Hartree-Fock polymer band-structure calculations with general atomic functions

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The momentum-space formulation of the Hartree-Fock equations for the linear chain of hydrogen atoms is studied using purely numerical methods to evaluate the necessary multicenter integrals. Modifications of the formulation to improve the convergence properties of the summations for the direct potential energy and the numerical treatment of the logarithmic singularity in the exchange potential energy are described. The feasibility of such calculations is illustrated by applying the methods using Slater orbitals and linear combinations of Gaussian orbitals. [S0163-1829(97)09604-5]

I. INTRODUCTION

To a very large extent, first-principles electronic structure calculations rely on bases of atomic Gaussian-type functions (GTO's) and large scale computer packages such as GAUSSIAN 94,[1] PLH-93,[2] and CRYSTAL92 (Ref. 3) are widely used for carrying out molecular and crystal structure calculations. However, deficiencies in these calculations may result from truncations coupled with the wrong asymptotic properties of the Gaussian form as discussed for example by Davidson and Feller.[4] Efforts to correct this situation mainly consist of designing larger expansions of Gaussian functions with parameters selected to match specific properties: total energy, electric and magnetic responses, molecular interactions, etc.[5] Enlarging basis sets, however, leads to additional problems such as linear dependences, which can rapidly become serious. In the case of extended systems, this problem is drastically amplified by its connection with the convergence of lattice sums.[6,7] In practice, problems arise as instabilities in the SCF convergence steps, unphysical values of the energy bands, etc. It may happen that lattice summations are not converged to sufficient accuracy, leading to errors that arise from linear dependences that are reminiscent of basis set overcompleteness. These problems become more severe for systems with narrow band gaps, particularly metallic systems. Attempts to improve on the quality of basis sets for extended systems thus cannot be separated from the problem of the convergence of lattice sums. In a recent study[8] using Gaussian 1s orbitals of an alternating chain of Li molecules, with a band gap of 2.5 eV, it was found that converged results for the exchange energy could not be obtained using the standard program PLH93.

In this paper we initiate a study of the feasibility of computing electronic structures of linear periodic systems as a model of polymers using methods that are largely numerical. With rapid advances in computer technology, it is becoming possible to carry out molecular calculations using orbitals that are given purely numerically,[9] thereby avoiding the less than satisfactory representation provided by GTO's. The problem investigated here is the calculation of the Hartree-Fock electronic structure of the hypothetical system of a linear chain of uniformly spaced H atoms $(H)_x$ with one Slater function centered on each nuclear site. The results are compared with increasingly large expansions of GTO's. We choose to work within the framework of the Fourier space method of Harris and Monkhorst[10] as formulated for model polymers by Delhalle and Harris[11] (to be referred to as DH) owing to its convenience for dealing with the critical aspect of carrying lattice summations to convergence within the Hartree-Fock approximation as discussed by Delhalle *et al.*[12]

The momentum-space representation of the Hartree-Fock equations for a one-dimensional chain[11] will be reviewed in the next section. In Sec. III two modifications of these equations to improve the numerical properties will be described. One of these is a splitting of the direct potential energy into two terms, one of which requires the evaluation of a screened electron-electron repulsion energy in direct space, and the other is a summation in momentum space for which the convergence rate is improved. The second modification involves the exchange potential energy and is constructed to improve the numerical treatment of the logarithmic singularity. The expansions of the various quantities (wave functions and densities) in spherical coordinates are described in Sec. IV. Sections VI and VII describe in detail the numerical aspects of the calculation, and the results of applying the method to the cases that the single atomic orbital on each site is a single GTO, a Slater orbital, and a linear combination of GTO's.

II. MATHEMATICAL FORMULATION

The Hamiltonian for the $(H)_x$ system, which will be considered to be a linear chain of N atoms with an internuclear spacing d and periodic boundary conditions, is, in atomic units,

$$H=\sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2+V_n(\mathbf{r}_i)\right]+\sum_{i<j=1}^{N}|\mathbf{r}_i-\mathbf{r}_j|^{-1}+U, \quad (1)$$

where $\mathbf{r}_i$ is the position vector of electron i. $V_n(\mathbf{r}_i)$ is the nuclear attraction potential energy of electron i given by

$$V_n(\mathbf{r}_i)=-\sum_{\mu=-N/2}^{N/2}|\mathbf{r}_i-\mu\mathbf{d}|^{-1} \quad (2)$$

where $\mathbf{d}$ denotes a vector of length d in the z direction. U is the nuclear-nuclear repulsion energy, given by

$$U=\sum_{\mu=-N/2}^{N/2}\sum_{\mu'=-N/2,\ \mu'\neq\mu}^{N/2}|(\mu-\mu')d|^{-1}. \quad (3)$$

An immediate difficulty is that the sums in Eqs. (1)–(3) are separately divergent in the limit $N\to\infty$ since the energy of the system is infinite and it is the energy per site that is of interest. The formulation in DH has been constructed to overcome this problem.

The Hartree-Fock wave function is the Slater determinant formed from Bloch functions $b(k,\mathbf{r})$ defined by

$$b(k,\mathbf{r})=\sum_{\mu=-N/2}^{N/2}e^{2\pi i\mu k}\chi(\mathbf{r}-\mu\mathbf{d}), \quad (4)$$

where $k=j/N$, $j=0,\ldots,(N-1)$. The function $\chi(\mathbf{r})$ can be chosen to minimize the energy; typically it is a linear combination of GTO's, but in the present calculation it can be arbitrary. The Bloch functions satisfy

$$\int b(k',\mathbf{r})^*b(k,\mathbf{r})d\mathbf{r}=N\delta_{k,k'}S(k), \quad (5)$$

where

$$S(k)=\sum_{\nu=-N/2}^{N/2}e^{2\pi i\nu k}\int\chi(\mathbf{r})^*\chi(\mathbf{r}-\nu\mathbf{d})d\mathbf{r} \quad (6)$$

and should be multiplied by $N^{-1/2}S(k)^{-1/2}$ to normalize them.

