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Author
Schaefer, H.F.

Publication Date
1982-06-01

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OPEN-SHELL MOLECULAR WAVE FUNCTIONS

Paul Saxe, Yukio Yamaguchi, and Henry F. Schaefer III

June 1982

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Analytic Second Derivatives in Restricted Hartree-Fock Theory.

A Method for High-Spin Open-Shell Molecular Wave Functions

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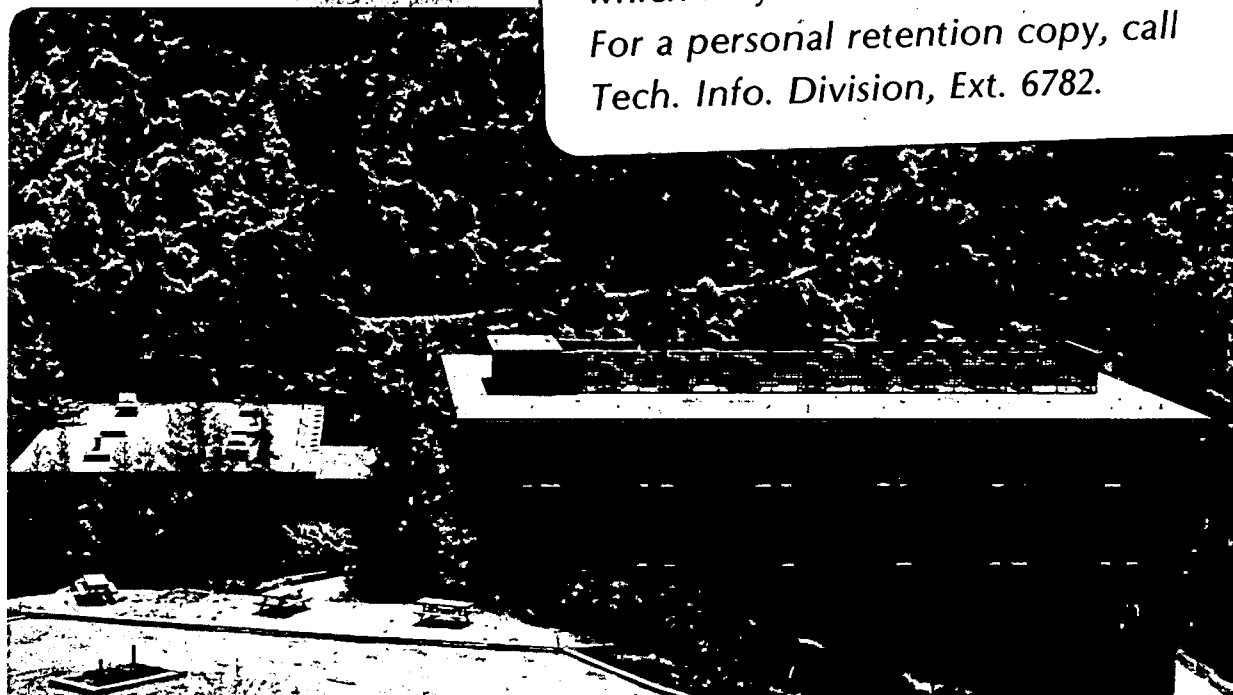Department of Chemistry and Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720

Abstract

Theoretical methods have been developed for the analytic determination of second energy derivatives (i.e., force constants) from restricted Hartree-Fock wave functions for certain types of open-shell systems. Specifically treated are systems for which all electrons outside closed shells have their spins parallel. Although the open shell formalism is somewhat complicated, its application, once implemented, is not greatly more arduous than the closed-shell theory presented in 1979 by Pople and coworkers. Like previous procedures for the evaluation of the second derivatives of electron repulsion integrals, the present method exploits the Rys polynomial concept. Beyond this general framework, however, significant departures appear, and these differences are described. Preliminary application of the new method has been to the two lowest triplet states of the formaldehyde molecule, for which both equilibrium geometry and harmonic vibrational frequencies have been evaluated.

Introduction

Electronic structure theorists are no longer content with variationally determining the energies of selected molecules at their equilibrium geometries.[1] The continuing progress in both theory and computation now allows much more complete ab initio studies to be undertaken for moderately large polyatomic systems.[2] However, the methods used in the past for the exploration and characterization of diatomic and triatomic potential energy surfaces are insufficient for the complicated hypersurfaces encountered with polyatomics.[3] Thus as methods and computers have become powerful enough for studies of polyatomic systems to be feasible, there has been a concomitant increase in interest in the analytic computation of the first and second derivatives[4] of the potential energy surface, in addition to the energy itself. This interest parallels the situation encountered with semi-empirical methods, which reached this stage some years ago,[5] inasmuch as semi-empirical calculations require less effort than their ab initio counterparts. First derivatives are particularly helpful in indicating in which direction to move on the potential energy surface when finding stationary points or following reaction paths.[6,7] Currently first derivatives also find extensive application in calculating second derivatives via finite difference methods;[8,9] of course, as analytic second derivative methods become widely available, this use will vanish. The second derivatives themselves are extremely useful, particularly since within local areas the potential energy surface is often approximately

quadratic .   The most direct use of the second derivative matrix is in the calculation of (harmonic) vibrational frequencies.[10] Additionally, as a tool for the theoretical chemist, the second derivatives are valuable in providing an indication of how large a step to take when following the gradients. Efficient algorithms to locate minima and transition states can be developed using the second derivative matrix.[11] Finally, having found a stationary point, the vibrational frequencies found for the second derivatives indicate whether the point is a minima, transition state, or some other type of stationary point.[12,13] It should be noted, of course, that normal coordinates for non-stationary points are also useful in that they give an accurate local representation of the potential.

