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### Publication Date

1983-05-01

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May 1982

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MOLECULAR SYMMETRY IV: THE COUPLED PERTURBED HARTREE-FOCK METHOD\*

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\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Grant No. CHE-7721305.

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## MOLECULAR SYMMETRY IV: THE COUPLED PERTURBED HARTREE-FOCK METHOD

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Abstract

Symmetry methods employed in the ab initio polyatomic program HONDO are extended to the coupled perturbed Hartree-Fock (CPHF) formalism, a key step in the analytical computation of energy first derivatives for configuration interaction (CI) wavefunctions, and energy second derivatives for Hartree-Fock (HF) wavefunctions. One possible computational strategy is to construct Fock-like matrices for each nuclear coordinate, in which the one- and two-electron integrals of the usual Fock matrix are replaced by the integral first derivatives. "Skeleton" matrices are constructed from the unique blocks of electron repulsion integral derivatives. The correct matrices are generated by applying a symmetrization operator. The analysis is valid for many wavefunctions, including closed- or open-shell spin restricted and spin unrestricted HF wavefunctions. To illustrate the method we compare the computer time required for setting up the coupled perturbed HF equations for eclipsed ethane using  $D_{3h}$  symmetry point group and various subgroups of  $D_{3h}$ . Computational times are roughly inversely proportional to the order of the point group.

Keywords: symmetry, coupled-perturbed Hartree-Fock, energy derivatives,  
HONDO.

## I. Introduction

The coupled perturbed Hartree-Fock (CPHF) theory outlined by Gerratt and Mills<sup>1</sup> for the calculation of one-electron second-order properties is a key step in the analytical computation of the energy first derivatives for configuration interaction (CI) wavefunctions<sup>2,3,4,5</sup> and of the energy second derivatives for Hartree-Fock (HF) wavefunctions.<sup>5</sup> The CPHF equations provide the derivatives of the molecular orbital coefficients with respect to the nuclear coordinates. The original formulation of the CPHF formalism for closed-shell HF wavefunctions<sup>1</sup> has been extended to open shell spin unrestricted HF wavefunctions by Pople, et al.<sup>5</sup> to open-shell spin restricted HF wavefunctions by Osamura, et al.<sup>3</sup> and to general multiconfiguration Hartree-Fock (MCHF) wavefunctions by one of us (MD).<sup>6</sup>

A possible and efficient computational strategy for setting up the CPHF equations involves constructing Fock-like matrices for each nuclear coordinate. In closed-shell HF cases (extension to open-shell HF cases is straightforward), these Fock-like matrix elements have the form

$$\tilde{F}_{\mu\nu}(A,a) = \frac{\partial}{\partial q_{A,a}} \langle \mu | h | \nu \rangle + \sum_{\rho,\sigma} D_{\rho\sigma} \left\{ \frac{\partial}{\partial q_{A,a}} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right] \right\} \quad (I-1)$$

where  $q_{A,a}$  represent the  $a^{\text{th}}$  cartesian coordinate ( $a = 1,2,3$ ) of center A. In Eq. (I-1)  $\langle \mu | h | \nu \rangle$  represents the usual bare nucleus hamiltonian operator integral,  $\langle \mu\nu || \rho\sigma \rangle$  the usual two-electron repulsion integral, and  $D_{\rho\sigma}$  is an electron density matrix element. The formal expression of  $\tilde{F}_{\mu\nu}(A,a)$  is closely related to the closed-shell Fock matrix element

$$F_{\mu\nu} = \langle \mu | h | \nu \rangle + \sum_{\rho, \sigma} D_{\rho\sigma} [2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle] \quad (\text{I-2})$$

The one- and two-electron integrals of Eq. (I-2) have been replaced by their derivatives with respect to the cartesian coordinate  $q_{A,a}$  in Eq. (I-1). Note that there are  $3N$  such matrices, one for each nuclear coordinate, where  $N$  is the number of nuclei.

The purpose of this paper is to show that the symmetry methods<sup>7,8,9</sup> employed in the ab initio polyatomic program HONDO can be extended to reduce the work required for the construction of the matrices  $\tilde{F}(A,a)$ . In Section II we present the key equations for the calculations of the energy first and second derivatives along with the CPHF equations. The reader is referred to refs. (1) and (5) for their derivations. In Section III we define the nomenclature closely following the notations of refs. (7), (8), and (9). In Section IV we define the projection operator which allows us to take advantage of symmetry in the construction of the Fock-like matrices of Eq. (I-1). In Section V we present some results of test calculations showing the computational savings. In what follows we will adhere to the following convention: the pair of indices "A,a" represents the " $a^{\text{th}}$ " coordinate of center A;  $\mu, \nu, \rho, \sigma \dots$  represent atomic basis functions;  $i, j, k, l \dots$  represent molecular orbitals; "q" stands for any nuclear displacement.



