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Computation of LCAO Wave Functions for Ground States of Polymers and Solids

J. M. ANDRE,[‡] J. DELHALLE,[‡] J. G. FRIPIAT[§]
AND G. LEROY

Laboratoire de Chimie Quantique, Celestijnenlaan 200 G, Héverlé, Belgium

Abstracts

The LCAO form of the Hartree-Fock method is discussed in its application to crystals. General formulae are given for obtaining Fourier coefficient of electronic density (in direct space) as well as of the band structure (in momentum space). Finally, it is shown that in its LCAO form, Slater-Hartree-Fock equations are very simple and that this method is of interest for numerical applications. Special integrals occurring in this formalism are evaluated for a Gaussian basis in the last part of this paper.

On discute de l'application de la méthode de Hartree-Fock aux solides, dans le cadre de l'approximation LCAO. On déduit les expressions des facteurs de structure de la densité électronique et des coefficients de Fourier des bandes d'énergie dans l'espace des moments. Il apparaît que, dans ces conditions, les équations de Slater-Hartree-Fock peuvent être résolues simplement. La forme des intégrales caractéristiques de ce formalisme est déduite pour une base Gaussian dans la dernière partie de ce travail.

Die Anwendung der Hartree-Fock-Methode auf Festkörper wird im Rahmen eines LCAO-Näherungsverfahrens beschrieben. Formeln für die Fourier-koeffizienten der Elektronendichte und der Bandstruktur werden angegeben. Die Hartree-Fock-Slater-Gleichungen werden mit diesem Formalismus vereinfacht. Spezielle Integrale werden für einen Basissatz von Gaussfunktionen berechnet.

1. Introduction

It is well known that the Hartree-Fock method furnishes the best set of wave functions of strictly mono-electronic character (i.e. the best band structure) for solids or polymers. In molecular quantum chemistry, the orbitals are usually expanded in terms of atomic solutions. Although this procedure has played a dominant role in the refinements of scf theories for molecules, its application to the description of energy bands in crystals was rather difficult; important problems being concerned with the evaluation of polycentre integrals. In that connection, it is to be noticed that LCAO computations were recently proved actually feasible

[‡] Fellow of "Fonds National Belge de la Recherche Scientifique".

[§] Fellow of "Institut Belge pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture".

if the one-electron Hamiltonian is known [1, 2], such procedures avoiding explicit calculations of scf-repulsion and exchange terms.

With the recent availability of Gaussian multicentre packages [3] and of polymer programs [4, 5], it seems that the main difficulties for an actual scf calculation are being removed [6], so that it is desirable to examine the type of information which can be obtained from such LCAO wave functions.

The purpose of the present paper is to discuss ground states of polymers or solids in the LCAO Hartree-Fock method. Particular attention will be given to the computation of electronic densities and of band structures. Finally we propose an approximate LCAO Slater-Hartree-Fock procedure for solving the wave equations. This procedure uses Fourier series for expressing the electronic density in the Slater-Hartree-Fock operator. The practicability of the method is confirmed by preliminary results.

2. The LCAO-SCF-CO Equations for Solids and Polymers

In band theory, the one electron approximation defines crystalline orbitals (co's) to represent the wave function of an electron in a periodic potential. The optimal co's for a given basis set are constructed in the usual way by solving the set of Hartree-Fock equations:

$$(1) \quad \left[-\frac{1}{2}\nabla^2(i) - \sum (h) \sum (p) \frac{Z_p}{|\mathbf{r}_i - \mathbf{R}_p - \mathbf{R}_h|} + \sum (\mathbf{k}'n') \{2J_{\mathbf{k}'n'}(i) - K_{\mathbf{k}'n'}(i)\} \right] \phi_n(\mathbf{k}, i) = \varepsilon_n(\mathbf{k}) \phi_n(\mathbf{k}, i)$$

Hereafter atomic units are used such as $\hbar^2/4\pi^2m = 1$ and $e^2/a_0 = 1$ (where \hbar is the Planck constant, m , the mass of an electron, e , its charge and a_0 , the Bohr radius = 0.529 Å). In Equation (1) Z_p refers to the nuclear charge of the atom p centred in cell h . $J_{\mathbf{k}'n'}$ and $K_{\mathbf{k}'n'}$ are the Coulomb and exchange operators, such as:

$$(2) \quad J_{\mathbf{k}'n'}(i) \phi_n(\mathbf{k}, i) = \left\{ \int \phi_{n'}^*(\mathbf{k}', j) \frac{1}{r_{ij}} \phi_n(\mathbf{k}, j) dv_j \right\} \phi_n(\mathbf{k}, i)$$

and

$$(3) \quad K_{\mathbf{k}'n'}(i) \phi_n(\mathbf{k}, i) = \left\{ \int \phi_{n'}^*(\mathbf{k}', j) \frac{1}{r_{ij}} \phi_n(\mathbf{k}, j) dv_j \right\} \phi_{n'}(\mathbf{k}', i)$$

The meaning of these electron-electron terms has been analysed in the classical paper by Slater [7].

With the aid of the LCAO approximation, we can describe the delocalized crystalline orbital $\phi_n(\mathbf{k}, r)$ as a periodic combination of functions centred at the atomic nuclei of polymers. For a system of $(2N + 1)$ cells in each direction of

space and with a basis set of length P describing the electronic distribution within a given cell, the \mathbf{k} th crystal orbital in the n th energy band is described as:

$$(4) \quad \phi_n(\mathbf{k}, r) = (2N + 1)^{-3/2} \sum (j) \sum (p) \exp(i\mathbf{k}\mathbf{R}_j) C_{np}(\mathbf{k}) \chi_p(\mathbf{r} - \mathbf{R}_j)$$

where j refers to the set of three cell indices (j_1, j_2, j_3) . $\sum(j)$ is a shorthand notation for $\sum_{j_1=-N}^N \sum_{j_2=-N}^N \sum_{j_3=-N}^N$ and $2N + 1$ is the number of cells explicitly used in the computation along \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 axes. \mathbf{R}_j defines the position vector, $\mathbf{R}_j = j_1\mathbf{a}_1 + j_2\mathbf{a}_2 + j_3\mathbf{a}_3$. $C_{np}(\mathbf{k})$ is an expansion coefficient of the linear combination. The basis set $\{\chi_p\}$ can be of several types. In our case, however, special formulae will be deduced for the Gaussian form:

$$(5) \quad \begin{aligned} \chi_p(\mathbf{r} - \mathbf{R}_a) &= \chi_p(\mathbf{R}_a, \alpha_p, l_p, m_p, n_p) \\ &= (x - X_a)^{l_p} (y - Y_a)^{m_p} (z - Z_a)^{n_p} \exp[-\alpha_p(x - X_a)^2] \\ &\quad \times \exp[-\alpha_p(y - Y_a)^2] \exp[-\alpha_p(z - Z_a)^2] \end{aligned}$$

Equation (5) defines the type of atomic orbital p centred on atom a (s -type: $l_p = m_p = n_p = 0$, p_x -type: $l_p = 1, m_p = n_p = 0$, etc.).