Because of their value, much effort has gone into developing methods for the determination of first and second derivatives of the energy for different types of wavefunctions.[14-24] Starting with the formalism described in the late 1960's by Pulay,[14] it is now possible to calculate the first derivatives for almost any type of theoretical   scheme, from unrestricted Hartree-Fock[8] to Moller-Plesset second order[4] and configuration interaction methods.[20-24] These first derivative programs have been found to be economical to use, since the first derivatives can usually be found in only two or three times the time needed for a single energy point. By comparison, for a system with N atoms, finite differences would require 3N+1 or 6N+1 energy points using one- or two-point differences respectively.

Second derivative techniques are just beginning to emerge as a practical alternative to finite differences of first derivatives.[4] The ultimate goal, of course, is the analytic determination of

second derivatives from any type of wavefunction. The first

such calculation for a self-consistent-field (SCF) wavefunction

was reported in 1973 by Thomsen and Swanstrom[25] for the water

molecule. Unfortunately, the reported calculation serves as a

reminder that no matter how elegant the theory may be, it is of

limited value if the implementation requires an unreasonable amount

of computer time. Thomsen and Swanstrom's calculation took more

than 18 hours on a CDC-6400, and appeared to confirm the prevalent

view that the only practical scheme for the evaluation of the

second derivatives was through finite differences of first derivatives.

Undaunted by this example, Pople and coworkers[4] in 1979 reported a

method based on Rys polynomial techniques[26] for the evaluation of

the first and second derivative integrals, and could reproduce

Thomsen and Swanstrom's result[25] in perhaps half an hour on a

comparable computer. This factor of 30 in time made the difference

between an interesting theoretical result[25] and a powerful tool[4]

for the exploration of the complex potential energy surfaces of

polyatomic systems. For SCF wavefunctions only, a second derivative

calculation requires about three or four times as much work

as the first derivatives, while the finite difference approach

again requires at least 3N+1 first derivative calculations. The

savings are again considerable for polyatomic systems.

The second derivative method of Pople, Krishnan, Schlegel,

and Binkley[4] is applicable to single-determinant self-consistent-

field (SCF) wavefunctions within the unrestricted Hartree-Fock

(UHF) framework.[27] However, for some systems, particularly excited

electronic states, the restricted Hartree-Fock (RHF) formalism

of Roothaan[28] is preferable. The RHF method of course guarantees

that the resulting wavefunction will be an exact eigenfunction

of S^2. A provocative recent example of the failure of the UHF

method is the work of Bell[29] on the structure of nitrosyl cyanide,

$O=N-C\equiv N$. In that case the ground state UHF wavefunction is so

severely contaminated by the low-lying $^3A'$ state that an equilibrium

geometry in poor agreement with experiment is predicted. It must

be emphasized of course that such cases are exceptions, with the

UHF method proving quite acceptable for most ground state molecules.

Nevertheless, it is fair to say that the RHF method is probably

preferable to UHF for the theoretical treatment of most excited

electronic states. Therefore, in the present research, analytic

methods have been developed for the evaluation of energy second

derivatives for RHF wavefunctions.

General Theory

1. Review for Closed-Shell Systems (see also reference 4)

A closed-shell system can be described in terms of one Slater determinant at the SCF level of theory. The Fock operator in Roothaan's RHF theory[30] is given by

$$F = H + 2J - K \tag{1}$$

where H is the one-electron operator, while J and K are the Coulomb and exchange operators. The electronic energy for this system may be expressed as

$$E_{elec} = \sum_{i}^{d.o.} (h_{ii} + \varepsilon_i) \tag{2}$$

where h_{ii} and ε_i are the one-electron molecular integrals and orbital energies defined in the equation

$$\varepsilon_i = h_{ii} + \sum_{j}^{d.o.} \{2(ii|jj)-(ij|ij)\} \tag{3}$$

In Eq. (3), (ii|jj) and (ij|ij) are the standard Coulomb and exchange molecular integrals, and the abbreviation d.o. is meant to imply a summation over the doubly-occupied molecular orbitals.

The energy derivative of Eq. (2) with respect to a nuclear cartesian coordinate "a" may be given by

$$E_{elec}^{(a)} = (\frac{\partial E_{elec}}{\partial a}) = 2 \frac{\partial}{\partial a} \sum_{i}^{d.o.} h_{ii} + \frac{\partial}{\partial a} \sum_{i,j}^{d.o.} \{2(ii|jj)-(ij|ij)\} \tag{4}$$

The one-electron part [first summation in Eq. (4)] is explicitly given by

$$E_{one}^{(a)} = 2 \sum_{i}^{d.o.} h_{ii}^{a} + 4 \sum_{i}^{d.o.} \sum_{r}^{all} U_{ri}^{a} h_{ri} \qquad (5)$$

where U_{ri}^{a} is the first order change in the ith molecular orbital (MO). In Eq. (5), the one-electron derivative integrals h_{ii}^{a} are given by

$$h_{ii}^{a} = \sum_{\mu,\nu} c_{\mu}^{i} c_{\nu}^{i} \left(\frac{\partial h_{\mu\nu}}{\partial a}\right) \qquad (6)$$

where c_{μ}^{i} is the coefficient of the μth basis function in the ith MO.