## II. Energy Derivatives and CPHF Equations

### a) First and second energy derivatives for HF wavefunctions

Let  $\tilde{F}$  denote the closed-shell HF Fock matrix with

$$F_{\mu\nu} = \langle \mu | h | \nu \rangle + \sum_{\rho, \sigma} D_{\rho\sigma} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right], \quad (\text{II-1})$$

where the density matrix element is expressed as a function of the molecular orbitals coefficients  $\{C_{\mu i}\}$ :

$$D_{\rho\sigma} = \sum_i^{\text{occ}} 2C_{\rho i} C_{\sigma i}. \quad (\text{II-2})$$

The energy of a closed-shell HF wavefunction has the form

$$E_{\text{HF}} = \frac{1}{2} \sum_{\mu\nu} \left[ D_{\mu\nu} \langle \mu | h | \nu \rangle + D_{\mu\nu} F_{\mu\nu} \right] + V_{\text{NUC}}, \quad (\text{II-3})$$

$V_{\text{NUC}}$  being the nuclear repulsion energy.  $E_{\text{HF}}$  may be written

$$E_{\text{HF}} = \sum_{\mu\nu} D_{\mu\nu} \langle \mu | h | \nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\mu\nu} D_{\rho\sigma} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right] + V_{\text{NUC}} \quad (\text{II-4})$$

The first derivative of  $E_{\text{HF}}$  with respect to the nuclear coordinate  $q$  is given by

$$\begin{aligned} \frac{\partial E_{\text{HF}}}{\partial q} &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial}{\partial q} \langle \mu | h | \nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\mu\nu} D_{\rho\sigma} \frac{\partial}{\partial q} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right] \\ &+ \frac{\partial}{\partial q} V_{\text{NUC}} - \sum_{\mu\nu} W_{\mu\nu} \frac{\partial}{\partial q} \langle \mu | \nu \rangle, \end{aligned} \quad (\text{II-5})$$

where  $W_{\mu\nu}$  is the energy weighted density matrix element

$$W_{\mu\nu} = \sum_i^{\text{OCC}} 2 \epsilon_i C_{\mu i} C_{\nu i} , \quad (\text{II-6})$$

$\langle \mu | \nu \rangle$  represents the usual overlap integral, and  $\epsilon_i$  is the energy of the  $i^{\text{th}}$  molecular orbital. At this point it is convenient to define a quantity  $\tilde{F}_{\mu\nu}(q)$  given by

$$\tilde{F}_{\mu\nu}(q) = \frac{\partial}{\partial q} \langle \mu | h | \nu \rangle + \sum_{\rho\sigma} D_{\rho\sigma} \frac{\partial}{\partial q} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right] . \quad (\text{II-7})$$

It can easily be seen that the derivative of  $F_{\mu\nu}$  of Eq. (II-1) is equal to

$$\frac{\partial}{\partial q} F_{\mu\nu} = \tilde{F}_{\mu\nu}(q) + \sum_{\rho\sigma} \frac{\partial D_{\rho\sigma}}{\partial q} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right] . \quad (\text{II-8})$$

In practice  $\tilde{F}_{\mu\nu}(q)$  is used to set up the CPHF equations which in turn provide  $\frac{\partial}{\partial q} D_{\rho\sigma}$  and make it possible to calculate  $\frac{\partial}{\partial q} F_{\mu\nu}$ . For this reason we will refer to  $\tilde{F}_{\mu\nu}(q)$  as a "Fock matrix derivative" element.

