



## A direct derivative MC-SCF procedure

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Received 24 November 1995; in final form 2 January 1996

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### Abstract

A direct method for the computation of energy second derivatives, and first derivatives which require the solution of the coupled perturbed MC-SCF equations, is presented. The two-electron derivative integral transformation is formulated in terms of 3/4 transformed integrals. The optimum strategy for the solution of the CP-MCSCF linear equations involves the solution in a Krylov space that involves all the right-hand sides. The feasibility of the method is demonstrated in a computation on the excited states of indene, styrene and octatetraene.

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### 1. Introduction

In direct methods the necessary integrals are never stored to disk but rather are evaluated during the solution of the quantum chemistry equations. Such methods are essential on large molecular systems. The direct SCF method pioneered by Almlöf et al. [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]. Taylor and Almlöf [7] have considered the possible strategies for the implementation of the 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 4-index transformation of the two-electron integrals that is similar to that used in perturbation methods [3–5]. In other

work [8] we have shown that a strategy based upon the use of Fock operators gives an efficient procedure for the MC-SCF problem.

While MC-SCF formalism for first derivatives [9] with respect to a nuclear perturbation is quite simple, the computation of force constants or the non-adiabatic coupling matrix elements is much more complicated because the solution of the coupled perturbed MC-SCF (CP-MCSCF) equations is required. The purpose of this Letter is to discuss a derivative MC-SCF method for the calculation of second derivatives which can be used to compute frequencies and to compute the non-adiabatic coupling and gradient difference which are used in gradient-directed searches for conical intersections.

### 2. Theory

The MC-SCF energy can be written in a compact form first suggested by Almlöf and Taylor [10],

$$E_{\text{MC-SCF}} = E_0 + \mathbf{E}^X \mathbf{X} + \frac{1}{2} \mathbf{X}' \mathbf{E}^{XX} \mathbf{X} + \frac{1}{2} \mathbf{E}^C \mathbf{C} + \frac{1}{2} \mathbf{C}' \mathbf{E}^{CC} \mathbf{C} + \frac{1}{2} \mathbf{X}' \mathbf{E}^{XC} \mathbf{C} + \frac{1}{2} \mathbf{C}' \mathbf{E}^{CX} \mathbf{X}. \quad (1)$$

We have used  $X_{ij}$  to denote the antisymmetric orbital rotation variables and  $C_{0K}$  to denote the rotation of the CI eigenvectors 0,  $K$ . The superscripts  $X$  and  $C$  denote differentiation with respect to  $C_{0K}$  and  $X_{ij}$  so that we have  $\mathbf{E}^X = \partial E / \partial X_{ij}$ ,  $\mathbf{E}^{XX} = \partial^2 E / \partial X_{ij} \partial X_{kl}$ ,  $\mathbf{E}^C = \partial E / \partial C_{0K}$ , etc. The  $\partial E / \partial X_{ij}$  are generalised Fock matrix elements. In this formalism the first derivative with respect to a nuclear variation  $\lambda$  is given as

$$E_\lambda = E^\lambda + \mathbf{E}^C \mathbf{C}_\lambda + \mathbf{E}^X \mathbf{X}_\lambda - \frac{1}{2} \mathbf{E}^Y \mathbf{S}_\lambda. \quad (2)$$

Throughout this Letter we shall follow the convention of Almlöf and Taylor [10] for subscripts and superscripts: subscripts denote total derivatives and superscripts denote partial derivatives. The nuclear perturbations are given greek symbols  $\lambda$  and  $\mu$ , etc. The quantity,  $S_\lambda$ , is the matrix of derivative overlap integrals,  $\mathbf{E}^Y = \partial E / \partial S_{ij}$  is a symmetric Lagrangian (see Ref. [10] for a full discussion of this term). We shall use the superscript  $Y$  in general to denote differentiation with respect to symmetric orbital rotations and the superscript  $X$  for the skew-symmetric transformation. The quantity  $E^\lambda$  is the MC-SCF energy evaluated with derivative integrals. This equation is general. If  $E^X$  etc. is computed with a transition density matrix, then the derivative corresponds to the CI derivative coupling [11,12], if  $E^X$  etc. is computed with a density difference, then the derivative is the gradient difference. The quantity  $E^X$  is zero in the case where the MC-SCF orbitals are optimised and there is no contribution from the perturbed orbital rotation coefficients  $\mathbf{X}_\mu$ . However, if the orbitals have been computed for state-averaged orbitals then one must solve the equations for the  $\mathbf{X}_\mu$ . The general form of the coupled perturbed MC-SCF equations is given as

