

An evaluation of three direct MC-SCF procedures

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The direct MC-SCF approach for modest active spaces is evaluated for (a) extended basis sets on small molecules and (b) modest sets on extended systems. An algorithm that scales as $n_a^2 N^4$ (n_a = number of active orbitals, N = number of AO) using Fock matrices appears to be quite efficient until n_a gets to 8 where an algorithm that scales as $n_a N^4$ using 3/4 transformed integrals begins to become competitive. The storage requirement for the J and K operators in the $n_a N^4$ algorithm has been removed with the cost of an additional direct Fock matrix construction.

1. Introduction

Traditionally in the standard algorithms of quantum chemistry the integrals were evaluated and stored on external storage to be processed later in an iterative solution of necessary equations. In *direct* methods the integrals are evaluated repeatedly during the iterative solution of the equations and never stored, thus avoiding the explosive growth in disk storage and *I/O* requirements in applications to large molecules. Such methods make quantum chemistry calculations on systems with up to several hundred atoms feasible. These methods are also becoming increasingly important because, in spite of the very fast general performance and large memories of the new generation of RISC workstation, disk access is slow.

The direct SCF method pioneered by Almlöf [1] has become the standard approach in the study of large molecules at the SCF level. Direct methods have since been applied to SCF second derivatives [2] and to perturbation theory [3-5]. A general discussion

of strategy in post-SCF direct methods can be found in refs. [6,7]. In this work we address the MC-SCF problem.

MC-SCF methods provide one of the only methods for obtaining a reliable zeroth order wavefunction in many chemical reactivity problems where homolytic bond cleavage occurs or one has bond exchange that may not be synchronous. In MC-SCF methods one usually has an *active space* consisting of a few orbitals and electrons treated by CI and a much larger number of *inactive* electrons in doubly occupied orbitals as in SCF theory. In order to extend MC-SCF computations to larger systems (for example to study the effects of phenyl substitution or to study a reacting group of centres in an extended system) direct MC-SCF must be used. Taylor and Almlöf [7] have considered the possible strategies for the implementation of direct MC-SCF problem in general. They have suggested two types of strategy, one based upon the use of Fock operators and a second based upon the usual methods for four-index transformation of the two-electron integrals that is similar to

that used in perturbation methods [3-5]. Our purpose in this Letter is the evaluation of three possible strategies for direct MC-SCF within the simplest first order MC-SCF approach. We believe that such an approach may be useful for modest active space but large numbers of inactive/virtual orbitals in studies requiring extended basis sets on small molecules or requiring more modest basis sets on large systems.

2. Three basic first order direct MC-SCF procedures

We shall limit our discussion to the simplest MC-SCF approach where the CI and orbital rotation parts of the problem are decoupled and the orbital rotation Hessian is approximated using Fock operators. We begin with a concise review of the basic elements of MC-SCF theory. We assume that we have an orthogonal set of starting orbitals. There are three types of orbitals; active (subscripts $\chi\nu\mu\eta$), with variable occupancy used in the CI expansion, inactive (subscripts $abcd$), which are double occupied in each CI configuration, and virtual (subscripts $rstu$), which have zero occupancy. The MC-SCF CI expansion is written as

$$\Psi = \sum_K C_K |K\rangle \quad (1)$$

and energy is simply

$$E = \epsilon_c + \sum_{\kappa L \eta \chi} \left(\langle \chi | h^c | \eta \rangle C_\kappa C_L A_{\eta\chi}^{KL} + \sum_{\chi\nu\mu\eta} [\chi\nu | \mu\eta] C_\kappa C_L B_{\chi\nu\mu\eta}^{KL} \right). \quad (2)$$

The $A_{\eta\chi}^{KL}$ and $B_{\chi\nu\mu\eta}^{KL}$ are numerical coefficients that depend upon the choice of CI configurations. The term ϵ_c is just the HF energy of the closed shell inactive orbitals and the operator h^c is the closed shell inactive orbital Fock operator while $[\chi\nu | \mu\eta]$ are the two-electron repulsion integrals.

