On the NonOrthogonality Problem Connected with the Use of Atomic Wave Functions in the Theory of Molecules and Crystals

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fixed constant, the entropy retained in the crystal is 

\[(1/n)R \ln 2 \text{ or } 1.38/n.\]

The maximum deficiency from the data is not far from the value for \(n = 3\), which, for a cyclic unit, would produce an arrangement exactly like one face of the tetrahedron of the ice structure.

This explanation appeals to the writer as a more probable one than the case for zero retention of entropy.

Quantitative consideration of the vapor heat capacity data will be deferred until this property has been accurately calculated from the molecular constants. The present required extrapolation of the table of Pitzer and Gwinn\(^{18}\) would introduce too large an uncertainty. Qualitatively, however, it is expected that the new dimensions will cause about the same decrease of the calculated barrier as in the case of the entropy. If this is true, the data of Eucken and Franck\(^{5}\) will lead to a barrier around 1200 cal./mole, that of Rowlinson\(^{6}\) to about 700 cal./mole.

**Note on Ethyl Alcohol**

In a recent analysis of the entropy of ethyl alcohol\(^{20}\) it was found that, for zero residual entropy, the sum of the barriers opposing the rotation of the methyl and hydroxyl groups was approximately 6000 cal./mole, possibly a little lower. If the situation is like the methyl alcohol case, the true sum could be almost as low as 4000 cal. The arbitrary assignment of 3000 to the methyl group would then leave 1000 for the hydroxyl group, exactly the value derived by Eucken and Franck\(^{5}\) from the vapor heat capacity.

The writer is indebted to Professor D. M. Dennison and Dr. D. G. Burkhard for permission to use their data and for stimulating discussions of this problem and related questions.

authors, e.g. Slater, Inglis, Van Vleck, but a complete treatment, including the Heitler-London method as well as the collective electron model, has up till now not been given. The purpose of this paper is to develop a simple method of taking the overlap integrals into consideration. We wish to emphasize that the overlap effects, instead of being negligible, are often of essential importance for the properties of molecules and crystals.

II. CONSTRUCTION OF MOLECULAR ORBITALS

Let us first consider a molecule by means of the method of molecular orbitals developed by Lennard-Jones, Hund, Mulliken, and others. In this theory the overlap integrals have been taken into account in a few cases: e.g. for some unsaturated and aromatic molecules by Wheland, for graphite by Bradburn, Coulson, and Rushbrooke, and for the linear chain by Hoffmann and Kónya. In some of his papers Mulliken and his collaborators have also retained the $S$-integrals.

A more complete treatment of the problem has recently been given by Chirgwin and Coulson in connection with the theory of conjugated systems developed by Coulson and Longuet-Higgins, and this paper will be discussed in greater detail below.

Let $H_\mu$ be the effective Hamiltonian operator for one electron of the system, moving in the self-consistent field of the nuclei and the other electrons, with the matrix elements

$$H_\mu = \int \phi_\mu^* H \phi_\mu d\tau,$$

with respect to the given $AO$. In the following we will denote matrices by the corresponding black type letters, and further we let $A^\dagger$ denote the hermitean adjoint of $A$, so that $A^\dagger = A^*$. We note that the matrices $H$ and $S$, formed by the elements $H_{\mu\nu}$ and $S_{\mu\nu}$, are self-adjoint.

The molecular orbitals $\psi_j$ ($j = 1, 2, \ldots \cdot n$) may be formed by linear combinations of the $AO$

$$\psi_j = \sum_{\mu=1}^{n} \phi_\mu x_{\mu j},$$

where the coefficients $x_{\mu j}$ are determined by the conditions

$$E = \int \psi_j^* H \psi_j d\tau = \text{extreme value},$$

$$\int \psi_j^* x \psi_j d\tau = 1.$$  

The Eqs. (4) and (5) are equivalent to the $n$ secular equations

$$\sum_{\mu=1}^{n} H_{\mu\nu} x_{\mu j} = \sum_{\mu=1}^{n} (\delta_{\mu\nu} + S_{\mu\nu}) x_{\mu j} E_j,$$

$$x_{\mu j} (\delta_{\mu\nu} + S_{\mu\nu}) x_{\mu j} = 1,$$

which also can be written in the matrix form

$$H x = (1+S) x E,$$

$$x^\dagger (1+S) x = 1.$$  

Here $x$ and $E$ are the matrices formed by the elements $x_{\mu j}$ and the diagonal elements $E_j$, respectively. Equation (9) is obtained by joining the normalization conditions (7) with the orthogonality theorem, which is a consequence of (6) and the hermitean character of $H$ and $S$. The fundamental Eqs. (8) and (9) can now be essentially simplified by introducing the substitution

$$x = (1+S)^{-1} C,$$

where $(1+S)^{-1}$ means the matrix

$$(1+S)^{-1} = 1 - \frac{1}{2} S + \frac{3}{8} S^2 - \frac{1}{16} S^3 + \cdots;$$

with the elements

$$(1+S)_{\mu\nu}^{-1} = \delta_{\mu\nu} - \frac{1}{2} S_{\mu\nu} + \frac{3}{8} \sum_a S_{\mu a} S_{a\nu} - \frac{1}{16} \sum_a \sum_{\alpha\beta} S_{\mu a} S_{a\alpha} S_{\alpha\beta} + \cdots.$$

Instead of (8) and (9) we now obtain

$$H^C = CE; \quad C^\dagger C = 1;$$

$$H^\dagger = (1+S)^{-1} H (1+S)^{-1}.$$  

Hence the following theorem is valid: The problem of solving the secular equations including the overlap integrals $S_{\mu\nu}$ can be reduced to the same form as if in the simplified theory (S neglected) if the matrix $H$ is replaced by the matrix (13). This new matrix $H^\dagger$ is also self-adjoint and can be expanded in the form

$$H_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} \sum_a (S_{\mu a} H_{a\nu} + H_{\mu a} S_{a\nu})$$

$$+ \frac{3}{8} \sum_{a\alpha} (S_{\mu a} S_{a\alpha} H_{\alpha\nu} + S_{\mu a} H_{\alpha a} S_{\alpha\nu}$$

$$+ H_{\mu a} S_{a\alpha} S_{\alpha\nu}) + \cdots.$$  

A more general definition of the matrix $H^{(1+S)^{-1}}$ can be given by the methods developed in P. A. M. Dirac, Quantum Mechanics (Oxford University Press, New York, 1947), 3rd edition p. 41.
We can easily obtain the same result in another way, which at once gives an interpretation of the elements $H_{\mu\nu}'$. The MO $\psi_{\mu}$ are formed from the AO by linear combinations, but in order to avoid the non-orthonormality difficulty we now first construct an orthonormalized set $\varphi_{\mu}$ from the set $\phi_{\mu}$ and then we build up our molecular orbitals with the aid of these new functions. Let $\phi$, $\varphi$, and $\psi$ denote the row matrices of order $n$ formed by the elements $\phi_{\mu}$, $\varphi_{\mu}$, and $\psi_{\mu}$, respectively. It is easily verified by using (1) that the functions $\varphi_{\mu}$ given by the matrix relations

$$
\varphi = \phi (1 + S)^{-1},
$$

(15)
or

$$
\varphi_{\mu} = \phi_{\mu} - \frac{1}{2} \sum_{\alpha} \phi_{\alpha} S_{\alpha\mu} + \frac{3}{2} \sum_{\alpha, \beta} \phi_{\alpha} S_{\alpha\beta} S_{\beta\mu} + \cdots,
$$

