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THE ANALYTIC EVALUATION OF THIRD AND FOURTH DERIVATIVES FOR HARTREE-FOCK WAVE FUNCTIONS

J.F. Gaw
(Ph.D. Thesis)

November 1984

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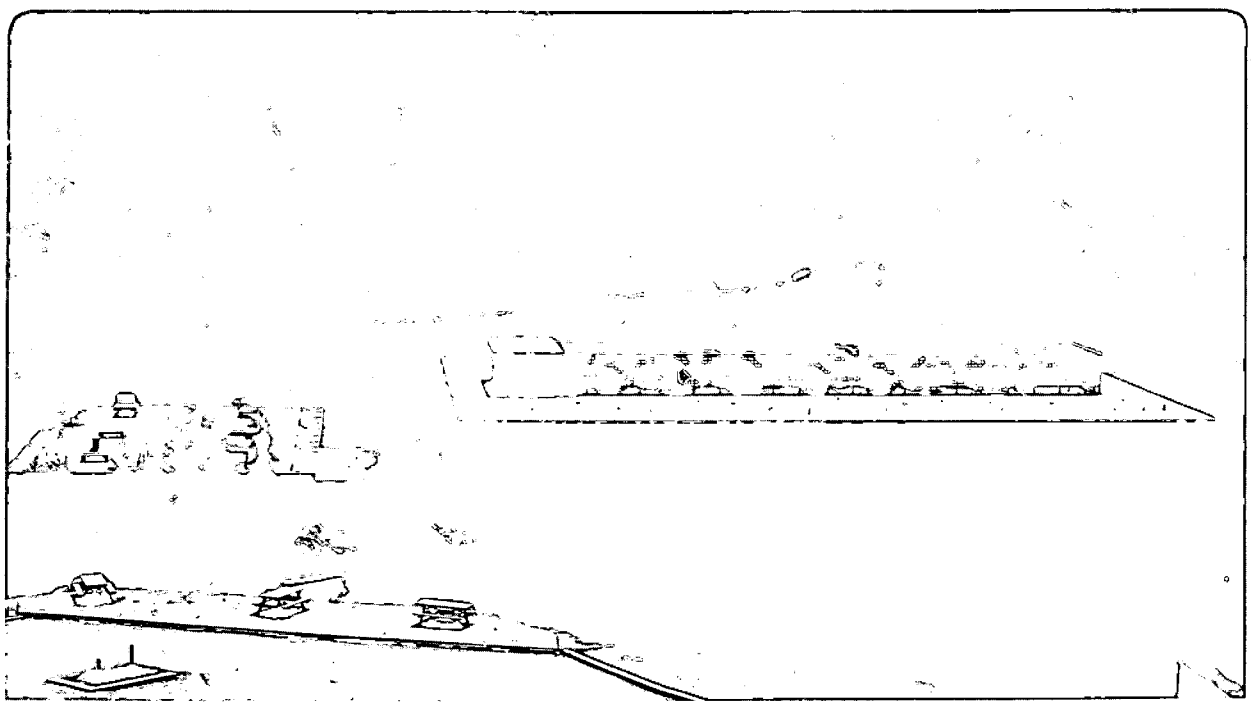

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THE ANALYTIC EVALUATION OF THIRD AND FOURTH DERIVATIVES FOR HARTREE-FOCK WAVE FUNCTIONS

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Ph.D. Thesis

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This work was supported by NSF grant CHE-8218785 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

The Analytic Evaluation of Third and Fourth Derivatives for Hartree-Fock Wave Functions

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ABSTRACT

First and second derivatives of the energy with respect to nuclear perturbations for Hartree-Fock wave functions have provided much information regarding the curvature and character of potential energy hypersurfaces. The introduction of analytic second derivatives not only allowed the calculation of quadratic force constants for molecular species that cannot be obtained through finite differences of energy gradients, but also increased accuracy and reduced computational time required to obtain these force constants. Third and fourth derivatives yield even more information concerning the potential energy surface by quantifying the anharmonicity. This work details the first implementation of the evaluation of analytic third derivatives with respect to nuclear perturbations for Hartree-Fock closed-shell molecules.

The calculation of analytic third derivatives divides neatly into two calculations: The first is the contribution from the perturbation of the basis set; and the second is the contribution from the perturbation of the molecular orbital coefficients. The perturbation of the basis set yields first, second, and third derivative atomic orbital integrals. These are calculated using Hermite gaussian functions and Rys quadrature. Details of the algorithms are presented.

The perturbation of the molecular orbital coefficients leads to first- and second-order coupled perturbed Hartree-Fock equations. These are reduced to first-order results. The ensuing energy equation coupling the two contributions is presented along with details concerning its evaluation.

Results comparing analytic cubic force constants in normal coordinate space to those derived from experimental data for the water molecule are reported. Agreement is excellent. Initial timing information indicates that the analytic evaluation of third derivatives is computationally less expensive than the calculation through finite differences of analytic second derivatives.

Henry F. Schaefer III

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My graduate studies have been greatly aided by the knowledge and encouragement of Professor H. F. Schaefer III. I would like to thank him for having enough confidence in my scientific ability to allow me a free hand in this and other projects on which I have worked while at Berkeley. I have benefited greatly from the inspired research environment created by Fritz and the many enlightening and spirited discussions over burgers, burritos, pizza and those interminal Risk games.

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Laurel. Our love has been my strength throughout our graduate studies. Laurel is an immunogeneticist at Stanford, and as such has had to put up with a lot, being married to an "Armchair scientist" from Berkeley. She has always been understanding and supportive, even when her sequences were garbled or clones the wrong length. Laurel has helped me in innumerable ways, not the least of which has been reading this thesis for spelling and grammatical errors. Without her, graduate school would have been impossible. Thanks.

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Preface

The analytic evaluation of energy derivatives requires an intimate knowledge of the evaluation of derivative atomic orbital integrals and the coupled-perturbed Hartree-Fock equations. Each of these subjects is complicated enough to warrant an entire thesis itself. Nevertheless, this thesis attempts to explain and provide the necessary information for the analytic evaluation of derivatives from "scratch".

The first chapter begins not with the theoretical background to the analytic solution of the derivative energy equations, but rather with experimental results. The reason for this is quite clear: The evaluation of cubic and quartic force constants, to be generally useful, must relate to something concrete. Chapter I outlines how this is accomplished. Chapter II details integral evaluation while chapter III deals with derivative integrals. The fourth chapter derives and presents the derivative energy equations providing computational remarks to the equations derived. Finally, the fifth chapter ties all the chapters together with the analytic calculation of the cubic force constants for the water molecule.

I. EXPERIMENTAL AND THEORETICAL BACKGROUND

I.1 INTRODUCTION

The effective rotational constants $B_v^{(\xi)}$ (ξ = a,b,c) and the vibrational energies $G_0(v_1, v_2, \ldots v_n)$ are two physical data directly derived from rotation and rotation-vibration spectroscopy. As the effective rotational constants are measured in a particular vibrational state, analysis over many states shows their dependence on a set of vibrational quantum numbers v_r.

$$B_v^{(\xi)} = B_e^{(\xi)} - \sum_r \alpha_r^{(\xi)} (v_r + g_r/2)$$

$$+ \sum_{r>s}\sum \gamma_{rs}^{(\xi)} (v_r + g_r/2) (v_s + g_s/2) + \ldots \qquad \text{(I.1.1)}$$

where g_r is the degeneracy of the vibrational state v_r, and g_s is the degeneracy of v_s. The $B_e^{(\xi)}$ are the equilibrium rotational constants defined by

$$B_e^{(\xi)} = \frac{\hbar^2}{2hc\ I_\xi} \qquad \text{(I.1.2)}$$

where I_ξ is the equilibrium moment of inertia about principal axis ξ. The constants $\alpha_r^{(\xi)}$ and $\gamma_{rs}^{(\xi)}$ describe the interaction of rotation and vibration and are experimentally obtained by a least-squares fit of the data.

The vibrational energies are given by

$$G_0(v_1, v_2, \ldots v_n) = G(v_1, v_2, \ldots v_n) - G(0,0,\ldots 0)$$

$$= \sum_r \omega_r^0 v_r + \sum_{r \geq s}\sum x_{rs}^0 v_r v_s \qquad (I.1.3)$$

with the expansion coefficients ω_r^0 and x_{rs}^0 found by a least-squares fit of the data. In the above observed vibrational energies, the expansion of the vibrational energy equation is truncated beyond second-order terms in the vibrational quantum numbers. In the absence of resonances this expansion is given by

$$G(v_1, v_2, \ldots v_n) = \sum_r \omega_r (v_r + g_r/2) + \sum_{r \geq s}\sum x_{rs} (v_r + g_r/2)(v_s + g_s/2) \qquad (I.1.4)$$

The ω_r are the zero-order frequencies and the x_{rs} are the anharmonic constants. The truncation beyond second-order implies that $x_{rs}^0 = x_{rs}$. The observed ω_r^0 are related to the zero-order frequencies by

$$\omega_r^0 = \omega_r + x_{rr} + 1/2 \sum_{r \neq s} x_{rs} g_s \qquad (I.1.5)$$

whereas the observed fundamentals ν_r are given by

$$\nu_r = \omega_r + x_{rr}(1+g_r) + 1/2 \sum_{r \neq s} x_{rs} g_s \qquad (I.1.6)$$

The experimental determination of these quantities is no trivial task. The anharmonic force constants are known only for a few relatively small polyatomic molecules. The advent of high resolution vibrational

spectroscopy has recently allowed the determination of ω_r and x_{rs} for as large a molecule as formaldehyde [1].

The basic theory on anharmonicity in polyatomic molecules is well known. See for example, the work of Nielsen [2], Cyvin [3], Kuchitsu [4,5], Oka [6], Morino [7], Watson [8,9] and Mills [10]. The theoretical evaluation of the anharmonic constants x_{rs} and the rotation-vibration interaction constants $\alpha_r^{(\xi)}$ begins with a series expansion of the potential energy function and a perturbation treatment of the rotation-vibration energy using the cubic and quartic terms in the potential series as the perturbation. In a review article of 1950, Nielsen [2] presented expressions for the x_{rs} and $\alpha_r^{(\xi)}$ constants correct through second-order in perturbation theory. The formulae expressed the anharmonic and interaction constants in terms of force constants and a number of complicated geometrically dependent quantities, all within normal coordinate space. It is the calculation of the anharmonic and interaction constants from _ab initio_ force constants that is the goal of this work.

Previous theoretical determinations of the anharmonic and interaction constants utilized a number of methods to obtain the necessary force constants. These methods include: the assumption of an analytic form of the potential that is mixed with experimental quantities so as to correctly describe the potential surface; the utilization of the experimental frequencies and interaction constants to iteratively solve for the force constants [11]; the fitting of _ab initio_ energy points to a polynomial [12]; and the utilization of finite differences of _ab initio_ energy gradients to calculate quadratic, cubic and quartic force constants [13]. In this study, however, analytic first,

second, and third energy derivatives of Hartree-Fock wave functions - the force constants themselves - will be calculated. No experimental data will be used. These force constants, along with the functions dependent on the geometry of the molecule, can then be used to determine the anharmonic and interaction constants.

In this chapter, the results of second-order perturbation theory of the complete rotation-vibration Hamiltonian will be presented for a potential energy function expanded as a power series. The question of the appropriate internal coordinates and the coordinate frame for the representation of the force constants will also be discussed.

I.2 RESULTS OF SECOND-ORDER PERTURBATION THEORY

The rotation-vibration Hamiltonian of Watson [8] is given by Mills [10] as

$$H = \sum_{\alpha,\beta} 1/2\ \mu_{\alpha\beta}\ \hbar^2\ (J_\alpha - \pi_\alpha)\ (J_\beta - \pi_\beta) + 1/2 \sum_r P_r^2 + V(Q_r) \tag{I.2.1}$$

The $\mu_{\alpha\beta}$, with α and β running over x, y, and z, are the elements of the μ tensor, which are related to the inverse moments of inertia (see reference 14 for details on its form); J_α are the components of the total angular momentum; π_α are the components of the vibrational angular momentum; and P_r is the rth normal mode conjugate momentum. The potential is given by

$$V/hc = 1/2 \sum_r \lambda_r Q_r^2 + 1/6 \sum_{rst} \Phi_{rst} Q_r Q_s Q_t + 1/24 \sum_{rstu} \Phi_{rstu} Q_r Q_s Q_t Q_u + \ldots\ldots \quad (I.2.2)$$

where the λ_r, Φ_{rst}, Φ_{rstu} are the quadratic, cubic, and quartic force constants. These force constants are the second, third, and fourth derivatives of the potential with respect to the normal coordinates. Mills [10] replaces P_r and Q_r with their dimensionless equivalents,

$$q_r = \gamma_r^{1/2} Q_r$$

and

$$p_r = P_r / \gamma_r^{1/2} \hbar \quad (I.2.3)$$

where

$$\gamma_r = \lambda_r^{1/2} / \hbar = 2\pi c \omega_r / \hbar \quad (I.2.4)$$

resulting in the potential being rewritten as

$$V/hc = 1/2 \sum_r \omega_r q_r^2 + 1/6 \sum_{rst} \phi_{rst} q_r q_s q_t + 1/24 \sum_{rstu} \phi_{rstu} q_r q_s q_t q_u + \ldots\ldots \quad (I.2.5)$$

It is for this form of the potential that the analytic force constants will be evaluated.

Much has been written on the intricacies of the terms that are a result of the perturbation treatment of the rotation-vibration energy. Nielsen's work [2] is perhaps the backbone for most recent treatments, however, we have found the work of Mills [10] the most enlightening. In

the following, the formulae derived by Mills [10] for the anharmonic constant x_{rs} and the rotation-vibration interaction constant $\alpha_r^{(\xi)}$ for the asymmetric top are presented to illustrate the uses of the third and fourth order force constants. The degeneracies of the vibrations for symmetric top increase the complexity of the formulae. As a result, the formulae lack the simple illustrative power of the asymmetric top and are not given here. The formulae for the symmetric top may be found in Mills [10], Nielsen [2], and Morino, Kuchistu, and Yamamoto [7].