The two-electron contribution is explicitly given by

$$E_{two}^{(a)} = \sum_{i,j}^{d.o.} \{2(ii|jj)^{a} - (ij|ij)^{a}\} + 4 \sum_{i}^{d.o.} \sum_{r}^{all} U_{ri}^{a} \sum_{j}^{d.o.} \{2(ri|jj) - (rj|ij)\}$$

$$(7)$$

In Eq. (7), each element of the first term, designated T_{i}^{a}, is obtained from

$$T_{i}^{a} = \sum_{j}^{d.o.} 2(ii|jj)^{a} - (ij|ij)^{a} = \sum_{\mu\nu} c_{\mu}^{i} c_{\nu}^{i} \sum_{j}^{d.o.} c_{\lambda}^{j} c_{\sigma}^{j} \{2 \frac{\partial}{\partial a} (\mu\nu|\lambda\sigma) - \frac{\partial}{\partial a} (\mu\lambda|\nu\sigma)\}$$

$$(8)$$

Combining Eqs. (5) and (7) leads to the following expression

for the first order energy derivative

$$E_{elec}^{(a)} = 2 \sum_i^{d.o.} h_{ii}^a + \sum_{i,j}^{d.o.} \{2(ii|jj)^a - (ij|ij)^a\} + 4 \sum_i^{d.o.} \sum_r^{all} U_{ri}^a \varepsilon_r \delta_{ri} \tag{9}$$

which is equivalent to

$$E_{elec}^{(a)} = \sum_i^{d.o.} (h_{ii}^a + \varepsilon_{ii}^a) + 4 \sum_i^{d.o.} \sum_r^{all} U_{ri}^a \varepsilon_r \delta_{ri} \tag{10}$$

In Eq. (10), ε_{ii}^a is defined as

$$\varepsilon_{ii}^a = h_{ii}^a + \sum_j^{d.o.} \{2(ii|jj)^a - (ij|ij)^a\} \tag{11}$$

The orthonormality condition for molecular orbitals provides the relationship

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0 \tag{12}$$

In Eq. (12), the overlap derivative integrals in terms of MO's are given straightforwardly as

$$S_{ij}^a = \sum_{\mu\nu} c_\mu^i c_\nu^j \left(\frac{\partial S_{\mu\nu}}{\partial a}\right) \tag{13}$$

Use of the relationship (12) simplifies the expression (10) to give a compact final result

$$E_{elec}^{(a)} = \sum_i^{d.o.} (h_{ii}^a + \varepsilon_{ii}^a) - 2 \sum_i^{d.o.} \varepsilon_i S_{ii}^a \qquad (14)$$

Similarly, we may obtain second derivatives of the Hartree-Fock energy by differentiating Eq. (14) with respect to a second variable "b". This leads to

$$E_{elec}^{(ab)} = \sum_i^{d.o.} (h_{ii}^{ab} + \varepsilon_{ii}^{ab}) + 4 \sum_i^{d.o.} \sum_r^{all} U_{ri}^b \varepsilon_{ri}^a$$

$$- 2 \sum_i^{d.o.} \varepsilon_i^{(b)} S_{ii}^a - 4 \sum_i^{d.o.} \sum_r^{all} \varepsilon_i U_{ri}^b S_{ri}^a$$

$$- 2 \sum_i^{d.o.} \varepsilon_i S_{ii}^{ab} \qquad (15)$$

where $\varepsilon_i^{(b)}$ are the derivatives of molecular orbital energies and quantities with superscript "ab" have similar definitions as in the first derivative case, i.e.,

$$h_{ii}^{ab} = \sum_{\mu\nu} c_\mu^i c_\nu^i \left(\frac{\partial^2 h_{\mu\nu}}{\partial a \partial b}\right) \qquad (16)$$

$$\varepsilon_{ii}^{ab} = h_{ii}^{ab} + T_i^{ab} \qquad (17)$$

$$T_i^{ab} = \sum_{\mu\nu} c_\mu^i c_\nu^i \sum_j^{d.o.} c_\lambda^j c_\sigma^j \{2 \frac{\partial^2}{\partial a \partial b}(\mu\nu|\lambda\sigma) - \frac{\partial^2}{\partial a \partial b}(\mu\lambda|\nu\sigma)\} \quad (18)$$

$$S_{ii}^{ab} = \sum_{\mu\nu} c_\mu^i c_\nu^i \left(\frac{\partial^2 S_{\mu\nu}}{\partial a \partial b}\right) \qquad (19)$$

In Eq. (15), the quantity ε_{ri}^a is defined in a manner analogous

to ε_{ii}^{a} in Eq. (11), namely

$$\varepsilon_{ri}^{a} = h_{ri}^{a} + \sum_{j}^{d.o.} \{2(ri|jj)^{a}-(rj|ij)^{a}\} \qquad (20)$$

In Eq. (15) the contribution from atomic orbital (AO) changes is given by the sum of first and last terms, while the contribution due to MO changes is reflected in the sum of second, third and fourth terms. The latter contribution can be evaluated using the results obtained by solving the coupled-perturbed Hartree-Fock equations.[4,31] By the same token, it is worthwhile to mention that the contribution due to MO changes can be calculated in the MO basis.

