

AB INITIO ENERGY DERIVATIVES CALCULATED ANALYTICALLY

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Abstract

The efficiency and accuracy of analytical differentiation in ab initio calculations are compared with the numerical approach. Formulae for computing integral derivatives are developed and the expression for the first derivative of the SCF energy is presented. The coupled-perturbed Hartree-Fock equations are solved for the first derivative of the molecular orbital coefficients. These are then used to calculate the second derivative of the SCF energy and the first derivatives of two energy schemes involving electron correlation: second order Møller-Plesset and all-doubles configuration interaction. Timing data indicate that as much as an order of magnitude increase in efficiency can be obtained through the use of derivative methods. Examples of geometry optimization and vibrational frequency calculation are given; additional applications to NMR magnetic shielding and electric polarizability are discussed briefly.

Introduction

To increase the efficiency of theoretical calculations, two general philosophies can be used:

- a) to perform the individual calculations faster, through the development of better algorithms and the use of higher speed computers or
- b) to extract more information from each calculation and to use that information effectively.

This chapter will be concerned with the latter approach applied to molecular orbital calculations. In particular, attention will be focused on computing energy derivatives analytically and using these energy derivatives in the determination of molecular structure and properties. The contents of this chapter follow closely a series of recent articles²⁻⁵ on the development and implementation of energy derivative methods. For details, the original work should be consulted.

A wide range of problems in quantum chemistry formally involves evaluation of derivatives of the electronic energy with respect to external parameters. Differentiation of the energy with respect to nuclear coordinates corresponds to calculation of forces and force constants determining nuclear motion. These nuclear displacement energy derivatives are important in the exploration of potential surfaces to find stationary points such as equilibrium structures and transition structures. Additional examples are the calculation of electric moments and polarizabilities (energy derivatives with respect to applied electric fields) and the calculation of magnetic properties such as diamagnetic susceptibilities and nuclear magnetic resonance chemical shifts (energy derivatives with respect to external and nuclear magnetic fields). A summary of the relation between these properties and energy derivatives is given in Table 1.

Energy derivatives could be calculated by a finite difference method of numerical differentiation. While it is easy to compute the energy $E(x)$ at two closely spaced points, and approximate the derivative by

$$\frac{\partial E(x)}{\partial x} \approx \frac{[E(x + \Delta x) - E(x)]}{\Delta x} \quad (1)$$

it is not very efficient if numerous first or higher derivatives are required. Nor is it accurate unless Δx is very small. An analytical differentiation is preferable if efficient algorithms can be devised.

Most of the work on first and second energy derivatives and associated properties has been carried out in conjunction with Hartree-Fock or single-determinant wave functions. The general theory of energy derivatives within this framework has been outlined by several authors. Bratoz⁶, Bishop *et al.*⁷ and Moccia⁸ have given analytical expressions for the first and second derivatives of the SCF energy for closed shells. Gerratt and Mills⁹ have outlined a perturbed Hartree-Fock theory to calculate one-electron second-order properties and have calculated force constants as the analytical derivative

TABLE 1
Molecular Properties as Energy Derivatives

	Coordinate	
	x = atom position	magnetic field
<u>First Derivative</u>	electric field	magnetic field
(dE/dx)	forces on the atoms in a molecule	dipole moment
		magnetic moment
<u>Second Derivative</u>		
(d ² E/dx ²)	force constants (vibrational frequencies)	dipole moment derivatives (infra red intensities)
y = atom position		dipole polarizability
electric field		
magnetic field		magnetic susceptibility
nuclear spin		magnetic shielding (NMR chemical shift)

of the Hellmann-Feynman force. Thomsen and Swanstrom¹² have analytically calculated the full second-derivatives of the energy for H₂O with a gaussian basis set. However, major applications to the computation of force constants have been with the force method of Pulay.^{10,11} In the force method the forces are obtained analytically and these are then differentiated numerically to obtain the force constants. This method has been used to calculate the force fields of a variety of molecules by Pulay and Meyer¹³⁻¹⁵ and by Schlegel, Wolfe and Bernardi.¹⁶⁻¹⁸ Ishida, Morokuma and Komornicki¹⁹ have used analytical energy derivatives to study reactions paths. Only a limited amount of work on energy derivatives has been carried out with wavefunctions beyond the Hartree-Fock level, most by the finite difference method,²⁰⁻²³ but a few with the analytical method.²⁴

The following sections outline methods for calculating the integrals and their derivatives, as well as various energies and their derivatives, in the manner that is implemented in the Carnegie-Mellon version of GAUSSIAN 80.³⁰

Wavefunctions

The Hartree-Fock wavefunction for an n-electron molecule can be written as a single determinant,

$$\psi_{\text{HF}} = (n!)^{-1/2} |x_1 x_2 \dots x_n| \quad (2)$$

where $x_1, x_2 \dots x_n$ are a set of orthonormal spinorbitals (one-electron functions of cartesian and spin coordinates). Wavefunctions that include electron correlation can be constructed from linear combinations of such determinants. The spinorbitals are written as linear combinations of a set of basis functions ω_μ ,

$$x_p = \sum_{\mu} C_{\mu p} \omega_{\mu} \quad (3)$$

Normally the ω_μ will be products of a set of cartesian coordinate basis functions ϕ_1, ϕ_2, \dots and the spin-functions α and β . If there are N ϕ -type functions, there will be 2N spinorbital basis functions ω_μ , viz. $\phi_1\alpha, \phi_1\beta, \phi_2\alpha \dots \phi_N\beta$. In turn, each of the cartesian basis functions is usually expressed as fixed linear combination of normalized gaussian type primitives

$$\phi_{\mu} = \sum_k \xi_{k\mu} g_k \quad (4)$$

Each primitive function is written as a polynomial times a spherical gaussian

$$g_a(\vec{l}_A, \vec{r}_A, \alpha) = N_a x_A^{l_{Ax}} y_A^{l_{Ay}} z_A^{l_{Az}} \exp(-\alpha |\vec{r}_A|^2) \quad (5)$$

where $\vec{l}_A = (l_{Ax}, l_{Ay}, l_{Az})$, $\vec{r}_A = \vec{r} - \vec{A} = (x_A, y_A, z_A)$, \vec{r} is the electron coordinate, N_a is the normalization coefficient, and $\vec{A} = (A_x, A_y, A_z)$, the gaussian center.

The gaussian centers are chosen to follow the nuclei rigidly. Thus, the basis functions depend on the nuclear coordinates directly. In the calculation of properties such as polarizability or magnetic shielding, there are significant advantages to be obtained by including an explicit dependence on the electric or magnetic field in the basis function.^{8,25,26} For example:

$$g_a^E = e^{-k \vec{E} \cdot \vec{r}} g_a \quad (6)$$

$$g_a^M = e^{-i \vec{H} \times \vec{r}_A \cdot \vec{r}} g_a \quad (7)$$

The higher order gaussians can also be expressed as derivatives of the corresponding spherical gaussian

$$g_a(\vec{l}_A, \vec{r}_A, \alpha) = M^{\hat{l}_{Ax}} M^{\hat{l}_{Ay}} M^{\hat{l}_{Az}} g_a(\vec{0}, \vec{r}_A, \alpha) \quad (8)$$

$$\text{where } M^{\hat{l}_{Ax}} = 1 \quad \text{for } l_{Ax} = 0 \quad (9)$$

$$= \frac{1}{2} \alpha \frac{\partial}{\partial A_x} \quad \text{for } l_{Ax} = 1 \quad (10)$$

$$\text{and } M^{\hat{l}_{Ax} + 1} = \frac{1}{2\alpha} M^{\hat{l}_{Ax}} \frac{\partial}{\partial A_x} + \frac{l_{Ax}}{2\alpha} M^{\hat{l}_{Ax} - 1} \quad (11)$$

$M^{\hat{l}_{Ay}}$ and $M^{\hat{l}_{Az}}$ are defined similarly. These relations are useful for the development of integral derivative expressions.

Integrals

The calculation of total energies for electronic wavefunctions can be divided into two parts,

- a) computing the integrals over the basis functions of the necessary one and two electron operators in the Hamiltonian and
- b) manipulating these integrals to determine the appropriate linear combination coefficients and energy.