It has been previously shown that the vectors $C_n(\mathbf{k})$ collecting the expansion coefficients $C_{np}(\mathbf{k})$ are the eigenvectors of the pseudoeigenvalue equations:

$$(6) \quad F_c(\mathbf{k}) C_n(\mathbf{k}) = S_c(\mathbf{k}) C_n(\mathbf{k}) E_n(\mathbf{k})$$

where $F_c(\mathbf{k})$ and $S_c(\mathbf{k})$ are the Fock and overlap matrices between Bloch orbitals:

$$(7) \quad F_c(\mathbf{k}) = \sum (j) \exp(i\mathbf{k}\mathbf{R}_j) F(j)$$

and

$$(8) \quad S_c(\mathbf{k}) = \sum (j) \exp(i\mathbf{k}\mathbf{R}_j) S(j)$$

$F(j)$ and $S(j)$ are the Fock and overlap matrices collecting the Fock and overlap integrals between atomic orbitals p centred in the origin unit cell and atomic orbital q centred in cell j .

The spectrum of the eigenvalues $E_n(\mathbf{k})$ for a given n with respect to \mathbf{k} is the n th energy band. The set of all energy bands describes the band structure of the polymer (or of the crystal). In connection with the eigenvalue Equation (6), the orthogonality constraints between Bloch orbitals for a given value of \mathbf{k} in the first Brillouin zone are:

$$(9) \quad C_n^\dagger(\mathbf{k}) S_c(\mathbf{k}) C_m(\mathbf{k}) = \delta_{mn}$$

For analyzing the electronic density, it is useful to define density matrices:

$$(10) \quad D_n(\mathbf{k}, o) = 2C_n(\mathbf{k}) C_n^\dagger(\mathbf{k}) (2N + 1)^{-3/2}$$

These quantities represent the contribution of the \mathbf{k} th orbital in the n th energy band to the electronic density of the basis functions in the unit cell. The contributions to the other cells are related to the ones in the unit cell by the formula:

$$(11) \quad D_n(\mathbf{k}, j) = \exp(i\mathbf{k}\mathbf{R}_j) D_n(\mathbf{k}, o)$$

These submatrices give rise to partial density submatrices for the n th energy band:

$$(12) \quad D_n(j) = \sum \langle k \rangle D_n(\mathbf{k}, j) = \sum \langle \mathbf{k} \rangle \exp(i\mathbf{k}\mathbf{R}_j) D_n(\mathbf{k}, o)$$

or total matrices:

$$(13) \quad D(j) = \sum_n D_n(j) = 2 \sum_{\mathbf{k}} \sum_n C_n(\mathbf{k}) C_n^\dagger(\mathbf{k}) (2N+1)^{-3/2} \exp(i\mathbf{k}\mathbf{R}_j)$$

Clearly:

$$\text{Tr} \sum (j)^\theta [S(j) D(j)] = 2n$$

(where n is the number of doubly occupied bands) is the normalization condition for the density submatrices.

It is to point out that in order to avoid cyclic properties, the value of N in Equation (13) must be greater than the one in Equation (4). Clearly, Equation (13) is an approximation (analogous to a numerical integration) to the correct expression:

$$(14) \quad D(j) = (2/\omega) \sum \langle n \rangle \int_{\omega} C_n^\dagger(\mathbf{k}) C_n(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_j) d^3k$$

where ω is the volume of the first Brillouin zone. The integration is done over all doubly occupied k points and the summation goes up to the last occupied band.

With the above definitions, we are in a position to deduce the electronic density associated to each point of direct space. We refer to a preceding paper [4] for discussions concerning selfconsistent and Hartree-Fock solutions.

3. Electronic Distribution in Polymers and Solids

In this section, we would like to consider the electronic density and express its structure factors in terms of LCAO integrals.

The contribution of an energy band to the electronic density within a given position \mathbf{r} is, in terms of crystalline orbitals:

$$(15) \quad \rho_n(\mathbf{r}) = \sum \langle \mathbf{k} \rangle \phi_n^*(\mathbf{k}, \mathbf{r}) \phi_n(\mathbf{k}, \mathbf{r})$$

or in terms of atomic orbitals:

$$(16) \quad \rho_n(\mathbf{r}) = (2N+1)^{-3} \sum \langle \mathbf{k} \rangle \sum \langle j \rangle \sum \langle h \rangle \sum \langle p \rangle \sum \langle q \rangle C_{np}^*(\mathbf{k}) C_{nq}(\mathbf{k}) \\ \times \exp[i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_h)] \chi_p(\mathbf{r} - \mathbf{R}_j) \chi_q(\mathbf{r} - \mathbf{R}_h)$$

From Equation (12), it appears that Equation (16) can be rewritten as a function of the density matrices $D_n(j)$:

$$(17) \quad \rho_n(\mathbf{r}) = \sum (j) \sum (h) \sum (p) \sum (q) D_{n,pq}^{h-j} \chi_p(\mathbf{r} - \mathbf{R}_j) \chi_q(\mathbf{r} - \mathbf{R}_h)$$

The summation in Equation (17) is extended to the cells of the crystal (j, h) and to the atomic orbitals in the unit cell (p, q).

