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Ewald-type formulas for Gaussian-basis studies of one-dimensionally periodic systems

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Abstract The history of computations at Namur and elsewhere on the electronic structures of stereoregular polymers is briefly reviewed to place the work reported here in the context of related efforts. Our earlier publications described methods for the formal inclusion of Ewald-type convergence acceleration in band-structure computations based on Gaussian-type orbitals, and that work is here extended to include a discussion of the calculation of total energies. It is noted that the continuous nature of the electronic density leads to different functional forms than are encountered for point-charge lattice sums. Examples are provided to document the correctness and convergence properties of the formulation.

Keywords Total energy · Stereoregular polymers · Ewald method

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1 Introduction

In the laboratories of the University of Namur, the authors and their colleagues have a long history in the development of methods for the study of one-dimensionally periodic systems described quantum-mechanically at the Hartree-Fock and correlation levels using expansions in Gaussian-type atomic orbitals. This work, which was started under the direction of Professor J. M. André, led to the creation of the program known as PLH [1]. That program, designed for the study of the structural and electronic properties of linear polymers, evaluated the lattice sums as direct-space expansions. Further work, directed by Professor J. Delhalle, led to the development of an approach that combined direct- and reciprocal-space concepts to yield an Ewald-type method [2]. That work appeared in the Ph.D. dissertation of Flamant [3], in a paper that included the present authors [4], and in later publications that are referred to where appropriate in the present communication.

The past 20 years have seen a renewal of interest in lattice summation methods, catalyzed by the advances in high-performance computing and the ability thereby provided to approach molecular dynamics and condensed-phase structural problems that had previously seemed inaccessible. In this respect, an important development was the so-called fast multipole method (FMM) [5]. With its help, the electrostatic energies of arrays of charged particles can be evaluated in computing times that are nearly linear in the number of particles. One of the strengths of FMM is that the charge distribution need not be periodic, and methods of Ewald character can be combined with FMM concepts for studies of periodic systems [6].

While FMM has opened the door to greatly improved efficiency in lattice sum evaluation, it may be useful to observe that (unlike the Ewald procedure) it is not a

fundamentally new algorithm. FMM is in our opinion better viewed as an intelligently designed direct-space approach wherein (1) the charges in various regions are described in terms of a (truncated) set of their multipole moments; (2) multipole moments from regions that are sufficiently separated are used to compute energy contributions; (3) the regions, their size, and their moment truncation levels are chosen to optimize efficiency at a specified level of accuracy, and (4) any short-range energetic contributions that cannot be described accurately as multipole interactions are computed exactly and explicitly.

The situation becomes more complicated when, instead of point-charge arrays, one encounters continuous charge distributions of known functional forms, as occurs when orbitals are introduced to describe localized electron distributions in systems with periodicity in one or more dimensions. It is possible to use FMM methods for such systems, as was shown, for example, by Strain et al. [7]. However, in addition to the possibility of simply representing an orbital by its moments (and thereby foregoing any processing based on its specific form), one may alternatively be able to use properties of the orbitals to make further mathematical analyses that lead to gains in computational efficiency. Such an approach is represented in two efforts of which we are aware:

1. the periodic-system code CRYSTAL [8] manipulates direct-space lattice sums involving Gaussian-type orbitals (GTOs) in a way such that (at least for systems with linear periodicity) they are represented using the Euler-Maclaurin summation formula [9]. Although the Euler-Maclaurin formula is asymptotic (i.e., formally not convergent), this approach leads to highly satisfactory results in typical computations.
2. The work of our group (cited above), which makes explicit use of the transformational properties of the GTOs to obtain rapidly convergent analytical formulas for all the lattice sums entering Hartree-Fock (HF) and post-HF computations.

At this juncture, it is not clear which of the three currently identified approaches (FMM or those discussed in the preceding paragraph) will be the most efficient for various classes of problems. However, the present authors' experience indicates that there are problems of practical importance in which a full exploitation of the analytical properties of the basis functions has been found advisable. It therefore seems appropriate to encourage researchers to proceed in accord with their individual interests.

