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Published in:
International Journal of Quantum Chemistry

Publication date:
2009

Document Version
Early version, also known as pre-print

Published in International Journal of Quantum Chemistry
Reference: International Journal of Quantum Chemistry 109, 2968 (2009)

Numerical orbital fourier space approach to polymer band-structure calculations

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(Dated: August 28, 2015)

The periodic symmetry of polymer chains can be applied via Bloch functions to polymer band structure calculations [Delhalle, J. and Harris, F.E. Phys Rev B 1985, 31, 6755]. The possibility of replacing Gaussian orbitals with numerically defined orbitals in this approach is discussed. Two modifications of the theory to overcome problems with the cancellation of divergent terms are described. Result for a LiH chain are compared with analytic Gaussian orbital results.

I. INTRODUCTION

The last two decades have witnessed the emergence of the field of nanoscience and nanotechnology where nano-objects exhibiting remarkable properties (electrical, thermal ...) have been synthesized (carbon nanotubes, organic and inorganic nanorods, metallic nanowires, graphene ribbons,...). These particles already play an essential role in the materials and/or devices in which they are incorporated and/or assembled, and this situation is expected to further develop. The properties of these particles, in addition to their composition and bonding, largely stem from their specific geometrical characteristics or high aspect ratio and require appropriate theoretical levels for their description and prediction.

As in the case of polymers, the quasi one-dimensionality of space of the particles makes them good candidates for a realistic modelling in which periodicity in one space direction is used. Despite this simplification through symmetry, these particles are of a structural complexity such that the most widely applied theoretical methods are based on density functional theory which treats electron correlation in an approximate way and lacks a firm backgound for systematic improvement. The drawbacks are especially important for the description of excitations. The Hartree-Fock theory and the methodologies that extend it are still the most consistent ones to deal with such questions. Implementations of them have been made in both direct and momentum spaces. However, basis set questions and difficulties linked to long-range effects require further progress. These constitute a research area that is at the basis of the present contribution.

Practically all quantum chemical calculations are based on the expansion of molecular orbitals in analytic bases of gaussian orbitals (GTOs). These provide methods for the evaluation of the multicenter integrals necessary for molecular variational calculations. The gaussian basis functions are often expressed as polynomials in x, y, z multiplying a s-type function $e^{-\alpha r^2}$ where the coordinates are the distances from one of the nuclei. An equivalent form of basis is a spherical harmonic basis, in which the polynomial factors are specifically solid harmonics, $r^l Y_{lm}(\hat{\mathbf{r}})$.

There has been some recent progress in a program to replace the gaussian factors by basis functions defined numerically on a radial mesh centered at a particular nucleus [1]. The basis functions are then of the form $f_{lm}(\mathbf{r} - \mathbf{R})$ where

$$f_{lm}(\mathbf{r}) = g_l(r) Y_{lm}(\hat{\mathbf{r}}). \tag{1}$$

Although the computational problems are greater than with the use of GTOs, this approach permits the optimization of the basis orbitals, thereby permitting the use of a much smaller basis, and reducing problems of linear dependencies [2].

Contributions to the theory of the electronic structure of polymers has been made by F.E. Harris, H.J. Monkhorst and one of us [3, 4] and applied to cases with GTO functions [5-12]. In this article, the one-dimensional periodic symmetry is invoked using Bloch functions and Fourier series expansions. This approach has been applied in several cases using GTO bases. These applications have, until now, been largely restricted to s orbitals. The infinite summations obtained in this method overcome the problems of slow convergence of the multipole sums used to compute the long-range contributions [13] that occur in direct methods [14].

In this article, the application of numerical orbital basis methods to this approach to the theory of one-dimensional periodic system will be described and applied to some simple systems. A previous application to the problem of a linear chain of H_2 molecules has been described previously [15]

II. THEORY

We follow closely the theory and notation of Delhalle and Harris. The system is an infinite chain of unit cells (in the z direction), with atoms centered at points $\mathbf{s}_i$ relative to an arbitrary origin within each cell. The energy of the system is, of course, infinite, and the quantity of interest is the energy/unit cell. The expressions for the various extensive physical quantities are per unit cell.

It is convenient to choose the units so that unit cell length is 2π; then the kinetic energy in atomic units is multiplied by $(2\pi/L_0)^2$ and potential energies in atomic units are multiplied by $2\pi/L_0$ where L_0 is the unit cell length in Bohr radii.

