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Exchange contributions in the electronic structure of systems with 1D-periodicity : importance and computation.

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Abstract

The purpose of this article is to point out to the scientific community interested in Hartree-Fock ab initio calculations that accurate calculations of the exchange contributions are essential. An extremely simple system such as the infinite chain of Be atoms, $(\text{-Be-})_\infty$, treated in direct space at the RHF level with the 3-21G basis fails to converge to physically meaningful results. An analysis based on the convergence properties of finite Fourier series points to the exchange contributions as the source of the problem. Owing to its capability of handling with the necessary accuracy all lattice summations, including the exchange sums, the Fourier representation is able to treat the problem effectively and is confirmed as a procedure of choice for RHF electronic structure calculations of systems with 1D periodicity.

Key words: restricted Hartree-Fock, direct space, Fourier space, polymers, band structure, exchange, lattice summations
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Introduction

This contribution is offered in commemoration of the scientific career of Per-Olov Löwdin. We hope it adequately reflects his emphasis on obtaining a good understanding of the physical and mathematical aspects of the phenomena under study.

Modern research on materials requires new and improved understanding of the relationships between structure and properties and how they can be engineered. With present-day experimental advances, polymer chains can be organized to a point where models characterized by one-dimensional (1D) periodicity are appropriate. Important questions range from the interpretation of spectroscopic measurements (infrared, NMR, electronic, etc.) to the design of new structures and/or organizations for which interesting properties (surface energy, corrosion protection via optimum bonding and organization of inhibitors, electric responses, optical and transport properties, etc.) can be calculated with the aim of engineering them in actual materials. For example, it has been possible to predict valence band spectra from the knowledge of the surface molecular structure of chain-like systems [1]. This approach can be inverted and from photoelectron experiments, which essentially probe the surface sample, it is possible to get information on the primary and secondary structures of the polymer chains forming the first layers of a substrate. Theoretical calculations have not only predicted this possibility, but also provided the basis for refined interpretation. They have also stressed the danger of relying on the simplified model of primary ionization lines, particularly in conjugated systems, as well as developing suitable levels of theory [2-5].

As just pointed out with this example, an adequate level of theory is critical to achieve a proper description of a system. Currently the most popular method for purely theoretical calculations of the electronic structure of extended systems is density functional theory (DFT), which is relatively inexpensive, but includes electron correlation approximately and suffers from a lack of systematic ways to improve the results. In that respect, methodologies based on the Hartree-Fock theory and beyond (many-body perturbation theory, many-body

Green's functions, etc.) remain the most consistent approaches. Efforts to master the points that make them difficult to apply should thus be continued.

Some of the main difficulties in the Hartree-Fock based methods originate, not surprisingly, from exchange. In the case of extended systems Hartree-Fock exchange contributions are obtained from lattice summations of which convergence properties and consequences on the quality of the calculations have been mostly overlooked and to some extent continue to be so. The purpose of this article is to provide an account of the recent understanding of the situation regarding restricted Hartree-Fock (RHF) exchange contributions for systems with 1D periodicity and the use of the Fourier representation method to compute them efficiently. Assuming that the reader has familiarity with the general RHF equations for systems with 1D periodicity, only the essential equations will be provided and commented on in the second section. The interested, but unfamiliar reader is referred to the original papers [6-8] and books [9,10] to trace additional information and/or details. The paper is divided into two complementary parts. With the RHF-LCAO matrix elements expressed in direct space, an analysis of the convergence properties of the lattice sums is presented and the consequences thereof are stressed considering the simple case of the infinite chain of beryllium atoms (third section). In the fourth section, the same equations expressed in the Fourier space [11-18] are very briefly discussed to point out the virtue of the approach for computing efficiently the problematic exchange contributions. The paper ends with some considerations regarding the future of calculations on 1D periodic systems using the Fourier transform (FT) approach.