The rotation-vibration interaction constant about the principal axis b, $\alpha_r^{(b)}$ is given by [10]:

$$-\alpha_r^{(b)} = \frac{2B^2}{\omega_r} \left\{ \sum_\xi \frac{3\left(a_r^{(b\xi)}\right)^2}{4\, I_\xi} + \sum_s \left(\zeta_{r,s}^{(b)}\right)^2 \frac{\left(3\omega_r^2 + \omega_s^2\right)}{\omega_r^2 - \omega_s^2} + \pi \left(\frac{c}{h}\right)^{1/2} \sum_s \phi_{rrs}\, a_s^{(bb)} \frac{\omega_r}{\omega_s^{3/2}} \right\} \qquad (I.2.6)$$

where the sum over ξ is over a, b, and c (the principal axes) while the sums over s are over all normal modes. ω_r is the harmonic force constant and ϕ_{rrs} the cubic force constant; both are in wavenumber units. The Coriolis coupling constant $\zeta_{r,s}^{(\xi)}$ in I.2.6 , may be reduced with the zeta sum rule

$$\sum_s \left(\zeta_{r,s}^{(\xi)}\right)^2 = A_{rr}^{(\xi\xi)} - \sum_\beta \frac{\left(a_r^{(\xi\beta)}\right)^2}{4\, I_{\xi\xi}} \qquad (I.2.7)$$

where $A_{rr}^{(\xi\beta)}$ and $a_r^{(\xi\beta)}$ are the expansion coefficients for the moment of inertia expressed in terms of normal coordinates.

$$I_{\xi\beta} = I_{\xi\beta}^e + \sum_r a_r^{(\xi\beta)} Q_r + \sum_r \sum_s A_{rs}^{(\xi\beta)} Q_r Q_s \qquad (I.2.8)$$

The coefficients are the derivatives of the moment of inertia with respect to normal coordinates. The $A_{rr}^{(\xi\beta)}$ and $a_r^{(\xi\beta)}$ are the geometrical quantities alluded to in the introduction.

The anharmonic constant x_{rs}, for r equal to s, is given by [10]:

$$x_{rr} = 1/16\ \phi_{rrrr} - 1/16 \sum_s \phi_{rrs}^2 \left\{ \frac{8\ \omega_r^2 - 3\ \omega_s^2}{\omega_s (4\ \omega_r^2 - \omega_s^2)} \right\} \tag{I.2.9}$$

where ϕ_{rrrr} is the quartic force constant defined by equation I.2.5. When r and s are not equal, the anharmonic constant is given by:

$$x_{rs} = 1/4\ \phi_{rrss} - 1/4 \sum_t \frac{(\phi_{rrt}\ \phi_{tss})}{\omega_t}$$

$$-1/2 \sum_t \phi_{rst}^2 \quad \omega_t \frac{(\omega_t^2 - \omega_r^2 - \omega_s^2)}{\Delta_{rst}}$$

$$+ \left(A(\zeta_{r,s}^{(a)})^2 + B(\zeta_{r,s}^{(b)})^2 + C(\zeta_{r,s}^{(c)})^2 \right) \left(\frac{\omega_r}{\omega_s} + \frac{\omega_s}{\omega_r} \right) \tag{I.2.10}$$

where

$$\Delta_{rst} = (\omega_r + \omega_s + \omega_t)\ (\omega_r - \omega_s - \omega_t)\ (-\omega_r + \omega_s - \omega_t)\ (-\omega_r - \omega_s + \omega_t) \tag{I.2.11}$$

These formulae are valid when there are no resonances. Resonances occur when two vibrational states are nearly degenerate, resulting in the denominator of terms in I.2.6, I.2.9, and I.2.10 approaching zero. Methods are available to treat such occurrences [10].

I.3 FORCE CONSTANTS AND COORDINATE SYSTEMS

The calculation of cubic and quartic force constants in an internal coordinate reference frame is complicated by the property that the nuclei are moving along arcs, not infinitesimal displacements along a rectilinear coordinate frame. This means that instantaneous values of the internal coordinate displacements must be obtained. Therefore, the traditional linear transformation between internal coordinates and cartesian displacement coordinates given below [14]

$$R_i = \sum_n B_i^n \, \delta x_n \tag{I.3.1}$$

must be expanded to [15,11]

$$\mathbf{R}_n = \sum_i B_n^i \, \delta x_i + 1/2 \sum_{i,j} B_n^{ij} \, \delta x_i \, \delta x_j + 1/6 \sum_{i,j,k} B_n^{ijk} \, \delta x_i \, \delta x_j \, \delta x_k + \ldots \tag{I.3.2}$$

where the B_n^i, B_n^{ij}, and B_n^{ijk} are the first, second, and third derivatives the nth internal coordinate with respect to δx_i. Such a set of $\mathbf{R}_n$ that describe the actual motion of the nuclei has been introduced by Hoy, Mills, and Strey [15].

The potential energy function in terms of these true internal coordinates is given by

$$V/hc = 1/2 \sum_{i,j} f^{ij} \, \mathbf{R}_i \, \mathbf{R}_j + 1/6 \sum_{i,j,k} f^{ijk} \, \mathbf{R}_i \, \mathbf{R}_j \, \mathbf{R}_k + 1/24 \sum_{i,j,k,l} f^{ijkl} \, \mathbf{R}_i \, \mathbf{R}_j \, \mathbf{R}_k \, \mathbf{R}_l + \ldots \tag{I.3.3}$$

In order to use the formulae presented in section I.2, the force constants f^{ij}, f^{ijk}, and f^{ijkl} calculated in terms of the true internal coordinates $\mathbf{R}_n$ must be transformed using a non-linear transformation to cartesian coordinates. The force constants with respect to cartesian coordinates are then linearly transformed to normal coordinate space.

Hoy, Mills, and Strey [15] have developed an alternative to the approach outlined above. In their technique, the force constants in terms of internal coordinates $\mathbf{R}_n$ are directly transformed to normal coordinate space by the L tensor. The elements of the L tensor are given by the non-linear transformation from internal coordinates $\mathbf{R}_n$ to normal coordinates Q_r.

$$\mathbf{R}_n = \sum_r L_n^r Q_r + 1/2 \sum_{r,s} L_n^{rs} Q_r Q_s + 1/6 \sum_{r,s,t} L_n^{rst} Q_r Q_s Q_t + \ldots \tag{I.3.4}$$

where the L_n^r, L_n^{rs}, and L_n^{rst} are the first, second, and third derivatives of $\mathbf{R}_n$ with respect to normal coordinates.

Substituting equation I.3.4 into I.3.3 and comparing the result to equation I.2.2, Hoy <u>et al.</u> [15] found that

$$\Phi_{rs} = \lambda_r = \sum_{i,j} f^{ij} L_i^r L_j^s \delta_{rs}$$

$$\Phi_{rst} = \sum_{i,j,k} f^{ijk} L_i^r L_j^s L_k^t + \sum_{i,j} f^{ij} \left(L_i^{rs} L_j^t + L_i^{rt} L_j^s + L_i^{st} L_j^r\right)$$

$$\Phi_{rstu} = \sum_{i,j,k,l} f^{ijkl} L_i^r L_j^s L_k^t L_l^u + \sum_{i,j,k} f^{ijk} \left(L_i^{rs} L_j^t L_k^u \right.$$

$$\left. + L_i^{rt} L_j^s L_k^u + L_i^{ru} L_j^s L_k^t + L_i^{st} L_j^r L_k^u + L_i^{su} L_j^r L_k^t + L_i^{tu} L_j^r L_k^s \right)$$

$$+ \sum_{i,j} f^{ij} \left(L_i^{rs} L_j^{tu} + L_i^{rt} L_j^{su} + L_i^{ru} L_j^{st} \right)$$

$$+ \sum_{i,j} f^{ij} \left(L_i^{rst} L_j^{u} + L_i^{rtu} L_j^{s} + L_i^{stu} L_j^{r} + L_i^{rsu} L_j^{t} \right) \tag{I.3.5}$$

This set of equations indicates that the cubic force constant in normal coordinate space contains cubic and quadratic force constant contributions from the internal coordinate representation; similarly for the quartic force constant Φ_{rstu}. This illustrates how quadratic potential surfaces in internal coordinates R_n can actually contain a large portion of the information concerning the higher force constants when transformed to normal coordinates. Pulay, Meyer, and Boggs [17], for example, found that the ϕ_{144} force constant in methane is comprised of roughly 75 percent f^{ij} and the remaining 25 percent f^{ijk}.

In the analytic calculation of the force constants, derivatives of the energy - the potential field under which the nuclei interact - are taken with respect to cartesian coordinates. These force constants are linearly related to the normal coordinate force constants, and thus the entire problem of choice of internal coordinates and the non-linear transformation of these coordinates is completely avoided.

The second derivative of the energy produces a set of cartesian coordinate force constants, f_x^{ij}, that are easily transformed to normal coordinates. The procedure is outlined as follows [14]: First the force constants are mass-weighted and then diagonalized. The eigenvalues are the frequencies λ_r, and the eigenvectors form the mass-weighted L_{xm} matrix $L^r_{xm,i}$. In this notation, the subscript i refers to a particular cartesian coordinate and the superscript r refers to a particular normal

coordinate. In the subscript xm, the x is used to indicate that the L matrix is for cartesian coordinates and the m is used to indicate that it is also masss-weighted. The mass-weighted L_{xm} matrix is transformed to the L_x matrix by

$$L^r_{x,i} = \sum_i m_i^{-1/2} L^r_{xm,i} \tag{I.3.6}$$

The L_x matrix is similar to the first component of the L tensor, except that the L matrix is between cartesian and normal coordinates rather than internal and normal coordinates. It is then used to generate the normal coordinates Q_r from the cartesian coordinates.

$$\delta x_i = \sum_r L^r_{x,i} Q_r \tag{I.3.7}$$

Note that for the L_{xm} matrix

$$\sum_{r,s} L^r_{xm,i} L^s_{xm,j} = \delta_{ij} \tag{I.3.8}$$

whereas for the L_x matrix

$$\sum_{r,s} L^r_{x,i} L^s_{x,j} = m_i^{-1} \delta_{ij} \tag{I.3.9}$$

The L_x matrix produces the frequencies λ_r by

$$\lambda_r = \sum_{i,j} L^r_i f^{ij}_x L^r_j \tag{I.3.10}$$

For third derivatives, the cartesian force constants f^{ijk}_x, are

linearly transformed to the normal coordinate representation by

$$\phi_{rst} = \sum_{i,j,k} \left(L_i^r \, f_x^{ijk} \, L_j^s \right) L_k^t \qquad (I.3.11)$$

The fourth derivatives of the cartesian force constant are treated similarly. This linear relationship between the cartesian coordinate force constants and the normal coordinate force constants allows the unambiguous calculation of the ϕ's. The ϕ's in turn are combined with geometrical data to produce the anharmonic constants x_{rs} and rotation-vibration interaction constants $\alpha_r^{(\xi)}$.

The calculation of the cartesian force constants is a lengthy process that necessitates the solution to the Schrodinger equation using the Born-Oppenheimer approximation to separate electronic and nuclear motions. The solution to the electronic problem, using ab initio wave functions, requires calculation of the integrals described in chapter II. The calculation of the force constants - the derivatives of the electronic and nuclear energies - requires the evaluation of derivative integrals described in chapter III. The derivative integrals must then be combined to produce the derivative energies, the force constants themselves. This process is described in chapter IV. Finally, in chapter V, the results of an actual cubic force constant calculation are discussed and compared to experimental data.

II ATOMIC ORBITAL INTEGRALS

II.1 INTRODUCTION

The n electron Hartree-Fock wave function is the antisymmetrized product of n one-electron molecular spin orbitals (MSO). Each MSO is a product of a spatial function ϕ_n and a spin function α_n or β_n. In order to better describe the molecular orbitals of a molecule, linear combinations of atomic orbitals χ_μ (LCAO) are used to build the spatial function ϕ_n.

$$\phi_n = \sum_\mu C_\mu^n \chi_\mu \qquad \text{(II.1.1)}$$

The self-consistent-field (SCF) method, as presented by Roothaan [18,19], proceeds to find the best ϕ_n - in the variational sense - by iterating through a set of equations known as the Roothaan equations (see reference 18 for closed-shell, and 19 for open-shell molecular system). The best ϕ_n is made up of the variationally optimized molecular orbital coefficients, C_μ^n , and a series of fixed atomic orbitals, χ_μ.

The atomic orbitals were orginally approximated by modifying the exact wavefunction for the hydrogen atom; such orbitals are called Slater-type orbitals (STO) given by

$$\chi_\mu = r^{n^*-1} \exp\left(-Z_{n^*} r / n^* \right) Y_l(\theta,\phi) \qquad \text{(II.1.2)}$$

where n^* is an effective principal quantum number and $Y_l(\theta,\phi)$ is a spherical harmonic in real form. The resulting integrals are not particularly simple to evaluate. This difficultly, coupled with the large number of integrals involved in a molecular calculation, has led to the demise of the STO as the basis function for atomic orbitals.

Integrals over gaussian functions are easier to solve than those over STO, making the gasussian functions the primary basis function for the one-electron atomic orbitals χ_μ. There are, however, a few deficiencies with gaussian functions: The nuclear cusp is not correctly described, and the gaussian function incorrectly tails off at large distances. In order to correct for these deficiencies, it is common practice to use a number of gaussians as the basis function, with varied exponents a_k and weights c_k, in a specific linear combination. Such a basis set is called a contracted basis set (see reference 20 for more details concerning the contraction of basis sets):

$$\chi_\mu = \sum_k c_k \exp(-a_k r^2) \qquad \text{(II.1.3)}$$

Many types of gaussians have been used with great success in quantum calculations: simple gaussian lobes [21], spherical gaussians [22], ellipsoidal gaussians [23], cartesian gaussians [24], trigonometric gaussians [25], and Hermite gaussians [26]. (See the review article by V.R. Saunders [22] for more details). In this chapter, the atomic orbital integrals involved in a molecular calculation will be examined for atomic orbitals where cartesian gaussians are employed as the basis, as well as for atomic orbitals where the cartesian gaussian basis has been expanded in terms of Hermite gaussians. Hermite gaussians will prove to

be ideally suited for the calculation of derivative integrals.