(16)
are normalized and orthogonalized, i.e., that

$$
\int \varphi_{\mu}^{\ast} \varphi_{\nu} d\tau = \delta_{\mu\nu},
$$

(17)

The functions (16) seem to have been first introduced in a paper by the author concerning the overlap effects in ionic solids. By means of these functions, it is then easy to construct the MO in the usual way. According to (3), (10), and (15) we now get

$$
\psi = \phi x = \phi (1 + S)^{-1} C = \varphi C,
$$

(18)
or

$$
\psi_{\mu} = \sum_{\nu=1}^{n} \varphi_{\nu} C_{\mu\nu},
$$

(19)
Using (13) and (15) we further obtain

$$
H_{\mu\nu}' = \int \varphi_{\mu}^{\ast} H \varphi_{\nu} d\tau,
$$

(20)
i.e. that $H_{\mu\nu}'$ are the matrix elements with regard to the functions $\varphi_{\mu}$. Since (19) also shows that $C_{\mu\nu}$ are the expansion coefficients with respect to the same functions, we get the following result: The solution of the problem of constructing the molecular orbitals, when taking the overlap integrals into consideration, is the same as if we consider the orthonormalized functions

$$
\varphi_{\mu} = \phi_{\mu} - \frac{1}{2} \sum_{\alpha} \phi_{\alpha} S_{\alpha\mu} + \frac{3}{2} \sum_{\alpha, \beta} \phi_{\alpha} S_{\alpha\beta} S_{\beta\mu} + \cdots
$$

(21)
as the real atomic orbitals.

We note that the functions $\varphi_{\mu}$ are reduced to the usual AO $\phi_{\mu}$ when the distances between the atoms increase, but that these orbitals are essentially deformed when the overlap is appreciable.13

13 P. O. Längdlin, Arkiv f. mat., astr. o. fysik, 35A, 9 (1947). The first two terms and a part of the third term of (16) were given by R. Landshoff, Zeits. f. Physik 102, 201 (1936). See also G. H. Wannier, Phys. Rev. 52, 191 (1937), who has the first two terms.

**Calculation of the Expansion Coefficients**

Now we will consider the problem of calculating $C$ in the case when the corresponding $C_{0}$ for the simplified theory (S neglected) is already known. We have

$$
HC_{0} = C_{0} E_{0}, \quad C_{0}^{\dagger} C_{0} = C_{0} C_{0}^{\dagger} = 1
$$

(22)
and

$$
C_{0}^{\dagger} H C_{0} = E_{0},
$$

(23)
where $E_{0}$ is the diagonal matrix formed by the elements $\epsilon_{0\alpha}$ which are the characteristic numbers of the matrix $H$. In the following we will use the theory of unitary transformations of matrices. Let us first introduce the new matrix

$$
S = C_{0}^{\dagger} S C_{0}.
$$

(24)
The matrix Eq. (12) can then by the substitution

$$
C = C_{0} Q
$$

(25)
be put into the form

$$
(1 + S)^{-1} E_{0} (1 + S)^{-1} Q = Q E,
$$

(26)
$$
Q^{\dagger} Q = Q Q^{\dagger} = 1.
$$

(27)
For the further development it is convenient to distinguish between two cases:

(i) The matrix $S$ commutes with the matrix $H$. This important case has been treated in considerable detail by Chirgwin and Coulson,9 but still the result obtained by the matrix method used here seem to be more surveyable and general. Now $S$ can be expressed as a function of $H$, and we assume that this function,14 $S = f(H)$, is of a simple polynomial type or can be expanded in a series of positive (and eventually negative) powers of $H$. Using (24) and general theorems concerning unitary transformations we immediately obtain

$$
S = f(H), \quad s = f(E_{0}), \quad s_{\mu} = f(\epsilon_{\mu}).
$$

(28)
We note that $s$ here is a diagonal matrix formed by the elements $s_{\mu} (= \epsilon_{\mu})$. The relations (13) and (14) can now be simplified:

$$
H' = (1 + S)^{-1} H = H (1 + S)^{-1},
$$

(29)
$$
H_{\mu\nu}' = H_{\mu\nu} - \sum_{\alpha} H_{\mu\alpha} S_{\alpha\nu} + \sum_{\alpha, \beta} H_{\mu\alpha} S_{\alpha\beta} S_{\beta\nu} + \cdots
$$

(30)
The Eq. (26) has the solution $Q = 1$, $C = C_{0}$, and we note that the necessary and sufficient condition for the existence of this solution is that $s$ is a diagonal matrix, i.e. that $S$ commutes with $H$—as has already been found by Chirgwin and Coulson in another way. If $F$ denotes an arbitrary polynomial or power series function, we get, by using (10), (24), and the laws of unitary transformations, that

$$
F(S)C = CF(s), \quad F(S)x = xF(s).
$$

(31)
According to (10), (18), (25), and (26), we then obtain

14 Wheland, Chirgwin, and Coulson and others have been mainly interested in the case of a linear connection between $S$ and $H$. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 168.234.75.2 On: Tue, 29 Oct 2013 21:29:36
the matrix relations
\[ C = C_0, \quad x = C(1+s)^{-1}, \quad E = E_0(1+s)^{-1}, \quad \psi = \phi C(1+s)^{-1}, \] (32)
and in components
\[ C_{\mu j} = (C_0)_{\mu j}, \quad x_{\mu j} = \frac{C_{\mu j}}{(1+s)^l}, \quad E_j = \frac{\epsilon_j}{1+s_j}, \quad \psi_j = (1+s_j)^{-1} \sum_\mu \phi_\mu C_{\mu j}. \] (33)

The relation for the energy \( E_j \) in (33) can be considered as a generalization of the expressions found by Wheland and Chirgwin-Coulson for the case of a linear connection between \( S \) and \( H \). The formula for \( \psi_j \) shows that the \( MO \) obtained in the simplified theory (\( S \) neglected) are quite correct but for a normalization constant \( (1+s)^{-l} \) depending on the overlapping.