It is shown in DH [Eq. (10)] that the total energy per site is given by

$$E=\int_{\mathrm{BZ}}P(k)\left[T(k)+V(k)+\frac{1}{2}J(k)+\frac{1}{2}K(k)\right]dk+U/N. \quad (7)$$

The function $P(k)=2/S(k)$ for the occupied states and 0 for the unoccupied states and BZ denotes the Brillouin zone. Since the single-particle states are doubly occupied, a factor of 2 is included. The Brillouin zone is the interval $[0,\ 2\pi/d]$ or, equivalently, $[-\pi/d,\ \pi/d]$. Since only half the Brillouin zone is occupied, the integral is effectively over the interval $[-\pi/2d,\ \pi/2d]$. It will be convenient to choose the length unit such that $d=2\pi$. It is then necessary to multiply the kinetic energy by C^2 and the potential energy terms by C, where $C=2\pi a_0/d$ and a_0 is the Bohr radius. Integrations in k are then on the interval $[-1/4,\ 1/4]$. Then

$$\int_{\mathrm{BZ}}P(k)S(k)dk=1. \quad (8)$$

The kinetic energy function $T(k)$ is given by [DH, Eq. (26)]

$$T(k)=-\frac{C^2}{2}\sum_{\nu=-N/2}^{N/2}e^{2\pi i\nu k}\int\chi(\mathbf{r})^*\nabla^2\chi(\mathbf{r}-\nu\mathbf{d})d\mathbf{r}. \quad (9)$$

The function $V(k)$, which stems from the nuclear attraction energy, can be expressed as

$$V(k)=-C\sum_{\mu=-N/2}^{N/2}\sum_{\nu=-N/2}^{N/2}e^{2\pi i\nu k}\times\int\chi(\mathbf{r})^*|\mathbf{r}-\mu\mathbf{d}|^{-1}\chi(\mathbf{r}-\nu\mathbf{d})d\mathbf{r}. \quad (10)$$

This result can also be expressed in momentum representation as

$$V(k)=-\frac{C}{2\pi^2}\sum_{\mu=-N/2}^{N/2}\int e^{i\mu\mathbf{q}\cdot\mathbf{d}}\frac{1}{q^2}\Phi(\mathbf{q},k)d\mathbf{q}, \quad (11)$$

where

$$\Phi(\mathbf{q},k)=\sum_{\nu=-N/2}^{N/2}e^{2\pi i\nu k}\int e^{-i\mathbf{q}\cdot\mathbf{r}}\chi(\mathbf{r})^*\chi(\mathbf{r}-\nu\mathbf{d})d\mathbf{r} \quad (12)$$

is the Fourier transform of

$$Q(\mathbf{r},k)=\sum_{\nu=-N/2}^{N/2}e^{2\pi i\nu k}\chi(\mathbf{r})^*\chi(\mathbf{r}-\nu\mathbf{d}). \quad (13)$$

It should be noted that

$$S(k)=\Phi(0,k). \quad (14)$$

The function $J(k)$, which is the direct electron-electron repulsion energy, is given by

$$J(k)=\frac{C}{2\pi^2}\int_{\mathrm{BZ}}dk'P(k')\times\sum_{\mu=-N/2}^{N/2}\int\frac{d\mathbf{q}}{q^2}e^{i\mu\mathbf{q}\cdot\mathbf{d}}\Phi(\mathbf{q},k)\Phi(-\mathbf{q},k'), \quad (15)$$

which can be identified as the interaction energy of charge distributions given by Eq. (13) separated by μd.

As discussed in DH, the separate contributions given by $V(k)$ and $J(k)$ are divergent, and it is necessary to combine one-half $V(k)$ with $J(k)/2$, and one-half with U/N, where U/N is also expressed as an integral on k. Equations (11) and (15) can then be combined to give

$$\frac{1}{2}[V(k)+J(k)]=\frac{C}{4\pi^2}\sum_{\mu=-N/2}^{N/2}\int\frac{d\mathbf{q}}{q^2}e^{i\mu\mathbf{q}\cdot\mathbf{d}}\Phi(\mathbf{q},k)\times\left[\int_{\mathrm{BZ}}dk'P(k')\Phi(-\mathbf{q},k')-1\right]. \quad (16)$$

The sum on μ is

$$\sum_{\mu=-N/2}^{N/2} e^{i\mu q_z d}, \tag{17}$$

which in the limit $N\to\infty$ can be expressed as

$$\sum_{\mu=-N/2}^{N/2} e^{2\pi i\mu q_z} \to \sum_{n=-\infty}^{\infty} \delta(q_z-n). \tag{18}$$

It is then possible to replace the q_z integration in Eq. (16) by a summation and write

$$\frac{1}{2}[V(k)+J(k)]=\frac{C}{4\pi^2}\sum_{n=-\infty}^{\infty}\int \frac{d\mathbf{u}}{u^2+n^2}\Phi(\mathbf{u}_n,k) \times\left[\int_{\mathrm{BZ}} dk' P(k')\Phi(-\mathbf{u}_n,k')-1\right]. \tag{19}$$

The integration on $\mathbf{u}$ in this expression is twofold in the plane perpendicular to the chain with z coordinate n; the argument $\mathbf{u}_n$ indicates the point with coordinates (u_x,u_y,n). The integral of the $n=0$ term in this result would be divergent if the two terms in the brackets were treated separately; because of Eq. (14) the two terms cancel for $\mathbf{u}_0\to 0$.

The function $K(k)$, which arises from the exchange potential energy, is given by

$$K(k)=-\frac{C}{4\pi^2}\int_{\mathrm{BZ}} dk' P(k') \times \sum_{\mu=-N/2}^{N/2}\int \frac{d\mathbf{q}}{q^2} e^{i\mu[\mathbf{q}\cdot\mathbf{d}+2\pi(k-k')]}\Phi(\mathbf{q},k)\Phi(-\mathbf{q},k'). \tag{20}$$

In the limit $N\to\infty$ this becomes, again applying Eq. (18),

$$K(k)=-\frac{C}{4\pi^2}\int_{\mathrm{BZ}} dk' P(k') \times\sum_{n=-\infty}^{\infty}\int \frac{d\mathbf{u}}{u^2+(n+k-k')^2}\Phi(\mathbf{u}_{n+k-k'},k) \times\Phi(-\mathbf{u}_{n+k-k'},k'). \tag{21}$$

The integration on $\mathbf{u}$ in this expression is twofold in the plane perpendicular to the chain with z coordinate $n+k-k'$; the argument $\mathbf{u}_{n+k-k'}$ indicates the point with coordinates $(u_x,\ u_y,\ n+k-k')$.