To determine the energy, we must first compute the following terms:

the overlap integrals

$$S_{\mu\nu} = \int \omega_{\mu}^* \omega_{\nu} d\tau \quad (12)$$

the Core-Hamiltonian integrals

$$H_{\mu\nu} = \int \omega_{\mu}^* \hat{H}^{\text{core}} \omega_{\nu} d\tau \quad (13)$$

and the two-electron integrals

$$\begin{aligned} (\mu\lambda || \nu\sigma) &= \iint \omega_{\mu}^*(1) \omega_{\lambda}^*(2) (1/r_{12}) \\ &\quad [\omega_{\nu}(1) \omega_{\sigma}(2) - \omega_{\sigma}(1) \omega_{\nu}(2)] d\tau_1 d\tau_2 \quad (14) \\ &= (\mu\nu | \lambda\sigma) - (\mu\sigma | \lambda\nu) \end{aligned}$$

where \hat{H}^{core} is the one-electron core Hamiltonian (kinetic energy + potential energy in the electrostatic field of the nuclei). The two-electron operator in (14) is the inter-electronic repulsion energy. Note that $(\mu\lambda || \nu\sigma)$ is antisymmetric in both the pairs $\mu\lambda$ and $\nu\sigma$.

The integrals over the basis functions are composed of integrals over the gaussian primitives. The overlap and kinetic energy integrals are relatively simple²⁹ and will not be considered here. The nuclear-electron attraction integrals can be treated as a special case of the two electron integrals discussed below.

The evaluation of the two electron integrals is the most time consuming part of the integral step in ab initio computations. Although the use of gaussian functions permits each

individual integral to be computed relatively rapidly, there are ca. N^4 integrals that must be calculated (where N is the number of primitives in the basis set). Thus, considerable attention has been paid to developing schemes to compute two electron integrals rapidly.

The general two electron integral involving four primitives on different centers can be denoted as:

$$(\vec{l}_A \vec{l}_B | \vec{l}_C \vec{l}_D) = \iint g_a(\vec{l}_A \vec{r}_A(1) \alpha) g_b(\vec{l}_B \vec{r}_B(1) \beta) \frac{1}{|\vec{r}(1) - \vec{r}(2)|} g_c(\vec{l}_C \vec{r}_C(2) \gamma) g_d(\vec{l}_D \vec{r}_D(2) \delta) dr_1 dr_2 \quad (15)$$

For efficiency in the evaluation of the integrals, the gaussians can be arranged in shells²⁸ such that all gaussians within a shell share the same exponent, but differ in the polynomial factor (e.g. and s type and three p type gaussians with the same exponent are used to form the 2sp shell of an STO-3G basis set). The collection of all two electron integrals in a product of four shells is termed a shell block (256 integrals for 4 sp type shells). When these are evaluated together, substantial savings in computation can be achieved since the integrals share a great deal of common information. For 1s spherical gaussians, the general 4 center two electron integral is:

$$(\vec{0}, \vec{0} | \vec{0}, \vec{0}) = (ss | ss) = N_{abcd} \theta F_0(\rho PQ^2) \exp(-uAB^2) \exp(-vCD^2) \quad (16)$$

where $p = \alpha + \beta$ $q = \gamma + \delta$ $\rho = pq/(p + q)$

$\theta = 2\pi^{5/2}/(pq \sqrt{p + q})$ $u = \alpha\beta/(\alpha + \beta)$ $v = \gamma\delta/(\gamma + \delta)$

$AB^2 = |\vec{A} - \vec{B}|^2$ $CD^2 = |\vec{C} - \vec{D}|^2$ $PQ^2 = |\vec{P} - \vec{Q}|^2$

$\vec{P} = (\alpha\vec{A} + \beta\vec{B})/p$ $\vec{Q} = (\gamma\vec{C} + \delta\vec{D})/q$

and

$$N_{abcd} = N_a N_b N_c N_d$$

The function $F_m(t)$ is closely related to the error function, and has the properties

$$F_m(t) = \int_0^1 u^{2m} \exp(-tu^2) du$$

$$\frac{dF_m(t)}{dt} = -F_{m+1}(t). \quad (17)$$

Two electron integrals over other types of gaussians can be derived integrating eq. (15) directly. Alternatively, the derivative operators used in eq. (8) to construct higher order gaussians can be applied to the two electron integrals over spherical gaussians,

$$\begin{aligned} (\vec{\ell}_A \vec{\ell}_B | \vec{\ell}_C \vec{\ell}_D) &= \left(\prod_{U=ABCD} \hat{M}^{U i} \right) (ss | ss) \\ &\quad i=xyz \\ &= \hat{M}(\omega) (ss | ss) \end{aligned} \quad (18)$$

There are a number of ways to expand eq. (18) to facilitate computation. For example, an expression can be obtained as a sum of terms containing $F_m(t)$ and angular factors,²⁹

$$\begin{aligned} (\vec{\ell}_A \vec{\ell}_B | \vec{\ell}_C \vec{\ell}_D) &= \sum_{m=0}^{m_{\max}} C_x^m C_y^m C_z^m F_m(t) \\ m_{\max} &= |\vec{\ell}_A| + |\vec{\ell}_B| + |\vec{\ell}_C| + |\vec{\ell}_D| \end{aligned} \quad (19)$$

The C_x^m 's depend on the exponents and only the x components of the gaussian coordinates and angular momenta; similarly for the C_y^m 's and C_z^m 's. Rotation to an intermediate, local axis system²⁸ can force many of the integrals in a shell block to be zero and also simplify the C^m 's. The net gain in speed is substantial, as demonstrated by the GAUSSIAN programs³⁰ which use this scheme to evaluate sp two electron integrals.

An alternate approach recently developed by Dupuis, Rys and King³¹ is especially efficient for higher angular momentum basis functions. Exploiting the properties of the Rys polynomials, they have used numerical integration techniques to derive an exact, analytical formula for the two electron integral:

$$(\vec{l}_A \vec{l}_A | \vec{l}_C \vec{l}_D) = \sum_{n=1}^{n_{\max}} IP_x(t_n) IP_y(t_n) IP_z(t_n) \omega_n \quad (20)$$

$$n_{\max} > (|\vec{l}_A| + |\vec{l}_B| + |\vec{l}_C| + |\vec{l}_D|)/2$$

and

$$IP_x = \exp(\rho PQ_x^2 t_n^2) \cdot (1 - t_n^2)^{-1/2} \\ \iint dx(1) dx(2) x_A(1)^{l_{Ax}} x_B(1)^{l_{Bx}} x_C(2)^{l_{Cx}} x_D(2)^{l_{Dx}} \\ \exp(-\alpha x_A(1)^2 - \beta x_B(1)^2 - \gamma x_C(2)^2 - \delta x_D(2)^2 \\ - t_n^2(x(1) - x(2))/(1 - t_n^2))$$

The t_n and ω_n are the roots and weights of the Rys polynomials, which have the property

$$F_m(X) = \sum_n t_n^{2m} \omega_n \exp(-X t_n^2)$$

Like the C_x^m 's, IP_x depends only on the x components of the gaussian coordinates and the angular momenta. The Rys polynomial approach offers two advantages:³¹

- a) the sum in eq. (20) contains only half as many terms as the sum in eq. (19)
- b) the small number of IP integrals can be evaluated readily.

For integrals involving d orbitals, the Rys polynomial method becomes the preferred approach.