(ii) The matrix \( S \) does not commute with the matrix \( H \). If the non-diagonal elements of the matrix \( S \) are very small, it often will be convenient to solve the Eq. (26) by the usual perturbation theory, treating
\[ V = (1+s)^{-1} E_0 (1+s)^{-1} - E_0 \] (34)
as the perturbation and \( E_0 \) as the unperturbed matrix. The formulas needed may be put up without difficulties. If the non-diagonal elements of \( S \) are not so small, it seems better to solve the secular Eqs. (12) directly. We will therefore finish this part with a more detailed investigation of the matrix elements \( H_{\mu \nu}' \).

Treatment of the Matrix \( H' \)
The fundamental matrix \( H_{\mu \nu}' \) has been naturally introduced into the theory by considering the orthonormalized functions \( \phi_\mu \) given by (16) as the real atomic orbitals. The matrix \( H' \) is self-adjoint \((H_{\mu \nu}'* = H_{\nu \mu}')\) and for real atomic orbitals this gives the simple symmetry relation
\[ H_{\mu \nu}' = H_{\nu \mu}'. \] (35)
which is of importance for the interpretation of the theory.

Another property of \( H' \) may also be emphasized. From the expansion (14) we can see that \( H_{\mu \nu}' \) depends on the \( AO \) \( \phi_\mu \) and \( \phi_\nu \) but also on all the other atomic orbitals \( \phi_\alpha (\alpha = 1, 2, \ldots, n) \) of the system. Hence the quantities \( H_{\mu \nu}' \) have a certain many-orbital-character arising from the overlapping of the \( AO \) of the free atoms. The author has pointed out the importance of such "many-orbital-effects" in some earlier papers, where it was shown that these effects could be considered responsible for the well-known failure of the Cauchy relations for the elastic constants in ionic crystal. More details about this question will be given in the later part of this paper.

Here we will also show a transformation property of \( H' \). The effective Hamiltonian operator \( H_{\mu \nu} \), belonging to the system under consideration, contains various electrostatic potentials having zero-points which may be chosen arbitrarily. Changing the zero-point of \( H_{\mu \nu} \) totally by an amount \( k \) we get the transformation
\[ H_{\mu \nu} \rightarrow H_{\mu \nu} + k. \] (36)
All energy quantities of the system, which are dependent on this zero-point, must then have the same change, whereas all other physical quantities must be invariant. Using (1), (2), and (36) we now immediately obtain
\[ H \rightarrow H + k(1+S), \] (37)
which shows that \( H \) cannot possibly have a direct physical interpretation. On the other hand, we get for our matrix \( H' \):
\[ H' \rightarrow H' + k(1+S), \] (38)
or
\[ H_{\mu \nu}' \rightarrow H_{\mu \nu}' + k, \quad H_{\mu \nu}' \rightarrow H_{\mu \nu}' (\mu \neq \nu). \] (39)
which means that the diagonal elements are changed by \( k \) and that the non-diagonal elements are invariant. The hermitean character of \( H' \) and the transformation property (38) therefore show that it is possible that \( H' \) has a direct physical significance, i.e. that there exist some close connections between the elements \( H_{\mu \nu}' \) and experimentally determined quantities.

Let us now introduce the notations
\[ H_{\mu \nu} = \alpha_{\mu \nu}, \quad H_{\mu \nu} = \beta_{\mu \nu} (\mu \neq \nu), \] (40)
\[ H_{\mu \nu} = H_{\mu \nu} = \gamma_{\mu \nu} (\mu = \nu). \] (41)
Here \( \gamma_{\mu \nu} \) is a generalization of the quantity \( \gamma \) originally introduced by Mulliken-Rieke-Brown in 1941. The importance of this quantity has later been stressed by several authors. Using (37) we get
\[ \alpha_{\mu \nu} \rightarrow \alpha_{\mu \nu} + k, \quad \beta_{\mu \nu} \rightarrow \beta_{\mu \nu} + k \gamma_{\mu \nu}, \] (42)
\[ \gamma_{\mu \nu} \rightarrow \gamma_{\mu \nu}. \] (43)
Here we emphasize that \( \gamma_{\mu \nu} \) is invariant, and, as far as the author knows, this transformation property has never been pointed out before. Because of (42) and (43) it seems convenient to express the matrix \( H' \) only in terms of the quantities \( \alpha_{\mu \nu} \) and \( \gamma_{\mu \nu} \). Starting from the expression (13) and using the identity \((1+S)^{-1} = (1+S)^{+1} - S(1+S)^{-1}, \) we easily derive the formula
\[ H_{\mu \nu}' = \sum_k \{ (1+S)^{-1} \alpha_{\mu \nu} (1+S)^{+1} \gamma_{\mu \nu} \}
+ \sum_{\lambda \neq \nu} (1+S)^{-1} \gamma_{\lambda \nu} (1+S)^{-1} \gamma_{\mu \nu}. \] (44)
In the special case (i) when \( S \) commutes with \( H \), we start instead from (29) and by using the identity \((1+S)^{-1} = 1 - S(1+S)^{-1} \) we get the result
\[ H_{\mu \nu}' = \alpha_{\mu \nu} + \sum_{\lambda \neq \nu} \gamma_{\mu \lambda} (1+S)^{-1} \gamma_{\lambda \nu}. \] (45)
For small $S$ the formulas (44) and (45) are very convenient for numerical computations, and in the case of (44) the result can be checked by the transformation property of $H'$ given by (39). As examples we have calculated the matrix $H_{\mu\nu}'$ for butadiene and benzene; considering only the interaction between nearest neighbors and taking $S=0.25$, we have got the same result as given by Chirgwin and Coulson in another way.

**Applications to the Theory of Conjugated Systems**

The conjugated system has been investigated by many authors, but here we will follow the treatment given in a series of papers by Coulson and Longuet-Higgins. For the simplified theory ($S$ neglected) they have introduced some useful concepts, as charge density, bond order, and polarizabilities, and now we will show how it is possible to generalize these concepts even to the more general theory with the overlap effects taken into account. The total energy $\varepsilon$ of the mobile electrons ($\pi$-electrons) is in the usual approximation given by

$$\varepsilon = \sum_{j=1}^{m} n_j E_j,$$  \hspace{1cm} (46)\

where we have to sum over all occupied MO ($j=1, 2, \ldots, m$), and $n_j$ is the number of electrons in the $j$th orbital. By using (4) and (18) we obtain

$$E_j = \int \psi_j^* H_{\alpha\beta} \psi \, d\tau = (C|H|C)_{jj},$$  \hspace{1cm} (47)\

$$\varepsilon = \sum_{j=1}^{m} \sum_{\alpha, \beta=1}^{n} n_{\alpha} C_{\alpha j}^* H_{\alpha\beta} C_{\beta j}.$$  \hspace{1cm} (48)\

