CROATICA CHEMICA ACTA CCACAA **72** (4) 945–952 (1999)

ISSN-0011-1643
CCA-2627 *Original Scientific Paper*

Self-Consistent Field Low Rank Perturbation Method

Dražen Horvat,[a] *Zorislav Đaković,*[a] *and Tomislav P. Živković* [b,*]

[a] *Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia*

[b] *Ruđer Bošković Institute, P.O.B. 1016, HR-10001 Zagreb, Croatia*

Received June 18, 1999; revised October 29, 1999; accepted October 29, 1999

The LRP-method is applied to the generalized perturbed eigenvalue equation, where the solution of the reference unperturbed equation is known. This method is generalized to the SCF approach. A simple case of rank one perturbation is considered. It is shown that the operation count required to perform a single SCF iteration is of the order $O(n^2)$, where n is the order of the matrices considered. This operation count is essentially independent of the magnitude of the perturbation. In addition, the number of SCF iterations increases very slowly with the magnitude of the perturbation. The SCF LRP method can be applied to those problems where the rank of the perturbation is relatively small. In particular, it can be applied to localized perturbations, where only a few perturbation matrix elements are nonzero. Such are, for example, substitution of an atom in a molecule by a heteroatom, formation or breaking of a chemical bond, *etc*.

Key words: Low Rank Perturbation, SCF method, generalized eigenvalue equation

INTRODUCTION

If the rank of the perturbation is small, the perturbed eigenvalue equation can be efficiently treated by the low rank perturbation method[1] (LRP). This method is applied to the generalized perturbed eigenvalue equation

* Author to whom correspondence should be addressed. (E-mail: zivkovic@rudjer.irb.hr)

$$(\boldsymbol{B} + \boldsymbol{V})\Psi_k = E_k\,(\boldsymbol{C} + \boldsymbol{P})\Psi_k \tag{1}$$

where $\boldsymbol{B}$, $\boldsymbol{V}$, $\boldsymbol{C}$ and $\boldsymbol{P}$ are n order matrices. In the LRP approach, the solution of the corresponding unperturbed equation

$$\boldsymbol{B}\Phi_i = \lambda_i \boldsymbol{C}\Phi_i \tag{2}$$

is assumed to be known. Matrices $\boldsymbol{B}$, $\boldsymbol{V}$, $\boldsymbol{C}$ and $\boldsymbol{P}$ are arbitrary, except for the requirement that matrix $\boldsymbol{C}$ should be nonsingular and matrix $\boldsymbol{C}^{-1/2}\boldsymbol{B}\boldsymbol{C}^{-1/2}$ nondefective.[1] By definition, a matrix is nondefective if it has a complete set of eigenvectors.[2,3] This is a very mild condition, and the LRP method can be applied to a large number of problems. In particular, matrices $\boldsymbol{B}$, $\boldsymbol{V}$, $\boldsymbol{C}$ and $\boldsymbol{P}$ are not required to be hermitian.

The LRP method can be applied to any perturbation, but the calculation is most efficient if the rank ρ of the perturbation ($\boldsymbol{V}$, $\boldsymbol{P}$) is small with respect to n.[1] One can show that the derivation of all the eigenvalues and all the eigenvectors of the perturbed eigenvalue equation (1) by the LRP method requires $O(\rho^2 n^2)$ operations.[1,4] If $\rho << n$, this operation count is essentially of the order $O(n^2)$. In addition, if the perturbation ($\boldsymbol{V}$, $\boldsymbol{P}$) is localized, that is, if matrices $\boldsymbol{V}$ and $\boldsymbol{P}$ are sparse with only a few nonzero matrix elements, the operation count to obtain a single selected eigenvalue and eigenvector is essentially of the order $O(n)$. In comparison, the well-known Householder QR-method, which applies to a much more restrictive hermitian eigenvalue problem, requires $O(n^3)$ operations to obtain all eigenvalues and eigenvectors.[2] A similar operation count is obtained by various other direct diagonalization methods.[2,3] These direct methods are not very suitable for the derivation of a single eigenvalue and eigenvector. On the other hand, various perturbation approaches that can be applied to the derivation of a single selected eigenvalue and eigenvector usually require that the perturbation should be small, in order for the perturbation expansion to converge sufficiently fast. Unlike these standard perturbation methods, the efficiency of the LRP method is not effected by the magnitude of the perturbation. Thus, the standard perturbation methods and the LRP method are complementary. The former methods are efficient if the magnitude of the perturbation is small, while the LRP method is efficient if the rank of the perturbation is small.