These results do not completely remove the divergences, since the energy terms U/N and the integral of $V(k)/2$ must be combined. To this end DH write

$$\begin{aligned}U/N&=\frac{C}{N}\sum_{\mu=-N/2}^{N/2}\ \sum_{\mu'=-N/2,\ \mu'\neq\mu}^{N/2}|(\mu-\mu')d|^{-1}\\
&=\frac{C}{2\pi^2 N}\int\sum_{\mu=-N/2}^{N/2}\ \sum_{\mu'=-N/2,\ \mu'\neq\mu}^{N/2} e^{i(\mu-\mu')\mathbf{q}\cdot\mathbf{d}}\frac{1}{q^2}d\mathbf{q}\\
&=\frac{C}{2\pi^2}\int\left[\frac{1}{N}\left(\sum_{\mu=-N/2}^{N/2}e^{i\mu\mathbf{q}\cdot\mathbf{d}}\right)^2-1\right]\frac{1}{q^2}d\mathbf{q}\\
&\to\frac{C}{2\pi^2}\int\left[\sum_{n=-\infty}^{\infty}\delta(q_z-n)-1\right]\frac{1}{q^2}d\mathbf{q}\\
&=\frac{C}{4\pi^2}\int_{\mathrm{BZ}}P(k)S(k)dk\int\left[\sum_{n=-\infty}^{\infty}\delta(q_z-n)-1\right]\frac{1}{q^2}d\mathbf{q},\end{aligned} \tag{22}$$

where we have used the identity

$$\frac{1}{N}\left[\sum_{\mu=-N/2}^{N/2}e^{2\pi i\mu q_z}\right]^2\to\sum_{n=-\infty}^{\infty}\delta(q_z-n). \tag{23}$$

It is now possible to write the terms in $V(k)/2$ and U/N in the total energy as

$$\frac{1}{2}\int_{\mathrm{BZ}}P(k)V(k)dk+\frac{U}{N} =\frac{C}{4\pi^2}\int_{\mathrm{BZ}}dkP(k)\left[\int\left(\sum_{n=-\infty}^{\infty}\frac{S(k)-\Phi(\mathbf{u}_n,k)}{u^2+n^2} -\frac{\pi S(k)}{u}\right)d\mathbf{u}\right], \tag{24}$$

where again the integration on $\mathbf{u}$ is twofold in the plane perpendicular to the chain. We have also used the simple identity

$$\int_{-\infty}^{\infty}\frac{1}{q^2}dq_z=\frac{\pi}{u},\quad u^2=q_x^2+q_y^2. \tag{25}$$

The apparent divergence of the integral in Eq. (24) at $\mathbf{u}=\mathbf{0}$ is removed because of Eq. (14). The integral is apparently also divergent at large $\mathbf{u}$. This divergence is canceled, however, by virtue of the identity

$$\sum_{n=-\infty}^{\infty}\frac{1}{u^2+n^2}=\frac{\pi}{u}\coth(\pi u). \tag{26}$$

Equation (24) then becomes

$$\frac{1}{2}\int_{\mathrm{BZ}}P(k)V(k)dk+\frac{U}{N}=\frac{C}{4\pi^2}\int_{\mathrm{BZ}}dkP(k)\times\left[\int\left(\frac{2\pi}{u(e^{2\pi u}-1)}S(k)-\sum_{n=-\infty}^{\infty}\frac{1}{u_n^2}\Phi(\mathbf{u}_n,k)\right)d\mathbf{u}\right]. \quad (27)$$

III. MODIFIED EQUATIONS

Equations (7), (9), (16), (21), and (24) determine the energy per atom of the system. Equations (16) and (21) present problems for numerical calculations, and these will be addressed in this section.

If the basis function $\chi(r)$ is an s-wave Slater orbital, the Fourier transform $\Phi(\mathbf{q},k)$ behaves like q^{-4} for $q\to\infty$. The integrand in the $\mathbf{q}$ integration in Eq. (16) then decreases like q^{-4} and this is reflected in a slow convergence of the sum in Eq. (19). In fact, carrying out the $\mathbf{u}$ integration for a fixed n and $\Phi(\mathbf{u}_n,k)=(u^2+n^2)^{-2}$ shows that the terms must decrease like n^{-4}, which is not very satisfactory. If $\chi(r)$ is a linear combination of GTO's, this problem would apparently be less severe. However, to represent even approximately the cusplike behavior of the electronic wave functions close to the nuclei, it is necessary to include short-range GTO's and these will require integration to large $|\mathbf{q}|$ values. In other words, physically the electron wave function has large momentum components stemming from the singular nuclear Coulomb potential, and these should be included to obtain a complete description of the system.

This problem has been reduced by writing Eq. (11) as

$$V(k)=V_1(k)+V_2(k), \quad (28)$$

where

$$V_1(k)=-\frac{C}{2\pi^2}\sum_{\mu=-N/2}^{N/2}\int e^{i\mu\mathbf{q}\cdot\mathbf{d}}\frac{\lambda^4}{q^2(q^2+\lambda^2)^2}\Phi(\mathbf{q},k)d\mathbf{q}, \quad (29)$$

$$V_2(k)=-\frac{C}{2\pi^2}\sum_{\mu=-N/2}^{N/2}\int e^{i\mu\mathbf{q}\cdot\mathbf{d}}\frac{q^2+2\lambda^2}{(q^2+\lambda^2)^2}\Phi(\mathbf{q},k)d\mathbf{q}. \quad (30)$$

It is now possible to write $V_2(k)$ in position space, in analogy to the transition from Eq. (10) to Eq. (11),

$$V_2(k)=-C\sum_{\mu=-N/2}^{N/2}\sum_{\nu=-N/2}^{N/2}e^{2\pi i\nu k}\times\int\chi(\mathbf{r})^*V_s(\mathbf{r}-\mu\mathbf{d})\chi(\mathbf{r}-\nu\mathbf{d})d\mathbf{r}, \quad (31)$$

where

$$V_s(r)=\frac{1}{r}\left(1+\frac{\lambda r}{2}\right)e^{-\lambda r} \quad (32)$$

is a screened Coulomb potential. It may be noted that the long-range Coulomb potential has been replaced by the screened potential in Eq. (32). There is therefore no problem in principle with the summation on μ, which should now converge exponentially, rather than diverge.

