PHYSICAL REVIEW A **82**, 052518 (2010)

Numerical solution of the Hartree-Fock equation in molecular geometries

James D. Talman[*]
Department of Applied Mathematics, University of Western Ontario, London, Ontario, Canada N6A 5B7

(Received 7 September 2010; published 23 November 2010)

Solutions of the restricted Hartree-Fock equations are obtained for small molecules using a combination of variationally optimized atomic orbitals centered on the nuclei and corrections computed on a Cartesian mesh. The problem of finding the corrections is reduced to the problem of solving the Hartree-Fock equations with inhomogeneous terms. An iterative method is developed in which the equation is treated as an inhomogeneous Helmholtz equation with the potential terms transferred to the inhomogeneous term. Terms in the equation that arise from rapid variation of the orbitals in the neighborhoods of the nuclei are treated analytically. The Helmholtz equation can then be solved using a fast Fourier transform method. Results for a number of small molecules that are accurate at the millihartree level are presented. The method for solving the inhomogeneous Hartree-Fock equation should be applicable to other problems of quantum chemistry.

DOI: 10.1103/PhysRevA.82.052518 PACS number(s): 31.15.A−, 31.15.xr

I. INTRODUCTION

The purpose of this article is to present a method for the numerical solution of the Hartree-Fock equations appropriate for the geometry of arbitrary molecules. Although the discussion is for the Hartree-Fock equations, the approach is equally applicable to other problems such as the Kohn-Sham equations of density functional theory. Major problems that attend the problem of electronic molecular orbitals are the facts that there is no natural coordinate system for the problem and that the potentials are singular at the nuclei so that the orbitals and densities have rapidly varying short-range behavior at the nuclei.

Contemporary molecular structure calculations are almost entirely based on the expansion of molecular orbitals in terms of Gaussian basis functions [Gaussian-type orbitals (GTOs)]. The reason is, of course, that the required multicenter integrals are almost trivial to obtain for GTOs and extremely difficult to obtain for other functional forms. That is not to say that GTOs are perfectly suited for the problem. Since electron densities are strongly peaked at the nuclei, a superposition of several GTOs is required for a satisfactory representation of densities and single-particle orbitals. This requirement for superpositions reduces the efficiency of the method and, in the case of superpositions of large numbers of functions, can cause instabilities.

Finite-difference approximate methods have been extensively and successfully used in atomic problems [1]. These approaches are successful because they are carried out in a spherical coordinate system centered at the nucleus. In addition, the mesh points are not uniform in the radial coordinate since the wave function is concentrated at, and most rapidly varying at, the nucleus. This simplification is not generally available in molecular geometries, although prolate spheroidal coordinates are usefully applied for diatomic molecules [2].

Various approaches have been taken to try to overcome this problem. For example, an adaptive grid method can be applied, with mesh points taken to be more dense in the vicinity of the nuclei [3]. Recently, Shiozaki and Hirata [4] have discussed a method for solution of the Hartree-Fock equation using a method introduced by Becke and Dickson [5]. This scheme is based on overlapping spheres centered at the nuclei, with integration points in the intersections assigned weights less than 1. However, this approach does not completely resolve the problem of the slow convergence of the angular momentum summations. Harrison and colleagues have employed, and obtained impressive results using, a multiresolution method and wavelets to represent the Poisson and Helmholtz kernels for the single-particle problem and the Hartree-Fock equations [6,7].

In the approach followed here, the problems associated with rapid variations at the nuclei are overcome in a variety of ways. Approximate molecular orbitals are constructed as linear combinations of basis atomic orbitals, as in the usual molecular orbitals (MO)–linear combination of atomic orbitals (LCAO) approach. These atomic orbitals are defined numerically on a radial mesh and are variationally optimized to minimize the Hartree-Fock energy. The correct behavior of the orbitals at the nuclei is therefore described. These atomic orbital basis functions are obtained using methods developed previously by the author [8]. The essential problems that arise are the calculation of the various multicenter integrals required for the energy calculation and the construction and solution of the variational equations for the orbitals. This approach yields Hartree-Fock results for small molecules close to the Hartree-Fock minimum, using minimal basis sets, that is, $1s$ on H and $1s$, $2s$, and $2p$ on the first-row atoms. However, it is difficult to improve on these results by adding polarization orbitals since the convergence in the angular momentum expansions is slow.

Subsequent to the construction of the molecular orbitals, corrections are constructed in spatial Cartesian coordinates. This calculation requires the inversion of the Hartree-Fock single-particle operator $\mathcal{F} - e_k$. This is effected iteratively by transferring the potential energy terms in the Hartree-Fock operator to the inhomogeneous term. The resulting Helmholtz inhomogeneous equation can then be solved numerically on the Cartesian mesh using the fast Fourier transform (FFT) method. A significant finding is that the iterative procedure converges satisfactorily.

In the neighborhood of a nucleus of charge Z_n at $\mathbf{R}_n$, a molecular orbital $\psi_k(\mathbf{r})$ behaves as $\psi_k(\mathbf{R}_n)e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}$, that is, as a Slater orbital. It will be shown in detail that it is possible to exploit this known behavior to improve the accuracy by treating such terms analytically.

---

[*] jtalman@uwo.ca

The approach described here is related to one proposed by Alexander and colleagues [9,10]. However, the present advantage is that the difficult structure of the wave functions in the neighborhood of the nuclei is described by the radial basis functions, and the increments are less rapidly varying.

An approach in which the behavior at the nuclei is treated by superpositions of Gaussian orbitals and the overall behavior is treated by the finite element method has been described by Yamakawa and Hyodo [11] and applied to small molecules within the local density approximation for exchange and correlation. A similar approach has been taken by Pahl and Handy [12] and applied within the Hartree-Fock approximation to the water molecule. In this method, basis functions are constructed within finite spheres centered on each nucleus and are augmented by plane waves.