Another advantage of the LRP method is its low storage requirement. In order to solve the LRP problem, one does not need to know all the matrix elements, but rather only all the unperturbed eigenvalues and all the components of the unperturbed eigenfunctions on the sites effected by the perturbation.[1,4] Thus, instead of $O(n^2)$ matrix elements, only n unperturbed eigenvalues and ρn unperturbed eigenfunction components are required. For

example, if $n = 1000$ and $\rho = 1$, and if the calculation is performed on a PC with double precision, the storage requirement for a single n order matrix is $8n^2 = 8 \cdot 10^6$ bytes of memory. If the matrix is symmetric, this can be reduced to $4n^2 = 4 \cdot 10^6$. On the other hand, the storage requirement for n unperturbed eigenvalues and n components of the unperturbed eigenfunctions is only $8 \cdot 2n = 16 \cdot 10^3$ bytes. This is almost three orders of magnitude less. Thus, even on the personal computer, one can apply the LRP method on very large matrices.

In this paper, we generalize the original LRP approach by including the SCF effects. We treat the most important case where matrices $\boldsymbol{B}$, $\boldsymbol{V}$, $\boldsymbol{C}$ and $\boldsymbol{P}$ are hermitian, and where, in addition, matrices $\boldsymbol{C}$ and $\boldsymbol{C} + \boldsymbol{P}$ are positive definite. This latter requirement is necessary in order for the generalized eigenvalue equations (1) and (2) to be equivalent to the hermitian eigenvalue equations.[5] In particular, this requirement warrants that the eigenvalues E_k and λ_i are real. In addition, we treat only the SCF LRP rank one case in this paper. If the perturbation is local, this corresponds formally to the change of the matrix element on a single site, and to the subsequent iterative adjustment of the effective charge q_{eff} on this site. There are, in principle, no obstacles to generalizing this rank one model to higher ranks, except for more involved programming. The operation count for these higher ranks should follow the rule $O(\rho^2 n^2)$, as already established in the case of the original LRP method.[1,4]

One additional point should be emphasized. If the SCF approach is applied to the eigenvalue equation $\boldsymbol{H\Theta}_i = \varepsilon_i \boldsymbol{\Theta}_i$, the matrix elements of matrix $\boldsymbol{H}$ are obtained iteratively, and these matrix elements depend on the eigenvectors Θ_i. Hence, if one introduces a local perturbation into the system, the effective perturbation will be spread all over the system, *i.e.* it will become delocalized. For example, if in an alternant hydrocarbon one replaces a particular carbon atom with a heteroatom, there will be a change of effective charges on all other carbon atoms. This means that, though the replacement of one atom by another can be represented by a local and hence low rank perturbation, the effective SCF perturbation is neither local nor of low rank. This and similar problems can be treated by the combined strategy of SCF LRP and standard perturbation approaches.[1] In the above example, though the effective SCF perturbation is spread all over the molecule, it is nevertheless mostly concentrated in the immediate vicinity of the point of substitution, and it decreases very rapidly in an oscillating exponentially decaying manner with the distance from this point.[6] Therefore, one can partition the effective perturbation into two parts. The low rank component that involves the point of the substitution and a few points close to this point. This component is large, and it is treated exactly by the SCF LRP ap-

proach. The remaining perturbation is relatively small, it is spread all over the molecule, and it is not of low rank. This component is treated then by the standard perturbation method.

This combined method is not considered here, and we explicitly consider only the first dominant component of the effective SCF perturbation. This dominant component is large, and it is treated by the SCF LRP method. Namely, the purpose of this paper is to test the SCF LRP idea, and not the standard perturbation method.

