J. Am. Chem. Soc. 1983, 105, 7506-7511

Analytic Energy Second Derivatives for Two-Configuration Self-Consistent-Field Wave Functions. Application to Twisted Ethylene and to the Trimethylene Diradical

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Abstract: A formalism for the analytic evaluation of force constants for two-configuration Hartree–Fock wave functions is presented. The method is the first to treat analytic energy second derivatives at a level of theory beyond the single-configuration picture. Twisted ethylene is chosen as an example of a system for which the single-configuration Hartree–Fock approximation is adequate for the determination of the total energy (within point group D_{2d}), but the new formalism is necessary for the evaluation of force constants. The trimethylene diradical in its singlet and triplet electronic states has also been investigated for three different conformers: edge-to-edge, edge-to-face, and face-to-face.

We recently reported in a short communication[1] the first working theoretical method for the analytic determination of energy second derivatives from post-Hartree–Fock wave functions. The case considered was the most straightforward, the two-configuration self-consistent-field (TCSCF) wave function,[2] which also happens to be one of the most useful of simple correlated wave functions. Specifically, TCSCF wave functions provide a reasonable starting point for the description of carbenes[3] and other organic diradicals, such as the trimethylene species[4] examined in this research.

Force constants (energy second derivatives with respect to nuclear coordinates) of course may be evaluated via successive finite differences of computed total energies, if great care is exercised.[5] However, such procedures are notoriously inaccurate,[6] and it has been shown earlier that for single-configuration Hartree–Fock wave functions, the direct analytic evaluation of

$$\frac{\partial^2\langle\psi|H|\psi\rangle}{\partial p\partial q}$$

may be formulated as an inherently simpler procedure.[7,8] Our short communication[1] attempted to describe in words the theoretical approach adopted, but space limitations precluded the presentation of the formal basis for the method. Here the new method is described in satisfactory mathematical detail. In addition two new examples[9] are presented that illustrate the power and usefulness of the TCSCF analytic second-derivative method.

Theory

We take as a starting point our earlier formal analysis[10] of the coupled perturbed Hartree–Fock equations for general MCSCF wave functions. However, that formalism may be greatly simplified when dealing with the two-configuration SCF case. Let us assume that two configurations

$$\Phi_1 = |...m\bar{m}| \tag{1}$$

$$\Phi_2 = |...n\bar{n}| \tag{2}$$

are used to construct the total wave function

$$\Psi = C_1\Phi_1 + C_2\Phi_2 \tag{3}$$

The electronic energy of the TCSCF wave function (eq 3) may be expressed via either configurations or density matrix elements as follows.

$$\begin{aligned} E &= \sum_{\mathrm{IJ}} C_\mathrm{I} C_\mathrm{J} H_\mathrm{IJ} \\ &= 2\sum_i^{\mathrm{occ}} f_i h_{ii} + \sum_{ij}^{\mathrm{occ}} \{\alpha_{ij}[ii;jj] + \beta_{ij}[ij;ij]\} \end{aligned} \tag{4}$$

In (4) H_IJ is the matrix element between configurations I and J and is written in terms of the one- and two-electron molecular orbital (MO) integrals, h_{ij} and $[ij;kl]$.

For the case of a TCSCF wave function,

$$\begin{aligned} H_{11} = 2\sum_i^{\mathrm{d.o.}} h_{ii} + \sum_{ij}^{\mathrm{d.o.}} \{2[ii;jj] - [ij;ij]\} + 2h_{mm} + \\ 2\sum_i^{\mathrm{d.o.}} \{2[mm;ii] - [mi;mi]\} + [mm;mm] \end{aligned} \tag{5}$$

$$\begin{aligned} H_{22} = 2\sum_i^{\mathrm{d.o.}} h_{ii} + \sum_{ij}^{\mathrm{d.o.}} \{2[ii;jj] - [ij;ij]\} + 2h_{nn} + \\ 2\sum_i^{\mathrm{d.o.}} \{2[nn;ii] - [ni;ni]\} + [nn;nn] \end{aligned} \tag{6}$$

$$H_{12} = [mn;mn] \tag{7}$$

Note that the coefficients appearing in (4) take on the values

$$\begin{aligned} f_m = \alpha_{mm} = C_1^2 \qquad f_n = \alpha_{nn} = C_2^2 \\ \alpha_{mn} = \beta_{mm} = \beta_{nn} = 0 \qquad \beta_{mn} = C_1C_2 \end{aligned} \tag{8}$$

Of course the coupling constants f_i, α_{ij}, and β_{ij} depend explicitly on the CI coefficients, whereas they are constant for the case of

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(8) Y. Osamura, Y. Yamaguchi, P. Saxe, M. A. Vincent, J. F. Gaw, and H. F. Schaefer, *Chem. Phys.*, **72**, 131 (1982).

(9) The test cases presented in ref 1 were singlet methylene and cyclopropyne.

(10) (a) Y. Osamura, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **77**, 383 (1982). (b) Note that the first formal presentation of coupled MCSCF perturbation theory is that of M. Jaszunski and A. J. Sadlej, *Theor. Chim. Acta*, **40**, 157 (1975); see also M. Jaszunski and A. J. Sadlej, *Int. J. Quantum Chem.*, **11**, 233 (1977).

