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UNIFIED THEORETICAL TREATMENT OF ANALYTIC FIRST AND SECOND ENERGY DERIVATIVES IN OPEN-SHELL HARTREE-FOCK THEORY

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Mark A. Vincent, Jeffrey F. Gaw, and Henry F. Schaefer III

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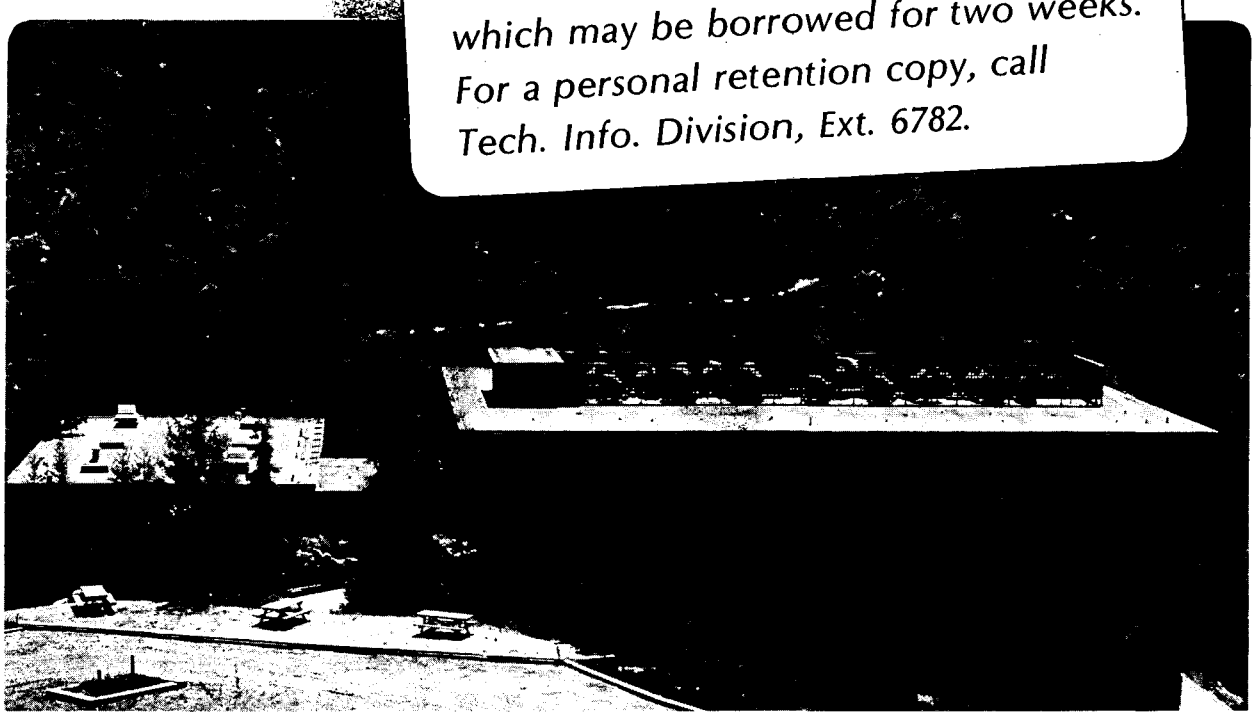

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Unified Theoretical Treatment of Analytic First and Second Energy Derivatives in Open-Shell Hartree-Fock Theory

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Abstract

Second derivatives of polyatomic potential energy hypersurfaces are of widespread importance to problems in theoretical chemistry. A formalism is presented which allows the analytic evaluation of energy second derivatives from restricted Hartree-Fock wave functions for arbitrary closed or open-shell molecular systems. The present method makes use of previously reported integral second derivative techniques and earlier advances in the solution of the open-shell coupled perturbed Hartree-Fock equations. The applicability of the new method is demonstrated in studies of the first excited singlet state of formaldehyde, for which the equilibrium geometry and vibrational frequencies have been determined with two different basis sets.