Integral Derivatives

To compute energy derivatives analytically, we must first calculate the corresponding derivatives of the one and two electron integrals over the basis functions, and hence over the primitive gaussians. The first derivative with respect to the gaussian center is

$$\frac{dg_a}{dA_x}(\vec{l}_A, \vec{r}_A, \alpha) = 2 \alpha g_a(\vec{l}_A^{+1}, \vec{r}_A, \alpha) - l_{Ax} g_a(\vec{l}_A^{-1}, \vec{r}_A, \alpha) \quad (21)$$

where $\vec{l}_A^{\pm 1} = (l_{Ax} \pm 1, l_{Ay}, l_{Az})$

and the second derivative is

$$\begin{aligned} \frac{d^2 g_a}{dA_x^2}(\vec{l}_A, \vec{r}_A, \alpha) &= 4\alpha^2 g_a(\vec{l}_A^{+2}, \vec{r}_A, \alpha) - (2l_{Ax} + 1) g_a(\vec{l}_A, \vec{r}_A, \alpha) \\ &\quad + l_{Ax}(l_{Ax} - 1) g_a(\vec{l}_A^{-2}, \vec{r}_A, \alpha) \end{aligned} \quad (22)$$

where $\vec{l}_A^{\pm 2} = (l_{Ax} \pm 2, l_{Ay}, l_{Az})$

For gaussians depending explicitly on the electric or magnetic field, derivatives with respect to the field can be expressed in terms of derivatives with respect to the gaussian centers.^{25,27} Thus it is sufficient to limit the discussion of integral derivatives to differentiation with respect to the gaussian function centers. Two different approaches can be taken to evaluate two electron integral derivatives.

a) Using Higher Angular Momentum Basis Functions

From eq. (21), the two electron integral derivative with respect to the x component of the gaussian at center A can be written as

$$\frac{\partial}{\partial A_x} (\vec{l}_A, \vec{l}_B | \vec{l}_C, \vec{l}_D) = 2\alpha (\vec{l}_A^{+1}, \vec{l}_B | \vec{l}_C, \vec{l}_D) - l_{Ax} (\vec{l}_A^{-1}, \vec{l}_B | \vec{l}_C, \vec{l}_D) \quad (23)$$

Similar expressions can be written for second derivatives. This approach leads to a relatively simple form for the derivatives provided integrals over the higher angular momentum functions are available. The analogues of eq. (23) for one electron integrals may be quite practical since one electron integrals for higher angular momentum gaussians can be calculated easily. However, for two electron integrals, the additional calculations involving the higher angular momentum functions are significantly more difficult to program and more costly to evaluate. Gradient calculations using this method are several times slower than the energy calculation alone, even when special steps are taken to optimize the derivative evaluation.

b) Avoiding Higher Angular Momentum Basis Functions

To compute the first derivative of the Hartree-Fock energy, the individual integral derivatives are not required explicitly, but can be combined with appropriate elements of the density matrix and summed. An algorithm can be constructed that takes advantage of this fact, while avoiding the use of code for higher angular momentum functions.²

For the two electron integral over spherical gaussians, eq. (16), the derivatives with respect to a cartesian component of a gaussian center, R_i ($R=A,B,C,D$; $i=x,y,z$), can be written as

$$\begin{aligned} \frac{d(ss|ss)}{dR_i} &= -\left(u \frac{d\overline{AB}^2}{dR_i} + v \frac{d\overline{CD}^2}{dR_i}\right) N_{abcd} \theta F_0(\rho\overline{PQ}^2) \exp(-u\overline{AB}^2) \exp(-v\overline{CD}^2) \\ &\quad \rho - \frac{d\overline{PQ}^2}{dR_i} N_{abcd} \theta F_1(\rho\overline{PQ}^2) \exp(-u\overline{AB}^2) \exp(-v\overline{CD}^2) \\ &= \Lambda(R_i) (ss|ss) + \Lambda'(R_i) (ss|ss)' \end{aligned} \quad (24)$$

where $(ss|ss)'$ is $(ss|ss)$ with F_n replaced by F_{n+1} , Λ and Λ' are linear functions of \vec{A} , \vec{B} , \vec{C} and \vec{D} .

The fact that the expression for a derivative has two similar terms, each of which is closely related to the integral, can be used to considerable advantage in obtaining expressions for higher angular momentum gaussians. As with the integrals themselves, the integral derivatives for higher angular momentum gaussians can be obtained by applying the operators \hat{M} to eq. (24)

$$\begin{aligned} \frac{d}{dR_i} (\vec{\ell}_A \vec{\ell}_B | \vec{\ell}_C \vec{\ell}_D) &= \frac{d}{dR_i} \hat{M}(\omega) (ss|ss) \\ &= \hat{M}(\omega) \frac{d}{dR_i} (ss|ss) \\ &= \hat{M}(\omega) (R_i) (ss|ss) + \hat{M}(\omega) (R_i)' (ss|ss)' \end{aligned} \quad (25)$$

Both parts of this expression for the integral derivative can be expanded in terms of the integral itself and integrals over lower angular momentum functions. Furthermore, much of the code for computing the primed and unprimed quantities is the same as needed for the original integral.

The first derivative of the Hartree-Fock energy does not require the integral derivatives individually (see below). Instead, they can be combined directly with the appropriate density matrix elements, denoted by $\mathbf{P}(\omega)$ in eq. (26), and summed. The special form of eq. (25) permits a great deal of factoring and simplification when the contributions of an entire shell block to all of the derivatives are computed at one time.

block

$$\begin{aligned} & \sum_{\omega} \mathbf{P}(\omega) d(\vec{l}_A \vec{l}_B | \vec{l}_C \vec{l}_D) / dA_x \\ & = \Lambda [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A \vec{l}_B | \vec{l}_C \vec{l}_D)] + \Lambda_A [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A^{-1} \vec{l}_B | \vec{l}_C \vec{l}_D)] \\ & \quad + \Lambda_B [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A \vec{l}_B^{-1} | \vec{l}_C \vec{l}_D)] + \Lambda' [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A \vec{l}_B | \vec{l}_C \vec{l}_D)'] \\ & \quad + \Lambda'_A [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A^{-1} \vec{l}_B | \vec{l}_C \vec{l}_D)'] + \Lambda'_B [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A \vec{l}_B^{-1} | \vec{l}_C \vec{l}_D)'] \\ & \quad + \Lambda'_C [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A \vec{l}_B | \vec{l}_C^{-1} \vec{l}_D)'] + \Lambda'_D [\sum_{\omega} \mathbf{P}(\omega) (\vec{l}_A \vec{l}_B | \vec{l}_C \vec{l}_D^{-1})'] \quad (26) \end{aligned}$$

where

$$\Lambda = \Lambda(A_x)$$

$$\Lambda_A = -1/2 \alpha \quad \partial \Lambda / \partial A_x$$

and

$$\vec{l}_A^{-1} = (l_{Ax}^{-1}, l_{Ay}, l_{Az}), \text{ etc.}$$

Such a scheme has been implemented for s and p gaussians and has proven to be one of the fastest algorithms for integral derivatives² of this type. This approach has also been applied to exponent derivatives² but it has not been practical to extend the method to include d orbitals.

The Rys polynomial method can also be adapted to the computation of first and second derivatives for s, p and d gaussians. Also, there is no particular disadvantage to computing each integral derivative individually. As will be seen below, the first derivatives of the integrals are required explicitly for the differentiation of correlated wavefunctions and the calculation of Hartree-Fock second derivatives. The first derivative is given by

$$\frac{d}{dA_x} (\vec{l}_A \vec{l}_B | \vec{l}_C \vec{l}_D) = \sum_{n=1}^{n_{\max}} IP'_x(t_n) IP_y(t_n) IP_z(t_n) \omega_n \quad (27)$$

$$n_{\max} > (|\vec{l}_A| + |\vec{l}_B| + |\vec{l}_C| + |\vec{l}_D| + 1)/2$$

$$IP'_x(t_n) = dIP_x(t_n)/dA_x$$

The $IP'(t_n)$ can be expressed in terms of the t_n and the IP 's for only the same and lower angular momenta. Similar formulae can be derived for the second derivatives.

