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Treatment of Coulomb interactions in Hartree-Fock calculations of periodic systems

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A computational scheme for the treatment of Coulomb sums in the Hartree-Fock approach to periodic systems in one, two, and three dimensions is presented. The philosophy is as follows: (a) The interaction of two charge distributions contributing to the total charge in cells $\vec{0}$ and $\vec{m}$ is treated exactly at short range; (b) when the reciprocal penetration of the distributions is sufficiently small, the charge distribution at $\vec{m}$ is partitioned into "shell-charge distributions" which are then expanded in a multipole series; (c) for $|\vec{m}|$ larger than a given threshold, a Madelung sum of atomic charges is performed. Results are reported for the SN_x polymer, the graphite, boron nitride, and beryllium monolayers, for the beryllium monolayer with hydrogen chemisorbed thereon, and for three-dimensional silicon, with a view to compare two charge-partitioning schemes, and the convergence of the results with respect to the order of the multipole expansions. It is shown that the inclusion of all terms to hexadecapole confines the error in the Coulomb contribution to the total energy for all the systems considered to within 0.001 a.u./atom, with the exactly treated zone reduced to a few neighbors, and that at this level the results are essentially independent of the particular charge-partitioning scheme adopted.

I. INTRODUCTION

In linear combination of atomic orbitals (LCAO) Hartree-Fock studies of periodic systems, infinite sums of Coulomb and exchange integrals must be evaluated both for the construction of the Fock matrix and for the calculation of the total energy. With few, though interesting exceptions,[1,2] exact formulas are not available for calculating these infinite summations, which run over several indices and depend in a complicated way on the crystal structure of the system and on the type and location of the basis functions. Approximate procedures are therefore adopted, based usually on the following two-step analysis: (a) The series is first rearranged by grouping together subsets that can be accurately summed, the purpose of which is to improve the convergence properties of the rearranged series, whose summation index corresponds as a rule to the direct-lattice vectors $\vec{m}$, ordered according to their length; (b) in the summation of the new series, a decreasing level of accuracy is adopted with increasing distance from a given reference cell.

Extreme care must be used in this procedure because convergence usually depends on a delicate balance of terms of opposite sign. Also connection problems may arise when passing from a zone of given accuracy to the next less precise one. Much ingenuity has been spent on devising effective ways to implement the above general scheme; the quality of a computer program and possibly its very structure depend critically on the kind of summation criteria adopted.

The problem of the exchange terms is a relatively minor one. The short-range character of exchange forces leads to a very rapid convergence if the series is appropriately rearranged.[3-5] Here we only consider the more difficult problem of accelerating the convergence of the Coulomb series. The importance of long-range Coulomb effects in Hartree-Fock calculations of infinite polymers has been discussed by Delhalle *et al.*[5] Similar problems have shown up in a study of beryllium films,[6] where a reliable estimate of the total energy required very large numbers of two-electron Coulomb integrals to be taken into account, while the wave function was affected to a lesser extent. It is the primary purpose of the present work to show how the use of multipole series expansions carried out to sufficiently high order may be used to reduce the computational burden to manageable proportions. Indeed the use of an exact summation formula specially designed for multipole expansions within one-dimensional periodic systems makes the procedure of Delhalle *et al.*[5] very effective in this context. The fact that it appears impossible to generalize such formulas to two- and three-dimensional structures is not the only, or even the main, reason why the Delhalle *et al.*[5] procedure is not applicable in these cases. A given radius that fixes the range where whole cells must be treated exactly can correspond to quite feasible computations with a simple polymer, while leading to explosively high numbers of integrals with a thin film or a three-dimensional crystal. More subtle criteria are therefore needed than those based on crystal-cell units. The present work has been carried out using the philosophy adopted in the CRYSTAL program that has been used for the beryllium slab calculations[6] and a number of other Hartree-Fock studies,[3,4,7] where the electronic charge is partitioned among atomic shells; the Coulomb interaction

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between the charge distribution of a given shell and a charge distribution associated with the reference cell was treated exactly if the degree of penetration of the two distributions is sufficiently high, or else evaluated using a multipole expansion of the shell about the corresponding nuclear position. This procedure satisfies the charge conservation conditions discussed by a number of authors.[5,8,9]

The present work may be regarded as an advance over that in Ref. 3 on two counts.

(a) The criteria for an exact partition of the electronic charge into partial contributions are discussed, with emphasis on the degrees of freedom in this essentially arbitrary process. It is demonstrated that the results obtained with two partitioning schemes are in very close agreement.

(b) The evaluation of multipolar expansions truncated at relatively high order (up to $l=6$) is discussed, then to be compared with calculations carried out at the dipole level ($l=1$) hitherto. The practical usefulness of such high-order expansions is related to an efficient technique for the evaluation of multipole and field integrals involving products of Gaussian-type functions (GTF's) to be described.

Results will be presented for the $(SN)_x$ polymer, boron nitride, graphite, and beryllium monolayers, for a hydrogen monolayer chemisorbed on a beryllium monolayer, and for silicon. We present these results to test the efficiency of different charge-partitioning schemes and of the truncation criteria, and to assess the importance of higher than dipole terms in the multipole expansions.

As a by-product of the much enhanced precision obtainable in the present work we have arrived at an explanation for the puzzling fact that the wave function appeared to be more stable than the total energy in previous work,[6] together with a suggestion for improvement of the energy expression. The results indicate that a solution of the Coulomb problem in the Hartree-Fock treatment of periodic systems is well within reach.

II. EVALUATION OF COULOMB INTERACTIONS

Infinite summations of Coulomb terms appear within two contexts in an LCAO Hartree-Fock program for periodic systems. First, when evaluating the electrostatic contribution to the elements of the Fock matrix,

$$(F_{jj'}^{\vec{g}})_{\rm Coul}=\int \rho_{jj'}^{\vec{0}\,\vec{g}}(\vec{r}\,')d\vec{r}\,' \int \rho(\vec{r})\,|r-r'|^{-1}d\vec{r}\ , \tag{1a}$$

$$\rho_{jj'}^{\vec{g},\,\vec{g}\,'}(\vec{r})=\chi_j^{\vec{g}}(\vec{r})\chi_{j'}^{\vec{g}\,'}(\vec{r})\ , \tag{1b}$$

and second, when estimating the Coulomb contribution to the total energy per cell,

$$E_{\rm Coul}=\frac{1}{2N}\int \rho(\vec{r}\,')d\vec{r}\,' \int_{\vec{r}\neq\vec{r}\,'} \rho(\vec{r})\,|\vec{r}-\vec{r}\,'|^{-1}d\vec{r}\ , \tag{2}$$

where $\rho(\vec{r})$ denotes the total charge density of the system, the condition $\vec{r}\neq\vec{r}\,'$ in Eq. (2) prevents the self-interaction of nuclear charges, and N denotes the number of cells taken into account (the limit $N\rightarrow\infty$ should be taken). To simplify notation, real atomic orbitals are assumed in Eq. (1b) and henceforth. The total charge density is composed of the following electronic and nucleic contributions:

$$\rho_{\rm nuc}(\vec{r})=\sum_{\vec{h}}\rho_{\rm nuc}^{\vec{h}}(\vec{r})\ , \tag{3a}$$

$$\rho_{\rm nuc}^{\vec{h}}(\vec{r})=\sum_A \rho_A^{\vec{h}}(\vec{r})=-\sum_A z_A\delta(\vec{r}-\vec{h}-\vec{f}_A)\ , \tag{3b}$$

and

$$\rho_{\rm elec}(\vec{r})=\sum_{j,\vec{g};j',\vec{g}\,'} P_{jj'}^{\vec{g}\,'-\vec{g}}\rho_{jj'}^{\vec{g},\,\vec{g}\,'}(\vec{r})\ , \tag{4}$$

where the symbols adopted here are as in previous work.[3] We now wish to rearrange the series implied by Eq. (4) so as to make it possible to write

$$\rho_{\rm elec}(\vec{r})=\sum_{\vec{h}}\rho_{\rm elec}^{\vec{h}}(\vec{r})\ , \tag{5a}$$

