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Improved coupled perturbed Hartree–Fock and Kohn–Sham convergence acceleration

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Received 11 October 2002; in final form 18 December 2002

Abstract

A derivative version of the well-known direct inversion in the iterative subspace (DIIS) algorithm is presented. The method is used to solve the coupled perturbed Hartree–Fock (CPHF) equation to obtain the first and second derivatives of the density matrix with respect to an external electric field which, in this case, leads to the electric molecular polarizability and hyperpolarizability. Some comparisons are presented and the method shows good convergences in almost all cases.

1. Introduction

A number of molecular properties [1] as for example: second-order geometric derivatives [2,3], non-linear optical properties [4–6], nuclear magnetic resonance [7,8], g tensor [9], Raman intensity [10], etc. can be formulated in terms of derivatives of the total energy E, with respect to the perturbational parameter(s), $x^a, x^b, \ldots$

$$E^{(a,b,\ldots)} = \frac{\partial}{\partial x^a} \frac{\partial}{\partial x^b} \cdots E. \tag{1}$$

The perturbation(s) $x^a, x^b, \ldots$ can include, for example: nuclear displacements, external electric and/or magnetic field, and nuclear magnetic spin moment. Thus a large variety of molecular prop-

erties can be computed in the framework of the coupled perturbed equations.

In this Letter, we present a method to reduce the number of iterations during the resolution of the coupled perturbed Hartree–Fock (CPHF) or Kohn–Sham (CPKS) equations.

We will show that an extension using derivatives of the well-known direct inversion in the iterative subspace algorithm (DIIS) [11,12] is well suited, in principle, for any kind and order of the CPHF or CPKS equations. To the best of our knowledge, it is the first use of such a kind of extension of the Pulay's method applied to the CPHF/CPKS equations. This algorithm has been implemented in our new quantum chemistry program package FREEMOL [13]. Using the proposed method we find a significant reduction of the number in iterations needed to reach convergence for a given threshold during the computation of both static polarizability and hyperpolarizability.

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Comparisons with the results obtained using the program GAMESS [14] show a gain factor between 1.7 and 3.9 for the set of molecules taken as test (see Tables 1–4).

This Letter is organized as follows: in Section 2 we present the methodology, Section 3 will be dedicated to the presentation of the results and finally the conclusions will be drawn in Section 4.

2. Methodology

In molecular orbital (MO) theory it is well-known that the convergence of the Roothaan–Hall self-consistent field iterations can be accelerated by several methods. The most simple being the constant or dynamic damping [15] method, and one of the most popular ones is the DIIS [11,12] or the new energy direct inversion in the iterative subspace (EDIIS) recently developed by Cancès and co-workers [16,17].

2.1. Constant damping algorithm

The constant damping algorithm is the simplest and rather trivial method to avoid convergence problems. It consists in mixing by a linear combination the old density matrix D_{k-1} and the new density D_k as

$$\tilde{D}_k = \alpha D_k + (1 - \alpha)D_{k-1}, \tag{2}$$

where α is a predefined constant factor in the interval $[0, 1]$.

2.2. Direct inversion in the iterative subspace

The DIIS method, introduced some time ago by Pulay [11,12], provides a significant acceleration of the SCF rate. The idea of the DIIS scheme consists in using the information accumulated during the preceding iterations by constructing an averaged effective atomic orbital (AO) Fock matrix $\tilde{F}_k$ at the kth iteration. This effective Fock matrix is then used instead of F_k to generate an improved set of molecular orbitals and thus an improved density matrix D_{k+1} on the basis of atomic orbitals (AO density matrix). In this manner, the SCF procedure is stabilized and the oscillations avoided.