Energies

In terms of the one and two electron integrals over the basis functions, the Hartree-Fock energy can be written (in the unrestricted formalism) as

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\lambda | | \nu\sigma) + V_{\text{nuc}} \quad (28)$$

where $P_{\mu\nu}$ is the spinorbital density matrix defined by

$$P_{\mu\nu} = \sum_{i=1}^n C_{\mu i}^* C_{\nu i} \quad (29)$$

and V_{nuc} is the nuclear-nuclear repulsion. Note that the sums over greek suffixes in eq. (28) and elsewhere in this section are over the $2N$ spinorbital basis functions. Thus $P_{\mu\nu}$ are elements of a $2N \times 2N$ matrix. With separate α - and β -type orbitals, this matrix will be blocked with $N \times N$ α - and β -parts and no $\alpha\beta$ interaction elements. Orthonormalization of the spinorbitals must be retained and requires the condition

$$\sum_{\mu\nu} C_{\mu p}^* S_{\mu\nu} C_{\nu q} = \delta_{pq} \quad (30)$$

Minimization of the Hartree-Fock energy with respect to the linear coefficients $C_{\mu p}$ (subject to the orthonormality conditions) leads to the Fock type equations

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_p S_{\mu\nu}) C_{\nu p} = 0 \quad (31)$$

Here $F_{\mu\nu}$ is the $2N \times 2N$ Fock matrix

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\lambda || \nu\sigma) \quad (32)$$

and ϵ_p is the one-electron energy of the p -th spinorbital. These are the Hartree-Fock self-consistent equations. For UHF theory they separate into two sets of coupled equations for the α - and β -spinorbitals.

Equations (31) will be soluble for $2N$ possible values of the one-electron energy ϵ_p , only n of which will correspond to occupied molecular spinorbitals. It is convenient to use suffixes i, j, k ($=1, 2, \dots, n$) for occupied spinorbitals and a, b, c, \dots ($=n+1, \dots, 2N$) for the remainder (usually described as virtual spinorbitals). We shall continue to use p, q, r, \dots for the entire set of $2N$ spinorbitals. It is convenient to define matrix elements with respect to the spin orbitals. The notation for matrix elements is

$$H_{pq} = \int \chi_p^* H^{\text{core}} \chi_q d\tau = \sum_{\mu\nu} C_{\mu p}^* C_{\nu q} H_{\mu\nu} \quad (33)$$

$$\begin{aligned} (pq || rs) &= \iiint \chi_p^*(1) \chi_q^*(2) \left(\frac{1}{r_{12}} \right) [\chi_r(1) \chi_s(2) - \chi_s(1) \chi_r(2)] d\tau_1 d\tau_2 \\ &= \sum_{\mu\nu\lambda\sigma} C_{\mu p}^* C_{\nu q}^* C_{\lambda r} C_{\sigma s} (\mu\nu || \lambda\sigma) \end{aligned} \quad (34)$$

Thus, the expression for the Hartree-Fock energy becomes

$$E_{\text{HF}} = \sum_{i=1}^n H_{ii} + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n (ij || ij) + V_{\text{nuc}} \quad (35)$$

To go beyond the Hartree-Fock approximation, the electronic wavefunction can be constructed from a linear combination of determinants. If we limit ourselves to double excitations from the Hartree-Fock reference determinant then the unnormalized wavefunction can be written as

$$\psi_{\text{corr}} = \sum_s a_s \psi_s = \psi_{\text{HF}} + \frac{1}{4} \sum_{ijab} a_{ij}^{ab} \psi_{ij}^{ab} \quad (36)$$

where ψ_{ij}^{ab} is a determinant in which the spinorbitals χ_i and χ_j are replaced by spinorbitals χ_a and χ_b respectively. The coefficients a_{ij}^{ab} and the energy corresponding to ψ_{corr} can be computed variationally or by perturbation theory.

Second order Møller-Plesset perturbation theory³² leads to

$$a_{ij}^{ab} = -(ij||ab) / \Delta_{ij}^{ab} \quad (37)$$

and a total energy of

$$E_{MP2} = E_{HF} - \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{virt} (ij||ab)^2 (\Delta_{ij}^{ab})^{-1} \quad (38)$$

where

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \quad (39)$$

Once the Hartree-Fock equations are solved for the coefficients $C_{\mu p}$, the matrix elements $(ij||ab)$ are easily obtained and eq. (38) then gives an easily computable expression for the total energy including correlation.

Calculation of a_{ij}^{ab} variationally results in a configuration interaction wavefunction which includes double excitations, Ψ_{CID} . The energy E_{CID} is given by the expectation value

$$E_{CID} = \langle \Psi_{CID} | \hat{H} | \Psi_{CID} \rangle / \langle \Psi_{CID} | \Psi_{CID} \rangle$$

$$= \sum_{st} a_s \mathcal{H}_{st} a_t / \sum_s a_s^2 \quad (40)$$

$$= \sum_{abij} a_{ij}^{ab} ((E_{HF} + \Delta_{ij}^{ab}) a_{ij}^{ab} + w_{ij}^{ab}) / \sum_{abij} (a_{ij}^{ab})^2 \quad (41)$$

The a_{ij}^{ab} are obtained by the iterative solution of:

$$a_{ij}^{ab} = w_{ij}^{ab} / (E_{CID} - E_{HF} - \Delta_{ij}^{ab}) \quad (42)$$

where

$$w_{ij}^{ab} = (ab||ij) + \frac{1}{2} \sum_{cd} (ab||cd) a_{ij}^{cd} + \frac{1}{2} \sum_{kl} (kl||ij) a_{kl}^{ab}$$

$$+ \sum_{kc} [- (kb||jc) a_{ik}^{ac} + (ka||jc) a_{ik}^{bc} - (ka||ic) a_{jk}^{bc} + (kb||ic) a_{jk}^{ac}] \quad (43)$$

Energy Derivatives

In this section, we finally combine the efforts of the previous sections on integrals, integral derivatives and energy expressions to develop the formulae for energy derivatives E/x_i and $\partial^2 E / x_i x_j$. Direct differentiation of the Hartree-Fock energy eq. (28) with respect to the parameter x gives

$$\begin{aligned} \partial E_{\text{HF}} / \partial x = & \sum_{\mu\nu} P_{\mu\nu} (\partial H_{\mu\nu} / \partial x) + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\partial / \partial x) (\mu\lambda || \nu\sigma) + \partial V_{\text{nuc}} / \partial x \\ & + \sum_{\mu\nu} (\partial P_{\mu\nu} / \partial x) H_{\mu\nu} + \sum_{\mu\nu\lambda\sigma} (\partial P_{\mu\nu} / \partial x) P_{\lambda\sigma} (\mu\lambda || \nu\sigma) \end{aligned} \quad (44)$$

The first three parts on the right-hand side of eq. (44) directly involve the derivatives of the integrals $H_{\mu\nu}$, $(\mu\lambda || \nu\sigma)$ and the nuclear repulsion energy V_{nuc} . The remaining terms involve the derivative of the density-matrix and hence of the spinorbital coefficients $C_{\mu i}$. However, explicit evaluation of $\partial P_{\mu\nu} / \partial x$ can be avoided at this point if we note that the final two parts of eq. (44) can be written

$$\begin{aligned} & \sum_{\mu\nu} \sum_{i=1}^n (\partial C_{\mu i}^* / \partial x) H_{\mu\nu} C_{\nu i} + \sum_{\nu\mu\lambda\sigma} \sum_{i=1}^n (\partial C_{\mu i}^* / \partial x) P_{\lambda\sigma} (\nu\lambda || \nu\sigma) C_{\nu i} + \\ & \hspace{15em} \text{complex conj.} \\ & = \sum_{\mu\nu} \sum_{i=1}^n (\partial C_{\mu i}^* / \partial x) F_{\mu\nu} C_{\nu i} + \text{complex conj.} \\ & = \sum_{\mu\nu} \sum_{i=1}^n (\partial C_{\mu i}^* / \partial x) \epsilon_i S_{\mu\nu} C_{\nu i} + \text{complex conj.} \end{aligned} \quad (45)$$

using eqs. (31) and (32). Further, differentiation of the orthonormality equation (30) leads to (with $p = q = i$)

$$\sum_{\mu\nu} [(\partial C_{\mu i}^* / \partial x) S_{\mu\nu} C_{\nu i} + C_{\nu i}^* (\partial S_{\mu\nu} / \partial x) C_{\nu i} + C_{\mu i}^* S_{\mu\nu} (\partial C_{\nu i} / \partial x)] = 0 \quad (46)$$