$$\begin{bmatrix} \mathbf{E}^{XX} & \mathbf{E}^{XC} \\ \mathbf{E}^{CX} & \mathbf{E}^{CC} \end{bmatrix} \begin{bmatrix} \mathbf{X}_\mu \\ \mathbf{C}_\mu \end{bmatrix} = - \begin{bmatrix} \bar{\mathbf{E}}^{\mu X} \\ \bar{\mathbf{E}}^{\mu C} \end{bmatrix}, \quad (3)$$

where

$$\begin{aligned} \bar{\mathbf{E}}^{\mu C} &= \mathbf{E}^{\mu C} - \frac{1}{2} \mathbf{E}^{CY} \mathbf{S}_\mu, \\ \bar{\mathbf{E}}^{\mu X} &= \mathbf{E}^{\mu X} - \frac{1}{2} \mathbf{E}^{XY} \mathbf{S}_\mu, \end{aligned} \quad (4)$$

where we use  $\lambda$ ,  $\mu$  etc. to denote differentiation with respect to the nuclear perturbation, and  $X$ ,  $Y$ ,  $C$  to denote differentiation with respect to orbital rotations ( $X$  and  $Y$ ) and CI coefficients ( $C$ ). In Eq. (4)  $\mathbf{E}^{\mu X}$  is the antisymmetric Lagrangian matrix ( $\mathbf{E}^X$ ) evaluated with derivative integrals. These equations are modified slightly for state-averaged MC-SCF orbitals [13–15].

In this notation, the expression for the second derivative can be written compactly as

$$\begin{aligned} E_{\lambda\mu} &= E^{\lambda\mu} - \frac{1}{2} \mathbf{E}^Y \mathbf{S}_{\lambda\mu} + \mathbf{C}_\lambda \bar{\mathbf{E}}^{\mu C} + \mathbf{X}_\lambda \bar{\mathbf{E}}^{\mu X} \\ &\quad - \frac{1}{2} \bar{\mathbf{E}}^{\lambda Y} \mathbf{S}_\mu - \frac{1}{2} \bar{\mathbf{E}}^{\mu Y} \mathbf{S}_\lambda + \frac{1}{2} \mathbf{E}^Y \mathbf{S}_\lambda \mathbf{S}_\mu \\ &\quad - \frac{1}{4} \mathbf{E}^{YY} \mathbf{S}_\lambda \mathbf{S}_\mu. \end{aligned} \quad (5)$$

We have defined

$$\bar{\mathbf{E}}^{\mu Y} = \mathbf{E}^{\mu Y} - \frac{1}{2} \mathbf{E}^{YY} \mathbf{S}_\mu \quad (6)$$

in the analogous fashion to Eq. (4) (i.e. in Eq. (6)  $\mathbf{E}^{\mu Y}$  is the symmetric Lagrangian matrix ( $\mathbf{E}^Y$ ) computed from derivative integrals). While  $-\frac{1}{2} \mathbf{E}^{YY} \mathbf{S}_\mu$  and  $E^{\lambda\mu}$  are conveniently evaluated in the AO basis in the same way as the MC-SCF gradients [9] during the computation of the derivative integrals, the remaining terms must be evaluated in the MO basis.