The present communication, which deals with computations of the total energy in one-dimensionally periodic systems, completes an exposition started in a recent paper from our group [10], in which we developed Ewald-type formulas for GTO-based band-structure computations in

stereoregular polymers. The work of our group showed how the integrations in the nonperiodic directions can be carried out analytically to yield exact closed formulas for the terms in the remaining one-dimensional lattice summations. Although the Ewald transformation for GTOs leads, for the direct-space part, to complementary error functions (as also found for expansions involving point charges), the reciprocal-space contribution was found to be significantly different, being expressible in terms of a family of incomplete Bessel functions [11] whose numerical features had not previously been fully investigated. Consequently, our research effort included not only the formal aspects of the manipulation of the lattice summations to reach rapid convergence, but also the development of methods for the numerical evaluation of the relevant special functions. A satisfying aspect of the analysis is that the use of a comprehensive formal development enables the subsequent pursuit of whatever numerical methods seem most appropriate, in contrast to a situation in which the formal problem is solved via the introduction of a specific numerical method that is then not easily modified.

Formulas for the total energy of course include the nuclear–nuclear repulsion, which during the computation must be offset by half the electron–nuclear attraction energy to reach a finite, convergent result. This, in turn, means that the formalism for the nuclear–nuclear term must be developed in a way consistent with that for the other energy contributions so that a proper divergence cancelation is achieved. This problem was addressed for spherically symmetric orbitals by Flamant [3], and the present communication extends the analysis to orbitals of general symmetry. Because our results are expressed in terms of the first-order density matrix, they can be further extended without essential modification to more general GTO-based calculations that include electron correlation.

2 Total energy—basic formulas

We assume that the Hartree-Fock orbitals of our problem have already been determined, based on a Fock matrix $F_{ab}(k)$ whose subscripts a and b label Bloch states built from basis GTO's and whose argument k is a Bloch-wave vector in units such that the Brillouin zone is of unit length. Our methods for the calculation of $F_{ab}(k)$ and related quantities were reported in detail in our previous work [10].

Included in $F_{ab}(k)$ are Coulomb and exchange electron–electron terms, as well as k-dependent electron–nuclear and kinetic-energy matrices $V_{ab}(k)$ and $T_{ab}(k)$. We also note that $F_{ab}(k)$, $V_{ab}(k)$, and $T_{ab}(k)$ are scaled such that the corresponding overlap matrix element has the value $S_{ab}(k)$. All these k-dependent quantities are assumed known.

From the occupied Hartree-Fock orbitals, we can obtain the first-order density matrix $P_{ab}(k)$, and the total energy (per unit cell) then takes the form

$$E_T = \frac{1}{2} \int\limits_{-1/2}^{1/2} \mathrm{d}k \sum_{ab} P_{ba}(k)$$
$$\times \left[F_{ab}(k) + T_{ab}(k) + V_{ab}(k) + n_e^{-1} S_{ab}(k) U \right], \quad (1)$$

where U is twice the nuclear–nuclear repulsion energy:

$$U = \frac{1}{a_0} \sum_{AB} Q_A Q_B u(\mathbf{B} - \mathbf{A}), \quad (2)$$

$$u(\mathbf{R}) = \sum_{v=-\infty}^{\infty}{}' \frac{1}{|\mathbf{R} + v\hat{\mathbf{z}}|}. \quad (3)$$

Here, n_e is the number of electrons per unit cell, and Q_A and Q_B are nuclear charges at respective points $\mathbf{A}$ and $\mathbf{B}$ in the unit cell, with positions expressed as fractions of the cell dimension, which is a_0. The unit vector $\hat{\mathbf{z}}$ is in the direction of periodicity, and the prime on the v summation indicates that the term $v = 0$ is to be omitted if $A = B$. The factor $n_e^{-1} S_{ab}(k)$ in Eq. (1) simply causes the summation and integration of the U term of Eq. (1) to reduce to U. The present placement of U facilitates the combined treatment of $V_{ab}(k) + n_e^{-1} S_{ab}(k) U$.