Using this notation the second derivative of  $E_{\text{HF}}$  with respect to nuclear coordinates  $p$  and  $q$  is

$$\begin{aligned} \frac{\partial^2}{\partial p \partial q} E_{\text{HF}} = & \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2}{\partial p \partial q} \langle \mu | h | \nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\mu\nu} D_{\rho\sigma} \frac{\partial^2}{\partial p \partial q} \left[ 2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle \right] \\ & + \frac{\partial^2}{\partial p \partial q} V_{\text{NUC}} - \sum_{\mu\nu} W_{\mu\nu} \frac{\partial^2}{\partial p \partial q} \langle \mu | \nu \rangle \end{aligned} \quad (\text{II-9})$$

$$+ \sum_{\mu\nu} \tilde{F}_{\mu\nu}(q) \frac{\partial}{\partial q} D_{\mu\nu} - \sum_{\mu\nu} \frac{\partial W_{\mu\nu}}{\partial p} \frac{\partial}{\partial q} \langle \mu | \nu \rangle .$$

To calculate the last two terms of Eq. (II-9), one needs to know the derivatives of the molecular orbital coefficients with respect to the nuclear coordinates. These derivatives are provided by the CPHF equations.

b) First energy derivatives for CI wavefunctions

The general form of a configuration interaction (CI) energy is

$$E_{CI} = \sum_{i,j}^{occ} \gamma^{ij} \langle i | h | j \rangle + \frac{1}{2} \sum_{ijhl}^{occ} \Gamma^{ijhl} \langle ij || kl \rangle . \quad (II-10)$$

Following refs. (2) and (6), we have

$$\begin{aligned} \frac{\partial}{\partial q} E_{CI} = & \sum_{\mu\nu} \gamma^{\mu\nu} \frac{\partial}{\partial q} \langle \mu | h | \nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma} \Gamma^{\mu\nu\rho\sigma} \frac{\partial}{\partial q} \langle \mu\nu || \rho\sigma \rangle \\ & + \sum_{i,j} U_{ij}^q \epsilon^{ij} \end{aligned} \quad (II-11)$$

In Eqs. (II-10) and (II-11)  $\gamma^{ij}$  and  $\Gamma^{ijhl}$  are the one- and two-particle density matrix elements of the CI wavefunction expressed in the molecular orbital basis,  $\gamma^{\mu\nu}$  and  $\Gamma^{\mu\nu\rho\sigma}$  are the one- and two-particle density matrix elements expressed in the atomic orbital basis. The matrix  $U^q$  is the matrix of molecular orbital coefficient derivatives given by the CPHF equations.

### c) The CPHF equations

In the CPHF theory we assume that the molecule with molecular orbitals  $\phi(o)$  is subjected to a small change in nuclear coordinate  $q$ .

The matrix  $U^q$  is defined in first-order approximation by:

$$C(q) = C(o) [1 + qU^q] \quad . \quad (II-12)$$

Where  $C$  is the matrix of molecular orbital coefficients. For a closed-shell HF wavefunction the CPHF equations are

$$\begin{aligned} U_{ai}^q (\epsilon_i - \epsilon_a) = & \tilde{F}_{ai}(q) - S_{ai}^q \epsilon_i \\ & - \sum_{m,n}^{\text{occ}} S_{mn}^q [2\langle aillmn \rangle - \langle amllin \rangle] \\ & + \sum_j^{\text{occ}} \sum_b^{\text{virt}} [4\langle aillbj \rangle - \langle abllij \rangle - \langle ajllbi \rangle] U_{bj}^q , \end{aligned} \quad (II-13)$$

where  $\tilde{F}_{ai}(q)$  is given by

$$\tilde{F}_{ai}(q) = \sum_{\mu\nu} C_{\mu a} \tilde{F}_{\mu\nu}(q) C_{\nu i}, \quad (II-14)$$

and

$$S_{ai}^q = \sum_{\mu\nu} C_{\mu a} \frac{\partial}{\partial q} \langle \mu | \nu \rangle C_{\nu i} \quad . \quad (II-15)$$

In ref. (7) we showed how point group symmetry can be used to reduce the computational task in forming  $F_{\mu\nu}$  given by Eq. (II-1). The method was extended to the second term of Eq. (II-5)<sup>8</sup>

$$\frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\mu\nu} D_{\rho\sigma} \frac{\partial}{\partial q} [2\langle \mu\nu || \rho\sigma \rangle - \langle \mu\rho || \nu\sigma \rangle] \quad ,$$

and to the second term of Eq. (II-9)<sup>9</sup>

$$\frac{1}{2} \sum_{\mu\nu\rho\sigma} D_{\mu\nu} D_{\rho\sigma} \frac{\partial^2}{\partial p \partial q} \left[ 2\langle\mu\nu||\rho\sigma\rangle - \langle\mu\nu||\nu\sigma\rangle \right] .$$

In what follows we propose a new extension of the method to deal with the formation of  $\tilde{F}(q)$  given by Eq. (II-7), to be used for HF energy second derivatives in Eq. (II-9), and for CI energy first derivatives in Eq. (II-13).

