 1 is a high-speed electronic digital computed located at M. I. T. and sponsored by the O. N. R. It was built and is maintained as a prototype for engineers and mathematicians in the development of circuitry and logic for digital computers. Time has been made available by the M. I. T. Committee on Machine Methods of Computation and Numerical Analysis (Professor P. M. Morse, Chairman), which supervises the scientific and engineering applications of the machine, to staff members and students at M. I. T.

The direct, or fast storage elements of the machine are magnetic cores. These are grouped into registers each of which can accommodate a word length of 16 binary digits. There are 2048 magnetic core registers and it is in these that sections of the program in operation are stored along with numbers to be operated upon. That is, control and arithmetic is done only with the core memory. As passive storage, whose contents when needed must be transferred into the cores at a relatively slow rate, there are reels of magnetic tape and a 22, 528 register magnetic drum. Another drum will be available soon and there is the outside storage of punched paper tape. Information is fed into the machine on punched paper tape passed through a photoelectric reader and the output can be had on automatic typewriter, punched tape, magnetic tape, or a photographed cathode-ray tube display.

The electronic speed of the machine is about 40, 000 operations per second, per se. The bare electronic machine, however, is not the easiest to code and needs to be polysyllabic in its words. The basic word length corresponds to about 4 decimal digits and necessitates fixed decimal (or binary) point arithmetic. Therefore, a programmed arithmetic has been written: numbers occupy two registers in the form $x2^y$ and the order to multiply, for example, transfers control to a slew of operations which perform the double-length, floating point multiplication. The programmed arithmetic

occupies a section of fast storage, numbers take up twice the space, and more time is spent on an arithmetic operation. In fact, programmed arithmetic is about 40 times slower than ordinary Whirlwind.

Associated with the programmed arithmetic is a wonderful system of service routines. These include:

Automatic conversion of a program written in almost basic English to the binary code of the machine.

The floating address system whereby a program is written with addresses referred to only as letters, algebraic symbols whose values are assigned by the machine itself.

Automatic cycle counters.

A set of buffer registers, each three ordinary registers long, to be used in the accumulation of partial sums without the intermediate round-off into two registers.

An elaborate system of program checks and post-mortem routines for mistake diagnosis.

All this and more leaves the machine with sufficient speed and capacity, but with a logic more malleable.

The service routines are developed by the staff of mathematicians at Whirl-wind. Programs for calculation are written by the originators of the problems who learn coding from the computer staff and who turn to the staff when the malicious mach-ine reacts absurdly to the unique and careful logic of their programs. The staff is most capable. It is always shown that what seems a fundamental incompatability is a simple lack of understanding which can be corrected.

There are two types of programs: the sub-routine and the production style. The sub-routine is a packaged unit ready to be inserted, to perform a complex opera-tion, into any large program. The external program sets up the data as required by the sub-routine, transfers control to the sub-routine which does what it should and re-turns control to the external program, which goes on from there. The programmed arithmetic is a sub-routine, and many of the matrical routines to be described are in sub-routine form, easily assembled into compound programs. The other type, a pro-duction style routine, is complete. As the data is read in, the program assembles it, has it manipulated through a series of smaller sub-routines, and then displays the output. Production style routines are not meant to be synthesized into larger routines; sub-routines are.

The Algebraic Routines

Much of matrix algebra has been programmed. To begin with, there is the diagonalization of Hermitian matrices. This method is this: Let H be a real sym-

metric matrix. It is transformed to diagonal form by a succession of 2×2 orthogonal transformations. Let u be an orthogonal matrix with unity for every diagonal element except the ith and j^{th}, and zero for every off-diagonal element except the i, j^{th} and the j, i^{th}. Schematically

$$
u = \begin{array}{c c} & \begin{array}{cc} i & \quad j \end{array} \\ \begin{array}{c} \\ i \\ \\ j \\ \\ \end{array} & \left| \begin{array}{ccccc} 1 & & & & 0 \\ & c & 0 & -s & \\ & 0 & 1 & 0 & \\ & s & 0 & c & \\ 0 & & & & 1 \end{array} \right| \end{array}
\qquad
u^t = \begin{array}{c c} & \begin{array}{cc} i & \quad j \end{array} \\ \begin{array}{c} \\ i \\ \\ j \\ \\ \end{array} & \left| \begin{array}{ccccc} 1 & & & & 0 \\ & c & 0 & s & \\ & 0 & 1 & 0 & \\ & -s & 0 & c & \\ 0 & & & & 1 \end{array} \right| \end{array}
$$

Under the transformation $u^t H u = H'$, only the elements in the ith and j^{th} rows and columns of H are affected.

$$H'_{mn} = H_{mn} \qquad\qquad m \neq i \text{ or } j, \ n \neq i \text{ or } j$$

$$H'_{im} = cH_{im} + sH_{jm} \qquad\qquad m \neq i \text{ or } j$$

$$H'_{jm} = -sH_{im} + cH_{jm} \qquad\qquad m \neq i \text{ or } j$$

$$H'_{ii} = c^2 H_{ii} + 2sc H_{ij} + s^2 H_{jj}$$

$$H'_{jj} = s^2 H_{ii} - 2sc H_{ij} + c^2 H_{jj}$$

$$H'_{kj} = (c^2 - s^2) H_{ij} + sc(H_{jj} - H_{ii})$$

c and s are determined by the trigonometric identity

$$c^2 + s^2 = 1$$

and the condition that $H'_{ij} = 0$. Under any orthogonal transformation the sum of the squares of all the elements of H is unchanged:

$$\sum_{mn} (H_{mn})^2 = \text{Trace}\left[H^2\right]$$

which is invariant. However, this particular transformation has increased the sum of the squares of the diagonal elements by $2H_{ij}^2$:

$$\sum_{m} (H'_{mm})^2 = (\text{Tr } H')^2 - \sum_{m \neq n} H_{mm} H_{nn}$$

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The invariance of the trace and determinant imply

$$\text{Tr } H' = \text{Tr } H$$

$$H'_{ii} H'_{jj} = H_{ii}H_{jj} - H^2_{ij}$$

so that

$$\sum_m (H'_{mm})^2 = (\text{Tr } H)^2 - \sum_{m \neq n} H_{mm} H_{nn} + 2H^2_{ij}$$

$$= \sum_m (H_{mm})^2 + 2H^2_{ij}$$

Weight has been shifted to the diagonal and, if for each 2×2 transformation the largest off-diagonal element is made to vanish, the process will converge. The total orthogonal transformation is the product of all the 2×2 transformations, and is calculated in parallel with the diagonalization. After each reduction, and beginning with a unit matrix, u is multiplied into the orthogonal matrix constructed up to that point, affecting only the ith and j^{th} columns. H is considered diagonal when the absolute largest off-diagonal element is less than a prescribed criterion.

In the machine, the upper half of the symmetric matrix is stored in fast storage, the orthogonal matrix is kept on the drum. The routine is amazingly fast and accurate, and exists as both a sub-routine and a production style program.

Complex Hermitian matrices have to be handled by enlargement. Let

$$H = A + iB$$

where A is real symmetric, B real antisymmetric. The eigenvalue-eigenvector equation reads as

$$(A + iB)(x + iy) = \lambda(x + iy)$$

or

$$Ax - By = \lambda x$$
$$Bx + Ay = \lambda y$$

The last two equations can be written in enlarged matrix form as

$$\begin{vmatrix} A & -B \\ B & A \end{vmatrix} \begin{vmatrix} x \\ y \end{vmatrix} = \lambda \begin{vmatrix} x \\ y \end{vmatrix}$$

so that a real symmetric matrix is to be diagonalized.