II.2 CARTESIAN GAUSSIANS

Since the introduction of cartesian gaussians by Boys in 1950 [24], the gaussian type function has become the primary basis function for the one-electron atomic orbitals used in the evaluation of molecular integrals. The unnormalized cartesian gaussian on center A is given by

$$G(a,A,n,l,m) = G(a,A) = x_A^n \, y_A^l \, z_A^m \exp(-ar_A^2) \qquad \text{(II.2.1)}$$

where x_A, y_A, and z_A are components of the vector $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$, with $\mathbf{r}$ being the position vector of an electron and $\mathbf{A}$ a nuclear center. The angular momentum of an atomic orbital is approximated by the products of x_A, y_A, and z_A and their associated powers n, l, and m. When n, l, and m are zero, G(a,A) simply describes a s-type orbital. Any higher angular momentum gaussian can be obtained by applying the following equation to a s-type orbital [27]:

$$G(a,A,n,l,m) = M^{n_{Ax}} \, M^{l_{Ay}} \, M^{m_{Az}} \, G(a,A,0,0,0)$$

where

$$M^{n_{Ax}} = 0 \text{ if } n_{Ax} < 0$$
$$= 1 \text{ if } n_{Ax} = 0$$

and

$$M^{n_{Ax}+1} = 1/2a \left(M^{n_{Ax}} \frac{\partial}{\partial Ax} + n_{Ax} M^{n_{Ax}-1} \right) \qquad \text{(II.2.2)}$$

with $M^{l_{Ay}}$ and $M^{m_{Az}}$ being similarly defined. The total angular momentum of the cartesian gaussian G(a,A) is defined by

$$\lambda_A = n_{Ax} + l_{Ay} + m_{Az} \qquad \text{(II.2.3)}$$

Note that the three-dimensional cartesian gaussian may be split along each of its coordinates; thereby a result for the x-coordinate can be generalized for the y and z coordinates. In this manner, the x-coordinate normalization constant is

$$N_n(a) = \frac{\left(2a/\pi \right)^{1/4} \left(4a \right)^{n/2}}{\left((2n - 1)!! \right)^{1/2}} \qquad \text{(II.2.4)}$$

Products of gaussians, referred to as overlap or charge distributions, reoccur in quantum chemistry with every integral. One of the most utilized properties of gaussians is the product rule [24,28]. It states that the product of two gaussians G(a,A) and G(b,B) is itself a gaussian G(p,P). The new gaussian is located at a point P with exponent p along the line connecting the centers A and B weighted by a constant K_{AB}.

$$G(a,A)\ G(b,B) = K_{AB}\ G(p,P) \qquad \text{(II.2.5)}$$

where

$$p = a + b$$

$$\mathbf{P} = (a\mathbf{A} + b\mathbf{B}) / p$$

$$\overline{\mathbf{AB}} = \mathbf{A} - \mathbf{B}$$

$$K_{AB} = \exp (-ab\ \overline{\mathbf{AB}}^2 / p) \qquad \text{(II.2.6)}$$

Products of cartesian gaussians naturally include products of the monomials x_A^n and $x_B^{n'}$, as well as those for the y and z coordinates.

The standard treatment, as given by Taketa et al. [29], is to recognize that

$$x_A = x_p + P_x - A_x = x_p + \overline{PA}_x$$
$$x_B = x_p + P_x - B_x = x_p + \overline{PB}_x \qquad \text{(II.2.7)}$$

and expand the products as polynomials in $(x_p + \overline{PA}_x)^n$ and $(x_p + \overline{PB}_x)^{n'}$.

$$x_A^n \, x_B^{n'} = \sum_k f_k(n,n',\overline{PA}_x,\overline{PB}_x) \, x^k \qquad \text{(II.2.8)}$$

where $f_k(n,n',a,b)$ is the coefficient of x^k in the expansion $(x+a)^n \, (x+b)^{n'}$. The end result is that a polynomial over two centers has been reduced to a polynomial about a common center. Equation II.2.8 is then substituted into the integral formulae, resulting in integrands that are averaged cartesian gaussians multiplied by a polynomial also based on the averaged positions.

II.3 HERMITE GAUSSIANS

In contrast to the above method, McMurchie and Davidson [30] used Hermite gaussians to expand the product of monomials and thus reduced the integrals from cartesian gaussians to integrals over Hermite gaussians. The following closely follows the work of McMurchie and Davidson [30] and Saunders [22]; however, the notation of Saunders is generally employed.

The Hermite gaussian is defined as

$$\Lambda(a,A,n,l,m) = \left(\frac{\partial}{\partial A_x} \right)^n \left(\frac{\partial}{\partial A_y} \right)^l \left(\frac{\partial}{\partial A_z} \right)^m \exp\left(-ar_A^2\right) \tag{II.3.1}$$

Like the cartesian guassian, the Hermite gaussian is separable into three components along the x,y, and z coordinates. The Hermite gaussian for the x coordinate is related to the Hermite Polynomial of order n for the x coordinate by

$$\Lambda_x(a,A,n) = a^{n/2} H_n[a^{1/2}x_A] \exp\left(-ax_A^2 \right)$$

$$= \lambda_x(a,A,n) \exp\left(-ax_A^2 \right) \tag{II.3.2}$$

where the λ_x is the scaled Hermite Polynomial of order n. Similar definitions hold for the y and z coordinates.

The product of monomials $x_A^n \; x_B^{n'}$ in the cartesian gaussian charge distribution can be expanded in terms of $\lambda_x(p,P,t)$ where the expansion is about the averaged gaussian.

$$x_A^n \; x_B^{n'} = \sum_{t=0}^{t=n+n'} e_x(n,n',t) \; \lambda_x(p,P,t) \tag{II.3.3}$$

where $e_x(n,n',t)$ are the linear expansion coefficients. Basically, this states that a polynomial in x_p ($x_A^n \; x_B^{n'}$ is a polynomial in x_p, see equation II.2.7) can be written as a linear combination of scaled Hermite Polynomials which themselves are in terms of x_p. To successfully utilize equation II.3.3, a general equation for the

production of the expansion coefficients e_x must be derived. Since the λ_x are scaled Hermite Polynomials, we begin with the recursion relationship for a Hermite Polynomial of order N and argument ε,

$$\varepsilon\, H_N(\varepsilon) = N\, H_{N-1}(\varepsilon) + 1/2\, H_{N+1}(\varepsilon) \qquad \text{(II.3.4)}$$

The mononial product

$$x_A^{n+1}\, x_B^{n'} = \sum_{t=0}^{t=n+n'} e_x(n,n',t)\, x_A\, \lambda_x(p,P,t) \qquad \text{(II.3.5)}$$

is easily expanded with the recursion relationship. Equations II.2.7 and II.3.4 give

$$x_A\, \lambda_x(p,P,t) = 1/2p\, \lambda_x(p,P,t+1) + \overline{PA}_x\, \lambda_x(p,P,t) + t\, \lambda_x(p,P,t-1) \qquad \text{(II.3.6)}$$

Substituting this back into II.3.5 yields

$$x_A^{n+1} x_B^{n'} = \sum_{t=0}^{t=n+n'} e_x(n,n',t) \left(\lambda_x(p,P,t+1)/2p + \right.$$

$$\left. + \overline{PA}_x\, \lambda_x(p,P,t) + t\, \lambda_x(p,P,t-1) \right) \qquad \text{(II.3.7)}$$

Equation II.3.7 is generalized as to obtain a general recursion relationship for the expansion coefficients, $e_x(n,n',t)$.

$$e_x(n+1,n',t) = e_x(n,n',t-1)/2p + \overline{PA}_x\, e_x(n,n',t)$$

$$+ (t+1)\, e_x(n,n',t+1) \qquad \text{(II.3.8)}$$

Similar recursion relationships hold for the e_y and e_z expansion coefficients. Using these recursion relations, any monomial product can be expanded. The overlap, or charge distribution, for example is now written as

$$G(a,A,n,l,m)\ G(b,B,n',l',m')$$

$$= K_{AB} \sum_{t=0}^{t=n+n} e_x(n,n',t)\ \exp\ (-px_P^2\ )\ \lambda_x(p,P,t)$$

$$\times \sum_{u=0}^{u=l+l'} e_y(l,l',u)\ \exp\ (-py_P^2)\ \lambda_y(p,P,u)$$

$$\times \sum_{v=0}^{v=m+m'} e_z(m,m',v)\ \exp\ (-pz_P^2)\ \lambda_z(p,P,v) \qquad \text{(II.3.9)}$$

By defining

$$E(t,u,v) = E(n,n',l,l',m,m',t,u,v)$$

$$= e_x(n,n',t)\ e_y(l,l',u)\ e_z(m,m',v) \qquad \text{(II.3.10)}$$

the charge distribution of equation II.3.9 reduces to

$$\text{II.3.9} = K_{AB} \sum_{t,u,v} E\ (t,u,v)\ \Lambda\ (p,P,t,u,v) \qquad \text{(II.3.11)}$$

The shorthand notation of E(t,u,v) will be used repeatedly in the forthcoming sections.

All of the atomic integrals contain at least one charge distribution, and thus each integral contains products of expansion

coefficients. By including the constants: K_{AB}, normalization constants N_{nlm}, and $N_{n'l'm'}$, and contraction coefficients c_k of A and $c_{k'}$ of B in the generation of the expansion coefficients, many multiplications can be eliminated, reducing the total number necessary for a given block of integrals. This property will become more evident in the cases of two-electron replusion integrals. Thus,

$$e_x(0,0,0) = K_{AB}\ c_k(A)\ c_{k'}(B)\ N_{nlm}\ N_{n'l'm'}$$
$$e_y(0,0,0) = e_z(0,0,0) = 1 \qquad \text{(II.3.12)}$$

The value of e_y and e_z are the result of equations II.3.2 and II.3.3 which imply that for n and n' equal to zero e_x is equal to one since $H_0(a^{1/2}x_A)$ is equal to one.

In the following sections, the use of Hermite gaussians will be examined for each of the types of integrals involved in a molecular SCF calculation. For the sake of clarity, sums over contraction coefficients will be omitted. As stated above, normalization constants, K_{AB}, and contraction coefficients are assummed to be premultiplied into the e_x coefficients.

The formulae presented for the zeroth order integrals, as well as the derivative integrals presented in chapter III, have been implemented in a series of integral programs. These programs evaluate integrals in terms of blocks, as do most recent integral packages. A block of integrals refers to the entire collection of integrals for a given interaction of shells, where a shell is defined as a group of gaussian primitives with a given exponent, centered on the same nuclear position. As an example, the block of integrals for the nuclear

attraction interaction between two different p shells (angular momentum equal to one) is made up of nine integrals: Vp_xp_x, Vp_xp_y, Vp_xp_z, Vp_yp_x, Vp_yp_y, Vp_yp_z, Vp_zp_x, Vp_zp_y, and Vp_zp_z. Many of the intermediaries needed for the evaluation of these integrals are the same, and much computer time may be saved by evaluating the integrals as a block. At the conclusion of section II.6. the use of intermediaries for this case is explicitly examined.

II.4 OVERLAP INTEGRALS

The overlap integral, which can be considered a charge distribution, is reduced from two centers to one center using the Gaussian product rule of equation II.2.5.

$$S_{\mu\nu} = \int_{-\infty}^{\infty} \chi_\mu \, \chi_\nu \, d\tau = \int_{-\infty}^{\infty} G(a,A) \, G(b,B) \, d\tau = \int_{-\infty}^{\infty} K_{AB} \, G(p,P) \, d\tau \tag{II.4.1}$$

Expanding the charge distribution about the point P in terms of Hermite gaussians leads to

$$\begin{aligned} S_{\mu\nu} = & \sum_{t=0}^{t=n+n'} e_x(n,n',t) \int_{-\infty}^{\infty} \Lambda_x(p,P,t) \, dx \\ \times & \sum_{u=0}^{u=l+l'} e_y(l,l',u) \int_{-\infty}^{\infty} \Lambda_y(p,P,u) \, dy \\ \times & \sum_{v=0}^{v=m+m'} e_z(m,m',v) \int_{-\infty}^{\infty} \Lambda_z(p,P,v) \, dz \end{aligned} \tag{II.4.2}$$

The x integral is over Hermite Polynomials, as are the y and z integrals. Examining it more closely,

$$\int_{-\infty}^{\infty} \Lambda_x(p,P,t)\ dx = \int_{-\infty}^{\infty} \exp\ (\ -px_p^2)\ p^{t/2}\ H_t(p^{1/2}x_p)\ dx \tag{II.4.3}$$

Due to the orthogonal properties of the Hermite Polynomials, the integral reduces to

$$\begin{aligned} \int_{-\infty}^{\infty} \Lambda_x(p,P,t)\ dx &= \quad 0 \quad \text{if } t\neq 0 \\ &= (\pi/p)^{1/2} \quad \text{if } t=0 \end{aligned} \tag{II.4.4}$$

This reduces the summation in equation II.4.2 to a single term giving

$$S_{\mu\nu} = e_x(n,n',0)\ e_y(l,l',0)\ e_z(m,m',0)\ (\pi/p)^{3/2} \tag{II.4.5}$$

If the constant factor $(\pi/p)^{3/2}$ is placed in the e_x expansion coefficient, along with the normalization constants, contraction coefficients, and K_{AB}, more multiplication steps can be eliminated.

II.5 KINETIC ENERGY INTEGRALS

The operator for the kinetic energy is

$$\mathbf{T} = -1/2\ \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \tag{II.5.1}$$

where the partials are with respect to the electronic position. The straight application of the operator on the cartesian gaussian G(b,B) yields

$$T_{\mu\nu} = \int_{-\infty}^{\infty} \chi_\mu T \chi_\nu \, d\tau = -1/2 \; \{ 4b^2 \; (\int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n'+2,l',m') \; d\tau +$$

$$\int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n',l'+2,m') d\tau + \int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n',l',m'+2) d\tau)$$

$$- 2b\big((2n'+1) + (2l'+1) + (2m'+1)\big) \int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n',l',m') \; d\tau$$

$$+ n'(n'-1) \int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n'-2,l',m') \; d\tau$$

$$+ l'(l'-1) \int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n',l'-2,m') \; d\tau$$

$$+ m'(m'-1) \int_{-\infty}^{\infty} G(a,A,n,l,m) \; G(b,B,n',l',m'-2) \; d\tau \; \} \qquad \text{(II.5.2)}$$

This is nothing more than a linear combination of overlap integrals. Using the results of section II.4, the above expression reduces to a sum of products of expansion coefficients. Overlap and kinetic energy integrals are thus conveniently solved at the same time, provided the table of expansion coefficients is created large enough by increasing the limits of generation in equation II.3.8. The final formula is

$$\begin{aligned} T_{\mu\nu} = -1/2 \; (\pi/p)^{3/2} \; \{ 4b^2 \; (& e_x(n,n'+2,0) \; e_y(l,l',0) \; e_z(m,m',0) \\ & + e_x(n,n',0) \; e_y(l,l'+2,0) \; e_z(m,m',0) \\ & + e_x(n,n',0) \; e_y(l,l',0) \; e_z(m,m'+2,0) \;) \\ - 2b \; (2(n'+l'+m') + 3) & \; e_x(n,n',0) \; e_y(l,l',0) \; e_z(m,m',0) \\ + n'(n'-1) & \; e_x(n,n'-2,0) \; e_y(l,l',0) \; e_z(m,m',0) \\ + l'(l'-1) & \; e_x(n,n,0) \; e_y(l',l'-2,0) \; e_z(m,m',0) \end{aligned}$$

$$+ \; m'(m'-1)\; e_x(n,n',0)\; e_y(1,1',0)\; e_z(m,m'-2,0) \;\Big\}$$

(II.5.3)

II.6 NUCLEAR ATTRACTION INTEGRALS

The nuclear attraction integrals (NAI), are

$$V_{\mu\nu} = \int_{-\infty}^{\infty} \chi_\mu \sum_C r_c^{-1} \chi_\nu \, d\tau \qquad \text{(II.6.1)}$$

where $r_c = |\mathbf{r} - \mathbf{C}|$, with $\mathbf{r}$ being the electronic position vector and $\mathbf{C}$ being the position vector of nucleus C. The summation over C is over all nuclear positions in the molecular system. For clarity sake it is usually dropped during the derivation of the solution to the NAI, and replaced in the final formula. This practice will be observed here. The NAI has no simple closed form, unlike the overlap and kinetic energy integrals presented in the previous sections.