2. **The RHF LCAO Matrix Elements for Systems with 1D Periodicity**

In the RHF approximation, the electronic wave function is an antisymmetrized product built from one-electron orbitals of Bloch type. The RHF-Bloch orbitals, $\varphi_n(k,\mathbf{r})$, are doubly occupied up to the Fermi energy, E_F, and are orthonormalized as shown in the following equation:

$$\int d\mathbf{r}\varphi_{n'}^{*}(k',\mathbf{r})\varphi_{n}(k,\mathbf{r}) = \delta_{k'k}\delta_{n'n} \tag{1}$$

where k and n are the wave numbers and the band index, respectively. In the notation used, k is expressed in units of $\frac{2\pi}{a_0}$, a_0 being the cell length, and is defined in the Brillouin zone (BZ), whose length is $\frac{2\pi}{a_0}$, i.e., $k \in \left[-\frac{1}{2},\frac{1}{2}\right]$. The Bloch orbitals,

$$\varphi_n(k,\mathbf{r}) = \sum_p b_p(k,\mathbf{r})C_{pn}(k) \tag{2}$$

are expressed in terms of Bloch sums, $b_p(k,\mathbf{r})$,

$$b_p(k,\mathbf{r}) = (2N+1)^{-1/2}\sum_{m=-N}^{N} e^{i2\pi km}\chi_p\left(\mathbf{r}-(\mathbf{p}+m\mathbf{e}_z)a_0\right) = (2N+1)^{-1/2}\sum_{m=-N}^{N} e^{i2\pi km}\chi_p^{m}(\mathbf{r}) \tag{3}$$

where p and the vector $\mathbf{p}$ (in units of cell length a_0), respectively, represent the label and the position of the atomic orbital χ_p in the reference cell. The quantity $(2N+1)^{-1/2}$ is the normalization factor for a polymer containing $2N+1$ $(N \to \infty)$ unit cells. In the following, the indices p, q, r and s denote atomic orbitals. The direction of periodicity is defined by the unit vector $\mathbf{e}_z$ and the lattice sites are identified by integers m, m' and m'' (with values $0, \pm 1, \pm 2, \ldots, \pm N$).

The normalization condition, in terms of Bloch sums and for $n = n'$ and $k = k'$, is

$$\sum_{p,q} C_{pn}^{*}(k)S_{pq}(k)C_{qn}(k) = 1 \tag{4}$$

where $S_{pq}(k)$ are the overlap matrix elements

$$S_{pq}(k) = \int d\mathbf{r} b_p^*(k,\mathbf{r}) b_q(k,\mathbf{r}) . \tag{5}$$

The density matrix elements, $P_{pq}(k)$, are given by

$$P_{pq}(k) = \sum_n C_{pn}^*(k) C_{qn}(k) \theta_n(k) \tag{6}$$

where the occupation function, $\theta_n(k)$, is equal to 2 for $E_n(k) \le E_F$ and 0 otherwise; $E_n(k)$ is the nth energy band.

The expansion coefficients, $C_{pn}(k)$, and one-electron energy eigenvalues, $E_n(k)$, are solutions of the following system of equations:

$$\sum_q F_{pq}(k) C_{qn}(k) = E_n(k) \sum_q S_{pq}(k) C_{qn}(k) \tag{7}$$

in which $F_{pq}(k)$ are the Fock matrix elements given by

$$F_{pq}(k) = T_{pq}(k) + V_{pq}(k) + J_{pq}(k) + X_{pq}(k) \tag{8}$$

$T_{pq}(k)$, $V_{pq}(k)$, $J_{pq}(k)$ and $X_{pq}(k)$ are the kinetic, electron-nuclear attraction, electron-electron repulsion and exchange contributions to $F_{pq}(k)$, respectively. They are defined as follows:

$$T_{pq}(k) = \int d\mathbf{r} b_p^*(k,\mathbf{r}) \left[-\frac{1}{2} \quad {}^2(\mathbf{r}) \right] b_q(k,\mathbf{r}) , \tag{9}$$

$$V_{pq}(k) = -\int d\mathbf{r} b_p^*(k,\mathbf{r}) \left[-\sum_{A,m'} Z_A \left| \mathbf{r} - \left(\mathbf{R}_A + m' \mathbf{e}_z \right) a_0 \right|^{-1} \right] b_q(k,\mathbf{r}), \tag{10}$$