In the second section, the theory underlying the Hartree-Fock approximation and the MO-LCAO approach will be reviewed. Section III will discuss aspects of the multicenter integral problem for arbitrary orbitals and the orbital optimization procedure. Section IV will develop the equations for the molecular orbital corrections and the correction to the total energy. The iterative procedure for the inversion of the Schrödinger-like operator is explained in Sec. IV. Spatial integrations for various matrix elements are complicated by the singular nuclear potentials, and methods to remove this problem analytically are proposed. The numerical methods applied will be described in Sec. V, and the factors that affect the accuracy will be discussed in a somewhat heuristic way. Results for a number of small molecules are presented in Sec. VI and compared with other, largely Gaussian-type orbital results. Possible avenues for future work and possible other extensions are described in the last section.

II. HARTREE-FOCK EQUATIONS

The molecular wave function in the Hartree-Fock approximation is a Slater determinant formed from orthonormal single-particle wave functions ψ_k. It is convenient to define functionals V and W by

$$V[\rho](\mathbf{r}) = \int \frac{1}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}')d\mathbf{r}', \tag{1}$$

$$\begin{aligned} W[f,g] &= \int f(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}g(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \\ &= \int f(\mathbf{r})V[g](\mathbf{r})d\mathbf{r}. \end{aligned} \tag{2}$$

The functional V is the potential stemming from a density ρ.

The total energy E, apart from nuclear-nuclear repulsion, in the restricted Hartree-Fock approximation is given by

$$\begin{aligned} E &= \sum_k \langle\psi_k|T+V_{\mathrm{N}}|\psi_k\rangle \\ &\quad + \sum_{kl}\left(\frac{1}{2}W\left[\psi_k^2,\psi_l^2\right] - \frac{1}{4}W[\psi_k\psi_l,\psi_k\psi_l]\right), \end{aligned} \tag{3}$$

where

$$\langle\psi_k|T+V_{\mathrm{N}}|\psi_k\rangle = \int \psi_k(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{N}}(\mathbf{r})\right]\psi_k(\mathbf{r})d\mathbf{r}, \tag{4}$$

$$V_{\mathrm{N}}(\mathbf{r}) = -\sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}. \tag{5}$$

The sums in Eq. (3) are over the occupied orbitals, and the sum in Eq. (5) is over the nuclei. Normally, a factor of 2 should be included with each summation.

The Hartree-Fock equations are

$$\mathcal{F}\psi_k(\mathbf{r}) = e_k\psi_k(\mathbf{r}), \tag{6}$$

where

$$\mathcal{F}\psi_k(\mathbf{r}) = \frac{1}{2}\frac{\delta E}{\delta\psi_k(\mathbf{r})}. \tag{7}$$

Explicitly, $\mathcal{F}$ operating on a spin-orbital f is defined by

$$\begin{aligned} [\mathcal{F}f](\mathbf{r}) &= \left[-\frac{1}{2}\nabla^2 + V_{\mathrm{N}}(\mathbf{r})\right]f(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r})f(\mathbf{r}) \\ &\quad - \sum_l \psi_l(\mathbf{r})V[\psi_l f](\mathbf{r}), \end{aligned} \tag{8}$$

where

$$V_{\mathrm{H}}(\mathbf{r}) = \sum_l V\left[\psi_l^2\right](\mathbf{r}) \tag{9}$$

and the sum on l is on the occupied orbitals, and ψ_l and f have the same spin quantum number in the exchange term.

In the standard MO-LCAO approach, approximate Hartree-Fock orbitals ψ_k are constructed as linear combinations of atomic basis functions χ_i defined by

$$\chi_i(\mathbf{r}+\mathbf{R}_i) = \chi_{0i}(r)Y_{l_i m_i}(\hat{\mathbf{r}}), \tag{10}$$

where χ_{i0} is the radial factor and $\mathbf{R}_i$ is usually a nuclear coordinate; that is, χ_i is an angular momentum wave function in the coordinate system centered at $\mathbf{R}_i$. The molecular orbitals are orthonormalized linear combinations of the atomic orbitals:

$$\phi_j(\mathbf{r}) = \sum_j d_{ij}\chi_i(\mathbf{r}). \tag{11}$$

The solutions of the Hartree-Fock equations are in turn linear combinations of the molecular orbitals:

$$\begin{aligned} \psi_k &= \sum_j u_{jk}\phi_j, \\ &= \sum_{ij} d_{ij}u_{jk}\chi_i, \\ &= \sum_i c_{ki}\chi_i. \end{aligned} \tag{12}$$

The coefficients c_{ki} in Eq. (12) are obtained from the solution of the Hall-Roothaan equation:

$$\mathbf{F}\mathbf{v}^{(k)} = e_k\Omega\mathbf{v}^{(k)}, \tag{13}$$

with the matrices $\mathbf{F}$ and Ω defined by

$$f_{ij} = \langle\chi_i|\mathcal{F}|\chi_j\rangle, \tag{14}$$

$$\omega_{ij} = \langle\chi_i|\chi_j\rangle. \tag{15}$$

The expansion coefficients are then given by $c_{ki} = \mathbf{v}_i^{(k)}$. This leads to the problem of computing the matrix elements of $\mathbf{F}$

and the overlap integals $\langle \chi_i | \chi_j \rangle$. The matrix equation can also be written as follows:

$$\langle \psi_k | \mathcal{F} | \psi_l \rangle = \delta_{kl} e_k. \tag{16}$$

In most molecular calculations, the radial factors χ_{oi} are constructed as linear combinations of Gaussian orbitals. In the present approach, the usually contracted Gaussian orbitals are replaced by functions in which the radial factors are defined numerically on a radial mesh uniformly spaced in the variable $\rho = \ln r$. This leads to a double optimization process, that is, the solution of the Hall-Roothaan equations and the optimization of the radial factors. This set of functions will be referred to as the atomic orbital basis.

III. ORBITAL OPTIMIZATION

Electronic molecular structure calculations using numerically defined orbitals is a multifaceted problem requiring the evaluation of the necessary multicenter integrals, translation of angular momentum wave functions centered at one point to a new point, expansion of products of angular momentum wave functions in terms of such functions, and solving the variational problem for the radial factors. In this section, the approaches to these problems followed here will be summarized.