The periodic properties of $\rho_n(\mathbf{r})$ make it readily adaptable to a Fourier development such as:

$$(18) \quad \rho_n(\mathbf{r}) = \sum (\mathbf{G}) F_{n\mathbf{G}} \exp(-i\mathbf{G}\mathbf{r})$$

The Fourier transforms $F_{n\mathbf{G}}$ are easily obtained by a straightforward integration. In the following, V means the total volume of the crystal ($= [2N + 1]^3 v$)

$$(19) \quad F_{n\mathbf{G}} = \frac{1}{V} \int_V \rho_n(\mathbf{r}) \exp(i\mathbf{G}\mathbf{r}) d^3r$$

$$(20) \quad = \frac{1}{v} \sum (j) \sum (p) \sum (q) D_{n,pq}^{oj} S_{pq}^{oj}(\mathbf{G})$$

when defining the "generalized" overlap integrals between atomic orbitals, introduced by Stewart [8], which are nothing but the Fourier transforms of an overlap charge distribution:

$$(21) \quad S_{pq}^{oj}(\mathbf{G}) = \int \chi_p(\mathbf{r} - \mathbf{R}_o) \exp(+i\mathbf{G}\mathbf{r}) \chi_q(\mathbf{r} - \mathbf{R}_j) d^3r$$

General formulae as well as special ones for s - s , s - p and p - p Gaussian orbitals are given in Section 6 of this paper.

The total electronic density is obtained by summing the partial ones (Equation 18) for all energy bands

$$(22) \quad \rho(\mathbf{r}) = \sum (n) \rho_n(\mathbf{r}) = \sum (\mathbf{G}) F(\mathbf{G}) \exp(-i\mathbf{G}\mathbf{r})$$

We may then make a further approximation, by using Equation (21) and obtain the electronic density in terms of density matrices D_{pq}^{oj} and of generalized overlap matrices $S_{pq}^{oj}(\mathbf{G})$, so that the electronic density can be rewritten as:

$$(23) \quad \rho(\mathbf{r}) = \frac{1}{v} \sum (\mathbf{G}) \sum (j) \sum (p) \sum (q) D_{pq}^{oj} S_{pq}^{oj}(\mathbf{G}) \exp(-i\mathbf{G}\mathbf{r})$$

so that

$$(24) \quad F(\mathbf{G}) = \frac{1}{v} \sum (j) \sum (p) \sum (q) D_{pq}^{oj} S_{pq}^{oj}(\mathbf{G})$$

We would like to point out the excellent convergency properties of Equation (23),

both in the direct space ($S_{pq}^{oj}(\mathbf{G})$) being proportional to $\exp [\alpha_p \alpha_q (\mathbf{R}_0 - \mathbf{R}_j)^2 / (\alpha_p + \alpha_q)]$ as seen in Section 6 and in reciprocal space $\{S_{pq}^{oj}(\mathbf{G}) \simeq \exp [-|\mathbf{G}|^2 / 4(\alpha_p + \alpha_q)]\}$. This makes Equation (23) of great utility for practical application.

To gain confidence about the practicality of the above described method, we undertook the evaluation of structure factors of a simple cubic structure (of length axis = 2 a.u.), with a nucleus of charge 2 at the origin of cell axis and two electrons per unit cell. The crystalline orbitals are taken to be Bloch functions of an *s* Gaussian orbital of screening ($\alpha = 0.817571$). Intermediate results (density matrices and structure factors) are given in Table I. Electronic densities in unit cell calculated by Equation (16) and by Equation (23) are given in Table II.

TABLE I. Density matrices and structure factors.

$h^2 + k^2 + l^2$ or $m^2 + n^2 + p^2$	Number of equivalent points in the set	Density matrices $D(m, n, p)$	Structure factors (Bohr ⁻³) $F(h, k, l)$
0	1	2.562152	0.250000
1	6	-0.520844	0.064800
2	12	0.105879	0.016796
3	8	-0.021523	0.004353
4	6	0.101023	0.000597
5	24	-0.020439	0.000155
6	24	0.004135	0.000040

TABLE II. Electronic densities in unit cell, $Y = Z = 0$.

$X a$	(Equation 16)	(Equation 23)			
		7 terms	19 terms	27 terms	125 terms
0.00	0.883488	0.638800	0.840352	0.875176	0.883488
0.25	0.577251	0.509200	0.576384	0.576384	0.577251
0.50	0.282111	0.379600	0.312416	0.277592	0.282111
0.75	0.577251	0.509200	0.576384	0.576384	0.577251

From another point of view, it would be tempting to have the following reasoning. Since D_{pq}^{oj} and $S_{pq}^{oj}(\mathbf{G})$ are important only for nearest neighbours, we could neglect, without too much approximation the intermolecular integrals of those types if we are concerned with a molecular crystal; so that the structure factor $F(\mathbf{G})$ seems, at first sight, to depend only on the molecular structure and not on the intermolecular structure arrangements. However it is important to note that, unlike the overlap integrals S_{pq}^{oj} , the generalized overlap integrals $S_{pq}^{oj}(\mathbf{G})$ usually depend on the absolute positions of centres *p* and *q* in the direct space as well as

on their relative positions. As a consequence the structure factors are very sensitive to intermolecular arrangements.

It is to be noted that the coefficients $F(\mathbf{G})$ in Equation (22) are the structure factors of the polymers, related to the experimentally observed ones in X-ray diffraction (except for a phase factor). It is usually assumed that this structure factor can be expanded in terms of the diffusion power of each atom:

$$(25) \quad F(\mathbf{G}) = F(hkl) = \sum (p) f_p \exp [-i(u_p h + v_p k + w_p l)]$$

In Equation (25), f_p is the diffusion factor of the p th atom and u_p, v_p, w_p the reduced components of the position vector of the p th atom in the origin unit cell. Furthermore, we neglect the temperature factor.

Clearly, the difference between the "semi-empirical" relation (Equation 25) and the theoretical expression (Equation 24) is mainly connected with the neglect of non-diagonal terms $S_{pq}^{oj}(\mathbf{G})$. Thus the diffusion term f_p can be understood as the intrinsic diffraction power of the p th atom corrected by the mean value of the diffracting power of electronic overlap populations.

