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Multipole expansion in tight-binding Hartree-Fock calculations for infinite model polymers

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The importance of long-range electrostatic contributions in Hartree-Fock-Roothaan calculations on model chainlike polymers is stated. The multipole expansion is used to handle them properly. General expressions and working formulas are deduced. Special attention is paid to the Gaussian lobe functions. Applications on $(LiH)_x$ and $(CH_2)_x$ chains are made to illustrate the points.

I. INTRODUCTION

Theoretical studies on model polymers, simple enough to be completely worked out on a rigorous basis, can be self-justified; however, it is expected in the long run that theory will eventually be confronted with experiment and produce mutual enrichment. Over this past decade, refinements in polymer-chain preparations and discovery of new compounds, development in spectroscopic techniques, and advances in elaborating firmly based theoretical methods have greatly contributed in making the quantum theory for polymers an attractive and rapidly growing field of research.[1-4]

Since 1968,[5] theoretical calculations of various degrees of sophistication have helped in the understanding of physical and chemical properties of polymers. One of the significant contributions is the affirmation of the validity of the conventional energy-band scheme in describing the valence electronic spectra of chainlike systems.[6]

Also promising is the quantum study of the vibrational properties of polymers and more specifically of the influence of the extended nature of the chains upon force constants and vibrational spectra; an interesting contribution has already been reported for the infinite chain of hydrogen fluoride molecules.[7] Another exciting field is the conformational study of the extended polymers. So far, most of the efforts have been made within the frameworks of molecular classical mechanics[8] and molecular quantum chemistry[9] but applied to oligomers rather than largely extended chains. In doing so, effects of the long-range type are often ignored. It would certainly be valuable to bridge this gap by bringing in the complementary point of view of polymer quantum calculations and deciding on a consistent footing wherever those effects play a significant role.

Methods including electron correlation would obviously correspond to the best choice but these are not yet ready for practical implementation. Yet a Hartree-Fock (HF) approach is routinely and successfully used for representing the ground-state properties of closed-shell molecules and crystals. In solid-state physics, HF calculations are important in determining the electronic properties of solids; indeed they yield good charge densities, Compton profiles, total energies, cell geometry, etc., and in addition they provide a useful conceptual basis for interpreting modifications in spectra [ir, XPS (x-ray photoemission spectroscopy), etc.] when homogeneous series of compounds are considered. The same trends hold true for molecular properties. With such a promising record it is reasonable to expect that a wide variety of properties related to the electronic structure and geometry of polymeric materials can also be investigated and predicted following the same way.

It is only recently that self-consistent Hartree-Fock-Roothaan calculations on realistic polymers have been made possible by the development of new mathematical techniques and faster computers. Practically all of them have been performed in the framework of the direct-space representation which is an extension to infinite systems of the linear combination of atomic orbitals–self-consistent-field–molecular orbitals (LCAO-SCF-MO) method originally deduced by Roothaan and Hall for molecules. For practical reasons those calculations did not include the long-range interactions basically present in the formalism. However, this had long ago been pointed out[10] as a source of problems, and indeed, both in three-dimensional solid-state physics[11,12] and polymer conformational analysis,[13] one can find examples where long-range interactions significantly affect the quality of the results. More recently this was also discovered in polymer quantum calculations.[14-17] It turns out that band structures, force constants, and total energy, most interesting quantities for ground-state investigations, are sensitive with respect to the number of neighbors included in calculations. To achieve proper computations it is first necessary to develop a technology capable of handling Madelung-type interactions in the direct space LCAO-SCF-CO (CO = crystalline orbitals) formalism which is at present the only one of routine applicability. These interactions can be accounted for by using either the Fourier representation method[18] for classical arrays of points or the multipole expansion (two-center expansion) of the Coulombic operator.[19]

The purpose of this paper is to present computational techniques based on the multipole expansion for performing polymer ground-state calculations in which the correct Hartree-Fock (HF) exchange operator is employed and the long-range Coulombic interactions are accounted for. We illustrate the method by applying it to infinite linear chains of lithium hydride molecules and of polyethylene using Gaussian lobe functions.[20] The results will be critically discussed in relation with the practice of quantum calculations.

II. BASIC FORMALISM AND THE MULTIPOLE EXPANSION

In this section we review the basic formalism of the multipole expansion[19] as it can be efficiently used in quantum calculations of the electronic properties of model polymers. During the developments, the stress will be put on the reduction in computational labor it brings into the Hartree-Fock-Roothaan method (LCAO-SCF-CO) for infinite chainlike systems. To provide this paper with a reasonable self-containedness and to introduce the quantities relevant to the subsequent discussions, we proceed first by giving a brief outline of the LCAO-SCF-CO formalism. For a detailed presentation we refer the reader to original papers.[21,22]

A. The LCAO-SCF-CO procedure

Let us consider a one-dimensional periodic lattice consisting of a macroscopic number, $2\mathfrak{N}+1$ ($\mathfrak{N}\to\infty$), of unit cells of length a, each containing Ω nuclei at positions $\vec{A}_1, \vec{A}_2, \ldots, \vec{A}_u, \ldots, \vec{A}_\Omega$ relative to the cell's origin $ja\vec{z}_0$, $j=0, \pm1, \pm2, \ldots, \pm\mathfrak{N}$, and $2n_0$ electrons distributed along the nuclear backbone. As will be shown later, a strict electroneutrality of the cells ($2n_0=Z_1+Z_2+\cdots+Z_\Omega$) is necessary for the stability of the system. The electrons are assumed to doubly occupy a set of one-electron orbitals, $\phi_n(k,\vec{r})$, of Bloch-type, written as periodic combinations of ω basis functions χ_p,

$$\phi_n(k,\vec{r})=(2\mathfrak{N}+1)^{-1/2}\sum_{j=-\mathfrak{N}}^{\mathfrak{N}}\sum_{p=1}^{\omega}C_{np}(k)e^{ikja}\chi_p(\vec{r}-ja\vec{z}_0), \tag{1}$$

where $\vec{r}$ is the position vector measured from an arbitrary but fixed origin, $\vec{z}_0$ is a unit vector in the direction of lattice periodicity, and k is a point in the first Brillouin zone (BZ), $(-\pi/a, \pi/a)$, of the polymer; L_{RC}, the length of this Brillouin zone, is equal to $2\pi/a$. In this paper the sets of indices (j,h,l), (u,v), (p,q,r,s), and (a,b,c,d) refer to cells, nuclei, contracted atomic functions, and primitive functions, respectively.

The $\phi_n(k,\vec{r})$'s represent the wave functions of a single electron in the periodic potential created by the nuclei and the other electrons. The optimal set of those polymer orbitals for a given atomic basis is obtained in the usual way by solving the Hartree-Fock equations. The SCF monoelectronic operator has the explicit form

$$F(\vec{r})=-\tfrac{1}{2}\nabla^2(\vec{r})-\sum_{h=-\mathfrak{N}}^{\mathfrak{N}}\sum_{u=1}^{\omega}Z_u\,|\vec{r}-(\vec{A}_u+ha\vec{z}_0)|^{-1}+L_{RC}^{-1}\int dk'\sum_{n'=1}^{n_0}[2J_{n'k'}(\vec{r})-K_{n'k'}(\vec{r})], \tag{2}$$

where n_0 is the number of doubly occupied bands. The terms included in Eq. (2) are, respectively, the kinetic operator, the attraction of a single electron with all nuclei centered in all cells, the averaged electrostatic potential of all electrons, and the averaged exchange interaction.

As is usually the case for complex problems where expansions into known functions are required, the ultimate equations are in matrix form. By applying the Hartree-Fock condition of minimum expectation value for the total energy of the many-electron crystal wave functions, we end up with the following system of equations:

$$\sum_p C_{np}(k)\left(\sum_j e^{ikja}[F^j_{pq}-E_n(k)S^j_{pq}]\right)=0, \qquad p,q=1,2,\ldots,\omega\,. \tag{3}$$

The solutions to this systems at various k points in the BZ provide the band structure $\{E_n(k)\}$, which is a multivalued function of k in the reduced-zone scheme, and the corresponding eigenvectors $\{C_{np}(k)\}$. We note that F^j_{pq} is a matrix element of the one-electron operator, $F(\vec{r})$, between the atomic orbital χ_p centered in the origin (or reference) cell and the atomic orbital χ^j_q centered in cell j. S^j_{pq}, an overlap integral, is the matrix element between the same orbitals χ_p and χ_q^j when the unit operator is used. Both F_{pq}^j and S_{pq}^j matrix elements decrease exponentially with the distance r between the orbitals giving rise to a natural convergence of the summations over cells appearing in the secular system (3).