The translation of an angular momentum wave function can be expressed [13] as

$$\begin{aligned} f_{lm}(\mathbf{r} - \mathbf{R}) = \sum_{LL'MM'} (-1)^m \begin{pmatrix} L & L' & l \\ M & M' & -m \end{pmatrix} \\ \times F_{LL'}(r, R) Y_{LM}(\mathbf{r}) Y_{L'M'}(\mathbf{R}), \end{aligned} \tag{17}$$

where

$$\begin{aligned} F_{LL'}(r,R) = i^{l+L'-L} \left[\frac{(2L+1)(2L'+1)}{4\pi(2l+1)} \right]^{1/2} \begin{pmatrix} L & L' & l \\ 0 & 0 & 0 \end{pmatrix} \\ \times \frac{2}{\pi} \int_0^\infty j_L(kr) j_{L'}(kR) \tilde{f}(k) k^2 dk, \end{aligned} \tag{18}$$

$$\tilde{f}(k) = \int_0^\infty j_l(kr) f(r) r^2 dr. \tag{19}$$

The functions $F_{LL'}(r,R)$ can be computed using an efficient approach applying Gaussian integration [14].

The product of two expansions of the form of Eq. (17) about a third center can be reduced using the familiar identity

$$\begin{aligned} Y_{l_1 m_1}(\hat{\mathbf{r}}) Y_{l_2 m_2}(\hat{\mathbf{r}}) = \sum_{LM} (-1)^M \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)} \right]^{1/2} \\ \times \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} Y_{LM}(\hat{\mathbf{r}}). \end{aligned} \tag{20}$$

However, if the three centers are collinear, a better method that avoids the rather slow convergence of the expansions is available [15].

The nuclear attraction three-center integrals are obtained by expanding each of the atomic orbitals and the nuclear potential about a third center, as described by Eq. (17). The Coulomb factor is expanded by the familiar Laplace expansion. The expansion center is chosen to optimize the convergence rate of the resulting summation [16]. The three sums are truncated at a common value $L_{\mathrm{N,max}}$.

The electron-electron repulsion integrals are obtained by expanding each product of orbitals about an intermediate center:

$$\chi^{(1)}_{l_1 m_1}(\mathbf{r} - \mathbf{R}_1) \chi^{(2)}_{l_2 m_2}(\mathbf{r} - \mathbf{R}_2) = \sum_{\Lambda\sigma} F_{\Lambda\sigma}(\mathbf{r} - \mathbf{R}_c), \tag{21}$$

where $F_{\Lambda\sigma}$ is again an angular momentum eigenfunction. The four-center integrals can be efficiently computed in momentum space by initially computing and storing the spherical Bessel transforms $\tilde{F}_{\Lambda\sigma}$. The expansions in Eq. (21) are truncated at a maximum Λ_{max}; $\Lambda \leqslant \Lambda_{\mathrm{max}}$. If the expansion centers coincide, the resulting integral will be relatively large, but there are many fewer terms in the summation. Therefore a large value of Λ_{max}, $\Lambda^{(1)}_{\mathrm{max}}$, can be chosen. Conversely, if the expansion centers differ, a smaller value, $\Lambda^{(2)}_{\mathrm{max}}$, is chosen. Details of the procedure can be found in [15]. The numerical spherical Bessel transforms are obtained using a procedure adapted for the logarithmic meshes that is efficient and gives valid results at large values of the transform variable [17].

The optimization problem being followed is twofold. The coefficients in the basis function are optimized by solving the Hall-Roothaan equation [Eq. (13)]. The numerically defined basis functions are then to be determined by constructing and solving an Euler-Lagrange equation, again with the constraint that the ψ_k should be orthonormal. There is some redundancy in this, however, from arbitrary factors in the basis functions. This is removed by requiring that the basis functions be normalized.

The energy, expressed in terms of the χ_i, is

$$\begin{aligned} E = \sum_{ij} w_{ij} \langle \chi_i | T + V_{\mathrm{N}} | \chi_j \rangle \\ + \sum_{ijkl} w_{ij} w_{kl} \left(\frac{1}{2} W[\chi_i \chi_j, \chi_k \chi_l] - \frac{1}{4} W[\chi_k \chi_j, \chi_i \chi_l] \right), \end{aligned} \tag{22}$$

where the w_{ij} are the elements of the density matrix obtained from the solution of Eq. (13):

$$w_{ij} = \sum_k o_k c_{ki} c_{kj}, \tag{23}$$

where $o_k = 2$ if orbital k is occupied, and 0 otherwise. We therefore consider a Lagrangian

$$\mathcal{L} = E - \sum_{kl} \lambda_{kl} \langle \psi_k | \psi_l \rangle, \tag{24}$$

$$\frac{\delta \mathcal{L}}{\chi_k(\mathbf{r})} = 0. \tag{25}$$

The variational derivative of E with respect to χ_i is given by

$$\frac{\delta E}{\delta \chi_i(\mathbf{r})} = 2 \sum_j w_{ij} \mathcal{F} \chi_j(\mathbf{r}). \tag{26}$$

The variational equations are therefore

$$\sum_j w_{ij} \mathcal{F} \chi_j - \sum_j \gamma_{ij} \chi_j = 0, \tag{27}$$

where $\mathcal{F}\chi_j$ is defined in Eq. (8). The multipliers γ_{ij} are determined from the equation

$$\sum_j w_{ij} f_{jk} = \sum_j \gamma_{ij}\omega_{jk}, \tag{28}$$

where f_{jk} and ω_{jk} are defined in Eqs. (14) and (15).

Equations (27) are coupled. They are solved separating the diagonal terms in w_{ij} and treating them as inhomogeneous equations with the off-diagonal terms being the inhomogeneity. This is feasible since the density matrix is positive semidefinite. The equations then take the form

$$[\mathcal{F}-\gamma_{ii}]\chi_i(\mathbf{r}) = -\frac{1}{w_{ii}}\sum_{i\neq j} w_{ij}[\mathcal{F}-\gamma_{ij}]\chi_j(\mathbf{r}). \tag{29}$$

The procedure is then to expand the terms in Eq. (29) about $\mathbf{R}_i$ using Eqs. (17) and (20). Since χ_i in these coordinates is of the form $\chi_i(r)Y_{l_i m_i}(\hat{\mathbf{r}})$, only terms proportional to $\chi_i(r)Y_{l_i m_i}(\hat{\mathbf{r}})$ contribute to the inhomogeneous term. However, terms proportional to χ_i are separated out and retained to define an effective central potential, in order to reduce the inhomogeneous terms.