The orbitals Φ^{i+1} at the $(i+1)$ th iteration are obtained from Φ^i of the i th iteration by unitary transformation as

$$\Phi^{i+1} = \mathbf{U} \Phi^i. \quad (3)$$

The unitary transformation \mathbf{U} is written in terms of its parameters as

$$\mathbf{U} = \exp(\mathbf{X}), \quad (4)$$

where \mathbf{X} is a skew-symmetric matrix of $\frac{1}{2}n(n-1)$ independent parameters. The SCF condition is

$$\mathbf{F}^x = \{\partial E / \partial X_{ij}\} = 0. \quad (5)$$

The $\partial E / \partial X_{ij}$ depend on two Fock-type operators,

$$\mathbf{F}^1 = \mathbf{h}^c + \sum_{\nu\mu} (\mathbf{J}_{\nu\mu} - \frac{1}{2}\mathbf{K}_{\nu\mu}) \gamma_{\nu\mu} \quad (6)$$

and

$$\mathbf{F}^2 = \sum_{i\chi} |i\rangle \left(\sum_{\nu\mu\eta} (\langle i | h^c | \eta \rangle \gamma_{\eta\chi} + 2[i\nu | \mu\eta] \Gamma_{\chi\nu\mu\eta}) \right) \langle \chi |, \quad (7)$$

where $\mathbf{J}_{\nu\mu}$ and $\mathbf{K}_{\nu\mu}$ are Coulomb and exchange operators, and $\gamma_{\nu\mu} / \Gamma_{\chi\nu\mu\eta}$ the one- and two-electron density matrices which are defined as

$$\gamma_{\nu\mu} = \sum_{KL} C_K C_L A_{\nu\mu}^{KL}, \quad (8)$$

$$\Gamma_{\chi\nu\mu\eta} = \sum_{KL} C_K C_L B_{\chi\nu\mu\eta}^{KL}. \quad (9)$$

The summations over $\chi\nu\mu\eta$ include the active orbitals and over i for either inactive, active and virtual orbitals. Specifically

$$\partial E / \partial X_{\nu\mu} = 2(\mathbf{F}^2)_{\nu\mu} - 2(\mathbf{F}^2)_{\mu\nu},$$

$$\partial E / \partial X_{a\mu} = 4(\mathbf{F}^1)_{\alpha\mu} - 2(\mathbf{F}^2)_{a\mu},$$

$$\partial E / \partial X_{ar} = 4(\mathbf{F}^1)_{ar},$$

$$\partial E / \partial X_{r\mu} = 2(\mathbf{F}^2)_{r\mu}.$$

The simplest possible MC-SCF algorithm involves two steps. The *first* step involves the solution of the CI problem to produce C_K and $\gamma_{\nu\mu} / \Gamma_{\chi\nu\mu\eta}$. This step needs the h^c operator and the integrals over the valence orbitals $[\chi\nu | \mu\eta]$. The *second* step performs the orbital rotations and requires \mathbf{F}^1 and \mathbf{F}^2 that in turn depend on the $\gamma_{\nu\mu} / \Gamma_{\chi\nu\mu\eta}$. In a direct MC-SCF method one has several strategies based upon methods already developed, for direct SCF theory [1] and for direct CPHF [2] theory, to construct all the Fock-like operators (h^c , $\mathbf{J}_{\nu\mu} / \mathbf{K}_{\nu\mu}$), and/or using methods developed for MP2 [4] for the four-index transfor-

small molecules and (b) v =number of AO) using 3/4 transformed integrals n has been removed with

methods can be found address the MC-SCF

one of the only methods of the only method order wavefunction problems where or one has bond exponential. In MC-SCF *ve space* consisting of ed by CI and a much ions in doubly occupied order to extend MC-tems (for example to titution or to study a extended system) di-ylor and Almlöf [7] strategies for the im-² problem in general. of strategy, one based and a second based ur-index transformals that is similar to