In the LCAO-CO procedure, the matrix elements F_{pq}^j are

$$F_{pq}^j = T_{pq}^j - \sum_h \sum_u Z_u V_{pq}^j(h, \vec{\mathrm{A}}_u) + \sum_h \sum_l \sum_r \sum_s D_{rs}^{hl}\left[2\begin{pmatrix} oj & hl \\ pq & rs \end{pmatrix} - \begin{pmatrix} oh & jl \\ pr & qs \end{pmatrix}\right] \tag{4}$$

when defining the following:

the kinetic integrals

$$T_{pq}^j = -\tfrac{1}{2}\int \chi_p(\vec{\mathrm{r}})\nabla^2(\vec{\mathrm{r}})\chi_q(\vec{\mathrm{r}} - ja\vec{\mathrm{z}}_0)d\vec{\mathrm{r}} , \tag{5}$$

the nuclear attraction integrals

$$V_{pq}^j = \int \chi_p(\vec{\mathrm{r}})\,|\,\vec{\mathrm{r}} - (\vec{\mathrm{A}}_u + ha\vec{\mathrm{z}}_0)\,|^{-1}\chi_q(\vec{\mathrm{r}} - ja\vec{\mathrm{z}}_0)\, d\vec{\mathrm{r}} , \tag{6}$$

the electron repulsion integrals

$$\begin{bmatrix} oj & hl \\ pq & rs \end{bmatrix} = \iint \chi_p(\vec{\mathrm{r}}_1)\chi_q(\vec{\mathrm{r}}_1 - ja\vec{\mathrm{z}}_0)r_{12}^{-1} \times \chi_r(\vec{\mathrm{r}}_2 - ha\vec{\mathrm{z}}_0)\chi_s(\vec{\mathrm{r}}_2 - la\vec{\mathrm{z}}_0)d\vec{\mathrm{r}}_1 d\vec{\mathrm{r}}_2 . \tag{7}$$

The iterative parts of the calculations involves elements of the density matrix D_{pq}^j; they are computed at each iteration by numerical integration over the occupied part of the first Brillouin zone of the polymer

$$D_{pq}^j = L_{RC}^{-1}\int_{\mathrm{BZ}} \sum_{n=1}^{n_0} C_{np}^*(k)\, C_{nq}(k) e^{ikja} dk . \tag{8}$$

The total energy E_T, where both electron and nuclear contributions are included, is obtained in the following way:

$$E_T = \sum_j \sum_p \sum_q D_{pq}^j(F_{pq}^j + I_{pq}^j) + \tfrac{1}{2}\sum_h{}' \sum_u \sum_v Z_u |\vec{\mathrm{A}}_v - (\vec{\mathrm{A}}_u + ha\vec{\mathrm{z}}_0)\,|^{-1} , \tag{9}$$

where I_{pq}^j collects one-electron quantities

$$I_{pq}^j = T_{pq}^j - \sum_h \sum_u Z_u V_{pq}^j(h, \vec{\mathrm{A}}_u) . \tag{10}$$

A prime on summations excludes the terms whose denominator vanishes.

B. Long-range problem

In actual applications it is obviously impossible to deal with arbitrary large values of $\mathfrak{N}$ since the two-electron part of an LCAO-CO calculation involves an enormous number of integrals $\left(\begin{smallmatrix} oj & hl \\ pq & rs \end{smallmatrix}\right)$, proportional to $\mathfrak{N}^3\omega^4$. There is a need for limiting $\mathfrak{N}$ to some amenable value N; in most of the reported polymer calculations, N ranges from 1 to 5. For a chosen basis set, N could be the number of neighboring cells still contributing a significant decaying tail of charge amplitude in the reference cell. The normalization condition is satisfied for every N:

$$2\sum_{l=h-N}^{h+N} \sum_r \sum_s D_{rs}^{hl} S_{rs}^{hl} = 2n_0 = 2\sum_{l=-N}^{+N} \sum_r \sum_s D_{rs}^{l} S_{rs}^{l} , \tag{11}$$

when the $C_{np}(k)$'s are properly normalized in Eq. (3) (the quantities D_{rs}^{hl} and D_{rs}^{hl} are identical with $D_{rs}^{(l-h)}$ and $S_{rs}^{(l-h)}$ respectively). However, long-range interactions, which behave like conditionally and slowly convergent series, are actually embodied in F_{pq}^j and E_T, and they are significantly contributing far beyond this number N. Owing to this particular behavior it would be unadvisable to cut off without insight all the three (j, h, l) summations after a few terms. An analysis to this problem as it arises in the direct-space LCAO-CO expressions[17] has been made and it turns out that one summation, to which we attach the index h, has to run from $-\mathfrak{N}$ to $+\mathfrak{N}$ ($\mathfrak{N} \rightarrow \infty$). The limits of the other two, j and l, can be given the values $-\mathfrak{N}$ and $+\mathfrak{N}$. In addition to the normalization constraint, exchange should be essentially and accurately contributed from the range $[-N, +N]$. As a result, F_{pq}^j and E_T can now be cast in more attractive form:

$$F_{pq}^j \simeq T_{pq}^j + \sum_{h=-N}^{+N}\left\{-\sum_u Z_u V_{pq}^j(h, \mathrm{A}_u) + \sum_{l=h-N}^{h+N}\sum_r \sum_s D_{rs}^{hl}\left[2\begin{pmatrix} oj & hl \\ pq & rs \end{pmatrix} - \begin{pmatrix} oh & jl \\ pr & qs \end{pmatrix}\right]\right\} + C_{pq}^j(N) , \tag{12}$$

with

$$C_{pq}^j(N) = \left(\sum_{h=-\infty}^{+\infty} - \sum_{h=-N}^{+N}\right)\left[-\sum_u Z_u V_{pq}^j(h, \vec{\mathrm{A}}_u) + 2\sum_{l=h-N}^{h+N}\sum_r \sum_s D_{rs}^{hl}\begin{pmatrix} oj & hl \\ pq & rs \end{pmatrix}\right] \tag{13}$$

and

$$E_T = \sum_{j=-N}^{+N}\sum_p \sum_q D_{pq}^j(F_{pq}^j + I_{pq}^j) + \tfrac{1}{2}\sum_{j=-N}^{N}{}' \sum_u \sum_v Z_u Z_v\,|\vec{\mathrm{A}}_v - (\vec{\mathrm{A}}_u + ja\vec{\mathrm{z}}_0)\,|^{-1} + C_T(N) , \tag{14}$$

with

$$C_T(N)=\left(\sum_{h=-\infty}^{+\infty}-\sum_{h=-N}^{+N}\right)\left(\tfrac{1}{2}\sum_u{}'\sum_v Z_u Z_v\,|\vec{\mathrm{A}}_v-(\vec{\mathrm{A}}_u+ha\vec{\mathrm{z}}_0)|^{-1}\right.$$
$$\left.-\sum_j\sum_u\sum_p\sum_q Z_u D^j_{pq}\,V^j_{pq}(h,\vec{\mathrm{A}}_u)\right). \tag{15}$$

$C^j_{pq}(N)$ is a part of the long-range contribution to the Fock matrix element F^j_{pq}, the other part being included in F^j_{pq} because of the long-range effect inducing a modification of the density matrix elements. Similarly, $C_T(N)$ is only a part of the long-range contribution to the total energy, the other one being already included in F^j_{pq} and D^j_{pq}. This partitioning formulates the fact that beyond a given distance of interactions, characterized by N, the contribution to the Fock matrix elements and to the total energy are essentially of the electrostatic and induction type. In the case of an atomic basis set including spherical Gaussian functions only, it can be further shown that these terms have the same expression as for classical point-charge interactions.[17]