NUMERICAL RESULTS

Our main goal was to assess the accuracy and the speed of the SCF LRP method. All the calculations were done on the PC–230 MHz Pentium computer. Due to the large order of matrices involved, the accuracy was tested indirectly, by verifying the mutual orthogonality of the obtained eigenfunctions. The accuracy of the LRP approach was directly tested for smaller matrices elsewhere.[4] The computer program was written by one of us (T. P. Živković) in the C++ language. We did test the SCF LRP rank one case. This rank one case is formally equivalent to the case of local perturbation involving a single site. Hence, the following simple model was applied. We assume the perturbation to involve only a single site, and in the iterative process we have to adjust the effective perturbation ω_{eff} and the effective charge q_{eff} on this site. We assume the effective perturbation on this site to be of the form $\omega_{\text{eff}} = \omega\,(1 + q_{\text{eff}})$. This is a very simple *ansatz* analogous to the so-called ω-technique that was used prior to more sophisticated SCF methods in order to improve Huckel MO.[7] Of course, the ω-technique is not a very advanced method, but it is good enough for testing the SCF LRP idea. In the first iteration, the effective charge on this site is set to zero ($q_{\text{eff}} = 0$), and the effective perturbation matrix element is $\omega_{\text{eff}} = \omega$. In each subsequent SCF iteration, one calculates coefficients of all occupied eigenfunctions on this site, these coefficients further determine the new effective charge, which then produces new effective perturbation matrix elements. To complete the iteration, a simple test is applied. If two consecutive effective charges agree up to 12 significant figures, iteration is completed.

The actual calculation was simulated by random matrices. Matrices of order $n = 100$ up to including $n = 8000$ were considered. In a range $n = (100, 2000)$, the order of matrices considered was increased in steps of 100, in a range $n = (2000, 4000)$, it was increased in steps of 250, and finally in a range $n = (4000, 8000)$, it was increased in steps of 500. As explained above, in the LRP approach the actual matrix elements are not required. All that is needed are unperturbed eigenvalues and coefficients of unperturbed eigen-

functions on perturbation sites.[1,4] These unperturbed eigenvalues were simulated as random numbers in the interval (–10.0, 10.0). Coefficients of the unperturbed eigenfunctions on the perturbation site were also simulated as random numbers, subject to the normalization condition. In order to assess the influence of the magnitude of the perturbation on the performance of the calculation, all calculations were done with four different perturbations spanning three orders of magnitude: $\omega = 1$, $\omega = 10$, $\omega = 100$ and $\omega = 1000$. Times needed to complete the SCF LRP calculation, as well as the numbers of SCF iterations were recorded. Since in the LRP approach the operation count required to obtain a single eigenvalue and eigenfunction is proportional to the matrix order n, these times were normalized per eigenvalue and eigenfunction, and per iteration. Such a presentation of the results is theoretically linear, and hence it is most suitable for the purpose of comparison. In addition, linear dependence on n has been confirmed here to hold very accurately. To obtain the actual times required to perform the complete SCF LRP calculation, one has to multiply these times by the matrix order n and by the number of SCF iterations. These normalized times for two extreme perturbation values ($\omega = 1$ and $\omega = 1000$) are shown in Figures 1 and 2. The results for $\omega = 10$ and $\omega = 100$ are intermediate, and for the sake of simplicity these results are omitted here.

It is obvious from Figures 1 and 2 that normalized times are to a very good approximation a linear function of the order n of the matrices involved.

