

Improved SCF Convergence Acceleration

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An improved version of the direct inversion in the iterative subspace algorithm is developed. The method is significantly more efficient than the previous version, and is applicable to intrinsically divergent or slowly convergent cases. Comparisons indicate that the method is superior to the recently proposed quadratically convergent (QC-SCF) method of Bacskay.

The direct inversion in the iterative subspace (DIIS) method, described in a recent communication¹ (hereafter referred to as part I), provides a significant acceleration of the SCF convergence rate, particularly toward the end of the SCF procedure when convergence, for reasons discussed in part I, is usually slow. It is important to have accurately converged SCF wavefunctions in a number of applications: for calculating correlation energy surfaces; in gradient programs; and in all cases where a subsequent numerical differentiation is involved, as in finite field methods.

The DIIS method can be briefly recapitulated as follows: In each SCF step, construct an error vector \mathbf{e}^i , where i is the step index. The vanishing of the error vector should be a necessary and sufficient condition for SCF convergence. The construction of a suitable error vector will be discussed later; basically, it is related to the gradient of the electronic energy with respect to the SCF parameters and thus vanishes for the SCF solution. Toward the end of the SCF procedure, changes in the wavefunction are small and it can be assumed that the error vector depends linearly on the parameters p used to characterize the wavefunction. As parameters, it is customary to use the elements of the density matrix or the Fock matrix, in order to avoid the phase difficulties of the wavefunction. It is then possible to find a linear combination of consecutive parameter vectors $\mathbf{p} = \sum_i c_i \mathbf{p}^i$ so that the corresponding error vector $\sum_i c_i \mathbf{e}^i$ approximates the zero vector in the least-squares sense. An interpolation like this violates, of course, the

idempotency of the density matrix in second order; however, this becomes insignificant as SCF convergence is approached. In practice, it was found that even interpolation between fairly different Fock matrices gave satisfactory results. As discussed in part I, the least-squares criterion, together with the condition that the coefficients c_i add up to 1, leads to a small set of linear equations:

$$\begin{pmatrix} 0 & -1 & -1 & \cdots & -1 \\ -1 & B_{11} & B_{12} & \cdots & \\ \cdots & & & & \\ -1 & \cdots & & & B_{ij} \\ \vdots & & & & \end{pmatrix} \begin{pmatrix} -\lambda \\ c_1 \\ \vdots \\ c_i \\ \vdots \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \\ \vdots \\ 0 \\ \vdots \end{pmatrix} \quad (1)$$

where $B_{ij} = \langle \mathbf{e}_i | \mathbf{e}_j \rangle$ with a suitably defined metric in the e space, and λ is a Lagrangian multiplier.

In part I, the error vector was defined as the change in the parameter vector in the course of the subsequent SCF step. This worked well in the semiempirical applications for which DIIS was originally developed. Nevertheless, an initial implementation in the *ab initio* SCF program TEXAS revealed several weaknesses: (1) In the *ab initio* Roothaan–Hall procedure, the main computational task is the construction of the Fock matrix. In the original algorithm¹ the determination of the error vector required the construction of an extra Fock matrix which was not used in any other way. (2) Due to the large number of arithmetic operations, the error vector constructed as the difference of two consecutive Fock matrices was not sufficiently accurate numerically. (3) Finally, the main objection against the algorithm presented in part I is that DIIS extrapolation was performed only

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periodically, after an arbitrary (5–12) number of conventional SCF cycles. This restricted the use of the method in intrinsically divergent or very slowly convergent cases. A constant damping² or level shifting³ often remedied this difficulty; however, the method presented below, in which extrapolation is applied in every step, is greatly superior.