$$J_{pq}(k) = (2N+1)\int_{BZ} dk' \sum_{r,s} P_{rs}(k') J_{pqrs}(k,k'), \tag{11}$$

where

$$J_{pqrs}(k,k') = \iint d\mathbf{r}_1 d\mathbf{r}_2 b_p^*(k,\mathbf{r}_1) b_q(k,\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} b_r^*(k',\mathbf{r}_2) b_s(k',\mathbf{r}_2) \tag{12}$$

and

$$X_{pq}(k) = -\frac{1}{2}(2N+1)\int_{BZ} dk' \sum_{r,s} P_{rs}(k') X_{psrq}(k,k'), \tag{14}$$

where

$$X_{psrq}(k,k') = \iint d\mathbf{r}_1 d\mathbf{r}_2 b_p^*(k,\mathbf{r}_1) b_s(k',\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} b_r^*(k',\mathbf{r}_2) b_q(k,\mathbf{r}_2) \tag{15}$$

The kinetic elements, $T_{pq}(k)$, raise no problem since they decay exponentially with the distance between the atomic orbital centers and can be computed to suitable accuracy with no difficulty.

The electron-nuclear attraction and electron-electron repulsion matrix elements, $V_{pq}(k)$ and $J_{pq}(k)$, must be combined under the cell electroneutrality condition to ensure convergence of their contributions to the Fock matrix elements. However, some of the resulting lattice sums are of slow convergence, N^{-2}, and require special techniques for practical evaluation. In direct space, multipole based approaches are classically used [19]. They turn out to be satisfactory for localized atomic basis functions, but much less so when the basis sets include diffuse functions. Furthermore, when the multipole approximation is

used in the case of continuous charge distributions, which is the case here, the associated series are semiconvergent.

Exchange matrix elements raise much less appreciated yet equally important problems as will be pointed out in the forthcoming sections.

3. Exchange Matrix Elements in Direct Space Representation

In direct space [6-10], $X_{pq}(k)$, can be written as,

$$X_{pq}(k) = \sum_{m=-\infty}^{\infty} e^{i2\pi km} X_{pq}^{0m} \tag{16}$$

with

$$X_{pq}^{0m} = -\frac{1}{2} \sum_{m'=-\infty}^{\infty} \sum_{m''=-\infty}^{\infty} \sum_{r,s} P_{rs}^{0,m'-m-m''} \left(p^{0} s^{m'} \middle| r^{m+m''} q^{m} \right) \tag{17}$$

where $P_{rs}^{0,m'-m-m'}$ is the finite Fourier transform of the LCAO density matrix element $P_{rs}(k')$,

$$P_{rs}^{0,m'-m-m''} = \int_{BZ} dk' e^{-i2\pi(m'-m-m')k'} P_{rs}(k') \tag{18}$$

and $\left(p^{0} s^{m'} \middle| r^{m+m''} q^{m} \right)$ a multicenter bielectronic integral,

$$\left(p^{0} s^{m'} \middle| r^{m+m''} q^{m} \right) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \chi_p^{0*}(\mathbf{r}_1) \chi_s^{m'}(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \chi_r^{m+m''*}(\mathbf{r}_2) \chi_q^{m}(\mathbf{r}_2). \tag{19}$$

In approaches like RHF, several properties (HOMO-LUMO gap, density of states, etc.) derive from the characteristics of the energy bands, $E_n(k)$, which are obtained after solving

the associated eigenvalue problem, Eq. (7). The analytical properties of the energy bands are thus directly connected, via a unitary transformation, to those of the Fock matrix elements, $F_{pq}(k)$, which in turn include the exchange contributions $X_{pq}(k)$, Eq. (16). Analyzing $X_{pq}(k)$ from the point of view of its dependence with respect to the continuous index k is thus important from the point of view of understanding the specific properties of the RHF method applied to systems with 1D periodicity.