2. Open-Shell Systems

A high-spin system, with all electrons outside closed shells having parallel spins, may also be described in terms of one Slater determinant at the SCF level of theory. The Fock operator in Roothaan's open-shell RHF theory is there given by[28]

$$F = H + 2J_T - K_T + 2(M_T-K_0) \qquad (21)$$

where H is the one-electron operator, J_T and K_T are the total Coulomb and exchange operators, M_T is the total exchange coupling operator, and K_0 is the exchange operator for open shells.

The electronic energy for such an open-shell system is given by

$$E_{elec} = \sum_{k}^{d.o.} (h_{kk}+\varepsilon_k) + \frac{1}{2} \sum_{m}^{h.o.} (h_{mm} + \varepsilon_m)$$

$$- \sum_{k}^{d.o.} K_{kk} - \frac{1}{4} \sum_{m}^{h.o.} K_{mm} \qquad (22)$$

where ε_i are the orbital energies

$$\varepsilon_i = h_{ii} + \sum_{k}^{d.o.} \{2(ii|kk)-(ik|ik)\}$$

$$+ \sum_{m}^{h.o.} (ii|mm) - \frac{3-2f_i}{2} K_{ii} \qquad (23)$$

and f_i is the occupation number of ith molecular orbital. Similarly in Eq. (22) K_{ij} is the sum of exchange integrals over open shell MO's

$$K_{ij} = \sum_{m}^{h.o.} (im|jm) \qquad (24)$$

In an analogous manner to the closed-shell case, the first derivative expression for the open-shell system is expressed as

$$E_{elec}^{(a)} = (\frac{\partial E_{elec}}{\partial a}) = \sum_{k}^{d.o.} (h_{kk}^a+\varepsilon_{kk}^a) + \frac{1}{2} \sum_{m}^{h.o.} (h_{mm}^a+\varepsilon_{mm}^a)$$

$$- \sum_{k}^{d.o.} K_{kk}^a - \frac{1}{4} \sum_{m}^{h.o.} K_{mm}^a - \sum_{i,j}^{occ} W_{ij}S_{ij}^a \qquad (25)$$

where h_{ii}^a and S_{ij}^a have the meanings established in the previous section.

In Eq. (25) the quantities ϵ_{ij}^a, K_{ij}^a and W_{ij} are given by

$$\epsilon_{ij}^a = h_{ij}^a + \sum_k^{d.o.} \{2(ij|kk)^a - (ik|jk)^a\}$$

$$+ \sum_m^{h.o.} (ij|mm)^a - \frac{3-f_i-f_j}{2} K_{ij}^a \qquad (26)$$

$$K_{ij}^a = \sum_m^{h.o.} (im|jm)^a \qquad (27)$$

$$W_{ij} = f_i \epsilon_i \delta_{ij} - \frac{1}{2} f_i f_j K_{ij} \qquad (28)$$

The matrix W defined by Eq. (28) is usually called the Lagrangian matrix.[23,24]

The second derivatives of the energy can be obtained by differentiating Eq. (25) with respect to a second variable "b".

$$E_{elec}^{(ab)} = \sum_k^{d.o.} (h_{kk}^{ab} + \epsilon_{kk}^{ab}) + \frac{1}{2} \sum_m^{h.o.} (h_{mm}^{ab} + \epsilon_{mm}^{ab})$$

$$- \sum_k^{d.o.} K_{kk}^{ab} - \frac{1}{4} \sum_m^{h.o.} K_{mm}^{ab} + 2 \sum_i^{occ} \sum_r^{all} U_{ri}^b W_{ri}^a - \sum_i^{occ} \sum_j^{occ} W_{ij}^{(b)} S_{ij}^a$$

$$- \sum_i^{occ} \sum_j^{occ} \sum_r^{all} W_{ij} (U_{ri}^b S_{jr}^a + U_{rj}^b S_{ir}^a) - \sum_i^{occ} \sum_j^{occ} W_{ij} S_{ij}^{ab}$$

$$(29)$$

where h_{ij}^{ab} and S_{ij}^{ab} are defined in

Eqs. (16) and (19). In Eq. (29) W_{ij}^a and $W_{ij}^{(b)}$ are given by

$$W_{ij}^a = f_i \, \epsilon_{ij}^a - \frac{1}{2} f_i \, f_j \, K_{ij}^a \tag{30}$$

$$W_{ij}^{(b)} = f_i \, \epsilon_i^{(b)} \, \delta_{ij} - \frac{1}{2} f_i \, f_j \, K_{ij}^{(b)} \tag{31}$$

In Eq. (31), the $\epsilon_i^{(b)}$ are derivatives of orbital energies and the $K_{ij}^{(b)}$ are defined as

$$K_{ij}^{(b)} = \sum_r^{all} (U_{ri}^b K_{rj} + U_{rj}^b K_{ir})$$

$$+ \sum_r^{all} \sum_m^{h.o.} U_{rm}^b \{(ir|jm) + (im|jr)\} + K_{ij}^b \tag{32}$$

In Eq. (29) the contribution from AO changes is given by the sum of first, second, third, fourth and last terms, while the contribution due to MO changes is reflected in the sum of fifth, sixth, and seventh terms.