Basis functions $\chi_i(\mathbf{r}-\mathbf{s}_i)$, $1 \le i \le N_b$, are defined on each nuclear site within the unit cell. Bloch functions

$$b_p(k,\mathbf{r}) = \sum_{\mu} e^{i2\pi\mu k}\chi_p^{\mu}(\mathbf{r}) \tag{2}$$

are formed as linear combinations of translated atomic orbital functions

$$\chi_p^{\mu}(\mathbf{r}) = \chi_p(\mathbf{r}-\mathbf{s}_p-2\pi\mu\mathbf{e}_z) \tag{3}$$

where is restricted to the Brillouin zone $(-1/2, 1/2]$. The basis functions are angular momentum functions of the form $\chi(r)Y_{lm}(\hat{\mathbf{r}})$. The inner product of two such Bloch functions is

$$\int b_p(k', \mathbf{r})^* b_q(k, \mathbf{r}) d\mathbf{r} = \delta(k' - k) S_{pq}(k) \tag{4}$$

where

$$S_{pq}(k) = \sum_{\nu} e^{2\pi i \nu k} \int \chi_p^0(\mathbf{r})^* \chi_q^{\nu}(\mathbf{r}) d\mathbf{r}. \tag{5}$$

The orthonormality condition is

$$\sum_{pq} c_{mp}(k)^* S_{mn}(k) c_{nq}(k) = \delta_{pq} \tag{6}$$

or, in a matrix notation

$$C^{\dagger}(k) S(k) C(k) = I. \tag{7}$$

The coefficients $C(k)$ can be obtained either by the Gram-Schmidt procedure or in a basis of eigenvectors of $S(k)$.

These functions are still subject to a unitary transformation which is determined from the Hartree-Fock matrix equations. Following the unitary transformation determined from the HF equation, the orthonormal Bloch waves are given by

$$\begin{aligned} \psi_i(\mathbf{r}, k) &= \sum_{pn} u_{ni}(k) c_{pn}(k) b_p(k, \mathbf{r}) \\ &= \sum_{p} v_{pi}(k) b_p(k, \mathbf{r}) \end{aligned} \tag{8}$$

where the u_{ni} are determined from the eigenvectors of the Hartree-Fock equation. In a matrix notation, we can write $V(k) = C(k)U(k)$.

The total energy per unit cell in the Hartree-Fock approximation is given by

$$\begin{aligned} E_T &= \int_{\mathrm{BZ}} \sum_{pq} P_{pq}(k) \left[T_{pq}(k) + V_{pq}(k) + \frac{1}{2} J_{pq}(k) + \frac{1}{2} K_{pq}(k) \right] dk + U \\ &= T + V_N + V_{\mathrm{ee}} + V_{\mathrm{ex}} + U \end{aligned} \tag{9}$$

and the matrix Hartree-Fock equation is

$$F(k)\mathbf{v}_i(k) = \epsilon_i(k) S(k) \mathbf{v}_i(k) \tag{10}$$

where the matrix $F(k)$ is

$$F(k) = T(k) + V(k) + J(k) + K(k) \tag{11}$$

The definition of the various quantities follows.

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

$$P_{pq}(k) = \sum_i n_i(k) u_{pi}(k)^* u_{qi}(k) \tag{12}$$

and $n_i(k)$ is the occupation number of $\psi(\mathbf{r}, k)$. The identity

$$\sum_{pq} \int_{\mathrm{BZ}} P_{pq}(k) S_{pq}(k) dk = \omega \tag{13}$$

which follows from Eqs. (8) and (12) will be used below.

The kinetic energy per unit cell is

$$T = \int_{\mathrm{BZ}} \sum_{pq} P_{pq}(k) T_{pq}(k) dk \tag{14}$$

where

$$T_{pq}(k) = \frac{1}{2} \sum_\nu e^{2\pi\nu k i} \int \vec{\nabla}\chi_p^0(\mathbf{r})^* \cdot \vec{\nabla}\chi_q^\nu(\mathbf{r}) d\mathbf{r} \tag{15}$$

The nuclear attraction potential energy per unit cell is

$$V_N = \int_{\mathrm{BZ}} \sum_{pq} P_{pq}(k) V_{pq}(k) dk \tag{16}$$

where

$$V_{pq}(k) = -\sum_u \sum_\nu e^{i2\pi\nu k} < \chi_p^0 | \sum_\mu \frac{Z_u}{|\mathbf{r} - \mathbf{s}_u + 2\pi\mu\mathbf{e}_z|} | \chi_q^\nu > \tag{17}$$

The nuclear charge density is

$$\rho_n(\mathbf{r}) = \sum_\nu \sum_i Z_i \delta(\mathbf{r} - \mathbf{s}_i - 2\pi\nu\mathbf{e}_z) \tag{18}$$

with the Fourier transform

$$\tilde{\rho_n}(\mathbf{q}) = \sum_\nu \sum_i Z_i e^{i\mathbf{q}\cdot(\mathbf{s}_i + 2\pi\nu\mathbf{e}_z)} \tag{19}$$

This can also be written

$$\tilde{\rho}_n(\mathbf{q}) = \sum_n \delta(q_z - n) W(\mathbf{q}) \tag{20}$$

with

$$W(\mathbf{q}) = \sum_i Z_i e^{i\mathbf{q}\cdot\mathbf{s}_i} \tag{21}$$

the sum being over the nuclei in a single unit cell.

