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Grid-based numerical Hartree-Fock solutions of polyatomic molecules

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Numerical solutions of the Hartree-Fock (HF) equation of polyatomic molecules have been obtained by an extension of the numerical density-functional method of Becke and Dickson [J. Chem. Phys. **89**, 2993 (1988); **92**, 3610 (1990)]. A finite-difference method has been used to solve Poisson's equation for the Coulomb and exchange potentials and to evaluate the action of the Laplace operator on numerical orbitals expanded on an interlocking multicenter quadrature grid. Basis-set-limit HF results for an atom and diatomic and triatomic molecules are presented with the total energies and the highest occupied orbital energies converged to within 10^{-5} Hartree without any extrapolation.

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The errors in the second-quantized electron-correlation methods arise from two sources—the truncation of a many-electron basis expansion of multidimensional wave functions and that of a one-electron basis expansion of orbitals. While various hierarchical electron-correlation methods have been devised to accelerate the summation of the former expansion, the convergence of energies and wave functions with respect to one-electron basis sizes is notoriously slow and is considered by many one of the most outstanding issues in modern electronic structure theory.

The slow convergence is traced to the lack of interelectronic (r_{12}) degrees of freedom in one-electron bases, e.g., linear-combination-of-atomic-orbital (LCAO) Gaussian bases [1,2]. Hence, this problem can be avoided by introducing r_{12} dependence in the LCAO determinant-based electron-correlation methods [3] or by constructing new electron-correlation methods with two-electron and higher-order bases [4,5]. In the latter category is a grid-based, numerical solution of the Sinanoğlu equation [6] (a first-quantized form of the second-order Møller–Plesset perturbation method) by McKoy and Winter [7], although it does not analytically eliminate the Coulomb singularity at the coalescence of two electrons [8].

A grid-based, numerical solution of the Sinanoğlu equation requires a grid-based representation of the Fock operator, which also enables a grid-based, numerical Hartree-Fock (HF) method. Such methods for atoms and diatomic molecules employing spherical or prolate spheroidal coordinates have been reviewed in Refs. [9] and [10]. The HF equation in a momentum space representation has been derived and solved with a complete plane-wave basis by Alexander *et al.* [11]. Becke and Dickson [12,13] have developed a numerical, real-space solver of density-functional theoretical (DFT) self-consistent field (SCF) equation for polyatomic molecules on the basis of an interlocking multicenter quadrature grid [14], which is now widely adopted in LCAO DFT implementations. Pahl and Handy [15] have used a mixed plane-wave and atom-centered radial polynomial basis functions and Yanai, Harrison, and co-workers [16,17] have introduced self-adjusting multiwavelet basis functions to obtain the HF solutions of polyatomic molecules in the complete-basis-set (CBS) limit. Talman have variationally optimized numerical atomic orbitals to solve the HF equation of polyatomic molecules [18,19].

In this paper, as an initial step to realizing grid-based, numerical electron-correlation methods, we report the implementation of a grid-based, numerical HF equation solver for polyatomic molecules without a basis-set error. Our implementation is an extension of the method developed by Becke and Dickson [12,13]: We employ Becke's multicenter grid to expand orbitals and potentials, solve Poisson's equation to obtain the Coulomb and exchange potentials, and represent the action of the Laplace operator (in the kinetic operator and Poisson's equation) on numerical orbitals in a finite-difference approximation. Becke and Dickson have also reported the numerical HF solutions of H_3^+ [13] and of other larger molecules [20,21] with the aim of describing dispersion interactions with smaller quadrature grids than those used in our work. The algorithmic details of their numerical HF methods beyond Refs. [12] and [13] have not been reported. Our grid-based method treats the HF exchange operator rigorously for general polyatomic molecules (albeit with a rather severe molecular size limit), necessitating an effective algorithm to solve an eigenvalue equation involving a non-Hermitian matrix. We present the exact HF solutions (within 10^{-5} Hartree) of an atom and diatomic and triatomic molecules obtained with the method.

Following the overall strategy of Becke and Dickson [12,13], we expand orbitals and potentials on an interlocking multicenter grid [14]. Whenever necessary, these functions are divided into the sum of atomic contributions, which are in turn expanded by atom-centered radial (Gauss-Chebyshev) and spherical (Lebedev) grids [22–27]. The Lebedev grid is characterized by its rank l_{quad} and is designed to integrate spherical harmonics Y_{lm} exactly up to $l=l_{\mathrm{quad}}$. Each atomic contribution is obtained by multiplying a weight function $w_A(\mathbf{r})$ that has significant amplitude within a Voronoi polyhedron centered at atom A and decays smoothly at its boundary, overlapping with the contributions from the adjacent cells [14].

