CONVERGENCE ACCELERATION OF ITERATIVE SEQUENCES. THE CASE OF SCF ITERATION

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Based on a recent method of Pople et al for the solution of large systems of linear equations, a procedure is given for accelerating the convergence of slowly converging quasi-Newton–Raphson type algorithms. This procedure is particularly advantageous if the number of parameters is so large that the calculation and storage of the hessian is no longer practical. Application to the SCF problem is treated in detail.

1. Introduction

Methods for determining a single eigenvalue and the associated eigenvector of a matrix, or those for the similar problem of solving a linear system of equations, can be classified as direct or iterative. Direct methods require (at least practically) a fixed number of arithmetical operations, depending on the dimension of the problem. They are independent of initial approximations or the specific properties of the matrix, such as diagonal dominance or the absence of nearly degenerate roots. A common disadvantage of the direct methods is that they require the modification of the matrix elements in random order. They are thus difficult to apply to very large matrices which must be kept on sequential files. Moreover, they cannot be applied if the matrix is available only in operator form, i.e. if its matrix elements have not been explicitly evaluated and only the effect of the matrix on an arbitrary vector can be calculated [1]. Iterative methods are free of the above disadvantages, as here the principal operation is the repeated multiplication of a trial vector by the matrix. However, these methods frequently suffer from slow convergence or even divergence.

Recently, ingenious combinations of iterative and direct methods have been suggested. For the eigenvalue problem, the first such method was given by Lánczos [2]. Better convergence is obtained, however, by the method of Davidson [3] and by the "nonlinear variation–perturbation method" of Brändas and Goscinski [4], the potentialities of which have been realized by Roos and Siegbahn [5]. A related technique has recently been used by Pople et al. [6] to solve a very large system of linear equations, arising in the problem of the analytical calculation of the second derivative of the molecular energy. The essence of the above methods is to set up an iterative method and perform a few ($\approx$5–15) iterations. The final result is then sought in the subspace spanned by the consecutive iterated vectors, using a direct method. It is an empirical fact that the convergence properties of this combined method are much superior to those of the original iterative method. The reason for this will be evident from the discussion below.

The purpose of the present note is to point out that a method similar in spirit to those mentioned can be used to advantage in two types of optimization problem commonly encountered in quantum chemistry: in SCF iteration and in gradient geometry optimization [7], particularly in the former.

2. Method

In both SCF iteration and geometry optimization, the aim is to find a stationary point (usually minimum) of the energy functional $E = E(p_1, p_2, \ldots, p_n)$ with respect to a set of parameters p_i. For the sake of convenience, the latter are considered independent at first. The number of parameters is the product of the number

of occupied and virtual orbitals in a closed-shell SCF problem, and $3N-6$ in general geometry optimization Near enough to the stationary point sought, both problems can be reduced to the solution of a large system of linear equations. However, the explicit construction of these equations is usually not practical, i.e. iterative algorithms must be used.

It is assumed that a trial set of parameters $\boldsymbol{p}^1 = (p_1^1, p_2^1, \ldots, p_n^1)^+$ is already available, and that this point in the parameter space is sufficiently close to the final solution $\boldsymbol{p}^f$ so that the energy can be considered quadratic in the parameters. In this case the simplest method for energy minimization is the quasi-Newton–Raphson procedure. Starting with $\boldsymbol{p}^1$, an improved parameter vector $\boldsymbol{p}^2$ is generated by acting on the gradient vector $\boldsymbol{g}^1$ ($g_i^1 = \partial E/\partial p_i$ at $\boldsymbol{p}^1$) by an approximate inverse hessian matrix $\mathbf{H}_0^{-1}$:

$$\boldsymbol{p}^2 = \boldsymbol{p}^1 - \mathbf{H}_0^{-1}\boldsymbol{g}^1 \tag{1}$$