Eq.(16) is a trigonometric series whose expansion coefficients, X_{pq}^{0m}, contain products of two factors, $P_{rs}^{0,m'-m-m''}$ and $\left(p\,s\,\middle|\,r\;q\right)^{0\;m'\;m+m''\;m}$, each depending on the summation index m. The ultimate convergence of the series and the resulting properties are thus determined by the decay of these two quantities as m tends to infinity. For a given m, the summations over m' and m'' converge exponentially and do not present numerical difficulties. However, the value of $|m|$ is a measure of the separation of the center of charge of the two distributions in X_{pq}^{0m}, and the contribution of the bielectronic integral to X_{pq}^{0m} decays only as $|m|^{-1}$. This factor alone is not sufficient for the series in Eq. (16) to converge to a finite value.

Thus, the factors $P_{rs}^{0,m'-m-m''}$ are crucial for the global convergence of the series. They correspond to the coefficients of the finite Fourier transform of $P_{rs}(k')$ and their decay is controlled by the analytic properties of $P_{rs}(k')$ which in turn depend on those of the LCAO expansion coefficients $C_{rn}(k')$ and $C_{sn}(k')$ as well as of the occupation function $\theta_n(k')$, Eq. (6). Two general cases must be distinguished:

1. $\theta_n(k')$ <u>is constant over the entire BZ</u>. This corresponds to a fully occupied BZ or a situation with non zero energy gap between the highest occupied and the lowest unoccupied levels. In this case the one-electron states are analytic functions of k' [20] and so are the LCAO density matrix elements $P_{rs}(k')$. Since Fourier coefficients of

analytic functions decrease exponentially [21], it turns out that that $\left|P_{rs}^{0,m'-m-m''}\right|$ decay exponentially with increasing $|m|$. In this case the series in Eq.(16) is formally of exponential decay.

2. $\theta_n(k')$ <u>exhibit discontinuities in the BZ</u>. This corresponds to a partially filled BZ or a situation of degeneracy between the highest occupied and the lowest unoccupied levels. In this case, the LCAO density matrix elements $P_{rs}(k')$ are obviously discontinuous, as may be seen from Eq. (6). Fourier coefficients (here $\left|P_{rs}^{0,m'-m-m''}\right|$) of sectionally continuous functions decrease like $|m|^{-1}$ [21]. This, combined with the convergence rate $|m|^{-1}$ of $\left|\begin{pmatrix} 0 & m' \\ p & s \end{pmatrix}^{m+m''} \begin{pmatrix} m \\ r & q \end{pmatrix}\right|$, leads to an overall $|m|^{-2}$ decay which ensures absolute convergence to the series in Eq. (16). However, it is not only very slow, but it is at the origin of the so-called anomalous behavior of the RHF approach when describing degenerate or metallic situations, the most dramatic expression of which is the vanishing of the density of states at the Fermi energy [22].

The importance of properly converged exchange contributions to the Fock matrix elements does not solely matter for cases with degeneracy between occupied and unoccupied levels. Discussions with practitioners of ab initio electronic structure calculations reveal that a significant number of attempted applications have not been completed, due to difficulties in getting physically meaningful results with the otherwise classical basis sets (3-21G, 6-31G, …) used in molecular quantum chemistry.

To illustrate the situation we have carried out direct space calculations with the PLH program [23] on the trivially simple infinite chain of Be atoms, $(\text{-Be-})_\infty$, using the rather common and somewhat limited 3-21G basis set. The unit cell length a_0 was arbitrarily set equal to 0.232 nm, a value based on previous calculations on Be clusters [24]. The number of explicitly interacting cells on each side of the reference unit cell was set to 10, and the number

of cells used in the intermediate region to correct for the long-range coulombic interactions was set to 49 (for more details about the meaning of these parameters see ref. [25]). It turns out that, under these conditions, the calculations failed to converge, after 28 cycles of SCF iteration yielding meaningless values. For instance, the maximum value of the LCAO density matrix $\left|P_{pq}^{0m}\right|$ for m = 10 is equal to 47.960 and the total energy per atom in the chain is -31.7192 hartree ! Yet the minimal eigenvalue of the overlap matrix, $\mathbf{S}(k)$, for all k points where it has been computed, is larger than 10^{-3}, which with the accuracy of the computers normally should not lead to problems related to linear dependency. As pointed out in an analysis by Suhai, Bagus and Ladik [26], the failure to converge arises from errors in the Fock matrix elements which are propagated and amplified during the SCF iteration cycles. In the present case the errors are due to a lack of accuracy in the exchange contributions to the Fock matrix elements. Forcing convergence is possible by removing some components of the basis [27]. However, doing so, in addition to the empirical and limited game of adding or subtracting interacting cells in the calculations, is not only frustrating, but raises questions about the reliability of such calculations on systems with 1D periodicity.