Now we define a new matrix $P$ by the relation  

$$P_{\mu\nu} = \frac{\partial \varepsilon}{\partial H_{\mu\nu}},$$  \hspace{1cm} (49)\

where we assume that all elements $H_{\mu\nu}'$ are formally independently varied. If we consider only real functions $\varphi_{\mu}$ and employ the symmetry relation (35), we must replace (48) by the two equations

$$P_{\mu\nu} = \frac{\partial \varepsilon}{\partial H_{\mu\nu}'}, \quad P_{\mu\nu} = \frac{1}{2} \frac{\partial \varepsilon}{\partial H_{\mu\nu}'},$$  \hspace{1cm} (50)\

Using the condition (4), giving $\partial \varepsilon/\partial C_{\mu\nu} = 0$, we have at once from (48) that

$$P_{\mu\nu} = \sum_{j=1}^{m} n_j C_{\alpha j}^* C_{\beta j},$$  \hspace{1cm} (51)\

and for real functions

$$P_{\mu\nu} = \sum_{j=1}^{m} n_j C_{\mu j}^* C_{\nu j},$$  \hspace{1cm} (52)\

Here $P$ is in general a self-adjoint matrix. In the following we will denote $P_{\mu\nu}$ as the charge density of the $\pi$-electrons at the atom $\mu$, and $P_{\mu\nu}(\mu \neq \nu)$ as the total mobile order of the bond $\mu \leftrightarrow \nu$, noting that both quantities include many-orbital effects. Using the formulas (19) and (20) in Coulson and Longuet-Higgins (reference 10, Part I), we find that these concepts may be considered as convenient generalizations of the corresponding quantities of the simplified theory ($S$ neglected), for in the case $S \to 0$ they are reduced to $q_{\mu}$ and $p_{\mu\nu}$, respectively.

Since $C_{\mu j}$ are the coefficients of the MO $\psi_j$ in their expansions (19) with regard to $\varphi_{\mu}$, we can also give another simple interpretation of the matrix $P$: The quantities $P_{\mu\nu}$ and $P_{\mu\nu}(\mu \neq \nu)$ constitute the charge densities and the bond orders in the sense of Coulson and Longuet-Higgins, if the orthonormalized functions $\varphi_{\mu}$ given by (21) are considered as the real atomic orbitals.

This result is in complete agreement with the theorem found on page 367, and it indicates the simplest way of transforming concepts from the simplified theory to the more general one including overlap effects. Hence the latter can be treated without further complications. All the theorems, for instance the useful integral formulas and the equations for the polarizabilities given by Coulson and Longuet-Higgins, are still valid: One has only to replace the matrix $H_{\mu\nu}$ with the new matrix $H_{\mu\nu}'$ in the fundamental secular determinant, and then to employ the characteristic values $E_j$ and the expansion coefficients $C_{\mu j}$ derived from this determinant.

**The Connection with the Theory of Chirgwin and Coulson**

Here we have also to investigate the connection between our theory and the treatment of the overlap effects given by Chirgwin and Coulson. Their theory is based on a "mixed tensor" $H_{\mu\nu}'$, which in our notation has the form $(1+S)^{-1}H$, and they define the new charge densities $q_{\mu}$ and bond orders $p_{\mu\nu}$ by

$$q_{\mu} = \sum_{j=1}^{m} n_j x_{\mu j} y_{\mu j},$$  \hspace{1cm} (53)\

$$p_{\mu\nu} = \sum_{j=1}^{m} n_j (x_{\mu j} y_{\nu j} + x_{\nu j} y_{\mu j}),$$  \hspace{1cm} (54)\

where $y$ is the matrix $y = (1+S)x$. At first we consider the case (i) when $S$ commutes with $H$. The relations (29) immediately show that the "mixed tensor" $H_{\mu\nu}'$ is now identical with our matrix $H'$; further we obtain, by using (31) and (33), that

$$x_{\mu j} = C_{\mu j} (1+z_j)^{-1},$$  \hspace{1cm} (55)\

which shows that their definitions of charge densities
and bond orders are in agreement with ours. In this case both theories seem to give identical results.

In the general case (ii) when $S$ and $H$ do not commute, the circumstances are, however, quite different. Instead of our simple generalization, based on the concept that the orthonormalized functions $\phi_r$ are the real atomic orbitals, Chirgwin and Coulson have a considerable work to carry out e.g. new formulas of the integral type and new equations for the polarizabilities. These complications seem to be closely connected with the fact that their "mixed tensor" $H_\alpha^\beta$ has lost the fundamental symmetry property, i.e. that $H_\beta^\alpha \neq H_\alpha^\beta$ for real $AO$. For complex atomic orbitals, $H_\alpha^\beta$ has a non-hermitean character which, of course, renders the physical interpretations more difficult. We note that no such complications occur in our treatment of the problem.

Even if the theory by Chirgwin and Coulson treats the simple case (i) in a very good way, our theory seems therefore to have considerable advantages in the general case (ii), for instance as regards the applications to heteromolecules.

III. CONSTRUCTION OF BLOCH ORBITALS IN A CRYSTAL

Let us now consider a crystal, where the atomic nuclei have fixed positions, forming a perfect and infinite lattice. The construction of crystal orbitals $\chi(r)$ by $LCAO$ was first given by Bloch, but, since he neglected all overlap-effects, we will here take up the problem again, taking these effects into full account. There is a close connection between the theory of Bloch orbitals and the theory of molecular orbitals, and in order to examine this in greater detail, we will again use the variation principle. However, there is a slight complication, since the integrals (4) and (5) over the whole space, in the following indicated by $(\infty)$, are divergent for an infinite crystal. They have therefore to be replaced by integrals over a cyclic domain—the microcrystal—denoted by $(G)$, which is defined below. The fundamental conditions for the BO then have the form

$$E = \int_{(G)} \chi^*H_\sigma\chi d\tau = \text{extreme value}, \quad (54)$$

$$\int_{(G)} \chi^*\chi d\tau = 1. \quad (55)$$

For the sake of simplicity we will at first assume that only one atomic orbit is associated with each nucleus. Let $\phi_r = \phi(r-y)$ be the normalized $AO$ connected with the nucleus at the lattice point $y = \mu_1a_1 + \mu_2a_2 + \mu_3a_3$, where $a_1, a_2, a_3$ are the basic vectors of the space lattice and $\mu_1, \mu_2, \mu_3$ are integers between $-\infty$ and $+\infty$. The microcrystal is then defined by the Born-von Karman boundary condition

$$\chi(r+Ga_k) = \chi(r), \quad k = 1, 2, 3 \quad (56)$$

where $G$ is a very large integer. At the same time we introduce the ordinary $k$-vectors,

$$k = (1/G)(k_1b_1 + k_2b_2 + k_3b_3), \quad (57)$$

where $b_1, b_2, b_3$ are the basic vectors of the reciprocal lattice, and $k_1, k_2, k_3$ are integers. In summations over the lattice points $y$ and $k$ in the ordinary space and the $k$-space, respectively, we let an index $(\infty)$ denote a summation over all lattice points and an index $(G)$ a summation only over the ground points, i.e. the $G^3$ lattice points of each type, satisfying the condition

$$\frac{G}{2} \leq \mu_k < \frac{G}{2}, \quad \frac{G}{2} \leq k < \frac{G}{2}, \quad k = 1, 2, 3. \quad (58)$$

