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An improved iterative solution to solve the electrostatic problem in the polarizable continuum model

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Abstract. We present a discrete iterative interpolation scheme (DIIS) to improve the convergence rate of electrostatic calculations in the polarizable continuum model (PCM) to describe solvent effects on molecular solutes. The electrostatic calculations may easily become the bottleneck of the calculation when the solute size is large. For large molecules iterative procedures turn out to be computationally more convenient than matrix inversion or closure methods. The DIIS scheme is compared here to another iterative procedure (DAMP) and to the biconjugate gradient (BCG) method. The comparisons show that DIIS leads to a sizeable saving of computational time for the C-PCM and IEF-PCM methods (average 40%) compared to DAMP, and more than 50% with respect to the BCG method.

Key words: Polarizable continuum model – Discrete iterative interpolation scheme – Conjugate gradient method – Molecular electrostatic

1 Introduction

The continuum solvent model is the origin of several useful computational methods for describing chemistry in condensed phases.

One of the strong points of this approach is the sharp reduction in the number of degrees of freedom one has to consider in treating a chemical problem in the liquid phase. Alternative methods, such as those based on computer simulations with explicit solvent, have to monitor a by far larger number of degrees of freedom, many of which have a very low direct influence on the final results. The heavy computational demand of such methods reduces their field of applicability.

A second strong point of the continuum approach is its versatility: continuum methods can be coupled to almost all molecular structure methods. Thus, the field of applicability ranges from accurate calculations of molecular properties at sophisticated levels of quantum mechanical (QM) theory to molecular mechanics calculations on molecules of very large size.

There exist at present a large number of continuum solvent procedures [1, 2], some expecially useful for high-quality QM calculations for small molecules, others addressing the problem of treating large solutes at a semiclassical level, and a few equipped to treat both large and small solutes over the whole range of quality in the description of the solute. Among the last of these there is the polarizable continuum model (PCM) [1–4], for which we present here a procedure to speed up the calculations. This procedure is based on the discrete iterative interpolation scheme (DIIS) [5], suggested years ago by Pulay to improve convergence in iterative calculations. DIIS is currently widely used in computational chemistry; it is available in computational packages, such as Gaussian [6], GAMESS [7], and MOPAC [8], to improve the convergence of the SCF cycle; a generalized version (GDIIS) is a powerful geometry optimizer [9]. The extension of this procedure to another problem is presented in the present article.

The article is organized as follows:

1. The basic PCM method is summarized, with attention to the different versions presently available for merging with DIIS to solve the electrostatic problem.
2. The DIIS–PCM procedure is compared to a simple damping procedure and to the biconjugate gradient (BCG) method.

2 Basic outlines of the PCM

The model is composed of a subsystem (the "solute") in which the necessary degrees of freedom are described in a detailed way and another subsystem (the "solvent"), which is described in terms of one or more continuous distribution functions (no explicit degrees of freedom are used in this part). As we have already said there are

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many choices available for describing the solute, from all-electrons all-nuclei in a QM version, to atoms alone (or a part of them) in semiclassical versions. There is also a large choice available for the continuous response functions of the solvent, including interactions of different types (electrostatic, dispersion, repulsion) and local as well as nonlocal characteristics of the medium (uniform homogeneous functions, position-dependent response functions, anisotropic distributions) covering various compositions of the solvent (pure solvent, mixed solvent, ionic solutions).

The DIIS procedure can be applied to all cases, but for simplicity we specialize the exposition to the basic model of uniform isotropic solvent distributions with interactions limited to the electrostatic component. Within this limited model we shall pay more attention to the application to solutes described at a low level. In fact it is just the particular case of large solutes that has motivated the implementation of DIIS–PCM, which is, however, also beneficial for full QM calculations.