This brief analysis of the analytic and numerical behavior of the RHF exchange contributions, $X_{pq}(k)$, stresses the importance of computing them properly to get results that are consistent with the RHF model. To our knowledge, attempts to implement the multipole expansion to compute with suitable accuracy the exchange contributions in direct space have not been successful so far . In the next section we call attention to the Fourier transform approach which is more propitious for handling the difficulties related to lattice summations in general.

4. Exchange Matrix Elements in Fourier Space Representation

Applying the Fourier transform [11-12],

$$\left[f(\mathbf{r})\right]^T(q) = f^T(\mathbf{q}) = \int d\mathbf{r}\, f(\mathbf{r}) \exp\left(i \frac{2\pi}{a_0}\, \mathbf{q}\cdot\mathbf{r}\right) \tag{20}$$

to the RHF equations yields different, but equivalent expressions of the RHF-LCAO matrix elements [14-18]. In particular, $X_{pq}(k)$, assumes the form [17],

$$\begin{aligned} X_{pq}(k) &= -\frac{1}{2}\int_{-1/2}^{1/2} dk' \sum_{r,s} P_{sr}(k')\, X_{psrq}(k,k') \\ &= -\frac{1}{2}\frac{1}{\pi a_0}\int_{-1/2}^{1/2} dk' \sum_{r,s} P_{sr}(k') \\ &\quad \times \sum_{m=-\infty}^{\infty} \int \frac{d\mathbf{q}_0}{\mathbf{q}_0^2 + (m+k-k')^2}\, S_{ps}(k', \mathbf{q}_{m+k-k'}) S_{rq}(k, -\mathbf{q}_{m+k-k'}) \end{aligned} \tag{21}$$

where $\mathbf{q}_0^2 = q_x^2 + q_y^2$ and $\mathbf{q}_{m+k-k'} = (q_x, q_y, m+k-k')$. The generalized overlap integrals $S_{pq}(k,\mathbf{q})$ arising in Eq.(20) are defined as:

$$\begin{aligned} S_{pq}(k,\mathbf{q}) &= \sum_{m=-\infty}^{\infty} \exp(2\pi i k m) \int d\mathbf{r}\, \chi_p^0(\mathbf{r})\, \chi_q^m(\mathbf{r}) \exp\left(i \frac{2\pi}{a_0}\, \mathbf{q}\cdot\mathbf{r}\right) \\ &= \sum_{m=-\infty}^{\infty} \exp(2\pi i k m) S_{pq}^m(\mathbf{q}) \end{aligned} \tag{22}$$

It would be beyond the scope of the present article to carry out an explicit and detailed analysis of the working expressions by which the $X_{pq}(k)$ matrix elements are actually computed. It suffices here to say that the Fourier transform concentrates near the origin of the **q**-space most of the problematic features of the exchange which can then be dealt with formally and practically. In the case of Gaussian basis sets, it has recently been possible to develop accurate summation procedures based on a combination of the Poisson summation formula and the Ewald method. These do require efficient algorithms to evaluate incomplete Bessel functions $K_n(x,y)$ [28, 29], which are new in the field of quantum chemistry. With

this it has become possible to carry out the exchange lattice summations to great accuracy and without approximations of the kind needed in the multipole expansion.

