Orbital-based direct inversion in the iterative subspace for the generalized valence bond method

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We present an algorithm that is a new combination of the direct inversion in the iterative subspace (DIIS) and the generalized valence bond (GVB) methods. The proposed algorithm is based on applying the DIIS directly to the orbitals updated via the GVB scheme as opposed to the conventional approach of applying DIIS to a series of composite Fock matrices (CFMs). The new method results in GVB convergence in situations where the CFM-based GVB-DIIS cannot be applied at all, e.g., when the original GVB method diverges. When both the new and the conventional methods converge, the former achieves the same reduction in the number of self-consistent field (SCF) iterations as the latter, but using considerably less storage and DIIS-related CPU time. Also, the orbital-based GVB-DIIS is less sensitive to the proximity of an initial guess to the exact wave function, and it does not depend on empirical criteria used in the CFM-based GVB-DIIS. Finally, the orbital-based DIIS formulation is not limited to GVB; it can be easily incorporated into any SCF approach that involves an iterative updating of the orbitals, such as, e.g., multiconfiguration SCF or Kohn–Sham density-functional theory. © *1995 American Institute of Physics.*

I. INTRODUCTION

Since the introduction of the direct inversion in the iterative subspace (DIIS) method by Pulay,[1] it has been widely accepted as a very successful means of accelerating convergence of various iterative processes, including self-consistent field (SCF) optimization of an electronic wave function.[2–5] For wave functions ranging from single determinant closed shell to multiconfiguration SCF such as the GVB-PP (generalized valence bond with perfect-pairing restriction) wave function,[6] DIIS has been used mostly within the framework of pseudoeigenvalue methods. In this formulation, the next approximation to molecular orbitals is obtained via diagonalizing an optimal linear combination of composite Fock matrices (CFMs) from current and previous iterations[1–3,5] rather than just the current CFM, as in conventional pseudoeigenvalue methods. Recipes for forming the CFM and the corresponding ''error vector'' have been proposed for several wave functions,[2,3,5,7] where the off-diagonal elements F_{ij} of the CFM are generally proportional to $\langle i|\mathscr{F}_j-\mathscr{F}_i|j\rangle$, and the diagonal elements are chosen so as to affect convergence in a favorable way.[7] Here $\mathscr{F}_i$ is the Fock operator associated with an orbital $|i>$; for virtual orbitals, it is zero.

In addition to combining DIIS with first-order pseudoeigenvalue methods, DIIS has been applied to second-order Hessian-based methods[4] as well. Since the computational cost of a single iteration of a second-order Hessian-based method is substantially higher than that of a pseudoeigenvalue method, the former will be the method of choice only for difficult cases where pseudoeigenvalue methods fail even if combined with DIIS.

Although the advantages of DIIS are hard to overestimate, CFM-based DIIS requires an initial guess that is sufficiently close to the exact solution,[1,5] and to establish initial convergence one often has to use such methods as damping,[8] level shifting,[9] or manual modification of an initial guess. The sensitivity of CFM-based DIIS to an initial guess calls for the introduction of a criterion that indicates if the DIIS can be turned on. The most commonly used criterion is that the maximum absolute value of the CFM's off-diagonal elements should drop below some threshold.[5,10] Such a criterion not only introduces an empirically adjustable value of a threshold, but also interferes with the practice of scaling CFM off-diagonal elements to accelerate convergence in certain cases.[3]

Recently, the DIIS procedure has been applied to the GVB-PP method via recasting the latter into the CFM formalism,[5] and, thus, GVB-DIIS inherited the problems associated with CFM-based DIIS. However, the original GVB-PP scheme for orbital optimization had several very attractive features as compared to CFM diagonalization. Indeed, unlike pseudoeigenvalue methods which are based on the first-order condition of the total energy being stationary, GVB-PP invokes changes in the occupied orbitals that minimize the total energy through the second order with respect to pairwise rotations between occupied orbitals and to mixing of virtual orbitals with each occupied orbital.[6]