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the general single-configuration open-shell SCF method.[8]

The first derivative of the electronic energy, eq 4, with respect to a nuclear coordinate "*a*" is simply written as[11]

$$E^a = 2\sum_i^{\text{occ}} f_i \sum_{\mu\nu} C_\mu^i C_\nu^i \frac{\partial\langle\mu|h|\nu\rangle}{\partial a} + \sum_{ij}^{\text{occ}} \sum_{\mu\nu\rho\sigma} \{\alpha_{ij} C_\mu^i C_\nu^i C_\rho^j C_\sigma^j + \beta_{ij} C_\mu^i C_\nu^j C_\rho^i C_\sigma^j\} \frac{\partial[\mu\nu;\rho\sigma]}{\partial a} - 2\sum_{ij}^{\text{occ}} \epsilon_{ij} S_{ij}^a \tag{9}$$

where

$$S_{ij}^a = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial\langle\mu|\nu\rangle}{\partial a} \tag{10}$$

and the Lagrangian matrix ϵ is defined as

$$\epsilon_{ij} = f_i h_{ij} + \sum_k^{\text{occ}} \{\alpha_{ik}[ij;kk] + \beta_{ik}[ik;jk]\} \tag{11}$$

The analytic second-derivative expression for TCSCF wave functions may be obtained by the differentiation of eq 9 with respect to the second nuclear coordinate "*b*".

$$E^{ab} = 2\sum_i^{\text{occ}} f_i \sum_{\mu\nu} C_\mu^i C_\nu^i \frac{\partial^2\langle\mu|h|\nu\rangle}{\partial a\partial b} + \sum_{ij}^{\text{occ}} \sum_{\mu\nu\rho\sigma} \{\alpha_{ij} C_\mu^i C_\nu^i C_\rho^j C_\sigma^j + \beta_{ij} C_\mu^i C_\nu^j C_\rho^i C_\sigma^j\} \frac{\partial^2[\mu\nu;\rho\sigma]}{\partial a\partial b} + 2\sum_{\mathrm{IJ}} \frac{\partial C_\mathrm{I}}{\partial b} \times C_\mathrm{J}\{H_\mathrm{IJ}^a - 2\sum_{ij}^{\text{occ}} S_{ij}^a \epsilon_{ij}^{\mathrm{IJ}}\} - 2\sum_{ij}^{\text{occ}} \{S_{ij}^{ab}\epsilon_{ij} + S_{ij}^a \epsilon_{ij}^b\} + 2\sum_i^{\text{all}} \sum_j^{\text{occ}} U_{ij}^b W_{ij}^a \tag{12}$$

where

$$W_{ij}^a = 2\epsilon_{ji}^a - \sum_k^{\text{occ}} \{(\epsilon_{ik} + \zeta_{ik}^j) S_{jk}^a + 2\epsilon_{jk} S_{ik}^a\} - \sum_{kl}^{\text{occ}} S_{kl}^a \{2\alpha_{jl}[ij;kl] + \beta_{jl}([ik;jl] + [il;jk])\} \tag{13}$$

and

$$S_{ij}^{ab} = \sum_{\mu\nu} C_\mu^i C_\nu^j \frac{\partial^2\langle\mu|\nu\rangle}{\partial a\partial b} \tag{14}$$

The derivative Lagrangian matrix ϵ^a and generalized Lagrangian matrix ζ appearing in eq 12 and 13 are defined as follows

$$\epsilon_{ij}^a = \sum_{\mu\nu} C_\mu^i C_\nu^j \left[f_i \frac{\partial\langle\mu|h|\nu\rangle}{\partial a} + \sum_k^{\text{occ}} \sum_{\rho\sigma} C_\rho^k C_\sigma^k \left\{ \alpha_{ik} \frac{\partial[\mu\nu;\rho\sigma]}{\partial a} + \beta_{ik} \frac{\partial[\mu\rho;\nu\sigma]}{\partial a} \right\} \right] \tag{15}$$

$$\zeta_{ij}^l = f_l h_{ij} + \sum_k^{\text{occ}} \{\alpha_{lk}[ij;kk] + \beta_{lk}[ik;jk]\} \tag{16}$$

The derivative Hamiltonian H_IJ^a can be similarly written by replacing the atomic orbital (AO) integrals with the derivative AO integrals in eq 5–7. Noting the relation

$$\epsilon_{ij} = \sum_{\mathrm{IJ}} C_\mathrm{I} C_\mathrm{J} \epsilon_{ij}^{\mathrm{IJ}} \tag{17}$$

one can find the "bare" Lagrangian matrices ϵ^{IJ}

$$\epsilon_{ik}^{11} = h_{ik} + \sum_j^{\text{d.o.}} \{2[ik;jj] - [ij;kj]\} + 2[ik;mm] - [im;km] \tag{18}$$

for k = d.o. and m

$$\epsilon_{ik}^{22} = h_{ik} + \sum_j^{\text{d.o.}} \{2[ik;jj] - [ij;kj]\} + 2[ik;nn] - [in;kn] \tag{19}$$

for k = d.o. and n

$$\epsilon_{im}^{12} = \epsilon_{im}^{21} = (1/2)[in;mn] \tag{20}$$

$$\epsilon_{in}^{12} = \epsilon_{in}^{21} = (1/2)[im;nm] \tag{21}$$

In eq 18–21 the index i includes all molecular orbitals, k includes only the doubly occupied MO's and m or n, while m and n are seen in eq 1 and 2 to refer to the two molecular orbitals with variable occupation numbers. The elements not included in the range of these indices are identically zero.

In order to evaluate eq 12, one may employ the first-order change matrices of MO coefficients U^a and the derivatives $\partial C_\mathrm{I}/\partial a$ (of the CI coefficients), obtained by solving the coupled perturbed multiconfiguration Hartree–Fock (CPHF) method.[10] The matrix

$$\begin{pmatrix} A^{11} & A^{21^+} \\ A^{21} & A^{22} \end{pmatrix} \begin{pmatrix} U^a \\ \partial C_\mathrm{I}/\partial a \end{pmatrix} = \begin{pmatrix} B_0^{a^1} \\ B_0^{a^2} \end{pmatrix} \tag{22}$$

elements of eq 22 for the TCSCF case are found to be

$$A_{ij,kl}^{11} = 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})[ij;kl] + (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{[ik;jl] + [il;jk]\} + \delta_{jk}(\epsilon_{il} - \zeta_{il}^j) - \delta_{ik}(\epsilon_{jl} - \zeta_{jl}^i) - \delta_{jl}(\epsilon_{ik} - \zeta_{ik}^j) + \delta_{il}(\epsilon_{jk} - \zeta_{jk}^i) \tag{23}$$