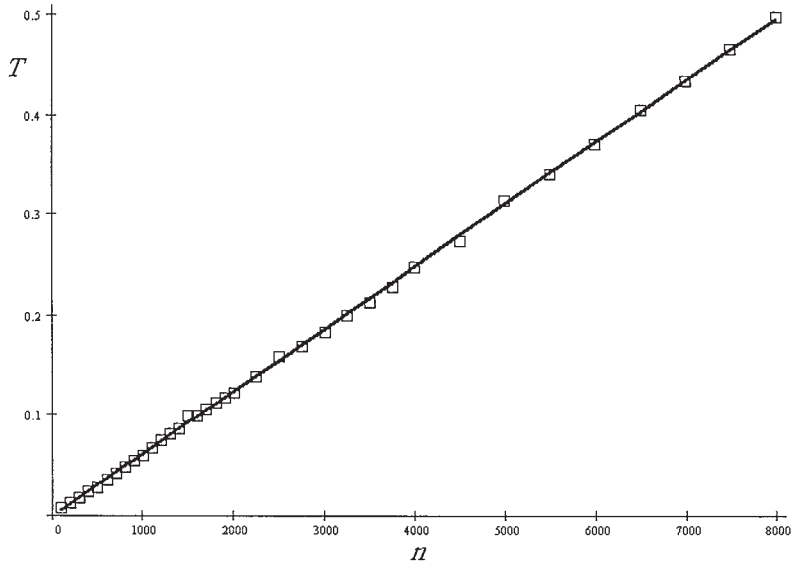

Figure 1. SCF LRP rank one calculations with perturbation $\omega = 1$. Normalized times T in arbitrary units are given as a function of matrix dimension.

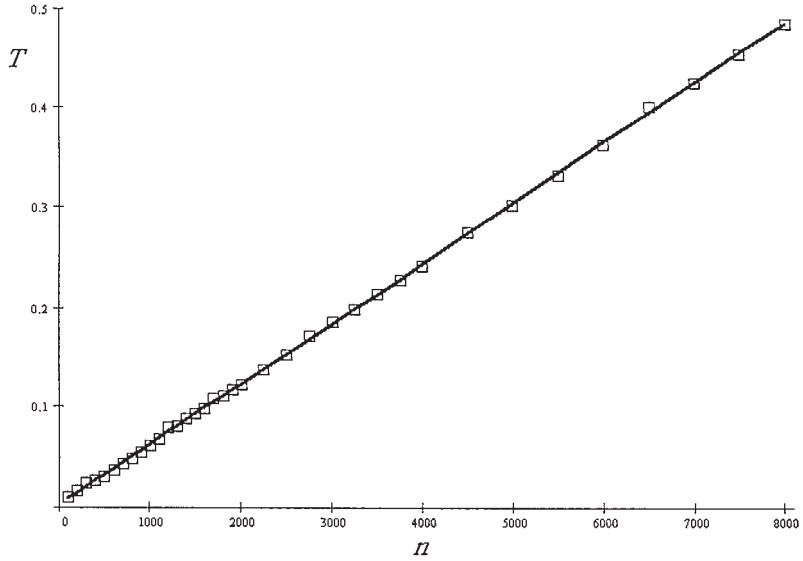

Figure 2. SCF LRP rank one calculations with perturbation $\omega = 1000$. Normalized times T in arbitrary units are given as a function of matrix dimension.

The correlation coefficient for data in Figure 1 is $k_1 = 0.99987$, while the correlation coefficient for data in Figure 2 is $k_{1000} = 0.99988$. Small fluctuations are due to the fact that in the LRP approach each particular eigenvalue is obtained in an iterative process, starting from an initial guess value. Hence, various random matrices require slightly different operation counts, which results in small fluctuations in the operation count per SCF LRP iteration. Further, the linear least square fit for data corresponding to the perturbation $\omega = 1$ (Figure 1) is very similar to the least square fit for data corresponding to the perturbation $\omega = 1000$ (Figure 2). The slope of the line in Figure 1 is $K_1 = 6.21 \cdot 10^{-5}$ while the slope of the line in Figure 2 is $K_{1000} = 6.03 \cdot 10^{-5}$. The slight decrease of the slope from the case $\omega = 1$ to the case $\omega = 1000$ indicates that the operation count per iteration slightly decreases with an increase of the magnitude of the perturbation. However, due to the extreme range of the perturbation considered (from $\omega = 1$ to $\omega = 1000$), this decrease is insignificant. One thus concludes that the operation count per iteration is highly insensitive to the perturbation magnitude.