Since the GVB-PP method is very robust, converges faster and has a greater radius of convergence than CFM-based diagonalization, it would be highly desirable to retain these properties when applying DIIS to GVB-PP. The main difficulty here is that GVB-PP is formulated in terms of orbitals, and their straightforward extrapolation would break the orthonormality condition $C^TSC=I$, where C is the matrix of orbital coefficients over basis functions, i.e. $|i>=\Sigma_{\mu=1}^{N}\ c_{\mu i}\chi_\mu$, S is the overlap matrix: $S_{\mu\nu}=<\chi_\mu|\chi_\nu>$, and I is the unit matrix. A known solution to avoid these difficulties is to use independent $N(N-1)/2$ rotational parameters (''angles'') along with some fixed set of orbitals serving as a reference,[11] so that every set of orbitals, C, can be obtained from the reference set, $C_{\rm ref}$, by

rotating it according to the angular matrix Θ as $C=C_{\rm ref}\exp\Theta$, where Θ is an antisymmetric matrix. This unitary transformation, obviously, preserves the orthonormality of the orbitals throughout the iterative process. Note that by determining rotational parameters *after* the next approximation to the exact orbitals is obtained via GVB-PP, instead of reformulating the SCF problem in terms of these parameters themselves, we still are able to use the GVB-PP scheme in order to advance iterations as opposed to the more expensive Hessian-based approaches.[4,11]

The idea of using $N(N-1)/2$ independent parameters within the DIIS framework has been pointed out by Pulay,[2] but his choice of an error vector called for two Fock matrix evaluations per iteration, so it was not practical. Our choice of the error vector (see Section II) requires only one Fock matrix evaluation per iteration, similar to the CFM-based DIIS algorithms[2,3,5] proposed after the original DIIS method[1] had been introduced. The other implementation of the orbital-based DIIS we would like to mention is that due to Fischer and Almlöf[4] where the independent parameters were used in a second-order Hessian-based algorithm,[4] which is very reliable but computationally expensive, as already mentioned.

As follows from the discussion above, one can expect superior performance from DIIS applied to orbitals that are updated via the GVB-PP scheme as compared to DIIS applied to the corresponding CFM. In the present paper, we demonstrate that this is indeed the case. The orbital-based GVB-DIIS results in the same reduction in the number of iterations as the CFM-based GVB-DIIS[5] when both methods converge, but at considerably less expense. Moreover, the new method is effective in cases where the CFM-based GVB-DIIS is not applicable, i.e., when the original GVB-PP scheme, used as a tool for establishing initial convergence, diverges.

II. METHOD

Among the methods used in SCF calculations, the GVB-PP method[6] has a computational cost similar to that of first-order pseudoeigenvalue methods and superior convergence properties characteristic of second-order Hessian-based techniques. The GVB-PP method is designed to converge a wave function of the form

$$\psi_{\rm GVB\text{-}PP}=\mathscr{A}\Bigg(\prod_{i=1}^{n_{\rm core}}\phi_i^c\phi_i^c\alpha\beta\prod_{i=1}^{n_{\rm pair}}(\sigma_{1i}\phi_{1i}\phi_{1i}+\sigma_{2i}\phi_{2i}\phi_{2i}+\cdots)(\alpha\beta-\beta\alpha)\prod_{i=1}^{n_{\rm open}}\phi_i^o\alpha\Bigg) \tag{1}$$

Here $\mathscr{A}$ is the antisymmetrizer, ϕ_i are orthogonal spatial orbitals, and α and β are spin coordinates. For every GVB-PP pair i, $i=1,...,n_{\rm pair}$, the coefficients σ_{ki}, $k=1,2,...$ satisfy the condition

$$\sigma_{1i}^2+\sigma_{2i}^2+\cdots=1. \tag{2}$$

The GVB-PP wave function provides the means to account for static electron correlation and serves as an excellent starting point for higher level calculations such as, e.g., multireference configuration interaction[12] or perturbation theory[13] calculations.