$$A_{\mathrm{I},ij}^{21} = 2\sum_\mathrm{J} C_\mathrm{J}(\epsilon_{ij}^{\mathrm{IJ}} - \epsilon_{ji}^{\mathrm{IJ}}) \tag{24}$$

$$A_{\mathrm{I,J}}^{22} = (1/2)\{H_\mathrm{IJ} - \delta_\mathrm{IJ}E + C_\mathrm{I}C_\mathrm{J}\} \tag{25}$$

$$B_{0_{ij}}^{a^1} = \epsilon_{ij}^a - \epsilon_{ji}^a + \sum_{k>l}^{\text{all}} \sum^{\text{occ}} S_{kl}^a [2(\alpha_{jk} - \alpha_{ik}) \times [ij;kl] + (\beta_{jk} - \beta_{ik})\{[ik;jl] + [il;jk]\} - \delta_{kj}(\epsilon_{il} - \zeta_{il}^j) + \delta_{ki}(\epsilon_{jl} - \zeta_{jl}^i)] + \sum_k^{\text{occ}} S_{kk}^a [(\alpha_{jk} - \alpha_{ik})[ij;kk] + (\beta_{jk} - \beta_{ik})[ik;jk]] \tag{26}$$

$$B_{0_\mathrm{I}}^{a^2} = -(1/2)\sum_\mathrm{J} C_\mathrm{J} H_\mathrm{IJ}^a + (1/2)C_\mathrm{I}E^a + \sum_\mathrm{J} C_\mathrm{J}\{2\sum_{i>j}^{\text{occ}} S_{ij}^a \epsilon_{ji}^{\mathrm{IJ}} + \sum_i^{\text{occ}} S_{ii}^a \epsilon_{ii}^{\mathrm{IJ}}\} \tag{27}$$

In the process of solving the TCSCF-CPHF eq 22, the problem may be simplified by exploiting the relationship[10a]

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \tag{28}$$

If the derivatives of the CI coefficients are assumed to be zero, then eq 22 reduces to

$$\sum_{kl} A_{ij,kl}^{11} U_{kl}^a = B_{ij}^{a^1} \tag{29}$$

which is identical with the CPHF equation for the general single-configuration SCF method.[8]

It should be noted that the derivatives of the CI coefficients with respect to nuclear coordinates are by no means always zero, even when the CI coefficients themselves are fixed for some geometries, e.g., $C_1 = C_2 = 2^{-1/2}$.

In the second derivative expression (eq 12) and the CPHF equation (eq 22), some quantities (Hamiltonian matrix elements, Lagrangian matrix, and their derivative terms) are written within the MO basis. Since the TCSCF formalism is based on Coulomb and exchange operators, not only H_IJ and $\epsilon_{ij}^{\mathrm{IJ}}$ but also H_IJ^a and ϵ_{ij}^a may be determined within the AO basis. In order to evaluate the derivative Hamiltonian and Lagrangian derivatives, it is convenient to define the Coulomb and exchange integral derivatives

$$J_{ij}^{k^a} = \sum_{\mu\nu} C_\mu^i C_\nu^j \sum_k^{(k)} \sum_{\rho\sigma} C_\rho^k C_\sigma^k \frac{\partial[\mu\nu;\rho\sigma]}{\partial a} \tag{30}$$

$$K_{ij}^{k^a} = \sum_{\mu\nu} C_\mu^i C_\nu^j \sum_k^{(k)} \sum_{\rho\sigma} C_\rho^k C_\sigma^k \frac{\partial[\mu\rho;\nu\sigma]}{\partial a} \tag{31}$$

where $\sum_k^{(k)}$ means that the running suffix k spans only the subset

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(11) For an alternate treatment of TCSCF gradients, see: (a) J. D. Goddard, N. C. Handy, and H. F. Schaefer, *J. Chem. Phys.*, **71**, 1525 (1979); or (b) S. Kato and K. Morokuma, *Chem. Phys. Lett.*, **65**, 19 (1979).

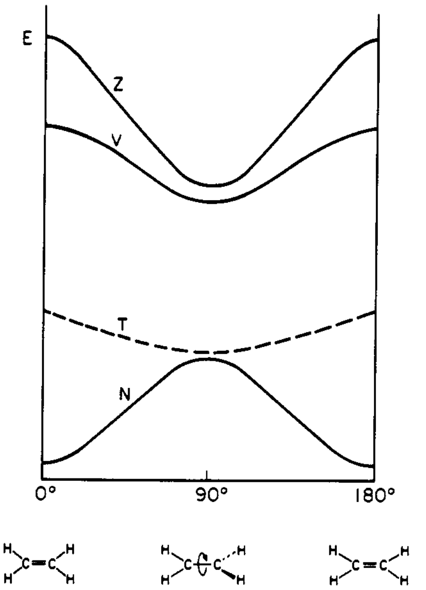

Figure 1. Qualitative shapes of four potential energy curves for the twisting of ethylene.

of MO's in question, i.e., doubly-occupied, orbital *m*, or orbital *n*.