$$\rho_{\rm elec}^{\vec{h}}=\sum_V \rho_V^{\vec{h}}(\vec{r})\ , \tag{5b}$$

where $\rho_V^{\vec{h}}(\vec{r})$ denotes a contribution to the electronic charge of the cell identified by translation vector $\vec{h},\rho_{\rm elec}^{\vec{h}}(\vec{r})$, while the index V symbolizes, for example, all the atomic orbitals (AO's) belonging to an atom within the cell, or to a shell of AO's, or even perhaps a single AO. To achieve our purpose, each of the terms on the right-hand side (rhs) of Eq. (4) is partitioned among the $\rho_V^{\vec{h}}(\vec{r})$ distributions. The criteria for the choice of the corresponding fractional weights, $\alpha(j,j',\vec{g},\vec{g}\,';V,\vec{h})$, are to some extent arbitrary, but the conditions of charge conservation,

$$\sum_{V,\vec{h}}\alpha(j,j',\vec{g},\vec{g}\,';V,\vec{h})=1\ , \tag{6}$$

and translational invariance,

$$\alpha(j,j',\vec{g},\vec{g}\,';V,\vec{h})=\alpha(j,j',\vec{0},\vec{g}\,'-\vec{g};V,\vec{h}-\vec{g})\ , \tag{7}$$

must be satisfied. It is also reasonable, if not absolutely essential, to require that a component of the charge distribution and its transpose be partitioned identically,

$$\alpha(j,j',\vec{g},\vec{g}\,';V,\vec{h})=\alpha(j',j,\vec{g}\,',\vec{g};V,\vec{h})\ . \tag{8}$$

For the moment, to keep notation simple, we let V denote a single AO, but ultimately it will denote an atomic shell. One of the most simple partitionings is to have all the fractional weights zero except when $V,\vec{h}$ is equal to $j,\vec{g}$ or $j',\vec{g}\,'$. We then have, using Eq. (4),

$$\rho_t^{\vec{h}}(\vec{r})=\sum_{t',\vec{h}\,'}\widetilde{P}_{tt'}^{\vec{h}\,'-\vec{h}}\rho_{tt'}^{\vec{h}\,\vec{h}\,'}(\vec{r}) \tag{9a}$$

$$\widetilde{P}_{tt'}^{\vec{h}\,'-\vec{h}}=2\alpha_{tt'}^{\vec{h}\,'-\vec{h}}P_{tt'}^{\vec{h}\,'-\vec{h}}\ , \tag{9b}$$

$$\alpha_{tt'}^{\vec{h}\,'-\vec{h}}=\alpha(t,t',\vec{0},\vec{h}\,'-\vec{h};t,\vec{0})\ . \tag{9c}$$

Equation (9) should be interpreted according to the convention that $\alpha_{tt}^{\vec{0}}=\frac{1}{2}$, rather than Eq. (6).

In a practical application, it is necessary to truncate the summations over t' and $\vec{h}\,'$ in Eq. (9a), and our procedure is as follows: We associate with each AO, $\chi_t^{\vec{h}}(\vec{r})$, an adjoined 1$s$-type Gaussian,[10] $g_t^{\vec{h}}(\vec{r})$, in such a way that the orbital exponent of the adjoin a_t measures the size of the corresponding AO. If the overlap integral between $g_t^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})$ and $g_{t'}^{\vec{\mathrm{h}}\,'}(\vec{\mathrm{r}})$ is less than a preset threshold t_1 the corresponding term in Eq. (9a) is discarded, thus reducing the summation to a finite number of terms. A Mulliken partition of the charge may be used, when $\alpha_{tt'}^{\vec{\mathrm{n}}}=\alpha_{tt'}^{\vec{0}}=\frac{1}{2}$, so that $\widetilde{P}_{tt'}^{\vec{\mathrm{n}}}=P_{tt'}^{\vec{\mathrm{n}}}$. A "weighted" Mulliken partition may be adopted instead. In the present work we have made use of the adjoined Gaussians to define such a weighted partition according to the formula

$$\alpha_{tt'}^{\vec{\mathrm{n}}}=\alpha_{tt'}^{\vec{0}}=a_t/(a_t+a_{t'}) \;, \tag{10}$$

which again guarantees charge conservation, Eq. (6), while correctly attributing a larger fraction of the overlap charge to the more localized AO. As partial justification for this weighted partition, consider the following. The product of the two adjoined Gaussians associated with a given overlap distribution may be considered to be a rough approximation to the overlap distribution itself. If we now replace the adjoined overlap distribution by two point monopoles located at the centroids of $\chi_t^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})$ and $\chi_{t'}^{h'}(\vec{\mathrm{r}})$ with charges $S_{tt'}^{\vec{\mathrm{h}}\,'}\alpha_{tt'}^{\vec{0}}$ and $S_{tt'}^{\vec{\mathrm{h}}\,'-\vec{\mathrm{h}}}\alpha_{t't}^{\vec{0}}$, respectively, where $S_{tt'}^{\vec{\mathrm{h}}\,'-\vec{\mathrm{h}}}$ denotes the overlap integral between the AO's, then it can be shown that the charge of the overlap distribution and the *dipole centroid* of the adjoined overlap distribution are conserved. The simple and weighted Mulliken partitions will be used in the present work; however, these are not the only possibilities, nor even perhaps the most sensible ones.

The expression for the Coulomb contribution to the Fock matrix elements, Eq. (1), may now be rewritten as

$$(F_{jj'}^{\vec{\mathrm{g}}})_{\mathrm{Coul}}=\int\rho_{jj'}^{\vec{0},\vec{\mathrm{g}}}(\vec{\mathrm{r}}\,')d\vec{\mathrm{r}}\,'\int\sum_{\vec{\mathrm{h}}}\left[\sum_{A}\rho_A^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})+\sum_{t}\rho_t^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})\right] \times|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\vec{\mathrm{r}} \tag{11}$$

The Coulomb contribution to the total energy per cell, Eq. (2), may now be written as half the energy of interaction of the total charge of the system with the reference-cell distribution. We have

$$E_{\mathrm{Coul}}=\tfrac{1}{2}(E_{NN}+E_{NE}+E_{EN}+E_{EE}) \;, \tag{12a}$$

$$E_{NN}=\int\rho_{\mathrm{nuc}}^{\vec{0}}(\vec{\mathrm{r}}\,')d\vec{\mathrm{r}}\,'\int_{\vec{\mathrm{r}}\neq\vec{\mathrm{r}}\,'}\sum_{\vec{\mathrm{h}}}\rho_{\mathrm{nuc}}^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\vec{\mathrm{r}} \;, \tag{12b}$$

$$E_{NE}=\int\rho_{\mathrm{nuc}}^{\vec{0}}(\vec{\mathrm{r}}\,')d\vec{\mathrm{r}}\,'\int\sum_{\vec{\mathrm{h}}}\rho_{\mathrm{elec}}^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\vec{\mathrm{r}} \;, \tag{12c}$$

$$E_{EN}=\int\rho_{\mathrm{elec}}^{\vec{0}}(\vec{\mathrm{r}}\,')d\vec{\mathrm{r}}\,'\int\sum_{\vec{\mathrm{h}}}\rho_{\mathrm{nuc}}^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\vec{\mathrm{r}} \;, \tag{12d}$$

$$E_{EE}=\int\rho_{\mathrm{elec}}^{\vec{0}}(\vec{\mathrm{r}}\,')d\vec{\mathrm{r}}\,'\int\sum_{\vec{\mathrm{h}}}\rho_{\mathrm{elec}}^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\vec{\mathrm{r}} \;. \tag{12e}$$

By noting the definition of the partitioned electronic charges, Eq. (9), and of the Fock matrix elements, Eq. (11), we may rewrite Eq. (12) as

$$E_{\mathrm{Coul}}=\tfrac{1}{2}\left[E_{NN}+E_{NE}+\sum_{j,j',\vec{\mathrm{g}}}F_{jj'}^{\vec{\mathrm{g}}}\widetilde{P}_{jj'}^{\vec{\mathrm{g}}}\right] . \tag{13}$$

It is easy to show that

$$E_{NE}=E_{EN} \;, \tag{14}$$

although this may not be true after approximations are introduced. The energy may thus also be written in the form

$$E'_{\mathrm{Coul}}=\tfrac{1}{2}\left[E_{NN}+E_{EN}+\sum_{j,j',\vec{\mathrm{g}}}F_{jj'}^{\vec{\mathrm{g}}}\widetilde{P}_{jj'}^{\vec{\mathrm{g}}}\right] . \tag{15}$$

We stress here that while E'_{Coul} is formally equal to E_{Coul}, the equality may not hold after approximation. In the present work, as previously,[3] we have evaluated E'_{Coul}, because computationally this is slightly simpler. However, it turns out that it would be preferable to evaluate E_{Coul}, which is more stable to the effects of approximation, and this provides the explanation for the hitherto puzzling observation[6] that the energy, evaluated as E'_{Coul}, is less stable than the wave function against approximation. We shall return to this point after a discussion of our approximations.