mation to obtain the $[\chi\nu|\mu\eta]$. The $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators can be produced during the first step (i.e. before the CI problem is solved) at the same time as \mathbf{h}^c using direct SCF methods as suggested by Taylor and Almlöf [6] and stored for subsequent use in the second step (method a). In this case the $[\chi\nu|\mu\eta]$ are found in the $\mathbf{J}_{\nu\mu}$. However, in this case one needs additional storage for the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$. Alternatively, the contribution of the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ to \mathbf{F}^1 (i.e. $\sum_{\nu\mu} (\mathbf{J}_{\nu\mu} - \frac{1}{2}\mathbf{K}_{\nu\mu})\gamma_{\nu\mu}$) can be computed after the CI step by forming the AO density matrix $\mathbf{P} = \sum_{\nu\mu} \gamma_{\nu\mu} \mathbf{D}_{\nu\mu}$ and then forming this contribution *in total* (with an additional integral evaluation) using direct SCF methods [1] while using a direct four-index transformation for the $[\chi\nu|\mu\eta]$. This scheme is implemented in method b. Finally, one can use methods developed for MP2 [4] for the four-index transformation, computing \mathbf{h}^c during the transformation of the first index and the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators during the transformation of the second index. Like method a this technique requires storage for the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators. This is referred to as method c.

The possible basic direct MC-SCF algorithms that we have evaluated are summarized below:

Method a. $n_a^2 + 1$ simultaneous Fock matrix constructions (one integral evaluation).

(1) Construct \mathbf{h}^c and all the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ simultaneously using the same methods as in direct CPHF [2] theory (via AO density matrices $\mathbf{D}_{\nu\mu}$). This step behaves as $n_a^2 N^4$.

(2) Solve for CI coefficients C_K .

(3) Construct $\gamma_{\nu\mu}/\Gamma_{\chi\nu\mu\eta}$ from CI coefficients.

(4) Construct $\partial E/\partial X_{ij}$ from \mathbf{F}^1 and \mathbf{F}^2 and solve for new orbitals.

Method b. Two Fock matrix constructions + 3/4 transformed integrals (four integral evaluations).

(1) Construct \mathbf{h}^c using the same methods as in direct SCF theory.

(2) Compute 3/4 transformed integrals $[p\nu|\mu\eta]$ using direct methods (p is AO basis index). This step behaves as $n_a N^4$.

(3) Generate $[\chi\nu|\mu\eta]$ then solve for CI coefficients C_K .

(4) Construct $\gamma_{\nu\mu}/\Gamma_{\chi\nu\mu\eta}$ from the CI coefficients.

(5) Form AO density matrix $\mathbf{P} = \sum_{\nu\mu} \gamma_{\nu\mu} \mathbf{D}_{\nu\mu}$ and then construct $\sum_{\nu\mu} (\mathbf{J}_{\nu\mu} - \frac{1}{2}\mathbf{K}_{\nu\mu})\gamma_{\nu\mu}$ via a single Fock

matrix formation using the same methods as direct SCF theory.

(6) Form $[i\nu|\mu\eta]\Gamma_{\chi\nu\mu\eta}$ and $\mathbf{F}^1/\mathbf{F}^2$ and solve for new orbitals.

Method c. 1/2 transformed integrals with \mathbf{h}^c and $\mathbf{K}_{\nu\mu}$ update (two integral evaluations).

(1) Compute one-index transformed integrals $[pq|r\eta]$ using vectorized direct methods (pqr are AO basis indices) producing \mathbf{h}^c via update. The $\mathbf{K}_{\nu\mu}$ are produced via update during the transformation of the second index. The update to produce $\mathbf{K}_{\nu\mu}$ is not vectorizable.

(2) Solve for CI coefficients C_K .