2.3. SCF based DIIS algorithm

The Pulay's DIIS scheme is based on the minimization of the norm of the error vector $\mathbf{e}_i$ given by the commutator

$$\mathbf{e}_i = [F(D_i), D_i]_S = F(D_i)SD_i - D_iSF(D_i), \tag{3}$$

with the quadratic coefficients being the products of the two error vectors

Table 1
Number of iterations needed for the calculation of the electric polarizability and first hyperpolarizability of sulfur hexafluoride with three different methods: CDA(α), DDIIS and CDA(α) and DDIIS or CDA(α) (see text), where α is the value of the damping factor

Method	α_{xx}	β_{xxx}	β_{yxx}
CDA(0.20)	19(30)	23(32)	23(34)
CDA(0.15)	17(28)	21(30)	21(31)
CDA(0.10)	17(26)	22(31)	20(29)
CDA(0.05)	24(29)	29(41)	19(28)
DDIIS and CDA(0.20)	9(12)	14(16)	9(11)
DDIIS and CDA(0.15)	9(11)	14(16)	9(11)
DDIIS and CDA(0.10)	8(11)	14(16)	9(11)
DDIIS and CDA(0.05)	8(11)	14(16)	9(11)
DDIIS or CDA(0.20)	8(10)	14(16)	9(11)
DDIIS or CDA(0.15)	8(10)	14(16)	9(11)
DDIIS or CDA(0.10)	8(10)	14(16)	9(11)
DDIIS or CDA(0.05)	8(10)	14(16)	9(11)

The number of iterations is given for a threshold on the first and second derivatives of the density matrices of $\Delta D_{1,max} = 10^{-4}$ a.u. ($\Delta D_{2,max} = 10^{-6}$ a.u. correspond to the values in parentheses) and a threshold for the tensor components of $\Delta \alpha_{max} = \Delta \beta_{max} = 10^{-4}$ a.u. have been used for all calculations.

Table 2
Comparison between the number of iterations needed for the calculation of the electric polarizability and first hyperpolarizability of sulfur hexafluoride with GAMESS [14] and FREEMOL

Method	α_{xx}	β_{xxx}	β_{yxx}
GAMESS	31	32	22
DDIIS and CDA(0.20)	8	14	9
DDIIS and CDA(0.15)	8	14	9
DDIIS and CDA(0.10)	8	14	9
DDIIS and CDA(0.05)	8	14	9
DDIIS or CDA(0.20)	8	14	9
DDIIS or CDA(0.15)	8	14	9
DDIIS or CDA(0.10)	8	14	9
DDIIS or CDA(0.05)	8	14	9

Two different methods are presented: DDIIS and CDA(α) and DDIIS or CDA(α) (see text), where α is the value of the damping factor. The number of iterations is given for a threshold on the first and second derivatives of the orbital rotation matrices $\Delta U_{\max} = 10^{-5}$ a.u. and a threshold on the tensor components of $\Delta\alpha_{\max} = \Delta\beta_{\max} = 10^{-4}$ a.u. have been used for all calculations.

$$f^{\mathrm{DIIS}}(c_0, \ldots, c_k) = \sum_{i,j=0}^{k} c_i c_j \mathbf{e}_i \cdot \mathbf{e}_j$$
$$= \left\| \sum_{i=0}^{k} c_i [F(D_i), D_i]_S \right\|^2, \qquad (4)$$

where $\|\cdot\|$ denotes the Frobenius norm and S the AO overlap matrix. It is worth mentioning that the error vector is proportional to the electronic gradient ($\nabla_\kappa E$) [18] with respect to the orbital rotation parameters κ_{pq} as

$$\nabla_\kappa E = 4[F, D]_S = 4\mathbf{e}. \qquad (5)$$

One solves in practice the constrained optimization problem

$$\inf \left\{ f^{\mathrm{DIIS}}, \sum_{i=0}^{k} c_i = 1 \right\}, \qquad (6)$$

where f^{DIIS} is given by (4). Once the optimal coefficients c_i^k have been obtained, it is then possible to find a linear combination of Fock matrices

$$\tilde{F}_k = \sum_{i=0}^{k} c_i^k F_i, \qquad (7)$$

so that the corresponding error vector $\tilde{\mathbf{e}}_k = \sum_{i=0}^{k} c_i^k \mathbf{e}_i$ approximates the zero vector in the least-squares sense. This interpolation – like violates the idempotency of the density matrix at the second-order, however, this becomes insignificant when the SCF convergence has been reached.