The superlinear convergence of the GVB-PP method arises from expansion of the total energy as a function of the orbital expansion coefficients C through second order. This allows one to find mixing coefficients between occupied orbitals that minimize this energy expansion for every pairwise rotation between the occupied orbitals. The mixing between the occupied and virtual orbitals is performed by a pseudoeigenvalue-type procedure (the detailed description of the GVB-PP method is given in Ref. 6).

Since the GVB-PP method is formulated in terms of orthogonal orbitals, DIIS cannot be applied to it in a straightforward fashion, as it will break the orthonormality condition $C^TSC=I$. Thus, our task is to find the object, as well as the corresponding ''error vector,'' that can be used within the DIIS framework. Following Yaffe and Goddard,[11] we find that it is very convenient to represent the orbital expansion coefficients C (which we will henceforth call ''orbitals'' for the sake of brevity) via some reference set of orbitals, $C_{\rm ref}$, and the unitary matrix U that transforms $C_{\rm ref}$ into C according to $C=C_{\rm ref}U$. Since every unitary matrix can be represented as $\exp\Theta$, where $\Theta^T=-\Theta$ (see, e.g., Ref. 14), the use of $N(N-1)/2$ *independent* orbital rotation angles Θ instead of the orbitals themselves can be advantageous.[4,11]

When the orbitals at the nth iteration are represented as

$$C_n=C_{\rm ref}\ \exp\Theta_n, \tag{3}$$

the relationship between the orbitals at the kth and nth iterations becomes

$$C_n=C_k\ \exp\Delta_{kn}, \tag{4}$$

where $\Delta_{kn}=\Theta_n-\Theta_k$. Using the fact that $C_n^TSC_n=I$ for every n, it is easy to show that

$$\Delta_{kn}=\ln(C_k^TSC_n)=\ln(I+C_k^TS(C_n-C_k)) \tag{5}$$

and, thus, we can use the power series

$$\ln(I+X)=\sum_{m=1}^{\infty}(-1)^{m+1}\frac{X^m}{m} \tag{6}$$

to calculate Δ_{kn}. Upon convergence, $\Delta_n=\Theta_n-\Theta_{n-1}$ should become zero, and, thus, we use Δ_n as an ''error vector'' corresponding to the nth iteration, where the orbitals C_n correspond to the rotational angles Θ_n, with the matrix Θ_n being treated as the object to be used in the DIIS procedure. Now we can formulate the orbital-based GVB-DIIS as follows.

1. Using the standard GVB-PP approach,[6] we obtain C_n (the next approximation to the orbitals) from the orbitals C_{n-1}. This is the most expensive part of the algorithm since it involves a Fock matrix evaluation.

2. If necessary, we change the sign of some orbitals in C_n and/or change the order of the occupied and, separately, the order of virtual orbitals in C_n in order to decrease the distance between C_n and C_{n-1}. This can be done in several

straightforward ways, and it is not even important to achieve the minimum of $\|C_n - C_{n-1}\|$. We have found that one pass over the columns of C_n that interchanges its ith column with the one that has minimal distance to the ith column of C_{n-1} and is chosen from the $i,...,n$ columns of C_n and their negative is sufficient.

3. Given the overlap matrix S and the orbitals C_n and C_{n-1}, we obtain Δ_n as described above. The matrix Δ_n represents an error vector associated with the iteration n. However, it accounts for changes in all orbitals, including the virtual ones, and, obviously, it is desirable to remove the virtual orbitals' contribution to the error vector. If the orbitals C_i, $i=i_0,...,n$ are partitioned into occupied and virtual parts as $C_i=(C_i^{\rm occ}|C_i^{\rm virt})$, then the same partitioning holds for the unitary matrix $U_n=\exp\Delta_n$ that transforms C_{n-1} into C_n, i.e., $U_n=(U_n^{\rm occ}|U_n^{\rm virt})$ and $C_n^{\rm occ}=C_{n-1}U_n^{\rm occ}$. However, the corresponding partitioning of Δ_n into $(\Delta_n^{\rm occ}|\Delta_n^{\rm virt})$ is approximate, since it is rigorous only within the linear approximation where $U_n=I+\Delta_n$. Nevertheless, if one uses $\Delta_n^{\rm occ}$ instead of Δ_n, the rotations between virtual orbitals are not taken into account, and they should not be. Our tests have also shown that the use of $\Delta_n^{\rm occ}$ as an error vector results in faster convergence as compared to the use of the full matrix Δ_n, and, therefore, we will use the former in all subsequent formulations.