In electrostatic continuum methods the solute is placed within a cavity in the solvent bulk, described as a polarizable continuum. This cavity is delimited in the more elaborate methods (such as the PCM) by a solvent accessible surface (SAS) [10]. There are various approaches to define the solute–solvent interaction between a charge distribution and a surrounding dielectric. In the PCM the apparent surface charge method is used. In this method a surface charge distribution, σ, is spread on the SAS to fulfill the boundary condition:

$$\partial V/\partial \hat{n}^- = \epsilon \partial V/\partial \hat{n}^+ \ , \tag{1}$$

where V is the electrostatic potential of the whole system of charges (apparent and real), ϵ is the dielectric constant, and $\hat{n}_\pm$ is the inward/outward unit orthogonal vector to the surface. This boundary equation is solved numerically by dissecting the SAS into a finite number of elements, each characterized by a representative point, $\vec{r}_i$, an orthogonal vector, $\hat{n}_i$, and a surface area, S_i. σ is thus discretized into a finite set of point charges, **q**.

The resulting procedure corresponds to the solution of a set of linear equations, which can be written in the following matrix form:

$$\mathbf{Dq} = \mathbf{g} \tag{2}$$

The vector **q** collects the unknown charges, and the vector **g** and the matrix **D** have different forms in the different PCM versions of the electrostatic problem. In any version the **q** charges are used to define an electrostatic interaction potential that gives an additional contribution to the energy of the isolated molecule and that modifies the charge distribution of the molecules in the cases in which the model allows it; namely, in quantum calculations and in classical mechanics calculations with force fields including polarization terms. In these cases there will be an iterative loop to reach self-consistency in the mutual solute–solvent polarization effects. Our primary concern is to present a procedure to speed up the first step of this procedure, the determination of the charges **q**. Actually there are different PCM versions that uses different formulations of Eq. (2). The three versions in current use for the homogeneous isotropic case are

1. D-PCM. This is the traditional formulation of the PCM based on the direct application of electrostatics as expressed in Eqs. (1) and (2). The **g** elements are the normal component of the electric field.
2. C-PCM. In this formulation the dielectric is approximated by a conductor, with the appropriate boundary condition (not corresponding to Eq. 1). The resulting **q** values are uniformly scaled to fulfill the Gauss theorem for the dielectric. The **g** elements are the local values of the electric potential.
3. Integral equation formalism (IEF)–PCM. This is the most sophisticated version, where the Green's function formalism used in D-PCM is supplemented by the use of Calderon operators [11, 12]. This advanced mathematical treatment has a large spectrum of applicability, including ionic solutions and liquid crystals. The **g** elements are a linear combination of the local values of the electric potential and the normal of the components of the electric field. In the case of isotropic solutions **g** can be expressed in function of the electric potential only [13].

D-PCM is related to the original Miertus–Scrocco–Tomasi version [3], C-PCM derives from Klamt and Schüürman semiempirical COSMO procedure [14], reformulated with changes for the PCM at the ab initio level by Barone and Cossi [15], and IEF–PCM has been elaborated by Mennucci and coworkers [11, 12]. Each formulation has different merits and defects.

D-PCM has the fastest spatial decay rate in the charge–charge interactions (Table 1) but is the most sensitive to the outlying solvent charge problem [16]. C-PCM is faster, less sensitive to the outlying charge, but less accurate for low ϵ values. IEF–PCM is the most accurate method over the whole range of solvent polarities and the least sensitive to outlying charges, but it is more complex to handle and a bit more costly, even in the version limited to isotropic liquids. The analytical expressions for **D** and **g** are reported in Table 1. There are several similarities between the C-PCM and

Table 1. Analytical expressions of the diagonal and nondiagonal elements of the **D** matrix and of the elements of the **g** vector (see Eq. 2) for all the polarizable continuum model (*PCM*) versions