Boys [24] introduced a solution for the NAI that employed a modified error function F(z) for s-type orbitals.

$$F(z) = \int_0^{\sqrt{z}} \exp\,(-\,\nu^2)\, d\nu$$

$$= 1/2 \left(\frac{\pi}{z} \right)^{1/2} \mathrm{erf}(\sqrt{z}) \qquad \text{(II.6.2)}$$

This function F(z) is a member of a class of integrals $F_m(z)$ that are closely related to the incomplete gamma function [28, 31].

$$F_m(z) = \int_0^1 \nu^{2m} \exp\,(-z\nu^2)\, d\nu \qquad \text{(II.6.3)}$$

Boys' solution for s-type orbitals about the average gaussian G(p,P) is obtained by employing a gaussian transformation to recast r_c^{-1}, with the final result being

$$V_{\mu\nu} = \frac{2\pi}{p} K_{AB} F_0(p \overline{PC}^2) \qquad \text{(II.6.4)}$$

The solution of the NAI for orbitals of higher angular momentum has been approached in a number of ways. One method is that pointed out by Boys, namely to apply equation II.2.2 to the NAI solution for s-type orbitals. The derivative of $F_0(z)$ with respect to a nuclear coordinate is a linear combination of $F_0(z)$ and $F_1(z)$. By the application of equation II.2.2 for n_{Ax} greater than zero, the NAI solution for any angular momentum function can be obtained.

Another method is that presented by Taketa et al.[29]. Using the charge distribution described at the end of section II.2, the products of $x_A^n x_B^{n'}$ and the other monomial products are described by equations II.2.7 and II.2.8. A fourier transformation is then used to recast the r_c^{-1} operator. Integration over x, y, and z yields an integral over Hermite Polynomials. The solution of this last integral is a linear combination of $F_m(z)$. The advantage of this method over repeated differentiation of the s-type orbital solution lies in the generation of the linear coefficients through a series of simple summation formulae.

A third approach is through the Hermite gaussian formalism.

$$V_{\mu\nu} = \sum_{t}^{t=n+n'} e_x(n,n',t) \sum_{l}^{u=l+l'} e_y(l,l',u) \sum_{v}^{v=m+m'} e_z(m,m',v)$$

$$\times \int_{-\infty}^{\infty} \Lambda(p,P,t,u,v)\, r_c^{-1}\, d\mathbf{r}$$

$$= \sum_{t,u,v} E\,(t,u,v) \int_{-\infty}^{\infty} \Lambda\,(p,P,t,u,v)\; r_c^{-1}\; dr \qquad \text{(II.6.5)}$$

Again, all constants are kept in the e_x expansion coefficients. The operator is recast with a gaussian transformation

$$r_c^{-1} = \int_0^{\infty} (\pi)^{-1/2}\; s^{-1/2} \exp\,(-s\; r_c^2\;)\; ds \qquad \text{(II.6.6)}$$

Rewriting the integral portion of equation II.6.5 and substituting equation II.6.6 for the operator gives

$$I_x\; I_y\; I_z \;=\; \int_{-\infty}^{\infty} \Lambda\,(p,P,t,u,v)\; r_c^{-1}\;\; dr$$

$$= (\pi)^{-1/2} \int_{-\infty}^{\infty} \int_0^{\infty}\; s^{-1/2}\; \Lambda\,(p,P,t,u,v)\; \exp(-sr_c^2)\; ds\; dr$$

(II.6.7)

Utilizing equation II.3.1, I_x is rewritten as (note that the $s^{-1/2}$ is dropped from the following derivation, but returned in equation II.6.12)

$$I_x = \int_{-\infty}^{\infty} \int_0^{\infty}\; \Lambda_x(p,P,t)\; \exp\big(\; -s(x-C_x)^2\;\big)\;\; ds\; dx$$

$$= \int_{-\infty}^{\infty} \int_0^{\infty}\; \left(\frac{\partial}{\partial P_x}\right)^{t} \exp\big(\; -p(x-P_x)^2 - s(x-C_x)^2\;\big)\; ds\; dx \qquad \text{(II.6.8)}$$

Expanding the squares results in

$$I_x = \int_{-\infty}^{\infty} \int_0^{\infty}\; \left(\frac{\partial}{\partial P_x}\right)^{t} \exp\big(-pP_x^2 - sC_x^2\big)\; \exp\big(-x^2(p+s) + 2x(pP_x + sC_x)\big)\; ds\; dx$$

(II.6.9)

The integral over x is a standard integral where the solution is of the form [28]:

$$\int_{-\infty}^{\infty} \exp\left(-x^2\alpha + 2\beta x \right) dx = \left(\pi/\alpha\right)^{1/2} \exp\left(\beta^2/\alpha \right) \qquad \text{(II.6.10)}$$

Performing the x integration and expanding the squares results in

$$I_x = \int_0^{\infty} \left(\pi/(p+s)\right)^{1/2} \left(\frac{\partial}{\partial P_x} \right)^t \exp\left(-ps/(p+s)\ (P_x - C_x)^2 \right) ds \qquad \text{(II.6.11)}$$

Following similar steps for I_y and I_z yields

$$V_{\mu\nu} = \sum_{t,u,v} E(t,u,v)\ I_x\ I_y\ I_z$$

$$= \sum_{t,u,v} E(t,u,v)\ (\pi)^{-1/2} \int_0^{\infty} \left(\pi/(p+s)\right)^{3/2}\ s^{-1/2}$$

$$\times \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v$$

$$\times \exp\left(-ps/(p+s)\ \overline{PC}^2 \right)\ ds \qquad \text{(II.6.12)}$$

where $\overline{PC}^2 = |\ \mathbf{P} - \mathbf{C}\ |^2$. In order to solve the remaining integral, the following variable transformation is made:

$$w^2 = s/(p+s) \qquad \text{(II.6.13)}$$

resulting in $$2\ \left(p^2/s\right)^{-1/2}(p+s)^{3/2}\ dw = ds\ . \qquad \text{(II.6.14)}$$

Note that as $s \to 0$, $w \to 0$ and that as $s \to \infty$, $w \to 1$.

Substitution gives

$$V_{\mu\nu} = 2\pi/p \sum E(t,u,v) \int_0^1 \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v \exp\left(-pw^2\, \overline{PC}^2\right) dw \tag{II.6.15}$$

This solution relates back to the solution for the s-type orbitals found by Boys. Letting $p\overline{PC}^2 = z$, equation II.6.15 reduces to

$$V_{\mu\nu} = 2\pi/p \sum E(t,u,v) \int_0^1 \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v \exp\left(-zw^2 \right) dw$$

$$= 2\pi/p \sum E(t,u,v) \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v F_0(z) \tag{II.6.16}$$

where Leibniz's rule has been used to move the differential operators out from under the integral. Instead of taking partials with respect to an actual nuclear position **A**, as the straight application of equation II.2.2 indicates, partials are being taken with respect to the average position, **P**. These relate back to the Hermite Polynomials.

With the aid of equations II.3.1 and II.3.2, equation II.6.16 can be recast in terms of Hermite Polynomials, where $f = t + u + v$

$$V_{\mu\nu} = 2\pi/p \sum E(t,u,v)\, p^{f/2} \int_0^1 dw\, \exp(-zw^2)\, w^f\, H_t(p^{1/2}\overline{PC}_x w)\, H_u(p^{1/2}\overline{PC}_y w)$$

$$\times\ H_v(p^{1/2}\overline{PC}_z w) \tag{II.6.17}$$

McMurchie and Davidson [30] defined $R^c(t,u,v)$ as

$$R^c(t,u,v) = p^{f/2} \int_0^1 dw\, \exp(-zw^2)\, w^f\, H_t(p^{1/2}\, \overline{PC}_x w)\, H_u(p^{1/2}\, \overline{PC}_y w)$$

$$\times \quad H_v(p^{1/2}\ \overline{PC}_z w) \qquad \text{(II.6.18)}$$

where the superscript c indicates that R is for a specific nuclear center C. Bringing the summation over C back into the formula results in

$$V_{\mu\nu} = 2\pi/p \sum_{t,u,v} E(t,u,v) \sum_{C} R^c(t,u,v) \qquad \text{(II.6.19)}$$

The evaluation of an entire block of integrals requires a table of $R^c(t,u,v)$ for a particular maximum of t, u , and v. McMurchie and Davidson [30] found that this table can be generated more easily through a general $R_j^c(t,u,v)$ defined as

$$R_j^c(t,u,v) = p^{f/2}\ (-2p)^j \int_0^1 dw\ \exp\ (-zw^2)\ w^{f+2j}\ H_t(p^{1/2}\ \overline{PC}_x w)$$

$$\times \quad H_u(p^{1/2}\ \overline{PC}_y w)\ H_v(p^{1/2}\ \overline{PC}_z w) \qquad \text{(II.6.20)}$$

The general $R_j^c(t,u,v)$ reduces to $R^c(t,u,v)$ via

$$R_0^c(t,u,v) = R^c(t,u,v)$$

$$R_j^c(0,0,0) = (-2p)^j\ F_j(z) \qquad \text{(II.6.21)}$$

By applying the recursion relations for Hermite Polynomials presented in equation II.3.4, a recursion relation for the general $R_j^c(t,u,v)$ is obtained. In the x coordinate, this recursion relation is

$$R^c_j(t+1,u,v) = -\overline{PC}_x\, R^c_{j+1}(t,u,v) \;+\; t\, R^c_{j+1}(t-1,u,v) \tag{II.6.22}$$

Similar formulae are easily derived for the y and z coordinates. The end result is that $R^c{}_j(t,u,v)$ can be generated from the recursion relation plus the appropiate $F_j(z)$. McMurchie and Davidson[30] provide a variety of formulae for the evaluation of $F_j(z)$, as does Shavitt [28], for various values of j and ranges of z.

Another approach to the solution of equation II.6.17, and the method adopted in the present series of integral programs, is through Rys quadrature, as introduced by Dupuis, Rys, and King [32]. In the method of Taketa et al. [29], and in that of McMurchie and Davidson [30], a specific $F_j(z)$ is evaluated, and then a table of $F_j(z)$ are produced by recursion relations. The members of this table are then combined in a linear manner to obtain the actual value of the integral. Rys quadrature approaches the problem radically differently. Equation II.6.17 is solved by a linear combination of the numerical values of the integrand evaluated at the zeroes of the Rys polynomials. A brief review of quadrature and Rys polynomials follows. See references 33 or 34 for more details concerning the nature of quadrature.

If a set of polynomials $P_i(x)$ is orthogonal to a weight function W(x) along a specified interval a,b

$$\int_a^b W(x)\, P_i(x)\, P_j(x)\, dx = h_i \delta_{ij} \tag{II.6.23}$$

then any integral along this same interval with the same weight function W(x) but including a function of x, f(x),

$$I = \int_a^b W(x)\ f(x)\ dx \qquad \text{(II.6.24)}$$

can be approximated by a quadrature formula of the form

$$I \approx \sum_{\gamma=0}^{N} w_\gamma(x)\ f(x_\gamma) \qquad \text{(II.6.25)}$$

where the sum is over N+1 quadrature points (roots) with w_γ being the weight factor of the N- order polynomial along the interval (a,b), and $f(x_\gamma)$ the value of the function f(x) evaluated at the γ root of the polynomial $P_\gamma(x)$. The number of quadrature points determines the accuracy of the summation in equation II.6.25. The summation becomes exact when the polynomial is of order less than or equal to 2N+1, where N is the limit of summation in equation II.6.25 [33,34].

The advantage of quadrature becomes clear when there is no simple closed form for an integral. Many orthogonal polynomials have simple formulae for the evaluation of weights and roots (see references 34 and 35), making the accurate solution of the integral in question tractable.