In computing the inhomogeneous terms, the nuclear attraction potentials and the orbitals are expanded about $\mathbf{R}_i$. These expansions are truncated at a common value $L_{\mathrm{max,opt}}$.

The variational equation is then a Schrödinger-like inhomogeneous equation:

$$-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d\chi_i}{dr} + \frac{l_i(l_i+1)}{2r^2}\chi_i(r) + [V(r)-\lambda_i]\chi_i(r) = Z_i(r), \tag{30}$$

where $V(r)$ stems from the terms proportional to χ_i and $Z_i(r)$ contains the remaining terms. This is a form of eigenvalue problem, with the eigenvalue λ_i being determined by the constraint that χ_i should be normalized. The procedure is describe in more detail in Ref. [8]. It should be mentioned that the total energy calculation is independent of the optimization procedure.

IV. ORBITAL CORRECTIONS

In this section, the equations for the corrections to the orbital wave functions and energies will be derived, and the approach to their solution will be described. The approximate solutions and single-particle energies will be denoted by ψ_k and ϵ_k. The Hartree-Fock operator constructed from the ψ_k will be denoted by $\mathcal{F}_0$. The error in the approximate solution is denoted by ϵ_k; that is,

$$[\mathcal{F}_0 - e_k]\psi_k = \epsilon_k. \tag{31}$$

It can be assumed that ϵ_k is orthogonal to ψ_k. The correction to the orbitals and the energy eigenvalues will be denoted by $\delta\psi_k$ and δe_k. It can also be assumed that $\delta\psi_k$ is orthogonal to ψ_l for all l.

The corrections must satisfy

$$(\mathcal{F} - e_k - \delta e_k)(\psi_k + \delta\psi_k) = 0. \tag{32}$$

The equations can be combined to give

$$(\mathcal{F}_0 - e_k)\delta\psi_k = -\epsilon_k - (\delta\mathcal{F} - \delta e_k)[\psi_k + \delta\psi_k], \tag{33}$$

where $\mathcal{F}$ is constructed from the exact solutions and $\delta\mathcal{F} = \mathcal{F} - \mathcal{F}_0$. Taking the product with ψ_k gives

$$\delta e_k = \langle\delta\psi_k|\epsilon_k\rangle + \langle\psi_k|\delta\mathcal{F}|\psi_k + \delta\psi_k\rangle. \tag{34}$$

The term $\delta\mathcal{F}[\psi_k + \delta\psi_k]$ arises from the increment in the direct and exchange potentials stemming from the $\delta\psi_k$.

Equation (33) can be rewritten as

$$\begin{aligned}\left[-e_k - \frac{1}{2}\nabla^2\right]\delta\psi_k &= -\epsilon_k - (\delta\mathcal{F} - \delta e_k)[\psi_k + \delta\psi_k] \\ &\quad + \sum_{n=1}^{N_n}\frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\delta\psi_k - V_{\mathrm{H}}(\mathbf{r})\delta\psi_k \\ &\quad + \sum_l \psi_l(\mathbf{r})V[\psi_l\delta\psi_k](\mathbf{r}).\end{aligned} \tag{35}$$

The equation is solved iteratively, writing it as

$$\left[-e_k - \frac{1}{2}\nabla^2\right]\delta\psi_k^{(n+1)} = -\epsilon_k + \sum_{n=1}^{N_n}\frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\delta\psi_k^{(n)} - I_k^{(n)}(\mathbf{r}), \tag{36}$$

where

$$\begin{aligned}I_k^{(n)} &= (\delta\mathcal{F}^{(n)} - \delta e_k)\big[\psi_k + \delta\psi_k^{(n)}\big] + V_{\mathrm{H}}(\mathbf{r})\delta\psi_k^{(n)} \\ &\quad - \sum_l \psi_l(\mathbf{r})V\big[\psi_l\delta\psi_k^{(n)}\big],\end{aligned} \tag{37}$$

with $\delta\psi_k^{(0)} = 0$, $\delta e_k^{(0)} = 0$.

The inhomogeneous Helmholtz equation

$$\big[-e - \tfrac{1}{2}\nabla^2\big]x(\mathbf{r}) = y(\mathbf{r}) \tag{38}$$

can be solved on a Cartesian mesh using Fourier transforms. If

$$\tilde{y}(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{r}}y(\mathbf{r})d\mathbf{r}, \tag{39}$$

then

$$x(\mathbf{r}) = \frac{1}{(2\pi)^3}\int\frac{2}{k^2+k_0^2}e^{-i\mathbf{k}\cdot\mathbf{r}}\tilde{y}(\mathbf{k})d\mathbf{k}, \tag{40}$$

where $k_0^2 = -2e$. In particular, if

$$y(\mathbf{r}) = e^{-Zr}, \tag{41}$$

$$x(\mathbf{r}) = \frac{2}{k_0^2 - Z^2}e^{-Zr} - \frac{4Z}{\left(k_0^2 - Z^2\right)^2}\frac{1}{r}[e^{-Zr} - e^{-k_0 r}], \tag{42}$$

and if

$$y(\mathbf{r}) = \frac{e^{-Zr}}{r}, \tag{43}$$

$$x(\mathbf{r}) = \frac{2}{k_0^2 - Z^2}\frac{1}{r}[e^{-Zr} - e^{-k_0 r}]. \tag{44}$$

As discussed in Sec. I, the problem of the behavior at the nuclei can be minimized by rewriting

Eq. (36) as

$$\begin{aligned}\left[-e_k - \frac{1}{2}\nabla^2\right] \delta\psi_k^{(n+1)} &= -\epsilon_k + \sum_{n=1}^{N_n} \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\left[\delta\psi_k^{(n)} - \delta\psi_k^{(n)}(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}\right] \\ &\quad - \left[I_k^{(n)}(\mathbf{r}) - \sum_n I_k^{(n)}(\mathbf{R}_n) e^{-|Z_n\mathbf{r}-\mathbf{R}_n|}\right] \\ &\quad + \sum_n \delta\psi_k^{(n)}(\mathbf{R}_n)\frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} e^{-Z_n|\mathbf{r}-\mathbf{R}_n|} \\ &\quad - \sum_n I_k^{(n)}(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}. \end{aligned} \tag{45}$$

The nuclear attraction term is finite at the nuclei, and the terms in $I_k^{(n)}(\mathbf{r})$ vanish at the nuclei. The solution for the latter two terms are obtained analytically using Eqs. (42) and (44).

