

Derivative Studies in Hartree-Fock and Møller-Plesset Theories

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Abstract

The complete spin-orbital formulation of the analytical first and second derivatives of the Hartree-Fock (HF) energy as well as the analytical first derivative of the correlated second-order Møller-Plesset perturbation energy (MP2) is presented. Some features of an efficient computational method to calculate these derivatives are described. The methods are applied to calculate the harmonic vibrational frequencies of ethylene, and the results are compared with experiment.

1. Introduction

A wide range of problems in quantum chemistry involves evaluation of derivatives of the electronic energy with respect to external parameters. Well-known examples are calculation of electric moments and polarizabilities (energy derivatives with respect to applied electric fields) and calculation of magnetic properties such as diamagnetic susceptibilities and nuclear magnetic resonance chemical shifts (energy derivatives with respect to external and nuclear magnetic fields). In addition, 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.

There are two general approaches to calculation of energy derivatives. The first is the finite-difference method in which calculation of the energy \mathcal{E} is repeated with a small but finite change Δx in a parameter x and the derivative obtained approximately by

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

The second is the analytic method in which formal differentiation of $\mathcal{E}(x)$ is first carried out and the resulting expression then computed directly. The finite-difference method has the advantage that the evaluation of the energy $\mathcal{E}(x)$ is usually much simpler than that of the first or second derivatives $\partial \mathcal{E} / \partial x$ or $\partial^2 \mathcal{E} / \partial x \partial y$. On the other hand, it has the disadvantage that the step size Δx must

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be small to avoid contaminating effects of higher derivatives, yet not so small that computational roundoff causes significant errors. If there are many variables, the number of individual computations becomes large in the finite-difference approach, particularly if second derivatives are needed. Clearly, the analytical differentiation method is preferable if the mathematics is tractable and efficient algorithms can be constructed.

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 wavefunctions. The general theory of energy derivatives within this framework has been outlined by several authors. Bratoz [1], Bishop and Randig [2], and Moccia [3] have given analytical expressions for the first and second derivatives of the SCF energy for closed shells. Gerratt and Mills [4] have outlined a perturbed Hartree-Fock theory to calculate one-electron second-order properties and have calculated force constants as the analytical derivative of the Hellmann-Feynman force. Thomsen and Swannstrom [7] have analytically calculated the full second derivative 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 [5, 6]. 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 Meyer [8-10] and by Schlegel, Wolfe, and Bernardi [11-13]. Ishida *et al.* [14] have used analytical energy derivatives to study reaction paths.

Only a limited amount of work on energy derivatives has been carried out with wavefunctions beyond the Hartree-Fock level [15-19]. The finite-difference approach has been used in these studies to calculate force constants for small molecules.

The main objectives of this article are (1) to give a general *spin-orbital formulation* of the analytical first and second derivatives of the HF energy, as well as the first derivative of the correlated second-order Møller-Plesset perturbation energy [20]; (2) to describe an efficient computational procedure for the evaluation of these derivatives in studying molecular force fields.

2. General Theory

Hartree-Fock theory is based on an n -electron single-determinant wavefunction,

$$\Psi_{\text{HF}} = (n!)^{-1/2} |\chi_1 \chi_2 \cdots \chi_n|, \quad (2)$$

where $\chi_1, \chi_2, \dots, \chi_n$ are a set of orthonormal spin orbitals (one-electron functions of Cartesian and spin coordinates). The corresponding expectation value of the nonrelativistic electronic Hamiltonian has the form

$$\mathcal{E}_{\text{HF}} = \sum_{i=1}^n H_{ii} + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n (ij||ij) + V_{\text{nuc}}. \quad (3)$$

The notation for matrix elements is

$$H_{pq} = \int \chi_p^* H^{\text{core}} \chi_q d\tau, \quad (4)$$

$$(pq||rs) = \iint \chi_p^*(1) \chi_q^*(2) (1/r_{12}) \times [\chi_r(1) \chi_s(2) - \chi_s(1) \chi_r(2)] d\tau_1 d\tau_2, \quad (5)$$

where H^{core} is the one-electron core Hamiltonian (kinetic energy plus potential energy in the electrostatic field of the nuclei). The two-electron operator in (5) is the interelectronic repulsion energy. Note that $(pq||rs)$ is antisymmetric in both the pairs pq and rs . Finally V_{nuc} is the nuclear repulsion energy, which is independent of the electronic coordinates. Orthonormality of the spin orbitals implies

$$\int \chi_p^* \chi_q dt = \delta_{pq}. \quad (6)$$

In practical computations, the spin orbitals are written as linear combinations of a set of basis functions ω_μ ,

$$\chi_p = \sum_{\mu} c_{\mu p} \omega_{\mu}. \quad (7)$$

Note that ω_μ are basis functions in the full one-electron space (Cartesian plus spin coordinates). Usually, the set of ω_μ will be products of a set of Cartesian coordinate basis functions $\varphi_1, \varphi_2, \dots$ (usually contracted Gaussian functions) and the spin functions α and β . If there are N φ -type functions, there will be $2N$ spin-orbital basis functions ω_μ , viz., $\varphi_1\alpha, \varphi_1\beta, \varphi_2\alpha, \dots, \varphi_N\beta$. The sum in (7), therefore, has $2N$ terms for the most general case. Normal practice is to constrain the spin orbitals so that they are pure α or pure β , in which case only N of the $2N$ terms in (7) would be nonzero. With no further restrictions, this would lead to the spin-unrestricted Hartree-Fock function (UHF), sometimes described as different orbitals for different spin (DODS). We shall develop the theory generally for the full expansion (7), particular constraints on the spin orbitals being imposed at a later stage.