However, it is obvious that this approximation can be justified in a certain way and related to Mulliken's definition of gross charges [9]. Let us examine the term $F(\mathbf{G})$ for $\mathbf{G} = 0$, which as a consequence of Fourier theorem is the mean value of the electronic density (i.e. the number of electrons per unit cell divided by the volume of the unit cell).

$$(26) \quad F^{\text{exp}}(0) = \frac{1}{v} \sum (p) f_p = \sum (p) Z_p / v$$

$$(27) \quad F^{\text{theor}}(0) = \frac{1}{v} \sum (j) \sum (p) \sum (q) D_{pq}^{oj} S_{pq}^{oj}$$

It is useful to write Equation (27) in terms of atoms a and b and orbitals α_a and β_b , centred on a and b respectively; in which case:

$$(28) \quad F^{\text{theor}}(0) = \frac{1}{v} \sum (j) \sum (a) \sum (b) \sum (\alpha_a) \sum (\beta_b) D_{\alpha_a \beta_b}^{oj} S_{\alpha_a \beta_b}^{oj}$$

which can be rewritten as

$$(29) \quad F^{\text{theor}}(0) = \frac{1}{v} \sum (a) \sum (\alpha_a) \{ \sum (j) \sum (b) \sum (\beta_b) D_{\alpha_a \beta_b}^{oj} S_{\alpha_a \beta_b}^{oj} \}$$

The quantity between parentheses is the partial gross population $N(\alpha_a, a)$ in atomic orbital α_a centred on a . If we go one step further,

$$(30) \quad F^{\text{theor}}(0) = \frac{1}{v} \sum (a) N(a)$$

where $N(a) = \sum (\alpha_a) N(\alpha_a, a)$ is the gross population on atom a . Clearly, Equation (30) is the number of electrons per unit cell divided by the volume of the unit cell. So that, in a way, we have justified for the factor $F(0)$ the breakdown into contributions due to each atom. In a physical sense, this corresponds to the Mulliken approximation where one allocates the whole electronic population among the atomic centres only.

However, it is important to remember that gross atomic populations are very dependent on the molecular or crystalline neighbouring and are not easily related to atomic density as assumed in Equation (25).

To conclude this section, we would like to point out that the empirical formula Equation (25) is to be implemented by considering the overlap populations as well as the gross populations (or the bond diffusion factors as well as the atomic ones).

4. Energy Spectrum in Reciprocal Space

It is obvious that energy bands in momentum space have analogous properties to those of the electronic density in direct space.

Similarly to Equation (15), the energy of a crystalline orbital can be expressed in terms of integrals of orbitals in direct space (corresponding to the summation over \mathbf{k} in Equation 15).

$$(31) \quad \varepsilon_n(\mathbf{k}) = \int \phi_n^*(\mathbf{k}, \mathbf{r}) h \phi_n(\mathbf{k}, \mathbf{r}) d^3r$$

or in terms of electronic integrals over atomic orbitals

$$(32) \quad \varepsilon_n(\mathbf{k}) = \sum (j) \sum (p) \sum (q) C_{np}^*(\mathbf{k}) C_{nq}(\mathbf{k}) \exp (i\mathbf{k}\mathbf{R}_j) \\ \times \int \chi_p(\mathbf{r} - \mathbf{R}_o) h \chi_q(\mathbf{r} - \mathbf{R}_j) d^3r$$

General theorems of solid state physics prove that $\varepsilon_n(\mathbf{k})$ is periodic in \mathbf{k} -space allowing us to define the Fourier series:

$$(33) \quad \varepsilon_n(\mathbf{k}) = \sum (\mathbf{R}_h) F_n(\mathbf{R}_h) \exp (-i\mathbf{R}_h\mathbf{k})$$

where \mathbf{R}_h are vectors of the direct lattice ($= h_1\mathbf{a}_1 + h_2\mathbf{a}_2 + h_3\mathbf{a}_3$ with h_1, h_2, h_3 integers). The Fourier transforms $F_n(\mathbf{R}_h)$ can be easily obtained in terms of Fock integrals F_{pq}^{oj} and elements of density matrices by a straightforward integration over the reciprocal cell in k -space:

$$(34) \quad F_n(\mathbf{R}_h) = \frac{1}{\omega} \int_{\omega} \varepsilon_n(\mathbf{k}) \exp (i\mathbf{k}\mathbf{R}_h) d^3k$$

$$(35) \quad = \frac{1}{\omega} \sum (j) \sum (p) \sum (q) F_{pq}^{oj} \int C_{np}^*(\mathbf{k}) C_{nq}(\mathbf{k}) \\ \times \exp [i\mathbf{k}(\mathbf{R}_j + \mathbf{R}_h)] d^3k$$

It can be seen from Equation (11) that the integrals in Equation (35) are half the elements of the density submatrix $D_n(\mathbf{k}, j + h)$.

Thus, the n th energy band, expressed in Fourier series is:

$$(36) \quad \varepsilon_n(\mathbf{k}) = \frac{1}{2} \sum (h) \sum (j) \sum (p) \sum (q) F_{pq}^{oj} D_{n,pq}^{o,j+h} \exp(i\mathbf{k}\mathbf{R}_h)$$

The convergency properties of Equation (36) can be considered to be very good since the product $F_{pq}^{oj} D_{n,pq}^{o,j+h}$ is negligible except for small values of indices j and h . Thus Equation (36) is of practical use for computing or plotting energy bands since the integrals F_{pq}^{oj} and $D_{n,pq}^{oj}$ are necessary quantities obtained at each iteration of the scf procedure.

Equation (36) enables us to define interesting properties of energy bands near points of high symmetry. Namely, the values for $\mathbf{k} = 0$ (Γ):

$$(37) \quad \varepsilon_n(0) = \sum (h) F_n(\mathbf{R}_h)$$

or in the neighbouring of $\mathbf{k} = 0$

$$(38) \quad \begin{aligned} \varepsilon_n(\mathbf{k} \rightarrow 0) &= \sum (h) F_n(\mathbf{R}_h) \left\{ 1 - \frac{(\mathbf{R}_h \mathbf{k})^2}{2!} + \dots \right\} \\ &= \varepsilon_n(0) - \sum (h) \frac{F_n(\mathbf{R}_h)}{2!} (\mathbf{R}_h \mathbf{k}) + \dots \end{aligned}$$