In terms of these Coulomb and exchange integral derivatives, one finds

$$\epsilon_{ij}^{a} = 2f_i h_{ij}^{a} + \sum_{(k)} \left(\alpha_{ik} J_{ij}^{k^a} + \beta_{ik} K_{ij}^{k^a}\right) \tag{32}$$

$$H_{11}^{a} = \sum_{i}^{\text{d.o.}} (2h_{ii}^{a} + 2J_{ii}^{i^a} - K_{ii}^{i^a} + 4J_{ii}^{m^a} - 2K_{ii}^{m^a}) + 2h_{mm}^{a} + J_{mm}^{m^a} \tag{33}$$

$$H_{22}^{a} = \sum_{i}^{\text{d.o.}} (2h_{ii}^{a} + 2J_{ii}^{i^a} - K_{ii}^{i^a} + 4J_{ii}^{n^a} - 2K_{ii}^{n^a}) + 2h_{nn}^{a} + J_{nn}^{n^a} \tag{34}$$

$$H_{12}^{a} = K_{nn}^{m^a} = K_{mm}^{n^a} \tag{35}$$

Since three "bare" Lagrangian matrices ϵ^{IJ} can be evaluated from AO integrals, the TCSCF-CPHF equations may be solved by using an iterative argorithm without MO transformation. Such a method has been proposed for the general single-configuration open-shell SCF treatment[12] of large molecular systems.

Computational Overview

Given the number of equations presented in the previous section, it may be helpful to note the order in which they are treated.

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

(2) Obtain the TCSCF molecular orbitals.

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

(4) Form the Lagrange multiplier matrix and ζ matrices in eq 11 and 16.

(5) Determine H_{11}, H_{22}, and H_{12} in eq 5–7 and form the bare Lagrangian matrices in eq 18–21.

(6) Evaluate the first derivative AO integrals, $S_{\mu\nu}^{a}$, $\langle\mu|h|\nu\rangle^{a}$, $[\mu\nu;\rho\sigma]^{a}$, and construct the derivative MO overlap integrals S^{a} in eq 10, the derivative Lagrange multiplier matrix ϵ^{a} in eq 32, and H_{11}^{a}, H_{22}^{a}, and H_{12}^{a} in eq 33–35.

(7) Evaluate the second-derivative AO integrals $S_{\mu\nu}^{ab}$, $\langle\mu|\text{h}|\nu\rangle^{ab}$, and $[\mu\nu;\rho\sigma]^{ab}$, and determine the first two terms in eq 12.

(8) Form the **A** matrices in eq 23–25.

(9) Form the $\mathbf{B}_0^a$ matrices in eq 26 and 27.

(10) Solve the simultaneous eq 22, directly or iteratively.

(11) Form the $\mathbf{W}^a$ and $\mathbf{S}^{ab}$ matrices in eq 13 and 14.

(12) Evaluate the last three terms in eq 12.

It should be noted that in step 4, there are three ζ matrices for the closed-shell TCSCF system.

Table I. Optimized Geometries and Vibrational Frequencies (cm^{-1}) for Three Low-Lying Electronic States of Planar Ethylene

	$S_0\ {}^1A_g$[a]	$V\ {}^1B_{1u}$	$T\ {}^3B_{1u}$
energy, hartrees	−78.01199	−77.68931	−77.91947
r_e(C-C), Å	1.334 (1.330)[b]	1.468	1.543
r_e(C-H), Å	1.075 (1.076)[b]	1.072	1.072
θ_e(HCH), deg	116.4 (116.6)[b]	117.9	119.3
a_g ν_1 CH_2 s stretch	3350 (3026)	3399	3352
ν_2 CC stretch	1809 (1623)	1243	1115
ν_3 CH_2 scis	1491 (1342)	1631	1599
a_u ν_4 CH_2 twist	1140 (1023)	10138 i	634 i
b_{1g} ν_5 CH_2 a stretch	3416 (3103)	3511	3465
ν_6 CH_2 rock	1356 (1236)	1311	1260
b_{1u} ν_7 CH_2 wag	1112 (949)	1384	506 i
b_{2g} ν_8 CH_2 wag	1143 (943)	447	423 i
b_{2u} ν_9 CH_2 a stretch	3448 (3106)	3533	3487
ν_{10} CH_2 rock	913 (826)	884	830
b_{3u} ν_{11} CH_2 s stretch	3321 (2989)	3386	3337
ν_{12} CH_2 scis	1614 (1444)	1590	1546

[a] Vibrational frequencies in parentheses are experimental values from the compilation of Shimanouchi.[19] [b] K. Kuchitsu, *J. Chem. Phys.*, 44, 906 (1966).

Twisted Ethylene

Twisted ethylene presents an interesting problem concerning the importance of the derivatives of CI coefficients with respect to nuclear coordinates. Rotating one CH_2 group around the C–C axis, the π and π^* orbitals of planar ground-state C_2H_4 become degenerate at the 90° twisted geometry.[13,14] At this point, four low-lying states corresponding to electron configuration e^2 may be described as[15]

$$\Psi_N({}^1B_1) = 2^{-1/2}\{|...e_1\bar{e}_1| - |...e_2\bar{e}_2|\} \tag{36}$$

$$\Psi_T({}^3A_2) = |...e_1e_2| \tag{37}$$

$$\Psi_V({}^1B_2) = 2^{-1/2}\{|...e_1\bar{e}_2| - |...\bar{e}_1e_2|\} \tag{38}$$

$$\Psi_Z({}^1A_1) = 2^{-1/2}\{|...e_1\bar{e}_1| + |...e_2\bar{e}_2|\} \tag{39}$$

The subscripts 1 and 2 in eq 36 and 37 are most commonly taken to be *x* and *y*.

Figure 1 schematically shows the well-known[16] dependence of the C_2H_4 potential curves on the twisting angle. These curves suggest that the N state is a transition state and the other three states are minima. The energies of these four states can be determined straightforwardly with Roothaan's open-shell RHF formalism[17] because there is no variational condition for the CI coefficients. The second derivatives might appear to be obtainable analytically by using the general open-shell formalism presented previously.[8] However, while the one-configuration formalism holds for the T and V states (which are open-shell triplet and singlet states), it does not apply to the N and Z states even if the CI coefficients are fixed within the confines of the D_{2d} point group.