4. Based on $\Delta_i^{\rm occ}$, $i=i_0,...,n-1$, from the previous iterations, we find the coefficients τ_i, $i=i_0,...,n$, that satisfy the condition

$$\sum_{i=i_0}^{n}\tau_i=1 \tag{7}$$

and that minimize the norm of the vector

$$\Delta_n^*=\sum_{i=i_0}^{n}\tau_i\Delta_i^{\rm occ}. \tag{8}$$

The sought-after τ_i, $i=i_0,...,n$ are found via solving the linear system

$$B(\lambda,\tau_{i_0},...,\tau_n)^T=(1,0,...,0)^T, \tag{9}$$

where the matrix B is formed from zeroes, ones, and $\langle\Delta_i^{\rm occ},\Delta_j^{\rm occ}\rangle$ as described in Ref. 1.

5. We construct the optimal orbitals C_n^* that correspond to the optimal rotation

$$\Theta_n^*=\sum_{i=i_0}^{n}\tau_i\Theta_i. \tag{10}$$

In order to do that, we first choose the base orbitals among C_i, $i=i_0,...,n$, that contribute the most to this linear combination, i.e., the orbitals that correspond to the maximum absolute value of τ_i, $i=i_0,...,n$, say C_k (the base orbitals C_k should not be confused with $C_{\rm ref}$ that allow us to map C_i onto Θ_i). Now we obtain

$$\begin{aligned}C_n^*=C_{\rm ref}\ \exp\Theta_n^*&=C_{\rm ref}\ \exp\left(\sum_{i=i_0}^{n}\tau_i\Theta_i\right)\\&=C_{\rm ref}\ \exp\left(\Theta_k+\sum_{i\neq k}\tau_i(\Theta_i-\Theta_k)\right)\\&=C_k\exp\left(\sum_{i\neq k}\tau_i\Delta_{ki}\right).\end{aligned} \tag{11}$$

From this expression it becomes clear why we choose the base orbitals C_k as described above, since in this case the norm of the rotation from the C_k to the C_n^* will be minimal and the power series for the exponential function will converge faster; however, this choice is not crucial and, actually, one can use any C_i as a base.

The expression for the optimal orbitals C_n^* obtained above can be interpreted as a series of rotations of the base orbitals C_k by the angles $\tau_i\Delta_{ki}$, where each Δ_{ki} is just the angle that brings C_k into C_i. If we would replace the rotations between orbitals by linear transformations, the optimal orbitals C_n^* obtained as described above would correspond to the linear combination of the orbitals C_i, $i=i_0,...,n$ with the coefficients τ_i, $i=i_0,...,n$. Thus, the orbital-based GVB-DIIS can be considered as an introduction of such interpretation of a linear combination of orbitals that preserves their orthonormality.

III. RESULTS AND DISCUSSION

In order to demonstrate the superior convergence properties of the orbital-based GVB-DIIS as compared to those of the CFM-based one, we first consider the example given in the paper that proposed the original CFM-based GVB-DIIS.[5] In this example, the GVB-PP wave function with one GVB pair is sought for the H_2O molecule with the 6-31G** basis set, where the correlated O–H σ-bond is stretched to different extents. Since we possess the same GVB2P5 program[15] as do the authors of the CFM-based GVB-DIIS, we are able to use initial guesses that must be similar to theirs, because our guesses require the same number of GVB2P5 iterations to meet the same convergence criterion as the guesses used in Ref. 5.