In the present article, a new algorithm, based on a new definition of the error vector, is presented which avoids the deficiencies of the previous method.¹

Consider a general SCF wavefunction with k groups of orbitals. It is assumed that the occupation number is constant within a group but is different for different groups; note that the virtual orbitals, with occupation number 0 are also considered; e.g., in the ordinary closed-shell case, $k = 2$, and in a simple open-shell RHF case, $k = 3$ (doubly occupied, singly occupied, and unoccupied orbitals). Let the corresponding density matrices be $\mathbf{D}_i = \mathbf{C}\mathbf{N}_i\mathbf{C}^+$, $i = 1, \dots, k$, where the \mathbf{N}_i s are density matrices in the orbital basis, i.e., diagonal matrices built from 0s and 1s, and \mathbf{C} is the transformation matrix from the basis function to the orbitals. Assume further that all orbitals are eigenfunctions of a single Fock matrix; Roothaan,⁴ Hirao,⁵ Davidson,⁶ Guest and Saunders,⁷ and Carbo, Gallifa, and Riera⁸ discuss the construction of suitable coupling operators. A necessary and sufficient condition for SCF convergence is the vanishing of the off-diagonal blocks of the Fock matrix in orbital basis between different orbital group. This is equivalent to the condition that the antihermitian matrix $\sum_{i>j} (\mathbf{N}_i \mathfrak{F} \mathbf{N}_j - \mathbf{N}_j \mathfrak{F} \mathbf{N}_i)$ vanishes. Here $\mathfrak{F} = \mathbf{C}^+ \mathbf{F} \mathbf{C}$ is the Fock matrix in orbital basis. In order to be useful for extrapolation purposes, these matrices (one in each iteration step) must be transformed to a common basis, e.g., to the original AO basis set. This leads to the following error matrix:

$$\mathbf{e} = \mathbf{f} - \mathbf{f}^+ = (\mathbf{C}^+)^{-1} \left\{ \sum_{i>j=1}^k a_{ij} \mathbf{N}_i \mathfrak{F} \mathbf{N}_j \right\} \mathbf{C}^{-1} - (\text{hermitian conjugate}) \quad (2)$$

Using the orthonormality condition $\mathbf{C}^+ \mathbf{S} \mathbf{C} = \mathbf{1}$, \mathbf{f} can be simplified to

$$\mathbf{f} = \sum_{i>j}^k a_{ij} \mathbf{S} \mathbf{D}_i \mathbf{F} \mathbf{D}_j \mathbf{S}$$

Here the a_{ij} are arbitrary nonzero coefficients which weigh the different off-diagonal blocks of the orbital density matrix. The arbitrariness of the a_{ij} can be used to simplify the error vector further.

Introduce the density matrix corresponding to the virtual orbitals,

$$\mathbf{D}_k = \mathbf{S}^{-1} - \sum_{i=1}^{k-1} \mathbf{D}_i$$

then \mathbf{e} can be written as

$$\mathbf{e} = \sum_{i>j}^{k-1} (a_{ij} + a_{ki} - a_{kj}) \mathbf{S} \mathbf{D}_i \mathbf{F} \mathbf{D}_j \mathbf{S} + \sum_{j=1}^{k-1} a_{kj} \mathbf{F} \mathbf{D}_j \mathbf{S} - (\text{hermitian conjugate}) \quad (3)$$

If the coefficients a_{ij} are chosen so that $a_{ij} = a_{kj} - a_{ki}$ ($i, j < k$), then the first term in eq. (3) vanishes and \mathbf{e} is given by the simple expression

$$\mathbf{e} = \sum_{j=1}^{k-1} a_j (\mathbf{F} \mathbf{D}_j \mathbf{S} - \mathbf{S} \mathbf{D}_j \mathbf{F}) = \sum_{j=1}^{k-1} (\mathbf{F} \mathbf{D} \mathbf{S} - \mathbf{S} \mathbf{D} \mathbf{F}) \quad (4)$$

where $a_j = a_{kj}$, $a_j \neq 0$, $a_j \neq a_i$, and $\mathbf{D} = \sum_{j=1}^{k-1} a_j \mathbf{D}_j$. It seems that the best choice for the arbitrary coefficients a_j is the occupation number, in which case \mathbf{D} becomes the charge density matrix. Indeed, it was pointed out long ago by McWeeny and Sutcliffe⁹ that the necessary and sufficient condition for an SCF solution is that the density matrix commutes with the Fock matrix, and that *this remains true in the open-shell case*. A further generalization to the case where the (spin-free) orbitals are not orthogonal and consequently cannot be the eigenfunctions of a single hermitian Fock matrix is straightforward; e.g., in the case of the spin-unrestricted (UHF) wavefunction, the error vector can be constructed from the separate error vectors for α and β spins.