	D-PCM	C-PCM
$D_{ij}\ i \neq j$	$S_i \hat{n}_i \cdot \frac{\vec{r}_i - \vec{r}_j}{\lvert\vec{r}_i - \vec{r}_j\rvert^3}$	$\frac{1}{\lvert\vec{r}_i - \vec{r}_j\rvert}$
D_{ii}	$2\pi \frac{\epsilon+1}{\epsilon-1} + 2.14\pi\sqrt{\frac{S_k}{4\pi R_k^2}}$	$1.07\ \sqrt{\frac{4\pi}{S_i}}$
g_i	$-S_i \frac{\partial}{\partial \hat{n}_i}\phi(\vec{r}_i)$	$-\phi(\vec{r}_i)$
IEF – PCM		
$\mathbf{D} = \left(\frac{1}{2}\mathbf{I} - \mathbf{B}\right)^{-1}$	$\left(\mathbf{B}_{S_J \hat{n}_J} - \frac{\epsilon+1}{\epsilon-1}\frac{1}{2}\mathbf{I}\right)\mathbf{A}$	
$A_{ij}\ i \neq j$	$\frac{1}{\lvert\vec{r}_i - \vec{r}_j\rvert}$	
A_{ii}	$1.07\ \sqrt{4\pi/S_i}$	
$B_{ij}\ i \neq j$	$S_J \hat{n}_j \cdot \frac{\vec{r}_i - \vec{r}_j}{\lvert\vec{r}_i - \vec{r}_j\rvert^3}$	
B_{ii}	$S_i \frac{A_{ii}}{2R_i}$	
g_i	$-\phi(\vec{r}_i)$	

IEF–PCM methods: they share the same expression for **g** and

$$\lim_{\epsilon\to\infty} \mathbf{D}_{\text{IEF–PCM}} = \mathbf{D}_{\text{C-PCM}} \ . \tag{3}$$

Because these similarities also hold from a numeric point of view, in the following we refer to potential methods (PMs) for IEF–PCM and D-PCM and to the field method (FM) for D-PCM. The classification is based upon the nature of **g** that is correspondent to the predominant nature of **D**.

Our experience in the use of these methods shows that PMs give more accurate results but the nonlocal nature of the off-diagonal part of **D** can lead to some numerical problems. These problems are discussed in Sect. 3.

In the following we shall focus our attention on an iterative solution of Eq. (2) and on its numerical behaviour. Thus, we do not treat the solutes at a QM level (that would imply having two nested iterative procedures), and so we shall limit ourselves to show, in the section dedicated to numerical results, numerical evidence regarding the effect of the DIIS procedure on calculations of the PM and FM type at the semiclassical level. The use of this procedure with QM levels does not present problems, and acutally it has already been used with satisfactory results in our laboratories.

At present the usual procedure to solve the electrostatic equation for the three versions of the PCM, as well as of other similar methods, is based on a matrix inversion:

$$\mathbf{q} = \mathbf{D}^{-1}\mathbf{g} \ . \tag{4}$$

This procedure was introduced into the PCM by Hoshi et al. [17] and was later adopted by us [18] to simplify the calculation of analytical geometric derivatives [19], replacing the preceding iterative version [3]. The inversion procedure is computationally stable and its effectiveness has been improved over the years. It remains, however, relatively expensive, with a large asymptotic scaling exponent, and it requires the allocation of considerable computer memory. These aspects are not serious drawbacks for high-quality QM calculations, but they become more important when attention is shifted to solutes of large size.

In recent years we have developed other approaches that are able to give analytical expressions of the geometry derivatives which alleviate this computational problem. They are based on closure methods [20–22] and on the iterative procedure again [23, 24]. The closure methods are essentially extrapolations of the iterative method that eliminate the inner loop in the iteration, but in their present form they have memory requirements similar to those of the inversion method. The most recent iterative methods use a Jacobi partition scheme [25] of the **D** matrix and can be implemented in a way that does not require massive memory allocations [23, 24]. In the present work we consider an improved iterative method where the new feature is the use of the DIIS interpolation scheme. As will be shown, this version maintains the low memory requirement, and it significantly reduces the number of iterations necessary to reach convergence for PMs.