The first approximation is effected by defining a "Madelung zone." If $\rho^{\vec{\mathrm{h}}}(r)$ is such that $|\vec{\mathrm{h}}|>M$, where M is a preset Madelung radius, it is assigned to the Madelung zone. A typical Coulomb contribution to the total energy is of the form

$$\int\rho_Y^{\vec{0}}(\vec{\mathrm{r}}\,')d\vec{\mathrm{r}}\,'\int\rho_X^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\vec{\mathrm{r}} \;,$$

where X and Y may denote either nucleic or electronic charge. If $\rho_X^{\vec{\mathrm{h}}}$ belongs to the Madelung zone, we make a bicentric expansion of the interaction operator, with origins located at the centroids of $\rho_X^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})$ and $\rho_Y^{\vec{0}}(\vec{\mathrm{r}}\,')$ for $\vec{\mathrm{r}}$ and $\vec{\mathrm{r}}\,'$, respectively.[11] The expansion is terminated at the $l=0$ term, and it is assumed that the Madelung radius is sufficiently large that the charge distributions are nonpenetrating. Clearly the partitioning criteria adopted for the electronic charge has some bearing on the accuracy of this approach. The lattice summations over the Madelung zone are performed by the Ewald method.[12] The Madelung contributions to the Fock operator are neglected entirely in the present work, as previously.[3] This approximation can be defined only if the Madelung radius is sufficiently large that the potential generated by the Madelung cells is constant within the reference cell, and this requirement presents no real difficulty in the case of one- and two-dimensional systems. However, in three-dimensional systems, the practical difficulties associated with a large Madelung radius are such that we now believe that it would be wise to incorporate the effects of the Madelung potential into the Fock operator. Work in this direction is now in progress, which it is hoped will greatly increase the accuracy of the method for three-dimensional ionic crystals, but meanwhile we refrain from a consideration of such systems.

Consider now the contributions of $\rho^{\vec{\mathrm{h}}}(\vec{\mathrm{r}})$ when $|\vec{\mathrm{h}}|<M$, that is, where the cells belong to the "quantum

zone." The quantum-zone contribution to the nuclear repulsion energy $\frac{1}{2}E_{NN}$ is easily evaluated without approximation. The quantum-zone contribution of the nucleic charges to the Fock operator,

$$H_{jj'}^{\vec{g}}=\sum_{|\vec{h}|<M}\sum_{A}\int\rho_{jj'}^{\vec{0}\,\vec{g}}(\vec{r}\,')d\vec{r}\,'\int\rho_{A}^{\vec{h}}(\vec{r})\,|\vec{r}-\vec{r}\,'|^{-1}d\vec{r}\,, \tag{16}$$

can also be evaluated without approximation. This also permits the exact evaluation of the quantum-zone contribution to the term E_{EN} which appears in E'_{Coul}, Eq. (15). Thus after combining Eqs. (9a), (12d), and (16), we find

$$E_{EN}=\sum_{j,j',\vec{g}}\tilde{P}_{jj'}^{\vec{g}}H_{jj'}^{\vec{g}}\,. \tag{17}$$

The Fock operator also requires the evaluation of terms such as

$$G(j,j',\vec{g};t,\vec{h})=\int\rho_{jj'}^{\vec{0}\,\vec{g}}(\vec{r}\,')d\vec{r}\,'\int\rho_{t}^{\vec{h}}(\vec{r})\,|\vec{r}-\vec{r}\,'|^{-1}d\vec{r}\,, \tag{18}$$

where $|\vec{h}|<M$. These are evaluated by one of two methods, according to the "degree of penetration" of $\rho_{jj'}^{\vec{0}\,\vec{g}}$ and $\rho_{t}^{\vec{h}}$ where the measure of the degree of penetration used in the present work is the same as that of Ref. 3. If the degree of penetration is greater than a preset threshold t_2, the integral, Eq. (18), is evaluated exactly as a linear combination of two-electron repulsion integrals. Thus using Eq. (9a), we find

$$G(j,j',\vec{g};t,\vec{h})=\sum_{t',\vec{h}\,'}\tilde{P}_{tt'}^{\vec{h}\,'-\vec{h}}(j,\vec{0};j',\vec{g}\,|\,t,\vec{h};t',h') \tag{19}$$

and we shall say that the density $\rho_{t}^{\vec{h}}$ is within the "bielectronic zone" with respect to $\rho_{jj'}^{\vec{0}\,\vec{g}}$.

However, if the degree of penetration of the two charge distributions is less than the given threshold, then Eq. (18) is evaluated by a multipole expansion of $\rho_{t}^{\vec{h}}(\vec{r})$ truncated at some given L value, and $\rho_{t}^{\vec{h}}(\vec{r})$ is said to belong to the "monoelectronic zone" with respect to $\rho_{jj'}^{\vec{0}\,\vec{g}}$. Thus let us indicate by $\rho_{t}^{\vec{h}L}(\vec{r})$ a multipole expansion of $\rho_{t}^{\vec{h}}(\vec{r})$ truncated at the Lth order. It is expedient and natural to make the origin of the expansion $\vec{h}+\vec{f}_t$, where the fractional vector identifies the centroid of $\chi_{t}^{\vec{0}}(\vec{r})$. We define un-normalized complex solid harmonics by means of

$$Y_{l}^{m}(\vec{C};\vec{r})=r_{C}^{l}P_{l}^{|m|}(\cos\theta)e^{im\phi}\,, \tag{20}$$

where θ and ϕ denote the angular coordinates of a spherical-polar system whose origin is $\vec{C}$ and where $\vec{r}_C=|\vec{r}-\vec{C}|$. Un-normalized real solid harmonics may be defined through

$$X_{l}^{m}(\vec{C};\vec{r})=[Y_{l}^{|m|}(\vec{C};\vec{r})+(\operatorname{sgn}m)Y_{l}^{-|m|}(\vec{C};\vec{r})]/(4\operatorname{sgn}m)^{1/2}\,. \tag{21}$$

The potential created at a point $\vec{r}\,'$, external to the distribution, $\rho_{t}^{\vec{h}}$, is given by

$$V_{t}^{\vec{h}L}(\vec{r}\,')=\sum_{l,m}^{L}\gamma_{lt}^{m}\Phi_{l}^{m}(\vec{h}+\vec{f}_t;\vec{r}\,')\,, \tag{22a}$$

$$\gamma_{lt}^{m}=\int X_{l}^{m}(\vec{f}_t;\vec{r})\rho_{t}^{\vec{0}}(\vec{r})d\vec{r}\,, \tag{22b}$$

$$\Phi_{l}^{m}(\vec{C};\vec{r})=N_{l}^{m}\Gamma_{l}^{m}(\vec{C};\vec{r})\,, \tag{22c}$$

$$\Gamma_{l}^{m}(C;r)=X_{l}^{m}(C;r)/r_{C}^{2l+1}\,, \tag{22d}$$

$$N_{l}^{m}=(2-\delta_{m0})[(l-m)!]/(l+m)!\,. \tag{22e}$$

Here, and in the following,

$$\sum_{l,m}^{L}$$

denotes the double summation

$$\sum_{l=0}^{L}\sum_{m=-l}^{l}\,.$$

Thus a monoelectronic-zone contribution to Eq. (18) is of the form

$$G(j,j',\vec{g};t,\vec{h})=\sum_{l,m}^{L}\gamma_{lt}^{m}\int\rho_{jj'}^{\vec{0}\,\vec{g}}(\vec{r}\,')\Phi_{l}^{m}(\vec{h}+\vec{f}_t;\vec{r}\,')d\vec{r}\,'\,. \tag{23}$$