Equation (46) may be used to eliminate the coefficient derivatives in eq. (45) and hence obtain the final formula

$$\begin{aligned} \partial E_{\text{HF}} / \partial x = & \sum_{\mu\nu} P_{\mu\nu} (\partial H_{\mu\nu} / \partial x) + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\partial / \partial x) (\mu\lambda || \nu\sigma) \\ & + \partial V_{\text{nuc}} / \partial x - \sum_{\mu\nu} W_{\mu\nu} (\partial S_{\mu\nu} / \partial x) \end{aligned} \quad (47)$$

where $W_{\mu\nu}$ is an 'energy-weighted density matrix'

$$W_{\mu\nu} = \sum_{i=1}^n \epsilon_i C_{\mu i}^* C_{\nu i} \quad (48)$$

We may obtain second derivatives of the Hartree-Fock energy by differentiating eq. (47) with respect to a second variable y . This leads to

$$\begin{aligned} \partial^2 E_{\text{HF}} / \partial x \partial y &= \sum_{\mu\nu} P_{\mu\nu} (\partial^2 H_{\mu\nu} / \partial x \partial y) + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\partial^2 / \partial x \partial y) (\mu\lambda || \nu\sigma) \\ &+ \partial^2 V_{\text{nuc}} / \partial x \partial y - \sum_{\mu\nu} W_{\mu\nu} (\partial^2 S_{\mu\nu} / \partial x \partial y) \\ &+ \sum_{\mu\nu} (\partial P_{\mu\nu} / \partial y) (\partial H_{\mu\nu} / \partial x) + \sum_{\mu\nu\lambda\sigma} (\partial P_{\mu\nu} / \partial y) P_{\lambda\sigma} (\partial / \partial x) (\mu\lambda || \nu\sigma) \\ &- \sum_{\mu\nu} (\partial W_{\mu\nu} / \partial y) (\partial S_{\mu\nu} / \partial x) \quad (49) \end{aligned}$$

The first four parts of eq. (49) involve the second derivatives of the integrals and V_{nuc} . They can be handled in a manner strictly analogous to eq. (47). The remaining terms involve the first derivatives of the density matrices $P_{\mu\nu}$ and $W_{\mu\nu}$; computation of these can no longer be avoided.

Differentiation of the Hartree-Fock wavefunction with respect to a variable y is accomplished by coupled perturbed Hartree-Fock theory (CPHF). The problem is to find solutions of the Fock-type equations (31) for values of y in the vicinity of a value $y=0$ for which solutions are already available. The necessary equations can be obtained expanding the terms in the Fock equations as powers of y , and insisting that the equations be satisfied for each power of y . Alternately, the same equations can be obtained by formal differentiation of the Fock equation and the orthonormality constraint.

$$\sum_{\nu} \left[\frac{\partial F_{\mu\nu}}{\partial y} - \frac{\partial \epsilon_{\mu}}{\partial y} S_{\mu\nu} - \epsilon_{\mu} \frac{\partial S_{\mu\nu}}{\partial y} \right] C_{\nu p} + (F_{\mu\nu} - \epsilon_{\mu} S_{\mu\nu}) \frac{\partial C_{\nu p}}{\partial y} = 0 \quad (50)$$

and
$$\left[\frac{\partial C_{\mu q}^*}{\partial y} S_{\mu\nu} C_{\nu p} + C_{\mu q}^* \frac{\partial S_{\mu\nu}}{\partial y} C_{\nu p} + C_{\mu q}^* S_{\mu\nu} \frac{\partial C_{\nu p}}{\partial y} \right] = 0 \quad (51)$$

These equations can be simplified by converting from the basis function space to the spin orbital space. The derivative of the orbital coefficients can be expressed in terms of the unperturbed coefficients

$$\frac{\partial C_{\nu p}}{\partial y} = \sum_r C_{\nu r} U_{rp} \quad (52)$$

Substituting into eq. (50) and transforming by $C_{\mu q}$ we obtain

$$\begin{aligned} \sum_{\mu\nu} [C_{\mu q}^* \left(\frac{\partial F_{\mu\nu}}{\partial y} - \frac{\partial \epsilon_p}{\partial y} S_{\mu\nu} - \epsilon_p \frac{\partial S_{\mu\nu}}{\partial y} \right) C_{\nu p} \\ + \sum_r C_{\mu q} (F_{\mu\nu} - \epsilon_p S_{\mu\nu}) C_{\nu r} U_{rp}] = 0 \end{aligned} \quad (53)$$

Simplifying, using eq. (30) and eq. (31)

$$\widetilde{F}_{qp} - \delta_{qp} \frac{\partial \epsilon_p}{\partial y} - \epsilon_p \widetilde{S}_{qp} + (\epsilon_q - \epsilon_p) U_{qp} = 0 \quad (54)$$

Similarly for the orthonormality constraint,

$$U_{qp}^* + \widetilde{S}_{qp} + U_{pq} = 0 \quad (55)$$

The following terms have been defined for the above two equations,

$$\widetilde{S}_{qp} = \sum_{\mu\nu} C_{\mu q}^* \frac{\partial S_{\mu\nu}}{\partial y} C_{\nu p} \quad (56)$$

$$\text{and } \widetilde{F}_{qp} = \widetilde{H}_{qp} + \widetilde{G}_{qp} \quad (57)$$

$$\text{where } \widetilde{H}_{qp} = \sum_{\mu\nu} C_{\mu q}^* \frac{\partial H_{\mu\nu}}{\partial y} C_{\nu p} \quad (58)$$

$$\begin{aligned} \text{and } \widetilde{G}_{qp} = \sum_i \sum_r^n [U_{ri}^* (qr||pi) + U_{ri} (qi||pr) \\ + \sum_{\mu\nu\lambda\sigma} C_{\mu q}^* C_{\nu p} P_{\lambda\sigma} \frac{\partial (\mu\lambda||\nu\sigma)}{\partial y}] \end{aligned} \quad (59)$$

Diagonal elements of eq. (54) give

$$\frac{\partial \epsilon_p}{\partial y} = \tilde{F}_{pp} - \tilde{S}_{pp} \epsilon_p \quad (60)$$

Off-diagonal elements of eq. (54) lead to

$$U_{qp} = [\tilde{F}_{qp} - \tilde{S}_{qp} \epsilon_p] / [\epsilon_p - \epsilon_q] \quad (61)$$

The sum over r in eq. (52) is conveniently separated into an occupied part (r=j=1...n) and virtual part (r=a=n+1,...2N). The occupied part U_{ij} can be simplified using eq. (51)

$$U_{ji}^* + U_{ij} = -\tilde{S}_{ij} \quad (62)$$

$$\text{for } U_{ai} = (Q_{ai} + \sum_b \sum_j [U_{bj}^* (ab||ij) + U_{bj} (aj||ib)] / (\epsilon_i - \epsilon_a)) \quad (63)$$

where

$$Q_{ai} = \tilde{H}_{ai} - \tilde{S}_{ai} \epsilon_i - \sum_{kl} \tilde{S}_{kl} (al||ik) + \sum_{\mu\nu\lambda\sigma} c_{\mu a}^* c_{\nu i} P_{\lambda\sigma} \frac{\partial}{\partial y} (\mu\lambda||\nu\sigma) \quad (64)$$

This set of equations can be used to solve for U_{ai} by some iterative process.

In the second-order derivative expression, eq. (49), we need $\partial P_{\mu\nu} / \partial y$ and $\partial W_{\mu\nu} / \partial y$. Again, separating the contributions from the occupied block and occupied virtual block, we obtain:

$$\begin{aligned} \frac{\partial P_{\mu\nu}}{\partial y} &= \sum_i^n \left(\frac{\partial C_{\mu i}^*}{\partial y} C_{\nu i} + C_{\nu i}^* \frac{\partial C_{\mu i}}{\partial y} \right) \\ &= - \sum_{ij} C_{\mu i}^* C_{\nu j} \tilde{S}_{ij} + \sum_{ia} (C_{\mu i}^* C_{\nu a} U_{ai}^* + C_{\mu a}^* C_{\nu i} U_{ai}) \quad (65) \end{aligned}$$

And similarly

$$\frac{\partial W_{\mu\nu}}{\partial y} = \sum_i^n \left[\frac{\partial \epsilon_i}{\partial y} C_{\mu i}^* C_{\nu i} + \epsilon_i \frac{\partial C_{\mu i}^*}{\partial y} C_{\nu i} + \epsilon_i C_{\mu i}^* \frac{\partial C_{\nu i}}{\partial y} \right]$$

$$= \sum_{ij} C_{\mu i}^* C_{\nu j} [\tilde{F}_{ij} - (\epsilon_i + \epsilon_j) \tilde{S}_{ij}] + \sum_{ia} \epsilon_i (C_{\mu i}^* C_{\nu a} U_{ai}^* + C_{\mu a}^* C_{\nu i} U_{ai}) \quad (66)$$