3 The DIIS–PCM method

Let us consider again the basic PCM electrostatic equation; we introduce the following partition

$$\mathbf{D} = \mathbf{D}_0 + \mathbf{D}_1 \ , \tag{5}$$

were $\mathbf{D}_0$ and $\mathbf{D}_1$ contain the diagonal and off-diagonal elements of **D** respectively. By considering the definitions of the **D** matrix elements reported in Table 1 and assuming typical values [26] of the following geometrical parameters,

$$\begin{aligned} S_i &= 0.4\,\text{Å}^2 \\ R_i &= 2.4 \ , \end{aligned} \tag{6}$$

one has

$$|D_{ii}/D_{ij}| \geq 6.78|\vec{r}_i - \vec{r}_j|^2 \tag{7}$$

for FM and

$$\frac{D_{ii}}{D_{ij}} \geq 8.68|\vec{r}_i - \vec{r}_j| \tag{8}$$

for PMs. For a well-tessellated cavity the value of r_{ij} is of the order of 0.5 Å for first neighbours and at least double for other couples of tesserae. Thus, there are very few i, j pairs for which the diagonal and off-diagonal elements of the **D** matrix have the same order or magnitude.

From the computational point of view the Jacobi iterative solution of a linear system works better if the diagonal elements are larger than the off-diagonal ones. This is true for FM and also, but less marked, for PMs. This fact is fundamental for the evaluation of the computational performances of the method proposed here and it will be discussed extensively in the final section.

By neglecting $\mathbf{D}_1$ we have a simple initial guess for the charges:

$$\mathbf{q}^{(0)} = \mathbf{D}_0^{-1}\mathbf{g} \ . \tag{9}$$

This guess can be refined iteratively according to the Jacobi scheme [25]:

$$\mathbf{q}^{(n)} = \mathbf{D}_0^{-1}(\mathbf{q}^{(0)} - \mathbf{D}_1\mathbf{q}^*) \ , \tag{10}$$

where the exponent (n) indicates the number of the iterative cycle and

$$\mathbf{q}^* = \mathbf{q}^{(n-1)} \ . \tag{11}$$

The iterative scheme defined by this equation is the simplest possible: each step depends only upon the previous one.

In Ref. [23] a more complex procedure was introduced:

$$\mathbf{q}^* = \lambda\mathbf{q}^{(n-1)} + (1-\lambda)\mathbf{q}^{(n-2)} \ , \tag{12}$$

where

$$\lambda = \frac{1/\mathrm{e}^{(n-1)}}{1/\mathrm{e}^{(n-1)} + 1/\mathrm{e}^{(n-2)}} \tag{13}$$

and

$$\mathbf{e}^{(k)} = \mathbf{q}^{(k)} - \mathbf{q}^{(k-1)} \tag{14}$$

If $\mathbf{e}^{(k)} > \mathbf{e}^{(k-1)}$, λ is set to 1. This is a typical DAMP procedure, where the intrinsic oscillatory nature of a iterative scheme is damped by retaining something from the previous iterative step. The use of a fixed damping procedure (where λ is fixed and given in input) was typical in SCF packages before the introduction of DIIS.

The DIIS interpolation procedure generalizes the two-step DAMP to an all-step procedure:

$$\mathbf{q}^{*} = \sum_{k=1}^{n-1} \lambda_k \mathbf{q}^{(k)} \quad . \tag{15}$$