Remembering[14] that the potential energy hypersurfaces for the N and Z states must be described minimally (for arbitrary geometry) by the two-configuration SCF method, it is apparent that the energy second derivatives of the N and Z states must likewise be obtained by using a TCSCF formalism. Since there is an orbital crossing at the twisted geometry (θ = 90°), the dominant configuration at θ = 0° will be the second most important at θ = 180°. Namely, the derivatives of the CI coefficients are non-zero at θ = 90°, although C_1 and C_2 themselves are constant by symmetry restriction.

Tables I and II show the geometries and vibrational frequencies of planar and twisted ethylene for several low-lying electronic

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(12) Y. Osamura, Y. Yamaguchi, P. Saxe, D. J. Fox, M. A. Vincent, and H. F. Schaefer, *J. Mol. Struct.*, **103**, 183 (1983).

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(15) L. Salem, "Electrons in Chemical Reactions: First Principles", Wiley, New York, 1982.

(16) See, for example, page 475 of N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, California, 1978.

(17) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

Table II. Optimized Geometries and Vibrational Frequencies (cm^{-1}) for Four Electronic States of Twisted Ethylene

	N $^1B_1$	T $^3A_2$	Z $^1A_1$	V $^1B_2$
energy, hartrees	−77.94169	−77.94351	−77.78038	−77.78641
r_e(C–C), Å	1.483	1.479	1.371	1.369
r_e(C–H), Å	1.076	1.076	1.092	1.090
θ_e(HCH), deg	117.6	117.6	110.8	110.7
a_1 ν_1 CH_2 s stretch	3305	3307	3171	3191
ν_2 CH_2 scis	1595	1594	1434	1430
ν_3 C–C stretch	1174	1179	1614	1609
b_1 ν_4 CH_2 twist	1693 i	650	1019	989
b_2 ν_5 CH_2 s stretch	3296	3297	3164	3184
ν_6 CH_2 scis	1571	1571	1514	1491
e ν_7 CH_2 a stretch	3414	3414	3193	3214
ν_8 CH_2 rock	1030	1020	1096	1042
ν_9 CH_2 wag	338	261	818	772

states. A standard double-ζ (DZ) basis set was used,[18] designated C(9s 5p/4s 2p), H(4s/2s). For the planar ground state the DZ SCF frequencies are all higher than the observed fundamentals, by 10.7, 11.5, 11.1, 11.4, 10.1, 9.7, 17.2, 21.2, 11.0, 10.5, 11.1, and 11.8%, respectively. Except for the two CH_2 wags, the DZ SCF harmonic vibrational frequencies all lie between 110 and 112% for the observed fundamentals.[19] This is consistent with the earlier findings of Yamaguchi and Schaefer[20] for this particular basis set. The average error for the 12 frequencies is 12.3%, of which two-thirds is typically due to correlation effects and one-third to anharmonicity corrections.[20]

Perhaps surprisingly, planar triplet ethylene is predicted to have *three* imaginary vibrational frequencies, one of which corresponds to the expected twist about the C–C bond. The two other imaginary frequencies correspond to the two CH_2 wagging motions. Note, however, in Table II that the *twisted* triplet state is a genuine minimum on the C_2H_4 potential energy hypersurface, although the degenerate ν_9(e) wag occurs quite low (261 cm^{-1}) compared to the standard value of ~940 cm^{-1} for ground-state C_2H_4.

Vibrational frequencies for the S_1 $^1B_{1u}$ ($\pi \rightarrow \pi^*$) state of planar ethylene are given in Table I. These were also computed by using analytic second-derivative methods. A very large (~10,000 i), unphysical imaginary frequency was calculated for the CH_2 twisting frequency, indicating that this state might suffer from variational collapse[8] for certain geometries having symmetry lower than D_{2h}. In general an unrealistically large imaginary vibrational frequency (corresponding to an extraordinarily large negative diagonal force constant) is an indication that such a variational collapse has occurred. However, finite difference studies with R. M. Pitzer showed the 10 138 i cm^{-1} result to be correct. This unphysical prediction appears to be a reflection of the fact that the planar $^1B_{1u}$ state is poorly described at this level of theory.

The D_{2h} stationary point geometry is given in Table I. Note that many previous studies[21] have shown that diffuse basis functions and correlation effects are very important for the realistic prediction of the excitation energy. As expected, both the V and T states have much longer bond distances (1.468 and 1.543 Å, respectively) than the ethylene ground state, confirming the absence of the π bond for these two electronic states.

Turning to the results for twisted ethylene, the results clearly show that the N state is a transition state for the twisting motion, as expected. The T, Z, and V states of twisted ethylene are all predicted to be minima at the DZ SCF level of theory. Table II gives the first theoretical predictions of the vibrational frequencies of these three states. However, previous work[14,22] has shown that correlation effects reverse the energetic ordering of the N and T states, and of the higher-lying Z and V states. In addition, the study of Brooks[14] suggests that correlation effects may give rise ultimately to a pyramidalized C_s equilibrium geometry for the Z state.

Table III. Optimized Geometry and Vibrational Frequencies (cm^{-1}) of Cyclopropane, C_3H_6[a]

energy, hartrees	−117.01870
r_e(C–C), Å	1.519 (1.512)[b]
r_e(C–H), Å	1.073 (1.083)[b]
θ_e(HCH), deg	113.8 (114.0)[b]

approximate type of mode	SCF	exptl	difference
a_1' ν_1 CH_2 s stretch	3340	3038	302 (9.9%)
ν_2 CH_2 scis	1660	1479	181 (12.2%)
ν_3 ring stretch	1288	1188	100 (8.4%)
a_1'' ν_4 CH_2 twist	1259	1126	133 (11.8%)
a_2' ν_5 CH_2 wag	1266	1070	196 (18.3%)
a_2'' ν_6 CH_2 a stretch	3438	3103	335 (10.8%)
ν_7 CH_2 rock	930	854	76 (8.9%)
e' ν_8 CH_2 s stretch	3320	3025	295 (9.8%)
ν_9 CH_2 scis	1618	1438	180 (12.5%)
ν_{10} CH_2 wag	1204	1029	175 (17.0%)
ν_{11} ring deform	931	866	65 (7.5%)
e" ν_{12} CH_2 a stretch	3416	3082	334 (10.8%)
ν_{13} CH_2 twist	1328	1188	140 (11.8%)
ν_{14} CH_2 rock	832	739	93 (12.6%)

[a] Experimental vibrational frequencies are from the compilation of Shimanouchi.[19] [b] R. J. Butcher and W. J. Jones, *J. Mol. Spectrosc.*, 47, 64 (1973).