2.4. Derivative based DIIS algorithm (DDIIS)

In this subsection we introduce the DDIIS method which is an extension of the Pulay's DIIS algorithm.

By straightforward differentiation of the error vector $\mathbf{e}_i$ defined in (3) with respect to the pertur-

Table 3
Number of iterations needed for the calculation of the electric polarizability and first hyperpolarizability of DP5 molecule with three different methods: CDA(α), DDIIS and CDA(α) and DDIIS or CDA(α) (see text), where α is the value of the damping factor

Method	α_{xx}	α_{yy}	α_{zz}	β_{xxx}	β_{yxx}	β_{yyy}	β_{zxx}	β_{zyy}	β_{zzz}
CDA(0.20)	44(47)	13(20)	19(33)	37(>50)	20(30)	16(30)	31(44)	18(27)	24(38)
CDA(0.15)	42(44)	13(18)	19(30)	34(48)	19(28)	16(28)	29(41)	17(25)	22(35)
CDA(0.10)	28(42)	12(17)	25(29)	32(45)	18(26)	19(28)	27(38)	16(24)	23(33)
CDA(0.05)	37(39)	11(16)	33(37)	36(48)	17(24)	24(36)	26(38)	15(22)	29(41)
DDIIS and CDA(0.20)	21(29)	7(11)	13(36)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS and CDA(0.15)	18(23)	7(10)	13(20)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS and CDA(0.10)	26(30)	7(10)	15(20)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS and CDA(0.05)	23(33)	7(10)	15(20)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS or CDA(0.20)	16(22)	7(10)	13(30)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS or CDA(0.15)	19(21)	7(10)	16(20)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS or CDA(0.10)	21(23)	7(10)	14(20)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)
DDIIS or CDA(0.05)	20(20)	8(10)	13(19)	24(31)	10(13)	12(19)	16(23)	8(12)	15(22)

The number of iterations is given for a threshold on the first and second derivatives of the density matrices of $\Delta D_{1,\max} = 10^{-4}$ a.u. ($\Delta D_{2,\max} = 10^{-6}$ a.u. correspond to the values in parenthesis) and a threshold for the tensor components of $\Delta\alpha_{\max} = \Delta\beta_{\max} = 10^{-4}$ a.u. have been used for all calculations.

Table 4
Comparison between the number of iterations needed for the calculation of the electric polarizability and first hyperpolarizability of DP5 molecule with Gamess [14] and Freemol

Method	α_{xx}	α_{yy}	α_{zz}	β_{xxx}	β_{yxx}	β_{yyy}	β_{zxx}	β_{zyy}	β_{zzz}
Gamess	43	14	45	42	19	31	36	17	36
DDIIS and CDA(0.20)	21	8	30	27	11	14	20	10	19
DDIIS and CDA(0.15)	18	8	16	27	11	14	20	10	19
DDIIS and CDA(0.10)	26	8	16	27	11	14	20	10	19
DDIIS and CDA(0.05)	23	8	15	27	11	14	20	10	19
DDIIS or CDA(0.20)	15	8	25	27	11	14	20	10	19
DDIIS or CDA(0.15)	16	8	16	27	11	14	20	10	19
DDIIS or CDA(0.10)	19	8	15	27	11	14	20	10	19
DDIIS or CDA(0.05)	19	8	15	27	11	14	20	10	19