The weight factors, λ_k, are determined by a least-squares procedure: the equation

$$S(\lambda) = \left| \sum_{k=1}^{n} \lambda_k \mathbf{e}^{(k)} \right|^2 \tag{16}$$

is minimized under the constraint

$$\sum_{k=1}^{n} \lambda_k = 1 \quad . \tag{17}$$

This is equivalent to minimizing the quantity

$$S(\lambda) + \mu \left(\sum_{k=1}^{n} \lambda_k - 1 \right) \tag{18}$$

or to solving the following linear system

$$\begin{pmatrix} 0 & 1 & 1 & 1 & \cdots & 1 \\ 1 & \mathbf{e}^{(1)} \cdot \mathbf{e}^{(1)} & \mathbf{e}^{(2)} \cdot \mathbf{e}^{(1)} & \mathbf{e}^{(3)} \cdot \mathbf{e}^{(1)} & \cdots & \mathbf{e}^{(n)} \cdot \mathbf{e}^{(1)} \\ 1 & \mathbf{e}^{(1)} \cdot \mathbf{e}^{(2)} & \mathbf{e}^{(2)} \cdot \mathbf{e}^{(2)} & \mathbf{e}^{(3)} \cdot \mathbf{e}^{(2)} & \cdots & \mathbf{e}^{(n)} \cdot \mathbf{e}^{(2)} \\ 1 & \mathbf{e}^{(1)} \cdot \mathbf{e}^{(3)} & \mathbf{e}^{(2)} \cdot \mathbf{e}^{(3)} & \mathbf{e}^{(3)} \cdot \mathbf{e}^{(3)} & \cdots & \mathbf{e}^{(n)} \cdot \mathbf{e}^{(3)} \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ 1 & \mathbf{e}^{(1)} \cdot \mathbf{e}^{(n)} & \mathbf{e}^{(2)} \cdot \mathbf{e}^{(n)} & \mathbf{e}^{(3)} \cdot \mathbf{e}^{(n)} & \cdots & \mathbf{e}^{(n)} \cdot \mathbf{e}^{(n)} \end{pmatrix} \times \begin{pmatrix} \mu \\ \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \cdot \\ \cdot \\ \cdot \\ \lambda_n \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix} \quad . \tag{19}$$

The DIIS interpolation scheme is valid if and only if the conditions

$$\mathbf{e}^{(n)} = 0 \tag{20}$$

and

$$\mathbf{q}^{(n)} = \mathbf{q} \tag{21}$$

are equivalent [5].

The definition of $\mathbf{e}^{(n)}$ previously given satisfies this requirement. In fact, rearranging Eq. (10), the relationship

$$\mathbf{D}\mathbf{q}^{(\mathrm{n})} = \mathbf{g} + \mathbf{D}_1 \mathbf{e}^{(\mathrm{n})} \tag{22}$$

holds.

4 Comparisons with other methods

The discussion of convergence improvements is not based upon "conventional" results such as molecular geometries, energies, and other molecular properties. A convergence improver does not affect the accuracy of the theory; it leads to the same results of the original implementation, but it permits one to reduce the numerical effort necessary to reach the result.

In this section the DIIS-like interpolation scheme is compared to the previously adopted DAMP procedure [23] and to a popular method to solve linear equations, namely the BCG method [25]. So-called conjugate gradient methods provide an alternative and quite general procedure for solving linear systems, which has been used recently in connection with Eq. (2). In particular the BCG method is able to solve the nonsymmetric linear system implied in the FM formulation using at most N iterations. We have tested the BCG method by using the subroutine *linbgc* from Ref. [25].

The initial guess is, as for the Jacobi scheme, that reported in Eq. (9).

The comparison is performed over a set of 108 molecules described at a classical level at a given geometry. This set is derived from the G2 set of molecular geometries [27]. We have removed from the original set the molecular systems that are of little interest in this framework: excited states, homonuclear diatomic molecules, and radicals. The sources of molecular electrostatics are partial atomic charges placed on every atom. These charges are determined by the charge equilibration method [28]. The criterion of convergence is that the norm of the difference between $\mathbf{q}^{(N_{\mathrm{it}})}$ and $\mathbf{q}^{(N_{\mathrm{it}}-1)}$, when N_{it} is the number of iterations needed to reach convergence, is less than 1.0×10^{-6}.