In spite of the partitioning already introduced we still have to handle an inifinite h summation involving bielectronic integrals, and Eqs. (13) and (15) remain untractable from the computational point of view. However, keeping in mind that l varies from $h-N$ to $h+N$, it is easily understood that the positions $\vec{\mathrm{G}}^j_{pq}$ and $\vec{\mathrm{G}}^{hl}_{rs}$, the centers of charge distributions $\chi_p(\vec{\mathrm{r}})\chi_q(\vec{\mathrm{r}}-ja\vec{\mathrm{z}}_0)$ and $\chi_r(\vec{\mathrm{r}}-ha\vec{\mathrm{z}}_0)\,\chi_s(\vec{\mathrm{r}}-la\vec{\mathrm{z}}_0)$, respectively, involved in the bielectronic integral $\left({}^{oj}_{pq}\middle|{}^{hl}_{rs}\right)$, are getting more and more distant as h increases. This goes up to a point where the overlap between these two distributions is virtually negligible. Similarly, for the nuclear attraction term $V^j_{pq}(h,\vec{\mathrm{A}}_u)$ and beyond a given lattice interdistance $|ha|$, there will be no significant overlap left between the charge distribution $\chi_p(\vec{\mathrm{r}})\chi_q(\vec{\mathrm{r}}-ja\vec{\mathrm{z}}_0)$ and the nuclei belonging to the cell h. At this point, electron repulsion, $\left({}^{oj}_{pq}\middle|{}^{hl}_{rs}\right)$, nuclear attraction, $V^j_{pq}(h,\vec{\mathrm{A}}_u)$, and of course nuclear repulsion, $|\vec{\mathrm{A}}_v-(\vec{\mathrm{A}}_u+ha\vec{\mathrm{z}}_0)|^{-1}$, decay roughly like $|ha\vec{\mathrm{z}}_0+b|^{-1}$ and thus behave clearly like individually divergent lattice sums; they are the classical conditionally convergent series encountered in evaluating Madelung constants. The cancellation of the divergence inherent in the problem is due to the electrical neutrality of the system and it is actually achieved by an approprite combination of the electron-electron terms with the nuclear-attraction ones in the case of $C^j_{pq}(N)$ and of the nuclear-repulsion terms with the nuclear-attraction ones in the case of $C_T(N)$. The next step is thus to find a way to conduct these summations up to infinity and at the same time to get rid of an infinite number of bielectronic integrals.

C. Calculation of $C^j_{pq}(N)$ and $C_T(N)$ via the multipole expansion

One way to bring this twofold objective to a successful end is to use[19] the bipolar expansion[23,24] of the Coulombic operators $|\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2|^{-1}$, $|\vec{\mathrm{r}}-(\vec{\mathrm{A}}_u+ha\vec{\mathrm{z}}_0)|^{-1}$, and $|\vec{\mathrm{A}}_v-(\vec{\mathrm{A}}_u+ha\vec{\mathrm{z}}_0)|^{-1}$ appearing in the electron-electron, nuclear-attraction, and nuclear-repulsion terms respectively. The merit of this approach is to separate the coupled variables $(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2)$, $(\vec{\mathrm{r}}_1,\vec{\mathrm{A}}_u+ha\vec{\mathrm{z}}_0)$, and $(\vec{\mathrm{A}}_v,\vec{\mathrm{A}}_u+ha\vec{\mathrm{z}}_0)$ and to expand the corresponding terms in convergent series of products of functions involving the coördinates of one particle only. The condition for convergence is that the interacting charge distributions must be enclosed inside nonoverlapping spheres. Since in the nuclear-repulsion contributions the nuclei are located at fixed positions, it is an easy matter to arrange things in such a way that this condition is satisfied. On the contrary, electron positions are characterized by probability distributions which extend throughout space and we can only speak of an asymptotic convergence.[25] Amos and Crispin[26] have made an explict analysis of the problem for Gaussian probability distributions. It is important to apply the bipolar expansion in those regions of configuration space where the values of the functions it represents can be calculated with a good degree of accuracy.

To our knowledge, Karpfen and Schuster[7] were the first to apply the bipolar expansion in the context of quantum calculations on polymers. They evaluated the long-range contributions to the total energy of a chain of hydrogen fluoride molecules interacting up to their third neighbors ($N=3$).[27] At the end of a conventional LCAO-SCF-CO calculation they applied an energy correction approximated as the sum of the electrostatic interactions of two isolated hydrogen fluoride molecules successively located at the lattice points. The calculations were repeated over 10^3 lattice points and the multipole expansion was carried out up to hexadecapole-hexa decapole term. In a recent paper, two of us[19] have shown how to include the long-range interactions in the Fock matrix elements and to combine correctly as well as to sum exactly up to infinity those contributions with the help of the Riemann zeta function, $\zeta(k)$. In this way the goal was given a complete and consistent solution. Indeed, the charge distributions of the system relax in the true field of an infinite chain and beyond a certain distance of interaction the problematic bielectronic integrals are eliminated with no loss of accuracy. The total energy, determinant for structural investigations, can thus be computed on a firm ground.

A detailed deduction of the multipole expansion formulas as they apply to polymers is given in Refs. 19 and 28; hereafter we restrict ourselves to the essentials. Introducing the bipolar expansion into Eqs. (13) and (15) we obtain

$$C^j_{pq}(N)=\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}U^{j\,(k,l)}_{pq}a^{-k-l-1}\Delta_N^{(k+l+1)} \tag{16}$$

and

$$C_T(N)=\tfrac{1}{2}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}U_T^{(k,l)}a^{-k-l-1}\Delta_N^{(k+l+1)}\ , \tag{17}$$

where

$$\Delta_N^{(n)}=\sum_{h=1}^{\infty}h^{-n}-\sum_{h=1}^{N}h^{-n}=\zeta(n)-\sum_{h=1}^{N}h^{-n}\ . \tag{18}$$

The quantities $U^{j\,(k,l)}_{pq}$ and $U_T^{(k,l)}$ correspond to the interaction of the 2^k-pole and 2^l-pole moments and are defined as

$$U^{j\,(k,l)}_{pq}=\sum_{m=-s(k,l)}^{s(k,l)}(k+l)!(-1)^m[(-1)^k+(-1)^l][(k+|m|)!(l+|m|)!]^{-1}M^{j\,(k,m)}_{pq}M^{(l,m)*} \tag{19}$$

and

$$U_T^{(k,l)}=\sum_{m=-s(k,l)}^{s(k,l)}(k+l)!(-1)^m[(-1)^k+(-1)^l][(k+|m|)!(l+|m|)!]^{-1}M_{\text{nuc}}^{(k,m)}M^{(l,m)*}\ . \tag{20}$$

In the above expressions, s is equal to the smaller of numbers k and l. Capital letter $M^{(l,m)}$ refers to the mth component of the 2^lth electric moment expressed in spherical coordinates and related to the charge distributions either associated with the orbital product $\chi_p(\vec{r})\,\chi_q(\vec{r}-ja\vec{z}_0)$,

$$M^{j\,(k,m)}_{pq}=\langle\chi_p(\vec{r})\,|r^kP_k^{|m|}(\cos\theta)e^{im\phi}\,|\chi_q(\vec{r}-ja\vec{z}_0)\rangle\ , \tag{21}$$

or with all nuclei,

$$M_{\text{nuc}}^{(k,m)}=-\sum_{u=1}^{\Omega}Z_ur_u^kP_k^{|m|}(\cos\theta_u)e^{im\phi_u}\ ,$$

or to the total charge (electrons + nuclei) associated with each translational unit,

$$M^{(k,m)}=-\sum_{u=1}^{\Omega}Z_ur_u^kP_k^{|m|}(\cos\theta_u)e^{im\phi_u}+2\sum_{j=-N}^{+N}\sum_p\sum_q D^j_{pq}\langle\chi_p(\vec{r})\,|r^kP_k^{|m|}(\cos\theta)e^{im\phi}\,|\chi_q(\vec{r}-ja\vec{z}_0)\rangle\ . \tag{22}$$

Compared to Ref. 19, simplified notations have been adopted by dropping the subscripts characterizing the coordinate systems 1 and 2, respectively, attached to the reference cell 0 and to cell h (here we use r_u instead of r_{0u} and r_{hu}). Indeed, due to translational symmetry, quantities evaluated in coordinate system 1 are identical to those of system 2. Moreover in the case of electron coordinates $\vec{r}_1$ and $\vec{r}_2$, over which separate integrations make the distinction irrelevant, we have ignored the indices 1 and 2 (we use r, θ, ϕ instead of r_{01}, θ_{01}, ϕ_{01} and r_{h2}, θ_{h2}, ϕ_{h2}).