The routine has been called for, of course, in those theories which approximate a wave function as a linear combination of orthogonal functions. The configuration interaction in the oxygen molecule, considered by the writer, was analyzed on Whirlwind. Kaplan's treatment of the ammonia molecule will require the solution of a 14×14 secular equation. For his tight binding computation, Koster took the subroutine, added a program which calculated the matrix elements, and ran through 220 independent points in k-space for the body-centered structure, 680 points for the face-centered. It should be realized that the ability to handle large matrices, once they exist, is not enough. There is the awful problem of the matrix elements, as to computation and transcription. The program written for Schultz, to be described in some detail, is lovely in the absolute minimum of input required for the mechanization of the theory. *

The existence of a fast and accurate diagonalization sub-routine makes feasible many other matrix computations. Determinants can be evaluated as the product of the eigenvalues. It seems best to evaluate any invariant of a matrix by first diagonalizing the matrix and then forming appropriate products of the eigenvalues. The calculation of the inverse of a matrix (or the square root of the inverse) has been programmed in this way. The matrix is first brought to diagonal form, the reciprocals of the diagonal elements are taken (or the square roots of the reciprocals), and then this diagonal inverse is brought back to non-diagonal form by the reverse of the orthogonal transformation. This inversion routine is in sub-routine form and in complete production style form. As a sub-routine it was incorporated into the impurity level calculation of Koster. He recognized a Green's function as the inverse matrix $(H - E)^{-1}$, where H is the unperturbed Hamiltonian and E is the sought energy level. The problem is solved in the space of a finite number of Wannier functions so that H becomes a finite matrix. For the body-centered structure 16 values of E were inserted for each of the 220 points in k-sapce.

The square root inversion routine was useful in the orthogonalization of a set of functions, and in the solution of the secular equation arising among a set of non-orthogonal functions. If a trial wave function be expressed as a linear combination of non-orthogonal functions

$$u_i(x) = \sum_j v_j(x) a_{ji}$$

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*The work of the Whirlwind users mentioned here is reported in the Progress Reports of this group and in the publications listed at the beginning of these reports biannually.

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the eigenvalue-eigenvector equation reads as

$$\sum_j H_{ij} a_{jk} = \sum_j S_{ij} a_{jk} E_k$$

with the side condition

$$\sum_{m,n} a^*_{mi} S_{mn} a_{nj} = \delta_{ij}$$

where H_{ij} is a matrix element of the Hamiltonian and S_{ij} is an overlap matrix element

$$H_{ij} = \int v_i^*(x) \, H \, v_j(x) \, dx$$

$$S_{ij} = \int v_i^*(x) \, v_j(x) \, dx$$

In matrix notation the simultaneous equations are

$$HA = SAE$$

$$A^\dagger S A = 1$$

Following a suggestion of Löwdin (M.I.T. lectures) define

$$U = S^{+1/2} A$$

so that

$$U^\dagger U = 1$$

$$(S^{-1/2} H S^{-1/2}) U = UE$$

and an ordinary secular equation is to be solved. * A program which carries out this Löwdin scheme has been written. As a production style routine it was used by McWeeny in his valence bond studies, and as a sub-routine it was used by Howarth in the last stage of the augmented plane wave method, and by Corbató in his tight binding calculation on graphite.

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*$S^{-1/2}$ is defineable since $S = V^\dagger V$ where $V_{xj} = v_j(x)$. S is therefore Hermitian and, if the columns of V are independent, positive definite.

Integrals that are needed in the molecular calculations done here are first evaluated among the basic set of atomic orbitals. The molecular orbitals, out of which are compounded the many-electron functions, are linear combinations of the atomic orbitals. The integrals which appear in matrix elements are integrals among the molecular orbitals. These are derived from the atomic orbital integrals by means of a congruent transformation $U^t A U$, where A is a suitably ordered matrix of atomic integrals, and U is a matrix whose elements are quadratic forms in the coefficients of the linear combinations.[1] A congruent transformation program exists in production style; it has been used by McWeeny and by Kaplan. As a prerequisite to it, a matrix multiplication sub-routine was written.

Special Programs

A colossal program to carry out the augmented plane wave method for copper was written by Howarth, and is being further developed by Saffren for application to sodium. From this specific program certain sub-routines can be pulled out for use elsewhere: Simpson's rule, generation of $P_l(\cos \theta)$, generation of spherical Bessel functions, and Gauss-Jackson numerical integration.

The adaptation to Whirlwind of Roothaan's self-consistent L. C. A. O. method is another large and specific program. It has been used by Kaplan for the ammonia molecule and will be used by Allen in his polarization study.

Finally, there is the program for the electron-lattice interaction model by Schultz. The model treats one otherwise free electron in interaction with the field of two degenerate lattice oscillators. The wave function of the system is expanded in a set of functions each belonging to the same total momentum, which is a good quantum number, and each distinguished by the number of quanta in the oscillator field. There are three parameters that Schultz wishes to vary independently and widely: the total momentum (η), the oscillator momentum (a), the coupling constant (γ). For each set of η, a, γ the convergence of the energy levels is to be followed as states of higher occupation numbers are brought in. The energy matrices, though large and many, can be computed easily by hand; there are an enormous number of zero elements and not many independent varieties of the non-zero ones. The matrix which allows up to three quanta in the field is shown in Fig. 6-1. The angle shaped lines are boundaries between states of different occupation numbers. Each occupation number brings in that number plus one new states -- the number of ways to distribute the quanta between the two oscillators.

Now, all these zeros, which present no computational problem, nevertheless would have to be written down on tape preparation forms, typed and punched out on paper tape, passed through the photoelectric reader on equal footing with the other numbers. Easy arithmetic though it may involve, the hand computation, transcription,

typing, and read in of the matrices, would be time consuming and greatly susceptible to error. The matrices must be formed in the machine. But is the machine to go along through the matrix, set itself at an i, j position, ask if the number to be inserted is zero, and if it is not, is the machine then to refer to a dictionary, somehow planted in storage which will direct it to a set of operations suitable to that value of i, j? This now rhetorical question was answered with a no. A block of registers can be cleared immediately by the program. There is no need to insert zero elements or even to pass through them. Rather than pick a position and decide what is to be placed there, pick up what is to be placed and decide where. This is how the program works: The problem has been solved up to a certain number of quanta and now the matrix is to be augmented by the introduction of states with one more quantum. Let m be this number of quanta plus one. The order of the matrix

$$n = \frac{m(m + 1)}{2}$$

The new off-diagonal elements are all of the form $\sqrt{k\gamma}$.

$$k = k_{max} - q$$

where

$$k_{max} = m - 1$$

and

$$0 \leqslant q \leqslant m + 2$$

Each k goes into two positions given by

$$j_q = j_o - q \qquad\qquad i_q = j_q - m$$

$$j_q' = j_o - (m - 1) + q \qquad\qquad i_q' = j_q' - (m + 1)$$

where

$$j_o = n - 1$$

The gross cycle is the one on m as it is set to increasing values beginning with m = 2. (The case of no quanta is a special one whose 1 × 1 matrix is computed

	0	1	2	3	4	5	6	7	8	9
0	η^2	$\sqrt{1}\gamma$	$\sqrt{1}\gamma$							
1		$2+(\eta-a)^2$		$\sqrt{2}\gamma$	$\sqrt{1}\gamma$					
2			$2+(\eta+a)^2$		$\sqrt{1}\gamma$	$\sqrt{2}\gamma$				
3				$4+(\eta-2a)^2$			$\sqrt{3}\gamma$	$\sqrt{2}\gamma$		
4					$4+(\eta)^2$			$\sqrt{1}\gamma$	$\sqrt{1}\gamma$	
5						$4+(\eta+2a)^2$			$\sqrt{2}\gamma$	$\sqrt{3}\gamma$
6							$6+(\eta-3a)^2$			
7								$6+(\eta-a)^2$		
8									$6+(\eta+a)^2$	
9										$6+(\eta+3a)^2$

Fig. 6-1

Schultz's matrix for $m_{max} = 4$

(Only the upper half of the symmetric is shown. Zero elements are left blank.)

immediately.) Pick an m. From this find n and k_{max}. Establish j_o. Set up a q counter and place the off-diagonal elements. The diagonal elements are of the form

$$t + \left[\eta + (\frac{t}{2} - 2q)\,a\right]^2$$

where $t = 2(m - 1)$ and $0 \leqslant q \leqslant \frac{t}{2}$. The address of the diagonal element is n - 1 - q, n - 1 - q.

The program input consists of m_{max}, η, a, γ. m begins at 2 and runs up to the m_{max} decided on by Schultz. Because the triangular Hermitian matrix has to be in fast storage, and because it would be costly timewise to break up the program into small bits which are transferred from the drum, the m_{max} cannot exceed 7, which corresponds to a maximum matrix order of 28.