It is apparent from Eqs. (29)-(32) that the open-shell formulation of analytic energy second derivatives is far more intricate than the analogous closed-shell theory. Nevertheless, once the equations have been properly derived, the amount of effort required to obtain the second derivatives is of the same order of magnitude as for the simpler closed-shell case. Moreover, the coupled-perturbed Hartree-Fock equations (needed to obtain the first-order changes U^a in the molecular orbitals) are just those solved earlier in our treatment of analytic first derivatives for open shell CI wavefunctions.[23]

Evaluation of the Second Derivatives of Integrals over Basis Functions

The most time-consuming portion of the second-derivative determination for either the closed- or open-shell cases is the evaluation of the first- and second-derivatives of the two-electron integrals. Therefore, for the method as a whole to be successful these integrals must be evaluated rapidly. The calculation reported by Thomsen and Swanstrom for water,[25] where the evaluation of the various integrals took about 18 hours on a CDC-6400, illustrates the impracticality of a method based on an inefficient procedure for calculating integrals. The essential problem is that for a typical (i.e., having a fairly uniform distribution of basis functions over four or more atoms) poly-atomic system most two-electron integrals are four-center ones and thus have 12 first and 78 second derivatives. It is quite simple to use translational invariance to reduce the number of derivatives explicitly calculated to 9 and 45 and this is indeed done in all current programs. The further use of rotational invariance[32] could reduce this still further to 6 and 21, but the implementation of such a scheme is by no means trivial and although quite worthwhile, none of the current generation of methods exploit this reduction. The difficulty with calculating the first- and second-derivatives of the two-electron integrals is clear--there are a large number of them. If it takes anything like 45 or even 21 times as long as the integral evaluation portion of the ordinary SCF procedure, the method will require a prohibitive amount of effort.

The various derivatives of an integral are intimately related

and by treating entire shell-blocks of integrals simultaneously

using the Rys quadrature method,[26,33] one can indeed determine

all the first and second derivatives of the two-electron integrals

with only about ten times the effort required for the original,

undifferentiated integrals. The crucial aspect of the Rys

quadrature method for evaluating two-electron integrals over

gaussian functions is that each integral is given as a sum over

quadrature points of a product of three two-dimensional integrals

(I_x, I_y, I_z) and a quadrature weight factor (W_a):

$$(ij|kl) = \sum_{a=1}^{n} 2\sqrt{\frac{\rho}{\pi}} \ I_x(a) \ I_y(a) \ I_z^*(a) \ W_a \quad (33)$$

Each two-dimensional integral contributes to several integrals;

for instance, for four different F shells, (here the capital letter

F designates the collection of seven f orbitals with the same

radial dependence[34]) there are 256 two-dimensional integrals per

cartesian coordinate for seven quadrature points, and thus 5376

different two-dimensional integrals combine to form all 10,000

integrals in the shell-block.

Perhaps the simplest approach to calculating the derivatives

of the integrals is through linear combinations of undifferentiated

integrals over functions of different angular momentum. The

derivative of a gaussian of angular momentum n is a combination of

functions with momentum n+1 and n-1; thus for example the

derivatives with respect to the first center for an [FF|FF] integral

block can be computed from the corresponding [DF|FF] and [GF|FF]

blocks. However, for second derivatives this strategy is unsatisfactory for several reasons. The main difficulty is that in the interests of efficiency all the second derivatives should be evaluated simultaneously, but the core storage needed for the intermediate blocks of integrals may be prohibitive. For the example with four F shells, the required space amounts to about 250,000 intermediate integrals. A second drawback is that the algorithms devised for the combination of the intermediate integrals to form the second derivatives may waste considerable computation time locating the various intermediates and may not be as efficient as the method to be outlined here.

Because of these considerations we have elected to calculate directly the first- and second-derivative integrals without forming intermediate integrals. This approach is not in itself novel--it is the approach used in Pople's method,[4] for instance. The idea is to form "derivative" two-dimensional integrals which when combined as in Eq. (33) give the appropriate derivative integrals. These are not strictly the derivatives of the two-dimensional integrals since for convenience certain terms arising from the derivatives of exponentials will be added to the true derivatives of the two-dimensional integrals. The undifferentiated integral is given by:

$$(ij|kl) = \int_0^1 \sqrt{\frac{\rho}{\pi}}\ I_x I_y I_z^* \exp(-G)\ \exp(-Xt)^2 dt \qquad (34)$$

The quadrature of this integral leads to Eq. (33). Now if we differentiate (34) with respect to say x_i, we have:

$$\frac{\partial}{\partial x_i} \ (ij|kl) \ = \ \int\limits_0^1 \ 2\sqrt{\frac{\rho}{\pi}} \ [\frac{\partial I_x}{\partial x_i} - (\frac{\partial X}{\partial x_i} t^2 + \frac{\partial G}{\partial x_i})I_x] \ I_y I_z^* \ \exp(-Xt^2)dt$$

$$(35)$$

Defining a modified derivative two-dimensional integral I_x' as

$$I_x' \ = \ \frac{\partial I_x}{\partial x_i} - (\frac{\partial X}{\partial x_i} t^2 + \frac{\partial G}{\partial x_i}) \ I_x \qquad (36)$$

and using the quadrature method employed before, we have

$$\frac{\partial}{\partial x_i} \ (ij|kl) \ = \ \sum_{a=1}^{m'} \ 2\sqrt{\frac{\rho}{\pi}} \ I_x' I_y I_z W_a \qquad (37)$$