Because of electroneutrality constraints which give $U^{j\,(k,0)}_{pq}=U_T^{(k,0)}=0$, Eqs. (16) and (17) can be simplified and, to avoid coordinate dependence of the results,[19,29,30] they deserve special attention when coming to the point of truncating the infinite summations over k and l. Taking these points into account, Eqs. (16) and (17) read[28]

$$C^j_{pq}(N)=\sum_{k=3,5,\ldots;\,k=\text{odd}}\Delta_N^{(k)}a^{-k}\sum_{l=1}^{k-1}U^{j\,(k-l-1,l)}_{pq}$$
$$=\sum_{k=3,5,\ldots;\,k=\text{odd}}\mathfrak{a}^{j\,(k)}_{pq}(N) \tag{23}$$

and

$$C_T(N)=\tfrac{1}{2}\sum_{k=3,5,\ldots;\,k=\text{odd}}\Delta_N^{(k)}a^{-k}\sum_{l=1}^{k-1}U_T^{(k-l-1,l)}$$
$$=\sum_{k=3,5,\ldots;\,k=\text{odd}}\mathfrak{a}_T^{(k)}(N). \tag{24}$$

In actual calculations, Cartesian coordinates are generally used and thus we provide the $U^{j\,(k,l)}_{pq}$'s expressed in these coordinates for the first powers of a^{-1} (See Table I). Note that in these expressions the summation over the index m has been performed as well as some grouping manipulations to obtain a final form almost ready for application (an explicit reference to the various powers of x, y, z, and r is also given in square brackets). To help the reader interested in the details, an illustrative deduction of $U^{j\,(3,1)}_{pq}$ is given in the Appendix. The content of Table I is restricted to a minimum, but any useful quantity can be deduced thereof. Only the terms $U^{j\,(k,l)}_{pq}$ for which $k\le l$ are listed, the missing ones, $U^{j\,(l,k)}_{pq}$, being obtained from $U^{j\,(k,l)}_{pq}$ after interchanging M^j_{pq} and M. Similarly all the quantities for evaluating $U_T^{(k,l)}$ are built up by replacing the notation ${}^j_{pq}$ by

TABLE I. $U_{pq}^{j(k,l)}$ expressed in Cartesian coordinates; the list is restricted to $k \leqslant l$. The Appendix contains explanations about the notation. $M_{pq}^{j(0)} \equiv S_{pq}^{j}$; $U_{pq}^{j(k,0)} = 0$.

$k+l+1$	
3	$U_{pq}^{j(0,2)} = M_{pq}^{j(0)} M^{(2)} [3z^2 - r^2]$
	$U_{pq}^{j(1,1)} = 2M_{pq}^{j(1)}[x]M^{(1)}[x] + 2M_{pq}^{j(1)}[y]M^{(1)}[y] - 4M_{pq}^{j(1)}[z]M^{(1)}[z]$
5	$U_{pq}^{j(0,4)} = \frac{1}{4}M_{pq}^{j(0)}M^{(4)}[35z^4 - 30z^2r^2 + 3r^4]$
	$U_{pq}^{j(1,3)} = 4M_{pq}^{j(1)}[z]M^{(3)}[3r^2z - 5z^3] + 3M_{pq}^{j(1)}[x]M^{(3)}[5xz^2 - r^2x] + 3M_{pq}^{j(1)}[y]M^{(3)}[5yz^2 - r^2y]$
	$U_{pq}^{j(2,2)} = 3M_{pq}^{j(2)}[3z^2 - r^2]M^{(2)}[3z^2 - r^2] - 24M_{pq}^{j(2)}[xz]M^{(2)}[xz] - 24M_{pq}^{j(2)}[yz]M^{(2)}[yz]$ $+ \frac{3}{2}M_{pq}^{j(2)}[x^2 - y^2]M^{(2)}[x^2 - y^2] + 6M_{pq}^{j(2)}[xy]M^{(2)}[xy]$
7	$U_{pq}^{j(0,6)} = \frac{1}{8}M_{pq}^{j(0)}M^{(6)}[231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6]$
	$U_{pq}^{j(1,5)} = -\frac{3}{2}M_{pq}^{j(1)}[z]M^{(5)}[63z^5 - 70z^3r^2 + 15zr^4] + \frac{15}{4}M_{pq}^{j(1)}[x]M^{(5)}[21z^4x - 14z^2xr^2 + xr^4]$ $+ \frac{15}{4}M_{pq}^{j(1)}[y]M^{(5)}[21z^4y - 14z^2yr^2 + yr^4]$
	$U_{pq}^{j(2,4)} = \frac{15}{8}M_{pq}^{j(2)}[3z^2 - r^2]M^{(4)}[35z^4 - 30z^2r^2 + 3r^4] - 30M_{pq}^{j(2)}[xz]M^{(4)}[7z^3x - 3xzr^2]$ $- 30M_{pq}^{j(2)}[yz]M^{(4)}[7z^3y - 3yzr^2] + \frac{15}{4}M_{pq}^{j(2)}[x^2 - y^2]M^{(4)}[7z^2(x^2 - y^2) - r^2(x^2 - y^2)]$ $+ 15M_{pq}^{j(2)}[xy]M^{(4)}[7z^2xy - xyr^2]$
	$U_{pq}^{j(3,3)} = -10M_{pq}^{j(3)}[5z^3 - 3zr^2]M^{(3)}[5z^3 - 3zr^2] + \frac{45}{4}M_{pq}^{j(3)}[5z^2x - xr^2]M^{(3)}[5z^2x - xr^2]$ $+ \frac{45}{4}M_{pq}^{j(3)}[5z^2y - yr^2]M^{(3)}[5z^2y - yr^2] - 45M_{pq}^{j(3)}[zx^2 - zy^2]M^{(3)}[zx^2 - zy^2]$ $- 180M_{pq}^{j(3)}[xyz]M^{(3)}[xyz] + \frac{5}{4}M_{pq}^{j(3)}[x^3 - 3xy^2]M^{(3)}[x^3 - 3xy^2]$ $+ \frac{5}{4}M_{pq}^{j(3)}[y^3 - 3x^2y]M^{(3)}[y^3 - 3x^2y]$

nuc wherever it appears.

As can be appreciated from Table I, all expressions are easy to implement into a computer program since they correspond to one-electron integrals only. The number of such integrals grows as the second power of the basis length, ω, and is proportional to the number of interacting cells (in the short-range sense), $2N+1$, as well as to the number of (k,l) couples included in the multipole expansion. As a consequence, the computing time required for including the long-range corrections is negligible with respect to the main part of an LCAO-CO calculation which involves the numerous two-electron multicenter integrals.

Another nicety of the bipolar decomposition is to provide a simple and direct understanding of the condition for the repeating unit cells of the polymer to be electrically neutral. To illustrate this point, let us factor out the first term $(k=l=0)$ of Eq. (17),

$$C_T(N) = \tfrac{1}{2}U_T^{(0,0)}a^{-1}\Delta_N^{(1)} + \tfrac{1}{2}\sum_{\substack{k=0\\(k,l)\neq(0,0)}}^{\infty}\sum_{l=0}^{\infty} U_T^{(k,l)}a^{-k-l-1}\Delta_N^{(k+l+1)}, \qquad (25)$$

and, from formulas (20) and (22), obtain $U_T^{(0,0)}$ explicitly:

$$U_T^{(0,0)} = 2\left(-\sum_u Z_u\right)\left(-\sum_v Z_v + 2\sum_l\sum_r\sum_s D_{rs}^l S_{rs}^l\right). \qquad (26)$$

Large parentheses contain precisely the total nuclear charge $(-\sum_u Z_u)$ and the number of electrons $(2n_0 = 2\sum_l\sum_r\sum_s D_{rs}^l S_{rs}^l)$ per unit cell. Note that $\Delta_N^{(l)}$ multiplies $U_T^{(0,0)}$ in Eq. (25) and it includes the Riemann zeta function $\zeta(1)$ which rapidly increases to infinity. To keep $C_T(N)$ finite or physical, one must add a constraint which forces the value in large parentheses to vanish identically (zero net charge in the unit cells). This corresponds to the well-known fact that isolated and charged infinite chains cannot exist. To consider charged polymers it is necessary to introduce complementary (opposite) charges such as counterions, chains bearing opposite electrical charges, etc. In such an event, however, a three-dimensional organization will be important to take into account and additional constraints[31] as to the dipole and second-moment tensors will be necessary.

III. BIPOLAR EXPANSION FOR GAUSSIAN LOBES AND APPLICATIONS

Up to this point no special attention has been paid as to the type of basis functions, and the expressions as well as conclusions of the preceding section are generally valid. However, when making a specific choice it is useful to take advantage of the favorable features of the basis set.