The Fourier transform of the product of two Bloch functions is given by

$$\begin{aligned}\tilde{\rho}_{pq}(\mathbf{q},k,k') &= \int b_p(k',\mathbf{r})^* e^{i\mathbf{q}\cdot\mathbf{r}} b_q(k,\mathbf{r}) d\mathbf{r} \\ &= \sum_{\nu'} e^{2\pi\nu'(k-k'+q_z)i} \sum_{\nu} e^{2\pi\nu k i} \int \chi_p^0(\mathbf{r})^* e^{i\mathbf{q}\cdot\mathbf{r}} \chi_q^{\nu}(\mathbf{r}) d\mathbf{r} \\ &= \sum_n \delta(k-k'+q_z-n)\Phi_{pq}(\mathbf{q},k) \end{aligned} \tag{22}$$

where

$$\Phi_{pq}(\mathbf{q},k) = \sum_{\nu} e^{i2\pi\nu k} \int \chi_p(\mathbf{r}) e^{i\mathbf{r}\cdot\mathbf{q}}\ \chi_q(\mathbf{r}-2\pi\nu\mathbf{e}_z) d\mathbf{r} \tag{23}$$

It follows from the definition that

$$\begin{aligned}\Phi_{pq}(\mathbf{q},k)^* &= \sum_{\nu} e^{-i2\pi\nu k} \int \chi_q(\mathbf{r}-2\pi\nu\mathbf{e}_z) e^{-i\mathbf{q}\cdot\mathbf{r}} \chi_p(\mathbf{r}) d\mathbf{r} \\ &= \sum_{\nu} e^{-i2\pi\nu k} \int \chi_q(\mathbf{r}) e^{-i\mathbf{q}\cdot[\mathbf{r}+2\pi\nu\mathbf{e}_z]} \chi_p(\mathbf{r}+2\pi\nu\mathbf{e}_z) d\mathbf{r} \\ &= \sum_{\nu} e^{-i2\pi\nu(k+q_z)} \int \chi_q(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \chi_p(\mathbf{r}+2\pi\nu\mathbf{e}_z) d\mathbf{r} \\ &= \Phi_{qp}(-\mathbf{q},k+q_z). \end{aligned} \tag{24}$$

where the sign of ν has been changed in the final sum. It can also be noted that

$$\Phi_{pq}(0,k) = S_{pq}(k) \tag{25}$$

The interaction energy of two charge distribution $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ with Fourier transforms $\tilde{\rho}_1(\mathbf{q})$ and $\tilde{\rho}_2(\mathbf{q})$is given in momentum space as

$$E = \frac{1}{2\pi^2} \int \frac{1}{q^2} \tilde{\rho}_1(-\mathbf{q}) \tilde{\rho}_2(\mathbf{q}) d\mathbf{q} \tag{26}$$

It follows directly from Eq. (20) that the the matrix $V_{pq}(k)$ defined in Eq. (17) can also be written

$$V_{pq}(k) = -\frac{1}{2\pi^2} \sum_n \int \frac{1}{q^2} \delta(q_z-n) \Phi_{pq}(-\mathbf{q},k) W(\mathbf{q}) d\mathbf{q} \tag{27}$$

The direct electron-electron repulsion energy per unit cell can similarly be expressed as

$$\begin{aligned} V_{ee} &= \frac{1}{4\pi^2}\sum_{nn'}\int \frac{d\mathbf{q}}{q^2}\delta(-q_z-n)\delta(q_z-n') \\ &\times\left[\sum_{pq}\int_{\mathrm{BZ}} P_{pq}(k)\Phi_{pq}(-\mathbf{q},k)dk\right]\left[\sum_{rs}\int_{\mathrm{BZ}} P_{rs}(k')\Phi_{rs}(\mathbf{q},k')dk'\right] \\ &= \frac{1}{2}\sum_{pq}\int_{\mathrm{BZ}} P_{pq}(k)J_{pq}(k)dk \end{aligned} \tag{28}$$

where

$$J_{pq}(k) = \frac{1}{2\pi^2}\sum_{rs}\sum_{n}\int \frac{d\mathbf{q}}{q^2}\delta(q_z-n)\Phi_{pq}(-\mathbf{q},k)\int_{\mathrm{BZ}} P_{rs}(k')\Phi_{rs}(\mathbf{q},k')dk' \tag{29}$$

The integrals in Eqs. (29) and (27) are separately logarithmically divergent. However, they can be combined to give a finite result:

$$\begin{aligned} V_{pq}(k)+J_{pq}(k) = \frac{1}{2\pi^2}\sum_{n}\int \frac{d\mathbf{q}}{q^2}\delta(q_z-n)[\Phi_{pq}(-\mathbf{q},k) \\ \times\left[\int_{\mathrm{BZ}}\sum_{rs} P_{rs}(k')\Phi_{rs}(\mathbf{q},k')dk' - W(\mathbf{q})\right] \end{aligned} \tag{30}$$