where the number of quadrature points needed may be one greater
than in Eq. (33). For each two-dimensional integral, we need
only derivatives with respect to three centers since the
derivatives with respect to the fourth can be generated using
translational invariance. Therefore to compute all derivatives
for a block of integrals we need the original three sets of two-
dimensional integrals in (33) and no more than nine sets of modified
derivatives. These are combined as in Eq. (37) using different
modified derivative two-dimensional integrals for each different
derivative. When we need the second-derivative integrals, these
modified first-derivative two-dimensional integrals are used in
27 of the 45 cases; the remaining 18 are constructed from modified
second-derivative two-dimensional integrals. For example, the

two-dimensional integral needed for the second derivative with respect to x_i is:

$$I_x'' = \frac{\partial^2 I_x}{\partial x_i^2} - 2\left(\frac{\partial X}{\partial x_i} t^2 + \frac{\partial G}{\partial x_i}\right) \frac{\partial I_x}{\partial x_i} + \left(\frac{\partial X}{\partial x_i} t^2 + \frac{\partial G}{\partial x_i}\right)^2 I_x \qquad (38)$$

This algorithm is quite efficient since all 9 first and 45 second derivatives are evaluated in exactly the same way, using the same array indices, etc.

There are several ways to evaluate the two-dimensional integrals needed; the approach outlined here is perhaps conceptually the simplest though not necessarily the most efficient algorithm. The undifferentiated ones are found using the recursion and transfer equations of Dupuis, et al.[34] Since the two-dimensional integrals are essentially polynomials the easiest way to obtain the derivatives is to differentiate the polynomials—or equivalently to differentiate the recursion and transfer equations. This leads to true derivatives, to which the extra terms in (35) and (38) can be added to yield the necessary modified derivatives. Again, this algorithm leads to the parallel evaluation of sets of 9 and 18 equations, which can be efficiently implemented on most types of computers.

In order to calculate the SCF second derivatives, there is no theoretical need to store the first- and second-derivative integrals. If sufficient central memory is available, they can be directly summed into the Fock-like matrices T^a of Eq. (8) (Fock matrices constructed with derivative AO integrals) and second-derivative

expression respectively. We currently take this approach, although other methods must be devised for larger cases and also for the second-order coupled perturbed Hartree-Fock (CPHF) procedure that is required for configuration interaction (CI) second derivatives. In our implementation, the first-derivative integrals over the contracted basis functions are actually constructed a block at a time and then used to form the Fock-like matrices. The second-derivatives over contracted gaussian functions are never formed; rather, each second-derivative integral over primitives is summed into the final second derivative expression as it is formed.

Molecular symmetry for D_{2h} and its subgroups is handled by the formalism of Dupuis as implemented in HONDO.[34] Indeed we gratefully thank M. Dupuis for allowing us to use several subroutines from HONDO and for guiding us in their use. Skeleton first- and second-derivative matrix contributions are formed from the petite list of integrals and then symmetrized to yield the correct contributions. The Fock-like matrices are handled in the same fashion. This approach to symmetry is ideally suited to the present application because a minimum number of integrals is calculated and then at the very end of the calculation of the derivative integrals, the various sets of matrices are symmetrized. Thus all computation associated with symmetry is removed from inside the loops over basis functions and contractions, and requires a negligible amount of time to complete.

To our knowledge, the only second derivative integral methods presently implemented are those of Pople[4] and Dupuis.[34] The method reported here has in common with these earlier developments the

exploitation of the Rys polynomial concept. The principal differences between the present method and that of Pople[4] are the approach to symmetry and to the evaluation of the modified derivative two-dimensional integrals. The use of recursion and transfer equations to generate these derivative integrals is unique to the present program. Pople's algorithm first generates the regular two-dimensional integrals using a scheme similar to the recursion and transfer equations, and then forms the modified derivative two-dimensional integrals from the regular ones. This step is computationally equivalent to our implementation, but is rather more complex and perhaps somewhat obscure. The program written by Dupuis, et al.[34] is radically different since the strategy employed is the formation of derivative two-electron integrals as combinations of undifferentiated integrals. This approach does not appear to offer any significant advantages and has a possible drawback in the amount of central storage needed to store the intermediate integrals.

Practical Overview

In light of the number of equations in the section above entitled "General Theory", it may be helpful to set out in plain terms the steps required to obtain analytic second derivatives for open-shell RHF wavefunctions. They are:

(1) Evaluate integrals over atomic orbitals (AO's), i.e., contracted gaussian basis functions.

(2) Obtain molecular orbitals (MO's) via standard open-shell restricted SCF procedures.[28]

(3) Evaluate the first and second derivatives of the AO integrals.

(4) Simultaneously, evaluate contributions of integral second derivatives to the different cartesian force constants via Eq. (29).

(5) Transform the AO integrals to the MO basis, via a standard four index transformation of two-electron integrals.

(6) Similarly transform the first derivative overlap [Eq. (13)] and Fock matrices [Eq. (26)] to the MO basis for use in the solution of the coupled perturbed Hartree-Fock (CPHF) equations.

(7) Obtain the elements of the A and B_0 matrices necessary for the CPHF equations.[23]

(8) Solve the simultaneous equations iteratively to obtain the MO changes U^a.

(9) Determine the electronic contribution to the second derivatives using Eq. (29).