Two different methods are presented: DDIIS and CDA(α) and DDIIS or CDA(α) (see text), where α is the value of the damping factor. The number of iterations is given for a threshold on the first and second derivatives of the orbital rotation matrices $\Delta U_{max} = 10^{-5}$ a.u. and a threshold for the tensor components of $\Delta\alpha_{max} = \Delta\beta_{max} = 10^{-4}$ a.u. have been used for all calculations.

bation parameters $x^a, x^b, \ldots$ one obtains the gradient error vector as

$$\mathbf{e}_i^{(a,b,\ldots)} = \partial_a \partial_b \cdots [F(D_i), D_i]_S, \tag{8}$$

where we have used the short-hand notation

$$\mathbf{e}_i^{(a)} \equiv \mathbf{e}_i^{(a)}(\mathbf{x}) \equiv \partial_a \mathbf{e}_i(\mathbf{x}) \equiv \frac{\partial \mathbf{e}_i(\mathbf{x})}{\partial x^a}. \tag{9}$$

The first and second derivatives are

$$\mathbf{e}_i^{(a)} = [F_i^{(a)}, S]_{D_i} + [F_i, S^{(a)}]_{D_i} + [F_i, S]_{D_i^{(a)}}, \tag{10}$$

and

$$\begin{aligned} \mathbf{e}_i^{(a,b)} = &[F_i^{(a,b)}, S]_{D_i} + [F_i, S^{(a,b)}]_{D_i} + [F_i, S]_{D_i^{(a,b)}} \\ &+ [F_i^{(a)}, S^{(b)}]_{D_i} + [F_i^{(b)}, S^{(a)}]_{D_i} \\ &+ [F_i^{(a)}, S]_{D_i^{(b)}} + [F_i^{(b)}, S]_{D_i^{(a)}} \\ &+ [F_i, S^{(a)}]_{D_i^{(b)}} + [F_i, S^{(b)}]_{D_i^{(a)}}. \end{aligned} \tag{11}$$

The derivative equivalent of the quadratic function (4) can be written as

$$f^{\mathrm{DDIIS}}(c_0, \ldots, c_k) = \sum_{i,j=0}^{k} c_i c_j \mathbf{e}_i^{(a,b,\ldots)} \cdot \mathbf{e}_j^{(a,b,\ldots)}. \tag{12}$$

One finally solves the constrained optimization problem

$$\inf \left\{ f^{\mathrm{DDIIS}}, \sum_{i=0}^{k} c_i = 1 \right\}. \tag{13}$$

Once the optimal coefficients c_i^k have been computed, it is then possible to find the extrapolated derivative Fock matrix $\tilde{F}_k^{(a,b,\ldots)}$ by

$$\tilde{F}_k^{(a,b,\ldots)} = \sum_{i=0}^{k} c_i^k F_i^{(a,b,\ldots)}. \tag{14}$$

3. Implementation

We have implemented the DDIIS in the DIIS routine of Freemol [13]. In order to take maximum advantage of the DDIIS method during the first few iterations, the routine uses only a constant damping scheme (CDA) with a constant parameter α. When the norm of the error vectors $\mathbf{e}_k$ is less than a certain threshold $\varepsilon_{\mathbf{e}}$, the subprogram can switch to a DDIIS with or without constant damping what we will call DDIIS and CDA and DDIIS or CDA, respectively.

At every CP iteration we compute the $\mathbf{B}$ matrices where the elements are $B_{ij} = \mathbf{e}_i^{(a,b,\ldots)} \cdot \mathbf{e}_j^{(a,b,\ldots)}$. We keep 10 previous matrices $F_i^{(a,b,\ldots)}$ and $\mathbf{e}_i^{(a,b,\ldots)}$ in a cyclic queue and replace the oldest one. As already mentioned by Pulay the DIIS is an extrapolation scheme. The optimal coefficients c_i^k are solution to the following quadratic programming problem:

$$\inf \left\{ -\frac{1}{2} \mathbf{c}^{\mathrm{T}} \mathbf{B} \mathbf{c}, \sum_{i=0}^{k} c_i = 1 \right\}, \tag{15}$$