If the basis expansion (7) is substituted in the Hartree-Fock energy expression (3), we obtain

$$\mathcal{E}_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\lambda||\nu\sigma) + V_{\text{nuc}}, \quad (8)$$

where $P_{\mu\nu}$ is the spin-orbital density matrix defined by

$$P_{\mu\nu} = \sum_{i=1}^n c_{\mu i}^* c_{\nu i}. \quad (9)$$

Note that the sums over Greek subscripts in (8) and elsewhere in this section are over the $2N$ spin-orbital 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 spin orbitals must be retained and requires the condition

$$\sum_{\mu\nu} c_{\mu p}^* S_{\mu\nu} c_{\nu q} = \delta_{pq}. \quad (10)$$

The matrix elements introduced in (8) and (10) are the overlap integrals,

$$S_{\mu\nu} = \int \omega_{\mu}^* \omega_{\nu} d\tau, \quad (11)$$

the core Hamiltonian integrals,

$$H_{\mu\nu} = \int \omega_{\mu}^* H^{\text{core}} \omega_{\nu} d\tau, \quad (12)$$

and the two-electron integrals,

$$(\mu\lambda||\nu\sigma) = \iint \omega_{\mu}^*(1) \omega_{\lambda}^*(2) (1/r_{12}) \times [\omega_{\nu}(1) \omega_{\sigma}(2) - \omega_{\sigma}(1) \omega_{\nu}(2)] d\tau_1 d\tau_2. \quad (13)$$

All of the integrals (11), (12), and (13) have to be evaluated given the nature and location of the basis functions ω_{μ} .

Minimization of the Hartree-Fock energy (8) with respect to the linear coefficients $c_{\mu p}$ [subject to the orthonormality conditions (10)] leads to the Fock-type equations

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_p S_{\mu\nu}) c_{\nu p} = 0. \quad (14)$$

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

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\lambda||\nu\sigma), \quad (15)$$

and ϵ_p is the one-electron energy of the p th spin orbital. These are the Hartree-Fock self-consistent equations. For UHF theory they separate into two sets of coupled equations for the α and β spin orbitals. If the Cartesian parts of these are identical in pairs, both sets of equations reduce to the closed-shell algebraic equations originally derived by Roothaan [21].

Equations (14) will be soluble for $2N$ possible values of the one-electron energy ϵ_p , only n of which will correspond to occupied molecular spin orbitals. It is convenient to use subscripts i, j, k ($= 1, 2, \dots, n$) for occupied spin orbitals and a, b, c, \dots ($= n+1, \dots, 2N$) for the remainder (usually described as *virtual* spin orbitals). We shall continue to use p, q, r, \dots for the entire set of $2N$ spin orbitals.

The virtual spin orbitals χ_a ($a = n+1, \dots, 2N$) are used in Møller-Plesset perturbation theory [20] to develop expressions for the correlation energy (measuring the error of the Hartree-Fock energy). The simplest significant level is second-order theory, which leads to a total energy

$$\mathcal{E}_{\text{MP2}} = \mathcal{E}_{\text{HF}} - \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} |(ij||ab)|^2 (\Delta_{ij}^{ab})^{-1}, \quad (16)$$

where

$$\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j. \quad (17)$$

Once the Hartree-Fock equations (14) are solved for the coefficients $c_{\nu p}$, the matrix elements $(ij||ab)$ are easily obtained and (16) then gives an easily computable expression for the total energy including correlation.

The general problem with which we are concerned in this section is finding changes that take place in the Hartree-Fock energy \mathcal{E}_{HF} and the Møller-Plesset energy \mathcal{E}_{MP2} when small changes take place in the matrix elements $S_{\mu\nu}$, $H_{\mu\nu}$, and $(\mu\lambda||\nu\sigma)$. As noted in Sec. 1, these changes may reflect addition of external perturbations or movement of the nuclei. The general theory is the same in all cases. We proceed by treating the change in the matrix elements as a perturbation represented by a number of parameters x_1, x_2, x_3, \dots (nuclear displacements or magnitudes of external fields). The objective is then evaluation of the energy derivatives $\partial\mathcal{E}/\partial x_i$ and $\partial^2\mathcal{E}/\partial x_i \partial x_j$ at the origin $x_1 = x_2 = \dots = 0$.

Direct differentiation of the Hartree-Fock energy (8) with respect to the parameter x gives

$$\frac{\partial\mathcal{E}_{\text{HF}}}{\partial x} = \sum_{\mu\nu} P_{\mu\nu} \left(\frac{\partial H_{\mu\nu}}{\partial x} \right) + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left(\frac{\partial}{\partial x} \right) (\mu\lambda||\nu\sigma) + \frac{\partial V_{\text{nuc}}}{\partial x} + \sum_{\mu\nu} \left(\frac{\partial P_{\mu\nu}}{\partial x} \right) H_{\mu\nu} + \sum_{\mu\nu\lambda\sigma} \left(\frac{\partial P_{\mu\nu}}{\partial x} \right) P_{\lambda\sigma} (\mu\lambda||\nu\sigma). \quad (18)$$