Introduction

Analytic gradient techniques in conjunction with *ab initio* self-consistent-field (SCF), multiconfiguration (MC) SCF and configuration interaction (CI) wave functions, have proven to be very efficient and accurate in characterizing potential energy hypersurfaces.[1-13] Recent developments of analytic *second* derivative techniques for closed shell[5,14,15] and high spin open-shell[15] SCF wave functions are also quite promising. Specifically, it now appears that the effort required to form a force constant (Hessian) matrix is five to ten times less than the corresponding work necessary using finite differences of analytic first derivatives.

Analytic second derivatives of the total energy may be utilized to explore the potential energy hypersurfaces of molecular systems in several important ways, some of which are;

1) As discussed by Murrell and Laidler[16] and McIver and Komornicki,[17] eigenvalues of the second derivative matrix (force constant matrix) give conclusive information concerning the nature of stationary points for the molecular system under consideration.

2) Vibrational frequencies can be readily obtained by diagonalizing a mass-weighted force constant matrix.[18] These frequencies and the corresponding vibrational eigenvectors can be further used to evaluate related physical properties, such

as vibrational contributions to the quantum statistical partition function, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distorsion constants.

3) In geometry optimization procedures, the second derivative matrix (Hessian matrix, H) for a certain point may be used to obtain an improved geometry employing the Newton-Raphson method,

$$\underset{\sim}{x}_{n+1} = \underset{\sim}{x}_n - \underset{\approx}{H}^{-1} \underset{\sim}{g}_n$$

where $\underset{\sim}{x}_n$ and $\underset{\sim}{x}_{n+1}$ are geometries for present and next steps, and $\underset{\sim}{g}_n$ is the gradient vector. It is also found that the Hessian matrix at a stationary point from a lower level of theory is very useful in geometry optimization at a higher level of theory. Furthermore, such an approximate Hessian has proved to be an excellent initial matrix for use in iterative geometry optimization techniques.[19-22]

4) Following one or a few specific eigenvectors of the second derivative matrix, one can find stationary points relatively easily, as discussed by Cerjan and Miller.[23]

5) The coordinate invariant minimum energy reaction pathway which is a mass-weighted steepest descent reaction coordinate, was independently suggested by Fukui[24] and Schaefer[25] about eight years ago. As demonstrated by Morokuma and coworkers,[26] the vibrational frequencies along this well-defined reaction pathway provide an illuminating way of discussing the mechanisms of chemical reactions.

6) The reaction path Hamiltonian method of Miller, Handy and Adams[27] allows detailed predictions of reaction dynamics to be made,[28-30] taking as input the energy second derivatives along the minimum energy path described in 5).

Here we present a compact, unified theoretical treatment of analytic first and second energy derivatives in the context of single configuration restricted Hartree-Fock (RHF) theory. Unlike previous second derivative methods,[5,15] the present formalism is not restricted to single determinant wave functions. This is explicitly demonstrated by applications to open-shell singlet RHF wave functions. Finally, it should be emphasized that this research is a logical outgrowth of our previous work on (a) integral second derivatives in the context of single determinant RHF theory[15] (b) the open-shell coupled perturbed Hartree-Fock equations, treated in the context of analytic first derivatives for large CI wave functions.[13]

Theory

I. The Coupled Perturbed Hartree-Fock (CPHF) Equations

In this section the derivation of CPHF equations is reviewed. Our approach here is similar in content to reference 13, but employs a simpler formalism which is also easier to apply. The generalized Fock operator[31] for a single configuration SCF wave function may be expressed as

$$F_i = f_i h + \sum_{\ell}^{occ} (\alpha_{i\ell} J_\ell + \beta_{i\ell} K_\ell) \qquad (1)$$

where f_i is a constant related to occupation of ith molecular orbital (MO), $\alpha_{i\ell}$ and $\beta_{i\ell}$ are constants unique to i^{th} and ℓ^{th} MO's, J and K are the standard Coulomb and exchange operators, respectively. The electronic energy for such a system is given by

$$E_{elec} = 2 \sum_{i}^{occ} f_i h_{ii} + \sum_{i}^{occ} \sum_{j}^{occ} \{\alpha_{ij}(ii|jj) + \beta_{ij}(ij|ij)\} \qquad (2)$$