As discussed in part I, a more balanced error vector can be obtained by transforming \mathbf{e} to an orthonormal basis. In the present case, this is equivalent to replacing \mathbf{e} by $\mathbf{e}' = \mathbf{A}^+ \mathbf{e} \mathbf{A}$, where $\mathbf{A}^+ \mathbf{S} \mathbf{A} = \mathbf{1}$; e.g., $\mathbf{A} = \mathbf{S}^{-1/2}$. This formula is used in the actual algorithm which can be summarized as follows:

(1) Construct the error vector according to eq. (4) and transform it to orthogonal basis. Note that the density matrix in eq. (4) is the density used to construct the Fock matrix. If the largest element of the error matrix, e_{\max} , is less than a threshold ($\approx 0.10 E_h$), initiate the DIIS procedure. If the e_{\max} is less than another threshold ($\approx 10^{-6} E_h$), the SCF procedure has converged.

(2) In each DIIS step, store both the error matrix and the current Fock matrix. Evaluate the necessary scalar products $B_{ij} = \text{Tr}(\mathbf{e}_i \mathbf{e}_j^+)$. Note that with

Table I. Decrease of the error parameter using the DIIS technique as compared to the traditional SCF procedure.^a

Cycle	A C E T Y L E N E ^b		Cycle	W A T E R ^c	
	DIIS	SCF		DIIS	SCF
1	0.29-2	0.29-2	1	0.27-1	0.27-1
4	0.58-4	0.15-3	4	0.68-4	0.63-3
6	0.82-6	0.34-4	6	0.32-5	0.28-3
8	0.13-7	0.75-5	8	0.43-7	0.12-3
10	...	0.17-5	10	...	0.53-4
14	...	0.78-7	15	...	0.67-5
16	...	0.14-7	20	...	0.82-6
			25	...	0.10-6
			27	...	0.44-7

^a The error parameter is defined as the largest element, in absolute value, of the error vector, eq. (4). The abbreviation 0.29-2 = 0.29×10^{-2} is used.

^b 4-21G Gaussian basis set, nonlinear geometry. The SCF iteration was begun with the wavefunction at a nearby (0.02 Å) geometry.

^c (12s6p2d/5s2p) → [5s4p2d/3s2p] Gaussian basis set, with an electric field of 0.01 a.u. parallel to the C₂ axis. The SCF iteration was begun with the wavefunction obtained without the field.

proper programming only the last row of **B** has to be evaluated in each SCF step. Set up and solve eq. (1). If eq. (1) becomes ill-conditioned, omit the first, second, etc., equation until its condition becomes acceptable.

(3) Replace the current Fock matrix by $\mathbf{F}' = \sum_{i=1}^n c_i \mathbf{F}_i$. Diagonalize the Fock matrix \mathbf{F}' ; determine the new density matrix and the new Fock matrix. Start again at step 1.

In spite of its simplicity, this method has proven greatly superior to the SCF procedure, particularly in the final stages when, for reasons discussed in part I, convergence is usually slow. It is also significantly superior to its predecessor.¹ Usually, the maximum element of the error vector decreases almost an order of magnitude per step toward the end of the iteration of DIIS is used, as contrasted with a decrease by a factor of about 2 in ordinary SCF. The extra computational effort associated with DIIS is negligible. We have found this method indispensable when a finite electric field is applied. An ingenious method has been recently suggested by Komornicki and McIver¹⁰ for the calculation of dipole moment and polarizability derivatives as the numerical derivatives of the exact SCF force¹¹

with respect to an external electric field. In these calculations high SCF accuracy is necessary, as the numerical derivatives of an unstable quantity, the force, are involved. We have found that, in general, ordinary SCF converges poorly in the presence of the field. As Table I shows, DIIS greatly decreases the number of necessary SCF steps in this case, and generally in every case where a high degree of self-consistency is needed.

Note finally that a method somewhat similar has been used to find the solution of the coupled Hartree-Fock equations by Sadlej.¹² A substantial restriction of his method is that only interpolation between two iteration steps are considered as in the method of Neilsen¹³ which is more similar to DIIS. An interesting feature of Sadlej's technique is that the criterion is the lowest total energy instead of the vanishing of the error vector. While this is perhaps desirable, the energy criterion can be used only if idempotency is exactly preserved. This is difficult to ensure and calls in any case for an extra evaluation of the Fock matrix.