Preliminary Applications

As a test case, we first considered the ethylene example reported by Pople, Krishnan, Schlegel, and Binkley (PKSB)[4] in their pioneering paper of three years ago. Their example involved the 6-31 G* basis set, which may be labeled C(10s 4p 1d/3s 2p 1d), H(4s/2s) in standard notation. This means that for ethylene there are 72 primitive gaussian functions and 38 contracted functions in the Pople basis set. PKSB reported timings for this test case on the Digital Equipment Corporation VAX-11/780 minicomputer with floating point accelerator.

Here the PKSB ethylene test case was repeated for a nearby (but not precisely the same) geometry on the Harris Corporation Series 800 minicomputer, estimated to be between 1.5 and 2.0 times the speed of the VAX in varying applications. A summary of the timing comparisons is given in Table I. Thus the two methods are seen to be roughly comparable. In the present work the ratio

$$\frac{\text{SCF plus first derivatives}}{\text{SCF energy only}} = 2.45 \tag{39}$$

while the further ratio

$$\frac{\text{SCF plus first and second derivatives}}{\text{SCF plus first derivatives}} = 3.34 \tag{40}$$

Both ratios are seen to strongly endorse the use of analytical derivative methods in molecular electronic structure theory.

The above timings beg the question "How long would it take to determine the force constants of ethylene via finite differences of analytic first derivatives?" Here of course a three-fold

reduction in effort is achieved by realizing that the cartesian

force constants of this six-atomic molecule may be related to

differences of first derivatives obtained for the unique atoms only,

i.e., one carbon and one hydrogen atom. Thus only nine first

derivative calculations (central differences of first derivatives

are necessary for accuracy in such cases) are actually required to

obtain the cartesian force constant matrix. However, of these nine

C_2H_4 calculations, none may be carried out in point group D_{2h}.

Specifically eight derivative calculations are carried out in point

group C_s and one gradient must be determined in point group C_1 (no

elements of symmetry except the identity). This is a significant point

because calculations in D_{2h} symmetry are significantly less time

consuming than those in the lower point groups. There are far more

unique nonzero integrals in the lower point groups and these require

not only computation but additional processing time in the SCF procedure.

Thus the finite difference determination of the force constant matrix

requires not nine times the effort to determine the forces but a

significantly larger multiplicative factor, perhaps 15. In this light

the factor of 3.34 obtained with the analytical second derivative

method is seen to represent a very significant advance.

The geometrical structures and vibrational frequencies of excited

electronic states of molecules are fundamentally important quantities

which are of difficult to determine experimentally.[35] Therefore it

was decided to consider two such cases, the two lowest triplet states

of formaldehyde, for preliminary application of the new open-shell

second derivative procedure. Ground state formaldehyde was previously

treated in an equivalent manner, but using only analytic first derivative methods.[36]

In C_{2v} symmetry, the ground state electron configuration of H_2CO is

$$^1A_1 \qquad 1a_1^2 \, 2a_1^2 \, 3a_1^2 \, 4a_1^2 \, 1b_2^2 \, 5a_1^2 \, 1b_1^2 \, 2b_2^2 \qquad (41)$$

while the lowest triplet state (traditionally designated $n \rightarrow \pi^*$) arises from[37] the single excitation $2b_2 \rightarrow 2b_1$

$$^3A_2 \qquad 1a_1^2 \, 2a_1^2 \, 3a_1^2 \, 4a_1^2 \, 1b_2^2 \, 5a_1^2 \, 1b_1^2 \, 2b_2 \, 2b_1 \qquad (42)$$

The second excited triplet state is usually labeled $\pi \rightarrow \pi^*$ and emanates from the $1b_1 \rightarrow 2b_1$ single excitation

$$^3A_1 \qquad 1a_1^2 \, 2a_1^2 \, 3a_1^2 \, 4a_1^2 \, 1b_2^2 \, 5a_1^2 \, 2b_2^2 \, 1b_1 \, 2b_1 \qquad (43)$$

It has long been known[38] that the first excited state of formaldehyde does not have a C_{2v} equilibrium geometry but rather a pyramidal (about carbon) C_s structure with the CH_2 plane making an angle of $\sim 38°$ with the CO internuclear axis. Thus the electron configuration for triplet formaldehyde is

$$^3A'' \qquad 1a'^2 \, 2a'^2 \, 3a'^2 \, 4a'^2 \, 5a'^2 \, 1a''^2 \, 6a' \, 2a'' \qquad (44)$$

We show here that the $\pi \rightarrow \pi^*$ triplet state of H_2CO has a comparable

structure, arising from the C_s electron configuration

$$^3A' \qquad 1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 1a''\ 2a'' \qquad (45)$$
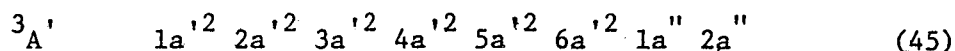
Standard Huzinaga-Dunning double zeta (DZ) and double zeta plus polarization (DZ+P) basis sets[39] were used here, the complete specification of the latter being C,O(9s 5p 1d/4s 2p 1d), H(4s 1p/ 2s 1p). Polarization function orbital exponents were $\alpha_d(C)$ = 0.80, $\alpha_d(O)$ = 0.8, $\alpha_p(H)$ = 1.0. Using analytic first and second energy derivatives, the geometrical structures of the lowest $^3A''$ and $^3A'$ electronic states of formaldehyde were quickly determined. Then a single second derivative calculation yielded all 78 cartesian force constants and hence the harmonic vibrational frequencies. These results are summarized in Table II. Note that the geometrical structures reported here are very similar to those of Bell,[40] and the reader is referred to Bell's paper for a discussion of the (relatively minor) differences between theory and experiment.