In order to take the overlap effects into consideration from the beginning, we start from the orthonormalized $AO$: 19

$$\varphi_\mu = \varphi_\mu - \frac{1}{2} \sum_a \varphi_\sigma S_{\alpha\mu} + \frac{1}{2} \sum_{\alpha\beta} \varphi_\alpha S_{\beta\mu} + \cdots, \quad (59)$$

where $S$ are the usual overlap integrals

$$S_{\mu\nu} = \int_{(G)} \varphi_\mu^* \varphi_\nu^* \delta_{\mu\nu}, \quad (60)$$

and the indices $\mu, \nu, \alpha, \beta, k, \cdots$ correspond to the vectors $y, v, \alpha, \beta, k, \cdots$, respectively. Then we construct our BO by means of $LCAO$:

$$\chi_k = \sum_\mu \varphi_\mu C_{\mu k}, \quad (61)$$

where the coefficients $C_{\mu k}$ according to (56) satisfy the periodicity condition

$$C_{\mu + a\alpha, k} = C_{\mu, k} \quad k = 1, 2, 3. \quad (62)$$

For each operator $F_\mu$, having the periodicity of the crystal, we obtain after some simple reductions the useful identity

$$\int_{(G)} \chi_k^* F_\mu \chi_{k'} d\tau = \sum_{\mu'} C_{\mu k} F_{\mu'} C_{\mu k'}, \quad (63)$$

$$F_{\mu k} = \sum_\chi \varphi_\mu^* \varphi_{\mu + a\alpha} \int_{(G)} \varphi_\nu^* \varphi_{\nu + a\beta} d\tau, \quad (64)$$

where $F_{\mu k}$ is the usual matrix element with respect to the functions (59), and $F_{\mu'k'}$ is the result of a summation, in which generally only one term is of real importance (because of the large magnitude of $G$). The fundamental Eqs. (54) and (55) are now equivalent with the

18 We note that Bloch instead employed a certain "orthogonality principle" in constructing the secular equations.

19 Here each function is characterized by three integers, but, since the lattice points are enumerable, they can also be characterized by only one integer, as before; see Eq. (21).
relations
\[ E_k = \sum_{\mu} \sqrt{\lambda} C_{\mu}^* \vec{H}_{\mu \alpha} C_{\mu \alpha} \text{ is extreme value,} \]
\[ \sum_{\mu} \sqrt{\lambda} C_{\mu}^* C_{\mu \alpha} = 1, \]
(65)
(66)
giving the secular equations
\[ \sum_{\mu} \vec{H}_{\mu \alpha} C_{\mu \alpha} = C_{\mu \alpha} \delta_{k \mu}, \mu \text{ in } (G). \]
(67)
We note that, because of the periodicity condition (62), our secular problem is now reduced to the finite order \( G^2 \); the indices being referred only to the ground points of \( y \) and \( k \).

Since we here are treating atomic orbitals \( \varphi_{y} = \varphi(r-y) \) of only one type, the matrix elements \( \vec{H}_{\mu \alpha} \) depend only on the difference \( \kappa = v-y \) between their indices. It is therefore convenient to introduce the new notation
\[ J_{\kappa} = \vec{H}_{\mu \alpha} = \sum_{\lambda} H_{\mu \alpha} \delta_{k \mu}. \]
(68)
Now it is well known (see Bloch, reference 17) that each cyclic matrix, having elements characterized only by the difference between their indices, can be transformed to the diagonal form by means of a similarity transformation \( \mathbf{C} \), given by
\[ C_{\mu \alpha} = G^{-1} \varphi_{\mu} \varphi_{\alpha}. \]
(69)
When the indices are referred only to the ground points of \( y \) and \( k \), \( \mathbf{C} \) is also a unitary matrix. Hence we obtain
\[ \mathbf{E} = \mathbf{C}^{\dagger} \vec{H} \mathbf{C}, \]
(70)
and
\[ \delta_{k \kappa} = J_{\kappa} = \sum_{\lambda} H_{\mu \alpha} \delta_{k \mu}. \]
(71)
It is easily verified that the expressions (69) and (71) really satisfy the secular problem, i.e. the Eqs. (67) and (66). Introducing (69) into (61), we get the corresponding crystal functions
\[ \chi_{\kappa}(r) = G^{-1} \sum_{\lambda} \varphi_{\kappa}(r), \]
(72)
the Bloch orbitals, which are automatically normalized and orthogonalized with respect to the ground domain \( (G) \), i.e.
\[ \sum_{\kappa} \chi_{\kappa}^* \chi_{\kappa} d\tau = \delta_{k \kappa}. \]
(73)
Besides they fulfill exactly the general Bloch condition
\[ \chi_{\kappa}(r+a_{\kappa}) = e^{i\kappa \cdot a_{\kappa}} \chi_{\kappa}(r), \quad \kappa = 1, 2, 3. \]
(74)
At first sight it seems to be somewhat surprising that we here got exactly the same coefficients (69) as Bloch obtained in his simplified theory (S neglected). In order to examine this fact we now try to construct our Bloch orbitals directly from the \( AO \phi_{\alpha} \), given originally:
\[ \chi_{\kappa} = \sum_{\alpha} \phi_{\alpha} \delta_{\kappa \alpha}. \]
(75)
The fundamental conditions (54) and (55) again give a secular problem of the finite order \( G^2 \) by introducing the matrices
\[ \vec{H}_{\mu \alpha} = \sum_{\lambda} H_{\mu \alpha} \delta_{k \mu}, \quad \vec{S}_{\mu \alpha} = \sum_{\lambda} S_{\mu \alpha} \delta_{k \mu}. \]
(76)
(77)
Since \( \vec{H}_{\mu \alpha} \) as well as \( \vec{S}_{\mu \alpha} \) depend only on the difference \( \kappa = v-y \), they can both be transformed to a diagonal form by the unitary transformation (69). This means that our matrices \( \vec{H} \) and \( \vec{S} \) commute, i.e. that our crystal problem belongs to the simple case (i) treated before. Here we have the explanation why the coefficients (69) are identical with the coefficients of the simplified theory. We note that the functions
\[ G^{-1} \sum_{\alpha} \varphi_{\kappa}(r), \]
(78)
given by Bloch, are really the correct crystal functions except for a normalization factor, which, however, is of essential importance. The normalization of (78) is a rather delicate problem (see Eq. 33), and in practical investigations it is therefore much better to start from the automatically normalized functions (72).