At this point it is convenient to define the Lagrangian matrix whose ij element is given

$$\varepsilon_{ij} = \langle i|F_i|j\rangle$$

$$= f_i h_{ij} + \sum_{\ell}^{occ} \{\alpha_{i\ell}(ij|\ell\ell) + \beta_{i\ell}(i\ell|j\ell)\} \qquad (3)$$

Using this quantity, the RHF variational conditions for the system are expressed as

$$\varepsilon_{ij} - \varepsilon_{ji} = 0 \qquad \text{for occupied-occupied orbital pairs} \tag{4}$$

and

$$\varepsilon_{ij} = 0 \qquad \text{for occupied-virtual orbital pairs} \tag{5}$$

The expansion of the molecular orbitals about the chosen reference geometry is given by

$$|i\rangle \rightarrow |i\rangle + \lambda \sum_j |j\rangle U^a_{ji} + \ldots \tag{6}$$

which implies that the atomic orbital (AO) integrals are expanded as

$$\langle\mu|h|\nu\rangle \rightarrow \langle\mu|h|\nu\rangle + \lambda\langle\mu|h|\nu\rangle^a + \ldots \tag{7}$$

$$(\mu\nu|\rho\sigma) \rightarrow (\mu\nu|\rho\sigma) + \lambda(\mu\nu|\rho\sigma)^a + \ldots \tag{8}$$

Substituting these expressions into Eq. (4) and collecting the first-order in λ, we find

$$- \sum_{k}^{all} U^a_{ki} \, (\varepsilon_{jk} - \zeta^i_{jk}) + \sum_{k}^{all} U^a_{kj} (\varepsilon_{ik} - \zeta^j_{ik})$$

$$+ \sum_{k}^{all} \sum_{\ell}^{occ} U^a_{k\ell} \, [2(\alpha_{i\ell} - \alpha_{j\ell})(ij|k\ell) + (\beta_{i\ell} - \beta_{j\ell})\{(ik|j\ell) + (i\ell|jk)\}]$$

$$+ \varepsilon^a_{ij} - \varepsilon^a_{ji} = 0 \tag{9}$$

where the generalized Lagrangian matrix $\underset{\approx}{\zeta}^j$ is

$$\zeta^j_{ik} = f_j h_{ik} + \sum_{\ell}^{occ} \{\alpha_{j\ell}(ik|\ell\ell) + \beta_{j\ell}(i\ell|k\ell)\} \tag{10}$$

It should be noted the following relationship holds for Eq. (10),

$$\zeta^i_{ik} = \zeta^k_{ik} = \varepsilon_{ik} \tag{11}$$

The derivative Lagrangian matrix ε^a appearing in Eq. (9) is defined by,

$$\varepsilon^a_{ij} = f_i \sum_{\mu\nu} c^i_\mu \, c^j_\nu \, \langle\mu|h|\nu\rangle^a$$

$$+ \sum_{\mu\nu\rho\sigma} \sum_{\ell}^{occ} \{\alpha_{i\ell} c^i_\mu c^j_\nu c^\ell_\rho c^\ell_\sigma + \beta_{i\ell} c^i_\mu c^\ell_\nu c^j_\rho c^\ell_\sigma\}(\mu\nu|\rho\sigma)^a \tag{12}$$

The orthonormality condition for molecular orbitals leads a significant decrease[13] in the number of independent elements of

the orbital change matrix U^a, following

$$U^a_{ij} + U^a_{ji} + S^a_{ij} = 0 \tag{13}$$

where

$$S^a_{ij} = \sum_{\mu\nu} C^i_\mu C^j_\nu \frac{\partial S_{\mu\nu}}{\partial a} \tag{14}$$