It may be wondered why a bicentric expansion of the interaction operator is not used to evaluate the monoelectronic-zone contribution to the Fock operator. The reason is that the charge partitions are actually allocated to atomic shells rather than individual atomic orbitals in the present work. The resultant shell-charge distributions are normally reasonably close to spherical symmetry. However the density $\rho_{jj'}^{\vec{0}\,\vec{g}}$ in Eq. (23) is often far from spherically symmetric, and the use of the monocentric expansion of the interaction operator allows account to be taken of all the multipole moments of this density. The criteria for assigning orbitals to the monoelectronic or bielectronic zone is then a function only of the shell to which the orbital belongs, and similar remarks apply also to the weighted partitioning criterion, Eq. (10), as well as to the truncation procedure associated with the summations over t' and $\vec{h}\,'$ in Eq. (9a). It may be useful to summarize our formula for the Coulomb contribution to the Fock matrix elements, after the various summations are organized by shells, the latter being denoted by T. We write

$$(F_{jj'}^{\vec{g}})_{\text{Coul}}=H_{jj'}^{\vec{g}}+\sum_{T}\left[\sum_{\vec{h}}^{\text{bi}}\sum_{t\in T}\sum_{t'\vec{h}\,'}\tilde{P}_{tt'}^{\vec{h}\,'-\vec{h}}(j,\vec{0};j',\vec{g}\,|\,t,\vec{h};t',\vec{h}\,')+\sum_{\vec{h}}^{\text{mono}}\sum_{l,m}^{L}\gamma_{lT}^{m}\int\rho_{jj'}^{\vec{0}\,\vec{g}}(\vec{r}\,')\Phi_{l}^{m}(\vec{h}+\vec{f}_T;\vec{r}\,')d\vec{r}\,'\right], \tag{24a}$$

$$\gamma_{lT}^{m}=\sum_{t\in T}\gamma_{lt}^{m}\,. \tag{24b}$$

It is convenient to rearrange the summations over the bielectronic zone as follows (let $\vec{k}=\vec{h}'-\vec{h}$):

$$\sum_{T}\sum_{\vec{h}}^{\text{bi}}\sum_{t\in T}\sum_{t',\vec{h}'}\tilde{P}_{tt'}^{\vec{h}'-\vec{h}}(j,\vec{0};j',\vec{g}\,|\,t,\vec{h};t',\vec{h}')=\sum_{T}\sum_{t\in T}\sum_{t',\vec{k}}\tilde{P}_{tt'}^{\vec{k}}\sum_{\vec{h}}^{\text{bi}}(j,\vec{0};j',\vec{g}\,|\,t,\vec{h};t',\vec{h}+\vec{k})\ . \tag{25}$$

In this way the summation over $\vec{h}$ may be performed prior to commencing the Hartree-Fock iterations, with a considerable saving in both computer time and backing store. For similar reasons the field integrals are summed over the $\vec{h}$ vectors of the monoelectronic zone for use in Eq. (24a),

$$M(j,j',\vec{g};T)=\sum_{\vec{h}}^{\text{mono}}\int\rho_{jj'}^{\vec{0},\vec{g}}(\vec{r}\,')\Phi_l^m(\vec{h}+\vec{f}_T;\vec{r}\,')d\vec{r}\,'\ . \tag{26}$$

It is now appropriate to discuss the differences between E_{Coul} and E'_{Coul}, Eqs. (13) and (15), respectively. The difficulty with E'_{Coul} is that the interaction of electrons associated with the reference cell and those belonging to the monoelectronic zone is evaluated approximately through a multipolar expansion of the monoelectronic-zone shell charges. However, no such approximation is made when one considers the interaction of the nuclei of the reference cell with the electrons of the more remote cells, because this term is evaluated exactly, using Eq. (14) to convert E_{NE} to E_{EN}. It is our opinion that a direct but approximate evaluation of E_{NE}, involving first a classification of the shell charges into those which are and are not penetration by the nuclei of the reference cell, would be preferable. In the nonpenetrating case, the interaction should then be evaluated by means of a multipole expansion of the shell charge (to the same order as used in the electron-electron interaction); the interaction is evaluated exactly in the penetrating case. In this way errors introduced in the evaluation of E_{EE} would be approximately counterbalanced by those in E_{NE}, and work is in hand to implement the evaluation of E_{Coul} by this method.

III. EVALUATION OF FIELD AND MULTIPOLE INTEGRALS

The field and multipole integrals involving products of GTF's that arise in the present work are evaluated using the method of McMurchie and Davidson[13] suitably generalized so that poles of arbitrarily high order can be evaluated. The first step in the McMurchie-Davidson procedure is to expand the overlap distributions of two GTF's with exponents a and b located at $\vec{A}$ and $\vec{B}$, respectively, as a linear combination of Hermite GTF's located at $\vec{Q}$ and with exponent q,

$$q=a+b\ , \tag{27a}$$

$$\vec{Q}=(a\vec{A}+b\vec{B})/q\ , \tag{27b}$$

so that

$$\chi_A(\vec{r})\chi_B(\vec{r})=\sum_{i,j,k}E_{ijk}\Lambda_{ijk}^{Q}(\vec{r})\ , \tag{28}$$

where E denotes the expansion coefficients to be generated according to the methods of Refs. 13 and 14, and where the Hermite GTF's denoted by Λ have the definition

$$\Lambda_{ijk}^{Q}(\vec{r})=\left[\frac{\partial}{\partial Q_x}\right]^i\left[\frac{\partial}{\partial Q_y}\right]^j\left[\frac{\partial}{\partial Q_z}\right]^k\exp(-qr_Q^2)\ , \tag{29}$$

with $r_Q=|\vec{r}-\vec{Q}|$. A common set of Hermite GTF's is used to expand all possible overlap distributions arising from a given shell-shell overlap, a feature which may be exploited to considerably accelerate the rate at which the integrals may be computed.[14]

A. Field integrals

We are here interested in integrals of the form

$$\int\chi_A(\vec{r})\chi_B(\vec{r})\Phi_l^m(\vec{C};\vec{r})d\vec{r}=\sum_{i,j,k}E_{ijk}J_l^m(\vec{Q},\vec{C},i,j,k)\ , \tag{30}$$

where $\Phi_l^m(\vec{C};\vec{r})$ has been defined in Eq. (22). We have used Eq. (28), and

$$J_l^m(\vec{Q},\vec{C},i,j,k)=N_l^m\int\Lambda_{ijk}^{Q}(\vec{r})\Gamma_l^m(\vec{C};\vec{r})d\vec{r}\ , \tag{31}$$

where N_l^m and $\Gamma_l^m(\vec{C};\vec{r})$ were defined in Eq. (22).

The solid harmonic, Eq. (21), is a homogeneous polynomial in x_C,y_C,z_C of order l,

$$X_l^m(\vec{C};\vec{r})=\sum_{\mu,\nu,\tau}D_l^m(\mu,\nu,\tau)x_C^{\mu}y_C^{\nu}z_C^{\tau}\ , \tag{32}$$

where the D coefficients are easily generated from the recursion relationships for the solid harmonics [see Eq. (45)].