The Band Structure

Equation (71) gives the energy band in the crystal associated with the atomic orbitals under consideration. The quantities \( J_{\kappa} \) characterize the band structure, and here we will consider them in greater detail.

Between the fundamental matrix elements \( H_{\mu \alpha}, H_{\mu \gamma}, \) and \( S_{\mu \alpha} \), there is a relation of the form (14). Using (64), (76), (77), and the transformation
\[ \sum_{\alpha} F_{\mu \alpha} = \sum_{\alpha} \vec{S}_{\mu \alpha}, \]
(79)
we obtain, after some simple reductions, for the finite matrices of order \( G^2 \):
\[ \vec{H}' = (1+\vec{S})^{-1} \vec{H}(1+\vec{S})^{-1}, \]
(80)
or, since \( \vec{S} \) commutes with \( \vec{H} \):
\[ \vec{H}' = (1+\vec{S})^{-1}. \]
(81)
In analogy to (42) and (43) we now introduce the notations
\[ \alpha = H_{00}, \quad \gamma_{\kappa} = H_{0\kappa} - \vec{H}_{0\kappa} \vec{S}_{0\kappa}. \]
(82)
In the same way as in deriving (45) we then get
\[ J_{\kappa} = \alpha \delta_{\kappa \kappa} + \sum_{\kappa' \neq \kappa} \gamma_{\kappa'} (1+\vec{S})^{-1} \delta_{\kappa \kappa'}. \]
(83)
where we also have neglected a term containing the quantity \( S_{06} \), which is practically zero. The formula (83) seems to be the best for practical purposes. The further development of the theory can be given in the usual way.

We note that, unlike the simplified theory (S neglected), the theory of band structure based on (59) and (83) is invariant with respect to the transformation (36), i.e., to an arbitrary change of the zero-point of the Hamiltonian operator. This is important, because in the simplified theory a very small change in the atomic potentials could cause considerable changes in the whole band structure.

Numerical applications\(^{20}\) of the simplified theory (S neglected) have given rather bad results, and from this fact one has usually drawn the conclusion that the whole LCAO-method represents a relatively bad and rough approximation for crystals. However, actual calculations in the complete theory, including overlap effects, show that the overlap integrals are of essential importance for the results, and therefore the whole problem must be reexamined. Numerical calculations on some typical crystals are now in progress, and the results will be published later.

Finally, we will say a few words about the connection between our orthonormalized atomic orbitals \( \phi_\mu \), given by (59), and the functions introduced by Wannier.\(^{21}\) He has treated the reverse problem, namely the construction of orthonormalized atomic orbitals by means of linear combinations from Bloch orbitals, and using the unitary property of (69), we obtain directly from (72) the two relations

\[
\chi_k = G^{-1} \sum_e \sum_{\tilde{e}} \sum_{\mu} \psi_{\tilde{e} k}^\dagger \phi_\mu, \quad (85)
\]

\[
\phi_\mu = G^{-1} \sum_k \sum_{\tilde{e}} e^{-2ik \cdot \tilde{r}} \psi_{\tilde{e} k}, \quad (86)
\]

Here (86) shows that, except for the different starting points, there is a very close connection between the functions \( \phi_\mu \) and Wannier's functions, since the latter are just given by a relation of this type. Slater\(^{22}\) has employed Wannier's functions in his theory of ferromagnetism, and now it is possible to reconsider this theory, starting from given atomic orbitals \( \phi_\mu \).

The theory of ferromagnetism, developed by Heisenberg, Bloch, Slater, and others, is based on the properties of certain "exchange integrals." It may here be pointed out that these integrals, referred to the orthonormalized atomic orbitals \( \phi_\mu \), are invariant with respect to an arbitrary change of the zero-point of the Hamiltonian operator. This does not apply to the corresponding quantities in the simplified theory (S neglected).

Here we have confined ourselves to the simple case when each unit cell \( \mathbf{y} \) contains only one atomic orbital \( \phi_\mu \), but we note that the theory is easily generalized even to the case when each unit cell \( \mathbf{y} \) contains \( p \) different atomic orbitals \( \phi_\mu^{(1)}, \phi_\mu^{(2)}, \ldots, \phi_\mu^{(p)} \), which may be associated with the same or different atomic nuclei in the cell \( \mathbf{y} \). The corresponding energy matrix

\[
H_{\mu,\nu}^{(s)}(r, s=1, 2, \ldots, p)
\]

can be essentially simplified by the unitary transformation (69), but instead of (71) we now get a determinant equation of the order \( p \). For each value of \( k \) we then have \( p \) different values of the energy \( E_k \), giving the \( p \) different energy bands belonging to the problem. It is not necessary to give more details, since the further development can be carried out following the conventional methods (see Mott and Jones, reference 20).

IV. THE NON-ORTHOGONALITY PROBLEM IN THE HEITLER-LONDON METHOD

Let us now consider a molecule or crystal, which contains \( N \) electrons having \( N \) atomic orbitals \( \phi_\mu (\mu = 1, 2, \ldots, N) \) at their disposal, by means of the Heitler-London method. As before the nuclei are assumed to be fixed; further we let \( Z_g \) be the atomic number of the nucleus situated at the point \( g \). The fundamental energy operator \(^{23}\) \( H_{\mu \nu} \) — different from the "effective" Hamiltonian in the theory of molecular orbitals — has now the form

\[
H_{\mu \nu} = W + \sum_{i=1}^{N} H_i + \sum_{k} G_{ik}. \quad (87)
\]

Here \( W \) represents the interaction between the nuclei, \( H_i \) the kinetic energy of the electron \( i \) plus its potential energy in the field of the nuclei, and \( G_{ik} \) the Coulomb interaction between the electrons \( i \) and \( k \):

\[
W = -\frac{e^2}{2} \sum_{\mu \nu} \frac{Z_\mu Z_\nu}{r_{\mu \nu}},
\]

\[
H_i = -\frac{e^2}{2m} \sum_{\mu \nu} \frac{Z_\mu}{r_{\mu i}} \quad G_{ik} = \frac{\epsilon^2}{2r_{ik}}. \quad (88)
\]

In the one-electron-approximation the wave function of each state of the system can be represented by a determinant of order \( N \), each element being a product of an \( AO \) \( \phi_\mu \) and a spin factor, \( \gamma^\uparrow \) or \( \gamma^\downarrow \). In the case under consideration we have a complicated spin degeneracy, which can be treated by the Heitler-London-Slater-\(^{23}\) relativistic effects being neglected.