Obviously, within the quadratic region $\boldsymbol{g} = \mathbf{H}(\boldsymbol{p} - \boldsymbol{p}^f)$, and therefore

$$\boldsymbol{p}^2 = \boldsymbol{p}^1 - \mathbf{H}_0^{-1}\mathbf{H}(\boldsymbol{p}^1 - \boldsymbol{p}^f)$$

$$= \boldsymbol{p}^f + (\mathbf{1} - \mathbf{H}_0^{-1}\mathbf{H})(\boldsymbol{p}^1 - \boldsymbol{p}^f), \tag{2}$$

where $\mathbf{H}$ is the accurate hessian, $H_{ij} = \partial^2 E/\partial p_i \partial p_j$ The next approximation is given by $\boldsymbol{p}^2$ replacing $\boldsymbol{p}^1$, etc This iterative method will be referred to as *simple relaxation* (SR) after its application in geometry optimization [7]. Obviously, SR is bound to converge in a single step within the quadratic region if $\mathbf{H}_0$ is equal to $\mathbf{H}$. Indeed, explicit evaluation of the hessian has been suggested [8] to achieve quadratic convergence in SCF iteration. However, this method is usually impractical, as the evaluation and inversion of $\mathbf{H}$ requires typically much more computational effort than even an extended SCF cycle †. The same holds for most cases of geometry optimization. Nevertheless, an acceptable approximation $\mathbf{H}_0$ is usually available in both problems. $\mathbf{H}_0$ has to be constructed explicitly in geometry optimization but it is implicit in the SCF process

The simple relaxation converges if the eigenvalues Λ_i of the matrix $\mathbf{A} = (\mathbf{1} - \mathbf{H}_0^{-1}\mathbf{H})$ are smaller than 1 in absolute value. However, convergence may be slow unless $\mathbf{H}_0$ approximates $\mathbf{H}$ well, i e. $|\Lambda_i| \ll 1$. In the spirit of the combined methods described in section 1, a much better approximation to the final solution can be constructed from the first m iterated vectors $\boldsymbol{p}^1, \boldsymbol{p}^2, \ldots, \boldsymbol{p}^m$ as

$$\boldsymbol{p} = \sum_{i=1}^{m} c_i \boldsymbol{p}^i, \tag{3}$$

by requiring that the residuum vector

$$\Delta\boldsymbol{p} = \sum_{i=1}^{m} c_i(\Delta\boldsymbol{p}^i) \tag{4}$$

(with $\Delta\boldsymbol{p}^i = \boldsymbol{p}^{i+1} - \boldsymbol{p}^i$) approximates the zero vector in the mean-square sense, and the condition

$$\sum_{i=1}^{m} c_i = 1 \tag{5}$$

holds. This leads to the following system of $m+1$ linear equations

$$\begin{pmatrix} B_{11} & B_{12} & \ldots & B_{1m} & -1 \\ B_{21} & B_{22} & \ldots & B_{2m} & -1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ B_{m1} & B_{m2} & \ldots & B_{mm} & -1 \\ -1 & -1 & \ldots & -1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_m \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ -1 \end{pmatrix}. \tag{6}$$

Here $B_{ij} = \langle \Delta\boldsymbol{p}^i | \Delta\boldsymbol{p}^j \rangle$ with a suitably defined scalar product in the parameter space, and λ is a lagrangian multiplier, the value of which yields the squared norm of the residuum vector (4). This method will be referred to as direct inversion in the iterative subspace (DIIS) ‡. DIIS is carried out in the following steps.

(1) Choose a starting vector $\boldsymbol{p}^1$ and an approximate inverse hessian $\mathbf{H}_0^{-1}$. Iterate by SR until the quadratic region is reached, as shown by the smallness of $\Delta\boldsymbol{p}$.

(2) From this point on, store the parameter vector after each SR iteration. Beginning with $m = 2$, set up and solve the linear system of equations (6). If the norm or, preferably, the largest element of the residuum

† An exception may be the case when a large integral transformation step must be redone in each SCF cycle, as in certain MC SCF procedures. In these cases, the saving due to genuine quadratic convergence may outweigh the cost of the evaluation of the hessian.

‡ Note that, in spite of some formal similarity, this is *not* an eigenvalue problem, as shown already by the form of the constraint condition, eq (5)

vector (4) becomes smaller than a predetermined limit, stop.

(3) Build a new parameter vector according to (3) and check, by a step of SR, whether convergence has been reached. If not, new Δp vectors can be added to the previous list.