The quantities $V_{ab}(k)$ and U are formally divergent, but when $V_{ab}(k)$ is used in $F_{ab}(k)$, the divergence cancels against a similar singularity in the electron–electron interaction. When both these kinds of contributions are treated by an Ewald procedure, the divergent contributions combine to give a finite (but nonzero) result. In Eq. (1) here, we can use for $V_{ab}(k)$ the same Ewald formulation as was used in our previous work, but will need to use a compatible Ewald formula for U and consider the limiting behavior of $V_{ab}(k) + n_e^{-1} S_{ab}(k) U$. Since the only divergence in the Ewald formulas is at the origin point of the Fourier-space sums, we may evaluate all the terms of $V_{ab}(k)$ and the decomposition of U individually except for the single divergent term of each and then for the divergent terms take the limit of their sum.

3 Nuclear–nuclear term

A rather direct way of obtaining the Ewald decomposition of the nuclear–nuclear lattice sum uses the error function, defined as

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}} \int\limits_0^x e^{-t^2} \mathrm{d}t, \quad (4)$$

and its complement $\mathrm{erfc}(x)$, defined as $1 - \mathrm{erf}(x)$. At $x = 0$, $\mathrm{erf}(x) = 0$ and $\mathrm{erfc}(x) = 1$, while at $x = \infty$, $\mathrm{erf}(x) = 1$ and $\mathrm{erfc}(x) = 0$. Thus, these functions

partition unity in a way dependent on the value of x. We use these properties by writing

$$u(\mathbf{R}) = \sum_{v=-\infty}^{\infty}{}' \frac{\mathrm{erf}\left(\frac{|\mathbf{R}+v\hat{\mathbf{z}}|}{\tau^{1/2}}\right) + \mathrm{erfc}\left(\frac{|\mathbf{R}+v\hat{\mathbf{z}}|}{\tau^{1/2}}\right)}{|\mathbf{R} + v\hat{\mathbf{z}}|}. \quad (5)$$

Here, τ is a separation constant (not necessarily equal to those used for V_{ab} or the electron–electron terms). Larger values of τ make the erfc term of the partitioning (the direct-space contribution) more important. Smaller values of τ cause emphasis on the erf term, which will be transformed into Fourier space.

The erf term of Eq. (5) is now subjected to a Poisson transformation, adding a contribution from $v = 0$ if it was missing and then subtracting it again external to the transformation. Before the Poisson transformation, this term, which we call $u_{\mathrm{FS}}(\mathbf{R})$, can be written as an integral:

$$u_{\mathrm{FS}}(\mathbf{R}) = \frac{2}{(\pi\tau)^{1/2}} \left[\sum_{v=-\infty}^{\infty} \int\limits_0^1 e^{-|\mathbf{R}+v\hat{\mathbf{z}}|^2 t^2/\tau} \mathrm{d}t - \delta_{\mathbf{R},0} \right]. \quad (6)$$

After the transformation, u_{FS} becomes (temporarily disregarding problems associated with the singularity at $\mu = 0$)

$$u_{\mathrm{FS}}(\mathbf{R}) = \sum_{\mu=-\infty}^{\infty} e^{2\pi i \mu R_z} K_0(\pi^2 \tau \mu^2, |\mathbf{R}_0|^2/\tau) - \frac{2\delta_{\mathbf{R},0}}{(\pi\tau)^{1/2}}. \quad (7)$$

In the right-hand side of Eq. (7) appear the component of $\mathbf{R}$ in the direction of periodicity, denoted R_z, and the two-dimensional remainder of $\mathbf{R}$ perpendicular to that direction, denoted $\mathbf{R}_0$. Reaching Eq. (7) requires a number of steps, but they are similar to those used for V_{ab} and other lattice sums in Ref. [10]. The function K_0 is an incomplete Bessel function that always occurs when a lattice of GTO's is subjected to a Poisson transformation, with integral representation

$$K_0(x, y) = \int\limits_1^{\infty} e^{-xt - y/t} \mathrm{d}t. \quad (8)$$

A detailed account of this function was recently published by one of the present authors [12], and methods for its numerical evaluation were reviewed by both of us [13].