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\(^{22}\) J. C. Slater, Phys. Rev. 52, 198 (1937).

\(^{23}\) Note added in proof: — J. C. Slater, Phys. Rev. 76, 1592 (1949), has recently shown that it is possible to treat electrons in perturbed periodic lattices by means of Wannier's functions in a simple way.
QUANTUM THEORY OF MOLECULES

TABLE I. Overlap integrals for LiCl and NaCl.*

<table>
<thead>
<tr>
<th></th>
<th>LiCl</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0 = 5.07 \ L_H$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S = 1 \ 1 \ 2$</td>
<td>0.0050</td>
<td>0.0092</td>
</tr>
<tr>
<td>$\alpha_0 = 5.20 \ L_H$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl/Na</td>
<td>3/3</td>
<td>3/0</td>
</tr>
<tr>
<td>$\phi_1(1)$</td>
<td>$\phi_2(1)$</td>
<td>$\phi_N(1)$</td>
</tr>
<tr>
<td>$\psi = \frac{1}{(N!)^N} \det \left[ \phi_1(1) \phi_2(1) \cdots \phi_N(1) \right]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\psi = \frac{1}{(N!)^N} \det \left[ \phi_1(2) \phi_2(2) \cdots \phi_N(2) \right]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\psi = \frac{1}{(N!)^N} \det \left[ \phi_1(N) \phi_2(N) \cdots \phi_N(N) \right]$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 1/3/3 etc. give the quantum numbers of the overlapping orbitals.

Pauling resonance theory. Here we are mainly interested in the overlapping effects, and, for the sake of simplicity, we will therefore confine ourselves to the simplest spin state, where all electrons have parallel spin. This state has the wave function

$$\Psi = \prod_{i=1}^{N} \phi_i(1)^{\uparrow} \phi_i(2)^{\downarrow} \cdots \phi_i(N)^{\uparrow}$$

The corresponding energy $E$ is then given by

$$E = \int \Psi^* H \Psi \ d\tau_1 \cdots d\tau_N'$$

where the integrations over $d\tau'$ include also summations over the spins. In (90) the calculation of the integrals is complicated by the non-orthogonality of the $AO$ $\phi_i$. Again we will use the formulas (15) and (16), giving

$$\phi = \frac{1}{\sqrt{1-|S_{12}|^2}},$$

or

$$\phi_\mu = \sum_{\sigma=1}^{N} \varphi_\sigma (1+S)^\mu \delta_\mu \delta_\nu.$$

Introducing the "overlap determinant"

$$\Delta = \det \left[ \delta_\mu + S_{\nu \mu} \right]$$

and using the law of determinant multiplication, we immediately obtain

$$\det \phi_\nu = \det \left[ \frac{1}{1-S_{13}} \cdots \frac{1}{1-S_{1N}} \right]$$

and

$$\Psi = \left( \frac{1}{N!} \right) \det \left[ \phi_\nu (1+S)^\mu \right].$$

Here the elements of the determinant are really orthogonal normalized functions, and hence we can directly employ the well-known formulas in the theory developed by Hartree-Slater-Fock. This simplification depends on the fact that a linear transformation of the $AO$ changes the determinant only by a constant factor. By using (94) we get directly

$$\int \Psi^* \Psi \ d\tau_1 \cdots d\tau_N' = \Delta = \det \left[ \delta_\mu + S_{\nu \mu} \right].$$

For $N = 2$ we have $\Delta = 1 - |S_{12}|^2$, and, for small values of $S_{12}$, the second term may be neglected in comparison to unity; i.e. the wave function is approximately normalized. However, this does not apply to higher values of $N$, since for increasing $N$ we get a rapidly increasing number of $S$-terms, which therefore no longer may be neglected in comparison to 1. For a crystal, where $N$ is an immense number, these terms are dominating.

The importance of the $S$-terms in this connection was first pointed out by Slater. Later Inglis stressed that for the theory of ferromagnetism the overlap integrals seemed to cause a real "non-orthogonality-catastrophe," but Van Vleck reexamined the problem and showed that probably the simplified theory ($S$ neglected) gives the best approximation. The latter also derived a semiquantitative formula for the error due to the non-orthogonality. Here we can now obtain a simple solution of the problem concerning the $S$-integrals.

In the energy expression (90) the numerator as well as the denominator contains the factor $\Delta$, which therefore cancels. Now we will introduce the following matrix elements:

$$\left[ \mu \left| H \right| \nu \right] = \int \phi_\mu^*(1) H \phi_\nu(1) d\tau_1,$$

$$\left[ \mu \left| G \right| \nu \right] = \int \phi_\mu^*(1) \phi_\nu^*(2) G_{12} \phi_\nu(1) \phi_\nu(2) d\tau_1 d\tau_2.$$

In the same manner we let brackets of the type () denote the corresponding elements associated with the original set $\phi_\nu$:

$$\left( \mu \left| H \right| \nu \right) = \int \phi_\mu^*(1) H \phi_\nu(1) d\tau,$$

$$\left( \mu \left| G \right| \nu \right) = \int \phi_\mu^*(1) \phi_\nu^*(2) G_{12} \phi_\nu(1) \phi_\nu(2) d\tau_1 d\tau_2.$$

**Table II. Survey of the various energy contributions in kcal./mol for LiCl, NaCl, and KCl.**

<table>
<thead>
<tr>
<th></th>
<th>Crystal energy</th>
<th>Exchange energy</th>
<th>S-energy</th>
<th>Cohesive energy</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>-210.4</td>
<td>-12.7</td>
<td>+35.4</td>
<td>-187.7</td>
<td>-198.1</td>
</tr>
<tr>
<td>NaCl</td>
<td>-218.5</td>
<td>-34.4</td>
<td>+69.7</td>
<td>-183.2</td>
<td>-182.8</td>
</tr>
<tr>
<td>KCl</td>
<td>-206.3</td>
<td>-53.7</td>
<td>+93.1</td>
<td>-166.9</td>
<td>-164.4</td>
</tr>
</tbody>
</table>

This idea of treating the non-orthogonality problem seems to have been first introduced by Landshoff, Zeits. f. Physik 102, 201 (1930), in an approximate way.
By using (94) and (96), we now get for the energy (90), according to a well-known formula in the Hartree-Slater-Fock theory,

\[ E = W + \sum_{\mu} [\mu | H | \mu] + \sum_{\mu\nu} \left[ [\mu\nu | G | \mu\nu] - [\mu\nu | G | \nu\mu] \right]. \tag{98} \]

In order to express the energy (98) in terms of the original matrix elements (97), we will use the matrix

\[ T = (1 + S)^{-1}. \tag{99} \]