From the investigations as to the most appropriate and convenient sets of basis functions, it turns out that various directions have been chosen according to preassigned criteria among which the labor associated with the evaluation of a huge number of electron-repulsion integrals is often determining. For that reason, Gaussian-type functions were soon preferred as the most popular functions because all integrals are expressed in closed form. The choice can be specialized further by considering 1*s* floating spherical Gaussians (Gaussian lobes) only since their analytical expressions are very simple. This direction has proven to be valuable with respect to the ability of predicting properties of interest with satisfactory accuracy,[32] provided enough flexibility is returned in the basis by expanding contracted functions, $\chi_p(\vec{r})$, into predetermined linear combinations of 1*s* Gaussian-type orbitals (GTO's) which can assume positions other than nuclear centers:

$$\chi_p^j(\vec{r}) = \sum_{a=1}^{\omega_p} g_{ap} G_a(\vec{r} - \vec{A}_p - ja\vec{z}_0). \tag{27}$$

In Eq. (27), ω_p is the number of 1*s* GTO's used to represent $\chi_p(\vec{r})$, which can be of $s, p, d, \ldots,$-type.[33] $G_a(\vec{r} - \vec{A}_p - ja\vec{z}_0)$, a primitive spherical Gaussian function, is given by

$$G_a(\vec{r} - \vec{A}_p - ja\vec{z}_0) = \left(\frac{2\alpha_{ap}}{\pi}\right)^{3/4} \exp[-\alpha_{ap}(\vec{r} - \vec{A}_p - ja\vec{z}_0)^2] . \tag{28}$$

The exponent α_{ap} and the center of the Gaussian $\vec{A}_p$, can be optimized variationally.

In this section, we show how for Gaussian lobe functions the moment integrals simplify and we report on actual calculations on two infinite chains: $(\mathrm{LiH})_n$ and $(\mathrm{CH_2{-}CH_2})_n$.

A. Simplification of moment integrals

In the case of Gaussian lobes the matrix elements $M_{pq}^{j\,(k,\,m)}$,

$$M_{pq}^{j\,(k,\,m)} = \langle \chi_p(\vec{r}) \,|\, r^k P_k^{|m|}(\cos\theta) e^{im\phi} \,|\, \chi_q^j(\vec{r}) \rangle = \sum_a^{\omega_p} \sum_b^{\omega_q} g_{ap} g_{bq} \langle \vec{G}_a(\vec{r} - \vec{A}_p) \,|\, r^k P_k^{|m|}(\cos\theta) e^{im\phi} \,|\, \vec{G}_b(\vec{r} - \vec{B}_q - ja\vec{z}_0) \rangle , \tag{29}$$

can be cast in a surprisingly simple form containing the overlap integral, S_{ab}^j, multiplied by a function of the powers of the components, (X_{ab}), (Y_{ab}), (Z_{ab}^j) of $\vec{G}_{ab}^j$, the center of the charge distribution $G_a(\vec{r} - \vec{A}_p)\, G_b(\vec{r} - \vec{B}_q - ja\vec{z}_0)$:

$$\langle G_a(\vec{r} - \vec{A}_p) \,|\, r^k P_k^{|m|} e^{im\phi} \,|\, G_b(\vec{r} - \vec{B}_q - ja\vec{z}_0) \rangle = S_{ab}^j \,|\vec{G}_{ab}^j|^k P_k^{|m|}(\cos\theta_{ab}^j) e^{im\phi_{ab}^j} , \tag{30}$$

where $|\vec{G}_{ab}^j|$, θ_{ab}^j, and ϕ_{ab}^j are the spherical coordinates of the vector $\vec{G}_{ab}^j$. This compactness contrasts with the widely used expression of moment integrals taken individually between two 1*s* GTO's:

$$\langle G_a(\vec{r} - \vec{A}_p) \,|\, r^k P_k^{|m|} e^{im\phi} \,|\, G_b(\vec{r} - \vec{B}_q - ja\vec{z}_0) \rangle \equiv \left\langle G_a \,\middle|\, \sum_{\alpha,\beta,\gamma} C_{\alpha\beta\gamma} x^\alpha y^\beta z^\gamma \,\middle|\, G_b^j \right\rangle \tag{31}$$

with $C_{\alpha\beta\gamma}$ being a constant:

$$\begin{aligned} \langle G_a(\vec{r} - \vec{A}_p) \,|\, x^\alpha y^\beta z^\gamma \,|\, G_b(\vec{r} - \vec{B}_q - ja\vec{z}_0) \rangle = {} & \left(\frac{2\alpha_{ap}}{\pi}\right)^{3/4} \left(\frac{2\alpha_{bq}}{\pi}\right)^{3/4} \exp\left(-\frac{\alpha_{ap}\alpha_{bq}}{\alpha_{ap} + \alpha_{bq}} \cdot (\vec{A}_p - \vec{B}_q - ja\vec{z}_0)^2\right) \\ & \times \sum_{i=0,2}^{\langle\alpha\rangle} \binom{\alpha}{i} (X_{ab})^{\alpha-i}\, \Gamma\!\left(\frac{i+1}{2}\right) (\alpha_{ap} + \alpha_{bp})^{-(i+1)/2} \\ & \times \sum_{j=0,2}^{\langle\beta\rangle} \binom{\beta}{j} (Y_{ab})^{\beta-j}\, \Gamma\!\left(\frac{j+1}{2}\right) (\alpha_{ap} + \alpha_{bq})^{-(j+1)/2} \\ & \times \sum_{k=0,2}^{\langle\gamma\rangle} \binom{\gamma}{k} (Z_{ab}^j)^{\gamma-k}\, \Gamma\!\left(\frac{k+1}{2}\right) (\alpha_{ap} + \alpha_{bq})^{-(k+1)/2} \end{aligned} \tag{32}$$

$\langle\nu\rangle$ corresponds to the largest even value such that $\langle\nu\rangle \leqslant \nu$.

Formula (30) is much more effective than formula (32) where a number of terms cancel each other but need to be computed, thus producing undesirable additional computation time. A formal proof of

(30) can be obtained in a simple way by using the modified regular spherical harmonics[34] defined as

$$\mathcal{Y}_l^m=(4\pi)^{1/2}[(2l+1)(l+m)!\,(l-m)!]^{-1/2}r^l Y_l^m(\theta,\phi)=\mathfrak{D}_{lm}r^l P_l^{|m|}(\cos\theta)e^{im\phi}\ , \tag{33}$$

with $|m|\leq l$ and $\mathfrak{D}_{lm}\neq 0$ as a constant. Let us now consider two 1*s* Gaussian functions G_a and G_b^j whose product yields another 1*s* Gaussian function centered at $\vec{G}_{ab}^j(X_{ab},Y_{ab},Z_{ab}^j)$[35]:

$$G_a(\vec{r}-\vec{A})G_b(\vec{r}-\vec{B}-ja\vec{z}_0)=D\exp-(\alpha_a+\alpha_b)(\vec{r}-\vec{G}_{ab}^j)^2\ , \tag{34}$$

where

$$\vec{G}_{ab}^j=\frac{\vec{A}\alpha_a+(\vec{B}+ja\vec{z}_0)\alpha_b}{\alpha_a+\alpha_b}\ ,\quad D=\exp\left(-\frac{\alpha_a\alpha_b}{\alpha_a+\alpha_b}\ [\vec{A}-(\vec{B}+ja\vec{z}_0)]^2\right)\left(\frac{2\alpha_a}{\pi}\right)^{3/4}\left(\frac{2\alpha_b}{\pi}\right)^{3/4}\ . \tag{35}$$

Now the matrix element $\langle G_a|r^l P_l^{|m|}e^{im\phi}|G_b^j\rangle$ is

$$\langle G_a|r^l P_l^{|m|}e^{im\phi}|G_b^j\rangle=\mathfrak{D}_{lm}^{-1}\langle G_a|\mathcal{Y}_l^m|G_b^j\rangle=D\,\mathfrak{D}_{lm}^{-1}\int\exp[-(\alpha_a+\alpha_b)(\vec{r}-\vec{G}_{ab}^j)^2]\,\mathcal{Y}_l^m(\vec{r})\,d\vec{r}\ . \tag{36}$$

Upon changing the variable $\vec{r}$ into $\vec{r}\,'=\vec{r}-\vec{G}_{ab}^j$, we get

$$\langle G_a|\mathcal{Y}_l^m(\vec{r})|G_b^j\rangle=D\int\exp[-(\alpha_a+\alpha_b)|\vec{r}|^2]\,\mathcal{Y}_l^m(\vec{r}+\vec{G}_{ab}^j)\,d\vec{r}\ . \tag{37}$$