The only apology that I can offer for going into the pattern of this program is that it was exciting to analyze, and I hope that the inversion of thought in the matrix formation will prove to be good experience for other problems.

Reference

1. This technique is described in the Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 28 and p. 32.

A. Meckler

7. APPLICATIONS OF WHIRLWIND TO PROBLEMS OF MOLECULAR AND SOLID-STATE PHYSICS

In the following report, various applications of the Whirlwind I computer to problems of molecular and solid-state physics are discussed in an attempt to illustrate the high versatility of such a machine. Inasmuch as the potentialities of high-speed computers are still not too well defined, the numerical techniques are sketched in some detail in order to indicate the scope of reasonable coding procedures. It is hoped that in this indirect fashion, it will be possible to display some of the shifts in numerical emphasis allowed by a modern computer.

Function Generators

In coding a problem for a digital computer, there often arises the need of knowing the value of a function for a given argument. There are two usual solutions to this problem: One may either use a table of the function values and an interpolation scheme if the values of the argument are non-uniform, or one may use a generation subroutine each time to form the function value from the argument. If the function varies rapidly over the range of the argument, or if many functions are required, the table method will require a great deal of the storage space in the computer. On the other hand, generation of a complicated function can be a time-consuming process even on a high-speed computer. In any case the problem of reading tables of function values into the computer is a serious one, for the unsatisfying task of proofreading is the only easy way to eliminate errors among the entries. Thus function generators are extremely useful in the coding of most problems, either in direct use or as the preliminary generators of tables for interpolation.

Because of their widespread application, the ordinary functions such as $\sqrt{x}$, $\sin x$, $\cos x$, $\sinh x$, $\cosh x$, $\exp x$, and $\ln x$ are available in the Whirlwind Subroutine Library which has been prepared by the computer staff. In general, when coding problems, these relatively simple functions are best obtained by the direct use of the generation subroutines.

In the writer's current work on the energy bands of graphite, the need arose for evaluating various types of two-center integrals involving analytic Slater AO's. By the use of prolate spheroidal coordinates, these integrals were all simple expressed in terms of the two sets of functions

$$C_n(x) \equiv x^{n+1} e^x \int_1^\infty t^n e^{-tx}\, dt = n! \sum_{j=0}^{n} \frac{x^j}{j!}$$

$$B_n(y) \equiv \int_{-1}^{1} t^n e^{-ty}\, dt = -\frac{1}{y^{n+1}} \left[e^{-y} C_n(y) + e^y C_n(-y) \right]$$

$$n:\ 0(1)\,N\ \begin{cases} 0 < x < \infty \\ -\infty < y < \infty \end{cases}$$

where x, y, and N are fixed for any particular integral. Since all ordinary two-center integrals of the Slater AO's (except exchange and hybrid integrals) are simply expressed in terms of the C_n and B_n, a general subroutine has been programmed for the generation of the two sets of functions for given x, y and N. Extensive application of this subroutine has been made by the writer and by Dr. A. Dalgarno of Queen's University Northern Ireland who was visiting M.I.T. this past summer.

It is perhaps interesting to examine in some detail the method used in coding the above subroutine, since it is illustrative of the numerical techniques which are applicable in a high-speed computer. The functions $C_n(x)$, being simply polynomials in x which is always positive, are sums with all positive terms, and thus offer no numerical cancellation problems. For greater computational efficiency though it is convenient to use the recursion formula

$$C_n(x) = x^n + n\,C_{n-1}(x)$$

to form the functions of higher n successively from $C_0(x) = 1$. The functions, $B_n(y)$, however, are considerably more difficult in that for the magnitude of y approximately less than n, the closed form given above has large numerical cancellations. To avoid this the following reformulation was made:

$$B_n(y) = 2(-1)^n \frac{d^n}{dy^n}\left[i_0(y)\right] = 2(-1)^n\,n!\ \sum_{j=0,1}^{n}{}' \frac{(2j+1)}{(n-j)!!\,(n+j+1)!!}\,i_j(y)$$

where

$i_n(x) \equiv (-\iota)^n\,j_n(\iota x)$ = spherical Bessel function of the first kind with imaginary argument (i.e. "modified spherical Bessel function")

$n!! \equiv n(n-2)(n-4)\ldots(2\ \text{or}\ 1)$

$\sum'$ = sum over: j even if n even; j odd if n odd.

Because the sign of $i_j(y)$ is always the same as that of y^j, it follows that the $B_n(y)$ are expressed as a sum of terms which are all positive or all negative. Now the power series for $i_N(y)$ and $i_{N+1}(y)$ converges rapidly when $20 \geqslant N \geqslant |y|$ and moreover contains terms of only one sign. Furthermore, the recursion relation,

$$i_{n-1}(x) = \left(\frac{2n+1}{x}\right) i_n(x) + i_{n+1}(x)$$

when used downward in n, does not contain cancellations so that significant figures are maintained. Thus the $B_n(y)$ are determined by numerically accurate methods for all $|y| \leqslant N$. For $|y| \geqslant N$, it was found empirically that the closed form is adequate. Finally, the round-off error propagation was minimized by appropriate use of buffer (i.e. higher accuracy) storage registers. Spot checks of the generated functions for various x and y indicated 6 to 7 significant figure accuracy for $N \leqslant 20$.

Inasmuch as it was a relatively simple modification of the preceding subroutine, a second subroutine has been developed for generating the set of $i_n(x)$ where n: 0(1) N. These modified spherical Bessel functions occur in the expansions often used in the evaluation of multicenter integrals and moreover in K. Ruedenberg's method of evaluating two-center exchange integrals of Slater AO's.[1] A general program for the latter method is currently being coded for Whirlwind by P. Merryman and K. Ruedenberg as a part of the general two-center integral evaluation program of Mulliken's group at the University of Chicago.

One-Electron, Two-Center Integrals[2]

Since a large number of one-electron, two-center integral values were desired by the writer and because such integrals occur often in other molecular calculations, a general production-style program was written. This program depends primarily on the C_n and B_n generation subroutine described earlier and allows the calculation of one-electron integrals involving wave functions which can be expressed as a linear combination of an arbitrary number of 1s, 2s, and 2p Slater AO's (e.g. a fitted HF wave function). Furthermore, by expressing potential functions in the form,

$$\frac{Z_p(r)}{r} = \frac{1}{r} \sum c_i e^{-d_i r}$$

the program can also be used to evaluate all of the potential-type one-electron integrals. The program in its final form can be manually modified in a trivial way by the computer operators to give any of the possible integral types (i.e. overlap, kinetic energy, etc.). The user gives as input data a listing of the composition of the wave functions (and potential, if required) in terms of the Slater AO parameters and coefficients. The results consist of a printed list containing the integral type, the integral value, and the wave function and potential compositions, so that identification is complete and data input mishaps are obvious. A major advantage of the program is that the lengthy intermediate results are processed without error within the machine and need not be brought out of the computer.

Fitting of HF Wave Functions[2]

Another application of Whirlwind has been a partial mechanization of the process of fitting a HF wave function with exponentials. The technique developed is an iterative one and is only suitable for a high-speed computer. After removing radial factors or r and node factors, $r_o - r$, from the tabulated HF wave function, there remains the exponential-like function, $E(r_l)$. For an n-exponential fit, n pairs of r_i' and r_i'' are chosen from the different regions of r_l such that $r_1' > r_1'' > r_2' > r_2'' > \ldots > r_n' > r_n''$. If we define

$$E^j(r) \equiv \sum_i a_i^{\,j} \exp(-b_i^{\,j} r)$$

to be the jth approximation to $E(r)$, then the following prescription of cyclical equations can be given where an iteration is comprised of i successively assuming the values from 1 to n. Defining

$$D^j(r_i) \equiv E(r_i) - (1 - \lambda^j)\left[\sum_{k < i} a_k^{j+1} \exp(-b_k^{j+1} r_i) + \sum_{k > i} a_k^{\,j} \exp(-b_k^{\,j} r_i)\right]$$

then

$$b_i^{j+1} = (r_i'' - r_i')^{-1} \ln\left[\frac{D^j(r_i')}{D^j(r_i'')}\right]$$

$$a_i^{j+1} = D^j(r_i') \exp(b_i^{j+1} r_i')$$

where

$$a_i^{\,o} = b_i^{\,o} = 0, \quad 0 < \lambda < 1$$

Examination of these equations reveals that as j increases to a large value, J, the coupling factor, $1 - \lambda^j$, approaches unity, and the cyclical equations express the 2n conditions of

$$E^J(r_i') = E(r_i') \text{ and } E^J(r_i'') = E(r_i'')$$

Thus, if λ is not too much smaller than one and J is large enough, the set of $a_i^{\,j}$ and $b_i^{\,j}$ will smoothly approach the desired parametric values. For convenience, after convergence is attained, the error function, $E^J(r_l) - E(r_l)$, is automatically plotted and photographed on the oscilloscope camera. From the shape of the error curve, new choices of the fitting points, r_i' and r_i'', can be made and with a few re-runs,

optimization of the fit can be essentially attained. Empirically it appears that all HF wave functions can be fitted in this manner.