Recently, Bacskay¹⁴ suggested an implementation of the quadratically convergent Hartree-Fock method (QC-SCF) which avoids the costly

Table II. Comparison of the performance of the modified DIIS and the QC-SCF^a methods.

Carbon monoxide ^b				H ₂ C ₂ N ⁺ ion ^b			
Iteration	DIIS	QC-SCF ^a		Iteration	DIIS	QC-SCF ^a	
0	SCF 1.3	9.2-1		0	SCF ^c 1.7	8.6-1	
1	" 3.4-1			3	" 1.8-1	7.1-1	
2	" 1.7-1			6	" 3.6-2	6.0-1	
3	" 1.6-1	5.8-1		7	DIIS 1.3-2		
4	DIIS 1.0-2			8	" 2.5-3		
5	" 1.8-3			9	" 6.7-4		
6	" 5.1-4			10	" 1.5-4	2.1-1	
7	" 7.9-5			11	" 1.5-5		
8	" 8.5-6			12	" 1.1-5		
9	" 3.4-6			13	" 5.5-6		
10	" 4.4-7	5.3-2		14	" 6.8-7		
11	" 2.2-9			15	" 1.5-7	9.1-2	
12	" 1.7-10			16	" 2.2-8		
...				17	" 1.1-9		
15		2.6-3		18	" 3.2-10		
...				19		6.0-3	
19		3.5-5		...			
...				25		6.1-5	
24		7.2-8		...			
...				31		1.1-6	
28		3.4-10		...			
				37		4.2-8	
				...			
				43		5.3-10	

^a See ref. 14. The iteration number is the number of microiterations.^b 4-31G basis set geometry as described by Bacskay in ref. 14.^c Damped with an interpolation factor of 0.5.²

four-index transformation of similar techniques. In essence, this is a damped Newton-Raphson-type optimization without the explicit evaluation of the Hessian; the latter is used only in operator form. A single diagonalization of the Hessian (a macroiteration) needs typically four to five microiterations, each comparable to one iterative cycle of conventional SCF. A comparison between Bacskay's method and the present scheme is shown for his more difficult cases, CO and the H₂C₂N⁺ ion in Table II. For a comparable computational effort, i.e., the same number of microiterations, DIIS significantly outperforms the QC-SCF technique; the difference is even greater if a moderate level shift parameter is used (not shown). The ability of DIIS to damp-out fairly large oscillations at the beginning is particularly pleasing. Most quadratically convergent multiconfig-

urational SCF (MC-SCF) methods are very efficient toward the end of the iteration but are not able to cope with the initial large oscillations. Efforts are under way to implement a DIIS-type procedure for certain types of MC-SCF wavefunctions and compare its performance to that of quadratically convergent schemes.

As mentioned in the Introduction, the DIIS technique violates the idempotency of the density matrices. Although this becomes insignificant as SCF convergence is approached, it might be preferable to perform the interpolation in a way which maintains idempotency if large changes in the orbitals are expected. The simplest way to do this is to use, instead of the Fock matrix elements, a set of independent parameters. E.g., by multiplying the coefficient matrices $C_1, C_2, \dots, C_i, \dots$ by C_1^{-1} from the left, a set of orthogonal matrices $U_i =$

$C_1^{-1}C_i$ are generated, each of which can be represented by the $n(n-1)/2$ independent elements of a real antisymmetric matrix \mathbf{K} . While the most commonly used representation is $\mathbf{U} = \exp(\mathbf{K})$, the pair of equations

$$\mathbf{U} = 2(\mathbf{K} - 1)^{-1} + 1, \quad \mathbf{K} = 2(\mathbf{U} - 2\mathbf{1})^{-1} + 1 \quad (5)$$

is simpler. Interpolation is performed in the \mathbf{K} space, and the interpolated \mathbf{K} matrix is transformed back to a coefficient matrix, from which a new Fock matrix is formed. A disadvantage of this method is that the most expensive part of the computation, the generation of the Fock matrix, has to be repeated twice. For this reason, this method is not recommended if a sufficiently good starting wavefunction is available, as it is usually the case in closed-shell calculations.

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