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A Multigrid Conjugate Residual Method for the Numerical Solution of the Hartree–Fock Equation for Diatomic Molecules

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Discretization of the Hartree–Fock equations in operational form leads to unsymmetric positive definite and indefinite linear equations. To solve these equations a combination of the multigrid method and the Orthomin method with Gauss–Seidel relaxation as preconditioner is used. The differential equations are approximated to the sixth order and the solution is extrapolated to the eighth order. The method is fully parallelized. The largest molecule treated is CuH. © 1992 Academic Press, Inc.

I. INTRODUCTION

To solve the Hartree–Fock equations for molecules, basis set methods have been the only methods able to solve the problem in a reasonable time. However, if highly accurate solutions are needed, it may be difficult to improve the basis set results, because the convergence to the exact result is slow and may be nonuniform. Numerical methods avoid the inherent limitations of expansion approaches. Using this technique it is possible to increase the accuracy of a calculation in a systematic fashion and to realistically predict its error.

Numerical 1D methods have been used for atoms and diatomic molecules. The first numerical 2D calculations on diatomics were carried out by Becke [1] in the Hartree–Fock–Slater or X_α approximation, using the variational form. Then, Laaksonen *et al.* [2] obtained the first numerical 2D solutions of the Hartree–Fock equations in operator form, using the successive overrelaxation (SOR) method. This latter approach will here be developed further.

Multigrid algorithms and Krylov subspace methods (conjugate gradient, conjugate residual, ...) with appropriate preconditioning are both efficient tools for the solution of equations which arise from the discretization of partial differential equations. We have used a combination of both methods in order to solve numerically the restricted Hartree–Fock (RHF) equations for diatomics in a reasonable time.

In Section II an iterative procedure is presented to solve the implicit RHF equations. The coordinate system and discretization are described in Section III and in Section IV a robust multigrid cycle is presented as a linear equation solver. In Section V computational details and results from both atomic and diatomic calculations are presented. Section VI, finally, contains our conclusions.

II. A PROCEDURE TO SOLVE THE HARTREE–FOCK EQUATIONS IN OPERATOR FORM

Consider a closed-shell diatomic molecule with nuclei of charges Z_A and Z_B separated by the distance R and containing $2N$ electrons in N doubly occupied orbitals. The ith orbital $\varphi_i(\mathbf{r})$ with orbital energy ε_i satisfies the (RHF) equation,

$$\hat{F}\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}),$$

where

$$\begin{aligned}\hat{F}\varphi_i(\mathbf{r}) = {} & \left[-\frac{1}{2}\nabla^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B}\right]\varphi_i(\mathbf{r}) \\ & + \sum_{j=1}^{N}\left[2\varphi_i(\mathbf{r})\int \frac{1}{|\mathbf{r}-\mathbf{r}'|}\varphi_j^*(\mathbf{r}')\,\varphi_j(\mathbf{r}')\,d\mathbf{r}' \right. \\ & \left. - \varphi_j(\mathbf{r})\int \frac{1}{|\mathbf{r}-\mathbf{r}'|}\varphi_j^*(\mathbf{r}')\,\varphi_i(\mathbf{r}')\,d\mathbf{r}'\right].\end{aligned}$$

This is an integro-differential equation, which can be formulated as a set of differential equations.

The SCF (self-consistent field) process to numerically solve the Hartree–Fock equation iteratively can be described as a generalized inverse iteration. In each iteration of the SCF process, two sets of equations have to be solved:

First, for $i = 1, ..., N$ and $j = 1, ..., i$ solve the Poisson equation for the potentials V^{ji}

$$-\nabla^2 V^{ji}(\mathbf{r}) = 4\pi\varphi_j(\mathbf{r})\,\varphi_i(\mathbf{r}). \tag{1}$$

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Next for $i = 1, \ldots, N$ calculate the orbital energy through the Rayleigh quotient,

$$\varepsilon_i = \frac{\langle \varphi_i | \hat{F} | \varphi_i \rangle}{\langle \varphi_i | \varphi_i \rangle},$$

where $\hat{F}$ is the Fock operator, and solve the linear equation,

$$\left[-\frac{1}{2}\nabla^2 - Z_A/r_A - Z_B/r_B + 2\sum_{j=1}^{N} V^{jj} - V^{ii} - \varepsilon_i \right] \varphi_i = \sum_{\substack{j=1 \\ j \neq i}}^{N} \varphi_j V^{ji} \tag{2}$$

which is the Hartree–Fock equation for the ith orbital. Then orthonormalize φ_i against $\varphi_1, \ldots, \varphi_{i-1}$.