Except for the twisting about the C–C bond, the vibrational frequencies for the N and T twisted equilibrium geometries are roughly comparable. In fact, except for ν_9(e), the CH_2 wag, the agreement is within 10 cm^{-1}. Qualitative agreement is also found between the Z and V state frequencies of twisted C_2H_4, the greatest difference being 54 cm^{-1} for ν_8(e). However, large differences occur between the N,T pair and the Z,V pair. Most conspicuously the C–C stretching frequencies of the N and T states are 1174 and 1179 cm^{-1}, typical for a C–C single bond at this level of theory. The Z and V state frequencies, however, are much higher, 1614 and 1609 cm^{-1}, though still below the 1809 cm^{-1} seen in Table I for the planar ground state. Similarly the CH_2 wagging frequencies for the zwitterionic[15] Z and V states are more than twice as large as those for the N and T states. Finally, twisting about the C–C bond is also more expensive energetically for the Z (1019 cm^{-1}) and V (989 cm^{-1}) states than for the T (650 cm^{-1}) state, but less so than for the planar ground state (1140 cm^{-1}). Thus the C–C bond for the zwitterionic states appears to be intermediate between the limiting single- and double-bond cases.

Trimethylene

The first substantive theoretical study of $\dot{C}H_2CH_2\dot{C}H_2$ was Hoffmann's investigation[23] using extended Hückel theory. Several previous ab initio studies[4,11b,24-26] for the trimethylene diradical

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[18] S. Huzinaga, *J. Chem. Phys.*, **42** 1293 (1965); T. H. Dunning, *ibid.*, **53**, 2823 (1970).

[19] T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", Consolidated Volume, National Bureau of Standards, Washington, D.C., 1972, NSRDS-NBS 39.

[20] Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **73**, 2310 (1980).

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[22] R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys.*, **9**, 75 (1976).

[23] R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).

[24] J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Am. Chem. Soc.*, **94**, 279 (1972).

Table IV. Vibrational Frequencies (cm^{-1}) of Edge-to-Edge or (0°,0°) Trimethylene Diradicals (note that the central methylene is labeled CH_{2A})

approximate type of mode	$^1A_1$ TCSCF	$^3B_1$ triplet	$^1B_1$ open-shell singlet
a_1 ν_1 CH_{2B} a stretch	3447	3448	
ν_2 CH_{2B} s stretch	3325	3326	
ν_3 CH_{2A} s stretch	3166	3146	
ν_4 CH_{2A} scis	1627	1633	
ν_5 CH_{2B} scis	1602	1606	
ν_6 CH_{2B} rock	1231	1251	
ν_7 CC s stretch	941	949	
ν_8 CCC deform	400	437	
a_2 ν_9 CH_{2A} twist	1273	1274	
ν_{10} CH_{2B} wag	259	310	
ν_{11} torsion (CH_{2B} twist)	156 i	185 i	
b_1 ν_{12} CH_{2B} a stretch	3443	3443	
ν_{13} CH_{2B} s stretch	3322	3322	
ν_{14} CH_{2B} scis	1579	1582	
ν_{15} CH_{2A} wag	1502	1512	
ν_{16} CC a stretch	1195	1189	
ν_{17} CH_{2B} rock	976	981	
b_2 ν_{18} CH_{2A} a stretch	3194	3166	
ν_{19} CH_{2A} rock	931	953	
ν_{20} CH_{2B} wag	323	311	
ν_{21} torsion (CH_{2B} twist)	73 i	168 i	
energy, hartrees	−116.96298	−116.96401	−116.77396

have appeared, beginning with the classic work of Salem and colleagues.[24] However, ours is apparently the first to determine vibrational frequencies for the different C_3H_6 stationary points. Moreover, we have considered both singlet and triplet electronic states in each of the edge-to-edge (E-E), edge-to-face (E-F), and face-to-face (F-F) conformers. The same Huzinaga-Dunning double-ζ (DZ) basis set[18] used above for ethylene was adopted in this research.

Here we first discuss the cyclopropane molecule, for which the experimental molecular structure and vibrational frequencies may be seen in Table III. The average DZ SCF harmonic vibrational frequency is 11.6% higher than the corresponding observed fundamental. The DZ SCF structure of cyclopropane is seen to be in good agreement with the experimental r_0 structure.

Hoffmann's pioneering study[23] of trimethylene led to the conclusion[27,28] that there should be a minimum for the edge-to-edge (E-E) singlet structure. This state is treated by the TCSCF method here, with vibrational frequencies determined via the new analytic second-derivative method. Our results are summarized in Figure 2 and Table IV. With all three conformers of trimethylene, the triplet and one of the two singlet states are energetically low lying. The second singlet state (for the E-E conformation this is the open-shell singlet) is always much higher in energy, by ~0.2 hartree. For the E-E case, it was not possible to predict realistic vibrational frequencies for the high-energy singlet state, since it is subject to variational collapse[8] for low-symmetry geometries.