The coupled equation which contains the independent elements of U^a can then be obtained by combining Eqs. (9) and (13);

$$\sum_{k>}^{all} \sum_{\ell}^{occ} A_{ijk\ell} U^a_{k\ell} = B^a_{0_{ij}} \tag{15}$$

where

$$\begin{aligned} A_{ijk\ell} &= 2(\alpha_{i\ell}-\alpha_{j\ell}-\alpha_{ik}+\alpha_{jk})(ij|k\ell) \\ &+ (\beta_{i\ell}-\beta_{j\ell}-\beta_{ik}+\beta_{jk})\{(ik|j\ell)+(i\ell|jk)\} \\ &+ \delta_{\ell j}(\varepsilon_{ik}-\zeta^j_{ik}) - \delta_{\ell i}(\varepsilon_{jk}-\zeta^i_{jk}) \\ &- \delta_{kj}(\varepsilon_{i\ell}-\zeta^j_{i\ell}) + \delta_{ki}(\varepsilon_{j\ell}-\zeta^i_{j\ell}) \end{aligned} \tag{16}$$

and

$$B^a_{0_{ij}} = -\varepsilon^a_{ij} + \varepsilon^a_{ji}$$

$$+ \sum_{k>}^{all} \sum_{\ell}^{occ} S^a_{k\ell}\Big[2(\alpha_{ik}-\alpha_{jk})(ij|k\ell)+(\beta_{ik}-\beta_{jk})\{(ik|j\ell)+(i\ell|jk)\}$$

$$+ \delta_{kj}(\varepsilon_{i\ell}-\zeta^j_{i\ell}) - \delta_{ki}(\varepsilon_{j\ell}-\zeta^i_{j\ell})\Big]$$

$$+ \frac{1}{2} \sum_{k}^{occ} S^a_{kk}\ [2(\alpha_{ik}-\alpha_{jk})(ij|kk) + 2(\beta_{ik}-\beta_{jk})(ik|jk)] \tag{17}$$

This is the CPHF equation for the general open-shell SCF wave function whose energy is given by Eq. (2). This equation must be solved for the pairs of orbitals i,j or U^a_{ij} :

(a) (i=virtual, j=doubly occupied) for closed shell SCF wave functions.

(b) (i=half occupied, j=doubly occupied), (i=virtual, j=doubly occupied), and (i=virtual, j=half occupied) for high spin open-shell wave functions.

(c) (i=half occupied, j=doubly occupied), (i=half occupied, j=half occupied), (i=virtual, j=doubly occupied), and (i=virtual, j=half occupied) for open-shell singlet wave functions.

In the general open-shell theory, a unitary transformation among unique shells, i.e., (doubly occupied - doubly occupied), (α spin - α spin), (β spin - β spin), and (virtual - virtual), does not change

total energy of the system. It is therefore advantageous to redefine these orbitals uniquely, when the entire U^a matrix is necessary in the later process. This can be done by separately diagonalizing each shell of the Fock matrix, constructed using the averaged Fock operator[32]

$$F^c = h + \sum_j f_j \, (2\, J_j - K_j) \tag{18}$$

The remaining (non-independent) elements of U^a may be obtained from

$$U^a_{ij} = \frac{1}{\varepsilon^c_j - \varepsilon^c_i} \Bigg[\sum_{k>}^{all} \sum_{\ell}^{occ} U^a_{k\ell} \, (f_\ell - f_k)\{4(ij|k\ell) - (i\ell|jk) - (ik|j\ell)\}$$

$$- \sum_{k>}^{occ} \sum_{\ell}^{occ} S^a_{k\ell} f_k \{4(ij|k\ell) - (i\ell|jk) - (ik|j\ell)\}$$

$$- \sum_{k}^{occ} S^a_{kk} \, f_k \{2(ij|kk) - (ik|jk)\}$$

$$+ \varepsilon^{c^a}_{ij} + \varepsilon^c_j \, S^a_{ij} \Bigg] \tag{19}$$

where

$$\varepsilon^{c^a}_{ij} = \sum_{\mu\nu} C^i_\mu C^j_\nu \langle \mu | h | \nu \rangle^a$$

$$+ \sum_{\mu\nu\rho\sigma} \sum_{\ell}^{occ} C^i_\mu C^j_\nu C^\ell_\rho C^\ell_\sigma f_\ell \{2(\mu\nu|\rho\sigma)^a - (\mu\rho|\nu\sigma)^a\} \tag{20}$$