In order to improve the SCF convergence the following procedure is adopted. Once an orbital has been corrected it is orthonormalized and damped between consecutive iterates by

$$\varphi^{i+1} = \alpha\varphi^{i+1} + (1-\alpha)\,\varphi^i,$$

where $0 < \alpha \leqslant 1$, and orthonormalized again. An alternative way is to perform the damping after all orbitals have been corrected and orthonormalized, but it has turned out to work less satisfactorily.

After all orbitals have been improved the Ritz projection process [3] for simultaneous computation of several eigenvalues and their eigenvectors is performed. That is, a unitary transformation which diagonalizes the matrix representation of the Fock operator in the subspace spanned by the orthonormalized orbitals is performed.

In the quadratic region it is possible to accelerate the convergence of the SCF process to the final solution by using the DIIS (direct inversion in the iterative subspace) method [4]. It uses the fact that a much better approximation to the final solution, in an iterative process, can be constructed from the first m iterated vectors $\mathbf{v}^1, \ldots, \mathbf{v}^m$ as

$$\mathbf{v} = \sum_{i=1}^{m} c_i \mathbf{v}^i$$

by requiring that the residuum vector

$$\Delta\mathbf{v} = \sum_{i=1}^{m} c_i\, \Delta\mathbf{v}^i$$

approximates the zero vector in the mean square sense, and the condition

$$\sum_{i=1}^{m} c_i = 1$$

holds. In this case $\mathbf{v}$ contains the orbitals. Note that for a DIIS(m) step, m differences, i.e., $m+1$ vectors, are necessary. After a DIIS step the orbitals are reorthonormalized.

III. COORDINATE SYSTEM AND DISCRETIZATION

A natural coordinate system for diatomic molecules is the prolate spheroidal coordinates, used in both Refs. [1, 2], which have axial symmetry and where the coordinate origins coincide with the positions of the nuclei. This coordinate system is defined by

$$x = a \sinh\mu \sin\nu \cos\phi$$

$$y = a \sinh\mu \sin\nu \sin\phi$$

$$z = a \cosh\mu \cos\nu,$$

where $a = R/2$ and

$$0 \leqslant \mu < \infty$$

$$0 \leqslant \nu \leqslant \pi$$

$$0 \leqslant \phi \leqslant 2\pi.$$

Using a constant step size for the prolate spheroidal coordinates gives a reasonably well-scaled grid for a diatomic wave function.

In prolate spheroidal coordinates, both Eq. (1) for the potentials and Eq. (2) for the orbitals can formally be written

$$(-\partial_\mu^2 - \partial_\nu^2 - \coth\mu\,\partial_\mu - \cot\nu\,\partial_\nu + f)u = g \tag{3}$$

which is the linear 2D differential equation we have to solve. The boundary conditions are given by symmetry conditions at the molecular axis and asymptotic expressions at a practical infinity.

The continuous Eq. (3) is discretized using central finite differences of order $O(h^l)$, where l is either 2, 4, or 6, see Refs. [2, 5]. The coefficient matrix of the second-order discretization is a tridiagonal block matrix. The diagonal blocks are themselves tridiagonal submatrices and the sub- and super-diagonal blocks are diagonal submatrices. Thus, for the fourth- or sixth-order discretizations the three diagonals are augmented to five or seven diagonals in the matrix and submatrices. Moreover, the matrix is unsymmetric, because of the first derivatives, and depending on f, positive definite for Eq. (1) and indefinite for Eq. (2).

IV. LINEAR EQUATION SOLVER

The efficiency of the multigrid method for the solution of the discretized time-independent Schrödinger equation has been demonstrated [6] for a two-dimensional model problem which includes the essential features present in actual scattering problems. In Ref. [6] Gauss–Seidel relaxation was used as a smoother in an accommodative multigrid algorithm, with a direct solver on the coarsest grid. The direct solver was used in order to circumvent the difficulties associated with the fact that the Schrödinger differential operator is not positive definite. This approach did in most cases not work satisfactorily for the Hartree–Fock equations, because of nearness to singularity, that is, the existence of nearly zero eigenvalues for the resulting matrix to Eq. (2). A more robust method is presented below.