We consider now the total energy correction. It is a standard result of Hartree-Fock theory that the total energy is the sum of the single-particle energies less the two-particle potential energy. Therefore the approximate energy obtained from the ψ_k is given by

$$E_0 = \sum_k e_k - \sum_{kl}\left(\frac{1}{2}W\left[\psi_k^2,\psi_l^2\right] - \frac{1}{4}W[\psi_k\psi_l,\psi_k\psi_l]\right). \tag{46}$$

Similarly, the total energy is given, from Eq. (34), by

$$\begin{aligned} E &= \sum_k e_k + \langle\delta\psi_k|\epsilon_k\rangle + \langle\psi_k|\delta\mathcal{F}|\psi_k+\delta\psi_k\rangle \\ &\quad - \frac{1}{2}\sum_{kl}\frac{1}{\left(1+\delta_k^2\right)\left(1+\delta_l^2\right)} W[(\psi_k+\delta\psi_k)^2,(\psi_l+\delta\psi_l)^2] \\ &\quad + \frac{1}{4}\sum_{kl}\frac{1}{\left(1+\delta_k^2\right)\left(1+\delta_l^2\right)} \\ &\quad \times W[(\psi_k+\delta\psi_k)(\psi_l+\delta\psi_l),(\psi_k+\delta\psi_k)(\psi_l+\delta\psi_l)] \\ &= E_0 + \sum_k \langle\delta\psi_k|\epsilon_k\rangle + \Delta V, \end{aligned} \tag{47}$$

where

$$\begin{aligned} \Delta V &= -\frac{1}{2}\sum_{kl}\frac{1}{\left(1+\delta_k^2\right)\left(1+\delta_l^2\right)}\Big\{-\left(\delta_k^2+\delta_l^2+\delta_k^2\delta_l^2\right)W\left[\psi_k^2,\psi_l^2\right] + 4W\left[\delta\psi_k\psi_k,\psi_l^2\right] + 4W[\delta\psi_k\psi_k,\delta\psi_l\psi_l] + 2W\left[\delta\psi_k^2,\psi_l^2\right] \\ &\quad + 4W[\delta\psi_k\psi_k,\delta\psi_l^2] + W\left[\delta\psi_k^2,\delta\psi_l^2\right]\Big\} + \frac{1}{4}\sum_{kl}\frac{1}{\left(1+\delta_k^2\right)\left(1+\delta_l^2\right)}\Big\{-\left(\delta_k^2+\delta_l^2+\delta_k^2\delta_l^2\right)W[\psi_k\psi_l,\psi_k\psi_l] + 4W[\delta\psi_k\psi_l,\psi_k\psi_l] \\ &\quad + 2W[\delta\psi_k\psi_l,\delta\psi_k\psi_l] + 2W[\psi_k\delta\psi_l,\delta\psi_k\psi_l] + 2W[\delta\psi_k\delta\psi_l,\psi_k\psi_l] + 4W[\delta\psi_k\delta\psi_l,\delta\psi_k\psi_l] + W[\delta\psi_k\delta\psi_l,\delta\psi_k\delta\psi_l]\Big\} \\ &\quad + \sum_k \langle\psi_k|\delta\mathcal{F}|\psi_k+\delta\psi_k\rangle, \end{aligned} \tag{48}$$

and $\langle\delta\psi_l|\delta\psi_l\rangle$ is denoted by δ_l^2.

The function $\delta\mathcal{F}[\psi_k+\delta\psi_k]$ is given by

$$\begin{aligned} \delta\mathcal{F}[\psi_k+\delta\psi_k] &= \sum_l \frac{1}{1+\delta_l^2}\left\{2V[\psi_l\delta\psi_l] + V\left[\delta\psi_l^2\right] - \delta_l^2 V\left[\psi_l^2\right]\right\}[\psi_k(\mathbf{r})+\delta\psi_k(\mathbf{r})] - \frac{1}{2}\sum_l\frac{1}{1+\delta_l^2}\Big\{V[\psi_k\psi_l]\left(\delta\psi_l-\delta_l^2\psi_l\right) \\ &\quad + V[\psi_k\delta\psi_l](\psi_l+\delta\psi_l) + V[\delta\psi_k\psi_l]\left(\delta\psi_l-\delta_l^2\psi_l\right) + V[\delta\psi_k\delta\psi_l](\psi_l+\delta\psi_l)\Big\}, \end{aligned} \tag{49}$$

$$\begin{aligned} \sum_k\langle\psi_k|\delta\mathcal{F}|\psi_k+\delta\psi_k\rangle &= \sum_{kl}\frac{1}{1+\delta_l^2}\Big\{2W\left[\psi_k^2,\psi_l\delta\psi_l\right] + 2W[\psi_k\delta\psi_k,\psi_l\delta\psi_l] + W\left[\psi_k^2,\delta\psi_l^2\right] + W\left[\psi_k\delta\psi_k,\delta\psi_l^2\right] - \delta_l^2 W\left[\psi_k^2,\psi_l^2\right] \\ &\quad - \delta_l^2 W\left[\delta\psi_k\psi_k,\psi_l^2\right]\Big\} - \frac{1}{2}\sum_{kl}\frac{1}{1+\delta_l^2}\Big\{2W[\psi_k\delta\psi_l,\psi_k\psi_l] + W[\psi_k\delta\psi_l,\psi_k\delta\psi_l] + W[\psi_k\delta\psi_l,\delta\psi_k\psi_l] \\ &\quad + W[\psi_k\psi_l,\delta\psi_k\delta\psi_l] + W[\psi_k\delta\psi_l,\delta\psi_k\delta\psi_l] - \delta_l^2 W[\psi_k\psi_l,\psi_k\psi_l] - \delta_l^2 W[\psi_k\psi_l,\delta\psi_k\psi_l]\Big\}. \end{aligned} \tag{50}$$