Generation of Matrix Elements

In view of the previous remarks concerning function generation, it is obvious that similar conclusions can be drawn concerning the generation of matrix elements in secular equation problems. In particular, when using the tight binding scheme in crystal problems, it is usually possible to cast the matrix elements in the general form of

$$H_{ij} = \sum_{\vec{R}_l} \left[C_{ij}(\vec{R}_l)(\cos \vec{k} \cdot \vec{R}_l) + D_{ij}(\vec{R}_l) \sin (\vec{k} \cdot \vec{R}_l) \right]$$

In writing a program for a specific crystal structure, one includes the properties of the $C_{ij}(\vec{R}_l)$ and $D_{ij}(\vec{R}_l)$. Consequently, one need only specify $\vec{k}$, the Brillouin zone vector, to completely generate the desired matrix to be solved in a secular equation. This procedure is found to be especially convenient in the writer's current work on graphite since the S and H matrices arising in the non-λ type secular equation, HX = SXλ, both have the same generation properties.

References

1. K. Ruedenberg, J. Chem. Phys. 19, 1459 (1951).
2. For further discussion, see F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 49.

F. J. Corbató

8. LIMITED CONFIGURATION INTERACTION TREATMENT OF THE NH_3 MOLECULE

The determination of molecular orbitals for the ammonia molecule as best linear combinations of atomic orbitals has been completed for both the equilibrium case and the planar case. Meckler's mechanization[1] of Roothaan's formalism[2] was used for this process. The criterion of self-consistency used was

$$\frac{E_n - E_{n-1}}{E_n} < 10^{-4},$$

where E_n is the total molecular energy after the nth cycle. The digital computer (Whirlwind) went through approximately forty cycles in order to achieve consistency.

The results are generally quite gratifying. For the equilibrium case the calculated binding energy, .840 a.u., is about 90 percent of the observed value, .930 a.u. The hump in the curve of molecular energy versus distance of the nitrogen atom from the plane of the hydrogens however is wrong by an order of magnitude: calculated .358 a.u., observed .019 a.u. Some error in this direction was expected due to the fact that the equilibrium N - H distance was used for the planar calculation. However, such a large error was not foreseen.

The one-electron functions exhibit the expected behavior. For each symmetry type there is one orbital somewhat concentrated between the nitrogen and the hydrogen plane which is occupied, and one exhibiting a node in this region which is unoccupied. For A_1 symmetry there is also a function which is primarily directed away from the binding region (Lennard-Jones lone pair) and a function consisting almost entirely of nitrogen 1 - s.

The results of the calculation are now being analyzed in more detail. In addition, preparation is being made to use the molecular orbitals as the basis of a limited configuration interaction described earlier.[3]

References

1. A. Meckler, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1954, p. 39.
2. C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).
3. H. Kaplan, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1953, p. 36.

H. Kaplan

9. VALENCE BOND THEORY. SIMPLE SATURATED MOLECULES

The revised valence bond theory, developed elsewhere[1,2] and already applied to the π-electron systems of simple conjugated molecules,[3] is now being applied in non-empirical calculations on simple saturated molecules. A preliminary treatment of the water molecule has been completed and calculations on ammonia are in progress. Both these molecules have been studied previously,[4,5] using the approximate self-consistent field (SCF) scheme,[6] reasonable binding energies being obtained. The present calculations have a different object; they are concerned with the following questions: (1) Can the valence bond approach lead more directly to results comparable with, or better than, those of SCF MO theory? (2) Can the directed "hybrid" orbitals, commonly employed in empirical valence theory, be used to advantage for this purpose? (3) Is it possible to use a model in which some electrons occupy a "closed shell" (composed of atomic inner shells and "lone pairs") and simply provide an effective field for those held responsible for binding?

The procedure being followed will be illustrated by the case of H_2O. The guiding principle upon which the qualitative interpretation of chemical valence and stereochemistry is usually based is that of "maximum overlapping" -- crudely put, bonds are best described by using those orbitals of the different atoms which overlap most strongly, and this principle is well founded insofar as the use of such orbitals provides a simple and direct way of describing an accumulation of electron density in the bond regions. In describing H_2O then, where the bond angle is considerably greater than the 90° between 2p orbitals, we first imagine the oxygen atom "promoted" from the ^3P ground state not to the valence state $(2s)^2 (2p_x)^2 (2p_y)^1 (2p_z)^1$ but to $(t_3)^2 (t_4)^2 (t_1)^1 (t_2)^1$ where t_1, t_2 are combinations of the 2s and 2p orbitals which "point" towards the hydrogen atoms H_1 and H_2 (see Fig. 9-1) so as to procure greater
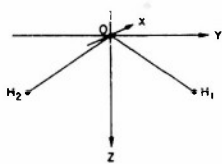

overlap with their 1s orbitals, h_1 and h_2 and t_3, t_4 are the residual orbitals, determined by symmetry and orthogonality, pointing away from the hydrogens and describing the lone pairs. We employ these orbitals in a preliminary treatment not because they are necessarily the most suitable, but because they are easily set up and chemically plausible; their deficiencies can always be corrected, if need be, by configuration interaction.

Fig. 9-1

Denoting oxygen orbitals by S, S, X, Y, Z, the following symmetry orbitals may be defined

$$S, \ S, \ Z, \ \sigma_1 (= 2^{-1/2}(h_1 + h_2)) \ : \ Y, \ \sigma_2 (= 2^{-1/2}(h_1 - h_2)) \ : \ X$$

where σ_1, σ_2 are left unnormalized since it is convenient to have them related to h_1 and h_2 by a <u>unitary</u> transformation. This basis of orbitals, which we shall denote by the row matrix $(A) = (S, S, Z, \sigma_1, Y, \sigma_2, X)$, is the one used by Ellison and Shull

who computed all the necessary integrals. We must now transform to the basis (a) = $(\mathcal{S}, t_1, t_2, t_3, t_4, h_1, h_2)$: writing (A) = (a)(T), the unitary matrix (T) is very easily determined. The straightforward VB procedure would now be to set up a spin eigen-function with orbitals t_1, h_1 and t_2, h_2 singly occupied and having "paired" spins -- this single "structure" representing the approximation of "perfect pairing": this course is complicated by the lack of orthogonality of the orbitals; but, as we have seen, [3] is certainly included in a "$\overline{VB}$" treatment where the orthogonalized orbitals $\overline{t}_1$, $\overline{t}_2$ -- are employed and "polar" structures (in which orbitals may be empty or doubly occupied) are admitted and the $\overline{VB}$ calculation can be carried out without the usual approximations of VB theory. We therefore form, from (a), a set of orthonormalized orbitals $(\overline{a})$, by the Löwdin method, i.e., $(\overline{a}) = (a)(S_a)^{-1/2}$. Here (S_a) is the matrix of overlap integrals (metrical matrix) for the (a) basis and is related to that for the (A) basis by $(S_a) = (T)(S_A)(T)^{\dagger}$: since (T) is unitary $(S_a)^{-1/2} = (T)(S_A)^{-1/2}(T)^{\dagger}$ and it follows that the orthonormalized AO's (directed AO's included) are related to the symmetry orbitals by $(\overline{a}) = (A)(\mu)$ where $(\mu) = (S_A)^{-1/2}(T)^{\dagger}$. All integrals referred to the (a) basis may now be expressed in terms of those given by Ellison and Shull.