This completes the evaluation of the terms required for the second derivative expression. The derivative of the second order Møller-Plesset energy can now be obtained. In addition to the derivative of Fock energies, ϵ_p , we require the derivatives of the transformed integrals $(ij||ab)$

$$\begin{aligned} \frac{\partial(ij||ab)}{\partial y} &= \sum_p [U_{pi}^* (pj||ab) + U_{pj}^* (ip||ab) + U_{pa} (ij||pb) \\ &\quad + U_{pb} (ij||ab) + (ij||ab)_x^\dagger] \quad (67). \end{aligned}$$

where

$$(pq||rs)_x^\dagger = \sum_{\mu\nu\lambda\sigma}^N C_{\mu p}^* C_{\nu q}^* C_{\lambda r} C_{\sigma s} (\partial/\partial x)(\mu\nu||\lambda\sigma) \quad (68)$$

Full algebraic details will not be given. In terms of a_{ij}^{ab} given by eq. (39), the final result for the derivative of the second-order correlation energy E_{MP2} is

$$\partial E_{MP2}/\partial x = \sum_{ij} \sum_{ab} a_{ij}^{ab} X_{ij}^{ab} \quad (69)$$

$$\begin{aligned} X_{ij}^{ab} &= \frac{1}{2} (ij||ab)_x^\dagger + \sum_k [(ij||ak)U_{kb} - \frac{1}{2} a_{ij}^{ab} \{\tilde{F}_{ki} - \epsilon_i \tilde{S}_{ki}\} \\ &\quad - \frac{1}{2} (kj||ab) \tilde{S}_{ik}] + \sum_c [(cj||ab)U_{ci} + \frac{1}{2} a_{ij}^{ac} \{\tilde{F}_{cb} - \epsilon_b \tilde{S}_{cb}\} \\ &\quad - \frac{1}{2} [(ij||ac) \tilde{S}_{bc}]] \end{aligned}$$

The first derivative of the configuration interaction energy using all double excitations involves considerably more effort. Since the expansion coefficients a_{ij}^{ab} have been optimized variationally we have $\partial E_{CID}/\partial a_{ij}^{ab} = 0$ in eq. (40). Differentiation of eq. (40) with respect to an external parameter x now gives

$$(\partial E_{CID}/\partial x) = \frac{\sum_{st} [a_s (\partial \mathcal{H}_{st}/\partial x) a_t]}{\sum_s a_s^2} \quad (71)$$

Hence the energy derivative can be reduced to the derivative of the Hamiltonian matrix which in turn is given in part by the set of anti-symmetrized two-electron integrals.

After some algebraic manipulation, the final CID energy derivative in terms of spin-orbitals can be given by

$$(\partial E_{CID}/\partial x) = (\partial E_{HF}/\partial x) + \sum_{ijab} a_{ij}^{ab} z_{ij}^{ab} / \sum_{ijab} (a_{ij}^{ab})^2 \quad (72)$$

where

$$\begin{aligned} z_{ij}^{ab} = & \frac{1}{2}(ij||ab)_x + \frac{1}{8} \sum_{cd} a_{ij}^{cd} (ab||cd)_x + \frac{1}{8} \sum_{kl} a_{kl}^{ab} (kl||ij)_x - \sum_{kc} a_{kj}^{cb} (ka||ic)_x \\ & + \frac{1}{2} \sum_c a_{ij}^{cb} [\tilde{F}_{ca} - \epsilon_a \tilde{S}_{ca}] - \frac{1}{2} \sum_k a_{kj}^{ab} [\tilde{F}_{ki} - \epsilon_i \tilde{S}_{ki}] \\ & + \sum_e U_{ei} [(ej||ab) + \frac{1}{2} \sum_{kl} a_{kl}^{ab} (ej||kl) - 2 \sum_{kc} a_{kj}^{cb} (ka||ec)] \\ & + \sum_m U_{ma} [(ij||mb) + \frac{1}{2} \sum_{cd} a_{ij}^{cd} (mb||cd) - 2 \sum_{kc} a_{kj}^{cb} (km||ic)] \\ & + \sum_m \tilde{S}_{mi} [-\frac{1}{4} w_{mj}^{ab} + \frac{1}{2} \sum_{cd} (ab||cd) a_{mj}^{cd} - \sum_{kc} (kb||jc) a_{mk}^{ac}] \\ & + \sum_e \tilde{S}_{ea} [-\frac{1}{4} w_{ij}^{eb} + \frac{1}{2} \sum_{kl} (kl||ij) a_{kl}^{eb} - \sum_{kc} (kb||jc) a_{ik}^{ec}] \quad (73) \end{aligned}$$

Illustrative Examples

a) Timing

If derivative methods are to represent a significant advance in the technology of quantum chemistry, they must permit more information to be calculated more accurately and/or more quickly than non-derivative methods. To demonstrate that this is indeed true, a series of calculations has been performed on ethylene at the 6-31G* basis set³⁵ level (this includes d orbitals on carbon). The timing data are collected in Table 2.

To calculate the energy and all of the first derivatives of the Hartree-Fock energy with respect to the positions of the nuclei requires approximately twice as much computer time as is needed to compute the Hartree-Fock energy alone, regardless of the size of the molecule or the number of degrees of freedom. In this highly symmetrical case the timing for the gradient is even more favorable because symmetry was used to reduce the number of integral derivatives calculated. Similar results are obtained with sp basis set. Since $3N-6$ derivatives are calculated for an N atom molecule at only double the cost of the energy alone this can represent an order of magnitude increase in efficiency for calculations on larger and less symmetrical molecules. Other gradient programs^{36,19} are reported to require 3-4 times as long as the SCF calculations. This difference in speed is directly attributable to the efficiency of the integral derivative algorithms outlined above.

The Hartree-Fock full second derivative calculation takes only 4 to 5 times as much time as the gradients. Early indications were that the direct analytical computation of the second derivatives might be prohibitively difficult¹², and that second derivatives could be calculated more practically by the finite difference method from the analytical gradients.^{10,11} The present work shows that even for a small highly symmetrical molecule, the analytical approach is competitive with the finite difference method. For larger, more general, problems the analytical approach should be superior, since the finite difference approach requires at least $3N-5$ calculations to determine the full second derivative matrix.

The second order Møller-Plesset energy can be computed very rapidly once the SCF orbitals are available. The derivatives of the MP2 energy take three times as long as the MP2 energy. More integrals must be transformed and the coupled-perturbed Hartree-Fock equations must be solved. Nevertheless, the calculation of gradients at this simple level of electron correlation is practical.

The configuration interaction calculations on ethylene are an order of magnitude more lengthy than the Hartree-Fock calculations. But similar to Hartree-Fock calculations, the timing for the CID energy plus gradients is very favorable, requiring only twice as long as the CID energy alone. Furthermore, this ratio should be relatively independent of the size of the configuration interaction calculation and the number of degrees of freedom in the molecule, since the most difficult sections of the CID gradient calculations scale in the same manner as the CID energy (N^5 in the number of functions). The MP2 or CID gradients and the Hartree-Fock second derivatives can be calculated together more efficiently

than both separately. The combination results in a very powerful method for geometry optimization that takes electron correlation into account.

b) Geometry Optimization

One of the most important and widespread applications of energy derivatives is geometry optimization. The wealth of information available in a gradient calculation can be used very effectively to locate the minima on a potential energy hypersurface both rapidly and accurately. Furthermore, analytical first and second energy derivatives make it feasible to search for more complicated stationary points on energy surfaces like saddle points and local maxima. Such features may be inaccessible by non-derivative methods.

A typical non-gradient minimization method proceeds by a series of one dimensional searches for each coordinate. Repeated cycles of varying each coordinate may be necessary for acceptable convergence to the minimum. There are more efficient optimization methods available such as the Fletcher-Powell³⁷ algorithm, but frequently it is still not practical to optimize all of the geometric parameters in a molecule using only the energy.