The multigrid method makes use of a sequence of subsequently coarsened meshes, where the coarsest mesh has to be fine enough to give a qualitative idea of the eigensolutions, while the final accuracy is determined by the finest mesh. These meshes are connected by restriction (fine-to-coarse transfer) and interpolation (coarse-to-fine transfer). Full weighting has been used as restriction and as interpolation the usual linear interpolation. When choosing a suitable smoother two problems have to be considered.

First, for indefinite problems, mode analysis shows [6] that the Gauss–Seidel relaxation is suitable if fine enough grids are considered. Smooth components may diverge on such grids, but slowly enough to be handled by the coarse-grid correction. On coarser grids, however, the divergence of smooth components in the Gauss–Seidel relaxation is faster; hence another relaxation scheme is needed.

Second, as was shown in Ref. [13], different singular behavior on different grids, causes large interpolation errors. This problem is more severe on the coarser grids and one may therefore to some extent avoid this problem by using only a few grids. This means that the coarsest grid may be too large to be efficiently solved by a direct method and, instead a Krylov subspace method [7, 8], the Orthomin algorithm is chosen for this purpose with Gauss–Seidel relaxation as preconditioner. The use of the Orthomin method will not only provide the smoothing but at the same time improve the coarse-grid correction. As a result the multigrid cycle will work satisfactorily also with few grids. Furthermore, Orthomin will offset to some extent the shortcomings of the basic smoother for the case of highly nonuniform meshes.

When the matrix is indefinite or unsymmetric, symmetric preconditioning is needed. The symmetrically preconditioned version of Orthomin(m), to solve the linear equation $Ax = b$, is

Choose x_0
Set $r_0 = b - Ax_0$

$$\tilde{r}_0 = M^{-1} r_0$$

$$p_0 = \tilde{r}_0$$

Start iterate

$$q_k = M^{-1} A p_k$$

$$\alpha_k = \langle q_k, \tilde{r}_k \rangle / \langle q_k, q_k \rangle$$

$$(\alpha_k = \langle A p_k, \tilde{r}_k \rangle / \langle A p_k, q_k \rangle)$$

$$x_{k+1} = x_k + \alpha_k p_k$$

$$\tilde{r}_{k+1} = \tilde{r}_k - \alpha_k q_k$$

$$o_k = M^{-1} A \tilde{r}_{k+1}$$

$$\beta_i = \langle o_k, q_i \rangle / \langle q_i, q_i \rangle$$

$$(\beta_i = \langle A \tilde{r}_{k+1}, q_i \rangle / \langle A p_i, q_i \rangle),\ i = 1, \ldots, m$$

$$p_{k+1} = \tilde{r}_{k+1} - \sum_{i=1}^{m} \beta_i p_i$$

$$A p_{k+1} = A \tilde{r}_{k+1} - \sum_{i=1}^{m} \beta_i A p_i,$$

where M^{-1} is an approximative inverse to A, $\tilde{r}$ is a generalized residual equal to $M^{-1} r$, and p is the direction of search. For the special case $m = 0$, Orthomin is identical to the minimal residual method and, for the case $m = 1$, Orthomin is equivalent to the conjugate residual method, when A is symmetric and positive definite.

Inside the parentheses, for comparison, we also give the simpler unsymmetric preconditioning which can be used when the matrix is positive definite and symmetric. If the matrix is indefinite a simple remedy is to add αI to the original matrix, where α is a scalar such that $A + \alpha I$ is positive real, and use as preconditioning the preconditioning associated with $A + \alpha I$. This can be effective in case α is not too large, see Ref. [10].

For the algorithm to work properly when the matrix is unsymmetric, a list of previous search directions must be kept. The length of the list depends on how large the asymmetric part of the matrix is. For this reason Orthomin(m) with m search directions is used on the coarsest grid, because here it is important for the solution to be converged, not only smoothed as on other grids. On the other coarser grids only a few iterations are needed and therefore Orthomin(1) works well.

When the number of iterations gets larger than m, the search direction corresponding to the smallest β relative to the norm of its associated vector is discarded. This is a much better policy than to use a first-in first-out policy, see [9] for a detailed discussion.

Let one work unit (WU) be equal to one relaxation on the finest grid. The work needed to form the vector Ax or to relax the equation $Ax = b$ is of equal size; therefore the main work for N iterations of the symmetric preconditioned Orthomin(1) on the finest grid is $3N + 1$ WU. The unsymmetric preconditioning is less expensive to use, but often two relaxation sweeps is necessary in the preconditioning step to achieve a convergence rate similar to that obtained with the symmetrical preconditioning, which gives $3N + 3$ WU.