The first three parts on the right-hand side of (18) 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 spin-orbital 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 (18) can be written

$$\begin{aligned} \sum_{\mu\nu} \sum_{i=1}^n \left(\frac{\partial c_{\mu i}^*}{\partial x} \right) H_{\mu\nu} c_{\nu i} + \sum_{\mu\nu\lambda\sigma} \sum_{i=1}^n \left(\frac{\partial c_{\mu i}^*}{\partial x} \right) P_{\lambda\sigma} (\mu\lambda||\nu\sigma) c_{\nu i} + \text{complex conjugate} \\ = \sum_{\mu\nu} \sum_{i=1}^n \left(\frac{\partial c_{\mu i}^*}{\partial x} \right) F_{\mu\nu} c_{\nu i} + \text{complex conjugate} \\ = \sum_{\mu\nu} \sum_{i=1}^n \left(\frac{\partial c_{\mu i}^*}{\partial x} \right) \epsilon_i S_{\mu\nu} c_{\nu i} + \text{complex conjugate}, \end{aligned} \quad (19)$$

using (14) and (15). Furthermore, differentiation of the orthonormality equation (10) leads to (with $p = q = i$)

$$\sum_{\mu\nu} \left[\left(\frac{\partial c_{\mu i}^*}{\partial x} \right) S_{\mu\nu} c_{\nu i} + c_{\mu i}^* \left(\frac{\partial S_{\mu\nu}}{\partial x} \right) c_{\nu i} + c_{\mu i}^* S_{\mu\nu} \left(\frac{\partial c_{\nu i}}{\partial x} \right) \right] = 0. \quad (20)$$

Equation (20) may be used to eliminate the coefficient derivatives in (19) and hence obtain the final formula

$$\frac{\partial\mathcal{E}_{\text{HF}}}{\partial x} = \sum_{\mu\nu} P_{\mu\nu} \left(\frac{\partial H_{\mu\nu}}{\partial x} \right) + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left(\frac{\partial}{\partial x} \right) (\mu\lambda||\nu\sigma) + \frac{\partial V_{\text{nuc}}}{\partial x} - \sum_{\mu\nu} W_{\mu\nu} \left(\frac{\partial S_{\mu\nu}}{\partial x} \right), \quad (21)$$

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

$$W_{\mu\nu} = \sum_{i=1}^n \epsilon_i c_{\mu i}^* c_{\nu i}. \quad (22)$$

We may obtain second derivatives of the Hartree-Fock energy by differentiating (21) with respect to a second variable y . This leads to

$$\begin{aligned} \frac{\partial^2 \mathcal{E}_{\text{HF}}}{\partial x \partial y} = & \sum_{\mu\nu} P_{\mu\nu} \left(\frac{\partial^2 H_{\mu\nu}}{\partial x \partial y} \right) + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left(\frac{\partial^2}{\partial x \partial y} \right) (\mu\lambda || \nu\sigma) \\ & + \frac{\partial^2 V_{\text{nuc}}}{\partial x \partial y} - \sum_{\mu\nu} W_{\mu\nu} \left(\frac{\partial^2 S_{\mu\nu}}{\partial x \partial y} \right) + \sum_{\mu\nu} \left(\frac{\partial P_{\mu\nu}}{\partial y} \right) \left(\frac{\partial H_{\mu\nu}}{\partial x} \right) \\ & + \sum_{\mu\nu\lambda\sigma} \left(\frac{P_{\mu\nu}}{\partial y} \right) P_{\lambda\sigma} \left(\frac{\partial}{\partial x} \right) (\mu\lambda || \nu\sigma) - \sum_{\mu\nu} \left(\frac{\partial W_{\mu\nu}}{\partial y} \right) \left(\frac{\partial S_{\mu\nu}}{\partial x} \right). \quad (23) \end{aligned}$$

The first four parts of (21) involve the second derivatives of the integrals and V_{nuc} . They can be handled in a manner strictly analogous to (21). 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) [4, 22, 23]. Here we give the general spin-orbital formulation of the CPHF theory, closely following the presentation of the theory for closed-shell systems by Gerratt and Mills [4]. The problem is to find solutions of the Fock-type equations (14) for values of y in the vicinity of a value y_0 for which solutions are already available. Without loss of generality, we may take $y_0 = 0$ and the problem is to find the derivative of the wavefunction with respect to y at $y = 0$. In equivalent perturbation terms, we have to find the first-order perturbation of the wavefunction for small y .

Let us write the Fock equations (14) for general y in the matrix form,

$$\mathbf{F}(y)\mathbf{c}_p(y) = \epsilon_p(y)\mathbf{S}(y)\mathbf{c}_p(y), \quad (24)$$

where $\mathbf{c}_p(y)$ is a column vector of coefficients for the spin orbital χ_p . Alternatively, if $\mathbf{C}(y)$ is the full matrix with $\mathbf{c}_p(y)$ as its columns, these equations can be written

$$\mathbf{F}(y)\mathbf{C}(y) = \mathbf{S}(y)\mathbf{C}(y)\mathbf{E}(y), \quad (25)$$

where $\mathbf{E}(y)$ is the diagonal matrix of one-electron energies $\epsilon_p(y)$. We also require that the orthonormality condition between spin orbitals is valid for all values of y , so that

$$\mathbf{C}^\dagger(y)\mathbf{S}(y)\mathbf{C}(y) = \mathbf{1}, \quad (26)$$

$\mathbf{1}$ being the unit matrix.

The theory is simplified if the spin-orbital coefficients $\mathbf{c}_p(y)$ are transformed to a basis corresponding to the unperturbed spin orbitals. Thus we write

$$\begin{aligned} \chi_p(y) &= \sum_q^{2N} u_{qp}(y) \hat{\chi}_q(y), \\ \hat{\chi}_q(y) &= \sum_\mu c_{\mu q}(0) \omega_\mu(y). \quad (27) \end{aligned}$$

$\hat{\chi}_q(y)$ is the form the spin orbital χ_q would take if the basis functions changed from $\omega_\sigma(0)$ to $\omega_\mu(y)$ but the c coefficients remained unaltered. Since the basis-set expansion of the perturbed orbital is

$$\chi_p(y) = \sum_\mu c_{\mu p}(y) \omega_\mu(y), \quad (28)$$

it follows from (27) and (28) that

$$c_{\mu p}(y) = \sum_q^{2N} c_{\mu q}(0) u_{qp}(y) \quad (29)$$

or

$$\mathbf{C}(y) = \mathbf{C}(0)\mathbf{U}(y). \quad (30)$$

Clearly $\mathbf{U}(0)$ is the unit matrix and our problem is to find $\mathbf{U}(y)$ for small y .