For the a' CH stretching frequency of the $^3A''$ state, the predicted DZ and DZ+P SCF harmonic frequencies are 115.3 and 113.7%, respectively, of the tentative experimental value, 2871 cm^{-1}. For comparison, the analogous ground state formaldehyde frequency predicted at the same two levels of theory is 115.9% and 113.2% of the observed fundamental.[9] Thus (for this CH stretching frequency) the lowest triplet state of formaldehyde displays the same relationship between theory and experiment as does the closed-shell ground state.

The predicted DZ+P SCF CO stretching frequency for the $n \to \pi^*$ triplet of formaldehyde is 1267 cm^{-1}, in very close agreement with the experimental values, which fall in the range 1240-1250 cm^{-1}. This is in contrast to the ground state comparison, where the DZ+P SCF prediction (1656 cm^{-1}) is 10.4% higher than the experimental C=O stretching frequency. Thus it may be that excited state theoretical predictions of vibrational frequencies are in less consistent agreement with experiment than is the case for closed-shell ground states.

Not surprising is the fact that the CH_2 pyramidalization frequency (924 cm^{-1} DZ+P SCF) is predicted to be about twice the fundamental frequency observed by Jones and Coon,[41] namely 452.8 cm^{-1}. The theoretical prediction refers to the harmonic frequency while the experimental frequency reflects the widely-discussed[41] anharmonicity associated with the $n \to \pi^*$ double minimum potential.

The remaining three vibrational frequencies of the $^3A''$ state and all six frequencies of $^3A'$ formaldehyde have not been determined in the laboratory. However, except for the highly anharmonic CH_2 wag (or pyramidalization motion) of the $^3A'$ state, all the DZ+P results are expected to be from zero to 12% greater than the true (unobserved) anharmonic frequencies.

Concluding Remarks

The formalism for the analytic determination of energy second derivatives from simple open-shell restricted Hartree-Fock wavefunctions has been spelled out in detail. The practical usefulness of these new techniques has been proven in a number of test cases. Specifically the comparison between theory and experiment for the vibrational frequencies of the lowest $n \to \pi^*$ triplet state of formaldehyde suggests that these methods will be very helpful is unraveling the properties of excited molecular electronic states.

One final advantage of analytic second derivatives is the precision afforded. An obvious test of this is provided by the six (five for linear molecules) residual frequencies remaining after the diagonalization of the 3Nx3N matrix of cartesian force constants. These residual frequencies correspond to the translational and rotational degrees of freedom of the molecule and should of course be identically zero. When the cartesian force constants are carefully calculated as finite differences of analytic first derivatives, the largest residual frequency is 51.0 cm^{-1} on our Harris Series 800 minicomputer (48 bit word length, 11 significant figures). Assuming that the stationary point has been precisely located, a residual of this magnitude is due to some combination of roundoff error and inappropriate central difference step sizes. However, when the cartesian force constants are determined analytically, the largest residual frequency is reduced to 1.5 cm^{-1}.

Acknowledgments

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Table I. Execution times for the SCF derivative programs (minutes) for ethylene using the 6-31G* basis set (38 contracted gaussians). Times are for the Harris 800, with those of PKSB[4] on the VAX 11/780 in parentheses.

Section	SCF Energy Only	SCF + First Derivatives	SCF + First and Second Derivatives
Integral evaluation	3.7 (10)	3.7 (10)	3.7 (10)
SCF iterations	0.4[a] (3)	0.4[a] (3)	0.4[a] (5)
Integral first derivatives	--	5.9 (7)	5.9 (16)
Two-electron integral transformation	--	--	1.0 (8)
Coupled-perturbed Hartree-Fock equations	--	--	2.8 (19)
Integral second derivatives	--	--	19.3 (31)
Total	4 (13)	10 (20)	33 (89)

[a]Time for 44 SCF iterations with method of R. M. Pitzer, Ohio State University.

Table II. Predicted equilibrium geometries and harmonic vibrational frequencies (cm^{-1}) for the two lowest triplet states of formaldehyde. Bond distances are given in angstroms.

	$^3A''$ $(n \to \pi^*)$			$^3A'$ $(\pi \to \pi^*)$	
	DZ SCF	DZ+P SCF	Experiment[a]	DZ SCF	DZ+P SCF
Energy (hartrees)	-113.77414	-113.81736	--	-113.74557	-113.78435
r_e(CO)	1.383	1.343	1.307±0.003	1.477	1.434
r_e(CH)	1.075	1.080	1.096±0.005	1.074	1.077
θ_e(HCH)	120.4°	118.5°	118.0 ± 1.0°	121.0°	119.1°
Out-of-plane angle	34.5°	39.2°	37.9°	32.0°	34.8°
Vibrational frequencies					
a' CH$_2$ symmetric-stretch	3309	3264	2871[a]	3320	3288
a' CH$_2$ scissor	1534	1542	--	1567	1590
a' C=O stretch	1170	1267	1240-1250[b,c]	1086	1176
a' CH$_2$ wag	812	924	452.8[b]	774	873
a" CH$_2$ asymmetric-stretch	3454	3390	--	3471	3420
a" CH$_2$ rock	1064	1066	--	1184	1232

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