In general, there are two issues that need to be addressed in the solution of the CP-MCSCF equations (3) and the subsequent computation of second derivatives via Eq. (5). Firstly, one needs MO-derivative integrals in the construction of  $\mathbf{E}^{\mu C}$  and  $\mathbf{E}^{\mu X}$ . Secondly, the orbital/CI rotation Hessian

$$\begin{bmatrix} \mathbf{E}^{XX} & \mathbf{E}^{XC} \\ \mathbf{E}^{CX} & \mathbf{E}^{CC} \end{bmatrix}$$

and quantities such as  $\mathbf{E}^{CY}$  cannot be kept in main memory for large systems, so an efficient *direct* method in which the Hessian is evaluated as the linear equations are solved needs to be considered.

We shall address the computation of the MO derivative integrals first. There are two derivative Fock type matrices [8,9] that are needed in the computation of  $\mathbf{E}^{\mu X}$  etc. that have the general form

$$\begin{aligned} {}^1 E_{ij}^{\lambda X} &= (h^c)_{ij}^\lambda + \sum_{mn} \left\{ (J_{mn}^\lambda)^{ij} - \frac{1}{2} (K_{mn}^\lambda)^{ij} \right\} \gamma_{mn}, \\ {}^2 E_{ij}^{\lambda X} &= \sum_m (h^c)_{im}^\lambda \gamma_{mj} + \sum_{mno} \Gamma_{imno} (on|mj)^\lambda, \end{aligned} \quad (7)$$

where we use the superscript  $\lambda$  to denote quantities constructed from derivative integrals and  $\gamma$  and  $\Gamma$  are the first and second order density matrices. The quantity  $(h^c)_{ij}^\lambda$  is the core Fock operator constructed from derivative integrals while  $(J^\lambda_{mn})$  and  $(K^\lambda_{mn})$  are Coulomb and exchange operators defined with  $m$  and  $n$  chosen to be active orbitals. The quantities  ${}^1E_{ij}^{\lambda X}$  and  ${}^2E_{ij}^{\lambda X}$  are combined to produce the  $\mathbf{E}^{\mu X}$  [8] in the same manner as  $\mathbf{E}^X$ . Clearly, the  $(ab|cd)^\lambda$  AO integrals could be pre-computed, written to disk as in a conventional SCF computation and then transformed to the MO basis. However, the  $(ab|cd)^\lambda$  AO-integral file gets large very fast as the number of atoms increases. Further, as we shall presently discuss, it is most efficient to process all the perturbations simultaneously and processing integrals from disk in this fashion, and transforming to the MO basis would be very inefficient. Thus the only efficient scheme must involve direct generation and transformation of the derivative integrals.

The most obvious approach for the computation of the  $\bar{\mathbf{E}}^{\mu X}$ ,  $\bar{\mathbf{E}}^{\mu C}$ , and  $\bar{\mathbf{E}}^{\mu Y}$  is based upon the direct computations of Fock operators (i.e. the  $(h^c)_{ij}^\lambda$ ,  $(J^\lambda_{mn})$  and  $(K^\lambda_{mn})$  are computed for all active indices  $m$  and  $n$  using the same approach as in direct MC-SCF itself [8]). This method will be efficient only if all the  $(J^\lambda_{mn})$  and  $(K^\lambda_{mn})$  can be held in main memory, which limits the technique to small numbers of atoms and modest basis sets. The second approach uses the methods similar to 4-index transformation of the two-electron integrals derivatives used in perturbation methods [16]. This type of technique turns out to be particularly efficient for MC-SCF integral derivatives. We now discuss our implementation of this method.