With the availability of rapidly calculated analytical gradients, more powerful optimization techniques can be used. A class of methods known as conjugate gradient or variable metric algorithms³⁸ guarantees exact convergence to an extremum in $N + 1$ steps on an N dimensional quadratic surface. The details of these and other optimization algorithms are discussed in another chapter. In practice, searches for equilibrium geometries seem to require ca. $N/2$ steps, for well chosen starting geometries and rough estimates of the second derivatives. Furthermore, gradient methods are well suited to optimize systems with strongly coupled coordinates such as polycyclic molecules that might be intractable otherwise.

Gradient optimization algorithms and Hartree-Fock first derivatives for s p and d type gaussian wavefunctions have been incorporated into the publicly available version of GAUSSIAN 80.³⁰ These gradient methods have made full geometry optimization with any standard basis set practically automatic and routine. In an attempt to organize the increasingly large amount of data on optimized molecular structures and total energies, a computer archiving system has been set up. The Carnegie-Mellon version of GAUSSIAN 80 now records directly into a computer readable file the essential information from all standard-route calculations. The first version of the

Carnegie-Mellon Quantum Chemistry Archive,³⁹ available in printed form or on magnetic tape, contains about 2000 fully optimized structures using the STO-3G, 321G and 6-31G* basis sets. Figure 1 illustrates a sample entry in the archive.

Gradient methods have also opened the way to locating transition structures. Unless the transition vector can be determined by symmetry, it is normally very difficult, if not impossible, to find the transition structure using only energy based optimization methods. Minimizing the gradient norm has been suggested,⁴⁰ but this can lead to false transition structures.⁴¹ A better approach is to use a modified conjugate gradient method. If the starting guess is within the quadratic region of the saddle point, optimization leads directly to the transition structure. However, no overall satisfactory and efficient algorithm seems to exist to solve the general transition structure problem.⁴¹

Computer programs have recently been developed to compute analytical second derivatives at the Hartree-Fock level.⁴ A one step optimization is possible for a quadratic function but quantum mechanically derived energy surfaces are rarely quadratic. In practice, a single second derivative computation followed by one or two gradient calculations are needed to carry out and confirm the optimization. The previous discussion on gradient optimization also pertains to first derivatives of correlated wavefunctions; however, there is a special advantage in combining MP2 or CID gradients with Hartree-Fock second derivatives. Once the MP2 or CID gradients are calculated, it is relatively cheap (see Table 2) to compute the HF second derivatives as well. The second derivatives are not strongly affected by correlation and thus provide an excellent estimate of the curvature of the correlated energy hypersurface. Usually only 2 to 3 additional MP2 or CID gradient calculations are needed to converge to the minimum. Until the advent of MP2 and CID first derivatives and HF second derivatives, geometry optimizations at a level that includes electron correlation, have been infrequent and costly.

Second derivatives are even more vital for transition structures. At a proper saddle point, the second derivative matrix has one and only one negative eigenvalue. Thus to verify that a geometry represents a true transition structure, not only must the gradient be zero, but also the second derivative matrix must be calculated to check that only one negative eigenvalue is present. Similar to the minimization problem, optimization of saddle points can be accomplished readily if the second derivatives are available and if the

HF/6-31G* ATOMS AND FULLY OPTIMIZED STRUCTURES. 225
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MOLECULE SYMM	TITLE	ENERGY	SEQ
B(1-)	KH B(1-) ... (1S)2 (2P)2 ... 6-31G*	-24.39726	4840
C3H7(1+)	EDGE-PROTONATED CYCLOPROPANE. 6-31G* OPT	-117.35073	265
CS	C3H7 (+). METHYL-STAGGERED 1-PROPYL CATION	-117.35111	3791
C2V	CORNER-PROTONATED CYCLOPROPANE. 6-31G* 0	-117.35916	187
C2V	2-PROPYL CATION. 6-31G* OPT.	-117.38076	513
O2(3)	D*H OXYGEN MOLECULE.6-31G* STRUCTURE! 001; D	-149.61791	2610

Key to full entries

FULL ENTRIES.

Sequence number ↓ author ↓ calculation type

265\20161\C3H7(1+)\KRISHNAN\14-OCT-1978\1\BP OPT 6-31G* NOBOP\EDGE=PRONATED CYCLOPROPANE. 6-31G* OPT.\1,1\X,C,1,R1,C,1,R2,2,90.\C,1,R2,2,90.0\H,1,R3,3,90.2,180.0\X,2,1,1,90.3,0.0\X,2,1,1,90.0\H,2,R4,7,THETA1,6,90.0\H,2,R4,7,THETA1,6,-90.0\X,4,1,1,THETA2,2,180.0\H,2,R5,10,THETA3,1,90.0\H,4,R5,10,THETA3,1,-90.0\X,3,1,1,THETA2,2,180.0\H,3,R5,13,THETA3,1,90.0\H,3,R5,13,THETA3,1,-90.0\X,3,1,1,THETA2,2,180.0\H,2=0.88307\HF=-117.3507286\RMSE=0.530D-07\KMSF=0.381D-03\FWG=C02V [C2(H1C1),SI GMAV(C2),SIGMAV(H2),X(H4)]\

Total Energy ↓ SCF convergence ↓ Residual forces after geometry optimization

optimized geometry

FIGURE 1 Sample extract from the Carnegie-Mellon Quantum Chemistry Archive (reference 39)

TABLE 2

Approximate Execution Times^e (in minutes) for Ethylene Using 6-31G* Basis (38 Basis Functions)

Program	HF	HF + 1st Deriv.	HF + 1st & 2nd Deriv.	MP2	MP2 + 1st Deriv.	CID	CID + 1st Deriv.	MP2 1st & HF 2nd Deriv.	CID 1st & HF 2nd Deriv.
Integrals	10	10	10	10	10	10	10	10	10
SCF	3	5 ^a	5 ^a	5 ^a	5 ^a	5 ^a	5 ^a	5 ^a	5 ^a
Transformation		8	8	5	15 ^d	15	15	15	15
CID					126	126	126		126
Integral									
1st Deriv.		7	16 ^{bc}		16 ^{bc}		16 ^{bc}	16 ^{bc}	16 ^{bc}
Integral									
2nd Deriv.			31 ^c					31 ^c	31 ^c
CPHF			13		13		13	13	13
HF 2nd Deriv. Eval.			6					6	6
MP2 or CID Deriv. Eval.					18		113	18	113
Total	13	22	89	20	77	156	298	107	335

^a SCF convergence on the density matrix tightened to get more significant figures in the M.O. coefficients.^b The integral derivatives are written out.^c Information about the symmetry of the molecule was used to aid in these parts of the calculation.^d More transformed integrals are calculated in this case as compared to a simple MP2 calculation.^e All the calculations were performed on a VAX-11/780 computer at Carnegie-Mellon University.

starting structure is in the quadratic region. More general algorithms for transition structure optimization are under study.

c) Force Constants and Vibrational Frequencies

The original applications of first derivatives were to the calculation of vibrational frequencies.¹⁰ Harmonic and anharmonic force constants were calculated by the finite difference method with gradients obtained analytically at the Hartree-Fock level.^{10,11,13-18} With the present programs it is possible to compute the Hartree-Fock second derivatives and, the vibrational frequencies in a single calculation. Furthermore, the effect of electron correlation can be assessed by calculating the force constants numerically from the MP2 gradients.

Table 3 lists the harmonic frequencies for ethylene * computed at the Hartree-Fock and MP2 level using the 6-31G basis set. The respective equilibrium geometry was used in each case. Also listed are the experimental frequencies corrected for anharmonicity.⁴² The HF theory appears to overestimate the harmonic frequencies by 55-180 cm^{-1} . Inclusion of correlation improves the agreement considerably. The MP2 calculation accounts for about 70% of the discrepancy in the HF theory, yielding frequencies that differ from experiment by only 10-90 cm^{-1} . Most of the frequencies are still overestimated but this may be due to the considerable uncertainty in the empirical anharmonicity corrections. Corrections to the harmonic vibrational frequencies can be computed from the cubic and quartic force constants. These are difficult to obtain experimentally for molecules larger than tetra-atomic. However, theoretical anharmonic force constants are predicted reliably even at the Hartree-Fock level.

