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MC SCF GRADIENT OPTIMIZATION OF THE $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ TRANSITION STRUCTURE

H. Bernhard SCHLEGEL*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

and

Michael A. ROBB**

Department of Chemistry, Queen Elizabeth College, London University, London W8 7AH, UK

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A compact algorithm is presented to obtain the two-electron integral derivative contribution to MC SCF gradients that avoids the storage of the integral derivatives or the back-transformed two-electron density matrix. The MC SCF gradients are applied to the optimization of the $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ transition structure at the 6-31G* basis-set level using a complete CI in a four-electron, four-orbital valence space.

1. Introduction

Hartree–Fock energy gradients have been used extensively to optimize equilibrium geometries [1] and are now being used to locate transition structures efficiently [2]. However, energy surfaces for some reactions cannot be described properly at the Hartree–Fock level. If correlation energy is included via configuration interaction (CI) or Møller–Plesset perturbation theory, energy gradients are more difficult to calculate, since the molecular orbital coefficient derivatives must be computed by solving the coupled perturbed Hartree–Fock (CPHF) equations [3]. Alternatively, it may be possible to describe the energy surfaces for many reactions with sufficient accuracy by using a multi-configuration SCF (MC SCF) approach with a modest size reference space (2–10 valence or active orbitals). Since the MC SCF calculations minimize the energy with respect to the MO and CI coefficients simultaneously, the CPHF equations can be avoided. Various formalisms and implementations of MC SCF gradients have been given in the liter-

ature [4–6][†]. In the present paper, we report equations and programming considerations for gradients based on the unitary group MC SCF procedure of Eade and Robb [8]. Special attention is given to the two-electron integral derivative term. As a preliminary application, the transition structure for the $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ reaction has been optimized and compared to previous calculations at the HF/6-31G* and MP2/6-31G* levels.

2. Method

Osamura et al. [5] have written the equation for energy gradients of a general wavefunction as

$$dE/dq = \sum_{ij} \gamma_{ij} dh_{ij}/dq + \sum_{ijkl} \Gamma_{ijkl} d(ij|kl)/dq + \sum_{ij} X_{ij} U_{ji} + dV_{\text{nuc}}/dq, \quad (1)$$

where γ_{ij} is the one-particle density matrix, Γ_{ijkl} is the two-particle density matrix, h_{ij} are the one-electron integrals, $(ij|kl)$ are the two-electron integrals

[†] For a general reference on gradient methods, see ref. [7].

* Fellow of the Alfred P. Sloan Foundation, 1981–83.

** Senior CIBA-GEIGY Fellow (1/1/82–31/8/82), Istituto di Chimica Organica, Università di Bologna, Bologna, Italy.

and V_{nuc} is the nuclear–nuclear repulsion energy. The lagrangian X_{ij} is given by

$$X_{ij} = \sum_k \gamma_{ik} h_{kj} + \sum_{klm} 2\Gamma_{iklm}(jk|lm). \quad (2)$$

For SCF and MC SCF calculations, X_{ij} is symmetric. Therefore, the MO coefficient derivatives, U_{ij} , can be obtained from the orthonormality constraint

$$U_{ij} + U_{ij}^T + dS_{ij}/dq = 0, \quad (3)$$

where S_{ij} is the overlap matrix.

In the notation of Eade and Robb [8], the lagrangian X_{ij} can be written in terms of the core and valence Fock matrices, F_1 and F_2 :

$$\begin{aligned} X_{ij} &= F_{1ij}, \quad i, j \in \text{core}, \\ X_{ij} &= F_{1ij}, \quad i \in \text{core}, j \in \text{valence}, \\ X_{ij} &= F_{2ij}, \quad i, j \in \text{valence}, \\ X_{ij} &= F_{2ij}, \quad i \in \text{valence}, j \in \text{core}. \end{aligned} \quad (4)$$

The configurations for the MC SCF calculation involve excitations within the set of valence orbitals while the core orbitals remain doubly occupied throughout. Often a complete CI can be carried out using the valence orbitals (also referred to as complete active space SCF or CASSCF). This separation of the orbitals into core and valence sets simplifies the structure of the two-particle density matrix. In the molecular orbital (MO) basis, Γ_{ijkl} can be written in terms of the one-particle density matrix and a smaller $\Gamma_{ijkl}^{\text{val}}$ that refers only to the valence space,

$$\begin{aligned} \Gamma_{ijkl} &= \Gamma_{ijkl}^{\text{val}}, \quad i, j, k, l \in \text{valence}, \\ \Gamma_{ijkl} &= \gamma_{ij}\gamma_{kl} - 0.25(\gamma_{ik}\gamma_{jl} + \gamma_{il}\gamma_{jk}), \\ &\quad \text{otherwise.} \end{aligned} \quad (5)$$

In practice, the integral derivatives are computed in the atomic orbital (AO) basis. This causes no difficulties for the one-electron integral derivatives, since the one-particle density matrix and the lagrangian can be transformed to the AO basis easily. In contrast, the calculation of the two-electron integral derivative contribution is less straightforward. The two-particle density matrix could be transformed to the AO basis by an N^5 algorithm that is the reverse of the usual integral transformation. However, this is rather costly in terms of both cpu time and storage. Alternatively,