Combining Eqs. (48) and (50) gives

$$\begin{aligned} \Delta V &= \frac{1}{2}\sum_{kl}\frac{1}{\left(1+\delta_k^2\right)\left(1+\delta_l^2\right)}\Big\{2\left(\delta_k^2-\delta_k^2\delta_l^2\right)W\left[\psi_k^2,\psi_l\delta\psi_l\right] + 4\delta_k^2 W(\psi_k\delta\psi_k,\psi_l\delta\psi_l] + 2\delta_k^2 W\left[\psi_k^2,\delta\psi_l^2\right] \\ &\quad + 2\left(\delta_k^2-1\right)W\left[\psi_k\delta\psi_k,\delta\psi_l^2\right] - \delta_k^2\delta_l^2 W\left[\psi_k^2,\psi_l^2\right] - W\left[\delta\psi_k^2,\delta\psi_l^2\right]\Big\} - \frac{1}{4}\sum_{kl}\frac{1}{\left(1+\delta_k^2\right)\left(1+\delta_l^2\right)}\Big\{2\left(\delta_k^2-\delta_k^2\delta_l^2\right)W[\psi_k\delta\psi_l,\psi_k\psi_l] \\ &\quad + 2\delta_k^2 \big(W[\delta\psi_k\delta\psi_l,\psi_k\psi_l] + 2\delta_k^2 W[\delta\psi_k\psi_l,\psi_k\delta\psi_l] + 2\delta_k^2 W[\psi_k\delta\psi_l,\psi_k\delta\psi_l] + 2\left(\delta_k^2-1\right)W[\psi_k\delta\psi_l,\delta\psi_k\delta\psi_l] \\ &\quad - \delta_k^2\delta_l^2 W[\psi_k\psi_l,\psi_k\psi_l]\Big\}. \end{aligned} \tag{51}$$

The leading term in the energy correction, $\sum_k \langle \delta\psi_k | \epsilon_k \rangle$, is the dominant contribution. The remaining terms are of cubic or higher order in ϵ_k.

V. NUMERICAL IMPLEMENTATION

As described earlier, approximate Hartree-Fock orbitals are constructed as linear combinations of atomic orbitals χ_i centered at the various nuclei. The molecular functions ψ_k are then obtained by interpolating the χ_i to the Cartesian mesh, in this case using seven-point interpolation, and applying Eq. (12).

One major difficulty in the approach is the determination of the functions ϵ_k defined in Eq. (31). Two approaches can then be followed. One is to calculate the functions $\mathcal{F}_0\chi_i$ as angular momentum expansions about the appropriate nucleus $\mathbf{R}_i$,

$$\mathcal{F}_0[\chi_i](\mathbf{r}) = \sum_{LM} D_{LM,i}(r) Y_{LM}(\hat{\mathbf{r}}), \tag{52}$$

and interpolate the resulting expansions to the Cartesian mesh. The alternative is to obtain the $\mathcal{F}_0\chi_i$ directly on the Cartesian mesh. The advantage of the former method is that the calculations on the radial mesh are much more accurate, but the purpose is defeated because of the truncation of the angular momentum sums. The disadvantage of the latter approach is that the requirements on the Cartesian mesh to obtain satisfactory accuracy are very demanding. On the other hand, less accuracy is required for the $\delta\psi_k$ and the energy corrections. The results in this article have been obtained using the latter approach.

If $\mathcal{F}_0[\psi_k]$ is constructed directly, singular canceling terms of the form $|\mathbf{r} - \mathbf{R}_n|^{-1}$ occur in the kinetic energy and nuclear attraction energy. Since the analytic form of the solutions at the nuclei is known, this problem is eliminated by separating out the singular terms of the form

$$\sum_n \psi_k(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}, \quad \sum_n \psi_k(\mathbf{R}_n) \frac{e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}}{|\mathbf{r}-\mathbf{R}_n|},$$

from $\mathcal{F}_0[\psi_k]$.

The kinetic and nuclear attraction terms in $\mathcal{F}_0[\psi_k]$ can then be written

$$\begin{aligned}\mathcal{F}_{0,\mathrm{sp}}[\psi_k] = {} & -\frac{1}{2}\nabla^2 \left[\psi_k - \sum_n \psi_k(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}\right] \\ & - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\left[\psi_k(\mathbf{r}) - \psi_k(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}\right] \\ & + \sum_n \psi_k(\mathbf{R}_n)\left[-\frac{1}{2}\nabla^2 - \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}\right] e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}.\end{aligned} \tag{53}$$

The Fourier transform of the counterterm in Eq. (53) is

$$-4\pi \sum_n \psi_k(\mathbf{R}_n) e^{i\mathbf{k}\cdot\mathbf{R}_n} \frac{Z_n^2}{\left(k^2 + Z_n^2\right)^2}.$$

Although less significant, terms of the form

$$\sum_n V_{\mathrm{H}}(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|} - \sum_{l,n} V[\psi_k\psi_l](\mathbf{R}_n)\psi_l(\mathbf{R}_n) e^{-Z_n|\mathbf{r}-\mathbf{R}_n|}$$

are also subtracted from the potential energy terms.

The Poisson equation for the potentials is solved in a similar way to the orbital equations. The potential produced by a charge density $\rho(\mathbf{r})$ is

$$V(\mathbf{r}) = \frac{1}{2\pi^2}\int \frac{1}{k^2} e^{-i\mathbf{k}\cdot\mathbf{r}} \tilde{\rho}(\mathbf{k}) d\mathbf{k}, \tag{54}$$

where

$$\tilde{\rho}(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r}) d\mathbf{r}. \tag{55}$$

At the nuclei, the densities behave as $\psi_k(\mathbf{R}_n)\psi_l(\mathbf{R}_n) e^{-2Z_n|\mathbf{r}-\mathbf{R}_n|}$. Therefore the potential for a modified density,

$$\psi_k(\mathbf{r})\psi_l(\mathbf{r}) - \sum_n \psi_k(\mathbf{R}_n)\psi_l(\mathbf{R}_n) e^{-2Z_n|\mathbf{r}-\mathbf{R}_i|}, \tag{56}$$

can be obtained. The correction term is then

$$\begin{aligned}\sum_n \psi_k(\mathbf{R}_n)\psi_l(\mathbf{R}_n) & \frac{\pi}{Z_n^3|\mathbf{r}-\mathbf{R}_n|} \\ & \times \left[1 - (1 + Z_n|\mathbf{r}-\mathbf{R}_n|) e^{-2Z_n|\mathbf{r}-\mathbf{R}_n|}\right],\end{aligned} \tag{57}$$

which incorporates the correct large $\mathbf{r}$ behavior.