Another point to be considered is the number of iterations. Average iteration numbers I, as well as the ranges ΔI of these numbers, are shown in Table I. There is a slight increase of the number of SCF iterations with the increase of the perturbation magnitude. However, this increase is also very small, since in the perturbation range of three orders of magnitude, it

amounts only to about 30%. It was further observed that in the case of each perturbation considered, the number of SCF iterations tends to decrease with the matrix dimension. Therefore, the operation count of the entire SCF LRP calculation is slightly sub quadratic.

TABLE I

Average number of iterations I and range of this number ΔI as a function of perturbation magnitude ω

ω	1	10	100	1000
I	3.06	3.39	3.75	3.87
ΔI	(3,4,5)	(3,4,5)	(2,3,4,5)	(3,4,5)

Considering the accuracy of this SCF LRP approach, it was tested indirectly by verifying mutual orthogonality of the obtained perturbed eigenfunctions. It was found that this orthogonality was satisfied up to approximately 14 significant figures. Since the data of type double that were used in the computer program are accurate approximately up to 15 significant figures, this result is entirely satisfactory.

CONCLUSION

The SCF LRP model can be efficiently applied to all those cases where the solution to the generalized eigenvalue equation of some reference system is known, and provided the perturbation is of low rank. We have tested the SCF LRP model on the simple case of rank one perturbation. It was shown that the operation count per SCF cycle and per eigenvalue and eigenfunction is to a high degree a linear function of the order n of the matrices considered. In other words, the operation count for one complete SCF cycle is a quadratic function of n. This operation count is highly insensitive to the magnitude of the perturbation. The number of SCF iterations slightly increases with the perturbation magnitude, but this effect is also very small and in the perturbation range of three orders of magnitude it amounts to only about 30%. In addition, the operation count slightly decreases with the increase of the matrix order n. One thus concludes that the SCF LRP method is quite robust, and that the operation count to perform complete SCF LRP calculation is slightly subquadratic in n. This result should be compared with operation counts of standard diagonalisation methods,[2] which are usually of the order $O(n^3)$.

REFERENCES

1. T. P. Živković, *Theor. Chem. Acta* **76** (1989) 331–351.
2. W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes*, Cambridge University Press, Cambridge, 1986.
3. G. H. Golub, C. F. Van Loan, *Matrix Computations*, Johns Hopkins Univ. Press, Baltimore, Md. 1983.
4. T. P. Živković, *J. Math. Chem.* **4** (1990) 143–153.
5. T. P. Živković, *J. Math. Chem.* **2** (1992) 55–73.
6. I. Gutman, *Theor. Chim. Acta* **50** (1979) 287–297.
7. A. Streitwieser, *J. Am. Chem. Soc.* **82** (1960) 4123–4135;
   A. Streitwieser and P. M. Nair, *Tetrahedron* **5** (1959) 149–165.

SAŽETAK

SCF perturbacijska metoda niskog ranga

Dražen Horvat, Zorislav Đaković i Tomislav P. Živković

Metoda LRP primjenjuje se na poopćenu jednadžbu vlastitih vrijednosti, gdje je poznato rješenje referentne neperturbirane jednadžbe. Ta je metoda poopćena na SCF pristup. Razmatran je jednostavan slučaj perturbacije ranga jedan. Pokazano je da je broj operacija potrebnih za jednu SCF iteraciju reda veličine $O(n^2)$, gdje je n red razmatranih matrica. Taj broj operacija uglavnom je neovisan o veličini perturbacije. Nadalje, broj SCF iteracija vrlo sporo raste s veličinom perturbacije. SCF LRP metoda može se primijeniti na sve one probleme gdje je rang perturbacije relativno malen. To posebno vrijedi za lokalizirane perturbacije, kod kojih nema mnogo matričnih elemenata različitih od nule. Takove perturbacije su na primjer supstitucija atoma u molekuli s heteroatomom, tvorba i kidanje kemijske veze, itd.