In the case of Rys quadrature, Dupuis, Rys, and King [32,36,37] introduced a set of even polynomials, R_n of order 2n, orthonormal on the interval 0 to 1, with respect to the weight function $W(x)=\exp(-zw^2)$ (see reference 36 for more details concerning the nature and properties of Rys polynomials).

$$\int_0^1 \exp\ (-zw^2)\ R_n(w^2,z)\ R_m(w^2,z)\ dw = \delta_{nm} \qquad \text{(II.6.26)}$$

If it is possible to express equation II.6.16 as an integral with

the weight function of $\exp(-zw^2)$ and the remainder of the integrand as a polynomial in w^2 of degree n, then a quadrature formula based on Rys polynomials can be obtained. By bringing the partial derivatives under the integral sign of $F_0(z)$ and performing the differentiation, equation II.6.16 becomes (this procedure is explicitly carried out in the case of the more complicated two-electron repulsion integrals discussed in section II.7)

$$V_{\mu\nu} = 2\pi/p \sum_{t,u,v} E(t,u,v) \int_0^1 P_t(w^2)\, P_u(w^2)\, P_v(w^2) \exp(-zw^2)\, dw \qquad \text{(II.6.27)}$$

where $P_t(w^2)$ is a polynomial of degree t in w^2. This can indeed be solved by Rys quadrature. Knowing that quadrature is possible, equation II.6.17 can be rewritten along the lines that Saunders [22,38] advocates for the two-electron repulsion integrals (section II.7). We define a scaled Hermite Polynomial

$$G_t(\beta,\overline{PC}_x) = \beta^t\, H_t(\beta\, \overline{PC}_x) \qquad \text{(II.6.28)}$$

where $\beta = p^{1/2}w$. Scaled Hermite Polynomials G_u and G_v are defined as in G_t, however they are directed along the y and z coordinates. Equation II.6.17 becomes

$$V_{\mu\nu} = 2\pi/p \sum E(t,u,v) \int_0^1 dw\, \exp(-zw^2)\, G_t(\beta,\overline{PC}_x)\, G_u(\beta,\overline{PC}_y)\, G_v(\beta,\overline{PC}_z) \qquad \text{(II.6.29)}$$

As this is still a polynomial in w^2 of order t, u, and v, Rys quadrature is performed, producing

$$V_{\mu\nu} = 2\pi/p \sum E(t,u,v) \sum_{\gamma=0}^{N} w_\gamma G_t(\beta_\gamma,\overline{PC}_x) G_u(\beta_\gamma,\overline{PC}_y) G_v(\beta_\gamma,\overline{PC}_z) \tag{II.6.30}$$

where w_γ are the weights and G_t, G_u, and G_v are evaluated at the roots of the Rys polynomials (indicated by the γ subscript on β). With the integrals calculated in blocks, the maximum value of t, u, and v for that block is passed to the quadrature scheme. The maximum value of t, u, and v is the sum of the total angular momentum about nuclear center **A** and nuclear center **B**. A block of integrals contains, however, integrals other than that for the maximum value of t, u, and v and thus a table of G_t, G_u, and G_v is needed to solve all the integrals of a given block. A simple recursion scheme based on that of the Hermite Polynomials, equation II.3.4, is required. The recursion relation for G_t is given by

$$G_{t+1}(a,b) = 2a^2 \left(b\, G_t\,(a,b) - t\, G_{t-1}(a,b)\right) \tag{II.6.31}$$

The quadrature becomes exact when

$$t < 2N + 1 \tag{II.6.32}$$

Remember that t, u, and v are all equal at this stage of the calculation and that $t=\lambda_A + \lambda_B$. In equation II.6.25, the summation over N is governed by the value of t. Naturally, it is desirable to obtain an accurate solution to II.6.25 using the minimum value of N (which is equivalent to the minimum number of quadrature points N', where N'=N+1). Equation II.6.32 is rewritten as

$$N' > [\ t/2\ ] + 1 \qquad \text{(II.6.33)}$$

where [t/2] indicates that decimals are rounded up to the nearest integer.

Equation II.6.30 can be simplified by recognizing that it is really

$$V_{\mu\nu} = \sum_{\gamma=0}^{N} 2\pi/p\ w_\gamma \Big\{ \sum_t e_x(n,n',t)\ G_t(\beta_\gamma,\overline{PC}_x)$$

$$\times \sum_u e_y(l,l',u)\ G_u(\beta_\gamma,\overline{PC}_y)$$

$$\times \sum_v e_z(m,m',v)\ G_v(\beta_\gamma,\overline{PC}_z) \Big\} \qquad \text{(II.6.34)}$$

which further reduces to

$$V_{\mu\nu} = \sum_{\gamma=0}^{N} X_\gamma^* Y_\gamma Z_\gamma \qquad \text{(II.6.35)}$$

where X_γ^* signifies that the $2\pi/p$ and the weights have been incorporated into the G_t. It is just as convenient to write equation II.6.35 in terms of γ going over N' quadrature points as going over the N orders of the polynomial. The above equation is ideally suited to solving integrals by blocks, as the table of X_γ^*, Y_γ , and Z_γ generated by performing the summations in II.6.34 will be used repeatedly. Returning to the example of a block of p shells presented in section II.3 , the repeated use of intermediaries is clearly illustrated. Equations II.6.34 and II.6.35 show that

$$X^*_\gamma(s,s) = X^*_\gamma(0,0) = w_\gamma\ 2\pi/p\ e_x(0,0,0)\ G_t(\beta_\gamma,0)$$

$$X^*_\gamma(p,s) = X^*_\gamma(1,0) = w_\gamma 2\pi/p\ \big(\ e_x(1,0,0)\ G_t(\beta_\gamma,0) + e_x(1,0,1)\ G_t(\beta_\gamma,1)\ \big)$$

$$X^*_\gamma(s,p) = X^*_\gamma(0,1) = w_\gamma 2\pi/p\ \big(\ e_x(0,1,0)\ G_t(\beta_\gamma,0) + e_x(0,1,1)\ G_t(\beta_\gamma,1)\ \big)$$

$$X^*_\gamma(p,p) = X^*_\gamma(1,1) = w_\gamma 2\pi/p\ \big(\ e_x(1,1,0)\ G_t(\beta_\gamma,0) + e_x(1,1,1)\ G_t(\beta_\gamma,1) + e_x(1,1,2)\ G_t(\beta_\gamma,2)\ \big) \qquad \text{(II.6.36)}$$

with similar definitions for the Y_γ and Z_γ. For this block of p shells equation II.6.35 becomes

$$Vp_xp_x = \sum_\gamma \{\ X^*_\gamma(p,p)\ Y_\gamma(s,s)\ Z_\gamma(s,s)\ \}$$

$$Vp_xp_y = \sum_\gamma \{\ X^*_\gamma(p,s)\ Y_\gamma(s,p)\ Z_\gamma(s,s)\ \}$$

$$Vp_xp_z = \sum_\gamma \{\ X^*_\gamma(p,s)\ Y_\gamma(s,s)\ Z_\gamma(s,p)\ \}$$

$$Vp_yp_x = \sum_\gamma \{\ X^*_\gamma(s,p)\ Y_\gamma(p,s)\ Z_\gamma(s,s)\ \} \qquad \text{(II.6.37)}$$

Note that many of the same intermediaries are used repeatedly. This reuse of intermediaries for blocks of integrals will be central to the algorithms employed in the two-electron repulsion integrals (ERI). As will become evident with the ERI, much of the results of this section

can be directly carried over for its evaluation.

II.7 TWO-ELECTRON REPULSION INTEGRALS

The evaluation of the two-electron repulsion integrals (ERI) is the bulk of most ab initio calculations. Without any reduction due to symmetry, the total number of integrals is proportional to n^4 where n is the number of gaussian primitives used in the basis set. For large molecules and small molecules with a large basis set, the evaluation of the integrals can become a significant step in the overall calculation. As a result, much attention has been focused on the algorithms used for the evaluation of the ERI. In this section, two algorithms based in the Hermite gaussian formalism will be examined, that of McMurchie and Davidson [30], and that of Saunders[38]. Recently Hegarty and Van Der Velde [39] have presented an algorithm that is based in Hermite gaussians, but allows more factorization than the McMurchie and Davidson [30] algorithm. Their algorithm, however, is sufficiently closely related to the McMurchie and Davidson scheme for the purpose of this discussion, and will not be included in the section. The ERI,

$$(\mu\nu|\rho\sigma) = \int_{-\infty}^{\infty}\int \chi_\mu(1)\ \chi_\nu(1)\ \ r_{12}^{-1}\ \ \chi_\rho(2)\ \chi_\sigma(2)\ \ d\tau_1\ d\tau_2 \tag{II.7.1}$$

is an integral over the positions of two electrons, with r_{12} equal to the distance between the electrons, and is hence six-dimensional.

The solution of the ERI begins by applying the gaussian product rule, equation II.2.5, to the gaussians approximating the orbitals of electron 1, χ_μ and χ_ν , reducing it to a single gaussian about a point

P. The same is done to χ_ρ and χ_σ , except that the averaged gaussian is about a point Q. The monomial products are then expanded in terms of Hermite gaussians, equation II.3.3.

$$(\mu\nu|\rho\sigma) = \int_{-\infty}^{\infty}\int \Big(G(a,A,n,l,m)\, G(b,B,n',l',m')$$

$$\times\ r_{12}^{-1}\ G(c,C,i,j,k)\, G(d,D,i',j',k') \Big)\, d\tau_1\, d\tau_2$$

$$= \sum_{t}^{n+n'} e_x(n,n',t) \sum_{u}^{l+l'} e_y(l,l',u) \sum_{v}^{m+m'} e_z(m,m',v)$$

$$\times \sum_{t'}^{i+i'} e_x(i,i',t') \sum_{u'}^{j+j'} e_y(j,j',u') \sum_{v'}^{k+k'} e_z(k,k',v')$$

$$\times \int_{-\infty}^{\infty}\int \Lambda(p,P,t,u,v)\ r_{12}^{-1}\ \Lambda(q,Q,t',u',v')\, d\tau_1 d\tau_2$$

(II.7.2)

where K_{AB} and K_{CD} have be incorporated into the appropriate e_x expansion coefficients. Using the shorthand notation introduced in equation II.3.10, the above equation can be rewritten

$$(\mu\nu|\rho\sigma) = \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times \int_{-\infty}^{\infty}\int \Lambda(p,P,t,u,v)\ r_{12}^{-1}\ \Lambda(q,Q,t',u',v')\ d\tau_1 d\tau_2$$

(II.7.3)

Proceeding along the lines used to reduce the NAI in section II.6, the r_{12}^{-1} operator is transformed by a gaussian transformation, resulting in

$$(\mu\nu|\rho\sigma) = (\pi)^{1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times \int_{-\infty}^{\infty} \int \int_{0}^{\infty} \exp\,(-sr_{12}^{2})\; s^{-1/2}\; \Lambda(p,P,t,u,v)\; \Lambda(q,Q,t',u',v')\; ds\; d\tau_1 d\tau_2 \tag{II.7.4}$$

By following much the same steps as those for the NAI, except that equation II.6.10 is applied twice, the ERI reduces to

$$(\mu\nu|\rho\sigma) = 2\,(\pi)^{5/2}\,(pq)^{-1}(p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times \left(\frac{\partial}{\partial P_x}\right)^{t} \left(\frac{\partial}{\partial P_y}\right)^{u} \left(\frac{\partial}{\partial P_z}\right)^{v} \left(\frac{\partial}{\partial Q_x}\right)^{t'} \left(\frac{\partial}{\partial Q_y}\right)^{u'} \left(\frac{\partial}{\partial Q_z}\right)^{v'} F_0(z) \tag{II.7.5}$$

where

$$z = \left(pq/\,(p+q) \right) \overline{PQ}^2 \tag{II.7.6}$$

$$\overline{PQ}^2 = \left| \mathbf{P} - \mathbf{Q} \right|^2 \tag{II.7.7}$$

and

$$F_m(z) = \int_0^1 w^{2m} \exp\,(-zw^2)\; dw \tag{II.7.8}$$

Equation II.7.5 connects the solution of the ERI to the solution of the ERI for s-type orbitals introduced by Boys, in the same way that equation II.6.16 connects the general NAI solution to that for s-type orbitals. It can be further reduced by noting that as z depends only on **P** - **Q**,

$$\left(\frac{\partial}{\partial P_x}\right) F_0(z) = (-1) \left(\frac{\partial}{\partial Q_x}\right) F_0(z) \tag{II.7.9}$$

By repeatedly applying equation II.7.9, equation II.7.5 reduces to

$$(\mu\nu|\rho\sigma) = 2\,(\pi)^{5/2}\,(pq)^{-1}\,(p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times \; (-1)^{t'+u'+v'} \left(\frac{\partial}{\partial P_x}\right)^{t+t'} \left(\frac{\partial}{\partial P_y}\right)^{u+u'} \left(\frac{\partial}{\partial P_z}\right)^{v+v'} F_0(z) \tag{II.7.10}$$

As Saunders points out, and McMurchie and Davidson allude to, placing the constants $2^{1/2}\ \pi^{5/4}\ p^{-1}$ into E(t,u,v) during its generation and $(-1)^{t'+u'+v'}\ 2^{1/2}\ \pi^{5/4}\ q^{-1}$ into E(t',u',v') during its production, a saving of multiplication time can be achieved. Modifying the generation of the e_x expansion coefficients, and utilizing equations II.3.1 and II.3.2, the ERI becomes

$$(\mu\nu|\rho\sigma) = (p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v') \;\; \alpha^{f/2}$$

$$\times \int_0^1 w^f \exp(-zw^2)\, H_{t+t'}(\alpha^{1/2}\, w\overline{PQ}_x)\, H_{u+u'}(\alpha^{1/2}\, w\overline{PQ}_y)$$

$$\times \; H_{v+v'}(\alpha^{1/2}\, w\overline{PQ}_z) \;\; dw \tag{II.7.11}$$

where $\qquad f = t+t'+u+u'+v+v'$ and $\alpha = pq(p+q)^{-1}$.

The introduction of w in equation II.7.11 is from equation II.7.8. Comparing the above equations to II.6.17 and II.6.18, it is clear that it can be rewritten in terms of $R^c(t,u,v)$ where $\overline{PC}_k$ (k is equal to a cartesian coordinate) of equation II.6.18 is replaced by $\overline{PQ}_k$. Doing this produces

$$(\mu\nu|\rho\sigma) = (p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')\; R(t+t',u+u',v+v') \tag{II.7.12}$$

It is at this point that the method of McMurchie and Davidson[30] and that

of Saunders [38] diverge. The McMurchie and Davidson algorithm solves the ERI as it is given in the above equation, whereas Saunders requires some additional definitions and reworking of equation II.7.12.

Saunders [22,38] defines a scaled Hermite Polynomial similar to equation II.6.28.

$$G_{t+t'}(\beta,\overline{PQ}_x) = \beta^{t+t'} H_{t+t'}(\beta\ \overline{PQ}_x) \qquad \text{(II.7.13)}$$

where

$$\beta = \alpha^{1/2} w = \left(pq(p+q)^{-1}\right)^{1/2} w \qquad \text{(II.7.14)}$$

$G_{u+u'}$ and $G_{v+v'}$ are similarly defined along the y and z axes.

Equation II.7.11 can now be rewritten

$$(\mu\nu|\rho\sigma) = (p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v') \int_0^1 \exp(-zw^2)$$

$$\times\ G_{t+t'}(\beta,\overline{PQ}_x)\ G_{u+u'}(\beta,\overline{PQ}_y)\ G_{v+v'}(\beta,\overline{PQ}_z)\ dw \qquad \text{(II.7.15)}$$

To be sure that it is possible to solve this with Rys quadrature, the partial derivatives of equation II.7.10 are brought under the integral sign of $F_0(z)$ giving:

$$(\mu\nu|\rho\sigma) = (p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times \int_0^1 \left(\frac{\partial}{\partial P_x}\right)^{t+t'} \left(\frac{\partial}{\partial P_y}\right)^{u+u'} \left(\frac{\partial}{\partial P_z}\right)^{v+v'} \exp(-zw^2)\ dw$$

(II.7.16)

Taking the partial derivative with respect to P_x , where $\xi = pq/(p+q)$, yields,

$$\left(\frac{\partial}{\partial P_x} \right)^{t+t'} F_0(z) = \int_0^1 \left(-2\xi w^2 (P_x - Q_x)^2\right)^{t+t'} \exp\left(-\xi (P_x - Q_x)^2 w^2 \right) dw \tag{II.7.17}$$

Similar results are obtained for the partial derivatives with respect to P_y and P_z. It is clear that the pre-exponential factor in the integrand is a polynomial of order t+t' in w^2. Thus equation II.7.10 has the form

$$(\mu\nu|\rho\sigma) = (p+q)^{-1/2} \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times \int_0^1 P_{t+t'}(w^2)\, P_{u+u'}(w^2)\, P_{v+v'}(w^2) \exp(-zw^2)\, dw \tag{II.7.18}$$

which according to section II.6, fits the requirements to be solved by Rys quadrature.