Other properties need the gradient and the Laplacian of the energy function with respect to \mathbf{k} . In the same way as before, we can expand the first and second derivatives of $\varepsilon_n(\mathbf{k})$ in Fourier series, by applying the derivation operators in Equation (32):

$$(39) \quad \nabla_{\mathbf{k}} \varepsilon_n(\mathbf{k}) = \mathbf{v}_k = v_{k_1} \mathbf{e}_{k_1} + v_{k_2} \mathbf{e}_{k_2} + v_{k_3} \mathbf{e}_{k_3}$$

where

$$(40) \quad \begin{aligned} v_{k_1} &= \frac{\partial \varepsilon_n(\mathbf{k})}{\partial k_1} = \sum (j) \sum (p) \sum (q) [C_{np}^{1*}(\mathbf{k}) C_{nq}(\mathbf{k}) + C_{np}^*(\mathbf{k}) C_{nq}^1(\mathbf{k}) \\ &\quad + ij_1 2\pi C_{np}^*(\mathbf{k}) C_{nq}(\mathbf{k})] F_{pq}^{oj} \exp(i\mathbf{k}\mathbf{R}_j) \\ &= \sum (R_h) F_n^1(R_h) \exp(-i\mathbf{k}\mathbf{R}_h) \end{aligned}$$

By this procedure, the Fourier transforms $F_n^1(R_h)$, $F_n^2(R_h)$ and $F_n^3(R_h)$ can be easily obtained in terms of F_{pq}^{oj} and elements of density matrices and their derivatives:

$$(41) \quad D_{n,p_1q}^{oj} = \frac{1}{\omega} \int_{\omega} C_{np}^{1*}(\mathbf{k}) C_{nq}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_j) d\mathbf{k}^3$$

such as

$$(42) \quad F_n^1(R_h) = \frac{1}{\omega} \int_{\omega} \sum (j) \sum (p) \sum (q) F_{pq}^{oj} [C_{np}^{1*}(\mathbf{k}) C_{nq}(\mathbf{k}) + C_{np}^*(\mathbf{k}) C_{nq}^1(\mathbf{k}) + ij_1 2\pi C_{np}^*(\mathbf{k}) C_{nq}(\mathbf{k})] \exp [i\mathbf{k}(\mathbf{R}_h + \mathbf{R}_j)] dk^3$$

$$(43) \quad = \sum (j) \sum (p) \sum (q) [D_{n,pq}^{o,h+j} + D_{n,pq}^{o,h+j} + ij_1 a D_{n,pq}^{o,h+j}] F_{pq}^{oj}$$

We obtain a similar (but more complicated) form for the second derivative. In the case of the first derivative and because of no spin-orbit coupling interactions, the coefficients of the Fourier series must be purely imaginary so we get a simpler form for $F_n^l(R_h)$, $l = 1, 2, 3$:

$$(44) \quad F_n^l(R_h) = \sum (j) \sum (p) \sum (q) F_{pq}^{oj} [ij_l 2\pi D_{n,pq}^{o,h+j}] F_{pq}^{oj}$$

The task for obtaining the $F_n^l(R_h)$'s is not more difficult than for computing the $F_n(R_h)$'s.

These procedures will be useful in order to approach the density of electronic states or the electronic effective masses near the points of high symmetry in terms of Fourier transforms and their derivatives.

Finally, other relations are easily deduced for investigating the form and the position of energy bands. We find that the centre of gravity of a band lies to the energetic values $F_n(0) = \sum (j) \sum (p) \sum (q) D_{n,pq}^{oj} F_{pq}^{oj}$, which is clearly the mean value of the entire n th energy band:

$$(45) \quad F_n(0) = \frac{\sum (\mathbf{k}) \sum (j) \sum (p) \sum (q) D_{\mathbf{k}n,pq}^{oj} F_{pq}^{oj}}{(2N+1)^3}$$

$$(46) \quad = \frac{1}{\omega} \int \varepsilon(\mathbf{k}, n) d^3k$$

By analogy with the population analysis given in Section 3, this term can be expressed as a sum of energies of each atom in the crystalline field:

$$(47) \quad F_n(0) = \sum (p) \varepsilon(p)$$

when

$$(48) \quad \varepsilon(p) = \sum (j) \sum (p) \sum (q) D_{n,pq}^{oj} F_{pq}^{oj}$$

Furthermore, since for very localized orbitals (1s-type orbital for instance in carbon polymers), the density matrices are negligible (of the order 10^{-1} , 10^{-2}) except for only one atom, the corresponding band will be characteristic of one type of atom (C, N or O) and will be localized around the energy of the atom in the crystal. The relation with the orbital energies of the separated atoms is in general not too immediate. However, if the corresponding crystalline orbitals are only slightly delocalized as compared to the isolated atoms and if the dominant part of the crystal field is the atomic field, then the orbital energies in the separated

atoms will resemble substantially the orbital energies in the polymer. This is the case of inner shell electrons.

Note that even in the case of 1s orbital energies, the spread of atomic levels is important (of the order of 0.2 a.u. or 5 eV). A measure of this broadening within the polymer or the solid is given by the difference between the level for $\mathbf{k} = 0$ and the centre of gravity of the band (mean value of the band). The important broadening is easily understood, since the inner shell electrons are highly energetic so that a small variation in density has a large effect on the energy.

As a consequence, only qualitative conclusions can be reached without explicit computations.

5. The LCAO-Slater-Hartree-Fock Equations

The excellent convergency properties of the Fourier series (24) enables us to formulate a LCAO form of the Slater-Hartree-Fock method.

The Slater-Hartree-Fock equations differ from the usual scf ones by the use of an approximate exchange potential. This approximation assumes that the exchange density and its corresponding potential depends mainly on the density of electronic charges. Thus, it allows us to approximate the exchange potential by a free-electron one corrected for non-uniform electronic distribution. By applying this procedure, we finally get the Slater-Hartree-Fock equations:

$$(49) \quad \left\{ -\frac{1}{2}\nabla^2(i) - \sum (h) \sum (p) \frac{Z_p}{|\mathbf{r}_i - \mathbf{R}_p - \mathbf{R}_h|} + \int \frac{\rho(j)}{r_{ij}} dv_j - \frac{3}{2} \left[\frac{3\rho(i)}{\pi} \right]^{1/3} \right\} \phi_n(\mathbf{k}, i) \\ = \varepsilon_n(\mathbf{k}) \phi_n(\mathbf{k}, i)$$

In practice, this equation replaces the non-local potential of Equation (1) by a local one and is very simple to apply. As pointed out by Slater [7], Equation (49) may be taken to be the basis of the ordinary form of the energy band theory of solids (i.e. it is assumed that we can imagine a model of a solid in which each electron moves independently in the same potential). It can be seen from Equation (3) that the Hartree-Fock method implies a different potential acting on each electron, while the Slater-Hartree-Fock method does not (Equation 49).