The spherical gradient operator $W_l^m(\vec{C})$ may be formally related[15] to the solid harmonic by the substitution $x_C\rightarrow\partial/\partial C_x$ (similarly for the y and z coordinate),

$$W_l^m(\vec{C})=\sum_{\mu,\nu,\tau}D_l^m(\mu,\nu,\tau)\left[\frac{\partial}{\partial C_x}\right]^{\mu}\left[\frac{\partial}{\partial C_y}\right]^{\nu}\left[\frac{\partial}{\partial C_z}\right]^{\tau}\ . \tag{33}$$

It can be shown (see pp. 124–127 of Ref. 16) that

$$W_l^m(\vec{C})r_C^{-1}=[(2l-1)!!]\Gamma_l^m(\vec{C};\vec{r})\ , \tag{34}$$

so that

$$J_l^m(\vec{Q},\vec{C},i,j,k)=\{N_l^m/[(2l-1)!!]\}\times\int\Lambda_{ijk}^{Q}(\vec{r})W_l^m(\vec{C})r_C^{-1}d\vec{r}\ . \tag{35}$$

The integrals in Eq. (31) may be shown to be uniformly convergent (in contrast to the case where Cartesian gradient tensor components are used, where Dirac δ functions may be involved). Thus after noting

$$\frac{\partial}{\partial C_x}r_C^{-1}=-\frac{\partial}{\partial x}r_C^{-1}\ , \tag{36a}$$

$$\frac{\partial}{\partial Q_x}\Lambda^{Q}_{ijk}(\vec{r})=-\frac{\partial}{\partial x}\Lambda^{Q}_{ijk}(\vec{r}) \;, \tag{36b}$$

and after successive integrations by parts, we find

$$J_l^m(\vec{Q},\vec{C},i,j,k)=\{(-1)^l N_l^m/[(2l-1)!!]\} \times \int W_l^m(\vec{Q})\Lambda^{Q}_{ijk}(\vec{r})r_C^{-1}d\vec{r} \;. \tag{37}$$

After noting the definition of the Hermite GTF's [Eq. (29)] and the spherical gradient operator [Eq. (33)], we arrive at the result

$$J_l^m(\vec{Q},\vec{C},i,j,k)=\{(-1)^l N_l^m/[(2l-1)!!]\} \times \sum_{\mu,\nu,\tau} D_l^m(\mu,\nu,\tau) \times J_0^0(\vec{Q},\vec{C},i+\mu,j+\mu,k+\tau) \;, \tag{38}$$

so that the general field integral has been reduced to a linear combination of nuclear attraction integrals, whose recursive evaluation has been given previously.[13,14]

Two practical points concerning the implementation of the above scheme are worth noting.

(i) The D coefficients are comparatively few in number even if high l values are used (for example, there are less than 200 finite coefficients for all l values less than seven), so that it is feasible to compute and store them at the outset. The factors $(-1)^l N_l^m/[(2l-1)!!]$ can be usefully incorporated into these tabulated coefficients.

(ii) In the evaluation of the Coulomb sums one actually requires sums over potentially large numbers of lattice vectors [see, for example, Eq. (26)]. Because the D and E coefficients are independent of these lattice vectors, it is convenient and extremely time saving (particularly if shell structure is exploited) to compute the quantities

$$I(\vec{Q},\vec{C},i,j,k)=\sum_{\vec{g}} J_0^0(\vec{Q},\vec{C}+\vec{g},i,j,k) \tag{39}$$

before effecting the contractions with the D or E coefficients. If the McMurchie and Davidson[13] algorithm is used for the evaluation of the two-electron repulsion integrals, a similar technique may also be used for the evaluation of Eq. (25).

B. Multipole integrals

These intregals are of the form

$$\int \chi_A(\vec{r})\chi_B(\vec{r})X_l^m(\vec{C};\vec{r})d\vec{r}=\sum_{i,j,k} E_{ijk}S_l^m(\vec{Q},\vec{C},i,j,k) \;, \tag{40a}$$

$$S_l^m(\vec{Q},\vec{C},i,j,k)=\int \Lambda^{Q(}_{ijk}\vec{r})X_l^m(\vec{C};\vec{r})d\vec{r} \;, \tag{40b}$$

where we have used Eq. (28). Actually, only the case $\vec{A}=\vec{C}$ arises in the present work, but the slightly more general form of Eq. (40) causes no additional complications. The Hermite GTF's have two important properties,[13,14] the definite integral,

$$\int \Lambda^{Q}_{ijk}(\vec{r})d\vec{r}=\delta_{i0}\delta_{j0}\delta_{k0}(\pi/q)^{3/2}=S_0^0(\vec{Q},\vec{C},i,j,k) \;, \tag{41}$$

and the recurrence relation,

$$x_Q\Lambda^{Q}_{ijk}(\vec{r})=\Lambda^{Q}_{i+1,j,k}(\vec{r})/(2q)+i\Lambda^{Q}_{i-1,j,k}(\vec{r}) \;, \tag{42}$$

with similar results for multiplication by y_Q and z_Q. First consider the case that the origin of the multipole operator is $\vec{Q}$. It is then obvious that $S_l^m(\vec{Q},\vec{Q},i,j,k)$ is zero if $i+j+k<l$, because of the orthogonality properties of the spherical harmonics. $S_l^m(\vec{Q},\vec{Q},i,j,k)$ is also zero if $i+j+k>l$; this becomes obvious after noting that the solid harmonic is a polynomial in x_Q,y_Q,z_Q of degree l, and using the recurrence relation, Eq. (42), and the definite integral, Eq. (41). Thus the only finite cases arise when $i+j+k=l$. By using the expansion of the solid harmonic, Eq. (32), and Eqs. (41) and (42), we can show that

$$S_l^m(\vec{Q},\vec{Q},i,j,k)=D_l^m(i,j,k)(i!)(j!)(k!)(\pi/q)^{3/2} \tag{43}$$

It should be carefully noted that it is unnecessary to consider the first term in the rhs of Eq. (42) in the derivation of Eq. (43), because this term will always give a null contribution after integration. This simplification does not apply if Cartesian multipole tensor components are considered, and represents an advantage of the spherical tensor system.

Consider now the more general case where the origin of the multipole operator is $\vec{C}$. The operator at $\vec{C}$ may be expanded (see pp. 137–140 of Ref. 16) as a linear combination of multipole operators at $\vec{Q}$,

$$X_l^m(\vec{C};\vec{r})=\sum_{l'=0}^{l}\sum_{m'=-l'}^{l'} V_{ll'}^{mm'}(\vec{Q}-\vec{C})X_{l'}^{m'}(\vec{Q};\vec{r}) \;, \tag{44a}$$

so that the multipole integrals can be evaluated from

$$S_l^m(\vec{Q},\vec{Q},i,j,k)=(i!)(j!)(k!)(\pi/q)^{3/2} \times \sum_{m'=-l'}^{l'} V_{ll'}^{mm'}D_{l'}^{m'}(i,j,k) \;, \tag{44b}$$

$$l'=i+j+k \;, \tag{44c}$$

and is zero unless $l\geq l'$. An alternative strategy used in the present work is based on the recursion formulas for the complex solid harmonics,

$$Y_{l+1}^{l+1}(\vec{C};\vec{r})=(2l+1)(x_C+\sqrt{-1}y_C)Y_l^l(\vec{C};\vec{r}) \;, \tag{45a}$$

$$Y_{l+1}^m(\vec{C};\vec{r})=[(2l+1)z_C Y_l^m(\vec{C};\vec{r})-r_C^2(l+|m|)Y_{l-1}^m(\vec{C};\vec{r})]/(l-|m|+1) \;. \tag{45b}$$

It is only necessary to consider the positive-*m* complex operators explicitly; integrals over negative-*m* counterparts are complex conjugates. Now

$$x_C=x_Q+(Q_x-C_x) \;, \tag{46}$$

so that we may derive from Eq. (42) a recursion relationship

$$x_C \Lambda^Q_{ijk}(\vec{r}) = \Lambda^Q_{i+1,j,k}(\vec{r})/(2q) + (Q_x - C_x)\Lambda^Q_{ijk}(\vec{r}) + i\Lambda^Q_{i-1,j,k}(\vec{r}) \; . \tag{47}$$

Now the first term of the rhs of Eq. (47) may be neglected in the present context, because it will always give a null contribution after integration, a result which we have already seen to be true for each term on the rhs of Eq. (42), and hence for the whole.