Once the Rys roots and weight factors are calculated, and a table of $G_{t+t'}$, $G_{u+u'}$, and $G_{v+v'}$ are obtained through recusion relations similar to equation II.6.31, quadrature is performed, yielding

$$(\mu\nu|\rho\sigma) = \sum_{\gamma=1}^{N'} (p+q)^{-1/2}\, w_\gamma \sum_{t,u,v} E(t,u,v) \sum_{t',u',v'} E(t',u',v')$$

$$\times\ G_{t+t'}(\beta_\gamma, \overline{PQ}_x)\, G_{u+u'}(\beta_\gamma, \overline{PQ}_y)\, G_{v+v'}(\beta_\gamma, \overline{PQ}_z) \tag{II.7.19}$$

where N' is the number of quadrature points and is found from

$$N' > [\ t+t'/2\ ] + 1\ , \tag{II.7.20}$$

with [t+t'/2] indicating that the sum of angular momentum about all four centers is divided by two and rounded up if it is not an even

multiple of two. β_γ is as given in equation II.7.14 except the roots of the Rys polynomial are used instead of w. Equation II.7.19 can be factored along each of its components, yielding

$$XX_\gamma = \sum_t e_x(n,n',t) \sum_{t'} e_x(i,i',t')\, G_{t+t'}(\beta_\gamma,\overline{PQ}_x) \qquad \text{(II.7.21)}$$

with similar definitions for $XY\gamma$ and $XZ\gamma$. By placing the weights in $G_{t+t'}$ along with $(p+q)^{-1/2}$, more savings in multiplication time may be realized. Doing so leaves the ERI solution as a very simple equation

$$(\mu\nu|\rho\sigma) = \sum_{\gamma=1}^{N'} XX_\gamma^* \, XY_\gamma \, XZ_\gamma \qquad \text{(II.7.22)}$$

Equation II.7.21 is also conveniently broken down to

$$XX_\gamma^* = \sum_{t'} e_x(i,i',t')\, YX_\gamma^*$$

where

$$YX_\gamma^* = \sum_t e_x(n,n',t)\, G^*_{t+t'}(\beta_\gamma,\overline{PQ}_x) \qquad \text{(II.7.23)}$$

The asterisks are used to indicate that the $G_{t+t'}$ has the weights and $(p+q)^{-1/2}$ premultiplied into it during its generation. A similar set of equations for the y and z coordinates is easily derived (without the asterisks).

The algorithms are presented in appendix A.1, in a detailed, almost Fortran 77-like, language. Note that the algorithms are presented so that they match the equations used throughout chapter II (and those in chapter III). Additional definitions required to understand the algorithms are at the beginning of the appendix A.1. The following

discussion concerning the efficiency of the algorithms uses these definitions.

In the McMurchie and Davidson algorithm[30], an intermediate array I contains, for a given Ishell and Jshell, all possible interactions for all Kshells and Lshells. This is illustrated Figure II.7.1.

The array I is the salient feature of the McMurchie and Davidson method. By forming it over all Kshells and Lshells for a particular Ishell and Jshell, integrals over highly contracted basis sets can be efficiently calculated. If a batch of integrals is more highly contracted on the Ishell and Jshell than on the Kshell and Lshell, then the algorithm should be flipped looping over Kshell and Lshell in the first step.

Saunders [22,38] and Hegarty and Van Der Velde [39] have examined the cost of the McMurchie and Davidson algorithm using two different approaches. Saunders counts the times a loop is executed as the angular momentum of the shell goes to infinity, while Hegarty and Van Der Velde have counted the number of multiplications encountered for specific blocks of integrals. Saunders' method best shows the differences between the two algorithms. In this approach, the depth of contraction of a shell is given by K (size of Ifns, etc in appendix A.1, or the length of the sum in equation II.1.3), and the total number of members of a given shell with a total angular momentum of λ is given by $(\lambda + 1)(\lambda + 2)/2$. The test case for the algorithm is a case of four shells of equal contraction depth K, with the same total angular momemtum.

The McMurchie and Davidson algorithm divides neatly into two blocks. The first block is the inside loop of figure II.7.1. The cost

Figure II.7.1

The McMurchie and Davidson Integral Evaluation Algorithm

```
Loop over Ishell, Jshell, and contractions on both shells
        Zero I
        Loop over Kshell, Lshell and contractions on both
        shells
                I is computed and expanded about the
                members of Kshell and Lshell
        I is expanded about the members of Ishell and Jshell
```

of this loop over the members of Kshell and Lshell and the calculation of I is

$$K^4 \{ (\lambda+1)(\lambda+2)/2 \}^2 (2\lambda+1)^3 (4\lambda+1)^3$$

times. As $\lambda \to \infty$, this limits as $K^4\lambda^{10}$. The outer loop, the second block of the algorithm, has a cost of

$$K^2 \{ (\lambda+1)(\lambda+2)/2 \}^2 N^2 (2\lambda+1)^3$$

where N is the total number of atomic orbitals. For a single block of integrals, $N = (\lambda+1)(\lambda+2)/2$ and the cost becomes

$$K^2 \{ (\lambda+1)(\lambda+2)/2 \}^4 (2\lambda+1)^3$$

which, as $\lambda \to \infty$, limits as $K^2\lambda^{11}$.

The Saunders algorithm is illustrated in Figure II.7.2. Notice that the Saunders algorithm does not have a K^2 loop as does the McMurchie and Davidson algorithm. In its favor, however, is the splitting of the integrand along each of the axes, allowing for multiple use of common intermediates. In section II.6, the intermediaries of a block of p shells for the NAI were examined. The use of intermediaries for the ERI is analogous to that of the NAI presented in section II.6.

There are three blocks to Saunders' algorithm that represent the bulk of the computation for the test block of integrals. The first block is the computation of YX, YY, and YZ. The cost for this loop over the angular momentum on Ishell and Jshell and the computation of YX, YY, and YZ is

$$K^4(2\lambda+1)\ \lambda^2\ (2\lambda)\ (2\lambda)$$

which limits as $K^4\lambda^5$ as $\lambda \to \infty$. The second block is the computation of XX, XY, and XZ which loops over the angular momentum on Kshell, Lshell, and t'. The cost of this is

Figure II.7.2

The Saunders Integral Evaluation Algorithm

```
Loop over Ishell, Jshell and contractions on both shells
    Loop over Kshell and Lshell and contractions on both
    shells
        Loop over the number of quadrature points
            loop over angular momentum on Ishell and Jshell
                Loop over sum of angular momentum on Kshell
                and Lshell
                    looping over t
                        compute YX, YY, and YZ
                Loop over angular momentum on Kshell and
                Lshell
                    looping over t'
                        compute XX, XY and XZ
            Expand XX, XY, and XZ about the members of all
            the shells
```

$$K^4 \ (2\lambda+1) \ \lambda^4 \ (2\lambda)$$

which limits as $K^4\lambda^6$. The third block is the expansion of XX, XY, and XZ about all the centers for all the shells and costs

$$K^4 \ (2\lambda+1) \ \{ \ (\lambda+1)(\lambda+2)/2 \ \}^4$$

which limits as $K^4\lambda^9$. Note that all three blocks are within the loop over Rys quadrature points.

The costs for both algorithms are collected in Table II.7.1. The table makes it clear that the McMurchie and Davidson algorithm will excel for heavily contracted basis sets, but expand rapidly for higher angular momentum functions. The Saunders algorithm pays heavily for contraction, but this deficiency is overcome for higher angular momentum functions.

For a third and fourth derivative integral package, the dependence on λ needs to be as small as possible as the fourth derivative of a $\lambda=2$ function (a d orbital) necessitates $\lambda=6$ functions. Thus, the Saunders algorithm was used as a base for the developement of the codes for first, second, third, and fourth derivatives. The actual form of the derivative integral algorithm, and the form of the derivative integrals themselves are discussed in the next chapter.

Table II.7.1

Costs of the Algorithms in Terms of the Total Angular Momentum λ and Contraction Depth K as λ Goes to Infinity

McMurchie and Davidson	Saunders
$K^4\lambda^{10}$	$K^4\lambda^5$
$K^2\lambda^{11}$	$K^4\lambda^6$
	$K^4\lambda^9$

Note that the McMurchie and Davidson algorithm is divided into two blocks, while the Saunders algorithm is divided in three. These blocks represent the most costly portions of each algorithm.

III DERIVATIVE ATOMIC ORBITAL INTEGRALS

III.1 INTRODUCTION

The first derivative with respect to a nuclear perturbation a_k (where a is the nuclear position and k the cartesian coordinate) of the Hartree-Fock closed-shell energy expression is given by

$$\frac{d}{dA_k} E^{SCF} = E^{a_k} = 2 \sum_i^{do} h_{ii}^{a_k} + \sum_i^{do} \sum_j^{do} \{ 2(ii|jj)^{a_k} - (ij|ij)^{a_k} \} - 2 \sum_i^{do} S_{ii}^{a_k} \varepsilon_i \qquad \text{(III.1.1)}$$

where

$$h_{ii}^{a_k} = \sum_\mu \sum_\nu C_\mu^i C_\nu^i h_{\mu\nu}^{a_k} \qquad \text{(III.1.2)}$$

$$(ii|jj)^{a_k} = \sum_\mu \sum_\nu \sum_\rho \sum_\sigma C_\mu^i C_\nu^i C_\rho^j C_\sigma^j (\mu\nu|\rho\sigma)^{a_k} \qquad \text{(III.1.3)}$$

$$S_{ii}^{a_k} = \sum_\mu \sum_\nu C_\mu^i C_\nu^i S_{\mu\nu}^{a_k} \qquad \text{(III.1.4)}$$

The summation limits in equation III.1.1 are all doubly occupied molecular orbitals, whereas the limits in equations III.1.2 through III.1.4 are all atomic orbitals. The C_μ^i are the molecular orbital coefficients that are variationally optimized (see section II.1), and ε_i is the orbital energy. Details of these equations will be discussed in chapter IV however, these equations are presented here as they illustrate the use of the derivative atomic orbital integrals.

The one-electron derivative atomic orbital integral, equation III.1.2, is given by

$$h_{\mu\nu}^{a_k} = \frac{\partial}{\partial A_k} \{ \int \chi_\mu (T + V) \chi_\nu \, d\tau \qquad \text{(III.1.5)}$$

with the two-electron and overlap derivatives defined similarly. This set of equations illustrates that an nth order derivative energy expression will involve n^{th} order derivative atomic orbital integrals.

As the derivatives are taken with respect to cartesian coordinates, certain derivatives are equivalent. (i.e. $\partial^2/\partial A_x \partial A_y$ is equivalent to $\partial^2/\partial A_y \partial A_x$). In order to minimize the computational effort, only the unique cartesian derivatives are evaluated. Table III.1.1 lists the number of unique degrees of freedom for the various order of derivatives.

Until recently, most quantum chemists believed that even analytic second derivative energies were computationally more expensive than those calculated by finite differences in analytic first derivatives, let alone higher derivatives. This was in part due to problems arising from the large number of degrees of freedom, plus the difficulty in evaluating the derivative integrals. The work of Thomsen and Swanstrøm [40] on the H_2O molecule supported this view. Their second derivative calculation used a near Hartree-Fock limit basis set on the oxygen and hydrogen, and took roughly 30 hours on the CDC 6400 computer, the derivative integrals taking roughly 10 hours. The dismay that the timings created is succinctly expressed by P. Pulay [41]: "...the analytic calculation of the second (and by the same token the third) derivative is not practical."

Table III.1

Number of Unique Degrees of Freedom for Various Orders of Derivatives

N = number of atoms

N3N = 3 (N)

Degree of Derivative	Number of Degrees of Freedom
1	N3N
2	(N3N) (N3N+1) / 2!
3	(N3N) (N3N+1) (N3N+2) / 3!
4	(N3N) (N3N+1) (N3N+2) (N3N+3) / 4!
.	
.	
NDER	(N3N) (N3N+1) (N3N+2) ...(N3N+NDER-1)/NDER!

In a landmark paper of 1979, Pople, Krishnan, Schlegel, and Binkley [42], demonstrated that it was possible to obtain second derivatives of SCF wave functions at the cost of only four to five times that of a single gradient calculation. Since this work, researchers using second derivative methods have repeatedly shown that the calculation of analytic second derivatives for Hartree-Fock wave functions is generally much faster and more accurate than second derivatives calculated through finite differences of first derivatives. Three techniques used for reducing computational times are: (a) the incorporation of translational [43] and rotational [44,45] invariance of the integrals, (b) the use of Rys polynomials in the derivative integral evaluation [32,42,46,47], and (c) the implementation of the iterative method of solving the coupled-perturbed Hartree-Fock equations (CPHF) [42]. In this chapter, formulae will be derived for the derivative atomic orbital integrals that occur in derivative energy studies taking advantage of points (a) and (b). CPHF equations will be discussed in Chapter IV.

III.2 TRANSLATIONAL AND ROTATIONAL INVARIANCE

The property that the integrals, in any basis, are invariant to translation was first used in derivative calculations by Komornicki *et al.* [43] in 1977. Since its introduction, translational invariance has become the primary computation-saving method in the calculation of derivative integrals. Translational invariance states that for an integral I, the sum of the derivatives with respect to all the centers A in I for a particular cartesian coordinate k, are zero:

$$\sum_{A} \left(\frac{\partial}{\partial A_k} \right) I = 0 \qquad \text{(III.2.1)}$$

The immediate consequence is that not all of the derivative integrals are independent. For a two center integral, the derivatives with respect to each center are equal, but of opposite sign. Thus only one derivative integral need actually be calculated, since the other is generated by multiplying the calculated derivative integral by minus one. Note also that the derivative of a one center integral is zero. The use of translational invariance greatly reduces the number of integrals to be calculated. Table III.2.1 shows the number of degrees of freedom that must be calculated so as to use translational invariance to eliminate the calculation of all the derivatives on one center of a multicenter integral. The total number of degrees of freedom are given in parentheses of table III.2.1. The number of integrals eliminated due to translational invariance is easily found by multiplying the difference in these two degrees of freedom by the number of members within a particular block.