A prototype program (FTCHAIN) based on the Fourier representation method has been implemented, but is presently limited to s-type Gaussian functions. To apply it to the study case of the infinite chain of beryllium atoms and demonstrate the potential of the Fourier approach, we simulated the 2p functions using a distributed basis set of s-type functions (DSGF). Thus, three s-type atomic functions are centered on the Be atom using the same contraction scheme (exponents and contraction coefficients) as in the standard 3-21G basis. Each p-type orbital is represented by two identical s-type Gaussian functions symmetrically centered about the nucleus, at distances corresponding to the position of the maximum of Be 2p orbital in the 3-21G basis set (0.1304 nm) with exponent equal to 0.3 $bohr^{-2}$. Total energies per atom and the occupied orbital energies for Be and Be_2 ($R_{Be\text{-}Be}$ = 0.232 nm) computed with the 3-21G and the DSGF bases are reported in Table I. These calculations carried out with the GAUSSIAN 98 program [30] confirm that the DSGF basis is reasonably representative of the 3-21G basis. Computations on the infinite chain of beryllium atom, $(\text{-Be-})_{\infty}$,, with the PLH program using the DSGF basis also fail to converge to physically meaningful values. After 32 cycles of SCF iteration, the maximum value of the LCAO density matrix $\left|P_{pq}^{0m}\right|$ for m = 30 is equal to 57.215 and the total energy per atom in the chain is -76.0220 hartree, while the minimal eigenvalue of the overlap matrix, $\mathbf{S}(k)$ is larger than 10^{-3}.

Table I. Total energies per atom and one-electron energies (in hartree) of the occupied orbitals of Be and Be_2.

	E_T	ε_{1s}	ε_{1s}	ε_{2s}	ε_{2s}
Be $_{(3\text{-}21G)}$	-14.4868	-4.6884	-	-0.3056	-
Be $_{(DSGF)}$	-14.4889	-4.6906	-	-0.3053	-
$Be_{2\ (3\text{-}21G)}$	-14.4058	-4.7306	-4.7301	-0.3599	-0.1633
$Be_{2\ (DSGF)}$	-14.4762	-4.6989	-4.6985	-0.4036	-0.2374
$Be_{\infty\ (FTCHAIN)}$	-14.7849	-4.6455	-4.6454	-0.4001	-0.0941

In the case of $(\text{-Be-})_\infty$ the reported values are the lowest and highest energy values of the two occupied bands.

Computation on the infinite chain of beryllium atoms, $(\text{-Be-})_\infty$, with the FTCHAIN converges, after 20 cycles of SCF iteration, yielding sensible values as seen in Table I. The total energy per beryllium atom has slightly decreased, as expected, compared to those of the isolated atom and the diatomic molecule. The one-electron energies correspond to the lowest and highest values obtained from energy bands $\varepsilon_1(k)$ and $\varepsilon_2(k)$. These values compare with those of Be atom and molecule. The fact that the FTCHAIN program treats this problem effectively indicates at least two points. First, it is not a problem of linear dependency that is at the origin of the failure with the direct space calculation. As a matter of fact, true linear dependencies, with double precision calculations, are usually diagnosed for eigenvalues of the metric or overlap matrix, $\mathbf{S}(k)$, smaller than 10^{-7}[26]. Second, it supports the idea that very careful and accurate calculations of all contributions to the Fock matrix elements are essential for successful ab initio calculations on extended systems. This applies to kinetic, Coulomb *and* exchange terms. In the latter case, one should once and for all eradicate the idea that these contributions scale with the overlap matrix decay and accordingly are of rapid convergence.

4. Conclusion and perspectives

The purpose of this article was to point out to the scientific community interested in Hartree-Fock ab initio calculations that accurate calculations of the exchange contributions are essential to get meaningful results. Even an extremely simple system with 1D periodicity, the infinite chain of beryllium atoms treated at the 3-21G level, requires this kind of attention. In that respect, the Fourier representation method appears to be capable of handling with the necessary accuracy all the terms, including exchange, needed for stable results. It has also been shown that this method can be turned into a very effective scheme [16-18]. However, it still awaits further development before it can be proposed for general use, including implementation for atomic functions of non zero angular momentum. It will also be important to go beyond the RHF approximation using perturbative or coupled-cluster techniques.