The results of such a comparison are shown in Table I. From this table it becomes clear that both the orbital-based and the CFM-based GVB-DIISs result in the same reduction in the number of iterations as compared to the original GVB-PP scheme implemented in the GVB2P5 program. However, to achieve such a reduction, the CFM-based algorithm has to rely on (and, thus, has to store) the CFMs from ten previous iterations.[5] The orbital-based scheme achieves comparable results by storing only two previous angle matrices, which not only greatly reduces the storage requirements that can be an issue even for moderate cases, but also practically eliminates the possibility of producing a poorly conditioned matrix B that is used to determine the coefficients τ_i according to Eq. (9). Note, that the latter problem appears to be quite common in CFM-based DIIS, since special techniques to alleviate it have been developed.[3,5]

TABLE I. The number of iterations to converge the GVB-PP wave function with one GVB pair for the H_2O molecule.

	Number of iterations					
			OB-DIIS			
			N_{store}^{c}			
ΔR[a]	GVB2P5	CFM-DIIS[b]	1	2	4	8
0.0	24	13	15	14	12	13
0.2	23	13	23	15	12	13
0.5	23	11	22	14	14	13
1.0	19	12	17	13	11	11
2.0	20	11	19	12	11	11

[a]The starting geometry is $R_{OH}=0.94$ Å, $\alpha_{HOH}=105.98^{o}$. One of the O–H bonds was stretched from its equilibrium position, with ΔR representing the increase in this bond length (in Å).

[b]From Ref. 5. In this case, 10 previous iterations were used in the DIIS procedure.

[c]N_{store} is the number of previous iterations used in the orbital-based GVB-DIIS (OB-DIIS).

The reason why the orbital-based GVB-DIIS relies on a substantially smaller number of previous iterations as compared to the CFM-based GVB-DIIS is rather transparent. Indeed, the GVB-PP algorithm[6] possesses a superlinear rate of convergence, and, thus, the error (i.e., the distance to the solution) changes substantially between consecutive iterations. This results in the earlier iterations being markedly farther away from the solution than the most recent ones, so that relatively few (two or three) of the latest iterations have comparable errors and give meaningful contributions to the optimal angles sought as a linear combination of the previous ones. In the case of linear convergence that is characteristic for an SCF based entirely on CFM diagonalization, a larger number of iterations have comparable errors and thus contribute to the optimal CFM.

Although the example considered above shows that the number of iterations is reduced approximately by half, it does not allow us to estimate the overhead incurred by the DIIS procedure, since the CPU time is very small (about 3 s on an HP-735 workstation) and is of the order of the start-up cost. In order to observe how the inclusion of the DIIS procedure into the GVB-PP algorithm affects the actual timing, we consider a larger case, where we find a GVB-PP wave function with three GVB pairs for a Na_6 cluster utilizing a valence double zeta (VDZ) basis and effective core potential due to Melius and Goddard.[16] We used a geometry that is a slightly distorted planar configuration believed to be the global minimum; its detailed description is given in Ref. 17. The results are shown in Table II, from which we see that the actual speedup (the reduction in the CPU time) resulting from employing the orbital-based GVB-DIIS is of the order of the reduction in the number of iterations, with the latter being even more impressive than for the small case of H_2O (nearly a factor of 3 less iterations required). We expect that thorough optimization of the computer code will decrease the DIIS-related overhead further. Unfortunately, we cannot compare the actual speedup for both the orbital-based and the CFM-based GVB-DIISs, since no timing data are given in Ref. 5.

TABLE II. The number of iterations and the corresponding CPU time (in s, for an HP-735 workstation) to converge the GVB-PP wave function with three GVB pairs for a Na_6 cluster. N_{store} is the number of previous iterations used in the orbital-based GVB-DIIS. GVB2P5 is the standard GVB-PP algorithm given in Ref. 6.