Substituting (30) in (25) and multiplying on the left by the Hermitian conjugate $\mathbf{C}^\dagger(0)$, we obtain

$$\mathbf{C}^\dagger(0)\mathbf{F}(y)\mathbf{C}(0)\mathbf{U}(y) = \mathbf{C}^\dagger(0)\mathbf{S}(y)\mathbf{C}(0)\mathbf{U}(y)\mathbf{E}(y). \quad (31)$$

This may be further simplified by defining ($2N \times 2N$) Fock and overlap matrices transformed by $\mathbf{C}(0)$,

$$\begin{aligned} \mathcal{F}(y) &= \mathbf{C}^\dagger(0)\mathbf{F}(y)\mathbf{C}(0), \\ \mathcal{S}(y) &= \mathbf{C}^\dagger(0)\mathbf{S}(y)\mathbf{C}(0). \quad (32) \end{aligned}$$

Then the Fock equations (31) become

$$\mathcal{F}(y)\mathbf{U}(y) = \mathcal{S}(y)\mathbf{U}(y)\mathbf{E}(y), \quad (33)$$

and the orthonormality condition (26) becomes

$$\mathbf{U}^\dagger(y)\mathcal{S}(y)\mathbf{U}(y) = \mathbf{1}. \quad (34)$$

$\mathcal{S}(0)$ is the unit matrix since the unperturbed spin orbitals are orthonormal. We have already noted that $\mathbf{U}(0)$ is the unit matrix. It follows from (33) that $\mathcal{F}(0)$ is identical with $\mathbf{E}(0)$ and is a $2N \times 2N$ diagonal matrix with diagonal elements equal to the unperturbed one-electron energies $\epsilon_p(0)$.

We now have to solve the basic equations (33) and (34) for small y . This is done by expanding the various matrices in powers of y and adopting a notation

$$\begin{aligned} \mathcal{F}(y) &= \mathbf{E}(0) + y\mathcal{F}^{(1)} + O(y^2), \\ \mathcal{S}(y) &= \mathbf{1} + y\mathcal{S}^{(1)} + O(y^2), \\ \mathbf{U}(y) &= \mathbf{1} + y\mathbf{U}^{(1)} + O(y^2), \\ \mathbf{E}(y) &= \mathbf{E}(0) + y\mathbf{E}^{(1)} + O(y^2). \quad (35) \end{aligned}$$

Note that $\mathbf{E}^{(1)}$ must be diagonal since $\mathbf{E}(y)$ is diagonal for all values of y . Substituting (35) into (33) and (34) and equating first-order terms in y , we obtain

$$\mathcal{F}^{(1)} + \mathbf{E}(0)\mathbf{U}^{(1)} = \mathcal{S}^{(1)}\mathbf{E}(0) + \mathbf{U}^{(1)}\mathbf{E}(0) + \mathbf{E}^{(1)}, \quad (36)$$

$$\mathbf{U}^{(1)\dagger} + \mathbf{U}^{(1)} + \mathcal{S}^{(1)} = 0. \quad (37)$$

Equations (36) and (37) now have to be solved to find the first-order changes $\mathbf{U}^{(1)}$ and $\mathbf{E}^{(1)}$.

At this point, it is convenient to revert to a subscript notation. Diagonal elements of (37) give

$$u_{pp}^{(1)*} + u_{pp}^{(1)} + \mathcal{S}_{pp}^{(1)} = 0. \quad (38)$$

We may choose $u_{pp}^{(1)}$ to be real, since multiplication of χ_p by an arbitrary phase factor is insignificant. Hence,

$$u_{pp}^{(1)} = -1/2 \mathcal{S}_{pp}^{(1)}. \quad (39)$$

Diagonal elements of (36) give

$$\epsilon_p^{(1)} = \mathcal{F}_{pp}^{(1)} - \mathcal{S}_{pp}^{(1)}\epsilon_p(0). \quad (40)$$

Off-diagonal elements of (36) lead to

$$u_{qp}^{(1)} = \frac{\mathcal{S}_{qp}^{(1)} - \mathcal{S}_{qp}^{(1)}\epsilon_p(0)}{\epsilon_p(0) - \epsilon_q(0)}. \quad (41)$$

Equations (39)–(41) give the required first-order quantities $\mathbf{U}^{(1)}$ and $\mathbf{E}^{(1)}$ in terms of the first-order changes $\mathcal{F}^{(1)}$, $\mathcal{S}^{(1)}$ of the Fock and overlap matrices. However, this is not yet a complete solution since $\mathcal{F}^{(1)}$ will itself depend on $\mathbf{U}^{(1)}$.