In the construction of the MO-derivative integrals required in Eq. (7) it turns out to be efficient to use 3/4 transformed integrals. Any MO derivative integral  $(im|no)^\lambda$  can be expressed [16] in terms of 3/4 transformed 1-index derivative integrals as

$$(im|no)^\lambda = \sum_a C_{ia}(a^\lambda m|no) + C_{ma}(a^\lambda i|no) + C_{na}(a^\lambda o|im) + C_{oa}(a^\lambda n|im), \quad (8)$$

where  $a^\lambda$  denotes an AO basis label,  $i$  runs over all orbitals and  $mno$  runs only over the active orbitals. The storage of the 3/4 transformed integrals

$(a^\lambda m|no)$  etc. is possible because the AO label for a given  $\lambda$  runs only over AO basis functions on the nuclear centres associated with  $\lambda$ . In Eq. (7) one of the indices  $j$  ranges over all the MO. Thus two sets of 3/4 transformed integrals need to be computed for the construction of the  $(a^\lambda m|no)$  etc. For each set, one index is associated with  $a^\lambda$ , one index runs over all the  $N_A$  orbitals ( $N_A = N_o + N_a + N_v$ ,  $N_o$  = the number of inactive orbitals,  $N_a$  = number of active orbitals and  $N_v$  = the number of virtual orbitals). The remaining indices run over the  $N_a$  active orbitals. We shall use  $N_{a^\lambda}$  to indicate all the AO basis functions on the nuclear centre associated with all  $\lambda$ . Thus the total number of integrals can be written as

$$3\{(N_{a^\lambda} N_a | N_A N_a) + (N_{a^\lambda} N_a | N_a N_a)\}. \quad (9)$$

In practical applications, for a small number of atoms/basis functions, one can hold all the  $(a^\lambda m|no)$  integrals in memory; otherwise several passes need to be carried out as we now discuss.

When the construction is performed in batches, the 3/4 transformed integrals for a subset (batch) of the complete range of  $a^\lambda$  are computed each pass. Effectively, the integrals associated with a batch of perturbations are constructed, requiring two arrays of size  $3(\tilde{N}_{a^\lambda} N_A | N_a N_a)$  where  $\tilde{N}_{a^\lambda}$  is the number of basis functions located on the nuclei associated with all the perturbations done in the current batch. In our implementation, the fully transformed integrals are obtained from these batches, and written to disk. This requires a file of length  $\tilde{N}_{a^\lambda} \times (N_A N_a N_a N_a)/2$ , where  $\tilde{N}_{a^\lambda}$  is the number of perturbations in this batch. Because all the stored integrals will be processed in the construction of the  $\bar{\mathbf{E}}^{\mu X}$ ,  $\bar{\mathbf{E}}^{\mu C}$ , and  $\bar{\mathbf{E}}^{\mu Y}$  before a new batch of 3/4 transformed integrals is computed, the disk space can be freed, and the storage of all the  $3(N_{\text{atoms}} - 1)(N_A N_a N_a N_a)/2$  integrals on disk is avoided.

The remaining quantities in Eq. (7) can be constructed using the same strategy as in the MC-SCF. The quantity  $\sum_{mn} \gamma_{mn}$  is transformed to the AO basis and then both  $\sum_{mn} \{(J^\lambda_{mn})^{ij} - \frac{1}{2}(K^\lambda_{mn})^{ij}\} \gamma_{mn}$  and  $(h^c)^\lambda$  are evaluated using direct derivative Fock matrix methods which requires one integral evaluation. Thus the overall construction of the derivative Fock matrices requires at least 2 derivative integral computations.

Now we turn our attention to the solution of the equation system (3) and the evaluation of terms such as  $\mathbf{E}^{YY} \mathbf{S}_\lambda \mathbf{S}_\mu$  which occur in the computation of second derivatives. The solution equation system (3) and the evaluation of terms such as  $\mathbf{E}^{YY} \mathbf{S}_\lambda \mathbf{S}_\mu$  requires operations of the form

$$\Omega'_\mu \leftarrow \mathbf{E}^{MN} \Omega_\mu, \quad (10)$$

where  $\mathbf{E}^{MN}$  is a Hessian contribution  $\mathbf{E}^{XX}$ ,  $\mathbf{E}^{XC}$  etc. and  $\Omega_\mu$  is a vector such as  $\mathbf{X}_\mu$ . The dimension of the orbital rotation Hessian  $\mathbf{E}^{XX}$ ,  $\mathbf{E}^{XY}$  etc. is of the order of  $(N_o + N_a)(N_v) + N_o N_a$ , where  $N_o$  is the number of inactive orbitals,  $N_a$  is the number of active orbitals and  $N_v$  is the number of virtual orbitals. Clearly, except for small systems, the hessian cannot be held in memory and one must solve the linear equations iteratively assembling the contributions from the Hessian directly from the integrals.