The next step in the $\overline{VB}$ calculation is to set up suitable $\overline{VB}$ structures in terms of the $\overline{AO}$'s. First we limit ourselves to those in which $\overline{\mathcal{S}}$, $\overline{t}_2$ and $\overline{t}_3$ are doubly occupied, and we deal explicitly only with the electrons occuping $\overline{t}_1$, $\overline{t}_2$, $\overline{h}_1$ and $\overline{h}_2$, us- ing an <u>effective</u> one-electron Hamiltonian, h, which takes into account the closed shell, instead of that for an electron in the field of the bare nuclei (f, say). This is a quite legitimate reduction (see Ref. 2) so long as we keep to configurations showing a filled closed shell and leads effectively to a four-electron problem. The effective Hamilton- ian h may be defined by its matrix elements between two of the valence orbitals, p and q say:

$$(p|h|q) = (p|f|q) + 2 \sum_x (xp|g|xq) - \sum_x (xp|g|qx)$$

where x is a closed shell orbital and summations are over all orbitals of the closed shell $(\overline{\mathcal{S}}, \overline{t}_3, \overline{t}_4)$. The energy calculated from the four-electron problem is then relative to a closed shell or "framework" energy

$$E_f = 2 \sum_x (x|f|x) + \sum_x (xx|g|xx) + 4 \sum_{xy} (xy|g|xy) - 2 \sum_{xy} (xy|g|yx)$$

summations again being over the closed shell (counting distinct <u>pairs</u> xy). The four- electron $\overline{VB}$ structures employed so far are shown, with an obvious symbolism, in Fig. 9-2. The first five are the "obvious" ones which would arise as the dominant terms in expansion of the perfect pairing approximation into $\overline{VB}$ structures, and which, in the charge-hopping interpretation should be capable of describing the two O-H bonds.
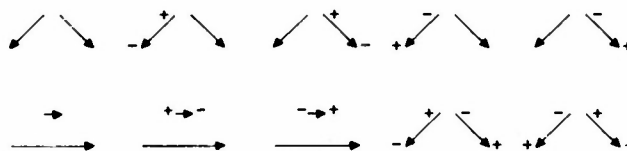
-32-

Fig. 9-2

The remainder correspond to intra-atomic atomic spin pairings and double "excitations" but either have low "energies" (diagonal matrix elements) or interact strongly with the first five. Thus, the "resonance" integral $(p|h|q)$, is associated with binding in the overlap region of p and q containing the interaction energy of the nuclei and a charge distribution pq in this region and governs the interaction between structures which show a charge shift between p and q. As anticipated, it is very large for the strongly overlapping orbitals of the bonds, but is small otherwise (e. g. when p and q belong to different bonds), and consequently structures showing intra-atomic charge shifts (Fig. 9-2) or crossed links should participate only weakly, doing little to stabilize the molecule. But the doubly polar structures are likely to be important -- though we are still omitting those showing a "doubly ionized" oxygen atom, which lie rather higher in energy.

This general picture is supported by the actual calculations. Unfortunately, detailed numerical results are not on hand (the writer being at present en route to King's College, Newcastle-on-Tyne, England) but the following qualitative conclusions are worthy of note.

There is no difficulty in handling the $\overline{VB}$ calculation by the methods already developed. The only real computational obstacle is the transformation to integrals over the $\overline{AO}$'s, and this is easily mechanized[6] being performed on Whirlwind in a very few minutes once the (28×28) matrices have been written down. * The iterative SCF procedure is replaced by the solution of a final secular determinant -- again easily mechanized -- and there is little doubt that the accuracy of the SCF result could be surpassed without too much trouble by adding a few more structures (e. g. breaking into the closed shell). But the whole object of these calculations was to find a simple way of setting up good wave functions, making use of the basic chemical concepts of directed valence and lone pairs and without any appeal to existing knowledge (e. g. the SCF results themselves), and from this point of view the results are not altogether encouraging. The decrease in total electronic energy, accompanying molecule formation, is found to be about 95 percent of that predicted using the full SCF method (and the wave function might therefore be reasonably good); but this decrease is completely offset by the increase in internuclear repulsion energy and the last 5 percent is found

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*I am indebted to Dr. Meckler for the use of his machine program for this purpose.

to be crucial in getting a binding energy. This is a familiar situation in binding energy calculations -- the electronic energy is good but the binding energy is very poor. The reason for this failure, however, does not lie wholly in the inadequacy of the $\overline{VB}$ structures selected, for at the outset we made a somewhat arbitrary choice of orbitals, upon which to base the limited configuration interaction calculation. Indeed, it is likely that the use of differently directed orbitals (describing "bent" or "strained" bonds) would have led to an improvement of the required order still within the framework of a closed-shell model with a simple chemical interpretation (inner shell, two lone pairs, two bonds). This belief, that the basic orbitals themselves are considerably at fault, was strengthened by making a limited SCF MO calculation, using one determinant based on the configuration $(\overline{S})^2$, $(\overline{t}_3)^2$, $(\overline{t}_4)^2$, $(\overline{T}_1)^2$, $(\overline{T}_2)^2$, where $\overline{T}_1 = N(\overline{t}_1 + \lambda \overline{h}_1)$ and $\overline{T}_2 = N(\overline{t}_2 + \lambda \overline{h}_2)$.

The only parameter admitted -- λ, which describes the polarity of the O-H bond and upon which the energy is quite strongly dependent -- was directly varied and the final minimum value was found to be no better than that reached in the $\overline{VB}$ calculation.

These results therefore suggest that a simple approach, in which attention is focussed upon the individual bonds, cannot be quantitatively successful unless the bond orbitals (localized MO's) of an MO treatment or the directed orbitals of a VB (or $\overline{VB}$) treatment are chosen with extreme care. Unless this can be done (as, in effect, it is in a full SCF treatment where none of the orbitals are chosen arbitrarily) there seems to be no alternative but to employ a "hammer and tongs" approach in which more and more configurations are thrown in to correct for an inappropriate choice. There can be no doubt that this procedure is feasible (many more configurations were handled in the calculations on benzene[3]) and the final results can always be given a simple pictorial interpretation by shifting attention onto the actual charge density (which can be calculated in many-configuration theories by the methods described elsewhere.[3, 7] But this is a clumsy way of getting a solution and it is to be hoped this procedure can be largely obviated by using intuition and previous experience in choosing more satisfactory basic orbitals. Again, it seems that a semi-empirical development is suitable; for binding is primarily associated with a few large integrals and these might well be regarded as disposable constants and the basic orbitals themselves would then no longer play a crucial part in the calculations.

The writer would like to take this opportunity of recording his gratitude to Professor Slater, and to members of the Solid-State and Molecular Theory Group, for the hospitality he has enjoyed at the Institute and for the benefit of many discussions during a most happy and stimulating year.

References

1. R. McWeeny, Proc. Roy. Soc. (London) A223, 63 (1954).

2. R. McWeeny, Proc. Roy. Soc. (London) A223, 306 (1954).

3. R. McWeeny, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., July 15, 1954, p. 31; Proc. Roy. Soc. (in the press).