To increment l and m simultaneously (when $m = l$) use a combination of Eqs. (45a) and (47) to yield

$$\begin{aligned} S^{l+1}_{l+1}(\vec{Q},\vec{C},i,j,k) = (2l+1)\{&(Q_x - C_x)S^l_l(\vec{Q},\vec{C},i,j,k) + iS^l_l(\vec{Q},\vec{C},i-1,j,k) \\ &+ \sqrt{-1}[(Q_y - C_y)S^l_l(\vec{Q},\vec{C},i,j,k) + jS^l_l(\vec{Q},\vec{C},i-1,j,k)]\} \; . \end{aligned} \tag{48}$$

To increment l alone, use a combination of Eqs. (45b) and (47) to yield

$$\begin{aligned} S^m_{l+1}(\vec{Q},\vec{C},i,j,k) = {} & [(2l+1)/(l-|m|+1)][(Q_z - C_z)S^m_l(\vec{Q},\vec{C},i,j,k) + kS^m_l(\vec{Q},\vec{C},i,j,k-1)] \\ & - [(l+|m|)/(l-|m|+1)]\{[(Q_x - C_x)^2 + (Q_y - C_y)^2 + (Q_z - C_z)^2]S^m_{l-1}(\vec{Q},\vec{C},i,j,k) \\ & + 2i(Q_x - C_x)S^m_{l-1}(\vec{Q},\vec{C},i-1,j,k) + 2j(Q_y - C_y)S^m_{l-1}(\vec{Q},\vec{C},i,j-1,k) \\ & + 2k(Q_z - C_z)S^m_{l-1}(\vec{Q},\vec{C},i,j,k-1) + i(i-1)S^m_{l-1}(\vec{Q},\vec{C},i-2,j,k) \\ & + j(j-1)S^m_{l-1}(\vec{Q},\vec{C},i,j-2,k) + k(k-1)S^m_{l-1}(\vec{Q},\vec{C},i,j,k-2)\} \; . \end{aligned} \tag{49}$$

Equations (48) and (49) define a recursive scheme for the evaluation of the multipole integrals commencing from S^0_0 as given by Eq. (41). The implementation of the above scheme is facilitated by noting the following.

(i) $S^m_l(\vec{Q},\vec{C},i,j,k) = 0$ for $i+j+k > l$.

(ii) The E coefficients, Eq. (28), are finite only for $i+j+k \le \mu$, where μ is the sum of the polynomial degrees of the nonexponential portions of $\chi_A(\vec{r})$ and $\chi_B(\vec{r})$. Therefore, at any stage in the recursive process it is only necessary to generate the $S^m_l(\vec{Q},\vec{C},i,j,k)$ for $i+j+k$ less than or equal to μ or l, whichever is the smaller. This is because the sum of i, j, and k quantum numbers of the terms on the rhs's of Eqs. (48) and (49) are always less than or equal to those on the lhs's.

(iii) To convert to real solid harmonic expectation values, it is necessary to use Eq. (21). The result is that the real and imaginary parts of $S^m_l(\vec{Q},\vec{C},i,j,k)$, with $m \ge 0$, give the corresponding real solid harmonic expectation values for positive and negative m, respectively.

IV. RESULTS AND DISCUSSION

The computational scheme discussed above will now be illustrated by the results of calculations of the $(SN)_x$ polymer, the graphite, boron nitride, and beryllium monolayers, for hydrogen chemisorbed on a beryllium monolayer, and for silicon. The geometries and basis sets adopted are shown in Table I. To completely define the conditions under which the data were collected, we briefly mention the following computational parameters not explicitly under investigation in the present work.

(i) The overlap threshold t_1 defined after Eq. (9) is set to 10^{-5}.

(ii) The number of stars of direct lattice vectors included in the exchange summations[3] is set to 3.

(iii) The irreducible part of the Brillouin zone has been sampled using a shrinking factor[3] equal to 12 for the one- and two-dimensional systems; 8 has been used for the three-dimensional system silicon.

(iv) The self-consistent procedure was terminated when the total energy was stable to 10^{-5} a.u./cell in successive cycles.

We now summarize the parameters under explicit consideration in the present work as follows.

(i) The "bielectronic" zone is characterized by a parameter, t_2. The interaction between an overlap distribution in the reference cell and a shell charge in cell $\vec{h}$ is treated

TABLE I. Geometries and basis sets, d is the lattice parameter, r_{SN} is the S—N distance (Å) for the symmetric zigzag structure; STO-3G is the Gaussian-type orbital basis set of Hehre *et al.* (Ref. 17). The monolayers are the (0001) planes of the corresponding hexagonal crystals with space groups $P6_3mc$ (graphite and BN) and $P6_3/mmc$ (Be). BeH is a two-layer system with the H atoms in "open" positions with respect to the Be atoms, and Z_H is the interlayer distance (Å).

System	Geometry	Basis set
SN	$r_{SN}=1.7$ $\theta_{SNS}=105°$	STO-3G
Graphite	$d=2.45$	STO-3G
Boron nitride	$d=2.45$	STO-3G
Beryllium	$d=2.29$	Extended (Ref. 6)
BeH	$d=2.29$ $Z_H=1.00$	Be: Extended (Ref. 6) H: STO-3G
Silicon	$d=5.42$	STO-3G

TABLE II. Radius (Å) of the bielectronic zone for the beryllium monolayer as a function of the penetration parameter T_2. b is the number of cells included in the bielectronic zone.

$\rho_{jj}^{\vec{0}\,\vec{0}}(\vec{r}\,')$	$\rho_T^{\vec{h}}(\vec{r}\,')$	$T_2=4$		$T_2=6$		$T_2=12$	
		R	b	R	b	R	b
core-core	core	0.0	1	0.0	1	0.0	1
core-core	valence	4.3	7	4.3	7	8.7	19
valence-valence	core	4.3	7	4.3	7	8.7	19
valence-valence	valence	7.5	13	8.7	19	15.0	43

exactly if the degree of penetration of the two distributions is greater than t_2. Results will be quoted in terms of $T_2=-\log_{10}t_2$. The size of the bielectronic zone is a function of the characteristics of both $\rho_{jj'}^{\vec{0},\vec{g}}(\vec{r}\,')$ and $\rho_t^{\vec{h}}(\vec{r})$. To show how the T_2 *parameter* is selective, typical dimensions of the bielectronic zone for the beryllium monolayer are reported in Table II. Note that interactions involving core orbitals are treated exactly in only a rather small region when compared with the region associated with valence orbitals. This selectivity of T_2 allows the study of systems containing atoms of the second and third row without large increases in computing time, and permits an economic treatment of inner shells without recourse to pseudopotential techniques. For example, the number of integrals to be computed in an all-electron calculation of silicon with a minimal basis set is approximately twice that of a corresponding valence-only calculation.[7]

(ii) For $|\,h\,| \geq M$ *(Madelung radius)* the interactions are treated classically in the energy expression and ignored in the Fock operator.

(iii) For $|\,h\,| < M$, and given negligible penetration, the contribution of a shell charge $\rho_T^{\vec{h}}(\vec{r})$ is evaluated using a multipole expansion truncated at the Lth order *(L parameter).*

(iv) The shell charges are assigned using one of two possible charge-partitioning criteria *(P parameter),* the "unweighted" and weighted Mulliken schemes.

Thus we must discuss the influence of four computational parameters (T_2,M,L,P) on the wave function and total energy. With hindsight, we can say that satisfactory results may be obtained with $T_2=4$, $L=4$, $M\sim 30$ Å, and using the unweighted Mulliken partition. Therefore, these parameters will be discussed separately one at a time, the other parameters being kept at the "standard" values, unless otherwise noted.

A. P parameter

The most pragmatic measure of success of a given partitioning technique is the rapidity of convergence of the multipole expansion of the total energy. In Table III we quote $E^{(l)}$, the contribution to the total energy (here and hereafter we use a.u./cell) from all poles of a given l value, for all the systems under consideration in the present work, and for $l=1$–6. The unweighted and weighted partition results are designated U and W, respectively. It is seen that the rate of convergence of the expansion is little affected by the partitioning criteria, and therefore we will

TABLE III. Influence of the charge-partitioning criteria on the convergence of the multipole expansion of the total energy (a.u./cell).