The exchange energy per unit cell is given in terms of the density defined in Eq. (22) and applying Eq. (24),

$$\begin{aligned} V_{\mathrm{ex}} &= -\frac{1}{8\pi^2}\int_{\mathrm{BZ}} dk\int_{\mathrm{BZ}} dk'\sum_{pqrs} P_{pq}(k)P_{rs}(k')\int \frac{1}{q^2}\tilde{\rho}_{ps}(-\mathbf{q},k,k')\tilde{\rho}_{rq}(\mathbf{q},k',k)d\mathbf{q} \\ &= -\frac{1}{8\pi^2}\int_{\mathrm{BZ}} dk\int_{\mathrm{BZ}} dk'\sum_{pqrs} P_{pq}(k)P_{rs}(k') \\ &\times\sum_{n}\int \frac{d\mathbf{q}}{q^2}\delta(q_z-n+k'-k)\Phi_{ps}(-\mathbf{q},k)\Phi_{rq}(\mathbf{q},k') \\ &= -\frac{1}{8\pi^2}\int_{\mathrm{BZ}} dk\int_{\mathrm{BZ}} dk'\sum_{pqrs} P_{pq}(k)P_{rs}(k') \\ &\times\sum_{n}\int \frac{d\mathbf{q}}{q^2}\delta(q_z-n+k'-k)\Phi_{sp}(\mathbf{q},k')^*\Phi_{rq}(\mathbf{q},k') \\ &= \frac{1}{2}\sum_{pq}\int_{\mathrm{BZ}} P_{pq}(k)K_{pq}(k)dk \end{aligned} \tag{31}$$

where

$$K_{pq}(k) = -\frac{1}{4\pi^2}\sum_{rs}\int_{\rm BZ} P_{rs}(k') \times \sum_n \int \frac{d\mathbf{q}}{q^2}\delta(q_z - n + k' - k)\Phi_{sp}(\mathbf{q},k')^*\Phi_{rq}(\mathbf{q},k')dk' \tag{32}$$

The nuclear-nuclear repulsion energy is given by

$$U = \frac{1}{2}\sum_{uu'\mu}\frac{Z_u Z_{u'}}{|\mathbf{s}_u - \mathbf{s}_{u'} + 2\pi\mu\mathbf{e}_z|} \tag{33}$$

where the term $u = u', \mu = 0$ is excluded. This can be expressed in momentum representation as

$$\begin{aligned} U &= \frac{1}{4\pi^2}\int\frac{d\mathbf{q}}{q^2}\left[\sum_n \delta(q_z - n)W(-\mathbf{q})W(\mathbf{q}) - \sum_i Z_i^2\right] \\ &= \frac{1}{4\pi^2\omega}\sum_{pq}\int_{\rm BZ} P_{pq}(k)\Phi_{pq}(0,k)dk \\ &\times\left[\int\frac{d\mathbf{q}}{q^2}\sum_n\delta(q_z-n)W(-\mathbf{q})W(\mathbf{q}) - \pi\int\frac{d\mathbf{q}}{|\mathbf{q}|}\sum_i Z_i^2\right] \end{aligned} \tag{34}$$

This integral is again logarithmically divergent, but can be combined with $V_N/2$ to give

$$\begin{aligned} U + \frac{1}{2}V_N &= \frac{1}{4\pi^2}\sum_{pq}\int_{\rm BZ} P_{pq}(k)dk \\ &\times\sum_\mu\int\delta(q_z-\mu)\frac{1}{q^2}W(-\mathbf{q})\left[\frac{1}{\omega}\Phi_{pq}(0,k)W(\mathbf{q}) - \Phi_{pq}(\mathbf{q},k)\right]d\mathbf{q} \\ &- \pi\sum Z_i^2\int\frac{d\mathbf{q}}{|\mathbf{q}|} \end{aligned} \tag{35}$$

where Eq. (13) has been applied.

The momentum space integrals in this expression do not exist separately but are combined to give well-defined integrals for analytic results. However, in the numerical approach being developed the terms can be treated independently provided the numerical integrations on $\mathbf{q}$ are performed consistently. This leads to the cancellation of large terms, but the loss of accuracy is trivial.

III. MODIFIED EXPRESSIONS

Although the integral of Eq. (30) is well-defined, its calculation is difficult since the integrands decrease rather slowly at large $\mathbf{q}$, as q^{-5} since the factor $\delta(q_z - \mu)d\mathbf{q}/q^2$ behaves

as q^{-1} and $\Phi_{pq}(\mathbf{q}_\mu, k)$ behaves as q^{-4} since the electronic densities have a cusp-like behavior at the nuclei. For example, the transform of the function $e^{-\alpha r}$ is $2\alpha(q^2+\alpha^2)^{-2}$. (If the basis functions are GTOs the decrease is much more rapid but contributions from very large exponent parameters may still cause difficulties.)