4. F. Ellison and H. Shull (unpublished).

5. H. Kaplan (unpublished).

6. R. McWeeny, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., April 15, 1954, p. 31.

7. R. McWeeny, Technical Report No. 7, Solid-State and Molecular Theory Group, M. I. T. (in preparation).

R. McWeeny

10. NATURAL ORBITALS FOR THE HELIUM ATOM

In his contribution to the last Quarterly Progress Report, P. O. Löwdin[1] introduces the concept of natural orbitals and discusses some of their interesting properties. He introduces them in the following manner. We imagine that we are trying to approximate the solution of an n electron problem with a Hamiltonian containing the usual kinetic and potential energy terms. In order to approximate the solution to this problem, we form antisymmetric states formed by taking linear combinations of Slater determinants each containing n one-electron spin orbitals selected from N spin orbitals, $\psi_1 \ldots \psi_N$. If we call the wave function described above $\Psi(x_1 \ldots \ldots x_n)$, a first order density matrix can be defined as

$$\gamma(x_1'|x_1) = N \int \Psi^*(x_1', x_2 \ldots x_n) \Psi(x_1, x_2 \ldots x_n) \, dx_2 \ldots dx_n \qquad (10.1)$$

This density matrix can be written in terms of our one-electron spin orbitals in the form

$$\gamma(x_1'|x_1) = \sum_1^N (k, \ell) \psi_k^*(x_1') \psi_\ell(x_1) \gamma_{\ell k} \qquad (10.2)$$

Here the constants $\gamma_{\ell k}$ consist of some forms in the constants that multiply the determinants in the wave function Ψ. If we go to another basis in the one-electron functions by a unitary transformation, we shall induce a unitary transformation on the coefficients $\gamma_{\ell k}$. Let us call the transformed functions

$$\phi_k = \sum(\alpha) \psi_\alpha U_{\alpha k} \qquad (10.3)$$

We can now look for the transformed density matrix which is diagonal. That is we can choose our unitary transformation such that

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

$$\gamma(x_1'|x_1) = \sum(k) n_k \phi_k^*(x_1') \phi_k(x_1) \qquad (10.4)$$

We can see that in general the natural spin orbitals will mix the original spin orbitals of α and β spin. Under the simplifying assumption that our total wave function Ψ has M_S (total z component of the spin) as a good quantum number this will not be the case since the density matrix $\gamma_{\ell k}$ will be blocked off into two parts. The one part we might denote as $\gamma_{\ell k}^+$ and the other part we shall call $\gamma_{\ell k}^-$. The constants $\gamma_{\ell k}^+$ are the coefficients of the products of orbitals with α spin in (3.2) and the $\gamma_{\ell k}^-$ are the coefficients of products of orbitals with β spin. There are no cross terms in this case. The reason for this can be seen by considering the origin of any term in the

expansion of the density matrix (10. 2). Any term in the sum in (10. 2) will arise from the integration of the product of two Slater determinants over $n - 1$ coordinates. If $\Psi_k(x_1')$ has α spin and $\Psi_\ell(x_1)$ has β spin the integration over the coordinates $x_2 \ldots x_n$ will yield zero since the integral over spins will be the integral of the product of two functions, one having spin $M_S + 1/2$ and the other having total spin $M_S - 1/2$. Since our density matrix is blocked off into two parts, one for α and the other for β spin, the unitary transformation which diagonalizes this matrix will also be blocked off. We shall thus have no mixing of α and β spin orbitals.

Part of the hope that Löwdin expressed in connection with the natural orbitals was that a configuration interaction treatment of the problem of the many-electron system would be more rapidly convergent in terms of the natural orbitals. In order to study the natural orbitals in a simple case and to study the convergence of the configuration interaction in terms of natural orbitals, it was decided to carry out a simple calculation on the helium atom.

For one-electron orbitals a 1s and a 2s wave function were chosen in the form

$$u_1 = \left[2/\sqrt{4\pi}(Z')^{3/2} \right] e^{-Z'r}$$

$$u_2 = \left[1/(2\sqrt{2}\sqrt{4\pi}) \right] (Z')^{3/2} (2 - Z') e^{-\frac{Z'r}{2}} \tag{10.5}$$

By making all possible ^1S states for this two-electron problem we arrive at three possible configurations: $(1s)^2$, $(1s2s)$, $(2s)^2$. Our many-electron wave function is now expressed as a sum of three terms

$$\Psi(x_1, x_2) = c_1(1s)^2 + c_2(1s2s) + c_3(2s)^2 \tag{10.6}$$

The expectation value of our Hamiltonian was taken with respect to this wave function for a given value of the effective charge Z' and the values of the energy and the c's were determined.[2] It was found that the best value of Z' was roughly 28/16 and that for this value the c's and the energy were

$$E = -5.70939$$

$$c_1 = .993173$$

$$c_2 = -.115706$$

$$c_3 = -.014819 \tag{10.7}$$

Table 10-1 contains a comparison of the energy obtained in this way with the Hartree-Fock energy, the experimental energy and the best possible energy obtainable from a

(NATURAL ORBITALS FOR THE HELIUM ATOM)

$(1s)^2$ configuration with the wave function of the type (10.5).

Table 10-1

Energy of the helium atom by various approximations
(energies in Rydbergs)

Experimental	- 5.80736
Hartree-Fock	- 5.75
$(1s)^2$ $Z' = 27/16$	- 5.6953
$(1s)^2 + (1s2s) + (2s)^2$ $Z' = 28/16$	- 5.709394

Knowing the wave function obtained in this manner it is possible to construct a density matrix for this problem.

$$\gamma(x_1|x_1') = .993085\, u_1(1')\, \alpha(1')\, u_1(1)\, \alpha(1) + .006914\, u_2(1')\, \alpha(1')\, u_2(1)\, \alpha(1)$$

$$- .080045\, u_1(1')\, \alpha(1')\, u_2(1)\, \alpha(1) - .080045\, u_2(1')\, \alpha(1')\, u_1(1)\, \alpha(1)$$

+ identical terms with all α's replaced by β's. (10.8)

Therefore

$$\gamma_{11}^+ = \gamma_{11}^- = .993085$$

$$\gamma_{12}^+ = \gamma_{21}^+ = \gamma_{12}^- = \gamma_{21}^- = -.080045$$

$$\gamma_{22}^+ = \gamma_{22}^- = .006914 \tag{10.9}$$

We notice here the factoring of the density matrix into a plus spin part and a minus spin part which we mentioned earlier. We also notice that the plus and minus spin parts of the density matrix are identical. This arises from the fact that the state we are considering is a singlet and therefore the density matrix must remain unchanged if we replace all α's by β's. In order to find the natural orbitals all we need do is to diagonalize the two by two matrix

$$\begin{pmatrix} \gamma_{11}^+ & \gamma_{12}^+ \\ \gamma_{21}^+ & \gamma_{22}^+ \end{pmatrix} \tag{10.10}$$

We find that if we diagonalize this matrix we get as the diagonal elements in the transformed matrix

$$n_1 = .999541$$
$$n_2 = .000459 \qquad (10.11)$$

The transformation which accomplishes this diagonalization has elements

$$U_{11} = .996764 \qquad U_{22} = .996764$$
$$U_{12} = -.080379 \qquad U_{21} = +.080379 \qquad (10.12)$$

Therefore our natural orbitals are given by

$$u_1' = .996764\, u_1 - .080379\, u_2$$
$$u_2' = .080379\, u_1 + .996764\, u_2 \qquad (10.13)$$

The new 1s function therefore has added to it a small amount of 2s and the new 2s function has added to it a small amount of 1s.

We are now in a position to determine the convergence of the configuration interaction treatment in terms of the natural and the original orbitals. We can construct from our natural orbitals configurations similar to those which we can construct from our original orbitals. We shall call these $(1s')^2$ $(1s'2s')$ and $(2s')^2$. We can now do our configuration interaction in three approximations. We can compare the energies of single $(1s)^2$ configurations made out of natural and our original orbitals, we can compare the energies we get from solving the two by two connecting the $(1s)^2$ and $(1s2s)$ and we can finally compare the energies that we get from the complete three by three done in both manners. In Table 10-2, we show the results of this comparison.

Table 10-2

Comparison of the energies of the helium atom arrived at
using natural orbitals and the original orbitals
(energies in Rydbergs)

$(1s)^2$	- 5.707462	- 5.6875
$(1s)^2 + (1s2s)$	- 5.707531	- 5.708464
$(1s)^2 + (1s2s) + (2s)^2$	- 5.709394	- 5.709394

(NATURAL ORBITALS FOR THE HELIUM ATOM)

We notice from this table that the natural orbitals give a much better energy for a single configuration than do the original orbitals. Adding the next configuration gives a very small improvement in the energy in the natural orbital framework. For two configurations, however, it would have been advantageous to use the original orbitals. For three configurations it makes no difference which one-electron functions we use as the basis. From this simple example it is not clear whether we have improved the convergence by using the natural orbitals. For one configuration it is better to use the natural orbitals, for two configurations it is better to use the original orbitals, for three it makes no difference which we use since we are doing the complete configuration interaction which can be carried out using our basic set of one-electron orbitals.