With this modification the term in Eq. (16) arising from $V_1(k)$ becomes

$$\frac{1}{2}[V_1(k)+J(k)]=\frac{C}{4\pi^2}\sum_{\mu=-N/2}^{N/2}\int\frac{d\mathbf{q}}{q^2}e^{i\mu\mathbf{q}\cdot\mathbf{d}}\Phi(\mathbf{q},k)\times\left[\int_{\mathrm{BZ}}dk'P(k')\Phi(-\mathbf{q},k')-\frac{\lambda^4}{(q^2+\lambda^2)^2}\right] \quad (33)$$

and similarly Eq. (19) becomes

$$\frac{1}{2}[V_1(k)+J(k)]=\frac{C}{4\pi^2}\sum_{n=-\infty}^{\infty}\int\frac{d\mathbf{u}}{u_n^2}\Phi(\mathbf{u}_n,k)\times\left[\int_{\mathrm{BZ}}dk'P(k')\Phi(-\mathbf{u}_n,k')-\frac{\lambda^4}{(u_n^2+\lambda^2)^2}\right]. \quad (34)$$

The terms in this last summation should now decrease like n^{-8} rather than n^{-4} because of the more rapid decrease of the screened Coulomb potential in momentum space.

The divergence problems associated with the long-range of the Coulomb potential are removed from Eq. (31) since the potential V_s is of short range. Evaluation of $V_2(k)$ does require the evaluation of three-center integrals. However, these reduce to two-center integrals that are readily calculated if two of the centers are the same, and are very small, because of the short-range nature of the potential, otherwise.

The term in Eq. (27) arising from $V_1(k)$ is

$$\frac{1}{2}\int_{\mathrm{BZ}}P(k)V_1(k)dk+\frac{U}{N}=\frac{C}{4\pi^2}\int_{\mathrm{BZ}}dkP(k)\left[\int\left(\frac{2\pi S(k)}{u(e^{2\pi u}-1)}-\sum_{n=-\infty}^{\infty}\frac{\lambda^4\Phi(\mathbf{u}_n,k)}{u_n^2(u_n^2+\lambda^2)^2}\right)d\mathbf{u}\right]. \quad (35)$$

It is seen that the convergence properties of the sum on n in this equation are also improved by the splitting of the nuclear attraction potential.

A numerical difficulty arises in computing the exchange energies detemined by Eq. (20). The $\mathbf{q}$ integration in the $n=0$ term leads to a factor of the form $\ln|k'-k|$ in the k' integral, which is therefore improper. The integral exists, but its numerical evaluation is computationally difficult. This problem can be reduced in a simple way by subtracting from the factor $\Phi(\mathbf{q},k)\Phi(-\mathbf{q},k')$ a term $S(k)S(k')f(\mathbf{q})$ in the $n=0$ term. This then eliminates the singularity at $\mathbf{q}=\mathbf{0}$ in the $\mathbf{q}$ integration. The function $f(\mathbf{q})$ can be chosen arbitrarily provided the $\mathbf{q}$ integral converges for $\mathbf{q}\to\infty$. In the present calculation we have chosen

$$f(\mathbf{q})=\frac{a^8}{(q^2+a^2)^4}. \quad (36)$$

A corresponding term is then subtracted from the $n=0$ term in Eq. (21). This leads to a correction term in $K(k)$, which can be written, since $P(k')S(k')=2$,

$$\Delta(k)=-\frac{C}{2\pi^2}S(k)\int_{-1/4}^{1/4}dk'\int\frac{d\mathbf{u}}{u^2+(k-k')^2}f(\mathbf{u}_{k-k'}). \tag{37}$$

Again, the $\mathbf{u}$ integration is twofold and $\mathbf{u}_{k-k'}$ denotes the vector $(u_x, u_y, k-k')$. The integral can be computed in cylindrical coordinates. Changing variables to $s=|\mathbf{u}_{k-k'}|$ gives, since $udu=sds$,

$$\Delta(k)=-\frac{C}{\pi}S(k)\int_{-1/4}^{1/4}dk'\int_{|k-k'|}^{\infty}\frac{1}{s}f(s)ds. \tag{38}$$

It can then be shown that

$$\Delta(k)=-\frac{C}{\pi}S(k)[F(1/4+k)+F(1/4-k)], \tag{39}$$

where

$$F(x)=x\int_x^{\infty}\frac{1}{s}f(s)ds+\int_0^x f(s)ds. \tag{40}$$

For the function f defined in Eq. (36),

$$F(x)=-\frac{1}{24}\frac{xa^4}{(x^2+a^2)^2}-\frac{3}{16}\frac{xa^2}{x^2+a^2}-x\ln\frac{x}{\sqrt{x^2+a^2}}+\frac{5}{16}a\arctan\left(\frac{x}{a}\right). \tag{41}$$

The contribution of $\Delta(k)$ to the total energy in Eq. (7) can be calculated analytically as

$$\begin{aligned}E_c&=-\frac{1}{2}\int_{-1/4}^{1/4}P(k)\Delta(k)dk\\&=-\frac{C}{\pi}\int_{-1/4}^{1/4}[F(1/4+k)+F(1/4-k)]dk\\&=-\frac{2C}{\pi}\int_0^{1/2}F(k)dk.\end{aligned} \tag{42}$$

In the present calculation

$$\int F(x)dx=-\frac{1}{48}\frac{a^2x^2}{a^2+x^2}-\frac{x^2}{2}\ln\frac{x}{\sqrt{x^2+a^2}}+\frac{5}{16}ax\arctan\left(\frac{x}{a}\right), \tag{43}$$

which is to be evaluated at $x=1/2$.

It should be noted that the term in $F(x)$ in $x\ln x$ leads to the well-known logarithmic singularity in $K'(k)$ at the top of the Fermi surface,[13] in this case at $k=1/4$.

An extension of this treatment to less singular terms in $\ln|k-k'|$ will be discussed in Sec. V.