The entire purpose of course in solving the CPHF equations is to

determine the matrix elements U^a_{ji}, which tell us [see Eq. (6)] for a cartesian nuclear displacement "a" to what degree the new SCF molecular orbital i takes on some of the character of MO j, determined at the reference geometry. It should be noted, however, that the non-independent elements of U^a in Eq.(19) are not required in the calculation of SCF second derivatives, as will be demonstrated in Section III.

II. First Derivative of Electronic Energy

The expression for the first derivative of the electronic energy of the system is obtained by differentiating Eq. (2) with respect to the cartesian nuclear coordinate "a",

$$\frac{\partial E}{\partial a} = 2 \sum_{i}^{occ} f_i \sum_{\mu\nu} c^i_\mu c^i_\nu \langle\mu|h|\nu\rangle^a$$

$$+ \sum_{i}^{occ} \sum_{j}^{occ} \sum_{\mu\nu\rho\sigma} \{\alpha_{ij} c^i_\mu c^i_\nu c^j_\rho c^j_\sigma + \beta_{ij} c^i_\mu c^j_\nu c^i_\rho c^j_\sigma\}(\mu\nu|\rho\sigma)$$

$$+ 4 \sum_{i}^{occ} \sum_{r}^{occ} U^a_{ri} \varepsilon_{ir} \qquad (21)$$

where ε_{ir} is an element of the Lagrangian matrix defined in Eq. (3). This equation can be simplified using the relationships shown in Eqs. (4), (5) and (13),

$$\frac{\partial E}{\partial a} = 2 \sum_{i}^{occ} f_i \sum_{\mu\nu} c^i_\mu c^i_\nu \langle\mu|h|\nu\rangle^a$$

$$+ \sum_{i}^{occ} \sum_{j}^{occ} \sum_{\mu\nu\rho\sigma} \{\alpha_{ij} c^i_\mu c^i_\nu c^j_\rho c^j_\sigma + \beta_{ij} c^i_\mu c^j_\nu c^i_\rho c^j_\sigma\}(\mu\nu|\rho\sigma)^a$$

$$- 2 \sum_{i}^{occ} \sum_{j}^{occ} S^a_{ij} \varepsilon_{ij} \qquad (22)$$

Equation (22) shows the well-known fact[1] any wave function which satisfies variational conditions given by Eqs. (4) and (5) does not require the orbital changes U^a to obtain the gradient of electronic energy.

III. Second Derivative of Electronic Energy

In a similar fashion the expression for the second derivative of the electronic energy may be obtained by differentiating Eq. (21) with respect to a second variable "b",

$$\frac{\partial^2 E}{\partial a \partial b} = 2 \sum_i^{occ} f_i \sum_{\mu\nu} c_\mu^i c_\nu^i \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b}$$

$$+ \sum_i^{occ} \sum_j^{occ} \sum_{\mu\nu\rho\sigma} \{\alpha_{ij} c_\mu^i c_\nu^i c_\rho^j c_\sigma^j + \beta_{ij} c_\mu^i c_\nu^j c_\rho^i c_\sigma^j\} \frac{\partial^2 (\mu\nu|\rho\sigma)}{\partial a \partial b}$$

$$+ 4 \sum_i^{occ} \sum_r^{all} U_{ri}^b \varepsilon_{ir}^a$$

$$- 2 \sum_i^{occ} \sum_j^{occ} \frac{\partial S_{ij}^a}{\partial b} \varepsilon_{ij} - 2 \sum_i^{occ} \sum_j^{occ} S_{ij}^a \frac{\partial \varepsilon_{ij}}{\partial b} \qquad (23)$$