In conclusion, if instead of performing v relaxations in a multigrid cycle, we perform v iterations of the preconditioned Orthomin with relaxation as preconditioning, then on the finest grid this will be too expensive to use, but on coarser grids we can afford it; therefore if work is considered, this method is better to use only on coarser grids. A V-cycle is a fixed multigrid algorithm. Let $V(v_1, v_2)$ be a V-cycle where v_1 is the number of relaxations or iterations before restriction and v_2 the number of relaxations or iterations after the coarse grid correction. The multigrid cycle used here on both Eqs. (1) and (2), is a $V(2, 3)$ cycle, with Gauss–Seidel relaxation on the finest grid and Orthomin(1) on the coarser grids, except for the coarsest grid where Orthomin(20) is used. The work needed to perform one $V(2, 3)$ cycle, if restriction is excluded, is approximately 11 WU.

Line relaxation is well suited for Eq. (1) for the potentials, because only the right-hand side of the equation changes between iterations. If banded LU factorization is performed in the first iteration and the LU decomposition is saved, then only forward and back substitution are needed to perform the relaxation in the following iterations.

The calculations were carried out on an Alliant FX-80/6 with more than one processor. By using zebra line relaxation, which implies that line relaxation is performed on two separate sets (colors), odd lines and even lines where the lines in each set are decoupled, for the second-order approximation and more colors for the higher order approximations for both Eqs. (1) and (2), the computations can be done in parallel.

A useful approximation to A^{-1} can be found, if the ILU (incomplete LU) factorization or the modified ILU factorization, which especially improves the low-frequency approximation, is used instead of relaxation. The block versions seem to be more efficient than the point versions, see, for example, [11]. Recently a block preconditioned conjugate gradient method [12] up to sixth order has been used to solve the Poisson equation in prolate spheroidal coordinates.

V. COMPUTATIONAL DETAILS AND RESULTS

Starting orbitals are taken from a basis set calculation. In the first iteration the potentials are initialized by a full multigrid cycle and thereafter as many multigrid cycles are performed as is necessary to make the norm of the residual for Eq. (1) smaller than a prescribed value. This value depends on the norm of the residuals in Eq. (2) for the orbitals involved in solving Eq. (1). In practice one multigrid cycle is enough for each potential. The equations for the orbitals are solved by using one multigrid cycle for each orbital.

TABLE I

Total and Orbital Energies (Hartree) for BH

Property	BH ($X^1\Sigma^+$)		
R(bohr)	2.336		
Grid	(193, 129)	(97, 65)	(97, 65)
E_T	−25.131598(9)70[a]	−25.131613[a]	−25.131609[b]
$\varepsilon(1\sigma)$	−7.686267(47)382	−7.686273	−7.686271
$\varepsilon(2\sigma)$	−0.6481872(8)7	−0.648188	−0.648188
$\varepsilon(3\sigma)$	−0.3484237(9)8	−0.348424	−0.348424

Note. For the largest grid the last figures for the sixth order values are given in parenthesis and the last extrapolated figures are given after the parenthesis.

[a] Present work.

[b] See Ref. [2].

The calculations presented here were carried out with sixth-order approximations, except in the first iteration for the potentials, where starting potentials were calculated with second-order approximations. The size of the grid was chosen to be $(n_\mu, n_\nu) = (193, 129)$ and μ-line relaxation was used. The number of grids used in the multigrid cycle was five, except three grids for the valence orbitals, to avoid the large interpolation errors associated with different singular behavior on different grids.

The damping factor for the orbitals was held constant during the SCF iterations. The SCF iterations were finished

TABLE II

Total and Orbital Energies (Hartree) for HF and CO

Property	HF ($X^1\Sigma^+$)	
R(bohr)	1.7328	
Grid	(193, 129)	(193, 129)
E_T	−100.07080(4)24[a]	−100.070804[b]
$\varepsilon(1\sigma)$	−26.29456(65)585	−26.2945664
$\varepsilon(2\sigma)$	−1.600985(13)07	−1.60098512
$\varepsilon(3\sigma)$	−0.7682476(5)0	−0.76824766
$\varepsilon(1\pi)$	−0.650393(60)55	−0.65039358
Property	CO ($X^1\Sigma^+$)	
R(bohr)	2.132	
Grid	(193, 129)	(113, 81)
E_T	−112.79090(9)71[a]	−112.79095[c]
$\varepsilon(1\sigma)$	−20.664521(8)26	−20.664531
$\varepsilon(2\sigma)$	−11.360051(5)33	−11.360055
$\varepsilon(3\sigma)$	−1.521489(91)84	−1.521491
$\varepsilon(4\sigma)$	−0.804529(84)79	−0.804531
$\varepsilon(5\sigma)$	−0.554923(43)38	−0.554925
$\varepsilon(1\pi)$	−0.640360(60)55	−0.640362

[a] Present work.