The overlap perturbation expression $\mathcal{S}^{(1)}$ can be handled easily since [from (32)]

$$\mathcal{S}_{\mu\nu}^{(1)} = \sum_{\mu\nu} c_{\mu q}^*(0) S_{\mu\nu}^{(1)} c_{\nu p}(0), \quad (42)$$

where $S_{\mu\nu}^{(1)}$ is the first-order contribution to the original overlap matrix $S_{\mu\nu}(y)$,

$$S_{\mu\nu}^{(1)} = \left(\frac{\partial S_{\mu\nu}}{\partial y} \right)_{y=0}. \quad (43)$$

The first-order Fock matrix contribution may be written

$$\mathcal{F}_{qp}^{(1)} = \mathcal{H}_{qp}^{(1)} + \mathcal{G}_{qp}^{(1)}, \quad (44)$$

where $\mathcal{H}_{qp}^{(1)}$ is the one-electron part,

$$\mathcal{H}_{qp}^{(1)} = \sum_{\mu\nu} c_{\mu q}^*(0) H_{\mu\nu}^{(1)} c_{\nu p}(0). \quad (45)$$

The two-electron part $\mathcal{G}_{qp}^{(1)}$ is the first-order term in the expansion of

$$\mathcal{G}_{qp}(y) = \sum_i \sum_{rs}^{2N} u_{ri}^*(y) u_{si}(y) (qr || ps)_y^\dagger. \quad (46)$$

Here $(qr || ps)_y^\dagger$ is written for the transformed integral,

$$(qr || ps)_y^\dagger = \sum_{\mu\nu\lambda\alpha} c_{\mu q}^*(0) c_{\lambda r}^*(0) c_{\nu p}(0) c_{\alpha s}(0) (\mu\lambda || \nu\sigma)_y, \quad (47)$$

which depends on y only through the original two-electron integrals. All three factors on the right of (46) give first-order contributions on expansion, so that

$$\mathcal{G}_{qp}^{(1)} = \sum_i \sum_r^{2N} [u_{ri}^{(1)*}(qr || pi) + u_{ri}^{(1)}(qi || pr)] + \sum_{\mu\nu\lambda\sigma} c_{\mu q}^*(0) c_{\nu p}(0) P_{\lambda\sigma}(0) \left(\frac{\partial}{\partial y} (\mu\lambda || \nu\sigma) \right)_{y=0}. \quad (48)$$

The sum over r in (48) is conveniently separated into an occupied part ($r = j = 1, \dots, n$) and a virtual part ($r = a = n + 1, \dots, 2N$). The occupied part can be simplified using (37), so that, substituting back in (44), the first-order Fock matrix expression becomes

$$\mathcal{F}_{qp}^{(1)} = \mathcal{H}_{qp}^{(1)} + \sum_i \sum_j^n \left\{ -\mathcal{S}_{ji}^{(1)}(qj || pi) + \sum_i \sum_a [u_{ai}^{(1)*}(qa || pi) + u_{ai}^{(1)}(qi || pa)] + \sum_{\mu\nu\lambda\sigma} c_{\mu q}^*(0) c_{\nu p}(0) P_{\lambda\sigma}(0) \left[\frac{\partial}{\partial y} (\mu\lambda || \nu\sigma) \right]_{y=0} \right\}. \quad (49)$$

This involves the occupied-virtual block $u_{ai}^{(1)}$, which again depends on $\mathcal{F}^{(1)}$ through (41). Substituting (49) into (41) and collecting terms we get

$$[\epsilon_i^{(0)} - \epsilon_a^{(0)}] u_{ai}^{(1)} = \mathcal{Q}_{ai}^{(1)} + \sum_j \sum_b [u_{bj}^{(1)*}(ab || ij) + u_{bj}^{(1)}(aj || ib)], \quad (50)$$

where

$$\mathcal{Q}_{ai}^{(1)} = \mathcal{H}_{ai}^{(1)} - \mathcal{S}_{ai}^{(1)} \epsilon_i(0) - \sum_{kl} \mathcal{S}_{kl}^{(1)}(al || ik) + \sum_{\mu\nu\lambda\sigma} c_{\mu a}^*(0) c_{\nu i}(0) P_{\lambda\sigma}(0) \left[\frac{\partial}{\partial y} (\mu\lambda || \nu\sigma) \right]_{y=0}. \quad (51)$$

The set of equations (50) can be used to solve for $u_{ai}^{(1)}$ by some iterative process. Once these are known, the whole matrix $\mathcal{F}_{qp}^{(1)}$ can be obtained directly from (49), since the right-hand side is then known.

To use the solutions of (49) in the second-order derivative expression (23), we need $\partial P_{\mu\nu}/\partial y$ and $\partial W_{\mu\nu}/\partial y$. These can be obtained by transformation of the corresponding matrices in the spin-orbital basis. Thus the electron density ρ is

$$\rho(y) = \sum_i \chi_i^*(y) \chi_i(y) = \sum_{rs}^{2N} P_{rs}(y) \hat{\chi}_r^* \hat{\chi}_s, \quad (52)$$

where

$$P_{rs}(y) = \sum_i u_{ri}^*(y) u_{si}(y). \quad (53)$$

Expansion of (51) to first order in y gives

$$\begin{aligned}\mathcal{P}_{ij}^{(1)} &= u_{ij}^{(1)*} + u_{ji}^{(1)} = -\mathcal{S}_{ji}^{(1)}, \\ \mathcal{P}_{ia}^{(1)} &= u_{ai}^{(1)}, \\ \mathcal{P}_{ab}^{(1)} &= 0.\end{aligned}\quad (54)$$

The required $P_{\mu\nu}$ derivative matrix is then

$$\left(\frac{\partial P_{\mu\nu}}{\partial y}\right)_{y=0} = \sum_{rs}^{2N} \mathcal{P}_{rs}^{(1)} c_{\mu r}^* c_{\nu s}(0). \quad (55)$$

In a similar way, the energy-weighted density matrix is

$$\mathcal{W}_{rs}(y) = \sum_i^n \epsilon_i(y) u_{ri}^*(y) u_{si}(y). \quad (56)$$

Expansion, together with (40) and (41), gives

$$\begin{aligned}\mathcal{W}_{ij}^{(1)} &= \mathcal{F}_{ji}^{(1)} - [\epsilon_i(0) + \epsilon_j(0)] \mathcal{S}_{ji}^{(1)}, \\ \mathcal{W}_{ia}^{(1)} &= \epsilon_i(0) u_{ai}^{(1)}, \\ \mathcal{W}_{ab}^{(1)} &= 0.\end{aligned}\quad (57)$$

Then

$$\left(\frac{\partial \mathcal{W}_{\mu\nu}}{\partial y}\right)_{y=0} = \sum_{rs}^{2N} \mathcal{W}_{rs}^{(1)} c_{\mu r}^* c_{\nu s}(0). \quad (58)$$

This completes evaluation of the second-derivative expression (23).