The integrals are also invariant to rotation [48]. Vincent, Saxe, and Schaefer [44,45] have pursued the use of rotational invariance in first and second derivative calculations, as have Page, Saxe, Adams, and Lensfield [49]. Vincent _et al._ have found the time savings to be on the order of fifty percent; however, the coding of the rotational invariance is a non-trivial matter and is presently limited to p-type orbitals. The code of Vincent _et al._ for the calculation of first and second derivative integrals expanded from roughly 5,400 lines to 34,000 once

Table III.2.1

Number of Degrees of Freedom for Derivatives on Various Centers Using Translational Invariance

Degree of Derivative	2 Centers	3 Centers	4 Centers
1	3 (6)	6 (9)	9 (12)
2	6 (21)	21 (45)	45 (78)
3	10 (56)	56 (165)	165 (364)
4	15 (126)	126 (495)	495 (1365)

Numbers in parentheses are the total number of degrees of freedom.

rotational invariance was included. As a result, rotational invariance has not been included in the present series of programs. Table III.2.2 lists the translational invariance relations used in this study, and is located at the end of the chapter.

III.3 DERIVATIVE OVERLAP INTEGRALS

The derivative of the atomic overlap integral is

$$S_{\mu\nu}^{a_k} = \frac{\partial}{\partial A_k} \left\{ \int_{-\infty}^{\infty} \chi_\mu \, \chi_\nu \, d\tau \right\}$$

$$= \int_{-\infty}^{\infty} \left(\frac{\partial}{\partial A_k} \chi_\mu \right) \chi_\nu \, d\tau + \int_{-\infty}^{\infty} \chi_\mu \left(\frac{\partial}{\partial A_k} \chi_\nu \right) d\tau \qquad \text{(III.3.1)}$$

If χ_μ and χ_ν are on the same center, then $S_{\mu\nu}^{a_k}$ is zero by translational invariance, and need not be calculated. Therefore, for the purpose of this section, it will be assumed that χ_μ is located on nuclear center **A**, and that χ_ν is located on nuclear center **B**. As a result, the second term in the above equation immediately drops out.

The derivative of the atomic orbital is simply the derivative of the cartesian gaussians that approximate the orbital itself. Thus, with k equal to x,

$$\frac{\partial}{\partial A_x} \chi_\mu = - n \, x_A^{n-1} \exp(-a x_A^2) + 2a \, x_A^{n+1} \exp(-a x_A^2)$$

$$= - n \, G(a,A,n-1,1,m) + 2a \, G(a,A,n+1,1,m) \qquad \text{(III.3.2)}$$

Substituting this back into equation III.3.1 for the A_x derivative

results in

$$S_{\mu\nu}^{a_x} = - n \int_{-\infty}^{\infty} G(a,A,n-1,l,m)\ G(b,B,n',l',m')\ d\tau$$

$$+ 2a \int_{-\infty}^{\infty} G(a,A,n+1,l,m)\ G(b,B,n',l',m')\ d\tau \qquad \text{(III.3.3)}$$

Using the results of section II.4, the above integrals each reduce to a single term, giving

$$S_{\mu\nu}^{a_x} = (\pi/p)^{3/2}\ \{ -n\ e_x(n-1,n',0)\ e_y(l,l',0)\ e_z(m,m',0)$$

$$+ 2a\ e_x(n+1,n',0)\ e_y(l,l',0)\ e_z(m,m',0)\ \} \qquad \text{(III.3.4)}$$

First, second, third, and fourth derivatives for cartesian gaussians are listed in table III.3.1.

The second derivative of the overlap integral with respect of A_k and A_k is obtained by integrating the charge distribution of the second derivative of the cartesian gaussian on **A** (from table III.3.1) and the undifferentiated cartesian gaussian on **B**. This is not one, but three separate charge distributions. As with the first derivative, section II.4 indicates that each distribution reduces to a single term. For $S_{\mu\nu}^{a_x a_x}$, the result is

$$S_{\mu\nu}^{a_x a_x} = (\pi/p)^{3/2}\ \{ 4a^2\ e_x(n+2,n',0)\ e_y(l,l',0)\ e_z(m,m',0)$$

$$- 2a\ (2n+1)\ e_x(n,n',0)\ e_y(l,l',0)\ e_z(m,m',0)$$

$$+ n(n-1)\ e_x(n-2,n',0)\ e_y(1,1',0)\ e_z(m,m',0)\ \} \qquad \text{(III.3.5)}$$

Third and fourth derivatives on the same center are easily obtained by applying the formulae of table III.3.1 and the results of section II.4, as was done above.

Up to this point, translational invariance has only been used to avoid the calculation of a derivative equal to zero for one center integrals. Table III.2.2 indicates that translational invariance can also be used to evaluate the derivative of the overlap distribution with respect to center **B**, while only calculating the derivative with respect to center **A**.

$$S_{\mu\nu}^{b_k} = - S_{\mu\nu}^{a_k}$$

$$S_{\mu\nu}^{b_k b_k} = S_{\mu\nu}^{a_k a_k}$$

$$S_{\mu\nu}^{b_k b_k b_k} = - S_{\mu\nu}^{a_k a_k a_k}$$

$$S_{\mu\nu}^{b_k b_k b_k b_k} = S_{\mu\nu}^{a_k a_k a_k a_k} \qquad \text{(III.3.6)}$$

When derivatives of order two or greater contain derivatives with respect to mixed cartesian coordinates, then the separability of the cartesian gaussian along each of the axes dictates that the total derivative is the product of the derivatives along each individual

Table III.3.1

Derivatives with Respect to A_n of a Cartesian Gaussian Centered on **A**

Degree of Derivative	Expression
0	$G(a,A,n)$
1	$2a\ G(a,A,n+1) - n\ G(a,A,n-1)$
2	$4a^2\ G(a,A,n+2) - 2a\ (2n+1)\ G(a,A,n)$ $+ n(n-1)\ G(a,A,n-2)$
3	$8a^3\ G(a,A,n+3) - 12a^2\ (n+1)\ G(a,A,n+1)$ $+ 6an^2\ G(a,A,n-1) - n(n-1)(n-2)\ G(a,A,n-3)$
4	$16a^4\ G(a,A,n+4) - 8a^3\ (4n + 6)\ G(a,A,n+2)$ $+ 12a^2\ (n^2 + (n+1)^2)\ G(a,A,n)$ $- 2a\ (2n(2n^2 - 3n + 1))\ G(a,A,n-2)$ $+ n(n-1)(n-2)(n-3)\ G(a,A,n-4)$

axis. For the case of $S_{\mu\nu}^{a_x a_y}$, this results in

$$S_{\mu\nu}^{a_x a_y} = (\pi/p)^{3/2} \{ nl\, e_x(n-1,n',0)\, e_y(l-1,l',0)\, e_z(m,m',0)$$

$$- 2na\, e_x(n-1,n',0)\, e_y(l+1,l',0)\, e_z(m,m',0)$$

$$- 2la\, e_x(n+1,n',0)\, e_y(l-1,l',0)\, e_z(m,m',0)$$

$$+ 4a^2\, e_x(n+1,n',0)\, e_y(l+1,l',0)\, e_z(m,m',0) \} \qquad \text{(III.3.7)}$$

Equation III.3.6 can now be generalized for cartesian coordinates x, y, and z indicated by the generic k, j, i, and h.

$$S_{\mu\nu}^{b_k b_j} = S_{\mu\nu}^{a_k a_j}$$

$$S_{\mu\nu}^{b_k b_j b_i} = - S_{\mu\nu}^{a_k a_j a_i}$$

$$S_{\mu\nu}^{b_k b_j b_i b_h} = S_{\mu\nu}^{a_k a_j a_i a_h} \qquad \text{(III.3.8)}$$

The translational invariance relations given in Table III.2.2 also indicate that the mixed center derivatives, whether the cartesian coordinates be the same or different, are equivalent to derivatives evaluated on one center.

$$S_{\mu\nu}^{a_k b_j} = - S_{\mu\nu}^{a_k a_j}$$

$$S_{\mu\nu}^{a_j a_i b_k} = - S_{\mu\nu}^{a_k a_j a_i}$$

$$S_{\mu\nu}^{a_i b_k b_j} = S_{\mu\nu}^{a_k a_j a_i}$$

$$S_{\mu\nu}^{a_j a_i a_h b_k} = S_{\mu\nu}^{a_h b_k b_j b_i} = - S_{\mu\nu}^{a_k a_j a_i a_h}$$

$$S_{\mu\nu}^{a_i a_h b_j b_k} = S_{\mu\nu}^{a_k a_j a_i a_h} \qquad \text{(III.3.9)}$$

Since mixed center derivatives are equivalent to derivatives on one center, many derivative integral packages do not store them. The one center derivatives are stored instead and expanded to the mixed centers when used in the derivative energy program.

III.4 DERIVATIVE KINETIC ENERGY INTEGRALS

Since the kinetic energy operator acts only on electronic coordinates, the application of a nuclear displacement will only affect the atomic orbitals. The first derivative is

$$T_{\mu\nu}^{a_k} = \frac{\partial}{\partial A_k} \left\{ \int_{-\infty}^{\infty} \chi_\mu \, \mathbf{T} \, \chi_\nu \, d\tau \right\}$$

$$= \int_{-\infty}^{\infty} \left(\frac{\partial}{\partial A_k} \chi_\mu \right) \mathbf{T} \, \chi_\nu \, d\tau + \int_{-\infty}^{\infty} \chi_\mu \, \mathbf{T} \left(\frac{\partial}{\partial A_k} \chi_\nu \right) d\tau \qquad \text{(III.4.1)}$$

Again, the derivative of an atomic orbital is the derivative of the cartesian gaussians used to approximate it. Tables III.2.2 and III.3.1, utilized in the previous section, provide the necessary relations for the derivative evaluation. As kinetic energy integrals are either over one or two nuclear centers, translational invariance dictates that the

derivative of any one center kinetic energy integral is zero, and hence need not be calculated. As a result, the χ_μ orbital is assumed to be located on nuclear center A, while the χ_ν orbital is assumed to be on B. The kinetic energy operator is assumed to operate on gaussian G(b,B), as in section II.4.

For k equal to x, $T^{a_k}_{\mu\nu}$ is given by

$$
\begin{aligned}
T^{a_x}_{\mu\nu} = -1/2\ (\pi/p)^{3/2}\ \{\ 4b^2\ \big(-n\ \big(\ & e_x(n-1,n'+2,0)\ e_y(1,1',0)\ e_z(m,m',0) \\
& + e_x(n-1,n',0)\ e_y(1,1'+2,0)\ e_z(m,m',0) \\
& + e_x(n-1,n',0)\ e_y(1,1',0)\ e_z(m,m'+2,0)\ \big) \\
+ 2a\ \big(\ & e_x(n+1,n'+2,0)\ e_y(1,1',0)\ e_z(m,m',0) \\
& + e_x(n+1,n',0)\ e_y(1,1'+2,0)\ e_z(m,m',0) \\
& + e_x(n+1,n',0)\ e_y(1,1',0)\ e_z(m,m'+2,0)\ \big)\ \big) \\
- 2b\ \big(\ 2(n'+l'+m') + 3\ \big)\ \big(\ & -n\ e_x(n-1,n',0)\ e_y(1,1',0)\ e_z(m,m',0) \\
& + 2a\ e_x(n+1,n',0)\ e_y(1,1',0)\ e_z(m,m',0)\ \big) \\
+ n'(n'-1)\ \big(\ & -n\ e_x(n-1,n'-2,0)\ e_y(1,1',0)\ e_z(m,m',0) \\
& + 2a\ e_x(n+1,n'-2,0)\ e_y(1,1',0)\ e_z(m,m',0)\ \big) \\
+ l'(l'-1)\ \big(\ & -n\ e_x(n-1,n',0)\ e_y(1,1'-2,0)\ e_z(m,m',0) \\
& + 2a\ e_x(n+1,n',0)\ e_y(1,1'-2,0)\ e_z(m,m',0)\ \big) \\
+ m'(m'-1)\ \big(\ & -n\ e_x(n-1,n',0)\ e_y(1,1',0)\ e_z(m,m'-2,0) \\
& + 2a\ e_x(n+1,n',0)\ e_y(1,1',0)\ e_z(m,m'-2,0)\ \big)\ \}
\end{aligned}
\tag{III.4.2}
$$

Although equation III.4.2 looks formidable, it is nothing more than a linear combination of derivative overlap integrals, and the results of section III.3 can be directly applied.

Again, only the derivatives on one center need be evaluated, as

derivatives on the second center, including mixed derivatives of both centers, can be calculated by translational invariance. Equations III.3.5 - III.3.7 of the derivative overlap integrals directly apply, except that derivatives are for kinetic energy integrals, rather than overlap integrals.