At this point we use a helpful identity satisfied by the modified regular solid spherical harmonics,[34] namely,

$$\mathcal{Y}_l^m(\vec{r}+\vec{G}_{ab}^j)=\sum_{k=0}^{l}\sum_{m'}\mathcal{Y}_k^{m'}(\vec{r})\mathcal{Y}_{l-k}^{m-m'}(\vec{G}_{ab}^j)\ , \tag{38}$$

with $\max(-k,-l+k+m)\leq m'\leq\min(k,l-k+m)$. Inserting (38) into (37) leads to

$$\langle G_a|\mathcal{Y}_l^m(\vec{r})|G_b^j\rangle=D\sum_{k=0}\sum_{m'}\mathcal{Y}_{l-m}^{m-m'}(\vec{G}_{ab}^j)\frac{4\pi}{[(2k+1)(k+m')!\,(k-m')!]^{1/2}}$$
$$\times\int_0^\infty e^{-(\alpha_a+\alpha_b)r^2}r^{2+k}\,dr\int Y_0^0(\theta,\phi)Y_k^{m'}(\theta,\phi)\sin\theta\ d\theta\ d\phi\ . \tag{39}$$

In the preceding equation we have expressed $\mathcal{Y}_k^{m'}$ according to (33) and expressed the unity as $(4\pi)^{1/2}\ Y_0^0(\theta,\phi)$. Integrations over θ and ϕ reduce to $\delta_{k0}\delta_{m'0}$ which finally leads to

$$\langle G_a|\mathcal{Y}_l^m(\vec{r})|G_b^j\rangle=S_{ab}^j\,\mathcal{Y}_l^m(\vec{G}_{ab}^j)\ , \tag{40}$$

where only the center of charge $\vec{G}_{ab}^j$ appears as the argument of $\mathcal{Y}_l^m$ which is multiplied by the overlap integral. Thus after some simple manipulations one ends with

$$\langle G_a|r^k P_k^{|m|}(\cos\theta)e^{im\phi}|G_b^j\rangle$$
$$=S_{ab}^j|\vec{G}_{ab}^j|^k P_k^{|m|}(\cos\theta_{ab}^j)e^{im\phi_{ab}^j}\ . \tag{41}$$

B. Results on $(LiH)_n$ and $(CH_2\text{-}CH_2)_n$ chains: Discussion

In response to interrogations raised by experimentalists trying to understand at an atomic level the physical and chemical properties of low-dimensional compounds, *ab initio* calculations on model systems tend to multiply. Unfortunately, the computational proficiency is not comparable to the one reached in atomic and molecular studies. In a recent paper, Karpfen[36] illustrated very well how equilibrium distances and one-electron energies of model chains change with respect to the basis used. These findings match similar conclusions previously obtained in atomic and molecular studies. Although a systematic search has yet to be made, it is reasonable to expect that computed properties of polymeric compounds with specific basis sets (minimal, extended, etc.) have generally the same weaknesses as their molecular counterparts.

There is one point at least which is not completely mastered or appreciated; it originates from the extended nature of the system, namely, the number of interacting neighbors one has to take into account to make certain that the model has been consistently solved and that nothing significant has been dropped. The model assumes an infinite number of interacting cells which usually leads to slowly convergent lattice sums. In principle, a finite but sufficient number of terms can very well yield accurate results but, as far as we know, there is no criterion which enables one to define *a priori* this number while achieving a satisfactory compromise between the computing cost and the quality of the results. One has very often the unpleasant experience of finding after a calculation that the included number of neighbors was either too small or could have been reduced.

In this part we want to analyze occurrences of long-range effects (the number of neighbors) either as a result of the basis-set type or as a true effect and the warning it gives for the practice of quantum-mechanical calculations on extended systems. The two test cases we have chosen to this aim are the ionic lithium hydride chain $(LiH)_n$ and polyethylene $(CH_2-CH_2)_n$, which is typically covalent and nonpolar. All calculations reported herein and using the bipolar expansion have been performed with the k-summation index limited to 7 in Eqs. (23) and (24). The neglect of bielectronic integrals has been made on the basis of a threshold of 10^{-8}.

1. $(LiH)_n$. This system models an ionic chain, a character known for generating long-range effects. The main reason for this somewhat artificial case is twofold: First the calculations are relatively easy to perform and second, it is one of the cases Karpfen[36] selected to carry out extensive numerical investigations on basis-sets effects and to which we want to compare our data where long-range effects have been included. As in Ref. 36 we consider the geometry where the two distances between atoms are equal.

As a preliminary we illustrate in Table II how the long-range Coulomb corrections, $\mathfrak{A}_T^{(k)}(N)$, defined in Eq. (24) modify the total energy value in the case of a strict floating spherical Gaussian-type orbital (FSGO) basis set. The center, $\vec{A}_p$, of the Gaussian describing the Li–H bond has been located at 0.3395 a.u. towards the hydrogen atom. One notices a rather slow convergence of $E_T^0(N)$ with respect to N, the number of neighboring cells, and it takes about 200 neighbors to achieve an accuracy of five decimal places.[18] The same result is readily obtained when introducing the long-range corrections which also indicate that beyond $N=2$ the contributions originate from the Coulomb field of the neighboring and remote cells. The individual contributions of the latters are small but their sum amounts to a significant correction. Compared to the direct evaluation, tedious and expensive, the bipolar expansion combined with the Riemann zeta function lends an accurate value with not much effort.

We now turn to the more sophisticated basis sets used by Karpfen which we have used exactly to compare his results to ours. We have carefully checked the molecular systems in which our sets of programs yielded the same charges, total and one-electron energies, etc., at the same level of accuracy as the one reported in Ref. 36. We have considered two basis sets denoted by A and B, respectively, in Table III. Basis set A is Huzinaga's $8s, 4s/5s, 3s$ basis for Li and H (Refs. 37 and 38): 8 primitive Gaussians contracted into 5 functions (the first one containing 4 Gaussians and the others 1 Gaussian) for describing the $1s$ and $2s$ Li shells and 4 primitive Gaussians contracted into 3 functions for the $1s$ H shell. In basis set B, one polarization function is added on each atom whose exponent is 0.5 a.u.$^{-2}$ for Li and 0.2 a.u.$^{-2}$ for H. Table III lists the equilibrium geometry, Mulliken population of the H atom, the total energy per unit cell, and the bandwidth of the 2σ band; these results were calculated with and without the long-range corrections and all values are in a.u.

From the data listed in Table III, one can make the following comments. First, the results, including long-range and using $N=2$, are essentially the same as those of $N=3$. This indicates that beyond $N=2$ the remaining interactions are Coulombic and the exchange and kinetic ones can be neglected for N outside the range $[-2,+2]$. It remains to devise practical expressions for estimating *a priori* the error when dropping these kinetic and exchange contributions outside $[-N,+N]$. For Gaussian-type orbitals, one way is to consider the magnitude of the overlap integrals which enter as multiplicative terms in the various

TABLE II. Evolution of the total energy $E_T^n(N)$ per unit cell of an infinite lithium hydride chain upon inclusion of the $\mathfrak{A}_T^{(k)}(N)$ corrections, Eq. (24). $E_T^n(N)$ is defined as $E_T^n(N)=E_T^0(N)+\sum_{k=3,5,\ldots}^{n} a_T^{(k)}(N)$ and $E_T^0(N)$ is the total energy per unit cell with no correction. Units in a.u.

N	$E_T^0(N)$	$E_T^3(N)$	$E_T^5(N)$	$E_T^7(N)$
1	−6.608 326 0	−6.617 573 3	−6.617 577 3	−6.617 574 7
2	−6.614 036 0	−6.617 574 0	−6.617 574 2	−6.617 574 1
3	−6.615 736 5	−6.617 574 0	−6.617 574 1	−6.617 574 1
4	−6.616 454 0	−6.617 574 1	−6.617 574 1	−6.617 574 1
5	−6.616 821 4	−6.617 574 1	−6.617 574 1	−6.617 574 1

$r_{\text{Li-H}}=3.2381$ a.u., $\alpha_{\text{Li}}=1.9815$ a.u.$^{-2}$, $\alpha_{\text{Li-H}}=0.1677$ a.u.$^{-2}$

TABLE III. Equlibrium distance, Mulliken population on the hydrogen, total energy per unit cell, and 2σ bandwidth for an equidistant infinite lithium hydride chain. Influence of long-range corrections on the results. Units in a.u.