[b] Unpublished results from private communication with Dage Sundholm.

[c] See Ref. [2].

TABLE III

Total and Orbital Energies (Hartree) for CuH

Property	CuH ($X^1\Sigma^+$)	
R(bohr)	2.764	
Grid	(193, 129)	
E_T	−1639.51(6)42[a]	−1639.5128[b]
$\varepsilon(1\sigma)$	−328.80(94)877	−328.8090
$\varepsilon(2\sigma)$	−40.8398(8)21	−40.8394
$\varepsilon(3\sigma)$	−35.6372(7)06	−35.6368
$\varepsilon(4\sigma)$	−5.0298(6)49	−5.0289
$\varepsilon(5\sigma)$	−3.3438(6)52	−3.3429
$\varepsilon(6\sigma)$	−0.5168(34)27	−0.5159
$\varepsilon(7\sigma)$	−0.33702(5)0	−0.3362
$\varepsilon(1\pi)$	−35.6383(8)4	−35.6380
$\varepsilon(2\pi)$	−3.3391(27)18	−3.3382
$\varepsilon(3\pi)$	−0.50777(8)3	−0.5069
$\varepsilon(1\delta)$	−0.5056(23)17	−0.5047

Note. The copper (20*s*, 12*p*, 9*d*) primitive set of Ref. [16] was extended to (20*s*, 15*p*, 10*d*, 6*f*, 4*g*) and contracted to (7*s*, 6*p*, 4*d*, 2*f*, 1*g*) using an ANO contraction [17]. The hydrogen (8*s*, 6*p*, 4*d*)/(4*s*, 3*p*, 2*d*) ANO basis was taken from [17].

[a] Present work.

[b] Unpublished basis set calculation made by Lars Pettersson.

when a DIIS(4) step gave no improvement. After having calculated a solution to the coarser grid (97, 65), a Richardson extrapolation was performed. Depending on the method used to converge the solution, there could be an iteration error in the last figure shown for the valence orbitals.

Results for the diatomic molecules BH, HF, CO, and CuH at the experimental bond length, are shown in Tables I, II, and III. For comparison, results from numerical RHF calculations by Laaksonen *et al.* [2] are also given for BH, HF, and CO. When the same gridsize is used, both methods yield nearly identical results. For CuH, also, results from a large basis set calculation are given. An error of about 1.4 mhartree in the total energy for the basis set seems reasonable, when the same basis set on the Cu atom gives a total energy of −1638.9629, which is in error by 0.8 mhartree compared with the exact RHF energy −1638.9637 [14].

TABLE IV

Total and Orbital Energies (Hartree) for the Zn Atom

Property	Zn (^1S)	
R(bohr)	3.0	
Grid	(193, 129)	
E_T	−1777.8(51)488[a]	−1777.8481[b]
$\varepsilon(1\sigma)$	−353.30(56)47	−353.304545
$\varepsilon(2\sigma)$	−44.361(81)74	−44.361726
$\varepsilon(3\sigma)$	−38.924(93)86	−38.9248455
$\varepsilon(4\sigma)$	−5.6378(33)19	−5.637821
$\varepsilon(5\sigma)$	−3.8393(89)77	−3.83937905
$\varepsilon(6\sigma)$	−0.7825(45)39	−0.78254215
$\varepsilon(7\sigma)$	−0.2925(11)08	−0.29250705
$\varepsilon(1\pi)$	−38.9248(8)5	−38.9248455
$\varepsilon(2\pi)$	−3.8393(83)76	−3.83937905
$\varepsilon(3\pi)$	−0.7825(43)39	−0.78254215
$\varepsilon(1\delta)$	−0.7825(43)39	−0.78254215

[a] Present work.

[b] See Ref. [15].

TABLE V

Spectroscopic Constants

	BH	HF	CO	CuH
r_e(bohr)	2.3052	1.6951	2.0820	2.98
D_e(eV)	2.79285	4.4067	8.0187	1.82
ω_e(cm^{-1})	2494	4479	2430	1750

In addition, a calculation was made on the Zn atom, to test the accuracy of the extrapolated solution against atomic 1D numerical calculations. The results in Table IV shows an error of 0.7 mhartree for the total energy while the errors in the orbital energies are in the last figure shown.