Equation (23) may be cast in a more tractable form using the readily derived relationships

$$\frac{\partial S_{ij}^a}{\partial b} = \sum_r^{all} (S_{rj}^a U_{ri}^a + S_{ir}^a U_{rj}^b) + S_{ij}^{ab} \qquad (24)$$

with

$$S_{ij}^{ab} = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} \tag{25}$$

and

$$\frac{\partial \varepsilon_{ij}}{\partial b} = \varepsilon_{ij}^b + \sum_r^{all} U_{ri}^b \zeta_{rj}^i + \sum_r^{all} U_{rj}^b \varepsilon_{ir}$$

$$+ \sum_r^{all} \sum_\ell^{occ} U_{r\ell}^b \left[2\, \alpha_{i\ell}(ij|r\ell) + \beta_{i\ell} \{(ir|j\ell)+(i\ell|jr)\}\right] \tag{26}$$

Combining Eqs. (23), (24) and (26), one obtains the final expression for the second derivative,

$$\frac{\partial^2 E}{\partial a \partial b} = 2 \sum_i^{occ} f_i \sum_{\mu\nu} C_\mu^i C_\nu^i \frac{\partial^2 h_{\mu\nu}}{\partial a \partial b}$$

$$+ \sum_i^{occ} \sum_j^{occ} \sum_{\mu\nu\rho\sigma} \{\alpha_{ij} C_\mu^i C_\nu^i C_\rho^j C_\sigma^j + \beta_{ij} C_\mu^i C_\nu^j C_\rho^i C_\sigma^j\} \frac{\partial^2 (\mu\nu|\rho\sigma)}{\partial a \partial b}$$

$$- 2 \sum_i^{occ} \sum_j^{occ} S_{ij}^{ab} \varepsilon_{ij} - 2 \sum_i^{occ} \sum_j^{occ} S_{ij}^a \varepsilon_{ij}^b$$

$$+ \sum_i^{all} \sum_j^{occ} U_{ij}^b \omega_{ij}^a \tag{27}$$

where

$$\omega_{ij}^a = 4\, \varepsilon_{ji}^a - \sum_k^{occ} \{4\, S_{ik}^a \varepsilon_{jk} + 2(\varepsilon_{ik} + \zeta_{ik}^j) S_{jk}^a\}$$

$$- 2 \sum_k^{occ} \sum_\ell^{occ} \left[2\, \alpha_{kj}(ij|k\ell) + \beta_{kj}\{(ik|j\ell)+(i\ell|jk)\}\right] \tag{28}$$

In this expression, the first four terms are due to changes in AO integrals, while the last term may be attributed to changes in the SCF molecular orbitals due to nuclear displacements from the reference geometry. In the last term, contributions from non-independent elements of U^a can be calculated without explicitly evaluating these elements because of the symmetric character of the ω^a matrix in Eq. (28) and the well-known relationship seen in Eq. (13). In other words, only the elements of the U^a matrix which are obtained from Eq. (15), are necessary to evaluate the last term in Eq. (27). The remaining part of the summation can be calculated by using the overlap derivatives S^a instead of explicit values of U^a.

Practical Overview

In light of the complexity of the formalism presented here, it may be of value to give some idea of the order in which the different steps of the problem are actually tackled. The computational procedure for the application of the general open-shell CPHF method may be concisely summarized as follows:

1. Evaluate the atomic orbital integrals, $\langle\mu|h|\nu\rangle$ and $(\mu\nu|\rho\sigma)$.

2. Obtain the RHF SCF molecular orbitals.

3. Transform the AO integrals to the MO basis set.

4. Form the Lagrangian matrix and ζ matrices defined in Eq. (10).

5. Evaluate the first derivative AO integrals, $S^a_{\mu\nu}$, $\langle\mu|h|\nu\rangle^a$ and $(\mu\nu|\rho\sigma)^a$, and construct the derivative MO overlap integrals S^a in Eq. (14) and the derivative Lagrangian matrix ε^a in Eq. (12).

6. Evaluate the second derivative AO integrals, $S^{ab}_{\mu\nu}$, $\langle\mu|h|\nu\rangle^{ab}$ and $(\mu\nu|\rho\sigma)^{ab}$, and determine first three terms in Eq. (27).