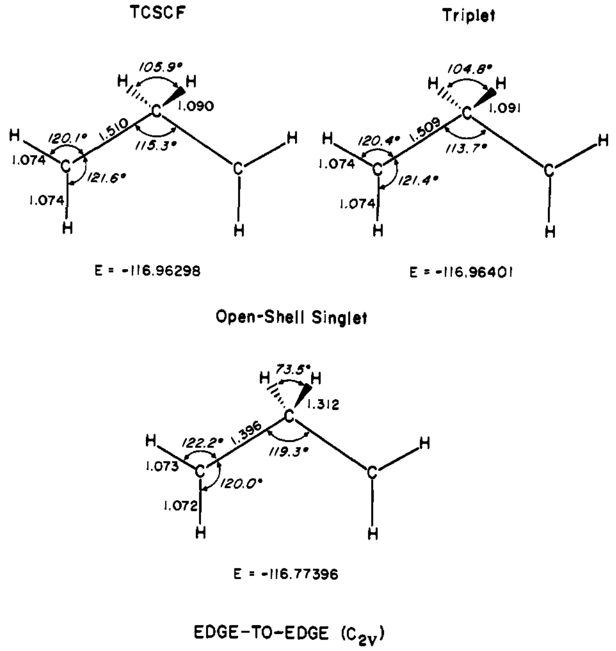

Figure 2. Predicted stationary point geometries for edge-to-edge [also called (0°,0°)] trimethylene. Bond distances are given in angstroms and energies in hartrees.

Table V. Vibrational Frequencies (cm^{-1}) of Edge-to-Face or (0°,90°) Trimethylene Diradicals (note that the central methylene group is labeled CH_{2A}, while the left-hand methylene group in Figure 3 is labeled CH_{2B})

approximate type of mode	$^3A''$ triplet	$^1A''$ open-shell singlet
a' ν_1 CH_{2B} a stretch	3442	3447
ν_2 CH_{2B} s stretch	3317	3321
ν_3 CH_{2C} s stretch	3312	3311
ν_4 CH_{2A} s stretch	3184	3184
ν_5 CH_{2A} scis	1641	1640
ν_6 CH_{2C} scis	1595	1594
ν_7 CH_{2B} scis	1580	1582
ν_8 CH_{2A} wag	1477	1486
ν_9 CC a stretch	1179	1180
ν_{10} CH_{2B} rock	1130	1142
ν_{11} CC s stretch	951	950
ν_{12} CH_{2C} wag	544	542
ν_{13} CCC deform	367	360
a'' ν_{14} CH_{2C} a stretch	3432	3431
ν_{15} CH_{2A} a stretch	3221	3220
ν_{16} CH_{2A} twist	1382	1384
ν_{17} CH_{2C} rock	1139	1134
ν_{18} CH_{2A} rock	836	835
ν_{19} CH_{2B} wag	351	333
ν_{20} torsion (CH_{2C} twist)	128	68
ν_{21} torsion (CH_{2B} twist)	148 i	155 i
energy, hartrees	−116.96429	−116.96125

In their earlier study[11b] Kato and Morokuma report a complete theoretical structure for the low-energy singlet state of E-E trimethylene, using a five-configuration SCF wave function in conjunction with a 4-31G basis set (slightly smaller than our standard DZ basis set). Kato and Morokuma note that the weights of the three configurations not included in the present study "are found to be less than a few percent". Thus it is not surprising that our TCSCF structure for E-E $(CH_2)_3$ is very similar to that of Kato and Morokuma. For example, the TCSCF C–C bond distance is 1.510 Å, while that of KM is 1.502 Å. The present stationary point geometry for *triplet* trimethylene is very similar to our TCSCF singlet structure, the largest difference (1.6°) being found for the C–C–C bond angle. The energies of the two stationary point geometries are also quite close, with the triplet lying 0.65 kcal lower. This energetic ordering is consistent with Doubleday, McIver, and Page's qualitative predictions.[25]

Both the triplet and low-energy singlet states of trimethylene are predicted in Table IV to have two imaginary vibrational frequencies for their E-E stationary points. This means that the energy is a maximum with respect to two degrees of freedom and

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(25) C. Doubleday, J. W. McIver, and M. Page, *J. Am. Chem. Soc.*, **104**, 6533 (1982).

(26) A. H. Goldberg and D. A. Dougherty, *J. Am. Chem. Soc.*, **105**, 284 (1983).

(27) For a helpful discussion, see P. B. Dervan and D. A. Dougherty, "Diradicals", W. T. Bordon, Ed., Wiley, New York, 1982, pp 107–149.

(28) See also J. J. Gajewski, "Hydrocarbon Thermal Isomerizations", Academic Press, New York, 1981, pp 27–35.

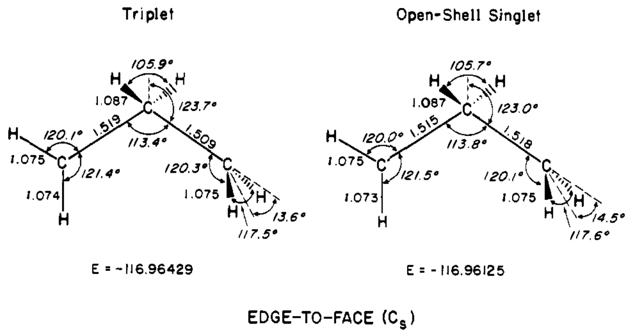

Figure 3. Predicted stationary point geometries for edge-to-face [also called (0°,90°)] trimethylene. Bond distances are given in angstroms and energies in hartrees.

a minimum with respect to the remaining 19 degrees of freedom. Not surprisingly, the two imaginary frequencies correspond to the conrotatory ($\nu_{11} = a_2$) and disrotatory ($\nu_{21} = b_2$) simultaneous rotations about the two carbon–carbon bonds. Note also that for both the triplet and low-energy singlet states, the magnitude of these frequencies is quite small, indicating the unusual flatness of the potential energy hypersurfaces with respect to these degrees of freedom.