IV. SPHERICAL HARMONIC EXPANSIONS

In order to carry out the numerical calculations, it is necessary to express the various functions in spherical coordinates, that is, to expand them in terms of spherical harmonics. In this section the relevant relations will be developed and the numerical methods will be described.

A basic problem is to expand an angular momentum eigenfunction centered at one point, $\mathbf{a}$, in terms of angular momentum eigenfunctions centered at another point, the origin. This expansion can be written[14] in the form

$$f_{lm}(\mathbf{r}-\mathbf{a})=\sum_{LM}\sum_{L'M'}f_{LL'}(r,a)(-1)^m\times\begin{pmatrix}L & L' & l\\ -M & -M' & m\end{pmatrix}Y_{LM}(\hat{a})Y_{L'M'}(\hat{r}), \tag{44}$$

where

$$f_{lm}(\mathbf{r})=f_l(r)Y_{lm}(\hat{r}) \tag{45}$$

and

$$f_{LL'}(r,a)=i^{l+L-L'}[4\pi(2l+1)(2L+1)(2L'+1)]^{1/2}\times\begin{pmatrix}L & L' & l\\ 0 & 0 & 0\end{pmatrix}\times\frac{2}{\pi}\int_0^{\infty}j_L(ka)j_{L'}(kr)\tilde{f}_l(k)k^2dk. \tag{46}$$

Here $\tilde{f}_l(k)$ is the spherical Hankel transform of $f_l(r)$:

$$\tilde{f}_l(k)=\int_0^{\infty}j_l(kr)f_l(r)r^2dr. \tag{47}$$

In the present case, $\mathbf{a}$ is in the z direction and $l=0$, so that the relations simplify to (omitting the factor Y_{00} from f)

$$f(|\mathbf{r}-\mathbf{a}|)=\sum_{L=0}^{\infty}(2L+1)P_L(\cos\theta)f_L(r,a), \tag{48}$$

$$f_L(r,a)=\frac{2}{\pi}\int_0^{\infty}j_L(ka)j_L(kr)\tilde{f}(k)k^2dk, \tag{49}$$

$$\tilde{f}(k)=\int_0^{\infty}j_0(kr)f(r)r^2dr. \tag{50}$$

The familiar plane wave expansion

$$e^{i\mathbf{q}\cdot\mathbf{r}}=4\pi\sum_{LM}i^LY_{LM}(\hat{r})^*Y_{LM}(\hat{q})j_L(qr) \tag{51}$$

applied in Eq. (12) leads to the expansion of $\Phi(\mathbf{q},k)$ in spherical coordinates:

$$\Phi(\mathbf{q},k)=\sum_{L=0}^{\infty}(2L+1)P_L(\cos\theta_q)\Phi_L(q,k), \tag{52}$$

where

$$\Phi_L(q,k)=4\pi\delta_{L0}\int_0^\infty j_0(qr)\chi(r)^2r^2dr+8\pi\sum_{\nu=1}^{\infty}\cos(2\pi(\nu k-L/4))\times\int_0^\infty j_L(qr)\chi_L(r,2\pi\nu)\chi(r)r^2dr, \quad (53)$$

where terms in ν and $-\nu$ have been combined. The function $\chi_L(r,2\pi\nu)$ comes from the translation of the basis orbital to the site $2\pi\nu$. It should be noted that

$$\Phi_L(q,-k)=(-1)^L\Phi_L(q,k). \quad (54)$$

The twofold integrations on $\mathbf{u}$ that occur in Eqs. (21), (34), and (35) are calculated in cylindrical coordinates by changing variables to $s=|\mathbf{u}_n|$, $|n|\leq s<\infty$, in the same way that Eq. (38) was obtained. With this change of variable,

$$\frac{d\mathbf{u}}{u_n^2}\to 2\pi\frac{ds}{s} \quad (55)$$

and

$$P_L(\cos\theta_q)=P_L(n/s). \quad (56)$$

Then Eq. (34) becomes

$$\frac{1}{2}[V_1(k)+J(k)]=\frac{C}{2\pi}\sum_{n=-\infty}^{\infty}\int_{|n|}^{\infty}\frac{ds}{s}\sum_{L\ \mathrm{even}}(2L+1)P_L(n/s)\Phi_L(s,k)\times\left[\int_{\mathrm{BZ}}P(k')\sum_{L'\ \mathrm{even}}(2L'+1)P_{L'}(n/s)\Phi_{L'}(s,k')dk'-\frac{\lambda^4}{(s^2+\lambda^2)^2}\right]. \quad (57)$$

In a similar way, Eq. (35) becomes

$$\frac{1}{2}\int_{\mathrm{BZ}}P(k)V_1(k)dk+\frac{U}{N}=\frac{C}{2\pi}\int_{\mathrm{BZ}}P(k)dk\int_0^\infty\left(\frac{2\pi}{e^{2\pi s}-1}S(k)-\frac{\lambda^4}{s(s^2+\lambda^2)^2}\Phi_0(s,k)\right)ds-\frac{C}{2\pi}\sum_{n=0}^{\infty}(2-\delta_{n0})\sum_{L\ \mathrm{even}}\int_{\mathrm{BZ}}P(k)dk\int_{|n|}^{\infty}\frac{\lambda^4}{s(s^2+\lambda^2)^2}(2L+1)P_L(n/s)\Phi_L(s,k)ds, \quad (58)$$

where the term $n=L=0$ is excluded from the summation, and Eq. (21) becomes

$$K(k)=-\frac{C}{2\pi}\int_{\mathrm{BZ}}P(k')dk'\sum_{n=-\infty}^{\infty}\sum_{L=0}^{\infty}\sum_{L'=0}^{\infty}(-1)^{L'}(2L+1)(2L'+1)\int_{|n+k-k'|}^{\infty}\frac{1}{s}P_L[(n+k-k')/s]P_{L'}[(n+k-k')/s]\times\left[\Phi_L(s,k)\Phi_{L'}(s,k')-\delta_{L0}\delta_{L'0}\delta_{n0}\frac{a^8}{(s^2+a^2)^4}S(k)S(k')\right]ds+\Delta(k), \quad (59)$$

where the final term in the square brackets comes from the counterterm which has been included to remove the logarithmic singularity.