### III. Basic Functions and Symmetry Transformations

Let  $\chi$  be a real cartesian basis function

$$\chi(A, n_x, n_y, n_z; r) = (x-A_x)^{n_x} (y-A_y)^{n_y} (z-A_z)^{n_z} g(|r-A|) \quad (\text{III-1})$$

where  $n_x, n_y, n_z$  are non-negative integers,  $A$  is the nuclear center of the function, and  $r$  the argument of the function. The radial factor,  $g$ , is usually a linear combination of Gaussian functions. We introduce the "rotational quantum number"

$$\lambda = n_x + n_y + n_z \quad (\text{III-2})$$

and refer to a function as being of type s, p, d, etc., when  $\lambda$  equals 0, 1, 2, etc., respectively. In what follows we may drop unimportant indices when it is felt that the meaning is obvious from the context. Let  $\chi^a$  denote the first derivative of  $\chi$  with respect to  $A_x, A_y$ , and  $A_z$  when  $a$  equals 1, 2, and 3, respectively. Basis functions are grouped into shells. Functions in the same shell I have the same  $A$  and  $\lambda$ , so an alternative notation is

$$\chi(I, m) = \chi(A, n_x, n_y, n_z; r) \quad (\text{III-3})$$

where I in the shell index.

Let G be the point group of the molecule, and  $\hat{R}$  an element of G. Operator  $\hat{R}$  maps point  $\underline{r}$  into  $\underline{r}'$ , function  $f(\underline{r})$  into  $f(\underline{r}')$  and shell I into I'. Shells I and I' have the same  $\lambda$  and their centers are related by

$$A_{I'} = \hat{R} A_I \quad (\text{III-4})$$

Basis function  $\chi(I, m)$  maps into a linear combination of functions in shell I' that is given by

$$\hat{R} \chi(I, m) = \sum_{m'=1}^{m(\lambda)} \chi(I', m') R(\lambda_I; m', m) \quad (\text{III-5})$$

where  $m(\lambda) = (\lambda + 1)(\lambda + 2)/2$  since we insist that a shell be closed under rotation about its own center, and thus include all combinations  $(n_x, n_y, n_z)$  consistent with a given  $\lambda_I$ . In ref. (8) we showed that the effect of a symmetry operation on a basis function derivative  $\chi^a$  is given by

$$\hat{R} \chi^a(I, m) = \sum_{m'} \sum_{a'} \chi^{a'}(I', m') R(1; a', a) R(\lambda; m', m) \quad (\text{III-6})$$

#### "Fock matrix derivatives" and symmetry operation

Let  $\underline{\chi}$  be a row vector denoting the molecular basis set and  $\hat{R}\underline{\chi} = \underline{\chi}'$  the set of images of these functions under  $\hat{R}$ .  $\underline{\chi}$  provides a basis for an n by n matrix representation of the group

$$\tilde{\chi}' = \tilde{\chi} R \quad (\text{III-7})$$

In ref. (7) we showed that the density matrix  $\tilde{D}$  defined by

$$\rho(r) = 2\tilde{\chi}\tilde{D}\tilde{\chi}^+ \quad (\text{III-8})$$

satisfies the equation

$$\tilde{D} = \tilde{R} \tilde{D} \tilde{R}^+ \quad (\text{III-9})$$

if the electron density  $\rho(r)$  has the symmetry of the molecule. In addition the matrix  $\tilde{F}$  of the closed-shell HF operator Eq. (II-1) satisfies the relation

$$\tilde{F} = \tilde{R}^+ \tilde{F} \tilde{R} \quad (\text{III-10})$$

Similarly one can show (Appendix A) that the Fock matrix derivative  $\tilde{F}(E,e)$  satisfies the following important property

$$\tilde{F}(E,e) = \sum_{e'} R(1;e',e) R^+ \tilde{F}(E',e') R, \quad (\text{III-11})$$

where  $E'$  is the image of  $E$  under the given  $R$ .

In ref. (7) we used Eq. (III-10) to show that it is possible to construct a "skeleton" Fock matrix from the "petite" list of unique electron repulsion integrals. The true Fock matrix is recovered by a final symmetrization projection. In the next section we show how to construct "skeleton" Fock matrix derivatives from the list of unique electron repulsion integral derivatives. The correct Fock matrix derivatives are recovered by a final symmetrization projection.