Comparisons between the DIIS method and the DAMP and BCG methods are reported in Fig. 1. The results are expressed as a percentage saving of effort:

$$\%\ \text{saving} = 100\left(N_{\mathrm{it}}^{x} - N_{\mathrm{it}}^{\mathrm{DIIS}}\right)/N_{\mathrm{it}}^{x} \quad , \tag{23}$$

where x = DAMP or BCG. The mean saving percentage and the mean number of iterations required to reach convergence are reported in Table 2. We found no relation between the type and size of the molecule and the performance of each convergence improver.

The performance of the BCG method is poor both in the PMs and FM formulations; furthermore each BCG iteration is computationally more expensive than an iterative step because it require a large number of operations on vectors and matrices than the Jacobi method. For this reason, the BCG performances will not be further discussed.

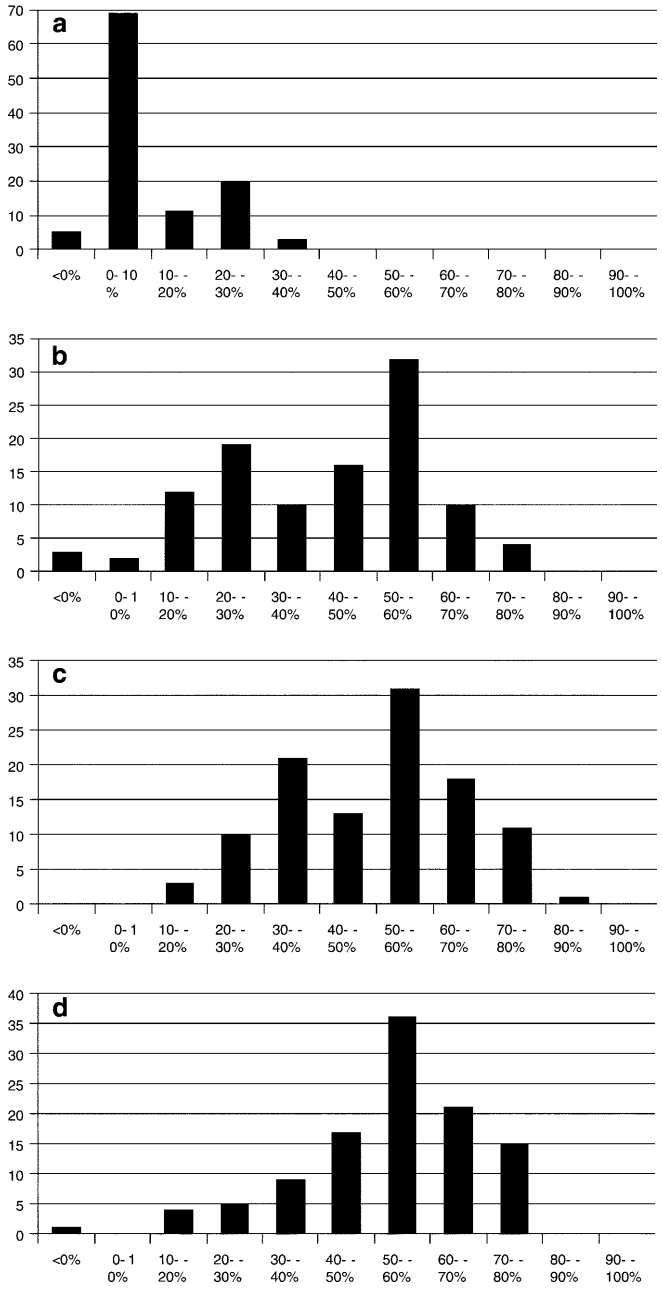

Fig. 1a–d. Comparison of the discrete iterative interpolation scheme (*DIIS*) with other procedures in terms of percentage saving. **a** DIIS versus DAMP (field method). **b** DIIS versus DAMP (potential methods). **c** DIIS versus the biconjugate gradient (*BCG*) method (field method). **d** DIIS versus the BCG method (potential method). The heights of the *bars* indicate the number of molecules for which the percentage savings lie in the range reported on the *x*-axis. The set is composed of 108 molecules