V. NUMERICAL METHODS

The numerical methods have been based to a large extent on an accurate and efficient method for computing spherical Hankel transforms,[15,16] as used in Eqs. (49), (50), and (53). In this method, the functions $f(r)$ and $\tilde{f}(k)$ are defined on logarithmic meshes, i.e., uniformly in variables $\rho=\ln r$, $\kappa=\ln k$. In these coordinates, it is possible to compute the transform by two applications of a numerical Fourier transform, which can be carried out very efficiently using the FFT algorithm. This approach furthermore yields accurate results at large values of the transform variable, which are very difficult to obtain using more conventional methods.

The ρ and κ values are given by $\rho_i=\rho_{\min}+(i-1)\delta\rho$, $\kappa_i=\kappa_{\min}+(i-1)\delta\rho$, $i=1,\ldots,N$, $N=2^n$. Typically, N will be 128 or 256. This method was used to compute all the spherical Hankel transforms, although it is true that the functions $f_L(r,a)$ defined in Eq. (50) can be obtained analytically for the Slater orbitals used here.

The infinite integrals on the intervals (n,∞) and $(n+k-k',\infty)$ required in Eqs. (57), (58), and (59) have been computed by translating them to the interval $(0,\infty)$. The integral on the interval (0,1) is computed using Gauss-Legendre integration on n_{GL} points and the integral on $(1,\infty)$ is transformed to $(0,\infty)$ by making the change of variable $s=e^t$ and using Gauss-Laguerre integration, again with n_{GL} points. It is necessary, however, to interpolate the functions $\Phi_L(s,k)$ from the logarithmic mesh to the new integration points. This has been done using six-point polynomial interpolation.

As remarked above, the function $V_2(k)$, as given in Eq. (31), is computed by expanding the third factor about the common center if two of the centers coincide, i.e., if $\mu=0$, $\nu=0$, or $\mu=\nu$. If the three centers are all different, $\chi(\mathbf{r})$ and

$\chi(\mathbf{r}-\nu\mathbf{d})$ are expanded about the nuclear center, i.e., $\mu\mathbf{d}$, using Eq. (48). In the first case, only the term $L=0$ contributes to the integral, and in the second case, the resulting sum on L converges rapidly.

The integrations on k and k' have been computed using Gauss-Legendre integration on n_k points on the interval $[-1/4, 1/4]$. A problem arises with this, however, in that the nonanalytic term in $|k-k'|$ cannot be handled properly by Gaussian integration, despite the fact that it is multiplied by a function that vanishes at $k=k'$. These logarithmic terms arise from the highest degree terms in the Legendre polynomials in Eq. (59), which are, for $n=0$,

$$\frac{(2L-1)!!}{L!}\left[\frac{k-k'}{s}\right]^L.$$

Therefore, Eq. (59) has been modified to

$$\begin{aligned}K(k)=&-\frac{C}{2\pi}\int_{\rm BZ}P(k')dk'\sum_{n=-\infty}^{\infty}\sum_{L=0}^{\infty}\sum_{L'=0}^{\infty}(-1)^{L'}(2L+1)\\&\times(2L'+1)\int_{|n+k-k'|}^{\infty}\frac{1}{s}\bigg(P_L[(n+k-k')/s]P_{L'}\\&\times[(n+k-k')/s]\Phi_L(s,k)\Phi_{L'}(s,k')\\&-\delta_{n0}(k-k')^{L+L'}\psi_L(k)\psi_{L'}(k')\frac{a^8}{(s^2+a^2)^4}\bigg)ds\\&+\Delta(k),\end{aligned}\tag{60}$$

where

$$\begin{aligned}\psi_L(k)=&\frac{(2L-1)!!}{L!}\lim_{s\to 0}s^{-L}\Phi_L(s,k)\\=&4\pi\delta_{L0}\int_0^\infty\chi(r)^2r^2dr+\frac{8\pi}{(2L+1)L!}\\&\times\sum_{\nu=1}^{\infty}\cos(2\pi(\nu k-L/4))\int_0^\infty r^L\chi_L(r,2\pi\nu)\\&\times\chi(r)r^2dr.\end{aligned}\tag{61}$$

The counterterms involve

$$\begin{aligned}\int_{|k-k'|}^{\infty}\frac{a^8}{s(s^2+a^2)^4}ds=&-\frac{1}{6}Q^3-\frac{1}{4}Q^2-\frac{1}{2}Q-\frac{1}{2}\ln Q+\ln a\\&-\ln|k-k'|,\end{aligned}\tag{62}$$

where

$$Q=\frac{a^2}{a^2+|k-k'|^2}.$$

All the terms but the last are analytic in k and k' and are included with the original terms in the numerical integration.

The term in $\ln|k-k'|$ in the total energy in Eq. (7) is treated separately by approximating the product $P(k)\psi_L(k)$ as a polynomial in k and evaluating the resulting integral analytically using

TABLE I. Dependence of results on n_s.

n_s	T	V_d	V_x	E
8	0.474 461	−0.648 750	−0.298 578	−0.472 867
10	″	−0.648 753	−0.298 592	−0.472 884
12	″	−0.648 746	−0.298 594	−0.472 879
14	″	−0.648 747	″	−0.472 880

$$\begin{aligned}&\int_{-1/4}^{1/4}\int_{-1/4}^{1/4}k^m k'^n(k-k')^\lambda\ln|k-k'|dk\,dk'\\&=\frac{1}{2^{2m+2n+\lambda+1}}\sum_{pq}(-1)^{\lambda+q}\binom{n}{p}\binom{m+n-p}{q}\\&\times\frac{2^{p+q}}{(p+\lambda+1)(p+q+\lambda+2)}\\&\times\left[-\ln 2-\frac{1}{p+\lambda+1}-\frac{1}{p+q+\lambda+2}\right]\end{aligned}\tag{63}$$

if $m+n+\lambda$ is even and is zero if $m+n+\lambda$ is odd. The polynomial approximation is obtained by expanding $P(k)\psi_L(k)$ in Legendre polynomials in $4k$ using Gaussian integration on $[-1/4, 1/4]$. Cancellation errors proved to be a problem in the calculation of these counterterms for large values of L; however, it was found that it was sufficient to include only terms with $L,L'\leqslant 2$ to overcome the problem with the numerical integration.