This problem can be considerably reduced by splitting the Coulomb potential in the electron-nuclear attraction energy into the sum of a short-range piece and a long-range piece:

$$\frac{1}{r} = V_L(r) + V_S(r) \tag{36}$$

where

$$V_L(r) = \frac{1}{r} - \frac{1}{r}\left(1+\frac{\lambda r}{2}\right)e^{-\lambda r} \tag{37}$$

$$V_S(r) = \frac{1}{r}\left(1+\frac{\lambda r}{2}\right)e^{-\lambda r} \tag{38}$$

This separation is quite arbitrary, and could be modified by, for example, adding a quadratic term to the linear factor in λr to give a more rapid decrease in k.

The Fourier transform of $V_L(r)$ is

$$\tilde{V}_L(k) = \frac{4\pi}{k^2}\beta(k) \tag{39}$$

where

$$\beta(k) = \left[\frac{\lambda^2}{k^2+\lambda^2}\right]^2 \tag{40}$$

The short-range piece contributes

$$V_{S,pq}(k) = -\sum_u Z_u \sum_\nu e^{i2\pi\nu k} < \chi_p^0 | \sum_\mu V_S(\mathbf{r} - (\mathbf{s}_u + 2\pi\mu e_z)) | \chi_q^\nu > \tag{41}$$

to the electron-nuclear attraction matrix and requires the calculation of three-center integrals. With this modification, Eq. (30) becomes

$$\begin{aligned} J_{pq}(k) + V_{pq}(k) = V_{S,pq}(k) + \frac{1}{2\pi^2}\sum_\mu \int \frac{d\mathbf{q}}{q^2}\delta(q_z-\mu)\Phi_{pq}(\mathbf{q}k) \\ \times \left[\int_{\mathrm{BZ}} dk' \sum_{rs} P_{rs}(k')\Phi_{rs}(-\mathbf{q},k') - \beta(q)W(-\mathbf{q})\right] \end{aligned} \tag{42}$$

for which the integrand decreases as q^{-9} and the terms in μ decrease as μ^{-9}.

Analogously to the separation of the electron-nuclear attraction, U can be separated into the sum of short- and long-range pieces U_l and U_s by writing

$$\frac{1}{r} = U_L(r) + U_S(r) \tag{43}$$

$$U_L(r) = \frac{1}{r} - \left[\frac{1}{r} + \frac{11}{16}\lambda + \frac{3}{16}\lambda^2 r + \frac{1}{48}\lambda^3 r^2\right] e^{-\lambda r} \tag{44}$$

$$U_S(r) = \left[\frac{1}{r} + \frac{11}{16}\lambda + \frac{3}{16}\lambda^2 r + \frac{1}{48}\lambda^3 r^2\right] e^{-\lambda r} \tag{45}$$

The short-range piece, stemming from $U_S(r)$, can be calculated directly without problem.

The contribution of the long-range piece is calculated in momentum space. The Fourier transform of $U_L(r)$ is given by

$$\tilde{U}_L(k) = \frac{4\pi}{k^2}\beta(k)^2 \tag{46}$$

It can be noted that $\tilde{U}_L(k)$ behaves like k^{-10} for $k \to \infty$.

$$\begin{aligned} U_l = &\frac{1}{4\pi^2}\sum_{uu'} Z_u Z_{u'} \sum_{\mu} \int \frac{d\mathbf{q}}{q^2}\beta(q)^2 e^{-i2\pi[\mathbf{q}\cdot(\mathbf{s}_u - \mathbf{s}_{u'}) + \mu q_z]} \\ &- \frac{1}{4\pi^2}\sum_u Z_u^2 \int \frac{d\mathbf{q}}{q^2}\beta(q)^2. \end{aligned} \tag{47}$$

The term with $u = u', \mu = 0$ has been added to the first term in U_1 and subtracted out explicitly. Then

$$\begin{aligned} U_l &= \frac{1}{4\pi^2}\int \frac{d\mathbf{q}}{q^2}\sum_{\mu} e^{i2\pi\mu\mathbf{e}_z}\beta(q)^2 W(-\mathbf{q})W(\mathbf{q}) - \frac{5\lambda}{32}\sum_u Z_u^2 \\ &= \frac{1}{4\pi^2}\sum_{\mu}\int \frac{d\mathbf{q}}{q^2}\delta(q_z - \mu)\beta(q)^2 W(-\mathbf{q})W(\mathbf{q}) - \frac{5\lambda}{32}\sum_u Z_u^2 \\ &= U_{l1} + U_{l2} \end{aligned} \tag{48}$$

The integral in the first term is again logarithmically divergent, but can be combined with half V_N to obtain a well-defined result. To this end U_{l1} can be written, using Eq. (13)

$$U_{l1} = \frac{1}{4\pi^2}\frac{1}{\omega}\sum_{pq}\int_{\mathrm{BZ}} P_{pq}(k)S_{pq}(k)\sum_{\mu}\int \frac{d\mathbf{q}}{q^2}\delta(q_z - \mu)\beta(q)^2 W(-\mathbf{q})W(\mathbf{q})dk \tag{49}$$