The following features of DIIS make it particularly suitable for SCF convergence acceleration:

(i) It is not necessary to store an approximate hessian, i e. n^2 or $\frac{1}{2}n(n+1)$ numbers. In the SCF problem, the number of parameters is usually so large that methods which require the storage of quadratic arrays, like the excellent variable-metric methods of Fletcher [9], become impractical. E g. a closed-shell calculation on PF_3 with 40 contracted basis functions, modest by today's standards, has already 399 independent parameters and would require about 80000 words of storage for the hessian (see the examples).

(ii) The independence of the parameters is not required in the present formulation. A redundant set of parameters (in the simplest case the same parameter occurring twice) corresponds to a modified metric in the parameter space. Within reasonable limits, this should not produce any gross change in the convergence properties of the method. This is important in SCF iteration where the easily accessible parameters are not independent. We have found it convenient to work with the independent elements of the Fock matrix [10]. An even better choice is the use of Fock matrix elements transformed to an orthonormal basis, such as $\mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}$ where $\mathbf{S}$ is the overlap matrix. This takes into account that a charge shift from a basis function to another is less important physically if the two functions overlap strongly ‡.

(iii) Explicit evaluation of the gradient vector (which requires independent parameters, cf. the previous point) is not necessary. Both the gradient and $\mathbf{H}_0$ are implicit in the prescriptions of the SCF procedure. Fortunately, this is all that is needed.

(iv) DIIS can converge in principle even if the underlying SR procedure diverges. However, it is difficult to arrive and remain in the quadratic region in this case. In the SCF case, DIIS is compatible with other convergence-controlling devices, such as the level-shifting technique of Saunders and Hillier [11], or the Fock matrix interpolation (e g. ref. [10]). These modifications of the SCF procedure correspond simply to other choices of $\mathbf{H}_0$. We shall return to this point because the results of DIIS allow the determination of the best interpolation parameter.

(v) In several modern SCF applications, e g. in gradient calculations [7,10], in finite-difference methods, and in orbital generation for large-scale CI calculations, a higher degree of SCF convergence is required than in the usual energy calculations. A failure to achieve full self-consistency manifests itself in numerical errors and, in the case of CI, in uneven potential surfaces. DIIS has been developed for these applications; it must be realized that it is of little or no use for establishing initial convergence. Another potential application is converging open-shell and multiconfigurational SCF wavefunctions which are notorious for poor convergence. Limited experience so far indicates that a reasonable criterion for the applicability of DIIS is that the matrix elements of $\mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}$ should not change more than 0.01 or 0.005 E_h between successive iterations.

In comparison to the SCF procedure, the application of DIIS to geometry optimization seems less promising, for two reasons: (1) At the present time, these problems usually involve only a moderate number of parameters, so that competitive, efficient methods which require the storage of the hessian [9] are applicable. (2) Very sharp geometry optimization is usually not required. Stated alternatively, regions on the energy hypersurface which are most important for geometry optimization are quite anharmonic.

In order to get a clearer picture of the convergence properties of the DIIS method, compared to SR, let us return to eq. (2). Recalling that $\mathbf{A} = \mathbf{1} - \mathbf{H}_0^{-1}\mathbf{H}$, we obtain for the nth step of SR

$$\boldsymbol{p}^n = \boldsymbol{p}^f + \mathbf{A}^{n-1}(\boldsymbol{p}^1 - \boldsymbol{p}^f), \tag{7}$$

where $\boldsymbol{p}^f$ is the desired solution. By a suitable linear transformation let us introduce new parameters $\boldsymbol{P}$ which diagonalize $\mathbf{A}$:

$$\boldsymbol{P}^n = \boldsymbol{P}^f + \boldsymbol{\Lambda}^{n-1}(\boldsymbol{P}^1 - \boldsymbol{P}^f), \tag{8}$$

where $\boldsymbol{\Lambda}$ contains the eigenvalues of $\mathbf{A}$. Assume that the

‡ Most workers use the density matrix instead of the Fock matrix. A difficulty is that the idempotency of the former is violated by any extrapolation scheme. The simplest and exact solution of this problem is the reconstruction of the density matrix from its occupied eigenvectors The remark about the Fock matrix holds for the density too. $\mathbf{S}^{-1/2}\mathbf{D}\mathbf{S}^{-1/2}$ is preferable to $\mathbf{D}$. However, we think that the Fock matrix in an orthogonalized basis is an even better alternative because of its energy weighting.