whose associated Euler–Lagrange equation reads

$$\begin{pmatrix} \mathbf{B} & \mathbf{1} \\ \mathbf{1}^{\mathrm{T}} & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{c} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ 1 \end{pmatrix}, \qquad (16)$$

where $\mathbf{0} = (0, \ldots, 0)^{\mathrm{T}}$ and $\mathbf{1} = (1, \ldots, 1)^{\mathrm{T}}$ are vectors whose all components are 0 and 1, respectively, and λ is the Lagrange multiplier of the constraint $\sum_{i=0}^{k} c_i = 1$. In our code, the set of linear equations are solved by inverting the left-hand side matrix. The inverse matrix is iteratively refined and thus if a linear set of equations is encountered, the oldest iterations are discarded until the system of equations becomes solvable as it is done in all common programs.

In the case of a perturbational independent basis set (for example, in the case of the perturbation due to an external electric field as considered in the following), the derivatives of the atomic overlap matrix S with respect to the external electric field E^a cancel identically ($S^{(a)} = S^{(a,b)} = 0$) and thus Eqs. (10) and (11) reduce to the following simpler expressions:

$$\mathbf{e}_i^{(a)} = [F_i^{(a)}, S]_{D_i} + [F_i, S]_{D_i^{(a)}}, \qquad (17)$$

and

$$\mathbf{e}_i^{(a,b)} = [F_i^{(a,b)}, S]_{D_i} + [F_i, S]_{D_i^{(a,b)}} + [F_i^{(a)}, S]_{D_i^{(b)}} \\ + [F_i^{(b)}, S]_{D_i^{(a)}}. \qquad (18)$$

In this way the number of matrix multiplications and consequently the computational effort are strongly reduced.

3.1. A simple example

In Section 4 we will present the results obtained for the resolution of the CPHF equation in the case of a static electric field perturbation as proposed by Sekino and Barlett [4] and Karna and Dupuis [5,6]. In this case the problem reads

$$\alpha_{\mu\nu} = -\mathrm{Tr}[H^{(\mu)} D^{(\nu)}] \quad \text{and} \quad \beta_{\mu\nu\xi} \\ = -\mathrm{Tr}[H^{(\mu)} D^{(\nu,\xi)}], \qquad (19)$$

where Tr stands for the trace of a matrix, $H^{(\mu)}$ is the AO matrix of the electric dipole moments in the μ directions and $D^{(\nu)}$ and $D^{(\nu,\xi)}$ are the first and

second derivatives of the density matrices w.r.t. the external static electric field components, respectively. The indices μ, ν and ξ run over Cartesian coordinates x, y and z. The matrices $D^{(\nu)}$ and $D^{(\nu,\xi)}$ are obtained at the CPHF level of theory by the following iterative schemes developed, among others, by Karna and Dupuis [6]. For the sake of clarity, the following explanations will be focused only on the first-order perturbation and the extension to higher order is straightforward. At each ith iteration, the derivative AO Fock matrix $F_i^{(\nu)}$ is set with the help of the AO density matrix $D^{(\nu)}$. At this stage the error vector for the current ith iteration $e_i^{(\nu)}$ is built up using Eq. (17) since the basis set is independent of the external electric field applied on the system. Once the **B** matrix is set up with the current and previous error vectors $\{e_i^{(\nu)}, e_{i-1}^{(\nu)}, \ldots, e_{i-n}^{(\nu)}\}$, where n is the number of vectors retained, then the Euler–Lagrange equation (16) are solved to give the set of coefficients $\{c_i^k\}$. At this stage, the extrapolated AO Fock matrix $\tilde{F}_i^{(\nu)}$ can be formed by a linear combination of the previous Fock matrix from (14). The iterations are repeated until the convergence is reached.