VI. NUMERICAL RESULTS

In this section we present results of the application of these methods for the cases that $\chi(r)$ is a linear combination of GTO's and a Slater orbital. The former is much more tractable numerically, since the Gaussian functions are smoother and decrease much more rapidly than Slater functions in both position and momentum space.

Initially we look at the single GTO case considered by DH:

$$\chi(r)=e^{-\zeta r^2},\tag{64}$$

with $\zeta=0.362\,08$, and an internuclear spacing of 1.915. The numerical accuracy is governed by a large number of parameters. These are the parameters that govern the numerical meshes: $N=2^n$, the number of mesh points in the ρ and κ meshes; n_k, the number of mesh points in $[-1/4, 1/4]$ in the

TABLE II. Dependence of results on n_k.

n_k	T	V_d	V_x	E
4	0.474 455	−0.648 745	−0.298 486	−0.472 776
6	0.474 461	−0.648 747	−0.298 595	−0.472 881
8	″	″	−0.298 594	−0.472 880
10	″	″	″	″

TABLE III. Dependence of results on $\nu_{\max}$, $L_{\max}$, and $n_{\max}$.

$\nu_{\max}$	$L_{\max}$	$n_{\max}$	T	V_d	V_x	E
1	2	0	0.454 271	−0.645 731	−0.289 169	−0.480 628
1	2	1	″	−0.645 823	−0.289 185	−0.480 737
1	2	2	″	″	″	″
2	2	2	0.472 145	−0.648 044	−0.297 213	−0.473 111
3	2	2	0.474 470	−0.648 098	−0.297 400	−0.471 028
4	2	2	0.474 461	−0.648 099	−0.297 399	−0.471 037
5	2	2	0.474 460	−0.648 099	−0.297 399	−0.471 038
5	3	2	″	−0.648 181	−0.298 511	−0.472 231
5	4	2	″	−0.648 782	−0.298 584	−0.472 906
5	5	2	″	−0.648 784	−0.298 598	−0.472 921
5	6	2	″	−0.648 747	−0.298 594	−0.472 880
5	7	2	″	−0.648 747	−0.298 592	−0.472 879
5	8	2	″	−0.648 736	−0.298 591	−0.472 867
5	9	2	″	″	″	″
5	10	2	″	−0.648 734	″	−0.472 865

k and k' meshes; n_s the number of mesh points in the integrations on s; and parameters that govern the truncations of the infinite summations: $\nu_{\max}$, the maximum of μ and ν in Eqs. (30) and (53); $L_{\max}$, the maximum of L in angular momentum sums; $n_{\max}$, the maximum of n in Eqs. (57), (58), and (59).

We consider first the dependence of the results on the numerical meshes. The results that are given are for truncation parameters $L_{\max}=6$, $\nu_{\max}=4$, and $n_{\max}=2$. The quantities computed are the kinetic energy T, the direct potential energy V_d, the exchange energy V_x, and the total energy E.

Results obtained for $N=128$ and $N=256$ with $n_s=20$ and $n_k=10$ differed by at most 10^{-6} for V_d. Presumably, then, results obtained with $N=256$ are valid to 10^{-6}; since the times required for the two calculations were virtually the same, all the calculations have been made with $N=256$.

Table I shows the dependence of the results on n_s, with $n_k=20$. It is evident that results accurate to 10^{-6} can be obtained with $n_s\approx 12$. Table II shows the dependence of the results on n_k, the number of points in the integrations on k and k'. It is seen that six-figure accuracy can be obtained with a very modest value of $n_k\approx 10$. This excellent result requires the careful treatment of the terms in $\ln|k-k'|$ described above; calculations without this treatment did not yield comparable accuracy with much larger values of n_k.

Table III shows the effect of truncating the infinite summations on the accuracy. It is observed that 10^{-6} accuracy is evidently obtained including only terms $n=0$ and ± 1 in the summation, and that comparable accuracy is obtained by limiting the sums on μ and ν in Eqs. (53) and (31) by $\nu_{\max}=4$. The results also indicate that the convergence of the sums on L is slower, although the summation for the exchange energy could apparently be restricted by $L_{\max}=6$ to obtain 10^{-6} accuracy, and by $L_{\max}=4$ to obtain 10^{-4} accuracy. It may be noted that the sums in Eqs. (57) and (58) scale like $L_{\max}$ whereas the calculation of Eq. (59) scales like $L_{\max}^2$. It would therefore be more efficient to use a larger value of $L_{\max}$ in the first two than in the third. It would apparently also be quite feasible to use a convergence acceleration technique on the L' and L sums in Eq. (57) and the L sum in Eq. (58).

TABLE IV. Dependence of results on n_s in the Slater orbital case.

n_s	T	V_d	V_x	E
8	0.548 187	−0.776 814	−0.300 003	−0.528 574
10	″	−0.777 080	−0.299 916	−0.528 809
12	″	−0.777 030	−0.299 929	−0.528 773
14	″	−0.777 035	−0.299 929	−0.528 776
16	″	−0.777 034	−0.299 928	−0.528 775

TABLE V. Dependence of results on n_k in the Slater orbital case.

n_k	T	V_d	V_x	E
4	0.548 021	−0.776 975	−0.314 386	−0.534 340
6	0.548 192	−0.777 036	−0.299 832	−0.528 677
8	0.548 187	−0.777 034	−0.299 932	−0.528 779
10	″	″	−0.299 928	−0.528 775

An accurate value of $E=-0.472\,139$ has been calculated by Delhalle *et al.*[12] for the above $\chi(r)$ and $d=2.0$. The corresponding numerical result, computed with $N=256$, $n_s=14$, $n_k=10$, $\nu_{\max}=5$, $L_{\max}=10$, and $n_{\max}=1$ is $E=-0.472\,141$. The small discrepancy apparently arises largely from the truncation of the angular momentum sums.

Similar calculations have been carried out for the Slater orbital

$$\chi(r)=e^{-\zeta r}, \tag{65}$$

where $\zeta=1.156$. Because of the long-range behavior of the Slater orbital in momentum space, it is difficult to obtain accuracies comparable to those obtained for the GTO's. For example, for $N=128$, 256, and 512, values of V_d of

TABLE VI. Dependence of results on $\nu_{\max}$, $L_{\max}$, and $n_{\max}$ in the Slater orbital case.