System		Total energy	$E^{(1)}$	$E^{(2)}$	$E^{(3)}$	$E^{(4)}$	$E^{(5)}$	$E^{(6)}$
SN	U	−446.807 05	−0.028 63	−0.036 23	0.000 74	−0.000 62	0.000 00	0.000 01
Polymer	W	−446.807 06	−0.016 32	−0.030 40	0.001 20	−0.000 69	0.000 02	0.000 01
BN	U	−78.284 10	0	−0.018 76	−0.001 59	−0.006 89	0.000 24	−0.000 53
Monolayer	W	−78.279 21	0	−0.002 07	−0.003 11	−0.006 24	0.000 24	−0.000 50
Be	U	−14.573 93	0	0.097 82	0	0.001 03	0	0.000 03
Monolayer	W	−14.573 93	0	0.100 40	0	0.001 20	0	0.000 01
BeH	U	−15.077 83	0.009 54	0.032 62	−0.000 73	−0.000 09	0.000 02	0.000 01
Monolayer	W	−15.078 17	0.011 43	0.040 02	−0.000 75	0.000 35	0.000 03	0.000 00
Graphite	U	−74.842 57	0	−0.013 02	0.000 30	−0.005 92	−0.000 14	−0.000 25
Monolayer	W	−74.842 57	0	0.001 30	0.000 40	−0.005 61	−0.000 12	0.000 26
Silicon	U	−571.318 84	0	0	−0.018 98	0.000 31	0	0.000 52
	W	−571.318 85	0	0	−0.023 91	−0.000 45	0	0.000 71

TABLE IV. Influence of the "Madelung radius" on the properties of the SN polymer. S and N denote the number of stars of cells and the number of cells, respectively, that are included in the quantum zone. $\gamma_0^0(\mathrm{N})$ is the valence shell charge of the nitrogen atom. ϵ_1 denotes the lowest valence eigenvalue at the Γ point and ϵ_F is the Fermi energy.

Madelung radius (Å)	S	N	Total energy	Kinetic energy	Madelung energy	$\gamma_0^0(\mathrm{N})$	ϵ_1	ϵ_F
15	4	7	−446.807 10	441.661 17	−0.000 04	5.3647	−1.180 87	−0.024 82
23	6	11	−446.807 10	441.660 80	−0.000 01	5.3651	−0.180 98	−0.024 86
36	8	15	−446.807 10	441.660 74	−0.000 01	5.3652	−1.181 00	−0.024 87

use the unweighted scheme henceforth, in view of its greater simplicity. This result is extremely encouraging for it means that our results are essentially invariant to criteria which must to some extent be arbitrary. Note, however, that this invariance to partioning technique is only achieved by carrying out the multipole expansions to at least the hexadecapole terms.

B. Madelung radius

Systems with null atomic charges have been found to be rather insensitive to variations in the M parameter for M values larger than 15–20 Å. The hypothesis that the Madelung zone does not affect the Fock operator is of course satisfied in the limit of large quantum zone (the complement of the Madelung zone, the union of the bielectronic plus monoelectronic zones); also the effects will certainly be much smaller in the polymer than in a chemically similar three-dimensional crystal. For one- and two-dimensional systems it is quite practical to use M values at which our hypothesis is satisfied. Thus in Tables IV and V the influence of the M parameter is reported for SN and BN, respectively. In both cases the total energy is stable to the fifth decimal figure for $M > 35$–40 Å. The kinetic energy is considerably more sensitive, particularly in the case of the BN monolayer, and small but not completely negligible changes are observed in the valence shell charges of BN, again pointing to the conclusion that the neglect of Madelung terms in the Fock operator is affecting the wave function. The Madelung-zone contribution to the total energy is of the order of 0.000 01 a.u./cell in the case of SN, but 2 orders of magnitude larger in BN, giving an indication of the scaling of the importance of this factor with the dimensionality of the system. For three-dimensional ionic crystals we have results which indicate rather large Madelung effects on the wave function; work now in progress to incorporate Madelung effects into the Fock operator is considered vital if such systems are to be studied accurately, and should be of some benefit in the case of two-dimensional systems.

C. L and T_2 parameters

When a shell-charge distribution $\rho_T^{\vec{h}}(\vec{r})$ is attributed to the monoelectric zone, the associated bielectronic integrals are approximated by field integrals, and two errors are introduced.

(i) A certain degree of penetration of the two charge distributions is inevitable. In practice, because of the exponential decay of penetration with the square of the distance, it is very easy to make this factor completely negligible.

(ii) The multipole expansion is truncated after L terms. This gives rise to errors which vary as $1/r^{L+2}$, consistently more slowly decaying than an exponential. The error depends on the size and shape of the shell-charge distributions. The latter are nearly spherical in ionic or metallic systems, whereas in covalent systems the contribution of high multipoles is non-negligible, and for this reason we have chosen the graphite monolayer and silicon as critical systems for testing the effects of T_2 and L.

Judicious values for the T_2 and L parameters are obviously linked, for the higher the L value the lower the T_2 value that can be tolerated, at least when penetration effects are negligible. One should choose T_2 and L so as to

TABLE V. Influence of the "Madelung radius" on the properties of the BN monolayer. Notation is the same as in Table IV.

Madelung radius (Å)	S	N	Total energy	Kinetic energy	Madelung energy	$\gamma_0^0(\mathrm{B})$	ϵ_1	ϵ_F
23	12	91	−78.283 82	77.726 20	−0.001 31	2.5199	−1.211 63	−0.2391
36	24	223	−78.284 10	77.750 94	−0.001 03	2.4941	−1.212 12	−0.2404
45	36	361	−78.284 09	77.761 18	−0.002 07	2.4840	−1.212 39	−0.2409

TABLE VI. Influence of the L parameter on the properties of the graphite monolayer. ϵ_1 and Δ denote the lowest valence eigenvalue and the valence-band width, respectively, at the Γ point. $\gamma_2^0(C)$ is the quadrupole moment of the carbon valence shell charge, while COST(1) gives the cost of computing the monoelectric integrals in Cray-1 seconds.

L	$E^{(L)}$	$E_L - E_{L-1}$	Kinetic energy	ϵ_1	Δ	$\gamma_2^0(C)$	COST(1)
0			74.130 46	−1.216 37	0.875 02		6.6
2	−0.013 023	−0.013 160	74.130 07	−1.218 27	0.875 07	0.062 23	11.9
3	0.000 301	0.000 301	74.130 21	−1.218 52	0.875 09	0.062 42	15.7
4	−0.005 924	−0.005 925	74.129 84	−1.219 17	0.875 13	0.062 05	20.6
5	−0.000 138	−0.000 138	74.129 82	−1.219 14	0.875 12	0.062 02	27.0
6	−0.000 249	−0.000 249	74.129 78	−1.219 16	0.875 14	0.061 97	34.6

minimize the overall cost of achieving a given accuracy. The cost is a rapidly increasing function of T_2, since it controls the number of two-electron integrals to be evaluated. A detailed analysis of the performance of the present version of CRYSTAL, our code for Hartree-Fock calculations on periodic systems, reveals that if one requires an accuracy of 0.0001 a.u./cell in the kinetic energy of graphite, this may economically be achieved by using $T_2=4$ and $L=4$. If an order-of-magnitude increase in precision is required, the $T_2=6, L=6$ values will economically provide this. These conclusions remain valid if one uses other measures of convergence (for example, eigenvalues, multipole moments of the shell charges, or total energy), and for other systems.

Let E_L denote the total energy computed using multipole expansions of order L. Now if the wave function were independent of the order of the expansion, we would have

$$E^{(L)}=E_L-E_L-1 \ . \tag{50}$$

Table VI gives a comparison of the $E^{(L)}$ with E_L-E_{L-1} values for graphite, and shows that Eq. (50) is obeyed to a remarkable degree of accuracy, indicating that the variation in E_L with L is not primarily due to variations in the wave function. This lends strong support to our argument concerning the superiority of the energy expression E [Eq. (13)] over E' [Eq. (15)], the former dealing with the interaction of the reference-cell electrons and nuclei with the electrons in the monoelectronic zone in a more balanced way. Table VI also documents the convergence of kinetic energy, the lowest eigenvalue ϵ_1 (in a.u.), the valence-band width Δ at the Γ point, and the quadrupole moment $\gamma_2^0(C)$ of the carbon valence shell as a function of L. The final column of Table VI gives an idea of how the cost of the calculation of the one-electron integrals rises with L, cost being measured in seconds of computing time on a Cray-1 computer.