The  $\mathbf{E}^{XX}$ ,  $\mathbf{E}^{XY}$  etc. involve 3 main types of contribution

$$\begin{aligned} (\mathbf{E}^{XX})_{ijkl} &\leftarrow F_{ik} \gamma_{jl}, \\ (\mathbf{E}^{XX})_{ijkl} &\leftarrow \sum_m \gamma_{km} (ml|ij), \\ (\mathbf{E}^{XX})_{ijkl} &\leftarrow \sum_{mn} \Gamma_{mnik} (mn|jl) + \Gamma_{mink} (mj|nl), \end{aligned} \quad (11)$$

which must be formed to do the ‘update’ of the form given in Eq. (10). The terms involving contraction with the one particle density matrix in Eq. (11) require all MO integrals with either one or two indices in the inactive space while the terms that involve the two-particle density matrix always have two indices in the active space. The treatment of the terms involving the two-particle density matrix in Eq. (11) needs to be carried out in the MO basis to avoid the transformation of the two-particle density matrix to the AO basis. Thus the disk based storage of the MO integrals in Eq. (11) requires  $\approx [(N_o + N_a)(N_v)]^2$  words. This can be reduced to  $[N_a N_v]^2$  words via ‘direct’ evaluation of the integrals that are needed for the contraction with the one particle density matrix as we now briefly describe. One must carry out operations of the form

$$(\Omega'_\lambda)_{ij} \leftarrow \sum_{lkm} (\Omega_\lambda)_{lk} \gamma_{km} (ml|ij). \quad (12)$$

Now if we define a ‘density matrix’  $Q$

$$Q_{lm}^\lambda = \sum_k (\Omega_\lambda)_{lk} \gamma_{km}, \quad (13)$$

then we can compute the update in Eq. (12) via the construction of a ‘Coulomb operator’  $J$  as

$$(\Omega'_\lambda)_{ij} \leftarrow J_{ij}^{\lambda Q} = \sum_{lm} Q_{lm}^\lambda (ml|ij). \quad (14)$$

If the  $Q_{lm}^\lambda$  are transformed to the AO basis, then one can use the strategy already implemented in direct MC-SCF [8] to evaluate quantities such as  $\mathbf{J}^{\lambda Q}$  for each  $\lambda$ . The penalty to be paid arises from the fact the integrals would need to be evaluated during each iteration of the of the linear equations, and again during the formation of  $\mathbf{E}^{YY} \mathbf{S}_\lambda \mathbf{S}_\mu$  etc. In the current implementation we have used the *direct* integral transformation methods to generate the all integrals storing the result on disk.

Thus assuming that the integrals required to form the contractions are held on disk, it remains to consider the strategy for the solution of the linear equations and the formation of terms such as  $\mathbf{E}^{YY} \mathbf{S}_\lambda$ . The major computational work involves assembling the parts of  $\mathbf{E}^{MN}$  ( $M, N = XCY$ ) (i.e. forming the contractions shown in Eq. (11)). Clearly it is desirable to do this work only once for each iteration of the linear equation solver. The optimum strategy is to operate on all right-hand sides at the same time,

$$(\Omega'_\mu \Omega'_\lambda \Omega'_\eta \dots) \leftarrow \mathbf{E}^{MM} (\Omega_\mu \Omega_\lambda \Omega_\eta \dots). \quad (15)$$