#### IV. Fock Matrix Derivatives and Symmetrization

Following closely the approach of ref. (7), we consider the  $\tilde{G}_2$  grande list of triplets  $(E; I, J)$  where  $E$  represents a nucleus and  $I$  and  $J$  represent shells.  $\tilde{G}_2$  is the direct product of the grande list  $G_2$  and the list of all the nuclei. Similarly  $\tilde{G}_4$  is the grande list of quintets  $(E; I, J, K, L)$ , the direct product of  $G_4$  and the list of all the nuclei.

Two triplets  $(E; I, J)$  and  $(E'; I'J')$  are said equivalent if there exists an  $\hat{R}$  which maps center  $E$  into center  $E'$ , and if the pair of shells  $IJ$  is equivalent to  $I'J'$  under  $T_2 \times G$ . ( $T_2$  is the permutation operator of two labels.) A similar relationship can be defined for the elements of  $G_4$ . The list of unique elements of  $\tilde{G}_2$  and  $\tilde{G}_4$  are the corresponding petite lists denoted  $\tilde{P}_2$  and  $\tilde{P}_4$ .

Let  $g$  be the order of the symmetry group,  $n(E; I, J)$  the number of operations that maps  $(E; I, J)$  into itself and  $n(E; I, J, K, L)$  the number of operations that map  $(E; I, J, K, L)$  into itself. We define the contituency numbers

$$\tilde{q}_2(E; I, J) = 2g/n(E; I, J) \quad , \quad (IV-1)$$

$$\tilde{q}_4(E; I, J, K, L) = 8g/n(E; I, J, K, L) \quad , \quad (IV-2)$$

and a symmetrization operator by the following equation: if  $E'$  is the image of  $E$  under operation  $\hat{R}$ :

$$M(E, e)_{\text{sym}} = \frac{1}{2g} \sum_{\hat{R}} \sum_{e'} R(1; e', e) R^+ [M(E', e') + M^+(E', e')] R \quad . \quad (IV-3)$$



Furthermore, to every element of  $\tilde{G}_2$  we assign a number  $\tilde{\lambda}_{E'I'J'}$  such that

$$\sum_{E', I', J'} \tilde{\lambda}_{E'I'J'} = \tilde{q}_2(E; I, J) \quad (\text{IV-4})$$

where  $(E; I, J)$  is in  $\tilde{P}_2$  and the summation is over all three-labels equivalent to  $(E; I, J)$ . Given a matrix  $M(E, e)$ , we define a "skeleton" matrix  $M^*(E, e)$  using

$$M^*(E, e)_{IJ} = \tilde{\lambda}_{EIJ} M(E, e)_{IJ} \quad (\text{IV-5})$$

An algebraic manipulation (see Appendix B) similar to the one developed in ref. (7) shows that the following theorem holds:

Theorem 1: Given an  $n$  by  $n$  hermitian matrix  $M(E, e)$  with the property

$$M(E, e) = \sum_{e'} R(1; e', e) R^+ M(E', e') R \quad (\text{IV-6})$$

for all  $R$  in the point group, and given an  $M^*(E, e)$  which satisfies Eqs. (IV-4) and (IV-5), it follows that

$$M(E, e) = M^*(E, e)_{\text{sym}} \quad (\text{IV-7})$$

We now define  $V^C(E, e; IJKL)$  and  $V^X(E, e; IJKL)$  two  $n$  by  $n$  matrices for each  $(E; IJKL)$  element of  $\tilde{G}_4$ . The matrix elements in block  $IJ$  are given by

$$V^C_{IJ}(E, e; IJKL) = D_{KL} \frac{\partial}{\partial q_{E, e}} (IJJ|KL) \quad (\text{IV-8})$$

and elements outside this block are zero. Similarly,

$$V_{IK}^X(E, e; IJKL) = D_{JL} \frac{\partial}{\partial q_{E, e}} (IJ \parallel KL) \quad (IV-9)$$

and all other matrix elements are zero. In Eqs. (IV-8) and (IV-9) the symbol  $(IJ \parallel KL)$  represents the block of electron repulsion integrals with indices belonging to shells I, J, K, L. Summation over indices in K and L shells is implied in (IV-8), and summation over indices in J and L shells is implied in (IV-9). Again, an algebraic manipulation (see Appendix C) similar to the one developed in ref. (7) shows that the following theorem holds:

Theorem 2: If  $\hat{R}$  maps the five label  $(E; IJKL)$  into  $(E'; I'J'K'L')$ , then

$$V^C(E, e; IJKL)_{\text{sym}} = V^C(E', e'; I'J'K'L')_{\text{sym}} \quad (IV-10)$$

$$V^X(E, e; IJKL)_{\text{sym}} = V^X(E', e'; I'J'K'L')_{\text{sym}} \quad (IV-11)$$

If we now define an n by n matrix by

$$V(E, e; IJKL) = V^C(E, e; IJKL) + V^C(E, e; KLIJ) - \frac{1}{4} \left[ V^X(E, e; IJKL) + V^X(E, e; JIKL) + V^X(E, e; IJLK) + V^X(E, e; JILK) \right], \quad (IV-12)$$

it follows from Theorem 2 that

$$V(E, e; IJKL)_{\text{sym}} = V(E', e'; I'J'K'L')_{\text{sym}} \quad (IV-13)$$

The Fock matrix derivative  $\tilde{F}(E, e)$  is given by

$$\tilde{F}(E, e) = \tilde{H}_0(E, e) + \sum_{\tilde{G}4} \left[ 2V^C(E, e; IJKL) - V^X(E, e; IJKL) \right], \quad (IV-14)$$

or equivalently

$$\tilde{F}(E, e) = \tilde{H}_0(E, e) + \sum_{\tilde{G}4} V(E, e; IJKL) \quad . \quad (IV-15)$$

It follows that

$$\tilde{F}(E, e) = \tilde{H}_0(E, e)_{\text{sym}} + \sum_{\tilde{G}4} V(E, e; IJKL)_{\text{sym}} \quad . \quad (IV-16)$$

The significance of Eq. (IV-13) is that equivalent members of  $\tilde{G}4$  make identical contributions to the sum in Eq. (IV-16), so we need to sum only over the petite list of five labels in  $\tilde{P}4$  and weight each contribution by  $\tilde{q}_4$ . We proceed by constructing a set of skeleton matrices

$$\tilde{F}^*(E, e) = \tilde{H}_0(E, e) + \sum_{\tilde{P}4} \tilde{q}_4(E; IJKL) V(E, e; IJKL) \quad (IV-17)$$

and then by performing a final symmetrization

$$\tilde{F}(E, e) = \tilde{F}^*(E, e)_{\text{sym}} \quad . \quad (IV-18)$$

## V. Results and Conclusions

We have implemented these ideas into a new version of HONDO<sup>10</sup> which computes the second derivatives of the energy for HF wavefunctions and the first derivatives of the energy for CI wavefunctions.

The computer code is the same as the one described in ref. (9). As the unique electron repulsion integrals derivatives are calculated their contributions are added into the proper skeleton Fock matrix derivatives. Once all the integrals derivatives have been processed, the skeleton matrices are "symmetrized."

Test calculations have been carried out for the  $C_2H_6$  molecule in the eclipsed conformation. We used a minimal basis set augmented with a set of d functions on the carbon atoms and a set of p functions on the hydrogen atoms. The energy, first derivatives of the energy, and the Fock matrix derivatives were calculated using the full  $D_{3h}$  symmetry and the entire calculation was then repeated using seven different subgroups. The present algorithm is a combination of similar methods for the calculation of energy derivatives and for the construction of the Fock matrix. In refs. (7), and (8) we pointed out that computation times are roughly inversely proportional to the order of the point group. Identical ratios were obtained in both cases when comparing computation times in  $D_{3h}$  symmetry, and in lower symmetry. The same ratios are obtained in this step, as shown in Table I.

In conclusion we have presented an extension of symmetry methods employed in HONDO to the calculation of Fock matrix derivatives. These matrices are used to solve the CPHF equations which provide the derivatives of the molecular orbitals coefficients with respect to the nuclear coordinates. They are also used as a contribution to the energy second derivative matrix.

In summary similar symmetry methods can be applied to all the time consuming steps of energy, energy first derivatives and energy second derivatives of HF wavefunctions. In all the cases we found that computation times are approximately inversely proportional to the order of the symmetry point group.

Table I. Ratio of computer time for constructing the "Fock matrix derivatives" for eclipsed ethane.

<u>Point Group</u>	<u>Order</u>	<u>Ratios</u> <u>(Gradient)</u>	<u>Ratios</u> <u>(Fock Derivatives)</u>
D <sub>3h</sub>	12	1.0	1.0
C <sub>3v</sub>	6	2.0	2.0
C <sub>2v</sub>	4	2.3	2.4
C <sub>3</sub>	3	2.8	2.6
C <sub>2</sub>	2	4.1	4.0
C <sub>s</sub> ( $\sigma_h$ )	2	4.1	3.9
C <sub>s</sub> ( $\sigma_v$ )	2	4.5	4.5
C <sub>1</sub>	1	8.0	8.2

### Acknowledgment

The authors gratefully acknowledge Dr. Y. Osamura for many stimulating discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Grant No. CHE-7721305.