Table VII documents the convergence of the above properties of graphite with respect to T_2 (in the range 3—24). The column labeled N_C gives the number of two-electron repulsion integrals calculated (scaled by 10^{-6}), and the column labeled b gives the number of cells included partially or completely in the bielectronic zone for valence-valence interactions.

Table VIII documents the convergence of silicon data with respect to T_2 (notation as in Table VII). The three-dimensional character of the silicon lattice makes high T_2 values very expensive, as can be seen from the last column

TABLE VII. Influence of the T_2 parameter on the properties of the graphite monolayer. N_C is the total number of two-electron Coulomb integrals computed, b denotes the number of cells involved in the bielectronic zone for valence-valence interaction, and COST(2) gives the cost of computing all the two-electron integrals (Coulomb and exchange) measured in Cray-1 seconds.

T_2	$10^{-6}N_C$	b	Total energy	Kinetic energy	$E^{(2)}$	$E^{(4)}$	$E^{(6)}$	COST(2)
3	0.85	19	−74.842 914	74.129 776	−0.015 85	−0.009 99	−0.001 80	42.3
4	1.36	31	−74.842 570	74.129 775	−0.031 02	−0.005 92	−0.000 25	47.3
6	2.03	37	−74.842 552	74.129 768	−0.010 26	−0.003 45	−0.000 21	54.3
12	4.62	61	−74.842 557	74.129 760	−0.006 29	−0.001 22	−0.000 03	79.0
24	9.68	121	−74.842 556	74.129 751	−0.003 50	−0.000 42	.000 01	127.3

TABLE VIII. Influence of the T_2 parameter on the properties of silicon. Notation is the same in Table VII.

T_2	$10^{-6}N_C$	b	Total energy	Kinetic energy	$E^{(3)}$	$E^{(4)}$	$E^{(6)}$	COST(2)
3	1.88	42	−571.317 89	563.380 73	−0.017 96	0.000 57	0.003 87	72.6
4	3.14	55	−571.318 84	563.380 83	−0.018 98	0.000 31	0.000 52	83.2
6	7.21	129	−571.319 87	563.381 03	0.002 11	0.000 26	−0.000 12	113.1

of Table VIII, giving the cost of evaluating the two-electron repulsion integrals, which rises more rapidly than the corresponding monolayer case (Table VII). Again we see that at $T_2=4$ the kinetic energy is in error by less than 0.0001 a.u./cell, while the total energy error is 1 order of magnitude larger.

In order to check if the T_2 convergence shown by graphite and silicon is confirmed by other systems, we have carried out calculations on systems with finite-atomic charges (SN, BN, and BeH) or with high quadrupoles (Be). The results are shown in Table IX. We first comment on the Be monolayer, which when treated at the $L=0$ level[6] showed a very slow convergence of the total energy with respect to T_2, requiring a very high T_2 value (25) and a very large number of electron-repulsion integrals to get a reasonable total energy. On the contrary, when one explicitly takes account of the very large quadrupole moment (higher poles are rather unimportant in this case) the energy becomes almost invariant with respect to T_2, and calculations at $T_2=4$ are reliable to 0.0001 a.u./cell.

When a hydrogen monolayer is chemisorbed onto the beryllium plane, atomic charges and dipoles are created as a consequence of bond formation, and all those effects are correctly allowed for by the multipole expansion, as evidenced by the stability of the total and kinetic energy with respect to T_2 (see Table IX). Similar comments hold true for SN and BN, and in all cases, comparing the $T_2=4$ and 6 results, the total energy is stable to the fifth decimal place. This result is rather promising, in particular with regard to systems where large polarization effects occur, as in regular chemisorption.

V. CONCLUSIONS

Our findings are summarized below.

(i) By means of high-order multipole expansions it is possible to compute Coulomb series in periodic systems of one, two, or three dimensions to high precision and reduced cost, the bielectronic interactions being computed exactly in only a relatively small region. An efficient technique for evaluating the necessary field integrals has been given.

(ii) The results are essentially invariant to the details of the charge-partioning scheme if the multipolar analysis is carried out to sufficiently high order ($L=4$).

(iii) An improved version of the total-energy expression has been given; work is currently in progress to implement it.

(iv) Given the greatly increased precision of the treatment of the quantum zone made possible by the present work, it has been possible to identify deficiencies in the treatment of the Madelung zone. In particular, the neglect of the effects of the Madelung zone on the Fock operator is now considered inadvisable in the case of three-dimensional ionic systems; work is in progress to incorporate Madelung zone terms into the Fock operator.

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TABLE IX. Convergence of the total kinetic energies of SN, Be, BN, and BeH with respect to T_2.

	Total energy			Kinetic energy		
System	$T_2=3$	$T_2=4$	$T_2=6$	$T_2=3$	$T_2=4$	$T_2=6$
SN	−446.807 57	−446.807 10	−446.807 15	441.661 01	441.660 80	441.660 82
Be	−14.573 91	−14.573 93	−14.573 90	14.802 16	14.802 11	14.802 38
BN	−78.283 44	−78.284 10	−78.284 06	77.750 43	77.750 94	77.750 73
BeH	−15.077 83	−15.077 83	−15.077 74	15.433 57	15.433 39	15.433 55

[1] F. E. Harris, in *Theoretical Chemistry, Advances and Perspectives,* edited by H. Eyring and D. Henderson (Academic, New York, 1975), Vol. 1, p. 147; M. L. Glasser and I. J. Zucker, *ibid.* (Academic, New York, 1980), Vol. 5, p. 67.

[2] N. E. Brener and J. L. Fry, Phys. Rev. B 17, 506 (1978).

[3] C. Pisani and R. Dovesi, Inter. J. Quantum Chem. 17, 501 (1980); R. Dovesi, C. Pisani, and C. Roetti, *ibid.* 17, 517 (1980).

[4] R. Dovesi, C. Pisani, F. Ricca, and C. Roetti, Phys. Rev. B 22, 5936 (1980).

[5] J. Delhalle, L. Piela, J.-L. Brédas, and J.-M. André, Phys. Rev. B 22, 6254 (1980).

[6] G. Angonoa, J. Koutecky, and C. Pisani, Surf. Sci. 122, 355 (1982).

[7] R. Dovesi, C. Pisani, C. Roetti, and P. Dellarole, Phys. Rev. B 24, 4170 (1981); R. Dovesi, M. Causà, and G. Angonoa, *ibid.* 24, 4177 (1981); R. Dovesi, C. Pisani, F. Ricca, and C. Roetti *ibid.* 25, 3731 (1982).

[8] S. Suhai, J. Chem. Phys. 73, 3843 (1980).

[9] T. H. Upton and W. A. Goddard III, Phys. Rev. B 22, 1534 (1980).

[10] E. Clementi and J. Mehl, IBMOL-5 Program, IBM Research Report RJ883 (unpublished); E. Clementi, in *Selected Topics in Molecular Physics* (Verlag Chemie, Weinheim, 1972); E. Clementi, Proc. Nat. Acad. Sci. 69, 2942 (1972).

[11] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 843.

[12] P. P. Ewald, Ann. Phys. (Leipzig) 64, 253 (1921).

[13] L. E. McMurchie and E. R. Davidson, J. Comput. Phys. 26, 218 (1978).

[14] V. R. Saunders, in *Methods in Computational Molecular Physics,* edited by G. H. F Diercksen and S. Wilson (Reidel, Dordrecht, 1983).

[15] B. F. Bayman, J. Math. Phys. 19, 2558 (1978).

[16] E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Cambridge University Press, London, 1931).

[17] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969).