In the FM case, the advantage of using DIIS instead of DAMP is very small. The first reason for this fact can be found in Eq. (7): the elements of $\mathbf{D}_1$ have a local character; thus $\mathbf{q}^{(0)}$ is a very good guess. In the FM case the iterative procedure converges in both versions in less than ten iterations in more than 95% of the cases (Fig. 2). Furthermore an analysis of the λ_k coefficients of the DIIS interpolation shows that, at the l^{th} iteration

Table 2. Average saving and average number of iterations of the discrete iterative interpolation scheme (*DIIS*) with respect to other procedures, DAMP and the biconjugate gradient (*BCG*) method for potential methods (*PMs*) and the field method (*FM*)

	Average saving	
PMs	DIIS versus DAMP	39.7%
	DIIS versus BCG	52.7%
FM	DIIS versus DAMP	5.3%
	DIIS versus BCG	52.1%

	Average number of iterations		
	DIIS	DAMP	BCG
PMs	10.92	20.46	24.20
FM	4.96	5.33	10.92

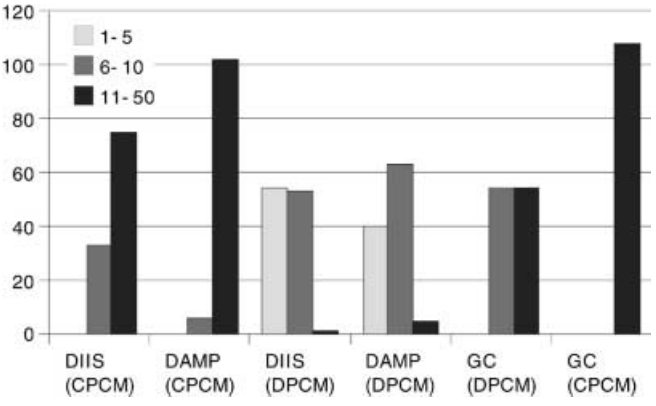

Fig. 2. Graphical comparison of DIIS with other procedures. For each method/formulation the distribution in classes with respect the number of iterations needed to reach the convergence threshold is reported. The heights of the *bars* indicate the number of molecules for which the number of iterations lies in the range reported in the legend. The three ranges were chosen on the basis of the authors' experience. They can be interpreted as fast (1–5), average (6–10), and slow (11–50) rate of convergence

$\lambda_l + \lambda_{l-1}$ is about 1. A synthesis of these considerations is that in the FM case the iterative procedure is intrinsically fast and cannot be significantly further improved.

The PM case is very different. In this case the non-local character of the $\mathbf{D}_1$ elements turn all the previous arguments upside down. The initial guess is not so good as in the FM and in the DAMP version more than ten iterations are required to reach the convergence threshold in about 95% of the cases. The introduction of DIIS substantially improves the convergence properties of the iterative procedure (Fig. 2). In this case almost all of the λ_k coefficients are significantly different from zero.

To test the behaviour of the DIIS method with respect the solute size, a test calculation was performed on a polyglycine peptide, in an all-trans configuration. The number of residues starts from ten and, in steps of ten, increases to 200. The DIIS procedure exhibits very regular behaviour: all the calculations converge in seven iterations for the FM and in 11 for the PMs. In contrast, the DAMP procedure show a totally irregular pattern:

almost all the calculations (expecially for the PMs) converge slowly or do not converge at all.

5 Conclusions

The introduction of DIIS does not significantly improve the convergence rate of the FM iterative procedure but it has very important consequences on the PM formulation because it significantly reduces the number of iterations required to reach the convergence threshold. This fast iterative scheme combined with a fast way of computing the iterative steps, like the fast multipole method [24, 29], leads to a PCM implementation that is computationally very efficient. This implementation can be coupled to molecular mechanics and/or semiempirical methods for which the traditional PCM procedures are too expensive. The DIIS procedure exposed here has been inserted into the development version of the Gaussian [6] package.

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