The operations required for the solution of the linear equations as well as terms such as  $\mathbf{E}^{YY} \mathbf{S}_\lambda$  are carried out in the same way. The linear equations are solved using the DIIS method (Direct Inversion in Iterative subspace [17]). This procedure requires updates of the form given in Eq. (15). The solution for all the right-hand sides  $\lambda, \mu, \nu$ , etc. are obtained simultaneously using the same Krylov space. We have tested the efficiency of this procedure against a Lanczos [18] procedure, solving for each right-hand side in turn. While the Lanczos procedure converges more rapidly for each right-hand side, the overall number of updates of the form of Eq. (10) was always more than the DIIS method.

The disk and memory requirements for the update involved in Eq. (15) is modest. One needs to allocate disk space for the  $\Omega_\mu$  and the  $\Omega'_\mu$  that is  $3(N_{\text{atoms}} -$

1) $(N_o + N_a)(N_p)N_{\text{iterations}}$  words, where  $N_{\text{iterations}}$  is the number of DIIS iterations required to converge. Since the  $\mathbf{E}^{MM}$  is assembled during the iteration procedure only a 'buffer' of the  $\Omega_\mu$  and the  $\Omega'_\mu$  and the associated  $\mathbf{E}^{MM}$  matrix elements needs to be in main memory at any time. This 'buffer' needs to be as large as possible to be able to use a machine dependant matrix multiply efficiently.

We now briefly comment on the computation of the perturbed CI eigenvector. Provided it is feasible to diagonalise the CI matrix, then one can express  $\bar{\mathbf{E}}^{\mu C}$  etc. in the basis of the CI eigenvectors and  $\mathbf{E}^{CC}$  becomes diagonal. Accordingly the  $\mathbf{C}_\mu$  can be obtained without iteration. The linear equations are thus solved only in the orbital rotation space with

$$\bar{\mathbf{E}}^{XX} = \mathbf{E}^{XX} - \mathbf{E}^{XC}(\mathbf{E}^{CC})^{-1}\mathbf{E}^{CX} \quad (16)$$

and

$$\bar{\mathbf{E}}^{\mu X} = \mathbf{E}^{\mu X} - \frac{1}{2}\mathbf{E}^{XY}\mathbf{S}_\mu - \mathbf{E}^{XC}(\mathbf{E}^{CC})^{-1}\bar{\mathbf{E}}^{\mu C}. \quad (17)$$

This strategy is feasible up to 8 active electrons. Otherwise, the solution of the perturbed eigenvector can be incorporated into the DIIS procedure.

### 3. An illustrative example

As we have discussed above the central issues in derivative MC-SCF focus on the generation of the MO-derivative integrals in the construction of  $\mathbf{E}^{\mu C}$  and  $\mathbf{E}^{\mu X}$  and the strategy for the formation of the

update of the form given in Eq. (15) that is used in the iterative solution of the linear equation system and quantities such as  $\mathbf{E}^{Y\lambda}\mathbf{S}_\lambda$ .

In Table 1 we give timing data for the various non-trivial steps in an excited state CAS(8, 8) frequency computation for indene ( $\text{C}_9\text{H}_8$ ) in a 3-21G basis (97 orbitals), styrene (16 atoms) in a 4-31G basis (88 orbitals) and octatetraene (18 atoms) in a 6-31G\* basis (140 basis functions).

The MO-derivative integrals can be computed via the construction of  $(J^\lambda_{mn})$  and  $(K^\lambda_{mn})$  for all  $\lambda$  and  $mn$  or through the use of 3/4 transformed integrals ( $a^\lambda m|no$ ). In lines 3 and 4 of Table 1 we present the MO-integral derivative times. It can be seen that the time required for the direct construction of  $\mathbf{E}^{\mu X}$  etc. via  $(J^\lambda_{mn})$  type operators (for the case of indene) is  $\approx 80$  times that for the generation of  $\mathbf{E}^{\mu X}$  via the 3/4 transformed integrals ( $a^\lambda m|no$ ). The origin of this difference results from the fact that 16 (one for each atom) passes are required to construct the  $(J^\lambda_{mn})$  and  $(K^\lambda_{mn})$  and that during each pass one must construct  $N_a^2$  operators. In contrast, all the 3/4 transformed integrals ( $a^\lambda m|no$ ) can be constructed in a single pass for indene in 5 MW. The larger computation time for octatetraene results from the fact that two batches are required using the same memory.