Method	Iterations	Total CPU time	CPU time per iteration
GVB2P5	76	285.5	3.76
$N_{store}=1$	27	112.0	4.15
$N_{store}=2$	27	114.4	4.24
$N_{store}=4$	25	105.9	4.24
$N_{store}=8$	25	106.5	4.26

The last example that we wish to consider illustrates the *qualitative* difference between the CFM-based GVB-DIIS and the orbital-based one. In this example, a GVB-PP wave function with five GVB pairs is sought for the $PtZrCH_3$ molecule. The conventional GVB2P5 program was unable even to approach the region of solution, since unstable behavior occurred from the very beginning of the iterative process. No option available within the GVB2P5 program to facilitate convergence (e.g., simple averaging with subsequent reorthonormalization of the orbitals) could remedy this situation. Thus, CFM-based GVB-DIIS could not even be started since it requires an initial guess that is close to the solution. It is the GVB2P5 program itself that is supposed to approach the region of solution in the CFM-based GVB-DIIS,[5] and if it fails, one has to resort to other means of establishing convergence apart from the DIIS; most often this involves a modifying an initial guess manually. (The dependence of the CFM-based GVB-DIIS on the convergence of the conventional GVB2P5 program can also be seen from the fact that in all examples considered in Ref. 5, the original GVB2P5 program always converges).

When we applied the orbital-based GVB-DIIS to this case that is difficult for the GVB2P5 program, convergence was achieved even for minimal DIIS, i.e., when only one previous angle matrix has been stored. The decrease in the number of iterations required to achieve convergence leveled off rapidly as we increased N_{store}, the number of previous angle matrices used in the DIIS expansion (10). Thus, for $N_{store}=1,2,3$ the number of iterations to convergence was, respectively, 50, 17, and 16. This is, of course, the expected behavior, as explained earlier.

The difference in convergence behavior of the conventional GVB-PP algorithm[6] and the orbital-based GVB-DIIS can be illustrated by Figs. 1–3. In these figures, every set of orbitals considered in the course of optimization (or, equivalently, the corresponding angle matrix Θ) is represented by a point, with the orbitals corresponding to the initial guess being at the origin. Each line segment represents a step of the regular GVB-PP orbital updating scheme,[6] where the points corresponding to input and output orbitals from this scheme are connected with a line. The length of a segment is taken to be equal to the norm of the corresponding error vector, Δ_n^{occ}, and the angle between two consecutive segments representing iterations $n-1$ and n is taken as an angle between the vectors Δ_{n-1}^{occ} and Δ_n^{occ}. The position of every point corresponding to the optimal linear combination (10) is taken as

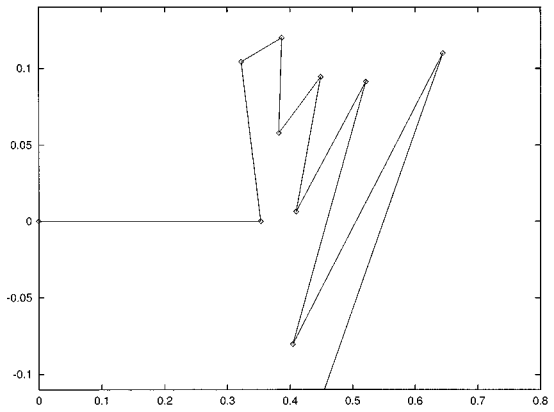

FIG. 1. The convergence behavior of the original GVB-PP scheme (as implemented in the GVB2P5 program, see Ref. 6) applied to the $PtZrCH_3$ molecule. See the text for the interpretation of these plots.

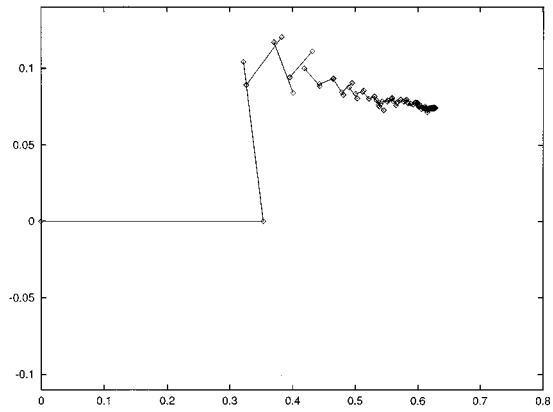

FIG. 2. The convergence behavior of the orbital-based GVB-DIIS with $N_{\text{store}}=1$ applied to the $PtZrCH_3$ molecule.

a linear combination of the positions of the corresponding points with the same coefficients as in Eq. (10).