4. Results and discussion

Throughout, we have kept 10 error vectors in memory to set up the DIIS matrix (16) and all test calculations were carried out with the 6–31G basis set [19] for the corresponding optimized geometries [20] at the Hartree–Fock level of theory. The modified DIIS subroutine was tested for sulfur hexafluoride and 1,10-diphenyl-deca-1,3,5,7,9-pentaene molecules (diphenylpolyene-5 or DP5). For DP5 the molecular chain has been oriented along the x axis. During the first step the subroutine uses the CDA with a given damping factor α. When the norm of the error vector $\|\mathbf{e}\|$ becomes smaller than the given threshold $\|\mathbf{e}\| < e_{\max}$ (which we choose to be $e_{\max} = 2.0$ a.u. throughout this work), the subroutine switches to the DDIIS procedure with a possibility to continue to use the CDA (see Tables 1–4).

The convergence criteria were based: firstly on the maximum absolute variation of the derived density matrix $\Delta D_i^{(a,b,\ldots)}$ as

$$\Delta D_i^{(a,b,\ldots)} = \max_{p,q} \left\{ \left| D_{pq,i}^{(a,b,\ldots)} - D_{pq,i-1}^{(a,b,\ldots)} \right| \right\}, \qquad (20)$$

where the indices p and q refer to the pq density matrix element at the ith iterations; and secondly on the absolute variation of the electric tensor component $\Delta\alpha_{\mu v}$ and $\Delta\beta_{\mu v \xi}$ as

$$\Delta\alpha_{\mu v} = |\alpha_{\mu v,i} - \alpha_{\mu v,i-1}|, \quad \Delta\beta_{\mu v\xi}$$
$$= |\beta_{\mu v\xi,i} - \beta_{\mu v\xi,i-1}|, \qquad (21)$$

where μ, v and ξ run over the Cartesian directions x, y and z. For the sake of comparison we have used another criterion based on the maximum absolute variation of orbital rotation derivative $\Delta U_i^{(a,b,\ldots)}$ as used in the GAMESS program package [14].

In Tables 1 and 3 the number of iterations needed to compute the polarizability and the first hyperpolarizability of SF_6 and DP5 is presented. The following criteria were set: $\Delta\alpha_{max} = \Delta\beta_{max} = 10^{-4}$ a.u. on the tensor elements and $\Delta D_{1,max} = 10^{-4}$ and $\Delta D_{2,max} = 10^{-6}$ on the density matrix elements.

In Tables 2 and 4 the number of iterations obtained with the program GAMESS and the DDIIS method within the precision fixed at the $\Delta U_i^{(a,b,\ldots)} < 10^{-6}$ a.u. matrices is presented. We can see that the convergence is significantly accelerated by a factor between 2.4 and 3.9 for the SF_6 and that the number of steps is not dependent on the type of the method used. In the case of DP5, the acceleration factor is obtained between 1.7 and 2.8 for the method started by the CDA followed by the DDIIS with a damping factor $\alpha = 0.15$.

One of the disadvantages of using the DDIIS method presented in this Letter is the significant number of commutators which needs to be evaluated, (10) and (11) in the case where the basis set depends on the perturbational parameter(s), thus the time spent for the evaluation of these commutators for big system (number of basis functions $N > 1000$) should be taken into consideration. Anyway with the currently available efficient sparse matrix linear algebra packages (among other SPARSKIT [21]) the problem of matrix product, which is in principle scaling as $O(N^3)$, should be strongly reduced toward $O(N)$.

5. Conclusion

The examples presented in this Letter show that the DDIIS is a useful tool for the calculation of first- and second-order analytic derivatives, with potential extension to any order, at the Hartree–Fock or Kohn–Sham level of theory. The cost of the calculations needed to reach the convergence is significantly reduced by the use of the DDIIS when the norm of the error vector is not too large ($e_{max} < 2.0$ a.u.). Some problems remain when the CDA cannot provide a stable derivative density matrix, thus the program cannot switch to the DDIIS subprogram. This aspect is currently under investigation.

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