Figure 3 and Table V summarize our results for E-F trimethylene. For this C_s geometry, the low-energy singlet state is the open-shell singlet state, here described by a single configuration. As noted by Doubleday, McIver, and Page,[25] the low-energy singlet state of E-F $(CH_2)_3$ may also be described as a linear combination of two closed-shell singlet configurations, *if* the MCSCF orbitals are themselves combinations of orbitals of different irreducible representations. For the E-F case, the conventional TCSCF wave function (constructed from symmetry-adapted molecular orbitals) describes the high-energy state, for which a complete geometry optimization was not attempted.

Our low-energy singlet structure in Figure 3 is in good agreement with that of Kato and Morokuma.[11b] The present C–C distances are slightly longer than those (1.502, 1.507 Å) of KM, but the ordering is the same. Also the present CCC angle of 113.8° agrees well with the 113.0° predicted by KM. There is no comparable theoretical prediction for the E-F triplet, and it is notworthy that the ordering of the two C–C bond distances (1.519, 1.509 Å) is reversed from the singlet low-energy structure. However, the other structural features of the triplet stationary point are very similar to those of the open-shell singlet.

Energetically, the E–F triplet is predicted to lie 1.91 kcal below the E-F low-energy singlet stationary point. Moreover, comparison of the total energies shows that the E-F triplet lies 0.18 kcal below the above-discussed E-E triplet. Inspection of Table V in fact shows the E-F triplet to be a true transition state, i.e., it has one imaginary vibrational frequency at the DZ SCF level of theory. Not surprisingly this reaction coordinate corresponds to rotation about the C–C bond to the left-hand (see Figure 3) terminal CH_2 group.

The low-energy E-F singlet (Figure 3) is also a transition state at the DZ SCF level of theory. This is consistent with the suggestion by Kato and Morokuma based on a limited number of calculations with broken symmetry. As noted earlier, the present work is the first to present explicit vibrational analyses for the different trimethylene stationary points.

Theoretical predictions for face-to-face (F-F) trimethylene may be seen in Figure 4 and Table VI. We were unable to locate a TCSCF stationary point for the low-energy singlet state. This does not mean that such a stationary point does not exist, although our efforts were more than casual. However, Kato and Morokuma[11b] were also unable to locate a minimum with respect to the terminal CH_2–terminal CH_2 separation.

The triplet F-F structure is a genuine transition state at the DZ SCF level of theory. Note, however, the exceedingly low vibrational frequency associated with the symmetric combination of CH_2 twisting motions about the two C–C single bonds. Note also that this is the highest lying energetically of the three triplet stationary points. It seems likely that there are several triplet relative minima of trimethylene, but of lower point group symmetry than the E-E (C_{2v}), E-F (C_s), and F-F (C_{2v}) conformations considered here. McIver's theoretical study[25] has emphasized the importance of triplet trimethylene, so a more detailed search for such potential minima may be in order.

Table VI. Vibrational Frequencies (cm^{-1}) of Face-to-Face or (90°,90°) Trimethylene Diradicals (note that the central methylene group is labeled CH_{2A})

approximate type of mode	$^3B_1$ triplet	$^1B_1$ open-shell singlet
a_1 ν_1 CH_{2B} s stretch	3316	3336
ν_2 CH_{2A} s stretch	3206	3138
ν_3 CH_{2A} scis	1642	1504
ν_4 CH_{2B} scis	1591	1540
ν_5 CC s stretch	1021	998
ν_6 CCC deform	561	426
ν_7 CH_{2B} wag	349	863
a_2 ν_8 CH_{2B} a stretch	3435	3489
ν_9 CH_{2A} twist	1421	1308
ν_{10} CH_{2B} rock	951	948
ν_{11} torsion (CH_{2B} twist)	27	385
b_1 ν_{12} CH_{2B} s stretch	3313	3333
ν_{13} CH_{2B} scis	1581	1519
ν_{14} CH_{2A} wag	1433	1263
ν_{15} CC a stretch	1157	1036 i
ν_{16} CH_{2B} wag	369	876
b_2 ν_{17} CH_{2B} a stretch	3439	3490
ν_{18} CH_{2A} a stretch	3254	3236
ν_{19} CH_{2B} rock	1293	1169
ν_{20} CH_{2A} rock	805	882
ν_{21} torsion (CH_{2B} twist)	101 i	196
energy, hartrees	−116.96234	−116.77389

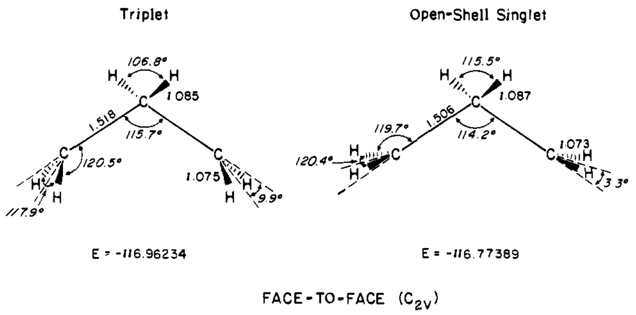

Figure 4. Predicted stationary point geometries for face-to-face [also called (90°,90°)] trimethylene. Bond distances are given in angstroms and energies in hartrees.

Concluding Remarks

Presented here is the theoretical formalism for the first implementation of analytic energy second derivatives for wave functions beyond the single-configuration Hartree–Fock approximation. The new method has been applied to two prototype diradicals, twisted ethylene and trimethylene. This work thus provides the first theoretical predictions of the vibrational frequencies of the lowest singlet and triplet states of these important species. Definitive results for these nonstandard electronic states will certainly require larger basis sets and a more complete treatment of electron correlation effects. Nevertheless, the present study gives a foundation from which one can move on to explore such problems in satisfactory detail.

Acknowledgment. This research was supported by the U.S. National Science Foundation, Grant CHE-8218785. We thank Mr. Douglas J. Fox, Dr. Michel Dupuis and Prof. Russell M. Pitzer for helpful discussions.

Registry No. Ethylene, 74-85-1; trimethylene diradical, 32458-33-6; cyclopropane, 75-19-4.