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### Appendix A: Property of $\tilde{F}(E,e)$

First we consider the electron-nucleus attraction operator

$$h(1) = - \sum_Q \frac{Z_Q}{r_{1Q}} \quad (A-1)$$

The derivative of  $h(1)$  with respect to coordinate "a" of center A is given by

$$\frac{\partial}{\partial q_{A,a}} h(1) = - Z_A \frac{[q_a(1) - Q_{A,a}]}{r_{1A}^{3/2}} \quad (A-2)$$

where  $q_a(1)$  represents the "a" cartesian coordinate of electron "1" when  $a = 1, 2$ , or  $3$ . Let B be the image of center A under symmetry operation  $\hat{R}$ . It follows

$$\hat{R} \frac{\partial}{\partial q_{A,a}} h(1) = - \sum_b \frac{Z_B}{r_{1B}^{3/2}} (q_b(1) - Q_{B,b}) R(1;b,a), \quad (A-3)$$

or

$$\hat{R} \frac{\partial h}{\partial q_{A,a}} = \sum_b \frac{\partial h}{\partial q_{B,b}} R(1;b,a) . \quad (A-4)$$

We now consider the matrix element

$$\frac{\partial}{\partial q_{E,e}} \langle \chi(I_A, m_A) | h | \chi(I_B, m_B) \rangle \quad (A-5)$$

and substitute Eqs. (III-5), (III-6), and (A-4) into Eq. (A-5). We find

$$\begin{aligned} \hat{R} \frac{\partial}{\partial q_{E,e}} \langle \chi(I_A, m_A) | h | \chi(I_B, m_B) \rangle = \\ \sum_{m'_A} \sum_{m'_B} \sum_{e'} R(1; e', e) R^+(\lambda_{I_A}; m_A, m'_A) R(\lambda_{I_B}; m_B, m'_B) \quad (A-6) \\ \times \frac{\partial}{\partial q_{E,e'}} \langle \chi(I_A, m'_A) | h | \chi(I_B, m'_B) \rangle . \end{aligned}$$

Similarly for the electron repulsion contribution of shells  $I_C$ , and  $I_D$  we get

$$\begin{aligned} \hat{R} \frac{\partial}{\partial q_{E,e}} \sum_{m_C} \sum_{m_D} D_{I_C m_C I_D m_D} \langle \chi(I_A, m_A) \chi(I_B, m_B) | \frac{1}{r_{12}} | \chi(I_C, m_C) \chi(I_D, m_D) \rangle = \\ \sum_{m'_A} \sum_{m'_B} \sum_{e'} R(1; e', e) R^+(\lambda_{I_A}; m_A, m'_A) R(\lambda_{I_B}; m_B, m'_B) \times \\ \sum_{m'_C} \sum_{m'_D} D_{I_C m'_C I_D m'_D} \times \quad (A-7) \\ \frac{\partial}{\partial q_{E,e'}} \langle \chi(I_A, m'_A) \chi(I_B, m'_B) | \frac{1}{r_{12}} | \chi(I_C, m'_C) \chi(I_D, m'_D) \rangle \end{aligned}$$

after using

$$D_{I_C m'_C I_D m'_D} = \sum_{m_C} \sum_{m_D} R(\lambda_{I_C}; m'_C, m_C) D_{I_C m_C I_D m_D} R^+(\lambda_{I_D}; m_D, m'_D). \quad (A-8)$$

Eqs. (A-6) and (A-7) are the basis of the property of Eq. (III-11) of  $\tilde{F}(E, e)$ .



### Appendix B: Proof of Theorem 1

Let us consider  $N(E, e) = M^*(E, e)_{\text{sym}}$ , or

$$N(E, e) = \frac{1}{2g} \sum_{\hat{R}} \sum_{e'} R(1; e', L) R^+ [M^*(E', e') + M^{*+}(E', e')] R, \quad (B-1)$$

which means that

$$N(E, e)_{IJ} = \quad (B-2)$$

$$\frac{1}{2g} \sum_R \sum_{I'J'} \sum_{e'} R(1; e', e) R_{II'}^+ [M^*(E', e') + M^{*+}(E', e')]_{I'J'} R_{J'J}.$$

The blocked form of  $\hat{R}$  (see ref. 7) implies that for each  $\hat{R}$  in Eq. (A-2) the summation over  $I'$  and  $J'$  reduces to a single non-vanishing term, namely the image of  $IJ$  under the given  $\hat{R}$ .