N	$r_{\mathrm{Li-H}}$	q_{H}	$E_T^n(N)$	$\Delta E_{2\sigma}$
	Basis set A without long range ($n=0$)			
2	3.262	1.801	−8.032 228	0.020 01
3	3.253	1.833	−8.033 735	0.018 52
4	3.248	1.845	−8.034 486	0.017 63
5	3.245	1.852	−8.034 896	0.017 35
6	3.243	1.856	−8.035 136	0.017 22
	with long range ($n=7$)			
2	3.239	1.866	−8.035 792	0.016 8
3	3.239	1.865	−8.035 791	0.016 8
	Basis set B without long range ($n=0$)			
2	3.194	1.735	−8.039 707	
3	3.191	1.767	−8.040 752	
4	3.190	1.781	−8.041 335	0.005 51
5	3.188	1.787	−8.041 667	0.004 89
6	3.187	1.792	−8.041 868	0.004 80
	with long range ($n=7$)			
2	3.184	1.802	−8.042 414	0.004 71
3	3.184	1.802	−8.042 415	0.004 78

integral expressions. This is of practical importance since it prevents the user from considering either too many interactions within the expensive scheme where all contributions (kinetic + exchange + Coulomb) are simultaneously processed or not enough. Second, when the long-range contributions are not included and even for $N=6$ in both A and B basis sets, the quantities reported in Table III are not yet stabilized within an accuracy of three decimal places. For example, the equilibrium distance in basis set A changes by 0.004 a.u. when going from $N=6$ to infinity; it illustrates how it could be misleading to extrapolate from the first few terms because they show little variations. This is done forgetting the slow but nevertheless effective building-up process of lattice sums into significant contributions. In the case we analyze ($N=6$), the differences are not dramatic enough to alter the conclusions drawn in Ref. 36, but there could be systems where the effects will be more pronounced. In fact, the Li-H case is so simple that it was possible to consider interactions up to $N=6$; however, in routine works on more common polymers, this will be just prohibitive. If we make then the same comparison as above with $N=2$, a normal number in actual calculations, the changes in equilibrium distance and total energy per unit cell upon including the long-range effects are 0.023 a.u. and 1.6 kcal mol^{-1}, respectively (basis A); the $\Delta E_{2\sigma}$ changes by 19%; these differences become nonnegligible. There is a third observation, which concerns the striking differences in speed of convergence of $E_T^0(N)$ in the FSGO basis compared to more extended basis sets (A and B). The discussion is made in comparison with the results on $(CH_2-CH_2)_n$.

TABLE IV. Evaluation of the total energy, $E_T^n(4)$, per unit cell of an infinite chain of polyethylene upon inclusion of the $\mathcal{Q}_T^{(k)}(4)$ corrections. Units in a.u.

$E_T^n(4)$	FSGO [a]	Molecular fragments [b]
$E_T^0(4)$	−32.979 304 7	−33.316 187 3
$E_T^3(4)$	−33.002 164 8	−33.316 183 6
$E_T^5(4)$	−33.002 202 2	−33.316 183 2
$E_T^7(4)$	−33.002 202 6	−33.316 183 4

[a] Basis parameters: $\alpha_{1s_C}=9.3064$ (a.u.)$^{-2}$, $\alpha_{C-C}=0.362\,94$ (a.u.)$^{-2}$, $\alpha_{C-H}=0.345$ (a.u.)$^{-2}$.

[b] Molecular fragments parameters: $\alpha_{1s_C}=9.3039$ (a.u.)$^{-2}$, $\alpha_{C-C}=0.357\,49$ (a.u.)$^{-2}$, $\alpha_{C-H}=0.357\,49$ (a.u.)$^{-2}$, $r/R=0.5$.

2. $(CH_2-CH_2)_n$. It is generally accepted that long-range effects are essentially important in polar systems. There are situations where nonpolar systems exhibit a behavior resembling long-range effects. This is the case of polyethylene computed with FSGO basis for which, unlike the usual atomic functions, the floating spherical Gaussians are located on bonds to simulate the Lewis structure. The reason for using the FSGO basis[39] is the low computing cost it requires to yield results (bond lengths, angles, conformers' stability, etc.) of an acceptable quality provided one is careful enough in using the numbers and one is aware of its major weaknesses. In the case of extended systems, where the computing effort is generally more important, this seems a promising approach for semiquantitative investigations.[40,41] However, in practice one finds unexpected convergence problems with respect to the number of neighbors even in favorable cases like polyethylene. Table IV contains total energies, $E_T^n(4)$, per unit cell of polyethylene computed with the FSGO basis and with the molecular fragment approach of Christoffersen.[42] The parameters used are reproduced at the bottom of Table IV according to the notation introduced in Fig. 1. While the FSGO basis causes trouble, the molecular fragment basis exhibits no convergence problem for usual atomic functions centered on the nuclei. Figure 1 helps

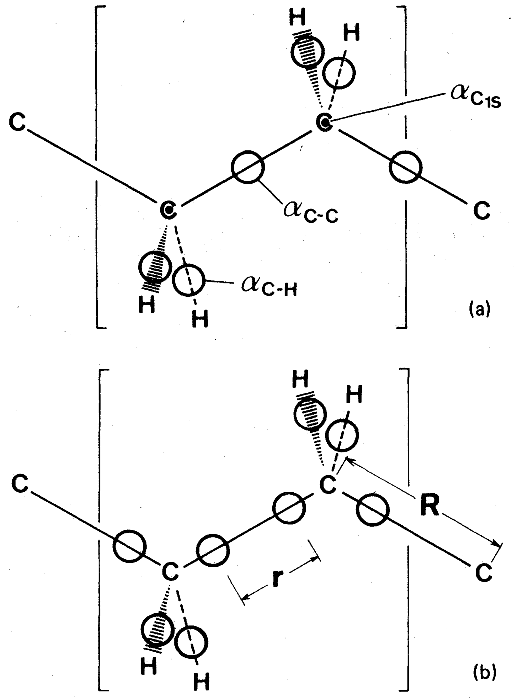

FIG. 1. Comparison of the FSGO basis sets decribing polyethylene. (a) Frost's basis set, (b) Christoffersen's basis set ($r/R=0.5$).

in interpreting this peculiar effect. In the case of the FSGO basis the C–C 1*s* Gaussian functions in each cell are located at the middle of the C–C bonds so that the resultant center of electron charges does not coincide with the center of nuclear charge, destroying (since the summation is made over cells' indices) the electrostatic interactions' balance which is only restored after including many neighbors. This is easily verified by considering a basis set of comparable quality but which remedies to the lack of symmetry in the unit cell, as is the case with the molecular fragment displayed in Fig. 1(b). Of course, this long-range type of effect is artificial, but nevertheless it can be faced in applications using bases which do not lead, *within the unit cell*, to a matching of the positive and negative centers of charges. The poor convergence of the LiH FSGO total energies has a similar origin: The basis is so limited that functions have to be located on bonds to obtain an energy minimum, and this induces an excess of polarity. Now, as pointed out by Harris,[3] a different description of the charge distribution along the chain can be made so as to decrease the number of terms to stabilize the energy. This is very system dependent, however, and less straightforward to implement into general programs designed for routine works. A cheap alternative is the use of the multipole expansion[19] or of any other technique[13] for handling lattice sums in closed forms.

From these two methodological examples we hope some light has been shed onto the so-called long-range problem. Its manifestations through corrections will depend upon the way the summations of terms have been carried out (cellwise as in most programs or atomwise[16]), on the choice of the repeating pattern,[31] and on the basis set used. In any case, it is sensible, in routine calculations, to include the long-range corrections in a systematic way since they will prevent, at low cost, the user either from considering more terms than actually needed in the expensive part of the calculations or simply from making serious mistakes.

IV. SYNOPSIS

At the beginning of this work we tried to demonstrate the importance quantum calculations on polymers will have in view of modern developments in polymer synthesis and in spectroscopic techniques. To perform reliable calculations there are points that should be solved first: influence of basis sets on the quality of the results and the size of the linear cluster required to reproduce accurately the properties of the infinite model. In the course of reviewing the LCAO-SCF-CO equations we have pointed out how to work actually on an infinite chain by recognizing the Coulombic nature of the interactions beyond a given number of neighbors. The bipolar expansion technique, familiar to chemists, was analyzed in the polymer context and shown to be a good candidate for summing to infinity these electrostatic interactions, thus making more attainable calculations on compounds of interest. A table of expressions, ready for programming, was also supplied. In the last part we specialized to floating spherical functions and discussed two manifestations of long-range effects. In the case of the infinite lithium hydride chain we pointed out the danger of extrapolating values from cluster-type results while for polyethylene, a nonpolar system, a type of long-range behavior was identified and interpreted. In all of the cases, the multipole expansion proved to be successful; it has also the definite advantage of being cheap to use and straightforward to implement. A more general conclusion would be that if an infinite and isolated chain of repeating structures is a good model for stereoregular polymers, it is also important for the sake of consistency to respect the definition and achieve calculations accordingly. Under this condition ground-state properties of polymers will be computed safely, and a broad spectrum of fundamental investigations will be opened to the quantum chemistry of polymers. Moreover, considering the importance Coulomb interactions have in those chains, one should estimate the effects of three-dimensional long-rangeness and try to elaborate methods which will take into account the specific nature of polymers as opposed to three-dimensional materials. This work is now in progress in our group.