7. Set up the A and $B_0{}^a$ matrices in Eqs. (16) and (17).

8. Solve the linear equations (15), directly or iteratively.

9. Evaluate the fourth and fifth terms in Eq. (27).

It should be noted that in step four there may be different numbers of ζ matrices depending on the number of unique shells in the system under consideration.

Application to Open-Shell Singlet Formaldehyde

One test of any new theoretical method is its applicability to previously difficult problems. An obvious example for the present formalism is the vibrational spectra of open-shell singlet states, examples of which occupy much of Herzberg's classic text[34] on polyatomic molecules. Most known electronic spectroscopy involves transitions of the type $S_0 \rightarrow S_1$ or $S_0 \rightarrow S_2$ and in the vast majority of these cases S_1 and S_2 are open-shell singlet electronic states. These states typically involve two unpaired electrons, residing in spatial orbitals a and b, and spin coupled in the manner

$$\frac{1}{\sqrt{2}} \cdot \ldots\ldots\ldots \quad [a\alpha b\beta - a\beta b\alpha] \tag{29}$$

In general the unrestricted Hartree-Fock (UHF) method[35] (in conjunction with which analytic second derivative methods already exist[5]) is not applicable to such problems since either of the two determinants in (29) taken separately does not come close to being a singlet (S=0) spin eigenfunction.

Although the failure of the UHF method to treat open-shell singlet states is well known, less widely appreciated is the fact that analytic restricted Hartree-Fock (RHF) first derivative methods are not in general applicable to the determination of harmonic vibrational frequencies. This arises from the fact that RHF wave functions for open-shell singlet states[33] only satisfy the variational principal if the spatial orbitals a and b in (29)

belong to different irreducible representations [or, at least to different rows of the same (degenerate) irreducible representation]. When the spatial orbitals a and b belong to the same irreducible representation, then the excited singlet is of the same symmetry as the ground state and the open-shell singlet RHF procedure may only serve to provide a poor description of the closed-shell ground state. Exactly this happens for the $\pi \rightarrow \pi^*$ singlet state of formaldehyde, for example.[36]

The above paragraph is pertinent here because for larger polyatomic molecules the determination of cartesian force constants as finite differences of analytic gradients usually requires consideration of geometries containing no elements of point group symmetry (other than the identity E), i.e., C_1 point group. For the molecular electronic system given as example here, the S_1 $n \rightarrow \pi^*$ open-shell singlet state of formaldehyde, the equilibrium geometry electron configuration is

$$\tilde{A}\ {}^1A'' \qquad 1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 1a''^2\ 6a'\ 2a'' \qquad (30)$$

Thus for C_s geometries the spatial orbitals a and b in (29) are of a' and a" symmetry, respectively, and the open-shell singlet RHF procedure provides an upper bound to the true energy of S_1, the lowest electronic state of ${}^1A''$ symmetry. However, it is <u>not</u> possible to obtain RHF cartesian force constants via analytic gradients,[6,7] since this would require the consideration of C_1 geometries, for which the RHF open-shell singlet procedure is of

dubious validity.

The application of analytic second derivatives to electronic states such as (30) never faces this problem since all force constants are calculated simultaneously at the (higher symmetry) equilibrium geometry. The practicality of this approach has been demonstrated for the $n \rightarrow \pi^*$ S_1 state of H_2CO using standard double zeta (DZ)[37] and double zeta plus polarization (DZ+P)[38] basis sets. These results are summarized in Table I. The predicted equilibrium geometries are presented for completeness but are of relatively little value otherwise, since very similar results were reported earlier by Bell.[39] For a discussion of the comparison between theoretical and experimental geometries, the reader is referred to Bell's fine paper.