The solution of linear equations treating all right-hand sides simultaneously, required 18–26 iterations. The full dimension of the Krylov space is  $\approx 30\%$  of the total number of orbital rotation variables. The equations are conditioned using an approximation to

Table 1  
Timing data (IBM RS6000/590) for an excited state, CAS(8, 8)  $S_1$  frequency computations on indene (17 atoms) in a 3-21G basis, styrene (16 atoms) in a 4-31G basis and octatetraene (18 atoms) in a 6-31G\* basis

Contribution	CPU time		
	indene	styrene	octatetraene
$\mathbf{E}^{\mu X}$ via ( $a^\lambda m no$ )	461	393	1850
$\mathbf{E}^{\mu X}$ via 'direct'	37952		
Fock matrix method (example for comparison)			
$\bar{\mathbf{E}}^{\mu C}$	165	132	605
$\bar{\mathbf{E}}^{\mu X}, \bar{\mathbf{E}}^{\mu Y}$	2840	1512	3582
solution for linear equations	37986	19649	67158
	18 iterations	17 iterations	26 iterations
	765/2414 variables	693/2010 variables	1097/3759 variables
$\mathbf{E}^{Y\lambda}\mathbf{S}_\lambda\mathbf{S}_\mu$	2741	1467	3447

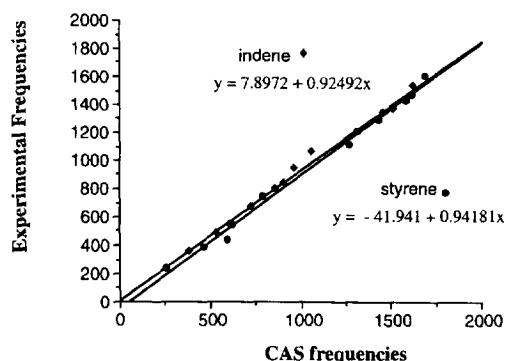


Fig. 1. Comparison of computed CAS frequencies for the  $S_1$  state of indene and styrene with the experimental data of Ref. [19] (indene) and Ref. [20] (styrene).

the diagonal elements of  $\mathbf{E}^{XX}$  (similar to the SCF case). The convergence is not quite as good as in the SCF case. This may be because the MCSCF Hessian is less diagonally dominant or the effects of two-electron terms is larger. From the timing data presented it can be seen that one iteration of solution of the linear equations, the computation of  $\bar{\mathbf{E}}^{\mu X}$ ,  $\bar{\mathbf{E}}^{\mu Y}$  and the computation of  $\mathbf{E}^{YY} \mathbf{S}_\lambda \mathbf{S}_\mu$  all require about the same time. This is essentially the time required to perform an operation of the form given in Eq. (15). If one divides the time for one iteration of solution of the linear equations by the number of perturbations, the timings are 25, 43 and 50 s for styrene, indene and octatetraene respectively. One would expect these times to be approximately in the ratio of the square of the numbers of rotation variables if the numbers of active orbitals is fixed.

In Fig. 1 we show a plot of the computed frequencies of the out-of-plane vibrations against experimental values (19) for indene and (20) styrene. The experimental values are known only to  $5 \text{ cm}^{-1}$ . Notice that the slope is 0.92–0.94, which is similar to the scale factor of 0.9 that is often used to scale SCF frequencies for comparison with experiment.

## Acknowledgements

This work was supported by the SERC (UK) under grant numbers GR/H94177 and GR/J25123.

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