$\nu_{\max}$	$L_{\max}$	$n_{\max}$	T	V_d	V_x	E
2	2	2	0.536 184	−0.771 438	−0.296 150	−0.531 404
3	2	2	0.549 269	−0.775 991	−0.298 961	−0.525 683
4	2	2	0.548 187	−0.775 578	−0.298 623	−0.526 014
5	2	2	0.547 857	−0.775 495	−0.298 546	−0.526 148
6	2	2	0.547 871	−0.775 470	−0.298 550	−0.526 150
6	2	3	″	−0.775 472	″	−0.526 152
6	2	4	″	−0.775 473	″	−0.526 152
6	3	4	″	−0.775 617	−0.299 952	−0.527 699
6	4	4	″	−0.776 844	−0.299 921	−0.528 894
6	5	4	″	−0.776 858	−0.299 935	−0.528 923
6	6	4	″	−0.776 936	−0.299 866	−0.528 932
6	7	4	″	″	−0.299 840	−0.528 908
6	8	4	″	−0.776 902	−0.299 814	−0.528 846
6	9	4	″	″	−0.299 703	−0.528 835
6	10	4	″	−0.776 874	−0.299 794	−0.528 797

TABLE VII. Total energy E, kinetic energy T, direct potential energy V_d, exchange potential energy V_x, the single-particle energy at 0, $\epsilon(0)$, and the single-particle energy at the top of the Fermi surface, $\epsilon(1/4)$, for approximations to the H 1s orbital given as a linear combination of N GTO's. The results are calculated for $d=1.8861$ and $\zeta=1.1253$.

N	E	T	V_d	V_x	$\epsilon(0)$	$\epsilon(1/4)$
1	−0.472 606	0.469 104	−0.643 740	−0.297 970	−0.6731	−0.0779
2	−0.514 150	0.503 001	−0.721 506	−0.295 645	−0.7216	−0.1000
3	−0.525 423	0.524 186	−0.752 618	−0.296 991	−0.7279	−0.1133
4	−0.528 021	0.528 108	−0.759 021	−0.297 109	−0.7294	−0.1165
5	−0.529 042	0.529 044	−0.760 940	−0.297 146	−0.7298	−0.1203
∞	−0.529 471	0.529 479	−0.761 806	−0.297 144	−0.7300	−0.1305

−0.776 797, −0.776 511, and −0.776 558 are obtained. (The values of T and V_x are much less dependent on N.) These results suggest that the errors for $N=512$ may be of the order of 5×10^{-6}. The calculations discussed below have been carried out with this value of N. Again, there is very little increase in computing time in going from $N=256$ to $N=512$, so that if memory limitations are not a consideration, this presents no difficulty.

Table IV presents results comparable to Table I, showing the dependence on n_s, and Table V, comparable to Table II, shows the dependence on n_k. These results indicate that for the integrations on s, and the integrations on k and k', the Slater orbital does not present significantly greater difficulty.

Table VI shows the dependence of the results on $\nu_{\max}$, $L_{\max}$, and $n_{\max}$. It is observed that it is necessary to go to much larger values of $\nu_{\max}$ in order to obtain accuracies comparable to the GTO case. The reason for this is clear: $\nu_{\max}$ governs the summations in Eqs. (31) and (53) and overlaps of Slater orbital are significant at much larger separations than are those of the GTO's. It is apparent also that the convergence of the angular momentum summations is slower than in the GTO case. These summations are governed by the behavior of the orbitals in momentum space, for which the Slater orbitals fall off much more slowly than the GTO's.

The energy minimum computed with the parameters as given in the last line of Table VI and $n_k=12$ is −0.529 471, obtained at a spacing $d=1.8861$ for $\zeta=1.1252$. The kinetic, direct potential, and exchange potential energies are, respectively, 0.529 479, −0.761 806, and −0.297 144. Since these results are obtained optimizing on both the spacing and ζ, the virial theorem should be satisfied exactly; the ratio T/E is in fact −1.000 015.

We have also carried out the calculation at the energy minimum with the H 1s orbital approximated by linear combinations of from 1 to 5 GTO's as given by Stewart.[17] Results for the energy, the three contributions to the energy, and the single-particle energy at 0 and at the top of the Fermi surface are given in Table VII. The percentage deviations from the accurate results have been found to be comparable to the percentage deviations of the approximate orbital as given by Stewart.

VII. DISCUSSION

The results presented in Tables I–III indicate that for GTO's the numerical methods discussed can give results accurate to one part in 10^{-6} with fairly modest calculational effort. Analytic methods are undoubtedly more economical; however, for linear combinations of n GTO's, the computational effort behaves like n^4, the purely numerical approach may become competitive for basis functions contracted on even a rather small number of GTO's.

The situation is more difficult for the Slater orbital calculation, for which the numerical approach can apparently give reliable results at the 10^{-4} level, but is open to some question at the 10^{-6} level. Certain improvements can probably be made in the approach. An obvious one is to introduce a convergence acceleration technique in the angular momentum sums in the direct Coulomb energy. It may also be noted that the computational effort in computing V_d is proportional to $L_{\max}$, whereas for V_x it is proportional to $L_{\max}^2$ so that it is possible to include much larger L values in the sum.

It is important to remember, however, that the problems with the Slater orbital arise because it gives a better representation of the actual single-particle wave function; i.e., if the parameters are chosen to conform to the nuclear charge, it can represent the cusp at the nucleus properly, and it gives a more reasonable representation of the wave function at large momenta. Another viewpoint is that although the energies are calculated much more accurately in the GTO case, they are actually in error by more than 0.05 a.u.

An important question is whether these methods can be extended to realistic polymers. Both the separation of $V(k)$ into $V_1(k)$ and $V_2(k)$ and the elimination of the logarithmic singularity in $K(k)$ can apparently be generalized to more complicated systems. A limitation that may be important is in data storage; the quantities $\Phi_L(s,k)$ require a large amount of memory that scales with the square of the number of basis orbitals. Another difficulty can arise for nuclei of large Z, for which the range of the orbitals in momentum space becomes large, and the calculation of the functions $f_L(r,a)$ defined in Eq. (49) becomes difficult, essentially because of the oscillatory behavior of the spherical Bessel functions. The problem of extending the methods to more complex chain systems will be considered in future studies.

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