Then

$$\begin{aligned} U_{l1} + \frac{1}{2}V_N = &\frac{1}{4\pi^2}\sum_{pq}\int_{\mathrm{BZ}} P_{pq}(k)\sum_{\mu}\int \frac{d\mathbf{q}}{q^2}\delta(q_z - \mu)\beta(q)W(-\mathbf{q}) \\ &\times \left[\frac{1}{\omega}S_{pq}(k)\beta(q)W(\mathbf{q}) - \Phi_{pq}(\mathbf{q},k)\right] dk \end{aligned} \tag{50}$$

The results should of course be independent of the value of λ in Eqs. (37)- (40). The extent to which this is not the case provides a rough indication of the effect of the truncation of the various infinite summations. It should be noted that the values of λ can be used in the calculation of $J_{pq}(k)$ and $U_l + V_N/2$ need not be the same.

IV. EXCHANGE LOGARITHMIC SINGULARITIES

The integral for $K_{pq}(k)$ determined by Eq. (32) is well-defined. However, the logarithmic singularities that occur for $\mu = 0$ and $\mu = \pm 1, k = \mp 1/2$ give rise to terms of the form $(1/2+k)\ln(1/2+k)$ and $(1/2-k)\ln(1/2-k)$ which cause numerical difficulties. To eliminate this difficulty, we define a function

$$\zeta_{pq}(k) = \sum_{rs} P_{rs}(k) S_{sp}(k)^* S_{rq}(k) \tag{51}$$

and rewrite Eq. (32) as

$$\begin{aligned} K_{pq}(k) = & -\frac{1}{4\pi^2} \sum_{rs} \int_{\mathrm{BZ}} P_{rs}(k') \sum_n \int \frac{d\mathbf{q}}{q^2} \delta(q_z - n + k' - k) \\ & \times \left[\Phi_{sp}(\mathbf{q}, k')^* \Phi_{rq}(\mathbf{q}, k') - S_{sp}(k')^* S_{rq}(k') h(\mathbf{q})^4 \right] dk' \\ & - \frac{1}{4\pi^2} \int_{\mathrm{BZ}} \sum_n \int \frac{d\mathbf{q}}{q^2} \delta(q_z - n + k' - k) \zeta_{pq}(k') h(\mathbf{q})^4 dk' \end{aligned} \tag{52}$$

where

$$h(s) = \left[\frac{\alpha^2}{s^2 + \alpha^2} \right] \tag{53}$$

The correction term to account for this requires an integral of the form

$$\begin{aligned} I(t, \alpha) &= \int_0^\infty \frac{s}{s^2 + t^2} \left[\frac{\alpha^2}{s^2 + t^2 + \alpha^2} \right]^4 ds \\ &= \frac{1}{2} \left[\ln(t^2 + \alpha^2) - \ln(t^2) - h(t) - \frac{1}{2} h(t)^2 - \frac{1}{3} h(t)^3 \right] \end{aligned} \tag{54}$$

and the correction term is

$$C_{pq}(k) = -\frac{1}{2\pi} \sum_{\mu} \int_{\mathrm{BZ}} dk' \zeta_{pq}(k') I(\mu + k - k', \alpha) \tag{55}$$

The logarithmic singularity leads to integrals of the form, in the case $\mu = 0$,

$$\begin{aligned}\int_{-1/2}^{1/2} \ln|k-k'| f(k')dk' = (1/2+k)\ln(1/2+k)\int_0^1 f(k-(1/2+k)y)dy \\ + (1/2+k)\int_0^1 \ln y f(k-(1/2+k)y)dy \\ + (1/2-k)\ln(1/2-k)\int_0^1 f(k+(1/2-k)y)dy \\ + (1/2-k)\int_0^1 \ln y f(k+(1/2-k)y)dy \end{aligned} \tag{56}$$

The integrals with the factor $\ln y$ are computed using the Gaussian integration procedure adapted for the non-standard weight function $-\ln x$ on [0,1]. The abscissae for this integration are the zeros of the $N+1$st polynomial orthogonal with respect to this weight function [16].

This result shows explicitly the terms in $(1/2+k)\ln(1/2+k)$ and $(1/2-k)\ln(1/2-k)$ in $K_{pq}(k)$. These can be separated out and integrated using the above prescription for integrands involving a logarithmic factor.

The result using this procedure should be independent of the parameter α. In fact, the result showed no dependence, at the level of 10^{-5} over a range of α. This independence also provides credibility for the numerical integration procedure applied.