As Table I shows, the vibrational spectroscopy of S_1 formaldehyde is essentially unique among molecules with more than three nuclei, in that all fundamentals have apparently been observed. Of these, the admittedly most tentative assignment is that of Hardwick and Till,[40] $\nu_3 \cong 1290$ cm^{-1}. The DZ+P SCF harmonic frequency for this methylene scissors vibration is 1544 cm^{-1}, or 19.7% higher than observed. Systematic studies indicate that closed-shell ground state SCF harmonic vibrational frequencies[41] are an average $\sim$ 12% higher than the observed fundamentals, so such a result is not entirely surprising. However, for ground state formaldehyde[41] the DZ+P SCF harmonic CH_2 scissor is 1656 cm^{-1} and the observed fundamental 1500 cm^{-1}, the difference being only 10.4%. It is also important to note

that the present theoretical predictions completely rule out the previously (i.e., prior to Hardwick and Till[40]) accepted experimental value[42] of ν_3 (S_1), namely 887 cm^{-1}.

Among the other observed fundamentals, the comparison with the theoretical harmonic frequency for the out-of-plane bending frequency ν_4 is obviously meaningless, since the two lowest vibrational states correspond to a tunneling splitting induced by the double minimum potential for this degree of freedom. This is nicely illustrated in Figure 1 of the paper by Jones and Coon.[43] More comparable to the DZ+P SCF harmonic frequency of 928 cm^{-1} are the differences $\Delta E(0^+ \rightarrow 1^+)$ = 542 cm^{-1} and $\Delta E(0^- \rightarrow 1^-)$ = 823 cm^{-1}, and agreement with the latter is quite acceptable.

The symmetric and asymmetric CH stretching harmonic frequencies at the DZ+P SCF level of theory are respectively 15.0% and 14.7% higher than the observed fundamentals, essentially comparable to the comparisons reported earlier[15,41] for both ground state H_2CO and its lowest triplet electronic state. The DZ+P SCF theoretical CO harmonic stretching frequency for S_1 H_2CO is 5.6% greater than the observed fundamental, and even better agreement has been reported[15] for T_1 H_2CO, while a +10.4% difference was found[41] for S_0 H_2CO. Finally the theoretical methylene rocking frequency is 19.3% greater than experiment. The general conclusion drawn from this work is that while excited state harmonic vibrational frequencies approaching the Hartree-Fock level of theory seem to be invariably higher than the observed fundamentals, they do not display the consistent errors of $\sim$ 12% which are more typical

for the analogous closed-shell singlet states.

Concluding Remarks

A unified theory for analytic first and second energy derivatives has been presented and is suitable for a broad range of open-shell molecular electronic states. The new method should be particularly valuable for use in the characterization of potential energy hypersurfaces for reactive chemical systems. A preview of the utility of the analytic second derivative technique is given by application to the vibrational frequencies of the first excited state of formaldehyde. This example should be the first of many for which earlier theoretical methods are not appropriate.

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Table I. Theoretical and experimental structures and vibrational frequencies for the $\tilde{A}\ ^1A''$ electronic state of formaldehyde. Theoretical vibrational frequencies were determined within the harmonic approximation, while the experimental results are the observed (anharmonic) fundamentals. Bond distances are given in Å and vibrational frequencies in cm^{-1}.

	DZ SCF	DZ+P SCF	Experiment
Energy (hartrees)	-113.76569	-113.80795	--
r_e(CO)	1.401	1.360	1.325±0.003[a]
r_e(CH)	1.074	1.079	1.095±0.005[a]
θ_e(HCH)	120.8°	118.8°	118±1° [a]
Out-of-plane angle	34.2°	38.7°	33.6° [a]
Vibrational Frequencies			
a' CH_2 symmetric stretch	3315	3275	2847[b]
a' CH_2 scissor	1533	1544	∿ 1290[c]
a' CO stretch	1141	1239	1173[b]
a' CH_2 wag	814	928	125[d]
a" CH_2 asymmetric stretch	3463	3403	2968[b]
a" CH_2 rock	1069	1078	904[b]

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[d] Note in references a and b of this Table that the double minimum potential associated with this degree of freedom gives rise to a tunneling splitting and an extraordinarily anharmonic set of vibrational energy levels.

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