Furthermore, the use of Slater-Hartree-Fock equations in their following LCAO form will provide a direct comparison with the general methods of solid state physics (APW, OPW) where the Slater-exchange potential has been traditionally used.

The periodic parts of the monoelectronic potential in Equation (49) can be developed in view of Section 3 of this paper by using Equation (24).

$$(50) \quad -\frac{1}{2}\nabla^2(i) - \sum (h) \sum (p) \frac{Z_p}{|\mathbf{r}_i - \mathbf{R}_p - \mathbf{R}_h|} + \sum (\mathbf{G}) F(\mathbf{G}) \int \frac{\exp(-i\mathbf{G}\mathbf{r}_j)}{r_{ij}} dv_j \\ - \frac{3}{2} \left[3 \sum (\mathbf{G}) F(\mathbf{G}) \frac{\exp(-i\mathbf{G}\mathbf{r}_i)}{\pi} \right]^{1/3}$$

The integrals which appear in Equation (50) are the usual ones found in the free electron exchange theory and which have been solved by Dirac [12], Bardeen [13] (see also Kittel [14]). The result is conditionally convergent:

$$(51) \quad \int \frac{\exp(-i\mathbf{G}\mathbf{r}_j)}{r_{ij}} d^3r_j = 4\pi \frac{\exp(-i\mathbf{G}\mathbf{r}_i)}{|\mathbf{G}|^2}$$

It turns out that the Coulomb potential exhibits repulsive divergency for $|\mathbf{G}| = 0$. This divergency combines with the corresponding part of the nuclear attraction terms which can be rewritten in Fourier series:

$$(52) \quad \sum (h) \sum (p) \frac{Z_p}{|\mathbf{r}_i - \mathbf{R}_p - \mathbf{R}_h|} = \frac{4\pi}{v} \sum (\mathbf{G}) \left\{ \sum (p) \frac{Z_p \exp[i\mathbf{G}(\mathbf{R}_p - \mathbf{r}_i)]}{|\mathbf{G}|^2} \right\}$$

If we remember that the structure factor $F(0)$ is equal to the number of electrons per unit cell (Equation 7) divided by the volume (v) of the unit cell, and that in order to save the neutrality of the system, the sum over nuclear charges ($\sum (p) Z_p$) must be equal to the number of electrons, we observe that the sum of terms ($\mathbf{G} = 0$) for the nuclear attraction part and for the repulsive coulomb potential is equal to zero.

A further simplification can be made in the exchange potential by using the binomial theorem:

$$(53) \quad V(i) = \frac{3}{2} \left[3 \sum (\mathbf{G}) F(\mathbf{G}) \frac{\exp(-i\mathbf{G}\mathbf{r}_i)}{\pi} \right]^{1/3}$$

$$(54) \quad = \left(\frac{81}{8\pi} \right)^{1/3} F(0)^{1/3} \left[1 + \sum (\mathbf{G} \neq 0) \frac{F(\mathbf{G})}{F(0)} \exp(-i\mathbf{G}\mathbf{r}_i) \right]^{1/3}$$

$$(55) \quad \simeq \left(\frac{81}{8\pi} \right)^{1/3} \left[F(0)^{1/3} + \sum (\mathbf{G} \neq 0) \frac{F(\mathbf{G})}{3F(0)^{2/3}} \exp(-i\mathbf{G}\mathbf{r}_i) \right]$$

$$(56) \quad \simeq \sum (\mathbf{G}) f(\mathbf{G}) \exp(-i\mathbf{G}\mathbf{r}_i) \begin{cases} f(0) = \left(\frac{81}{8\pi} \right)^{1/3} F(0)^{1/3} \\ f(\mathbf{G}) = \left(\frac{81}{8\pi} \right)^{1/3} \frac{F(\mathbf{G})}{3F(0)^{2/3}} \end{cases}$$

In a way, this approximation could be justified by observing that if we integrate the contributions for $\mathbf{G} \neq 0$ over all space, the net result is zero. However, the validity of approximation from Equation (54) to Equation (55) will depend on the ratio $F(\mathbf{G})/F(0)$, which have been seen in Section 3 to converge rapidly enough to zero.

We note that if we do not allow this simplification, the only way to compute matrix elements will be by numerical integration.

Under these conditions, the monoelectronic operator is now:

$$(57) \quad -\frac{1}{2}\nabla^2(i) + \frac{4\pi}{v} \sum (\mathbf{G} \neq 0) \{vF(\mathbf{G}) - \sum (p)Z_p \exp(-i\mathbf{G}\mathbf{R}_p)\} \\ \times \frac{\exp(-i\mathbf{G}\mathbf{r}_i)}{|\mathbf{G}|^2} + \sum (\mathbf{G})f(\mathbf{G}) \exp(-i\mathbf{G}\mathbf{r}_i)$$

It is straightforward to deduce the matrix elements in terms of kinetic integrals $\{\int \chi_p(\mathbf{r}_i - \mathbf{R}_0)[- \frac{1}{2}\nabla^2(i)]\chi_q(\mathbf{r}_i - \mathbf{R}_j) dv_j\}$ and of generalized overlap integrals (Equation 21). Let us note that the Fourier coefficients $f(\mathbf{G})$ depend only upon the same generalized overlap integrals and on the density matrices (Equation 13). The accuracy of the method would be achieved to any degree by simply increasing the size of the Fourier series. Let us notice that, although we have no convergence in the nuclear attractive potential of Equation (57), an excellent convergence will come from the multiplication of Fourier coefficients ($\sim 1/|\mathbf{G}|^2$) and corresponding generalized overlap integrals [$\sim \exp -|\mathbf{G}|^2/4(\alpha_p + \alpha_q)$], demonstrating that this procedure is very adequate for computing LCAO matrix elements.