Turning now to the term of u_{FS} with $\mu = 0$, which we denote χ_{nn}, we identify its limiting behavior as $\mu \to 0$, first for the case $\mathbf{R}_0 \neq 0$. Using Eq. (C12) of Ref. [10], we find

$$\chi_{\mathrm{nn}} = -2\ln\mu - \ln(\pi^2|\mathbf{R}_0|^2) - 2\gamma_{\mathrm{E}} - E_1(|\mathbf{R}_0|^2/\tau). \quad (9)$$

Here, γ_{E} is the Euler-Mascheroni constant, and E_1 is an exponential integral [14]. The quantity χ_{nn} contains the only singular contribution to U; it diverges logarithmically as $\mu \to 0$.

Summarizing and simplifying,

$$
U = \frac{1}{a_0} \sum_{AB} Q_A Q_B
$$

$$
\times \left[\sum_{\mu \neq 0} e^{2\pi i \mu (B_z - A_z)} K_0(\pi^2 \tau \mu^2, |\mathbf{B}_0 - \mathbf{A}_0|^2/\tau) + \chi_{nn} \right.
$$

$$
\left. + \sum_{v=-\infty}^{\infty}{}' \frac{\mathrm{erfc}(\tau^{-1/2}|\mathbf{B} - \mathbf{A} + v\hat{\mathbf{z}}|)}{|\mathbf{B} - \mathbf{A} + v\hat{\mathbf{z}}|} - \frac{2\delta_{AB}}{(\pi\tau)^{1/2}} \right] \quad (10)
$$

4 Singularity cancellation

To see how the singularities cancel, we first note that the only singular term of $V_{ab}(k)$ (from Ref. [10]) arises from the $\mu = 0$ limit of its term with all the quantum numbers $n = l = m = 0$. Thus, we write

$$
V_{ab}(k) = V_{ab}(k)|_{\text{nonsing}} - \frac{S_{ab}(k)}{a_0} \sum_A Q_A \chi_{ne}(A), \quad (11)
$$

where

$$
\chi_{ne}(A) = \lim_{\mu \to 0} K_0 \left(\pi^2 (\eta_{ab} + \tau_{ne}) \mu^2, \frac{|\mathbf{P}_0 - \mathbf{A}_0|^2}{\eta_{ab} + \tau_{ne}} \right). \quad (12)
$$

Here, τ_{ne} is the separation constant for $V_{ab}(k)$, $\eta_{ab} = 1/(\alpha_a + \alpha_b)$, where α_a and α_b are GTO screening parameters, and $\mathbf{P}_0$ is the component perpendicular to $\hat{\mathbf{z}}$ of the centroid of the GTO product ab, as given in Eq. (7) of Ref. [10]. Note that χ_{ne} also depends upon the orbitals a and b; the notation for χ becomes too cumbersome if that dependence is shown explicitly.

Evaluating the limit in Eq. (12), we find

$$
\chi_{ne}(A) = -2 \ln \mu - \ln(\pi^2 |\mathbf{P}_0 - \mathbf{A}_0|^2) - 2\gamma_E
$$

$$
- E_1 \left(\frac{|\mathbf{P}_0 - \mathbf{A}_0|^2}{\eta_{ab} + \tau_{ne}} \right). \quad (13)
$$

The χ_{ne} exhibit a logarithmic divergence as $\mu \to 0$ that must cancel against the similar divergence in χ_{nn}.

Combining all the χ terms, and inserting for those coming from $V_{ab}(k)$ the quantity $n_e^{-1} \sum_B Q_B$ (which is unity), the singularities and several finite contributions cancel, and we have

$$
\left[V_{ab}(k) + n_e^{-1} S_{ab}(k) U \right]_{\text{sing}} = \frac{S_{ab}(k)}{a_0 n_e} \sum_{AB} Q_A Q_B [\chi_{nn} - \chi_{ne}(A)]
$$

$$
= \frac{S_{ab}(k)}{a_0 n_e} \sum_{AB} Q_A Q_B \left[\ln \left(\frac{|\mathbf{P}_0 - \mathbf{A}_0|^2}{|\mathbf{B}_0 - \mathbf{A}_0|^2} \right) \right.
$$

$$
\left. + E_1 \left(\frac{|\mathbf{P}_0 - \mathbf{A}_0|^2}{\eta_{ab} + \tau_{ne}} \right) - E_1 \left(\frac{|\mathbf{B}_0 - \mathbf{A}_0|^2}{\tau} \right) \right]. \quad (14)
$$