The integral in Eq. (54) is improper since the denominator vanishes at $\mathbf{k} = 0$. This problem is treated by defining

$$\tilde{\rho}_c(\mathbf{k}) = \tilde{\rho}(\mathbf{k}) - \tilde{\rho}(0)\left[\frac{\lambda^2}{k^2 + \lambda^2}\right]^2, \tag{58}$$

where

$$\tilde{\rho}(0) = \int f(\mathbf{r}) d\mathbf{r}. \tag{59}$$

The solution of the Poisson equation is then

$$\begin{aligned}v(\mathbf{r}) = {} & \frac{1}{2\pi^2}\int \frac{1}{k^2} e^{-i\mathbf{k}\cdot\mathbf{r}} \tilde{\rho}_c(\mathbf{k}) d\mathbf{k} \\ & + \frac{\tilde{\rho}(0)}{\lambda^3 r}\left[1 - \left(1 + \frac{\lambda r}{2}\right) e^{-\lambda r}\right].\end{aligned} \tag{60}$$

The solution is independent of λ within a reasonable range.

Cartesian meshes are defined in both position and momentum spaces on intervals $[-X, X]^3$ and $[-P, P]^3$. The application of the FFT procedure constrains the meshes by $\Delta x \Delta p = 2\pi/N$. This would appear to be a serious restriction on the approach. However, the reciprocal scaling in space and momentum space is appropriate to the problem. The program package FFTW has been applied [18]. This package permits the number of mesh points to be a product of small prime factors, for example, 64, 100, 144, and 200.

Valence electron energies are typically ~0.5 so that valence orbitals should behave roughly as e^{-r} at large r. Therefore an X of 10.0 should be reasonable for small molecules near equilibrium. The momentum space behavior presents a more difficult problem. The momentum space orbitals in Eq. (40) behave as $\sin kr/(kr)^4$ in spherical coordinates. The length scale in k is determined by the maximum nuclear charge. Therefore, to obtain accuracy at the 0.001 level, P should be $\sim 4Z_{\max}$. The integrands for the energy corrections behave as k^{-10} and should not be a problem.

TABLE I. Energies for small molecules compared with results from Ref. [19], denoted HJO, showing the energy differences in millihartrees. The total energies from HJO are in hartrees. LCAO: results from the orbital basis. $N = 100$, etc: Cartesian correction results. The geometries are those of Ref. [19].

Molecule	HJO	LCAO	$N = 100$	$N = 144$	$N = 200$
H_2	−1.1336	5.1	0.0	0.0	0.0
CH_2	−38.8960	39.8	−0.4	−0.2	−0.2
CH_4	−40.2171	27.8	0.6	1.0	1.0
NH_3	−56.2249	52.8	−1.9	−0.4	−0.3
H_2O	−76.0674	54.1	−3.8	−0.8	−0.5
C_2H_2	−76.8556	64.4	−0.5	−0.5	−0.3
C_2H_4	−78.0707	76.9	−0.6	1.9	2.5
HF	−100.0708	33.9	−8.5	−1.5	−0.6
N_2	−108.9930	197.2	−9.5	−1.2	−1.2
N_2	−108.9930	124.8	−5.3	−2.2	0.6
CO	−112.7908	162.2	−17.7	−2.6	−1.5
CO	−112.7908	114.2	−14.9	−1.7	−2.6
HCN	−92.9157	110.2	−4.4	−0.9	−0.9
HNC	−92.9003	95.9	−5.8	−1.8	−1.8

VI. RESULTS

Results have been obtained for a number of small molecules for which accurate Hartree-Fock equations have been recorded by Helgaker *et al.* [19]. The calculated results depend on many parameters, as defined in the preceding sections. Obviously, some are more critical than others. The radial parameters in the radial factor optimizations are $r_{\min} = 0.0001$, $r_{\max} = 15.0$, and $k_{\max} = 200.0$, with 256 mesh points. The dependence on these parameters is probably insignificant within a reasonable range. The nuclear attraction integrals are computed with $L_{\mathrm{N},\max} = 8$. The values of $\Lambda^{(1)}_{\max}$ and $\Lambda^{(1)}_{\max}$ applied in the electron-electron repulsion integrals are 16 and 6, respectively. $L_{\max,\mathrm{opt}} = 16$ in the truncations in constructing Eq. (29). These parameters determine the accuracy of the atomic orbital basis. Checks varying these parameters indicate that the energy results should be accurate to ≈0.1 millihartrees. The most sensitive parameters are X and P, defining the Cartesian meshes in real and momentum space. The results given are for 100, 144, and 200 mesh points with $X = 10.0$ and $P \approx 15.4, 22.3$, and 31.1.

Results for the total energies are are given in Table I and are compared with those of [19] at the same geometries. These are denoted by HJO. Table I also shows the energies, denoted LCAO, obtained in the atomic orbital basis. The results agree with those given in HJO within a few millihartrees in all cases. However, it can be observed that the results for molecules containing nuclei of smaller Z are more accurate in the $N = 100$ case and that for larger Z values, the results are more dependent on N. This is suggests that the factor limiting the accuracy is P, the maximum momentum. The iterative procedure is terminated after 10 iterations, and the results may be ≈0.1 millihartrees high.