eigenvalue spectrum of **A** forms a dense, uniformly distributed set on the interval (a,b) If all components of the starting error vector $(\boldsymbol{P}^1 - \boldsymbol{P}^f)$ are of comparable magnitude then the convergence in SR comes from the matrix $\mathbf{A}^{n-1}$ converging toward the zero matrix; a measure for this is provided by the mean-square deviation of the function x^{n-1} from the zero function in (a,b) DIIS, on the other hand, corresponds to the least-squares polynomial approximation of the zero function, subject to the constraint that the sum of coefficients is 1. It is easy to evaluate these polynomials numerically and compare their mean-square deviation with that of the function x^{n-1}. This has been done in table 1 for two intervals, (−0 5, +0 5) and (−0 3, +0.7), the latter being fairly typical for SCF iteration. Although little is known about the eigenvalue spectrum of **A** (see however below), the comparison with realistic values of a and b should give a picture of the expected performance of DIIS versus SR: for a 9-term DIIS, the gain should be about 10^3, equivalent to ≈10 iteration steps, if the spectrum of **A** is real or nearly real

3. Examples and concluding remarks

Results obtained in CNDO/2 and ab initio SCF calculations are shown in tables 2 and 3. In the case of the CNDO/2 butadiene calculation, basic SCF convergence is fair and therefore the gain by DIIS is moderate, although significant. In the very slowly convergent case of the singlet CN^+ ion, DIIS yields dramatic improvement. The ab initio calculation on PF_3 is equally promising, the 7-term DIIS procedure yielding 3 orders of magnitude improvement in the convergence parameter, equivalent to 10 additional SCF cycles

It is interesting to note that the form of the polynomial

$$f(x) = \sum_{i=1}^{m} c_i x^{i-1} \tag{9}$$

yields information about the eigenvalue spectrum of the matrix **A**. For the 7-term DIIS expansion of table 3, this function is plotted in fig. 1. Obviously, the eigenvalues of **A** lie in the interval where $|f(x)|$ is small, say smaller than 0.002; this is the interval (−0.105, +0.565) The presence of small (≈0) *and* large (≈0 6) eigenvalues together explains the common observation that the convergence of the SCF procedure, as measured by some sort of mean-square deviation between consecutive steps, is fast at first and slows down as the final solution is approached Indeed, eq (8) shows that those components of the initial error vector $(\boldsymbol{P}^1 - \boldsymbol{P}^f)_i$ which correspond to small eigenvalues $|\Lambda_i| \ll 1$ are quickly annihilated. Those (generally few) components which correspond to large eigenvalues remain and cause slow convergence In such a case DIIS is expected to bring significant improvement.

The information about the eigenvalue spectrum of **A** can be used to accelerate basic SCF convergence.

Table 1
Comparison of the mean-square deviation of the best polynomial (DIIS) and the function x^{n-1} (SR) from the identically zero function on the intervals (−0 5, +0 5) and (−0 3, +0 7)

n	(−0 5, +0 5)			(−0 3, +0.7)		
	SR	DIIS	SR/DIIS	SR	DIIS	SR/DIIS
2	8 333 − 2 [a]	7 692 − 2	1 083	1.233 − 1	1.152 − 1	1 071
4	2.232 − 3	4 572 − 4	4 882	1.180 − 2	2 021 − 3	5 836
6	8 878 − 5	2 443 − 6	36 34	1.798 − 3	3 225 − 5	55.92
7	1 878 − 5	1.770 − 7	106 1	7.453 − 3	4 004 − 6	186.1
8	4.069 − 6	1 279 − 8	318 2	3.165 − 4	4.971 − 7	636 7
9	8 976 − 7	9 227 − 10	972 8	1 268 − 4	6.160 − 8	2222
10	2 008 − 7	6 650 − 11	3019	5.999 − 5	7.622 − 9	7871

[a] 8 333 − 2 means 8 333 × 10^{-2}

Table 2
SCF convergence of CNDO/2 calculations on butadiene [a] and on the singlet CN^+ ion