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The action of kinetic $\hat{T}$, nuclear attraction $\hat{V}$, and Coulomb $\hat{J}$ operators on numerical orbitals on the grid can be evaluated according to the computational prescription of Refs. [12] and [13]. Specifically, Poisson's equation is solved for the Coulomb potential given an electron density [12]. The Laplacian operator appearing in Poisson's equation and in the kinetic operator can be handled by letting it act on the atom-centered contributions which are expandable by spherical harmonics, which are eigenfunctions of the operator, up to $l_{\mathrm{max}}=\frac{1}{2}(l_{\mathrm{quad}}-1)$. The second derivatives of the radial parts are obtained by a seventh-degree finite-difference method [12,13].

The action of an exchange operator $\hat{K}$ on a trial function $\phi_p(\mathbf{r})$ is expressed as

$$\hat{K}\phi_p(\mathbf{r}_1)=\sum_i^{\mathrm{occ}}\int\frac{\phi_p(\mathbf{r}_2)\psi_i(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2\psi_i(\mathbf{r}_1)=\sum_i^{\mathrm{occ}}V_{pi}(\mathbf{r}_1)\psi_i(\mathbf{r}_1), \tag{1}$$

where an exchange potential V_{pi} is defined for each pair of an occupied orbital and the trial function $\phi_p\psi_i$ and satisfies Poisson's equation [28]

$$\nabla^2V_{pi}(\mathbf{r})=-4\pi\phi_p(\mathbf{r})\psi_i(\mathbf{r}). \tag{2}$$

The pair density $\phi_p\psi_i$ is divided into atomic contributions and, for each, atomic exchange potential V_{pi}^A is obtained:

$$\nabla^2V_{pi}^A(\mathbf{r})=-4\pi w_A(\mathbf{r})\phi_p(\mathbf{r})\psi_i(\mathbf{r}), \tag{3}$$

$$V_{pi}(\mathbf{r})=\sum_A^{\mathrm{atoms}}V_{pi}^A(\mathbf{r}). \tag{4}$$

This step of constructing V_{pi} from its atomic contributions $\{V_{pi}^A\}$ is the most time consuming one because it requires the evaluation of V_{pi}^A on the grids centered on atoms other than A by interpolation. This is carried out by a cubic spline interpolation, which is accelerated by noticing that the Gauss-Chebyshev radial grid points are evenly spaced after some coordinate conversion.

With the grid representation of the Fock operator $\hat{F}=\hat{T}+\hat{V}+\hat{J}-\hat{K}$, we solve the HF equation iteratively. Defining the residual $r_i(\mathbf{r})$ by

$$r_i(\mathbf{r})=(\hat{F}-\tilde{e}_i)\tilde{\psi}_i(\mathbf{r}), \tag{5}$$

where $\tilde{\psi}_i(\mathbf{r})$ and $\tilde{e}_i$ are approximate orbital and orbital energy, we consider the convergence is achieved when $|r_i|^2\leq 10^{-6}$ and the self-consistency is satisfied. With this threshold, orbital and total HF energies are accurate to within 10^{-5} Hartree. The iterative solution of Eq. (5) proceeds by a subspace diagonalization of $\hat{F}$ within the space spanned by trial functions, i.e., $\tilde{\psi}_i(\mathbf{r})=\Sigma_kC_k\phi_k(\mathbf{r})$. The efficiency of this process hinges on an effective scheme of generating trial functions that expand the occupied orbitals accurately and compactly. Conventional schemes [31,32] presume the diagonal dominance of the matrix, which facilitates the approximate inversion of $(\hat{F}-\tilde{e}_i)$. The finite-difference representation of $\hat{F}$ is far from diagonally dominant and we generate a useful trial function ϕ_i' by approximately breaking down $\hat{F}$ into spherically averaged atomic contributions $\{\hat{F}_{\mathrm{sph}}^A\}$ and acting $(\hat{F}_{\mathrm{sph}}^A-\tilde{e}_i)^{-1}$ on the residuals [13]:

$$\phi_i'(\mathbf{r})=\sum_A^{\mathrm{atoms}}(\hat{F}_{\mathrm{sph}}^A-\tilde{e}_i)^{-1}w_A(\mathbf{r})r_i(\mathbf{r}), \tag{6}$$

with

$$\hat{F}_{\mathrm{sph}}^A=\hat{T}+\hat{V}_{\mathrm{sph}}^A+\frac{1}{2}\hat{J}_{\mathrm{sph}}^A, \tag{7}$$

where $\hat{V}_{\mathrm{sph}}^A$ and $\hat{J}_{\mathrm{sph}}^A$ are also spherically averaged atomic contributions of the respective operators. The empirical factor of 1/2 multiplying $\hat{J}_{\mathrm{sph}}^A$ has been introduced to ensure swifter convergence. The evaluation of $(\hat{F}_{\mathrm{sph}}^A-\tilde{e}_i)^{-1}$ is straightforward since different angular components do not couple with one another by virtue of the spherical averaging. Unlike Becke and Dickson [13], the subspace size (the number of trial functions) increases until convergence in our scheme. Since this procedure yields only occupied orbitals, first-quantized equations (with no explicit reference to virtual orbitals) should be employed in a subsequent treatment of electron correlation.