TABLE II. Orbital energies obtained in this study.

n	H_2	CH_2	CH_4	NH_3	H_2O	HF
1	−0.5947	−11.292	−11.203	−15.537	−20.561	−26.290
2		−0.893	−0.943	−1.141	−1.350	−1.599
3		−0.566	−0.546	−0.628	−0.716	−0.769
4		−0.397	−0.546	−0.628	−0.587	−0.649
5			−0.546	−0.431	−0.509	−0.649

TABLE III. Orbital energies for heavier molecules.

n	C_2H_2	N_2	CO	HCN	HNC	C_2H_4
1	−11.244	−15.681	−20.674	−15.595	−15.598	−11.221
2	−11.240	−15.678	−11.352	−11.297	−11.293	−11.220
3	−1.030	−1.471	−1.521	−1.237	−1.266	−1.040
4	−0.768	−0.777	−0.803	−0.814	−0.878	−0.814
5	−0.682	−0.634	−0.641	−0.582	−0.522	−0.653
6	−0.411	−0.611	−0.641	−0.497	−0.522	−0.601
7	−0.411	−0.611	−0.555	−0.497	−0.493	−0.518
8						−0.377

Results for two cases for N_2 and CO are given. One is for the minimal basis on each atom, and the second adds 3s orbitals to the basis. These are added because the optimum $m = 0$ 2p orbital may be quite different from the $m = \pm 1$ solution.

Results for the single-particle energies of the occupied orbitals are presented in Tables II and III. The near-degeneracy of the valence $3\sigma_g$ and $1\pi_u$ in N_2 may be noted. The energies differ only slightly between the two calculations.

VII. DISCUSSION

Methods have been developed to overcome the problems associated with the rapid variation of molecular orbitals in the neighborhoods of the atomic nuclei and to obtain numerical solutions of the restricted Hartree-Fock equations for molecules. An important aspect is the method of separating out the Slater orbital-like contributions at the nuclei and treating them analytically.

A significant result of this work is that it presents an iterative procedure for the solution of the Hartree-Fock operator with inhomgeneous terms. It should therefore be applicable to other problems. For example, it should be feasible to add external static potentials to obtain polarizabilities. Evidently, exchange and/or correlation density-dependent potentials can be included in a straightforward way.

The convergence of the iterative procedure is rather slow and appears to be geometric, with the error decreasing by 1/2 to 2/3 at each iteration in the later stages. This may be a consequence of the self-consistent-field procedure for the direct and exchange potentials rather than the iteration on the $\delta\psi_k$. This is indicated since the energy iterations decrease monotonically.

There is considerable current interest in the possibility of applying the optimized effective potential (OEP) method to molecules [20–22]. The usual basis set expansion methods can lead to ambiguous results, as illustrated recently [23], in that matrix solutions of the single-particle Schrödinger equation may not provide faithful pointwise solutions. In future work, it is hoped to apply these methods to this single-particle problem and develop a Cartesian method for the OEP for molecules.

This approach is obviously very demanding of computer resources. It is also clearly most practical for molecules near equilibrium and is inapplicable to dissociation behavior. The method would be much improved if the large momentum properties of the orbitals and orbital increments could be treated in a more satisfactory fashion. Future work will be directed toward this issue. Other areas to be investigated are the convergence properties of the angular momentum expansions of the error terms ϵ_k. Evidently, the results should be independent of the atomic orbital basis chosen. However, including additional polarization orbitals in the atomic orbital basis may improve the convergence of the iterative process, and this will also be investigated.

ACKNOWLEDGMENTS

I am grateful to R. J. Bartlett, So Hirata, and H. J. Monkhorst of the Quantum Theory Project, University of Florida, for discussions and encouragement. I have also benefited from visits to the Chemistry Department, University of Namur; the Physics Department, University of Bordeaux; and the Donostia International Physics Center. This research has been supported by the Natural Sciences and Engineering Reseach Council of Canada. This work was made possible by the facilities of the Shared Heirarchical Academic Research Computing Network (SHARCNET) and Comput/Calcul Canada.

---

[1] C. Froese Fischer, *The Hartree-Fock Method for Atoms: A Numerical Approach* (Wiley, New York, 1977).
[2] L. Laaksonen, J. Kobus, and D. Sundholm, Comput. Phys. Commun. **98**, 346 (1996).
[3] T. L. Beck, Int. J. Quantum Chem. **65**, 477 (1997).
[4] T. Shiozaki and S. Hirata, Phys. Rev. A **76**, 040503 (2007).
[5] A. D. Becke and R. M. Dickson, J. Chem. Phys. **89**, 2993 (1988); **92**, 3610 (1990).
[6] R. J. Harrison, G. I. Fann, T. Yanai, and Z. Gan, J. Chem. Phys. **121**, 11587 (2004).
[7] T. Yanai, G. I. Fann, Z. Gan, and R. J. Harrison, J. Chem. Phys. **121**, 6680 (2004).
[8] J. D. Talman, Phys. Rev. Lett. **84**, 855 (2000); Int. J. Quantum Chem. **95**, 442 (2003); see also D. Andrae, Mol. Phys. **99**, 327 (2001).
[9] S. A. Alexander and H. J. Monkhorst, Int. J. Quantum Chem. **32**, 361 (1987).
[10] S. A. Alexander, R. L. Coldwell, and H. J. Monkhorst, J. Comput. Phys. **76**, 263 (1988).
[11] S. Yamakawa and S. Hyodo, Phys. Rev. B **71**, 035113 (2005).
[12] F. A. Pahl and N. C. Handy, Mol. Phys. **100**, 3199 (2002).
[13] J. D. Talman, Int. J. Quantum Chem. **93**, 72 (2003).
[14] N. Sovic and J. D. Talman, Collect. Czech. Chem. Commun. **70**, 1035 (2005).
[15] J. D. Talman, Int. J. Quantum Chem. **107**, 1578 (2007).
[16] J. D. Talman, J. Chem. Phys. **84**, 6879 (1986).
[17] J. D. Talman, Comput. Phys. Commun. **180**, 332 (2009).
[18] M. Frigo and S. G. Johnson, Proc. IEEE **93**, 216 (2005).
[19] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic Structure Theory* (Wiley, New York, 2000).
[20] S. Ivanov, S. Hirata, and R. J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999).
[21] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).
[22] A. Görling and M. Levy, Int. J. Quantum Chem., Symp. **56**, 93 (1995).
[23] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, J. Chem. Phys. **124**, 141103 (2006).