Γ_{ijkl} can be written in a partially factored form:

$$\begin{aligned} \Gamma_{ijkl} &= \Gamma_{ijkl}^{\text{fac}} + \Delta\Gamma_{ijkl}^{\text{val}}, \\ \Gamma_{ijkl}^{\text{fac}} &= \gamma_{ij}\gamma_{kl} - 0.25(\gamma_{ik}\gamma_{jl} + \gamma_{il}\gamma_{jk}), \\ &\quad i, j, k, l \in \text{core or valence}, \end{aligned}$$

$$\Delta\Gamma_{ijkl}^{\text{val}} = \Gamma_{ijkl}^{\text{fac}} - \Gamma_{ijkl}^{\text{val}}, \quad i, j, k, l \in \text{valence only}. \quad (6)$$

The factored portion of the two-particle density matrix, $\Gamma_{ijkl}^{\text{fac}}$, can be constructed in the AO basis directly from the one-particle density matrix in the AO basis. Thus without loss of generality^{††}, the problem has been reduced to transforming $\Delta\Gamma_{ijkl}^{\text{val}}$ for the valence space only. Since the valence space is typically 2–10 orbitals, $\Delta\Gamma_{ijkl}^{\text{val}}$ can be held in central memory and the transformation can be carried out without disk access. Furthermore, explicit storage of the transformed Γ_{ijkl} can be avoided, if the transformation is carried out during the integral derivative computation. Since the integrals and the integral derivatives are computed in shell blocks [9,10] (s, sp and d shells consist of 1, 4 and 6 functions, respectively) only a small portion of the transformed Γ_{ijkl} is needed at any one time (1–1296 values). For each shell block, a simple N^5 transformation is carried out on $\Delta\Gamma_{ijkl}^{\text{val}}$, the results added to $\Gamma_{ijkl}^{\text{fac}}$ and the total Γ in the AO basis combined directly with the integral derivatives. This procedure has been incorporated in the integral derivative programs in GAUSSIAN 80 [11].

3. Application

The reaction $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ has drawn considerable experimental [12] and theoretical [13–17] attention. Previous calculations have optimized the structure of the transition state at SCF, MP2 and CISD levels using 6-31G*, DZ and DZ + polarization basis sets. Recent calculations indicate [16] that triple excitations are important in determining the energy, suggesting that multi-reference determinant calculations may be required.

Fig. 1 compares the transition structures optimized at the Hartree–Fock (HF), second-order Møller–Plesset (MP2) and MC SCF levels using the 6-31G* basis set. The MC SCF calculations involve a complete

^{††} Further factoring can be achieved if the MC SCF wavefunction is restricted to be in GVB form [6].

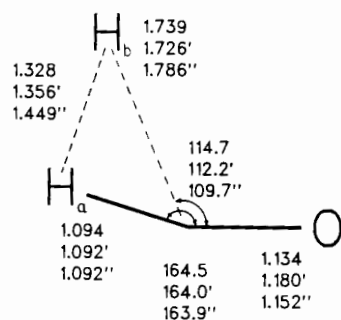


Fig. 1. Comparison of optimized geometries of the transition structure for $H_2CO \rightarrow H_2 + CO$, computed at the Hartree-Fock (unprimed), second-order Møller-Plesset (primed) and MC SCF (double primed) levels using the 6-31G* basis set.

CI in a valence space of four orbitals and four electrons chosen to describe CH bond breaking and HH bond formation. This choice also allows a proper description of dissociation to $CO + 2H$. The most prominent feature of the MC SCF optimized geometry is that H_b has moved away from the H_aCO moiety, compared to the HF or MP2 optimized structures. Goddard et al. [14] find a similar elongation at the CISD level (configuration interaction including all single and double excitations from the reference determinant) using a double-zeta basis set*. This can be understood by noting that neither the HF nor the MP2 calculations have the proper asymptotic behavior for $H_2CO \rightarrow HCO + H$ whereas the MC SCF and CISD calculations behave correctly in this limit. However, basis set effects can be similar in magnitude to the differences between HF/6-31G*, MP2/6-31G* and MCSCF/6-31G* calculations [14,17]. Dupuis et al. [17] have recently reported similar results for more extensive calculations with larger basis sets and optimization at the MC SCF and CI levels.

Table 1 summarizes the timing data for the MC SCF gradient calculations. Preliminary calculations indicated that convergence on the energy of at least 10^{-6} au is necessary. After the first or second MC SCF calculation in a geometry optimization run, the step size is sufficiently small so that this level of convergence is not difficult to achieve. The gradient evaluation requires only $\approx 20\%$ of the total time per optimization step. Approximately half of the gradient computation

* This elongation is not found when polarization functions (p on H and d on CO) are added to the DZ basis set [14].

Table 1
Timing data for $H_2 + CO$ transition structure optimization a)

Optimization cycle	Number of MC SCF iterations	Fraction of cpu time b)	
		MC SCF	gradient c)
0	12	0.77	0.13
1	9	0.71	0.16
2	6	0.65	0.20
3	3	0.53	0.27
4	4	0.57	0.24

a) Six core orbitals, four valence orbitals, complete CI in valence space.

b) Computations were performed on the CDC 7600 at the University of Bologna.

c) Including back-transformation of the two-electron density matrix.

time is due to the transformation of Γ_{ijkl} . Thus, any further improvement in the handling of the two-particle density matrix would have only a small effect on the total cpu time. This should also be true for calculations with a larger valence space, since the MC SCF step has an N^5 dependency as well and would still dominate the calculation.

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