Furthermore, we see that the average nuclear attractive and electronic repulsive potentials averaged over all space is zero in the expression of Equation (57). Consequently, we have to add an additive constant to the expression of Equation (57) in order to make the average potential take on the desired value. This constant is straightforwardly deduced from the second and third term of Equation (49).

Table III gives the numerical values of parts of matrix elements for the simple cubic case precedently described in Section 2 of this paper; when programmed straightforwardly the computation of 343 matrix elements of this type with 343 terms in the Fourier series were found to take about 50 secs (100 m/sec each) on IBM 360/75 equipment. A general program based on the above described method is now in the testing phase and will be applied to determination of band structures of first row solids. We feel confident in stating that this procedure could be of general interest in solid state physics. In our opinion, it avoids the difficulty of the expansion of wave functions in plane waves which needs many terms to represent the oscillations near nuclei. Our procedure develops the electronic density which has much less oscillations.

Furthermore, it also avoids the difficulty pointed out by Parmenter [15], where the Fourier expansion for the periodic part of crystalline orbital, is used since we have kept the general structure of LCAO methods which has been proved successful when they were possible to apply.

Finally, it should be pointed out that following the work available for the last 35 years [16-19], the correlation energy is generally assumed to mainly depend on the electron density and its first derivatives, which would be easily obtained in the framework of the present method. Indeed, such a procedure will not give

TABLE III. Convergence properties of matrix elements of a simple cubic lattice ($a = 2$ a.u.) with two electrons per unit cell, described by a $1s$ Gaussian orbital ($\alpha = 0.817571$) centred at the origin of axis. Results are given in atomic units.

$h^2 + k^2 + l^2$	Number of terms in the Fourier series	Kinetic term	Averaged nuclear term	Nuclear attractive term	Electronic repulsive term	Exchange term	Matrix element
0	7	1.226356	-0.345692	-0.422336	0.109385	-1.037116	-0.469403
	19	1.226356	-0.345692	-0.515729	0.115650	-1.049325	-0.568740
	27	1.226356	-0.345692	-0.524908	0.115809	-1.049792	-0.578227
	125	1.226356	-0.345692	-0.527011	0.115813	-1.049805	-0.580339
	343	1.226356	-0.345692	-0.527011	0.115813	-1.049805	-0.580339
1	7	-0.021536	-0.067384	-0.027441	0.007107	-0.188308	-0.297562
	19	-0.021536	-0.067384	-0.021373	0.006700	-0.187515	-0.291108
	27	-0.021536	-0.067384	-0.019584	0.006669	-0.187424	-0.289259
	125	-0.021536	-0.067384	-0.019850	0.006670	-0.187426	-0.289526
	343	-0.021536	-0.067384	-0.019850	0.006670	-0.187426	-0.289526
2	7	-0.054992	-0.013135	0.005348	-0.001385	-0.034006	-0.098170
	19	-0.054992	-0.013135	0.006532	-0.001464	-0.033851	-0.096910
	27	-0.054992	-0.013135	0.006183	-0.001459	-0.033869	-0.097271
	125	-0.054992	-0.013135	0.006152	-0.001459	-0.033869	-0.097303
	343	-0.054992	-0.013135	0.006152	-0.001459	-0.033869	-0.097303
3	7	-0.020620	-0.002560	0.003128	-0.000810	-0.006102	-0.026964
	19	-0.020620	-0.002560	0.002434	-0.000764	-0.006193	-0.027703
	27	-0.020620	-0.002560	0.002502	-0.000765	-0.006189	-0.027632
	125	-0.020620	-0.002560	0.002501	-0.000765	-0.006189	-0.027633
	343	-0.020620	-0.002560	0.002501	-0.000765	-0.006189	-0.027633

“correlated” wave functions for polymers or solids but only provide good estimates of the correlation energy.

6. General Formulae for the Generalized Overlap Integrals $S_{pq}^{oj}(\mathbf{G})$

In this section, we give the analytical solutions for the generalized overlap needed for the computation of electronic densities or for the computation of matrix elements in the LCAO-Slater-Hartree-Fock method, described in Section 5 of this paper. No derivation will be given here since it is very similar to procedures used in solving overlap integrals S_{pq}^{oj} (see for instance Bibliographies [20-22]). In defining the integrals over Gaussian functions, the following auxiliary functions are used:

$$(58) \quad F_i(l, m, a, b) = \sum_{s=0}^i \binom{l}{s} \binom{m}{i-s} a^{l-s} b^{m-i+s}$$

so that:

$$(59) \quad (x - X_p)^{l_p} (y - Y_p)^{m_p} (z - Z_p)^{n_p} \exp[-\alpha_p(\mathbf{r} - \mathbf{R}_p)^2] \\ \times (x - X_q)^{l_q} (y - Y_q)^{m_q} (z - Z_q)^{n_q} \exp[-\alpha_q(\mathbf{r} - \mathbf{R}_q)^2] \\ = \sum_i^{\langle l_p+l_q \rangle} \sum_j^{\langle m_p+m_q \rangle} \sum_k^{\langle n_p+n_q \rangle} f_i(l_p, l_q, \mathbf{P}_{px}, \mathbf{P}_{qx}) \\ \times f_j(m_p, m_q, \mathbf{P}_{py}, \mathbf{P}_{qy}) f_k(n_p, n_q, \mathbf{P}_{pz}, \mathbf{P}_{qz}) x_p^i y_p^j z_p^k \\ \times \exp[-(\alpha_p + \alpha_q)\mathbf{r}_P^2] \exp\left[\frac{-\alpha_p\alpha_q(\mathbf{R}_p - \mathbf{R}_q)^2}{(\alpha_p + \alpha_q)}\right]$$

Where we have used the position vectors \mathbf{R}_p (or \mathbf{R}_q) of centre of orbital p (or q) with components X_p, Y_p, Z_p (or X_q, Y_q, Z_q). \mathbf{R}_P is the vector position of the product of the two Gaussians p and q :

$$\mathbf{R}_P = \frac{\alpha_p \mathbf{R}_p + \alpha_q \mathbf{R}_q}{\alpha_p + \alpha_q} \quad \text{and} \quad \mathbf{r}_P = \mathbf{r} - \mathbf{R}_P$$

with components x_P, y_P, z_P . P_{pi} (or P_{qi}) is the i th projection (x, y or z) of the distance between the centre of orbital p (or q) and the centre of (P) of the two Gaussians. The normalization factor for the Gaussian functions is well-known:

$$(60) \quad N\alpha_p = \left(\frac{\pi}{2\alpha_p}\right)^{3/4} \left[\frac{(2l_p - 1)!! (2m_p - 1)!! (2n_p - 1)!!}{2^{2(l_p+m_p+n_p)} \alpha_p^{(l_p+m_p+n_p)}} \right]^{-1/2}$$