Even the result that the one configuration energy is improved by the use of natural orbitals is an uncertain result as we can show by a simple argument. Imagine that we did our configuration interaction problem for helium using the Hartree-Fock 1s and 2s functions as our basic set of functions rather than the ones in (3.5). In this case we would certainly have a three by three configuration interaction problem and could once again find the natural orbitals. In this case the natural orbital would turn out to be some mixture of the 1s and 2s Hartree-Fock functions. If we now used the natural orbitals formed in this manner to form the $(1s)^2$ configurations, we could ask if the energy of the singlet state would be improved by the use of the natural orbitals. It would certainly not be improved since the original Hartree-Fock functions were defined in such a way that they gave the best possible energy which can arise from a single determinant. An admixture of 2s to the Hartree-Fock 1s could only have the effect of raising the energy.

From the simple example and the discussions it would seem that it is doubtful that natural orbitals are going to increase the speed of convergence of a configuration interaction approach to the many-electron problem.

References

1. P. O. Löwdin, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 4.

2. For a complete discussion of simple configuration interaction calculations on the helium atom including the one described here see G. R. Taylor and R. G. Parr, Proc. Nat. Acad. Sci. 38, 154 (1952).

G. F. Koster

11. HARTREE-FOCK-SLATER SELF-CONSISTENT FIELD FOR Fe $(3d)^6 (4s)^2$

Solution of the one-electron wave functions for Fe with an unbalanced spin configuration, namely five 3d electrons with spin up, one 3d electron with spin down, and two 4s electrons (one of each spin) has reached self-consistency according to the criterion established by Hartree. The 3d and 4s functions show the most striking variations. In both cases, the spin-up function is shifted, with respect to the spin-down function, toward the origin (see Table 11-1). Both the 3d and 4s electrons spend considerable time in regions where the averaged exchange potential is a sizable fraction of the total potential function appearing in the radial wave equation. Thus, the two exchange potentials become important in determining the behavior of the radial wave functions for 3d and 4s.

<p style="text-align:center">Table 11-1</p>

P	r	r(M.G.)
1s+	.035	
1s-	.035	.037
2s+	.225	
2s-	.225	.221
2p+	.180	
2p-	.180	.181
3s+	.700	
3s-	.705	.735
3p+	.705	
3p-	.715	.735
3d+	.680	
3d-	.700	.735
4s+	2.240	
4s-	2.360	2.697

The charge density for the other functions (1s, 2s, 2p, 3s, 3p) is essentially the same with respect to spin interchange. The above-mentioned shift is not prominent, although still present. The total potential seen by these electrons is largely made up of ordinary $2Z_p$ plus the angular momentum term, the exchange potentials being here less important.

In Table 11-2 we list the radii of the electronic orbits (maxima of $P^2(r)$) for our final self-consistent functions and for those determined by Manning and Goldberg. This table is of limited value, but it serves to indicate the general trend of our calculations. The exchange has tended to pull the charge distribution in toward the origin and to lower the one-electron energies as one might guess. However, starting with

(HARTREE-FOCK-SLATER SELF-CONSISTENT FIELD FOR Fe $(3d)^6 (4s)^2$

Table 11-2
Energies (- Rydbergs)

M.G.	Present Calculations	Ionization Potentials
1s 523.0	584.5 (+) 584.2 (-)	523.9
2s 60.79	61.19 (+) 60.67 (-)	62.5
2p 53.02	57.09 (+) 55.90 (-)	52.2
3s 6.973	7.463 (+) 6.930 (-)	6.9
3p 4.600	5.061 (+) 4.540 (-)	4.1
3d 0.7578	1.1223 (+) 0.6636 (-)	0.60
4s 0.4836	0.5315 (+) 0.4275 (-)	0.58

3s in the energy table, the spin-down functions have a higher energy than do the Manning-Goldberg functions.

The inward shift of the one-electron radial charge densities is more marked for the functions starting with 3s, and the amount of shift seems to follow an argument like that given for the differences between the spin-up and spin-down functions; one is on less firm ground here, however, in view of the self-consistency of the two sets of calculations (Manning-Goldberg and present calculations).

J. H. Wood

12. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

The calculation of polarizability effects in F^- is being carried out in the revised scheme discussed in a previous Progress Report.[1] Unfortunately, this new formulation has rearranged the problem to such an extent that it has been necessary to re-evaluate the integrals. However, the experience gained previously has been helpful and work is proceeding rapidly.

Reference

1. L. C. Allen, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1954, p. 34.

L. C. Allen

13. ELECTRON-LATTICE INTERACTIONS

The problem of interaction between conduction electrons or impurity-bound electrons and lattice vibrations where the interactions are too strong to be handled by perturbation methods (e. g. ionic crystals) has been approached in a variety of different ways. Fröhlich, Pelzer, and Zienau[1] and Gross[2] have worked in a Fock space for the phonon assembly introducing cutoffs at one, two, or three quanta, then attempting an exact solution of the approximate problem remaining. Lee, Low, and Pines,[3] and Gurari[4] have applied intermediate coupling theory in what amounts to a Hartree-Fock approach in the momentum representation of Fock space. Various Russian writers including Bogolyubov,[5] Tyablikov,[6] and Pekar[7] have worked in an electron-lattice configuration space making various approaches to an adiabatic approximation.

Basic to all these approaches are certain assumptions. The periodic potential of the lattice is taken into account through the introduction of an effective mass. The lattice is treated as a harmonically vibrating continuum of polarization charge described by a phenomenological Hamiltonian introduced by Fröhlich.[8] The analyses are restricted to small momenta, that is slow electrons.

Several questions have been raised: Haken[9] in treating a highly specialized model has suggested that the effect of the actual periodic potential on the effect of interaction may be considerable. Lee and Pines claim to obtain an exact solution in the limit of strong coupling, yet Pekar using a variational method seems to obtain lower energies for sufficiently strong coupling. Lastly, the Fock-space methods suggest an effective mass increasing sharply with momentum, but these methods are valid only for small momenta. Attempts are now being made to resolve these uncertainties.

First an unsuccessful attempt has been made to investigate higher momenta of the electron-lattice system by a variational calculation in the Fock-space momentum representation in which the correlation between different phonons was explicitly included in the trial function. The Fröhlich Hamiltonian for an electron described by variables $\vec{q}$, $\vec{p}$ and a system of traveling-wave oscillators, the kth having frequency ω_k, creation operator $a_k{}^*$ and annihilation operator a_k is

$$H = \frac{p^2}{2m} + \sum_k g_k \, a_k \, e^{i\vec{k} \cdot \vec{q}} + g_n{}^* \, a_k{}^* \, e^{-i\vec{k} \cdot \vec{q}} + \sum_k \hbar \, \omega_k \, a_k{}^* \, a_k$$

neglecting zero-point energies. Introducing $\mathscr{H} = U^{-1} H U$ by the unitary operator

$$U = e^{i\hbar \sum_k \vec{k} \, a_k{}^* \, a_k \cdot \vec{q}} \quad ,$$

one obtains

$$\mathcal{H} = \frac{(\vec{p} - \hbar \sum_k \vec{k}\, a_k{}^* a_k)^2}{2m} + \sum_k g_k\, a_k + g_k{}^* a_k{}^* + \sum_k \hbar \omega_k\, a_k{}^* a_k$$

in which $\vec{q}$ is absent and its conjugate $\vec{p}$, now obviously the total momentum, is conserved. Restricting ourselves to states of definite total momentum $\vec{p}$, we may consider the operator $\vec{p}$ as a c-number. If $\zeta_n(\vec{k}_1 \ldots \vec{k}_n; \vec{p}) \equiv <\vec{k}_1 \ldots \vec{k}_n \vec{p} \,|\, U^{-1} \Psi>$ is the probability amplitude that a system in the state $|U^{-1} \Psi>$ has n quanta of momenta $\hbar \vec{k}_1, \hbar \vec{k}_2 \ldots \hbar \vec{k}_n$ respectively and total momentum $\vec{p}$, then

$$<\Psi | H - E | \Psi> = \sum_n \sum_{k_1} \sum_{k_2} \cdots \sum_{k_n} \left\{ \zeta_n(\vec{k}_1 \ldots \vec{k}_n; \vec{p})\left[\frac{\hbar^2}{2m}(\frac{\vec{p}}{\hbar} - \sum_i \vec{k}_i)^2 + \hbar \sum_i \omega_{k_i} - E \right] \right.$$

$$+ \sqrt{n+1}\; g(\vec{k}_i)\, \zeta_n{}^*(\vec{k}_1 \ldots \vec{k}_n; \vec{p})\, \zeta_{n+1}(\vec{k}_1 \ldots \vec{k}_n \vec{k}_i; \vec{p})$$

$$+ \sqrt{n}\; \zeta_n{}^*(\vec{k}_1 \ldots \vec{k}_n; \vec{p})\, g^*(\vec{k}_n)\, \zeta_{n-1}(\vec{k}_1 \ldots \vec{k}_{n-1}; \vec{p}) \Big\}$$

$$\equiv I(E; \vec{p})$$

The requirement that $H\Psi = E\Psi$ is equivalent to $\delta I = 0$ for arbitrary variations symmetric in all $\vec{k}_i$'s in the infinite set of functions $\left\{ \zeta_i \right\}$.