(3) Construct $\gamma_{\nu\mu}/\Gamma_{\chi\nu\mu\eta}$ from CI coefficients.

(4) Construct $\partial E/\partial X_{ij}$ from \mathbf{F}^1 and \mathbf{F}^2 and solve for new orbitals.

Method a was first proposed by Taylor and Almlöf [6]. It needs $n_a^2 N^2$ storage for the \mathbf{h}^c and $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators. While it would appear to be inefficient because of the n_a^2 dependence, it has the advantage that the integral pre-screening based upon density matrix cutoffs used in direct SCF procedures are applicable. This will be beneficial for extended molecules in highly contracted basis sets. In method b one can use the very efficient methods for four-index integral transformation that have been developed for other post-SCF procedures [4]. Further, there is no need to store the $n_a^2 N^2 \mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators so that only $n_a^3 N$ storage is required. Finally in method c one has the advantage of fewer integral evaluations compared with method b, however, the update to produce $\mathbf{K}_{\nu\mu}$ is not vectorizable and there is the need to store the $n_a^2 \mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ and \mathbf{h}^c operators. The problem of the $\mathbf{K}_{\mu\nu}$ in method c has been discussed by Taylor [6]. One can compute the integrals in batches so that the construction of the $\mathbf{J}_{\nu\mu}$ reduces to matrix multiplications. However the integrals are required in a different order for the $\mathbf{K}_{\nu\mu}$. Thus one must either compute the integrals again in the new order or use a scalar update to produce the $\mathbf{K}_{\nu\mu}$ at the same time as the $\mathbf{J}_{\nu\mu}$. Note that each generation of the transformed integrals via in the $n_a N^2$ methods requires effectively two canonical integral evaluations since one must generate "square" batches $[pq|rs]$ for all rs in order to vectorize the transformation. These algorithms have been implemented in Gaussian 91 [8]

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Table 1
Timing da

Basis
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benzene n
STO-3C
4-31G (G)
4-31G (G)
6-31G (G)
D95 (D)

quinone n
STO-3C
4-31G (G)
6-31G (G)

ergosterol
STO-3C

using standard utility routines [9,10] for direct construction of multiple Fock matrices [2] and 3/4 transformed integrals [4]. The only other implementation of direct MC-SCF methods that we are aware of is the unpublished work of Almlöf, Knowles and Werner [11].

3. Cost comparison of three algorithms for direct MC-SCF

In table 1 we present the timing data for a single MC-SCF iteration for each of the three methods described in section 2. (The timings are CPU time in seconds on an IBM RS/6000 model 540, 60 Mflops theoretical peak performance.) Two sets of data for method a are provided. The column a' is data obtained using density matrix cutoffs [7] of 10^{-10} in the direct computation of the Fock matrices while for the data a no cutoffs were used. We have also implemented an incremental Fock matrix construction in method a' and this can reduce the time significantly (in ergosterol the timing for method a' in incremental Fock matrix [7] construction was 2698 s compared with 3650 s for the full iteration); however, this is not possible for method c so we have not included these data in general. For method b we present the total time and the times for steps 1, 2 and

5. The default 10^{-10} density cutoffs in steps 1 and 5 were used of method b. For method c only the total CPU time for one iteration is presented.

Clearly, one expects method a' to perform at its best for a molecule with a large spatial extent and heavily contracted basis with a modest number of active orbitals. The results on ergosterol (78 atoms) for six active orbitals in the 1,3,5-hexatriene moiety in an STO-3G basis illustrate the efficiency of this algorithm. The major reason for the efficiency of method a, for the case of six active orbitals, arises from the formation of many Fock matrices at once [2]. Method b/c only begins to become competitive as the active space gets quite large (quinone $n_a=8$) and for six active orbitals method a'/a remains the best choice. In comparing methods b and c one must remember that utility of method c is limited by the additional storage required for the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators. Further, in method c one has the overhead of the non-vectorizable construction of $\mathbf{K}_{\nu\mu}$ and the computation of \mathbf{h}^c . Comparison of the timing data for step b(2) with the timing data for step c in table 1 indicates that these overheads are quite large. In fact, the major overhead in method c appears to be the computation of \mathbf{h}^c . In the 6-31G(D, P) computations on benzene in table 1 this overhead is about 200 s. Thus the algorithm used in method b could be improved by incorporating a vectorizable con-