If \( \Delta_{\mu\nu} \) is the cofactor of the determinant (92) associated with the element \( (\mu, \nu) \), we have

\[ T_{\mu\nu} = \Delta_{\mu\nu} / \Delta. \tag{100} \]

According to (91) we get \( \phi = \Phi T \), and, using the law of matrix multiplication, we then directly obtain

\[ \sum_{\mu} [\mu | H | \mu] = \sum_{\mu\nu} T_{\mu\nu}(\mu | H | \nu), \]

\[ \sum_{\mu\nu} [\mu\nu | G | \mu\nu] = \sum_{\mu\nu\lambda} T_{\mu\nu} T_{\nu\lambda}(\mu \nu | G | \kappa \lambda), \tag{101} \]

\[ \sum_{\mu\nu} [\mu\nu | G | \nu\mu] = \sum_{\mu\nu\lambda} T_{\nu\mu} T_{\mu\lambda}(\mu \nu | G | \kappa \lambda). \]

Putting (101) into (98), we get the result

\[ E = W + \sum_{\mu\nu} T_{\mu\nu}(\mu | H | \nu) + \sum_{\mu\nu\lambda} (T_{\mu\nu} T_{\nu\lambda} - T_{\nu\mu} T_{\mu\lambda})(\mu \nu | G | \kappa \lambda). \tag{102} \]

The last term can be transformed by using Jacobi's formula

\[ \Delta_{\mu\nu} \Delta_{\kappa\lambda} - \Delta_{\mu\kappa} \Delta_{\nu\lambda} = \Delta \cdot \Delta_{\mu\nu, \kappa \lambda}, \tag{103} \]

where \( \Delta_{\mu\nu, \kappa \lambda} \) is the determinant, obtained by striking out from \( \Delta \) the rows \( \mu \) and \( \nu \) together with the columns \( \kappa \) and \( \lambda \), multiplied by a sign factor \( (-1)^{\beta + \alpha + \sigma + \tau} \). From (100) and (102) we then get the final expression

\[ E = W + \sum_{\mu\nu} \Delta_{\mu\nu}(\mu | H | \nu) + \frac{1}{\Delta} \sum_{\mu\nu\lambda} \Delta_{\mu\nu, \kappa \lambda}(\mu \nu | G | \kappa \lambda), \tag{104} \]

which has a very simple symmetry.\(^{25}\)

We note that there is no "non-orthogonality-catastrophe," because the critical determinant \( \Delta \) does not appear alone but only in the connection

\[ T_{\mu\nu} = \frac{\Delta_{\mu\nu}}{\Delta} S_{\mu\nu} + \sum_{\sigma} S_{\mu\sigma} S_{\sigma\nu} - \cdots \tag{105} \]

Putting the expansion (105) in (102), we get an energy expression which is well fitted for numerical computations. However, we wish to emphasize that, even if there is no "S-catastrophe," the overlap integrals are still of essential importance for the results, which will be shown by the following examples.\(^{26}\)

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effects in the calculations, before one draws any conclusion as to the accuracy of the LCAO-method.

Now we will treat another property of the ionic crystals, closely connected with the overlap effects. Because of the perfect spherical symmetry of the complete electron-shells of the free ions, it has earlier often seemed to be natural to assume that the ions in the crystal, too, interact with central forces. As has been shown by the author, this is, however, not true because of the overlap effects.

The electrostatic energy as well as the exchange energy in (106) can be expressed in the form

$$\frac{1}{2} \sum_{\alpha \alpha'} E_{\alpha \alpha'}(r_{\alpha \alpha'})$$

(107)

where \(E_{\alpha \alpha'}\) is a function which depends only on the distance \(r_{\alpha \alpha'}\) between the nuclei of two ions. In the following we will therefore call forces, corresponding to potentials of this type, two-body-forces.

In an ionic crystal even the \(S\)-energy is a function only of the distances between the nuclei of the ions:

$$E_S = E_S(\mathbf{r}_{12}, \mathbf{r}_{13}, \ldots)$$

(108)

but this energy is now of a more complicated form than (107), since the corresponding expansion in addition to the two-body-terms also contains terms depending on the distances between the nuclei of three and more ions. The \(S\)-energy is therefore said to correspond to many-body-forces, and these forces add interesting new features to the properties of ionic crystals, e.g. as regards the elastic constants, the relative stability of different lattice types, and so on.

Let us here consider the problem of the elastic constants \(c_{ij}\) \((i, j = 1, 2, \ldots, 6)\). It is well known that if the forces in a general crystal are of two-body type, then these constants satisfy the six additional Cauchy relations:

$$c_{12} \equiv c_{66}, \quad c_{23} \equiv c_{44}, \quad c_{13} \equiv c_{46}, \quad c_{24} \equiv c_{64}, \quad c_{14} \equiv c_{66}, \quad c_{16} \equiv c_{66}$$

(109)

On the other hand, in references (15) and (16) the author has shown that these relations are no longer valid for the many-body potential derived there. This is of some interest, since experiments have shown that the Cauchy relations in reality are not valid for the crystals in nature. A comparison between the theoretical values of \(c_{ij}\), derived from the expression (106), and the experimental data would therefore also be a good test on the validity of our theoretical discussion concerning the overlap effects.

The alkali halides constitute the simplest case; they have only three independent elastic constants \(c_{11}, c_{12}, \text{ and } c_{44}\) with the Cauchy relation

$$c_{12} \equiv c_{44}$$

(110)

The calculations have been carried out for some of them, starting from the atomic orbitals \(\phi_n\), numerically given by Hartree-Hartree and Fock-Petrashen. Table III gives a survey of the importance of the overlap effects for the elastic constants.

The agreement between the theoretical and experimental values are almost better than one could really expect with regard to the approximations involved in the starting point as well as is the Heitler-London method. Hence, it seems probable that, in ionic crystals, the overlap effects with their many-body-forces are able to give an explanation of the well-known failure of the Cauchy relations.

As a summary of this paper we can thus draw the conclusion that, even if there is no "non-orthogonality-catastrophe," the overlap integrals are of essential importance in treating molecules and crystals by the LCAO-method.

**ACKNOWLEDGMENT**

Part of this work was carried out during a stay at H. H. Wills Physical Laboratory, University of Bristol, and I wish to express my gratitude to Professor N. F. Mott for his great hospitality and for fruitful discussions concerning crystal problems. Further, I take this opportunity of thanking Professor T. Waller, Upsala, for pointing out to me the problem connected with the elastic constants of the ionic crystals and the usefulness of Landshoff's work as a starting point for treating this problem. I am also indebted to Professor C. A. Coulson, London, for valuable discussions as to the conjugated systems. Finally, I should like to thank Dr. G. Wyllie, Bristol, for his kind help in reading the manuscript.