Butadiene		CN^+ ion	
cycle	convergence parameter [b]	cycle	convergence parameter [b]
1 [c]	2 20–8	1	1.09–4
8	1.17–11	8	3.25–5
9	6.73–12	9	2.85–5
10	3.19–12	10	2.45–5
15	1 27–13		
16	7.74–14	81	8.62–10
17	4.72–14	82	7.56–10
8-term DIIS(1–9) [d]	1 09–13	5-term DIIS(7–12)	2 64–13
9-term DIIS(1–10)	4 80–14		

a) A nonsymmetrical, nonplanar geometry was chosen to increase the number of variational parameters.
b) Average mean-square deviation between consecutive Fock matrices.
c) Iteration was started with the wavefunction of a nearly symmetrical geometry.
d) The Fock matrices utilized in the DIIS procedure are given in parentheses. Note that for an 8-term DIIS, 8 differences, i.e. 9 Fock matrices, are necessary.

Consider the extrapolation procedure formulated for the Fock matrix:

$$\mathbf{F}'_{i+1} = q\,\mathbf{F}_{i+1} + (1-q)\,\mathbf{F}_i,$$

where i and $i+1$ are step numbers, $q = 1$ corresponds to ordinary SCF iteration, $q < 1$ to interpolation and $q > 1$ to extrapolation. The effect of extrapolation is to change the matrix $\mathbf{A}$, and with it its eigenvalues, to $\mathbf{A}' = q\,\mathbf{A} - (q-1)\mathbf{1}$. The limiting convergence rate of the modified procedure will be superior to the original one if the largest eigenvalue decreases in absolute value. Elementary algebra shows that the best value of the

Table 3
SCF convergence of an ab initio calculation on PF_3 [a]

Cycle	Convergence parameter [b]
4	1 49–2
8	7 48–4
9	2 87–4
10	1.80–4
11	1.01–4
21	7.29–8
7-term DIIS(4–11) [c]	9.07–8

a) The basis set consists of 40 contracted gaussians, for P. 4-3-21G [14], for F· 4-21G [15].
b) Absolute difference between consecutive electron repulsion energies
c) See table 2. The extrapolated Fock matrix is accurate to $0\,5 \times 10^{-8}\,E_h$.

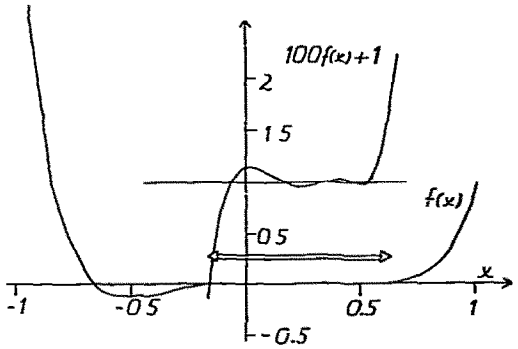

Fig 1 The polynomial $f(x)$, eq. (9), for the ab initio PF_3 calculation shown in table 3. The absolute value of $f(x)$ is less than 0.01 in the interval (–0.17, +0 62), shown by the thick arrow. This part of the curve is shown at 100× scale, shifted 1 unit upward for clarity. Within (–0 105, +0.565) the absolute value of $f(x)$ is less than 0.002.

interpolation parameter q is given by $q = [1 - \frac{1}{2}(\Lambda_{min} + \Lambda_{max})]^{-1}$ where Λ_{min} and Λ_{max} are the largest and smallest eigenvalues of **A**. For the example in fig 1, we obtain $q = 1.30$, and an improvement in the limiting convergence rate $\Lambda_{max}/(q\Lambda_{max} - q + 1) \approx 1.3$. This is confirmed by experience

The determination of the best extrapolation parameter may seem academic, as the result becomes available only after the run has been completed However, in the usual case a large number of similar calculations are performed, and the best parameter for one of them is sufficiently accurate for the others

The fact that consecutive SCF density matrices are frequently linearly dependent was observed by Neilsen [12]. In fact, his method of interpolating between two consecutive densities is practically equivalent to the simplest case of DIIS with $m = 2$ However, his method brings a significant improvement only if **A** has a single, well-separated large eigenvalue, in contrast to the general applicability of DIIS Note further that a good review about SCF convergence has been published recently [13]

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