The main source of the error comes from the orbital with lowest energy, which gives a larger error for Zn than for CuH.

The computed equilibrium bond length r_e, the dissociation energy D_e, and the harmonic frequency ω_e are given for BH, HF, CO, and CuH in Table V. The spectroscopic parameters were computed by cubic interpolation in r. For CuH the extrapolated values were used, but to give a reliable ω_e, higher numerical accuracy is needed.

Data about the calculations, with three processors in the cluster, are given in Table VI. The computational time behavs like $O(N)$, where N is the number of unknowns. This is what could be expected for this kind of problem with a multigrid method [7]. However, if a small damping factor is needed to obtain convergence, the computational time is increased.

The computational times for using one, two, or three processors for HF were 6663 s, 3334 s, and 2573 s, respectively. As a result, the computational time was reduced with a factor of 0.5 or 0.39 with two or three processors, respectively.

Finally, the residual history for the orbitals in the HF

TABLE VI

Computational Details

	BH	HF	CO	CuH	Zn
Number of orbitals	3	4	6	11	11
Number of potentials	6	11	22	76	76
Damping factor	0.54	0.54	0.4	0.3	0.3
Number of iterations	18	18	25	35	30
Computational time (h)	0.4	0.7	1.9	6.5	5.5
Comp. time (ms) per unknown	7.1	6.9	9.6	10.8	9.1

TABLE VII

Residual History for the Orbitals in the HF Molecule

Orbital SCF iteration	1σ	2σ	3σ	1π
1	5.3 (0.014)	1.8 (0.020)	1.9 (0.043)	1.1 (0.037)
2	2.4 (0.014)	8.5–1(0.021)	8.5–1(0.042)	5.2–1(0.037)
3	1.1 (0.014)	3.4–1(0.021)	4.0–1(0.042)	2.5–1(0.037)
4	5.3–1(0.015)	1.9–1(0.021)	1.9–1(0.041)	1.2–1(0.038)
5	2.5–1(0.015)	8.9–2(0.022)	9.1–2(0.042)	5.6–2(0.038)
6	2.6–2(0.016)	7.6–3(0.019)	9.2–3(0.059)	2.6–3(0.036)
7	1.2–2(0.016)	3.7–3(0.020)	4.3–3(0.059)	1.1–3(0.033)
8	5.6–3(0.016)	1.8–3(0.021)	5.0–3(0.145)	5.5–4(0.035)
9	2.6–3(0.016)	8.3–4(0.021)	2.8–3(0.156)	2.7–4(0.036)
10	1.2–3(0.016)	4.3–3(0.023)	1.3–3(0.143)	1.4–4(0.039)
11	1.4–3(0.016)	4.4–4(0.019)	3.0–4(0.038)	1.2–4(0.033)
12	6.7–4(0.016)	2.1–4(0.020)	1.6–4(0.043)	6.2–5(0.034)
13	3.1–4(0.016)	9.8–5(0.020)	8.0–5(0.046)	2.9–5(0.035)
14	1.4–4(0.016)	4.7–5(0.021)	3.8–5(0.045)	1.4–5(0.036)
15	6.8–5(0.016)	2.2–5(0.021)	2.0–5(0.052)	6.9–6(0.038)
16	2.2–5(0.015)	6.5–6(0.017)	9.4–6(0.070)	2.2–6(0.033)
17	1.0–5(0.015)	3.0–6(0.018)	3.1–6(0.047)	9.6–7(0.032)
18	4.8–6(0.015)	1.4–6(0.018)	1.8–6(0.058)	5.0–7(0.035)

Note. The multigrid cycle reduction of the residuals in each iteration are given inside the parenthesis. The short notation $-n = 10^{-n}$ is used for the residuals.

molecule is shown in Table VII. Especially for the 3σ valence orbital, the reduction of the residual depends on the DIIS method.

VI. CONCLUSIONS

The multigrid cycle, with Gauss–Seidel relaxation on the finest grid and the Orthomin method on the coarser grids with Gauss–Seidel relaxation as preconditioner, used as a linear equation solver in a generalized inverse iteration, has been shown to be very efficient to solve numerically the restricted Hartree–Fock (RHF) equations for diatomic molecules. The numerical results presented in this work are in good agreement with results given in the literature.

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