Equation (14) requires further manipulation if any of the quantities $\mathbf{B}_0 - \mathbf{A}_0$ or $\mathbf{P}_0 - \mathbf{A}_0$ vanish. In any such case, we

must replace the exponential integral by its small-argument limit, which then causes cancellation of the corresponding logarithm. The substitution involved corresponds to

$$
E_1 \left(\frac{|\mathbf{R}|^2}{\tau} \right) \longrightarrow -\gamma_E + \ln \tau - \ln |\mathbf{R}|^2, \quad (15)
$$

and has the result that if the entire system is linear, Eq. (14) reduces to

$$
\left[V_{ab}(k) + n_e^{-1} S_{ab}(k) U \right]_{\text{sing}} = \frac{n_e S_{ab}(k)}{a_0} \ln \left(\frac{\eta_{ab} + \tau_{ne}}{\tau} \right). \quad (16)
$$

5 Convergence rates

The ultimate rate of convergence of the μ and v summations in Eq. (10) is determined by the asymptotic behavior of the functions $\mathrm{erfc}(x)$ and $K_0(x, y)$, and in particular, the dominant contributions thereto at large x, which are exponentially decaying:

$$
\mathrm{erfc}(x) \sim e^{-x^2} f(x), \qquad K_0(x, y) \sim e^{-x-y} f(x, y); \quad (17)
$$

$f(x)$ and $f(x, y)$ are not important for the ultimate convergence rate. From Eq. (17), we see that when $\tau \neq 0$, both the summations converge at a quadratically exponential rate, with their relative rates dominated (for μ) by the decay of $\exp(-\pi^2 \tau \mu^2)$ and (for v) by the decay of $\exp(-\tau^{-1} v^2)$. Both these forms are in contrast to the slow and conditional convergence obtained when terms of $1/\mu$ dependence (but opposing signs) are summed.

The above analysis is consistent with our original objective in partitioning the energy contributions: larger τ enhances the convergence rate of the Fourier-space sum (that containing K_0) while diminishing its importance to the overall result. Smaller τ enhances the convergence rate of the direct-space sum (that containing erfc) while moving energetic contributions to the Fourier representation.

The optimum overall summation extent (in the limit of high accuracy) may now be obtained by requiring that both summations converge at the same ultimate rate; this objective is achieved by setting their exponential rates equal when $\mu = v$, yielding

$$
\pi^2 \tau = \tau^{-1}, \quad (18)
$$

with solution $\tau = 1/\pi \approx 0.32$.

A similar analysis can be applied to the partitioning of the energetic contributions of V_{ab}. As indicated in Ref. [10], the condition for equal direct- and Fourier-space ultimate convergence rates reduces to

$$
\pi^2 (\eta_{ab} + \tau_{ne}) = \frac{1}{\eta_{ab} + \tau_{ne}}, \quad (19)
$$

with solution $\tau_{ne} = \pi^{-1} - \eta_{ab}$. This result is meaningful only if $0 < \eta_{ab} < \pi^{-1}$. If this condition is not met, the

optimum value of τ_{ne} is zero, corresponding to computation entirely in Fourier space.

We close this section with two observations. First, the number of summation terms is only a partial criterion for maximizing computational efficiency. The relative effort of evaluating individual terms of the two summations is also relevant; current evaluation methods are faster for a direct-space term than for a Fourier-space term, indicating that Eqs. (18) and (19) are only starting points for highly tuned evaluations.

Second, the ultimate convergence rate may not be relevant if the accuracy we seek causes summation terms to be deemed negligible before the limiting behavior is reached. We observe this phenomenon in the examples to follow.