We now turn to the first derivative of the second-order Møller–Plesset energy (16). This requires derivatives of the transformed integrals $(ij||ab)$ as well as those of the Fock energies $\epsilon_p(ij||ab)$ to be written

$$(ij||ab) = \sum_{pqrs}^{2N} u_{pi}^* u_{qj}^* u_{ra} u_{sb} (pq||rs)_x^\dagger, \quad (59)$$

where $(pq||rs)_x^\dagger$ is given by (47). Differentiation of $(pq||rs)^\dagger$ gives a contribution to $(\partial/\partial x)(ij||ab)$, which is

$$\sum_{\mu\nu\lambda\sigma} c_{\mu i}^*(0) c_{\nu j}^*(0) c_{\lambda a}(0) c_{\sigma b}(0) \left(\frac{\partial}{\partial x}\right) (\mu\nu||\lambda\sigma). \quad (60)$$

Differentiation of the u and ϵ quantities may be carried out in the same way as previously, giving results in terms of the first-order matrices $\mathcal{S}_{qp}^{(1)}$ and $\mathcal{F}_{qp}^{(1)}$.

Full algebraic details will not be given. The final result is conveniently expressed in terms of the first-order Møller–Plesset wavefunction coefficients

$$a_{ij}^{qb} = -(ij||ab)/\Delta_{ij}^{qb}. \quad (61)$$

Then the derivative of the second-order correlation energy $\mathcal{E}^{(2)}$ is

$$\frac{\partial \mathcal{E}^{(2)}}{\partial x} = \sum_{ij} \sum_{ab} a_{ij}^{qb} X_{ij}^{qb}, \quad (62)$$

$$\begin{aligned}X_{ij}^{qb} &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} c_{\mu i}(0) c_{\nu j}(0) c_{\lambda a}(0) c_{\sigma b}(0) \left(\frac{\partial}{\partial x}\right) (\mu\nu||\lambda\sigma) \\ &+ \sum_k \left\{ (ij||ak) u_{kb}^{(1)} - \frac{1}{2} a_{kj}^{qb} [\mathcal{F}_{ki}^{(1)} - \epsilon_i(0) \mathcal{S}_{ki}^{(1)}] - \frac{1}{2} (kj||ab) \mathcal{S}_{ik}^{(1)} \right\} \\ &+ \sum_c \left\{ (cj||ab) u_{ci}^{(1)} + \frac{1}{2} a_{ij}^{qc} [\mathcal{F}_{cb}^{(1)} - \epsilon_b(0) \mathcal{S}_{cb}^{(1)}] - \frac{1}{2} (ij||ac) \mathcal{S}_{bc}^{(1)} \right\}.\end{aligned}$$

This can be calculated from a knowledge of the first-order matrices $\mathcal{S}^{(1)}$ and $\mathcal{F}^{(1)}$ (occupied, occupied and virtual, virtual blocks) and the first-order coefficients $U^{(1)}$ (occupied, virtual block).

3. Computational Procedures

Computation of the derivatives of \mathcal{E}_{HF} and \mathcal{E}_{MP2} uses much common information. In the GAUSSIAN 78 program, this is accomplished in the following principal steps:

Step 1. Evaluation of the integrals $S_{\mu\nu}$, $H_{\mu\nu}$, and $(\mu\nu||\lambda\sigma)$ by standard techniques [24–28]. The evaluation of the one-electron parts ($S_{\mu\nu}$ and $H_{\mu\nu}$) involves $O(N^2)$ operations, while the two-electron part $(\mu\nu||\lambda\sigma)$ requires $O(N^4)$ steps. The entire matrices containing $H_{\mu\nu}$ and $S_{\mu\nu}$ are stored on the disk. Only the nonzero two electron integrals are saved.

Step 2. Obtain the SCF coefficients $c_{\mu p}$ and Fock energies ϵ_p by conventional methods.

Step 3. Transformation of integrals to the molecular basis. For the calculation of \mathcal{E}_{MP2} and the second derivatives of \mathcal{E}_{HF} , only the set of transformed integrals with a maximum of two virtual spin orbitals $[(ij||ab)$ and $(ia||jb)]$ is required. However, differentiation of \mathcal{E}_{MP2} requires the larger set $(ia||bc)$ with three virtual spin orbitals. The Møller–Plesset energy and wavefunction coefficients a_{ij}^{qb} are available at this stage. This step involves $O(nN^4)$ arithmetic operations.

Step 4. Evaluation and storage of the first derivatives of the integrals $S_{\mu\nu}$, $H_{\mu\nu}$, and $(\mu\nu||\lambda\sigma)$. See step 7 for more details on the integral evaluation techniques. This step requires $O(N^4)$ arithmetic operations.