V. NUMERICAL EVALUATION OF THE DENSITIES

The principal problem in the numerical approach is the evaluation of the Fourier transforms of the products as defined in Eq. (23). This requires the expansion of the product of two angular momentum functions centered at different points $\mathbf{R}_1$ and $\mathbf{R}_2$, followed by the calculation of their Fourier transforms. One approach is to expand the product in angular momentum functions centered at some intermediate point $\mathbf{R}_c$ between the centers. In the case of GTOs the choice of centers is obvious and the expansion consists of a finite number of terms (a single term for s orbitals). More generally, the expansion is infinite, and the truncation is the major source of error in the procedure. The expansion of a density about $\mathbf{R}_c$ can be expressed as

$$\rho(\mathbf{r}) = \sum_{lm} \rho_{lm}(r) Y_{lm}(\theta,\phi) \tag{57}$$

Given an expansion center, each factor can be expressed as an angular momentum expansion by obtaining the so-called Löwdin functions. The resulting series can be multiplied and the product compressed using the familiar reduction expression for products of spherical harmonics. These methods are described extensively in [1] However, an approach that avoids these rather slowly convergent intermediate expansions has recently been devised. [17].

The density functions $\Phi_{pq}(\mathbf{q}, k)$ require the Fourier transforms of the product expansions. The Fourier transform of an angular momentum function $f_{lm}(\mathbf{r}) = f(r)Y_{lm}(\hat{\mathbf{r}})$ is given by

$$\tilde{f}_{lm}(\mathbf{q}) = 4\pi i^l Y_{lm}(\hat{\mathbf{q}})\tilde{f}(q) \tag{58}$$

where

$$\tilde{f}(q) = \int_0^\infty j_l(qr)f(r)r^2 dr. \tag{59}$$

Therefore the transform of the function $\rho(\mathbf{r})$ in Eq. (57) is

$$\tilde{\rho}(\mathbf{q}) = 4\pi \sum_{lm} i^l \tilde{\rho}_{lm}(q)Y_{lm}(\theta_q, \phi_q). \tag{60}$$

If the radial coordinates in both the $\mathbf{r}$ and $\mathbf{q}$ spaces are uniform in the variables $\rho = \ln(r)$ and $\kappa = \ln(q)$, the spherical Bessel transforms $\tilde{f}$ can be computed very efficiently and very accurately [18]. This method is used to obtain the transforms of the product functions in coordinates centered at the expansion center. It is then necessary to transform to the fixed coordinate system by multiplying by $e^{i\mathbf{q}\cdot\mathbf{R}_c}$.

The calculations are made in cylindrical coordinates (Q, ϕ, q_z) for $\mathbf{q}$ and (R_c, Φ_c, Z_c) for $\mathbf{R}_c$. It is then necessary to interpolate the transforms obtained in spherical coordinates and to expand the plane wave in cylindrical coordinates. An arbitrary function is expanded as

$$\begin{aligned} f(\mathbf{q}) &= \sum_{lm} f_{lm}^{\mathrm{sph}}(q)Y_{lm}(\theta_q, \phi_q) \\ &= \sum_m f_m^{\mathrm{cyl}}(Q, q_z)e^{im\phi_q} \end{aligned} \tag{61}$$

Since $q = [Q^2 + q_z^2]^{1/2}$ and $\theta_q = \cos^{-1}(q_z/q)$,

$$f_m^{\mathrm{cyl}}(Q, q_z) = \sum_l f_{lm}^{\mathrm{sph}}([Q^2 + q_z^2]^{1/2})Y_{lm}(\cos^{-1}(q_z/q), 0) \tag{62}$$

The translation factor to the fixed coordinate system is

$$e^{i\mathbf{Q}\cdot\mathbf{R}_c} = \sum_m J_m(QR_c)e^{im(\phi-\Phi_c)}e^{iZ_c q_z} \tag{63}$$

in cylindrical coordinates. Finally, the transform of the density functions Φ in cylindrical coordinates are given by

$$\begin{aligned}\Phi(Q,\phi_q,q_z) &= 4\pi \sum_{LMm'} i^l \tilde{\rho}_{LM}([q^2+q_z^2]^{1/2}) Y_{LM}(\theta_q,0) J_{m'}(QR_c) \\ &\times e^{iZ_c q_z} e^{iM\phi} e^{im'(\phi-\Phi_c)} \\ &= \sum_m \Phi_m(Q,q_z) e^{im\phi} \end{aligned} \tag{64}$$

where

$$\Phi_m(Q,q_z) = 4\pi \sum_{LM} i^L \tilde{\rho}_{LM}([Q^2+q_z^2]^{1/2}) Y_{LM}(\theta_q,0) J_{m-M}(QR_c) e^{i(m-M)\Phi_c} e^{iZ_c q_z} \tag{65}$$

Values of $\tilde{\rho}_{LM}(q)$ are interpolated using 6-point interpolation to obtain the functions $\Phi_m(Q,q_z)$.

The short-range potential matrix elements defined in Eq. (41) are obtained by expanding each of the orbital factors in spherical harmonics about a center chosen to optimize the convergence rate of the resulting series [19]. The resulting product of the two expansions can be reduced as discussed previously. The resulting integral is of the form

$$\int V_S(|\mathbf{r}-\mathbf{R}) f_{LM}(\mathbf{r}) d\mathbf{r} = 8 Y_{LM}(\hat{\mathbf{R}}) \int_0^\infty j_L(kR) \tilde{V}_S(k) \tilde{f}_{LM}(k) k^2 dk. \tag{66}$$

The transforms $\tilde{f}_{LM}(k)$ can be accurately and efficiently obtained in logarithmic coordinates, as previously described [18].