The method of FPZ was to set $\zeta_n = 0$ for all $n > m$, $m = 1$ and to solve the two remaining equations. Gross[2] attempted an extension to m = 2 and 3 and was led to m + 1 coupled integral equations. This method has the advantage of including correlations between two or three phonons accurately, but it is a good approximation only if the probability of more than m phonons being excited is very small. Furthermore, for more than one phonon, the integral equations cannot be solved exactly, and for more than two even the approximate methods become extremely cumbersome. Lee, Low, and Pines and Gurari have specified that

$$\zeta_n(\vec{k}_1 \ldots \vec{k}_n; \vec{p}) = \frac{C_{\vec{p}}}{\sqrt{n!}} \prod_{i=1}^{n} f_{\vec{p}}(\vec{k}_i)$$

where C is a normalization constant, and Lee and Pines have generalized this approach somewhat. Nevertheless, the wave functions thus derived do not explicitly include correlation.

It was suggested by Hylleraas's calculations on helium to set up a Fock-space momentum representative $(\zeta_0(\vec{p}), \zeta_1(\vec{k}_1; \vec{p}), \zeta_2(\vec{k}_1, \vec{k}_2; \vec{p}) \ldots)$ in which the form of each function $\zeta_n(\vec{k}_1 \ldots \vec{k}_n; \vec{p})$ is specified but depends on a few arbitrary parameters. The functional $I(E; \vec{p})$ becomes a function of these parameters with respect to which it is minimized. It was hoped that if a set of functions could be

found whose form was suggested by Gross's accurate wave functions for the one- and two-quantum cutoffs yet which would lead to tractable integrals, the minimization procedure could be performed by the Whirlwind digital computer for a cutoff of as high as 30 quanta.   Functions of the form

$$c_n e^{-\frac{1}{\sigma^2}\left[\sum_i k_i^2 + \mu \sum_{ij} \vec{k}_i \cdot \vec{k}_j\right]}$$

have the proper symmetry, explicitly include the correlation and lead to multi-dimensional integrals which can be evaluated analytically, at least for zero total momentum.   Preliminary hand computations indicated that though some improvement could be obtained if μ were allowed to vary from zero (case of no correlation), nevertheless the depressions of energy due to the interaction were only about half those obtained by other methods due to the poor fit of the one quantum trial function to the "exact" one quantum function.   Attempts at constructing trial functions better approximating the functions found by Gross led to seemingly impossible many-dimensional integrals for any significant number of quanta.

The fundamental difficulty is that one is trying to fit a series of unknown functions rather than just one as in the many-electron problem.   If an undetermined linear combination of m prescribed functions is constructed to approximate each ζ_n then the matrix to be diagonalized for n-quanta cutoff is roughly of order m × n so that n must be quite small.   If instead, more complicated single functions are used for a better approximation, the integrals become impossible.   The work of Lee and Pines has perhaps gone as far as possible by not introducing correlation into the trial functions and thus retaining simple integrals regardless of the number of quanta. Further attempts along this line have been abandoned, at least temporarily, since the dependence of energy on the correlation parameter and on the total momentum are meaningless if the trial functions at best are poor approximations.   Other methods of extrapolating to high momenta are being considered.

A second investigation now under way is stimulated by the desire to construct a model which can be solved with sufficient exactness to serve as a yardstick in determining the validity of the various adiabatic approaches and the validity of accounting for the periodic potential through an effective mass.   Gross[10] has determined the exact solutions to the eigenvalue problem arising when a free electron is allowed to interact with only one traveling lattice wave and all motion is confined to one dimension.   For sufficiently strong coupling he finds the state with minimum energy has non-zero momentum.   Since the one-phonon analysis is essentially spatially asymmetric, the problem of an electron with two degenerate modes (right- and left-going) in one dimension has been set up and programmed for Whirlwind by Meckler, using a cutoff of six quanta.   An investigation of the energy-momentum curves for intermedi-

ate and strong coupling, the dependence on lattice wave length of the effect of the interaction, and the convergence of the cutoff procedure are being investigated. It is hoped to push the one- or two-oscillator model as far as possible with regard to the periodic potential and the validity of the adiabatic approximation. The Fock-space approaches are not applicable here, depending as they do on the presence of a large number of independent oscillators.

References

1. H. Fröhlich, H. Pelzer and S. Zienau, Phil. Mag. 41, 221 (1950).

2. E. Gross, Technical Report No. 55, Laboratory for Insulation Research, M.I.T., December, 1952.

3. T. D. Lee, F. Low and D. Pines, Phys. Rev. 90, 297 (1953); T. D. Lee and D. Pines, Phys. Rev. 92, 883 (1953).

4. M. Gurrari, Phil. Mag. 44, 329 (1953).

5. N. N. Bogolyubov, Ukr. Mat. Zhurnal 2, 3 (1950).

6. S. V. Tyablikov, Zh. Eksper. Teor. Fiz. 21, 377 (1951); Zh. Tekh. Fiz. 22, 325, (1952); Zh. Eksper. Teor. Fiz. 22, 513 (1952); Zh. Eksper. Teor. Fiz. 23, 381 (1952).

7. S. I. Pekar, J. Exp. Theor. Phys. (USSR) 19, 796 (1949); Zh. Tekh. Fiz. 21, 1544 (1951); Zh. Tekh. Fiz. 22, 1062 (1952); Zh. Tekh. Fiz. 22, 1076 (1952); Usp. Fiz. Nauk. 50, 197 (1953); Issledovaniia po Elektronnoi Feorii Kristallov, Gostekhizdat, 1951 or German translation, Untersuchungen zur Elektronentheorie der Kristalle, Akad.-Verlag, Berlin, 1953.

8. H. Fröhlich, Proc. Roy. Soc. (London) A160, 230 (1937).

9. H. Haken, Z. Physik 135, 408 (1953).

10. E. Gross, Phys. Rev. 84, 818 (1953).

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14. THERMAL VIBRATIONS IN Cu-Zn SYSTEM CRYSTALS

The work described in the previous report is nearing completion, and it is anticipated that a paper will soon be written on this investigation of the atomic force constants in copper, in addition to a Ph. D thesis. The expressions for the change in conduction electron charge density ($\Delta\rho$) produced by the displacement of an ion core have been extensively investigated. $\Delta\rho$ has been calculated at a number of points in the lattice as a function of edge-width of the finite lattice used, both for cubic and for parallelopiped macroscopic shapes. The convergence shown is of the nature of damped oscillation about a constant value as asymptote, and the convergence pattern is the same at different points, except far from the origin, where spurious structure appears. For two lattices extensive plots of $\Delta\rho$ as a function of position in the lattice have also been made, and found in general agreement. A lattice of ten atomic planes' width has been settled upon for final calculations, as the best compromise between accuracy and ease of calculation. The numerical Coulomb integration of $\Delta\rho$ to get its contribution to the atomic force constants is now underway. and appropriate tables have been constructed for comparison of the results with experimental, nuclear dipole, closed-core interaction, Thomas-Fermi, and multipole expansion atomic force constants.

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