Eq. (IV-6) implies that if a given  $\hat{R}$  maps  $(E; IJ)$  into  $(E', I'J')$  then

$$M(E, e)_{IJ} = \sum_{e'} R(1; e', e) M(E', e')_{I'J'} R_{I'I} R_{J'J}. \quad (B-3)$$

The hermitian property of  $M(E, e)$  together with Eq. (IV-5) implies that

$$[M^*(E', e') + M^{*+}(E', e')]_{I'J'} = (\tilde{\lambda}_{E'I'J'} + \tilde{\lambda}_{E'J'I'}) M(E', e')_{I'J'}. \quad (B-4)$$

Substitution of Eqs. (B-4) and (B-3) into Eq. (B-2) yields

$$N(E, e)_{IJ} = \frac{1}{2g} M(E, e)_{IJ} \sum_{(E'I'J')} \tilde{\lambda}_{E'I'J'}, \quad (B-5)$$

where  $(E'; I'J')$  in the image of  $(E; IJ)$  under an element of  $T_2 \times G$ , and the sum runs over the direct product group. In the sum of Eq. (A-5) each member of the subset is repeated  $n(E; IJ)$  times. Thus Eqs. (IV-1), (IV-5), and (B-5) combine to give (Q.E.D.)

$$N(E, e)_{IJ} = M(E, e)_{IJ} \quad . \quad (B-6)$$

### Appendix C: Proof of Theorem 2

Let us operate  $\hat{R}$  and  $V^C(E, e; IJKL)$  defined by Eq. (IV-8). According to Eqs. (A-7) and (A-8), we have

$$V_{IJ}^C(E, e; IJKL) = \quad (C-1)$$

$$\sum_{e'} R(1; e'e) D_{KL} R_{II}^+ R_{J'J} R_{K'K} R_{LL}^+ \frac{\partial}{\partial q_{E', e'}} (I'J'K'L') ,$$

which can be written

$$V_{IJ}^C(E, e; IJKL) = \sum_{e'} R(1; e', e) R_{II}^+ \left[ D_{K'L'} \frac{\partial}{\partial q_{E', e'}} (I'J'K'L') \right] R_{J'J} . \quad (C-2)$$

or

$$V_{IJ}^C(E, e; IJKL) = \sum_{e'} R(1; e', e) R_{II}^+ V_{I'J'}^C(E', e'; I'J'K'L') R_{J'J} . \quad (C-3)$$

Since all other blocks of  $V^C$  are zero, Eq. (C-3) can be restated as a matrix equation

$$V^C(E, e; IJKL) = \sum_{e'} R(1; e'e) R^+ V^C(E', e'; I'J'K'L') R \quad (C-4)$$

Substituting Eq. (C-4) into Eq. (IV-3) leads to

$$V^C(E, e; IJKL)_{\text{sym}} = \quad (C-5)$$

$$\frac{1}{2g} \sum_{\hat{R}} \sum_{e'} R(1; e', e) R^+ \left\{ \sum_{e'} R'(1; e'', e') R'^+ [V^C(E'', e''; I''J''K''L'') + V^{C+}(E'', e''; I''J''K''L'')] R' \right\} R$$

which can be rewritten

$$V^C(E, e; IJKL)_{\text{sym}} = \quad (C-6)$$

$$\frac{1}{2g} \sum_{\hat{R}} \sum_{e'} \sum_{e''} \left( R(1; e', e) R'(1; e'', e') \right) R^+ R'^+ [V^C(E'', e''; I''J''K''L'') + V^{C+}(E''e''; I''J''K''L'')] R' R .$$

The closure property of the symmetry group yields

$$V^C(E, e; IJKL)_{\text{sym}} = \quad (C-7)$$

$$\frac{1}{2g} \sum_{\hat{R}''} \sum_{e''} R''(1; e'', e) R''^+ [V^C(E'', e''; I''J''K''L'') + V^{C+}(E''e''; I''J''K''L'')] R''$$

or

$$V^C(E, e; IJKL)_{\text{sym}} = V^C(E'', e''; I''J''K''L'')_{\text{sym}} \quad \text{Q.E.D.} \quad (C-8)$$

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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