Of course, the pictures shown in Figs. 1–3 are not unique, since there are two choices for the orientation of every segment when only its initial point, length and angle with the previous segment are known. However, we find it very helpful to view such pictures since they provide a qualitative description of the iterative process. For instance, Fig. 1 illustrates the hopelessly diverging GVB2P5 program when it is applied to $PtZrCH_3$. Note that each line segment here starts from the end of the previous segment since no DIIS expansion (10) is implemented and the output of the previous iteration serves as an input to the next. By contrast, Fig. 2 shows the regular convergence pattern of the orbital-based GVB-DIIS applied to the same case. The picture shown corresponds to the minimal DIIS, i.e., $N_{\text{store}}=1$ which is equivalent to a two-point extrapolation between the end points of two consecutive segments. Figure 3 illustrates the last 37 iterations of the GVB2P5 program applied to the Na_6 cluster. It explicitly shows the type of convergence behavior that is regular but very slow, again illustrating the need for the orbital-based GVB-DIIS.

IV. CONCLUSION

The present paper describes the orbital-based GVB-DIIS orbital optimization scheme that is based on combining the convergence-accelerating DIIS approach[1] with the GVB-PP algorithm.[6] Since the GVB-PP method is robust, has a superlinear rate of convergence and is not very sensitive to the initial guess, it results in better performance when combined with the DIIS than the previously proposed CFM-based GVB-DIIS.[5] In fact, this difference is true in even a qualitative sense, since the orbital-based GVB-DIIS is successful in cases not amenable to the CFM-based GVB-DIIS. By this we refer to the fact that the latter uses the original GVB-PP scheme in order to approach the vicinity of the solution and experiences difficulties when the conventional GVB-PP method diverges.

The orbital-based GVB-DIIS requires substantially less storage than the CFM-based GVB-DIIS, since the former relies on two or three previous iterations as opposed to ten used by the latter to achieve a comparable reduction in the total number of iterations. Consequently, the orbital-based GVB-DIIS incurs very little DIIS-related costs and, also, it is not likely to encounter an ill-defined system of linear equations (9), which is a known problem for the CFM-based DIIS.

Furthermore, in the orbital-based GVB-DIIS, the same orbital updating scheme is used throughout the entire optimization process, and, therefore, one is not concerned with choosing an empirically-adjustable criterion that indicates if and when the conventional GVB-PP algorithm used to approach the region of solution may be replaced by the CFM diagonalization scheme used in the final stage of the CFM-based GVB-DIIS.

Finally, we note that the orbital-based DIIS procedure presented herein is independent of the SCF method used to update the orbitals. We have illustrated it for GVB-PP, but it is also applicable to any SCF algorithm that involves an orbital optimization, including, e.g., general MCSCF or Kohn-Sham Density-Functional Theory.

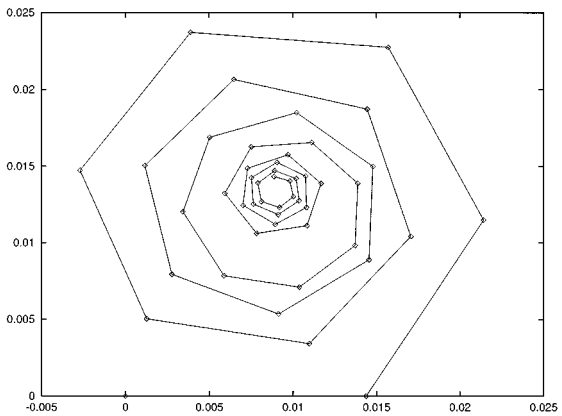

FIG. 3. A typical pattern of slow convergence, demonstrated by the GVB2P5 program applied to the Na_6 cluster.

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