Step 5. Use of the integral derivatives to set up and solve the simultaneous linear equations (50) for the wavefunction derivative coefficient $u_{ai}^{(1)}$. This equation can be written in general matrix form as

$$(\mathbf{1} - \mathbf{A}) \mathbf{B} - \mathbf{B}_0 = 0. \quad (63)$$

Here \mathbf{B} is the vector of the unknown $u_{ai}^{(1)}$ which we are trying to determine. \mathbf{B}_0 is the vector with $n \times (2N - n)$ elements given by

$$B_{0(ai)} = \frac{Q_{ai}^{(1)}}{\epsilon_i^{(0)} - \epsilon_a^{(0)}}. \quad (64)$$

Here, $B_{0(ai)}$ refers to the ai th element of \mathbf{B}_0 where a and i are taken together as a single suffix. \mathbf{A} is the square matrix of the same dimension given by (for the real case)

$$A_{(ai,bj)} = \frac{(ab||ij) + (aj||ib)}{\epsilon_i^{(0)} - \epsilon_a^{(0)}} \quad (65)$$

Note that \mathbf{A} is not a symmetric matrix.

The vector \mathbf{B}_0 is first evaluated by processing the stored one- and two-electron integral derivatives.

Equation (63) now gives

$$\mathbf{B} = \sum_{n=0}^{\infty} \mathbf{A}^n \mathbf{B}_0. \quad (66)$$

Direct use of (66) to get the unknown \mathbf{B} is usually a slowly convergent process and involves a large number of iterations. [An iteration consists of getting one more term in the series in (66).] This convergence can be improved considerably by the following process.

Define orthogonal vectors $\mathbf{B}_0, \mathbf{B}_1, \dots, \mathbf{B}_k$ by

$$\mathbf{B}_{n+1} = \mathbf{A}\mathbf{B}_n - (\text{projection of } \mathbf{A}\mathbf{B}_n \text{ on } \mathbf{B}_n, \mathbf{B}_{n-1}, \dots, \mathbf{B}_0),$$

i.e.,

$$\mathbf{B}_{n+1} = \mathbf{A}\mathbf{B}_n - \sum_{l=0}^n \frac{\langle \mathbf{B}_l | \mathbf{A} | \mathbf{B}_n \rangle}{\langle \mathbf{B}_l | \mathbf{B}_l \rangle} \mathbf{B}_l. \quad (67)$$

Put

$$\mathbf{B} = \alpha_0 \mathbf{B}_0 + \alpha_1 \mathbf{B}_1 + \dots + \alpha_k \mathbf{B}_k. \quad (68)$$

The coefficients $\alpha_0, \dots, \alpha_k$ may be obtained by requiring that the projection of the left-hand side of (63) on $\mathbf{B}_0, \mathbf{B}_1, \dots, \mathbf{B}_k$ vanish. Typically, about four to six terms are sufficient to give sufficient convergence (RMS deviation of 10^{-6}).

The number of arithmetic operations involved in this step is $O(n^2N^2)$ for each nuclear variable. Note that although the above equations are given for just one variable, it is easy to handle all of them together.

Step 6. Use of the first derivative of the wavefunction to evaluate $\partial \mathcal{E}^{(2)} / \partial x$ [Eq. (62)] and the final three parts of the second-derivative expression (23). In the evaluation of $\partial \mathcal{E}^{(2)} / \partial x$, all the terms that are independent of the variable x are summed first in intermediate arrays. These are then contracted with the necessary first-order terms. For example, the term involving $u_{kb}^{(1)}$ is evaluated as follows:

$$Y_{kb} = \sum_{ija} a_{ij}^{ab} (ij||ak). \quad (69)$$

Contribution to $\partial \mathcal{E}^{(2)} / \partial x = \sum_{kb} Y_{kb} u_{kb}^{(1)}$: Note that Y_{kb} is the same for all the variables. The number of arithmetic operations involved in the evaluation of $\partial \mathcal{E}^{(2)} / \partial x$ is $O(nN^4)$.

The final three parts of the second-derivative expression can be calculated from the density matrix derivatives and the written-out integral derivatives. Note that a number of variables can be handled at the same time in one pass through the integral derivative list. The number of arithmetic operations involved in this step is $O(N^4)$.

These integrals, the first derivatives, and those two-electron integrals $(\mu\nu||\lambda\sigma)$ involving at least one d function are evaluated by the method of Rys polynomials [26]. In this method, an integral over the primitive Gaussian functions is written as a sum whose terms are products of the Rys polynomial and a weighting factor. The sum goes over a discrete range, namely, the zeros of the polynomial. The polynomial can be factored into Cartesian x , y , and z components which involve integration in the x , y , and z directions, respectively.

In practice, basis functions sharing a common center and exponents are grouped together into a "shell." The basis functions are located on the nuclear centers, and throughout the differentiation process remain rigidly attached to these centers. The program structure is such that the outermost loops go over shells. The next level of loops goes over the primitive Gaussians that make up each shell. At this level, the necessary geometric and exponent information is combined to determine the roots and weights of the Rys polynomial. For each root, the necessary x , y , and z components of the polynomial are determined. The techniques by which the roots, weights, and components are evaluated are described elsewhere [28]. The next level involves the combination of the weights and the components to make each primitive integral. The final integrals over basis functions χ_μ are built up by looping over the Gaussian contractions. These are written out to the disk (integrals and first derivatives) or used directly in the computer memory (second derivatives).

The program structure outlined above can be used to calculate the integrals and their first and second derivatives. In the case of the integral derivatives, the derivatives of the components are necessary. These are readily obtained since they are simply the components that would be required in evaluating integrals containing functions of the next higher angular momentum. For the basic integrals $(\mu\nu||\lambda\sigma)$ the computer time is roughly divided between evaluation of the components and combining them with the weights to get the primitive integrals. The evaluation of the first and second derivatives of the integrals is dominated by the combination step.