Table 1
Timing data for a single MC-SCF iteration for methods a, b and c (CPU time in s on an IBM RS/6000 model 540)

Basis (basis/primitives)	Method						
	a'	a	b				c
			total	1	2	5	
benzene $n_a=6$ (12 atoms)							
STO-3G (36/108)	18	25	55	15	28	11	31
4-31G (66/144)	66	95	140	40	70	32	95
4-31G(D, P) (120/198)	429	496	616	169	294	152	559
6-31G(D, P) (120/210)	475	551	753	206	370	178	658
D95(D, P) (126/222)	698	960	1442	412	714	316	1042
quinone $n_a=8$ (12 atoms)							
STO-3G (44/132)	33	46	88	23	46	19	51
4-31G (80/176)	154	199	236	66	114	56	170
6-31G(D, P) (140/252)	1055	1250	1221	320	603	298	1136
ergosterol $n_a=6$ (78 atoms)							
STO-3G (189/567)	3650	10351	9879	2424	5300	2155	5925

struction of \mathbf{h}^c into step b(2) thus eliminating one integral evaluation and a similar improvement in method c is possible. It can thus be seen that for very large active spaces on compact molecular systems method b has many advantages but for modest active spaces method a' is always preferable.

4. Conclusions

For direct MC-SCF, an algorithm that scales as $n_a^2 N^4$ (method a) using Fock matrices appears to be quite efficient until n_a gets to 8 where an algorithm (method b/c) that scales as $n_a N^4$ using 3/4 transformed integrals begins to become competitive. The efficiency of method a arises from the direct formation of many Fock matrices at once [2]. The limitation in the $n_a^2 N^4$ approach, method a, and in method c arises from the need to store the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ operators in main memory ($n_a^2 N^2$ words). This difficulty is removed in method b by forming the contribution of the $\mathbf{J}_{\nu\mu}/\mathbf{K}_{\nu\mu}$ to \mathbf{F}^1 (i.e. $\sum_{\nu\mu} (\mathbf{J}_{\nu\mu} - \frac{1}{2}\mathbf{K}_{\nu\mu})\gamma_{\nu\mu}$) using direct SCF methods [11] via the AO density matrix $\mathbf{P} = \sum_{\nu\mu} \gamma_{\nu\mu} \mathbf{D}_{\nu\mu}$ with the cost of a second integral evaluation. An improved version of the algorithm used in method b (i.e. incorporating a vectorizable construction of \mathbf{h}^c into step b(2) thus eliminating one integral evaluation) will be the optimum approach for very large active spaces on compact molecular systems while method a seems the best approach for more extended systems with modest active spaces.

In this implementation we have discussed a two-step method. One can couple the orbital rotation and CI problems to simultaneously update the CI vector and the orbitals. Here method b looks promising because the contribution of $\sum_{\nu\mu} (\mathbf{J}_{\nu\mu} - \frac{1}{2}\mathbf{K}_{\nu\mu})\gamma_{\nu\mu}$ via the AO density matrix \mathbf{P} can be formed at the same time as \mathbf{h}^c using direct SCF methods [1]. Further,

these same techniques are applicable to second order methods that use the orbital rotation Hessian.

Finally, we should point out that these same methods are applicable to the coupled perturbed MCSCF (CP-MCSCF) problem (vibrational frequencies) as well. We have also implemented method a for the computation of the derivative Fock matrices in CP-MCSCF, thus eliminating the need to store the derivative integrals.

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