Under those conditions, the generalized overlap integrals are (when using vectors \mathbf{R}_j with components X_j, Y_j, Z_j to define the origin of the j th cell $[\mathbf{R}_j = j_1\mathbf{a}_1 + j_2\mathbf{a}_2 + j_3\mathbf{a}_3]$):

$$\begin{aligned}
 (61) \quad S_{pq}^{oj}(\mathbf{G}) &= N\alpha_p N\alpha_q \int (x - X_p - X_o)^{l_p} (y - Y_p - Y_o)^{m_p} \\
 &\quad \times (z - Z_p - Z_o)^{n_p} \exp[-\alpha_p(\mathbf{r} - \mathbf{R}_p - \mathbf{R}_o)^2] \\
 &\quad \times (x - X_q - X_j)^{l_q} (y - Y_q - Y_j)^{m_q} (z - Z_q - Z_j)^{n_q} \\
 &\quad \times \exp[-\alpha_q(\mathbf{r} - \mathbf{R}_q - \mathbf{R}_j)^2] \exp(+i\mathbf{G}\mathbf{r}) d^3r \\
 &= N\alpha_p N\alpha_q \exp\left[-\frac{\alpha_p\alpha_q(\mathbf{R}_p + \mathbf{R}_o - \mathbf{R}_q - \mathbf{R}_j)^2}{(\alpha_p + \alpha_q)}\right] \\
 &\quad \times [\pi/(\alpha_p + \alpha_q)]^{3/2} \exp\left[-\frac{|\mathbf{G}|^2}{4(\alpha_p + \alpha_q)}\right] \\
 &\quad \times \exp(+i\mathbf{G}\mathbf{R}_P) \sum_{j_1}^{(l_p+l_q)} \sum_{j_2}^{(m_p+m_q)} \sum_{j_3}^{(n_p+n_q)} i^{(j_1+j_2+j_3)} \\
 &\quad \times \left(\frac{1}{2(\alpha_p + \alpha_q)^{1/2}}\right)^{(j_1+j_2+j_3)} f_{j_1}(l_p, l_q, \mathbf{P}_{px}, \mathbf{P}_{qx}) \\
 &\quad \times f_{j_2}(m_p, m_q, \mathbf{P}_{py}, \mathbf{P}_{qy}) f_{j_3}(n_p, n_q, \mathbf{P}_{pz}, \mathbf{P}_{qz}) \\
 &\quad \times H_{j_1}\left[+\frac{G_x}{2(\alpha_p + \alpha_q)^{1/2}}\right] H_{j_2}\left[+\frac{G_y}{2(\alpha_p + \alpha_q)^{1/2}}\right] \\
 &\quad \times H_{j_3}\left[+\frac{G_z}{2(\alpha_p + \alpha_q)^{1/2}}\right]
 \end{aligned}$$

$H_l(a)$ are the Hermite polynomials:

$$(62) \quad H_l(a) = l! \sum_{j=0}^{(l/2)} \frac{(-1)^j (2a)^{l-2j}}{j! (l-2j)!}$$

Special formulae for integrals between s - s , s - p or p - p type orbitals are easily derived. Hereinafter, the subscripts $l(k)$ define the directionality of p -type orbital

functions and each is to be replaced with the value x or y or z as appropriate. i is the imaginary number ($i^2 = -1$).

$s-s$

$$(63) \quad S_{pq}^{oj}(\mathbf{G}) = N\alpha_p N\alpha_q \left[\frac{\pi}{\alpha_p + \alpha_q} \right]^{3/2} \exp \left[- \frac{\alpha_p \alpha_q (\mathbf{R}_p + \mathbf{R}_o - \mathbf{R}_q - \mathbf{R}_j)^2}{(\alpha_p + \alpha_q)} \right] \\ \times \exp \left[- \frac{|\mathbf{G}|^2}{4(\alpha_p + \alpha_q)} \right] \exp [+i\mathbf{G}\mathbf{R}_P]$$

$s-p_l$

$$(64) \quad S_{pq}^{oj}(\mathbf{G}) = N\alpha_p N\alpha_q \left[\frac{\pi}{\alpha_p + \alpha_q} \right]^{3/2} \exp \left[- \frac{\alpha_p \alpha_q (\mathbf{R}_p + \mathbf{R}_o - \mathbf{R}_q - \mathbf{R}_j)^2}{(\alpha_p + \alpha_q)} \right] \\ \times \exp \left[- \frac{|\mathbf{G}|^2}{4(\alpha_p + \alpha_q)} \right] \exp [+i\mathbf{G}\mathbf{R}_P] \\ \times \left[\mathbf{P}_{ql} - i \frac{G_l}{2(\alpha_p + \alpha_q)} \right]$$

p_l-p_k

$$(65) \quad S_{pq}^{oj}(\mathbf{G}) = N\alpha_p N\alpha_q \left[\frac{\pi}{\alpha_p + \alpha_q} \right]^{3/2} \exp \left[- \frac{\alpha_p \alpha_q (\mathbf{R}_p + \mathbf{R}_o - \mathbf{R}_q - \mathbf{R}_j)^2}{(\alpha_p + \alpha_q)} \right] \\ \times \exp \left[- \frac{|\mathbf{G}|^2}{4(\alpha_p + \alpha_q)} \right] \exp [+i\mathbf{G}\mathbf{R}_P] \\ \times \left[\mathbf{P}_{pl}\mathbf{P}_{qk} - i \frac{G_l \mathbf{P}_{qk} + G_k \mathbf{P}_{pl}}{2(\alpha_p + \alpha_q)} - \frac{G_l G_k}{4(\alpha_p + \alpha_q)^2} + \frac{\delta_{lk}}{2(\alpha_p + \alpha_q)} \right]$$

It is easily shown that these formulae reduce to the usual expressions for overlap integrals when $\mathbf{G} = 0$.

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