6 Numerical tests

In order to demonstrate the correctness and the convergence of this formulation, we now present illustrative computations of that portion of the total energy that includes the nuclear–nuclear repulsion and the offsetting electron–nuclear attraction. This contribution to the total energy arises from the last two terms within the square brackets of Eq. (1) and contains the singular terms that must cancel; we denote it E_{ne} and observe that it has the form

$$E_{ne} = \frac{1}{2} \int\limits_{-1/2}^{1/2} dk \sum_{ab} P_{ba}(k) \left[V_{ab}(k) + n_e^{-1} S_{ab}(k) U \right]. \quad (20)$$

Our test system consists of a linear chain of H_2 molecules, with a single $1s$ Gaussian orbital, of functional form $\exp(-\alpha r^2)$, on each atom. We used two geometries, with the first, designated $H_{2\parallel}$, consisting of molecules that are aligned on the z-axis (the direction of translational periodicity). The second geometry, designated $H_{2\perp}$, consists of molecules whose orientation is perpendicular to the z-axis. All computations were made for a unit cell of length $a_0 = 3.0$ bohr and containing one H_2 molecule with its internuclear distance fixed at 1.42 bohr. For computational simplicity, we used a density matrix with diagonal elements $P_{pp} = S_{pp}^{-1}$ ($p = a$ and b) and with off-diagonal elements set to zero.

In the case $H_{2\parallel}$, the vectors $\mathbf{R}_0$, $\mathbf{A}_0$, and $\mathbf{P}_0$ (which describe "projections" perpendicular to the direction of periodicity) vanish for all choices of orbitals and nuclei. This causes all the incomplete Bessel functions appearing in the computations to reduce to exponential integrals, with all the singular terms collapsing to the form given in Eq. (16) of the present communication. A more comprehensive test is provided by the case $H_{2\perp}$, because the

projection vectors do not vanish for $a \neq b$ and $A \neq B$, thereby providing a test for the general case of Eq. (14).

The first test we applied was to verify that our formulas for E_{ne} can give the same results as conventional "direct-space" (DS) computations. Fixing the separation constant τ at the near-optimum value 0.3 and setting τ_{ne} also to 0.3 (a value that will sometimes be far from optimal), we computed E_{ne} for several values of the GTO exponent α, both by the method of the present communication and by a conventional DS formula. The results are shown in Table 1. Because of the wide range of the α values and the non-optimal choice of τ_{ne} some of the summations needed for Table 1 converged extremely slowly. We arranged to keep up to 1001 terms in the lattice summations, achieving adequate convergence for all the table entries except for the DS sums at $\alpha = 0.1$. It is clear that the present and conventional methods are in agreement.

We next considered issues related to the rate of convergence of E_{ne}, restricting attention to the single GTO exponent $\alpha = 0.5$ bohr^{-2}. We carried out two sets of computations; in the first set, summarized in Table 2, we kept the electron–nuclear partitioning constant τ_{ne} at 0.3 and varied the nuclear–nuclear constant τ over a wide range of values. The table reports the overall value of E_{ne}, which should be (and is) independent of the value of τ, and also indicates the numbers of terms N larger in absolute value than 10^{-8} in the direct-space (DS) and Fourier-space (FS) series for U appearing in Eq. (10). The N values are expressed as ranges when they differ significantly for different atom pairs. As expected, an increase in τ increases the importance of the direct-space summation of U and reduces its convergence rate; the opposite trends are noted for for the Fourier-space summation of U.

The table also includes the total number of significant terms, $N_{DS} + N_{FS}$; we see that it is a minimum in a broad

Table 1 Energies E_{ne}, hartrees: this work ($\tau = \tau_{ne} = 0.3$) and by conventional direct-space computation (DS), for various GTO exponents α

	α bohr^{-2}	E_{ne} (this work)	E_{ne} (DS)
$H_{2\parallel}$	0.1	−0.003 139	−0.003 141
	0.5	−1.080 911	−1.080 911
	1.0	−1.591 596	−1.591 596
	10.0	−5.046 265	−5.046 265
	100.0	−15.957 691	−15.957 691
$H_{2\perp}$	0.1	−0.194 889	−0.194 890
	0.5	−1.104 350	−1.104 350
	1.0	−1.592 786	−1.592 786
	10.0	−5.046 265	−5.046 265
	100.0	−15.957 691	−15.957 691

Table 2 Electrostatic energy E_{ne} (hartrees) and the numbers of significant terms in the direct-space and Fourier-space series of Eq. (10) as a function of the separation constant τ