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References

1. Delhalle, J.; Deleuze, M. J Mol Struct (Theochem) 1992, 261, 187.
2. Deleuze, M.; Denis, J. P.; Delhalle, J.; Pickup, B. T. J Phys Chem 1993, 97, 5115.
3. Deleuze, M.; Cederbaum, L. S. Phys Rev B 1995, 53, 13326.
4. Deleuze, M. Adv Quantum Chem 1999, 35, 77 and refs. therein.
5. Sun, J. Q.; Bartlett, R. J Phys Rev Lett 77, 3669 (1996).
6. Yomosa, S. J Phys Soc Jpn 1964, 19, 1718.
7. Del Re, G.; Ladik, J.; Biczo, G. Phys Rev 1967, 155, 977.
8. André, J. M.; Gouverneur, L.; Leroy, G. Int J Quantum Chem 1967, 1, 427.
9. Ladik, J. J. *Quantum theory of polymers as solids*; Plenum Press: New York, 1988.
10. André, J. M.; Delhalle, J.; Brédas, J. L *Quantum Chemistry Aided Design of Organic Polymers*; World Scientific: London, 1991.
11. Harris, F. E.; Monkhorst, H. J Phys Rev B 1970, 2, 4400.

12. Harris, F.E. J. Chem Phys 1972, 56, 4422.
13. Delhalle, J.; Harris, F. E. Theor Chim Acta 1978, 48, 127.
14. Delhalle, J.; Harris, F. E. Phys Rev B 1985, 31, 6755.
15. Delhalle, J.; Cizek, J.; Flamant, I.; Calais, J. L.; Fripiat, J. G. J Chem Phys 1994, 101, 10717.
16. Flamant, I. Ph.D. Dissertation, *Fourier Space Restricted Hartree-Fock Method for the Electronic Structure Calculation of Stereoregular Polymers;* Presses Univ. Namur: Univ. Namur, 1998.
17. Flamant, I.; Fripiat, J. G.; Delhalle, J.; Harris, F. E. Theor Chem Acc, 2000, 104, 350.
18. Fripiat, J. G.; Flamant, I.; Harris, F. E.; Delhalle, J. Int J Quantum Chem, 2000, 80, 856.
19. Piela, L.; Delhalle, J. Int J Quantum Chem, 1978, 13, 605.
20. Bulyanitsa, D.S.; Svetlow, Yu. E. Soviet Phys-Solid State 1962, 4, 981 and refs. therein.
21. Bary, N.K. *Treatise on trigonometric series*; Pergamon, Oxford, 1964.
22. Seitz, F. *The modern theory of solids*, McGraw-Hill, New York, 1940.
23. Fripiat, J. G. ; Champagne, B.; Castet, F. ; Poulsen, T. D. ; Mosley, D. H.; Brédas, J. L.; Bodart, V.; Delhalle, J.; Vercauteren, D. P.; André, J. M. *PLH-2000*; Facultés Universitaires N.D. de la Paix , B-5000 Namur, Belgium
24. Flamant, I.; Mosley, D. H.; Delhalle, J.; André, J. M.; Fripiat, J. G. Int J Quantum Chem, 1996, 57, 871.
25. André, J. M.; Mosley, D. H. ; Champagne, B.; Delhalle, J. ; Fripiat, J. G.; Brédas, J. L.; Vanderveken, D. J. ; Vercauteren, D. P. *Methods and Techniques in Computational Chemistry (METECC-94),* Clementi, E (Ed); Stef: Cagliari, 1993, B, pp. 429.
26. Suhai, S.; Bagus, P. S.; Ladik, J. Chem Phys Lett 1982, 68, 467.
27. Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*,1st ed. rev., McGraw-Hill: New York, 1989.
28. Harris, F.E. Int J Quantum Chem 1997, 63, 913.
29. Harris, F.E. Int J Quantum Chem 1998, 70, 623.
30. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J. ; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D. ; Raghavachari, K.; Stefanov, B. B. ; Liu, G. ; Liashenko, A. ; Piskorz, P. ; Komaromi, I.; Gomperts, R. ; Martin, R. L. ; Fox, D. J. ; Keith, T. ; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A. ; Gonzalez, C. ; Challacombe, M.; Gill, P. M. W. ; Johnson, B.; Chen, W. ; Wong, M. W. ; Andres, J. L.; Gonzalez, C. ; Head-Gordon, M.; Replogle, ; E. S.; Pople, J. A. *Gaussian-98*; Gaussian Inc.: Pittsburgh PA, 1998.