The most time-consuming step is, as mentioned before, the interpolation of atomic exchange potentials and the overall computational cost scales as $O(n_{\mathrm{occ}}n_{\mathrm{trial}}n_{\mathrm{atom}}^2n_{\mathrm{radial}}n_{\mathrm{angular}}^2)$, where each factor denotes the number of occupied orbitals, the number of trial functions, the number of atomic centers, the numbers of radial and angular grid points per atom (i.e., not proportional to the number of atoms), respectively.

The first test has been performed on the Ne atom. Unlike polyatomic molecules, an atomic orbital is a single spherical harmonic times a radial function and a small angular grid is sufficient. For Ne, the spherical harmonics only up to $l_{\mathrm{max}}=2$ (correspondingly $n_{\mathrm{angular}}=14$) suffice so that a product of four p-type orbitals can be integrated exactly by the Lebedev quadrature. As Table I shows, the converged total HF energy and the highest occupied molecular orbital (HOMO) energy are obtained at $n_{\mathrm{radial}}=100$, which are in agreement to all shown digits with the results of Koga *et al.* [29]. The convergence of the total HF energy with respect to n_{radial} shows the nonvariational nature of the method (i.e., the Fock matrix on the grid is not Hermitian).

TABLE I. The total HF (E_{HF}) and HOMO (e_{HOMO}) energies (in hartree) of Ne.

Grid[a]	E_{HF}	e_{HOMO}
50 × 14 (2)	−128.547127	−0.850412
70 × 14 (2)	−128.547100	−0.850410
100 × 14 (2)	−128.547098	−0.850410
200 × 14 (2)	−128.547098	−0.850410
Koga *et al.*[b]	−128.547098	−0.850410

[a] $n_{\mathrm{radial}}\times n_{\mathrm{angular}}(l_{\mathrm{max}})$.

[b] Reference [29].

TABLE II. The total HF (E_{HF}) and HOMO (e_{HOMO}) energies (in hartree) of BH (bond length of 2.3289 a.u.).

Grid[a]	E_{HF}	e_{HOMO}
100 × 434 (17)	−25.131636	−0.348324
100 × 770 (23)	−25.131639	−0.348324
100 × 1202 (29)	−25.131639	−0.348324
Yanai *et al.*[b]	−25.131639	−0.348324
Pahl and Handy[c]	−25.131639	−0.348290
Halkier *et al.*[d]	−25.131639	

[a] $n_{\text{radial}} \times n_{\text{angular}}(l_{\max})$.
[b] Reference [16].
[c] Reference [15].
[d] Reference [30].

Once there are two (or more) atomic centers in the molecule, its orbitals are no longer proportional to spherical harmonics. A considerably larger grid becomes necessary to obtain accurate orbitals and energies and, in particular, to represent functions at the Voronoi cell boundary. We used $n_{\text{radial}}=100$ or 150 and $n_{\text{angular}}=434$, 770, or 1202 ($l_{\max}=17$, 23, or 29) for diatomic tests as the use of smaller grids resulted in a computational instability.

The converged total HF energy of the BH molecule (Table II) agrees perfectly with the values obtained by Yanai *et al.* [16] and by Pahl and Handy [15] and also with the value quoted by Halkier *et al.* [30]. Our HOMO energy is also in agreement with the result of Yanai *et al.* within 1 μhartree. The corresponding value of Pahl and Handy is in error by 34 μhartree.

TABLE III. The total HF (E_{HF}) and HOMO (e_{HOMO}) energies (in hartree) of FH (bond length of 1.7328 a.u.).

Grid[a]	E_{HF}	e_{HOMO}
100 × 434 (17)	−100.070741	−0.650392
100 × 770 (23)	−100.070775	−0.650389
150 × 770 (23)	−100.070788	−0.650393
100 × 1202 (29)	−100.070791	−0.650389
150 × 1202 (29)	−100.070799	−0.650392
Yanai *et al.*[b]	−100.070803	−0.650394
Pahl and Handy[c]	−100.070795	−0.650380
Sundholm *et al.*[d]	−100.07082	

[a] $n_{\text{radial}} \times n_{\text{angular}}(l_{\max})$.
[b] Reference [16].
[c] Reference [15].
[d] Reference [33].