Zero point vibrational energy is frequently ignored when theoretical energy differences are compared with experiment. The analytical second derivative programs permit this quantity to be evaluated in a single calculation, eliminating one more possible source of error in the comparison between theory and experiment.

d) Electrical and Magnetic Properties

With simple atomic orbitals, very large basis sets with extensive polarization are required to obtain second order ³³ magnetic and electrical properties to a reasonable accuracy. In contrast, rather modest basis sets can be used, if a field

TABLE 3
Vibrational Frequencies for Ethylene (cm⁻¹)

Symmetry	HF/6-31G* ^a	MP2/6-31G* ^b	Experimental Harmonic Frequencies ^c
b _{2u}	897.0	851.1	842.9
b _{2g}	1099.4	942.6	958.8
b _{1u}	1095.0	991.8	968.7
a _u	1154.9	1085.5	1043.9
b _{1g}	1352.5	1265.9	1244.9
a _g	1496.9	1415.7	1369.6
b _{3u}	1610.2	1520.8	1473.0
a _g	1856.2	1721.1	1654.9
b _{3u}	3320.9	3213.3	3146.9
a _g	3344.2	3230.9	3152.5
b _{1g}	3394.6	3300.4	3231.9
b _{2u}	3420.7	3323.3	3234.3

^a At the HF/6-31G* equilibrium geometry ($r_{CC} = 1.317$, $r_{CH} = 1.076$, $\angle HCH = 116.4$).

^b At the MP2/6-31G* equilibrium geometry ($r_{CC} = 1.335$, $r_{CH} = 1.085$, $\angle HCH = 116.5$).

^c Anharmonicity corrections are made on the observed experimental frequencies to get these estimated values.⁴²

dependence is built into the basis functions.²⁵⁻²⁷ Gauge-dependent atomic orbitals have been especially successful in NMR chemical shift calculations.^{25,26}

Summary

In the preceding sections, a number of expressions have been derived for the analytical calculation of energy derivatives. Formulae are discussed for the first derivatives or gradients of the Hartree-Fock energy and also for the second order Møller-Plesset and the double excitation configuration interaction energies, which include electron correlation. Timing data for the computer programs written to calculate these derivatives indicate that such computations are not only practical but indeed very efficient. In fact, derivative calculations represent an order of magnitude increase in the information that can be generated about energy hypersurfaces with a given amount of computer time. Geometry optimization and vibrational frequency calculations have been discussed as applications of analytically computed energy derivatives.

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References

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2. H. B. Schlegel, *J. Comput. Phys.*, to be published; Ph.D. thesis, Queen's University, Kingston, Ont. Canada, 1975.
3. H. B. Schlegel and J. S. Binkley, *J. Comput. Phys.*, to be published.
4. J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, *Int. J. Quantum Chem.: Quantum Chem. Sym.* **13**, 225 (1979).
5. R. Krishnan, H. B. Schlegel and J. A. Pople, *J. Chem. Phys.* **72**, 4654 (1980).
6. S. Bratoz, *Colloq. Intern. Centre Natl. Rech. Sci. (Paris)* **82**, 287 (1958).
7. D. M. Bishop and M. Randic, *J. Chem. Phys.* **44**, 2480 (1966).
8. R. Moccia, *Chem. Phys. Lett.* **5**, 260 (1970); *Int. J. Quantum Chem.* **8**, 293 (1974).
9. J. Gerratt and I. M. Mills, *J. Chem. Phys.* **49**, 1719 (1968); *J. Chem. Phys.* **49**, 1730 (1968).

10. P. Pulay, *Mol. Phys.* 17, 197 (1969).
11. P. Pulay, *Modern Theoretical Chemistry* (Vol. 4), H. F. Schaefer III, Ed., (Plenum Press, New York, 1977).
12. K. Thomsen and P. Swanstrom, *Mol. Phys.* 26, 735 (1973).
13. P. Pulay and W. Meyer, *J. Mol. Spec.* 40, 59 (1971).
14. W. Meyer and P. Pulay, *J. Chem. Phys.* 56, 2109 (1972).
15. P. Pulay and W. Meyer, *Mol. Phys.* 27, 473 (1974).
16. H. B. Schlegel, S. Wolfe and F. Bernardi, *J. Chem. Phys.* 63, 3632 (1975).
17. H. B. Schlegel, S. Wolfe and F. Bernardi, *J. Chem. Phys.* 67, 4181 (1977).
18. H. B. Schlegel, S. Wolfe and F. Bernardi, *J. Chem. Phys.* 67, 4194 (1977).
19. K. Ishida, K. Morokuma and A. Komornicki, *J. Chem. Phys.* 66, 2153 (1977).
20. W. Meyer and P. Rosmus, *J. Chem. Phys.* 63, 2356 (1975).
21. U. Wahlgren, J. Pacansky and P. S. Bagus, *J. Chem. Phys.* 63, 2874 (1975).
22. B. J. Rosenberg, W. C. Ermler and I. Shavitt, *J. Chem. Phys.* 65, 4072 (1976).
23. a) P. Pulay, W. Meyer and J. E. Boggs, *J. Chem. Phys.* 68, 5077 (1978);
b) P. R. Taylor, G. B. Bacskay, N. S. Hush and A. C. Hurley, *J. Chem. Phys.* 69, 1971 (1978).
24. a) J. D. Goddard, N. C. Handy and H. F. Schaefer III, *J. Chem. Phys.* 71, 1525 (1979);
b) S. Kato and K. Morokuma, *Chem. Phys. Lett.* 65, 19 (1979);
c) B. R. Brooks, W. D. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi and H. F. Schaefer III, *J. Chem. Phys.* 72, 4652 (1980).
25. R. Ditchfield, *J. Chem. Phys.* 56, 5688 (1972); *Mol. Phys.* 27, 789 (1974).
26. F. R. Prado, C. Giessner-Prettre and B. Pullman, *Int. J. Quantum Chem., Quant. Bio. Sym.* 6, 491 (1979).
27. A. J. Sadlej, *Chem. Phys. Lett.* 47, 50 (1977).
28. J. A. Pople and W. J. Hehre, *J. Comput. Phys.* 27, 161 (1978).
29. H. Taketa, S. Huzinaga and K. O-Ohata, *J. Phys. Soc. Japan* 21, 2313 (1966).
30. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople, "GAUSSIAN 80, an Ab Initio Molecular Orbital Program", Carnegie-Mellon University, Pittsburgh, PA, USA (1980).
31. a) M. Dupuis, J. Rys and H. F. King, *J. Chem. Phys.* 65, 111 (1976);
b) H. F. King and M. Dupuis, *J. Comput. Phys.* 21, 1 (1976).

32. C. Møller and M. S. Plesset, *Phys. Rev.* 46, 618 (1934).
33. R. M. Stevens, R. Pitzer and W. N. Lipscomb, *J. Chem. Phys.* 38, 550 (1963).
34. T. C. Caves and M. Karplus, *J. Chem. Phys.* 50, 3649 (1969).
35. P. C. Hariharan and J. A. Pople, *Theo. Chim. Acta* 28, 213 (1973).
36. P. Pulay, *Theo. Chim. Acta* 50, 299 (1979).
37. a) R. Fletcher and M.J.D. Powell, *Compt. J.* 6, 163 (1963);
b) J. B. Collins, P.v.R. Schleyer, J. S. Binkley and J. A. Pople, *J. Chem. Phys.* 64, 5142 (1976).
38. K. W. Brodlie, *Math Programming* 12, 344 (1977) and references cited.
39. R. A. Whiteside, J. S. Binkley, R. Krishnan, D. J. DeFrees, H. B. Schlegel and J. A. Pople, "Carnegie-Mellon Quantum Chemistry Archive", Carnegie-Mellon University, Pittsburgh, PA., USA (1980).
40. J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.* 94, 2625 (1972).
41. K. Mueller, *Angew. Chem. Int. Ed. Engl.* 19, 1 (1980).
42. J. L. Duncan, D. C. McKean and P. D. Mallinson, *J. Mol. Spec.* 45, 221 (1973).