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APPENDIX: DEDUCTION OF $U_{pq}^{j(3,1)}$

In Table I we have listed working formulas expressed in Cartesian coordinates to evaluate the interaction terms $U_{pq}^{j(k,l)}$. For the sake of illustration and to help the reader become familiar with the method, we provide hereafter a detailed deduction of a simple but nontrivial term: $U_{pq}^{j(3,1)}$. First we reorganize the original equation (19) into a form which leads to the $U_{pq}^{j(k,l)}$ terms directly as they are displayed in Table I:

$$U_{pq}^{j(k,l)}=A_{k,l}^{0}M_{pq}^{j(l,0)}M^{(k,0)}+2\sum_{m=1}^{s}A_{k,l}^{|m|}[\mathrm{Re}(M_{pq}^{j(l,m)})\,\mathrm{Re}(M^{(k,m)})+\mathrm{Im}(M_{pq}^{j(l,m)})\,\mathrm{Im}(M^{(k,m)})]\,. \tag{A1}$$

The relationships $M_{pq}^{j(l,m)*}=M_{pq}^{j(l,-m)}$ and $M^{(k,m)*}=M^{(k,-m)}$ enable us to write

$$\begin{aligned}U_{pq}^{j(k,l)}&=B_{k,l}^{0}M_{pq}^{j(l,0)}[x,y,z]M^{(k,0)}[x,y,z]\\&\quad+2\sum_{m=1}^{s}B_{k,l}^{|m|}\{M_{pq}^{j(l,m)}[x,y,z]M^{(k,m)}[x,y,z]+M_{pq}^{j(l,-m)}[x,y,z]\,M^{(k,-m)}[x,y,z]\}\end{aligned} \tag{A2}$$

when

$$\begin{aligned}M_{pq}^{j(l,m)}[x,y,z]&\equiv\mathrm{Re}(M_{pq}^{j(l,m)})=\langle\chi_p|r^lP_l^{|m|}(\cos\theta)\cos(m\phi)|\chi_q^j\rangle\,,\\M_{pq}^{j(l,-m)}[x,y,z]&\equiv\mathrm{Im}(M_{pq}^{j(l,m)})=\langle\chi_p|r^l P_l^{|m|}(\cos\theta)\sin(m\phi)|\chi_q^j\rangle\,,\\M^{(k,m)}[x,y,z]&\equiv\mathrm{Re}(M^{(k,m)})=-\sum_u Z_u r_u^k P_k^{|m|}(\cos\theta_u)\cos m\phi_u+2\sum_{l=-N}^{+N}\sum_r\sum_s D_{rs}^l\langle\chi_r|r^k P_k^{|m|}(\cos\theta)\cos m\phi|\chi_s^j\rangle\,,\\M^{(k,-m)}[x,y,z]&\equiv\mathrm{Im}(M^{(k,m)})=-\sum_u Z_u r_u^k P_k^{|m|}(\cos\theta_u)\sin m\phi_u+2\sum_{l=-N}^{+N}\sum_r\sum_s D_{rs}^l\langle\chi_r|r^k P_k^{|m|}(\cos\theta)\sin m\phi|\chi_s^j\rangle\,.\end{aligned} \tag{A3}$$

With this preliminary let us now turn to the particular example we have selected, $U_{pq}^{j(3,1)}$. In this case we have $s(k,l)=s(3,1)=1$, $A_{3,1}^{0}=-(4!2)/(3!1!)=-8$, $A_{3,1}^{1}=A_{3,1}^{-1}=(4!2)/(4!2!)=1$, and

$$M_{pq}^{j(1,0)}=\langle\chi_p|rP_1(\cos\theta)|\chi_q^j\rangle=\langle\chi_p|r\cos\theta|\chi_q^j\rangle\equiv M_{pq}^{j(1,0)}[z]\,,$$

$$\mathrm{Re}(M_{pq}^{j(1,1)})=\langle\chi_p|rP_1^1(\cos\theta)\cos\phi|\chi_q^j\rangle=\langle\chi_p|x|\chi_q^j\rangle\equiv M_{pq}^{j(1,1)}[x]\,,$$

$$\mathrm{Im}(M_{pq}^{j(1,1)})=\langle\chi_p|rP_1^1(\cos\theta)\sin\phi|\chi_q^j\rangle=\langle\chi_p|y|\chi_q^j\rangle\equiv M_{pq}^{j(1,-1)}[y]\,,$$

$$\begin{aligned}M^{(3,0)}&=-\sum_u Z_u r_u^3 P_3(\cos\theta_u)+2\sum_l\sum_r\sum_s D_{rs}^l\langle\chi_r|r^3P_3(\cos\theta)|\chi_s^l\rangle\\&=-\sum_u Z_u\frac{r_u^3}{2}(5\cos^3\theta_u-3\cos\theta_u)+2\sum_l\sum_r\sum_s D_{rs}^l\left\langle\chi_r\left|\frac{r^3}{2}(5\cos^3\theta-3\cos\theta)\right|\chi_s^l\right\rangle\\&=\frac{1}{2}\left(-\sum_u Z_u(5z_u^3-3z_ur_u^2)+2\sum_l\sum_r\sum_s D_{rs}^l\langle\chi_r|(5z^3-3zr^2)|\chi_s^l\rangle\right)\equiv\tfrac{1}{2}M^{(3,0)}[5z^3-3zr^2]\,,\end{aligned}$$

$$\begin{aligned}\mathrm{Re}(M^{(3,1)}) &= -\sum_u Z_u r_u^3 P_3^1(\cos\theta_u)\cos\phi_u + 2\sum_l\sum_r\sum_s D_{rs}^l \langle \chi_r | r^3 P_3^1(\cos\theta)\cos\phi | \chi_s^l\rangle \\ &= -\sum_u Z_u \frac{3r_u^3}{2}\sin\theta_u(5\cos^2\theta_u - 1)\cos\phi_u + 2\sum_l\sum_r\sum_s D_{rs}^l\langle\chi_r|\tfrac{3}{2}r^3\sin\theta(5\cos^2\theta - 1)\cos\phi|\chi_s^l\rangle \\ &= \frac{3}{2}\left(-\sum_u Z_u(5z_u^2x_u - x_u r_u^2) + 2\sum_l\sum_r\sum_s D_{rs}^l\langle\chi_r|(5z^2x - xr^2)|\chi_s^l\rangle\right) \equiv \tfrac{3}{2}M^{(3,1)}[5z^2x - xr^2],\end{aligned}$$

$$\mathrm{Im}(M^{(3,+1)}) \equiv \tfrac{3}{2}M^{(3,-1)}[5z^2y - yr^2].$$

The final expression will then be

$$U_{pq}^{j(3,1)} = -8M_{pq}^{j(1,0)}[z]\tfrac{1}{2}M^{(3,0)}[5z^3 - 3zr^2] + 2M_{pq}^{j(1,1)}[x]\tfrac{3}{2}M^{(3,1)}[5z^2x - xr^2] + 2M_{pq}^{j(1,-1)}[y]\tfrac{3}{2}M^{(3,-1)}[5z^2y - yr^2]. \quad (A4)$$

If we drop the m index for the components of the electric moments and proceed further in simplifying the expression (A4) we find the form given in Table I, i.e.,

$$U_{pq}^{j(3,1)} = 4M_{pq}^{j(1)}[z]M^{(3)}[3zr^2 - 5z^3] + 3M_{pq}^{j(1)}[x]M^{(3)}[5z^2r - xr^2] + 3M_{pq}^{j(1)}[y]M^{(3)}[5z^2y - yr^2]. \quad (A5)$$

In the case of Gaussian lobe functions (χ_p and χ_q^j), the effort for obtaining $U_{pq}^{j(k,l)}$ will just amount to introducing the indicated powers of r_u, x_u, y_u, z_u for nuclei and $|\vec{G}_{pq}^j|, X_{pq}, Y_{pq}, Z_{pq}^j$ for orbitals according to the expression given between brackets (as demonstrated in Sec. III of the work). Note also that $M_{pq}^{j(0)}$ is identically S_{pq}^j, the traditional overlap integral.

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