4. Illustrative Calculations

The derivative programs at the HF and the MP2 level have been used to calculate the harmonic vibrational frequencies of ethylene using the 6-31G* basis [30] (split valence plus polarization functions on the heavy atoms). At both levels, the respective equilibrium geometry was used. Use of some other geometry (e.g., the experimental geometry) may lead to ambiguities in the harmonic frequencies. As Pulay [6] comments, "Cartesian and internal force constants may lead to different harmonic vibrational frequencies if they are not calculated at the

theoretical equilibrium geometry." At the HF level, a single calculation of the energy second derivatives at the equilibrium geometry gives all the frequencies. However, at the MP2 level, a series of calculations involving the first derivatives of \mathcal{E}_{MP2} was performed to build the force constant matrix and hence obtain the frequencies. These are listed in Table I along with the experimental frequencies [29]. Anharmonicity corrections to the experimental frequencies have been made by Duncan *et al.* [29] to get estimated harmonic frequencies. These aid in direct comparison with theory and are listed in Table I.

It is seen immediately that HF theory overestimates the harmonic frequencies by 55–180 cm^{-1} . Inclusion of correlation, even at the simple MP2 level, improves the agreement considerably. It accounts for about 70% of the difference between the HF theory and experiment yielding frequencies that differ from experiment by only 10–90 cm^{-1} . Most of the frequencies are still overestimated. Unfortunately, there is a lot of uncertainty in the anharmonicity corrections. To avoid this problem, Pulay and Meyer [10] have corrected their calculated HF force constants (10% for diagonal stretching force constants and 20% for diagonal bending force constants) and get good agreement with experiment. However, this does not appear to be a satisfactory solution to this problem. The remaining difference between theory and experiment may be due to this uncertainty in the anharmonicity corrections or due to the deficiency in the basis set or the higher-order effects of electron correlation.

TABLE I. Vibrational frequencies for ethylene (cm^{-1}).

Symmetry of Vibration	HF/6-31G* ^a	MP2/6-31G* ^b	Experiment ^c	Estimated Harmonic Frequencies From Expt. ^d
b_{2u}	897.0	851.1	826.0	842.9
b_{2g}	1099.4	942.6	939.6	958.8
b_{1u}	1095.0	991.8	949.3	968.7
a_u	1154.9	1085.5	1023	1043.9
b_{1g}	1352.5	1265.9	1220	1244.9
a_g	1496.9	1415.7	1342.2	1369.6
b_{3u}	1610.2	1520.8	1443.5	1473.0
a_g	1856.2	1721.1	1630	1654.9
b_{3u}	3320.9	3213.3	3021	3146.5
a_g	3344.2	3230.9	3026.4	3152.5
b_{1g}	3394.6	3300.4	3102.5	3231.9
b_{2u}	3420.7	3323.3	3104.9	3234.3

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

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

^c The experimental frequencies are from ref. 29.

^d Anharmonicity corrections are made on the observed. Experimental frequencies to get these estimated values [29].

TABLE II. Execution times^d for the HF derivative programs (min) for ethylene using 6-31G* basis (38 basis functions).

Program	HF	HF + First Derivative	HF + First and Second Derivative
Integral evaluation	10	10	10
SCF	3	3	5 ^a
Evaluation of integral first derivatives		7 ^c	16 ^{b,c}
Two-electron integral transformation			8
CPHF + evaluation of density matrix derivative contribution to second derivatives			19
Evaluation of integral second derivatives			31 ^c
Total	13	20	89

^a The convergence on the density matrix in the SCF is tightened to get more significant figures in the MO 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 All the calculations were performed on a VAX-11/780 computer at Carnegie-Mellon University.

5. Comparison of the Execution Times for the Derivative Programs

In order to test the applicability of these derivative techniques, the execution times for the various steps outlined in Sec. 3 are listed in Tables II and III. Table II gives the execution times for the HF first- and second-derivative steps. Table III gives the corresponding execution times for the MP2 derivative programs.

TABLE III. Execution times^b for the MP2 derivative programs (min) for ethylene using 6-31G* basis (38 basis functions).

Program	MP ₂	MP ₂ + First Derivative
Integral evaluation	10	10
SCF	5	5
Two-electron integral transformation	5	15 ^a
Evaluation and writing out the integral first derivatives		16
CPHF + calculation of MP2 derivative		31
Total	20	77

^a More transformed integrals are calculated in this case as compared to a simple MP2 calculation.

^b All the calculations were performed on a VAX-11/780 computer at Carnegie-Mellon University.

It is seen from Table II that the calculation of \mathcal{E}_{HF} and its first derivatives takes approximately twice the computer time taken to calculate the energy alone. Pulay [31] and Ishida *et al.* [14] report that their gradient programs take about three to four times as long as the SCF programs. This speed-up is attributable to the increased efficiency of the Rys method relative to older integral evaluation techniques.

It is also seen that a full second-derivative calculation (which is sufficient to determine the harmonic vibrational frequencies) takes only four to five times as much computer time as a gradient calculation. Pulay [5, 6] has mentioned that the calculation of the analytical second derivatives may not be practical and that the calculation of the force constants by the finite-difference method on the gradients may be cheaper. However, the above results show that the evaluation of the harmonic force constants from the analytical second derivatives of the energy is an efficient and practical method. This is especially true since the number of gradient points required in the finite-difference method (for the general case) is $O(3m)$, where m is the number of atoms. Note also that the integral gradient times are strongly affected by the degree of contraction of the atomic orbital basis. New basis sets are currently under development that use fewer primitive Gaussians [32] and these give considerable timing improvements.

Analytical evaluation of the first derivatives of \mathcal{E}_{MP2} is also efficient. The evaluation of \mathcal{E}_{MP2} along with its derivatives takes about four times as much computer time as the calculation of the energy alone. This should be very useful for the exploration of potential surfaces at this level. It also gives improved accuracy in the calculation of force fields and harmonic frequencies. Extension of these techniques to higher perturbation orders of the correlation energy as well as applications to configuration interaction are currently in progress.

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