	τ	E_{ne}	N_{DS}	N_{FS}	$N_{DS} + N_{FS}$
$H_{2\parallel}$	0.001	−1.080 911	1	79	80
	0.01	−1.080 911	1	25	26
	0.1	−1.080 911	3	7	10
	0.3	−1.080 911	5	5	10
	1.0	−1.080 911	7–9	3	10–12
	10.0	−1.080 911	25	1	26
	100.0	−1.080 911	73	1	74
$H_{2\perp}$	0.001	−1.104 350	1	13–79	14–80
	0.01	−1.104 350	1	13–25	14–26
	0.1	−1.104 350	3	7	10
	0.3	−1.104 350	5	5	10
	1.0	−1.104 350	7	3	10
	10.0	−1.104 350	25	1	26
	100.0	−1.104 350	73	1	74

Table 3 Electrostatic energy E_{ne} (hartrees) and the numbers of significant terms in the direct-space and Fourier-space series appearing in Eqs. (53)–(55) of Ref. [10] as a function of the separation constant τ_{ne}

	τ_{ne}	E_{ne}	N_{DS}	N_{FS}	$N_{DS} + N_{FS}$
$H_{2\parallel}$	0.0	−1.080 911	0	7	7
	0.1	−1.080 911	5–7	5	10–12
	0.3	−1.080 911	7–9	3	10–12
	1.0	−1.080 911	11–13	3	14–16
	2.0	−1.080 911	13–15	1	14–16
	10.0	−1.080 911	25–27	1	26–28
	100.0	−1.080 911	73–75	1	74–76
$H_{2\perp}$	0.0	−1.104 350	0	7	7
	0.1	−1.104 350	7	5	12
	0.3	−1.104 350	7–9	3	10–12
	1.0	−1.104 350	11	3	14
	2.0	−1.104 350	15	1	16
	10.0	−1.104 350	27	1	28
	100.0	−1.104 350	75	1	76

region centered about the theoretical value, 0.32. Finally, we note that N_{FS} has a wide range of values for $H_{2\perp}$ at small τ. This behavior is caused by a combination of extremely slow convergence and the fact that when $A \neq B$, the large nonzero value of the second argument of the Bessel function K_0, namely $|\mathbf{B}_0 - \mathbf{A}_0|^2/\tau$, makes all the summation terms smaller, see Eq. (17), and fewer of them remain larger in magnitude than 10^{-8}.

Our second set of test computations was with the nuclear–nuclear separation constant τ set to 0.3, with the nuclear–electron constant τ_{ne} varied. These studies are summarized in Table 3, where we are studying the rates of convergence of the series for V_{ab}, given as Eqs. (53)–(55) of Ref. [10]. Again, we verify that the overall value of E_{ne} is independent of the separation constants. We also see, as expected, that the number of significant terms (greater in absolute value than 10^{-8}) in the direct-space series for V_{ab} increases with τ_{ne}.

If we now look at the total number of significant terms in the V_{ab} expansions, we see that they do not indicate a minimum at any intermediate value of τ_{ne}. Because of the presence of the quantity η_{ab}, which in this case is $1/2\alpha = 1$, Eq. (19) does not predict an optimum positive value of τ_{ne}, and the best choice for this parameter is predicted to be zero. The data in Table 3 are consistent with this prediction: The table shows the total number of terms, $N_{DS} + N_{FS}$, to be a minimum at $\tau = 0$, indicating that the optimum partitioning of V_{ab} is entirely to Fourier space.

The data in Table 3 do not show the wild variation in N_{FS} that was exhibited by the expansion of U for $H_{2\perp}$. The difference in behavior is due to the fact that for V_{ab} the second argument of K_0 depends upon $(\eta_{ab} + \tau_{ne})^{-1}$, and not on τ^{-1} as in the nuclear–nuclear contribution.

7 Conclusions

This paper completes the work presented in Ref. [10] by showing how the Ewald technique can be applied to compute the Hartree-Fock total energy for infinite systems of one-dimensional periodicity in a basis of Gaussian-type orbitals. A key aspect of the present contribution is the method for combining correctly the singularities appearing in the nuclear–nuclear and nuclear–electron interaction terms. These singularities are a manifestation of the fact that these two terms diverge if treated separately. The correctness and adequacy of the approach are validated by the presentation of sample computations.

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