VI. LITHIUM HYDRIDE AS A NUMERICAL EXAMPLE

The methods described above have been applied to the chain of LiH molecules in a minimal basis. The Li $2s$ orbital is quite diffuse, and therefore presents a challenge for the sum for the short range contributions of Eq. (41) and (45). On the other hand, since the nuclear charges are small, momentum space integrations should not be a problem. Results for this system and basis have been given by Flamant in her Ph.D thesis [6] and can be applied to assess the accuracy of numerical approach. The Li and H atoms are uniformly spaced, with a spacing of 3.24 a_0. The parameters for the Gaussian orbitals are given in Table I.

The maximum value of ν in the evaluation of the functions $\Phi(\mathbf{q},k)$ defined in Eq. (23), $\nu_{\max} = 4$. The maximum of n in Eq. (30), $n_{\max} = 24$. The maximum of μ in Eq. (41),

TABLE I. Gaussian orbital parameters for the LiH case.

Li 1 s		Li 2s		H 1s	
ζ	C	ζ	C	ζ	C
16.11957	0.1543290	1.652210	-0.05994475	3.425251	0.1543290
2.936201	0.5353281	0.1003278	0.5960385	0.6239137	0.5353281
0.7946505	0.4446345	0.03851733	0.4581786	0.1688554	0.4446345

$\mu_{\max} = 5$. Evidently, if λ is large, $\mu_{\max}$ can be fairly small, but since $\tilde{V}_L(k)$ will have large k components, $n_{\max}$ will need to be large, and conversely.

Results for the matrix elements of $V_{pq}(k) + J_{pq}(k)$ for several values of λ are given in Table II and compared with those obtained by Flamant. The results for the sum of the nuclear attraction energy, the direct electron-electron repulsion energy and the nuclear-nuclear repulsion energy, denoted by $U + V + J$ which should also be independent of λ are also given. It seen that the results are consistent at the level of 1 mH across the table, but in some cases are not in quite as good agreement with those of Flamant.

In future articles, results for the exchange energy, total energy and the single-particle spectra will be reported, together with applications using basis functions of higher quality.

Acknowledgments

This research was supported by the Natural Sciences and Engineering Research Council of Canada and the facilities of the Shared Hierarchical Academic Research Computing Network.

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TABLE II. Real part of the matrix elements of $V_{pq}(k) + J_{pq}(k)$ for k=0, 0.25, and 0.5. The labels 1,2,3 refer to Li 1s, Li 2s and H 1s respectively. The values of the sum of the nuclear attraction energy and the direct electron-electron energy are also given.

p q	IF	$\lambda = 0.25$	$\lambda = 0.5$	$\lambda = 1.0$	$\lambda = 2.0$	$\lambda = 5.0$
			k=0			
1 1	-5.06208	-5.06198	-5.06208	-5.06208	-5.06208	-5.06208
1 2	-0.46051	-0.46038	-0.46041	-0.46041	-0.46042	-0.46042
1 3	-0.18688	-0.18686	-0.18687	-0.18687	-0.18687	-0.18687
2 2	-0.26984	-0.26901	-0.26959	-0.26979	-0.26988	-0.27004
2 3	-0.18167	-0.18120	-0.18136	-0.18141	-0.18144	-0.18151
3 3	-0.44768	-0.44750	-0.44761	-0.44762	-0.44762	-0.44761
			$k = 0.25$			
1 1	-5.06207	-5.06198	-5.06208	-5.06208	-5.06208	-5.06208
1 2	-0.37512	-0.37517	-0.37519	-0.37519	-0.37519	-0.37519
1 3	-0.09344	-0.09343	-0.09344	-0.09344	-0.09344	-0.09344
2 2	-0.18493	-0.18512	-0.18484	-0.18464	-0.18456	-0.18453
2 3	-0.08479	-0.08494	-0.08492	-0.08488	-0.08486	-0.08487
3 3	-0.44046	-0.44032	-0.44043	-0.44043	-0.44043	-0.44043
			$k = 0.5$			
1 1	-5.06208	-5.06198	-5.06208	-5.06208	-5.06208	-5.06208
1 2	-0.29217	-0.29223	-0.29225	-0.29225	-0.29225	-0.29225
1 3	0	0.00000	0.00000	0.00000	0.00000	0.00000
2 2	-0.11340	-0.11333	-0.11374	-0.11394	-0.11401	-0.11392
2 3	0	0.00011	0.00007	0.00002	0.00000	-0.00001
3 3	-0.43330	-0.43314	-0.43325	-0.43325	-0.43325	-0.43326
			$U + V + J$			

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