The convergence of energies with respect to grid sizes is slower in the FH molecule (Table III) and the large grid (150 × 1202 points per atom) is needed. The results with this grid are in generally good agreement with the previously reported values [15–17] within 5 μhartree. Again, the HOMO energy of Pahl and Handy [15] suffers from a slightly greater error from our results and those of Yanai *et al.*, which agree with each other within 2 μhartree. The total energy depends on n_{radial} and n_{angular} in a rather systematic fashion, possibly lending itself to an extrapolation, but the energy changes upon the increases in n_{radial} and n_{angular} do not appear to be additive.

TABLE IV. The total HF (E_{HF}) and HOMO (e_{HOMO}) energies (in hartree) of H_2O (see Ref. [16] for the geometry used).

Grid[a]	E_{HF}	e_{HOMO}
100 × 770 (23)	−76.065592	−0.509705
150 × 770 (23)	−76.065593	−0.509711
100 × 1202 (29)	−76.065592	−0.509706
Yanai *et al.*[b]	−76.065596	−0.509721
aug-cc-pVQZ	−76.064122	−0.509676
aug-cc-pV5Z	−76.065429	−0.509704

[a] $n_{\text{radial}} \times n_{\text{angular}}(l_{\max})$.
[b] Reference [16].

Table IV lists the exact HF results of H_2O at a geometry of Yanai *et al.* [16], i.e., oxygen placed at the origin and hydrogens at (±1.4375, 0.0000, 1.1500) in a.u. The largest grid afforded by our calculations leads to the total energy within 3 μhartree and HOMO energy within 10 μhartree of Yanai *et al.*'s values [16], which appear slightly more accurate. These values are consistent with LCAO Gaussian HF results with huge basis sets (aug-cc-pVQZ or 5Z) [34]. However, the results obtained with the aug-cc-pV5Z basis set seem to suffer from errors of around 170 μhartree that are two orders of magnitude greater than our basis-set-free calculations.

Figures 1 and 2 illustrate the rapid exponential convergence of the total and HOMO energies and all five occupied orbitals with respect to the number of iterations. Here, the iterations refer to those for subspace diagonalization of the Fock operator and simultaneously for achieving SCF. In fact, the convergence of the total energy (Fig. 1) appears to be

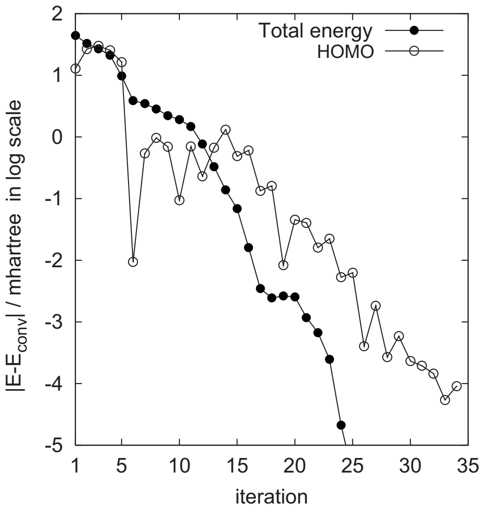

FIG. 1. The errors in the total HF and HOMO energies of H_2O as a function of the number of iterations for the subspace diagonalization of the Fock operator and SCF.

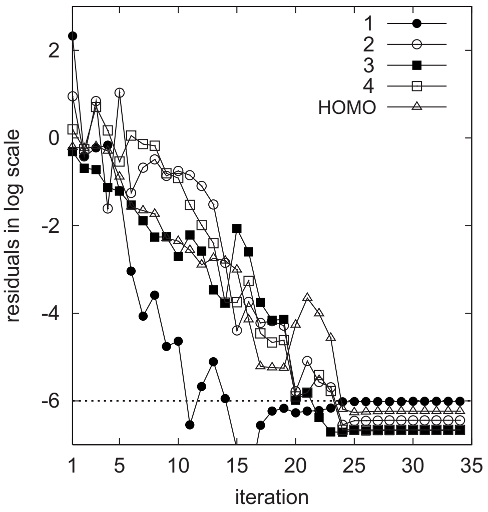

FIG. 2. The norm of the residual [Eq. (5)] of the occupied orbitals of H_2O as a function of iterations. The orbitals are numbered in the ascending order of energies.

faster than a single exponential decay, which might be due to the rapid convergence (Fig. 2) of the 1*s* core orbital that contributes the most to the total energy. The rates of convergence of orbitals are roughly in the order of the absolute values of the orbital energies.

For H_2O, the action of the Fock operator on five trial functions in the first iteration took 10 min on the 100×770 grid and 24 min on the 100×1202 grid with an IBM Power5 2.1 GHz workstation (1 CPU). The CPU time increases linearly with the number of trial functions. The most time-consuming step (the interpolation of the exchange potentials), however, can be effectively parallelized.

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