III.5 DERIVATIVE NUCLEAR ATTRACTION INTEGRALS

The nuclear attraction operator acts on the distance between an electron and a nuclear center, and is thus affected by a nuclear perturbation. The first derivative is given by

$$V_{\mu\nu}^{a_k} = \frac{\partial}{\partial A_k} \left\{ \int_{-\infty}^{\infty} \chi_\mu \sum_c r_c^{-1} \chi_\nu \, d\tau \right\}$$

$$= \int_{-\infty}^{\infty} \left(\frac{\partial}{\partial A_k} \chi_\mu \right) \sum_c r_c^{-1} \chi_\nu \, d\tau + \int_{-\infty}^{\infty} \chi_\mu \left(\frac{\partial}{\partial A_k} \sum_c r_c^{-1} \right) \chi_\nu \, d\tau$$

$$+ \int_{-\infty}^{\infty} \chi_\mu \sum_c r_c^{-1} \left(\frac{\partial}{\partial A_k} \chi_\nu \right) d\tau \qquad \text{(III.5.1)}$$

The first and third terms of the above equation are the derivatives of the cartesian gaussians, both of which have been encountered in the previous two sections. The second term, a Hellmann-Feynman-like term, vanishes unless A is equal to c. This term would be the one-electron Hellman-Feynman term if the kinetic energy operator were included in III.5.1. For A equal to c and k equal to x, this term gives

$$\int_{-\infty}^{\infty} \chi_\mu \left(\frac{\partial}{\partial A_k} \sum_c r_c^{-1} \right) \chi_\nu \, d\tau = \int_{-\infty}^{\infty} \chi_\mu \left(\frac{\partial}{\partial C_x} r_c^{-1} \right) \chi_\nu \, d\tau$$

$$= \int_{-\infty}^{\infty} \chi_\mu \, x_c \, r_c^{-3} \, \chi_\nu \, d\tau \qquad \text{(III.5.2)}$$

This is the electric field integral. Its evaluation is accomplished by returning to section II.6, the zeroth order NAI section. From section II.6, the general solution for the NAI is equation II.6.16

$$V_{\mu\nu} = 2\pi/p \sum_{t,u,v} E(t,u,v) \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v F_0(z) \qquad \text{(III.5.3)}$$

where $z = p\,\overline{PC}^2 = p\left((P_x - C_x)^2 - (P_y - C_y)^2 - (P_z - C_z)^2 \right)$

Rewriting equation III.5.2 in terms of the above equation, remembering that A is now equal to C, yields

$$\int_{-\infty}^{\infty} \chi_\mu \left(\frac{\partial}{\partial C_x} r_c^{-1} \right) \chi_\nu \, d\tau = 2\pi/p \sum_{t,u,v} E(t,u,v) \left(\frac{\partial}{\partial C_x} \right) \left(\frac{\partial}{\partial P_x} \right)^t$$

$$\times \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v F_0(z) \qquad \text{(III.5.4)}$$

where χ_μ and χ_ν have been reduced to an averaged gaussian about **P**. Since z depends only on **P** - **C**, then

$$\left(\frac{\partial}{\partial C_x} \right) F_0(z) = - \left(\frac{\partial}{\partial P_x} \right) F_0(z) \qquad \text{(III.5.5)}$$

Equation III.5.4 now becomes

$$\int_{-\infty}^{\infty} \chi_\mu \left(\frac{\partial}{\partial C_x} r_c^{-1} \right) \chi_\nu \, d\tau = -2\pi/p \sum_{t,u,v} E(t,u,v) \left(\frac{\partial}{\partial P_x} \right)^{t+1} \left(\frac{\partial}{\partial P_y} \right)^u$$

$$\times \left(\frac{\partial}{\partial P_z} \right)^v F_0(z)$$

$$= -\ 2\pi/p \sum_{t,u,v} E(t,u,v)\ \ R^{c}(t+1,u,v) \qquad \text{(III.5.6)}$$

where $R^{c}(t+1,u,v)$ is defined as in equation II.6.18. Again the superscript c is used to designate that this $R^{c}(t+1,u,v)$ is for a specific nuclear center C.

In a similar manner, electric field integrals in the y and z cartesian coordinates can be derived. The results are

$$\int_{-\infty}^{\infty} \chi_{\mu} \left(\frac{\partial}{\partial C_y} r_c^{-1} \right) \chi_{\nu}\, d\tau = -2\pi/p \sum_{t,u,v} E(t,u,v)\ R^{c}(t,u+1,v)$$

$$\int_{-\infty}^{\infty} \chi_{\mu} \left(\frac{\partial}{\partial C_z} r_c^{-1} \right) \chi_{\nu}\, d\tau = -2\pi/p \sum_{t,u,v} E(t,u,v)\ R^{c}(t,u,v+1)$$

(III.5.7)

Higher derivatives of the operator are also possible since

$$\left(\frac{\partial}{\partial C_x} \right)^{n} F_0(z) = (-1)^{n} \left(\frac{\partial}{\partial P_x} \right)^{n} F_0(z) \qquad \text{(III.5.8)}$$

Mixed cartesian derivatives are easily found as well, since

$$\left(\frac{\partial}{\partial C_x} \right) \left(\frac{\partial}{\partial C_y} \right) F_0(z) = \left(\frac{\partial}{\partial P_x} \right) \left(\frac{\partial}{\partial P_y} \right) F_0(z)$$

(III.5.9)

Before equations III.5.6 - II.5.9 and table III.3.1 are applied to the evaluation of the NAI derivative integral, it is beneficial to break the problem into three classes and examine a specific case from each class. The first class is comprised of derivatives with respect to one of the nuclear centers on which χ_{μ} and χ_{ν} are located. We will consider the general case of derivatives with respect to **A** where χ_{μ} is located

on nuclear center **A** and χ_ν is located on nuclear center **B.** The second class includes derivatives where χ_μ and χ_ν are located on the same center and the derivatives are taken with respect to this center. The specific case of interest will be when χ_μ and χ_ν are located on center **A** and the derivatives are with respect to **A.** The third class contains derivatives that are taken with respect to centers on other than where χ_μ and χ_ν are located. The specific case will be χ_μ located on **C** and χ_ν on **D**, while the derivatives are taken with respect to **A.**

In order to simplify notation, dirac notation will be employed. Derivatives are denoted by superscripts of the appropriate cartesian coordinates, and atomic orbitals are represented by μ or ν with a subscript denoting the nuclear center. The operator r_c^{-1} is denoted by V_c. As an example, consider

$$\int_{-\infty}^{\infty} \left(\frac{\partial}{\partial A_k} \chi_\mu \right) \sum_c r_c^{-1} \chi_\nu \, d\tau = \langle \mu_A^k \mid \sum_c V_c \mid \nu_B \rangle \tag{III.5.10}$$

<u>Case 1 : χ_μ on A χ_ν on B</u>

$$V_{\mu\nu}^{a_k} = \langle \mu_A^k \mid \sum_C V_c \mid \nu_B \rangle + \langle \mu_A \mid V_A^k \mid \nu_B \rangle \tag{III.5.11}$$

For k equal to x:

$$V_{\mu\nu}^{a_x} = 2\pi/p \left\{ -n \sum_{t=0}^{t=n-1+n'} e_x(n-1,n',t) \sum_{u=0}^{u=l+l'} e_y(l,l',u) \sum_{v=0}^{v=m+m'} e_z(m,m',v) \sum_C R^C(t,u,v) \right.$$

$$+ 2a \sum_{t=0}^{t=n+1+n'} e_x(n+1,n',t) \sum_{u=0}^{u=l+l'} e_y(l,l',u) \sum_{v=0}^{v=m+m'} e_z(m,m',v) \sum_C R^C(t,u,v)$$

$$- \sum_{t=0}^{t=n+n'} e_x(n,n',t) \sum_{u=0}^{v=l+l'} e_y(l,l',u) \sum_{v=0}^{v=m+m'} e_z(m,m',v)\ R^A(t+1,u,v)\ \} \tag{III.5.12}$$

<u>Case 2 : both χ_μ and χ_ν on A</u>

$$V_{\mu\nu}^{a_k} = \langle \mu_A^k \mid \sum_C V_c \mid \nu_A \rangle + \langle \mu_A \mid \sum_C V_c \mid \nu_A^k \rangle$$

$$+ \langle \mu_A \mid V_A^k \mid \nu_A \rangle \tag{III.5.13}$$

For k equal to x:

$$V_{\mu\nu}^{a_x} = 2\pi/p\{[\sum_{t=0}^{t=n+n'-1} -(n+n')\big(e_x(n-1,n',t) + e_x(n,n'-1,t)\big) + \sum_{t=0}^{t=n+n'+1} (2a+2b)$$

$$\big(e_x(n+1,n',t) + e_x(n,n'+1,t)\big)] \sum_{u=0}^{u=l+l'} e_y(l,l',u) \sum_{v=0}^{v=m+m'} e_z(m,m',v) \sum_C R^C(t,u,v)$$

$$- \sum_{t=0}^{t=n+n'} e_x(n,n',t) \sum_{u=0}^{u=l+l'} e_y(l,l',u) \sum_{v=0}^{v=m+m'} e_z(m,m',v)\ R^A(t+1,u,v)\ \} \tag{III.5.14}$$

<u>Case 3 : χ_μ on C and χ_ν on D</u>

$$V_{\mu\nu}^{a_k} = \langle \mu_C \mid V_A^k \mid \nu_D \rangle \tag{III.5.15}$$

For k equal to x:

$$V_{\mu\nu}^{a_x} = -2\pi/p \sum_{t=0}^{t=n+n'} e_x(n,n',t) \sum_{u=0}^{u=l+l'} e_y(l,l',u) \sum_{v=0}^{v=m+m'} e_z(m,m',v)\ R^A(t+1,u,v) \tag{III.5.16}$$

Equations similar to these are readily produced for the higher derivatives; they involve higher deivatives of the gaussians (Table

III.3.1) and larger limits for R^A. The only drawback to these formulae is the amount of work needed to solve them. Equations III.5.11 - III.5.16 take no advantage of translational invariance.

The NAI is at most a three center integral. For a specific three center case, section III.2 and the translational invariance relations of Table III.2.2 yield

$$< \mu_A^k \mid V_C \mid \nu_B > + < \mu_A \mid V_C^k \mid \nu_B > + < \mu_A \mid V_C \mid \nu_B^k > = 0 \tag{III.5.17}$$

All three of the quantities in III.5.17 are not independent, one of them can be calculated by knowing the other two. Choosing the electic field integral to be the dependent integral,

$$< \mu_A \mid V_c^k \mid \nu_B > = - < \mu_A^k \mid V_c \mid \nu_B > - < \mu_A \mid V_c \mid \nu_B^k > \tag{III.5.18}$$

This means that the formulae for the NAI derivatives can now be rewritten purely in terms of derivatives on μ and ν.

Returning to the three general cases, and substituting equation III.5.18 for the electric field integral (note that this substitution requires that V_c in equation III.5.18 be changed to V_A) one obtains:

<u>Case 1 :</u>

$$V_{\mu\nu}^{a_k} = < \mu_A^k \mid \sum_{C \neq A} V_c \mid \nu_B > - < \mu_A \mid V_A \mid \nu_B^k > \tag{III.5.19}$$

<u>Case 2 :</u>

$$V_{\mu\nu}^{a_k} = < \mu_A^k \mid \sum_{C \neq A} V_c \mid \nu_A > + < \mu_A \mid \sum_{C \neq A} V_c \mid \nu_A^k > \tag{III.5.20}$$

Case 3 :

$$V_{\mu\nu}^{a_k} = - < \mu_C^k \mid V_A \mid \nu_D > - < \mu_C \mid V_A \mid \nu_D^k > \qquad \text{(III.5.21)}$$

The most obvious advantage to the above set of equations over equations III.5.11 through III.5.15 is that their solution involves less work. The summations are more restricted and the electric field integral is never explicitly solved.

Translation invariance relations that relate $V_{\mu\nu}^{a_k}$ to $V_{\mu\nu}^{b_k}$ are not simple due to the summation over all centers inherent in the r_c^{-1} operator. If translational invariance is used to eliminate the electric field integral, then maximum use is already being made of translational invariance, and no more is possible. Assuming this to be the case, the only way to obtain $V_{\mu\nu}^{b_k}$ is by direct evaluation. This has a hidden benefit. $V_{\mu\nu}^{b_k}$ is given by

$$V_{\mu\nu}^{b_k} = < \mu_A \mid \sum_{C\neq B} V_c \mid \nu_B^k > - < \mu_A^k \mid V_B \mid \nu_B > \qquad \text{(III.5.22)}$$

Note that the second term in III.15.19 is calculated in the summation of III.5.22, and that the second term in III.5.22 is calculated in the summation in III.5.19. By calculating $< \mu_A \mid V_A \mid \nu_B^k >$ and placing it in both $V_{\mu\nu}^{a_k}$ and $V_{\mu\nu}^{b_k}$ and by placing $< \mu_A^k \mid V_B \mid \nu_B >$ in $V_{\mu\nu}^{a_k}$ and $V_{\mu\nu}^{b_k}$ when it is calculated, then the two derivatives are calculated for the price of $< \mu_A^k \mid \sum_{c\neq A} V_c \mid \nu_B >$ plus $< \mu_A \mid \sum_{c\neq B} V_c \mid \nu_B^k >$. This is clearly superior to equation III.5.11, which for $V_{\mu\nu}^{a_k}$ and $V_{\mu\nu}^{b_k}$ is comprised of both of these terms including the missing term in the summation, and $< \mu_A \mid V_A^k \mid \nu_B >$ and $< \mu_A \mid V_B^k \mid \nu_B >$. The use of translational invariance to eliminate the electric field integrals produces formulae

that will require the least amount of work.

For second, third, and fourth derivatives, using translational invariance to eliminate the integrals of the derivatives of the operator yields the set of equations that require the minimum amount of computation. For each degree of differentiation, n, a new translational invariance relation must be obtained. The simplest method to obtain it is to differentiate the translational invariance relation of degree n-1. For second derivatives, the new translational invariance relation is obtained by differentiating equation III.5.18 with respect to C_j.

$$< \mu_A \mid V_c^{kj} \mid \nu_B > = - < \mu_A^k \mid V_c^j \mid \nu_B > - < \mu_A \mid V_c^j \mid \nu_B^k > \tag{III.5.23}$$

The terms on the right of the above equation are also found from equation III.5.18. For the first term, the equation is first redefined in terms of the derivative with respect to C_j, not C_k ($k \rightarrow j$ in equation III.5.18). Then the derivative with respect of A_k is taken resulting in

$$< \mu_A^k \mid V_c^j \mid \nu_B > = - < \mu_A^{kj} \mid V_c \mid \nu_B > - < \mu_A^k \mid V_c \mid \nu_B^j > \tag{III.5.24}$$

The second term on the right in equation III.5.23 begins as did equation III.5.24 ($k \rightarrow j$ in equation III.5.18), but then it is differentiated with respect to B_k, yielding

$$< \mu_A \mid V_c^j \mid \nu_B^k > = - < \mu_A^j \mid V_c \mid \nu_B^k > - < \mu_A \mid V_c \mid \nu_B^{kj} > \tag{III.5.25}$$

Substituting both of these into equation III.5.23 produces

$$< \mu_A \mid V_c^{kj} \mid \nu_B > = < \mu_A^{kj} \mid V_c \mid \nu_B > + < \mu_A^k \mid V_c \mid \nu_B^j >$$

$$+ < \mu_A^j \mid V_c \mid \nu_B^k > + < \mu_A \mid V_c \mid \nu_B^{kj} >$$

(III.5.26)

Naturally, if the cartesian coordinates k and j are equal, then the middle two terms of the above equation are the same. Using these relations, all the second derivatives for the three general cases are straightforwardly derived.

<u>Case 1:</u>

$$V_{\mu\nu}^{a_k a_j} = < \mu_A^{kj} \mid \sum_C V_c \mid \nu_B > + < \mu_A^j \mid V_A^k \mid \nu_B > + < \mu_A \mid V_A^{kj} \mid \nu_B > +$$

$$+ < \mu_A^k \mid V_A^j \mid \nu_B > \qquad \text{(III.5.27)}$$

Substituting for the terms with derivatives on the operator with equations III.5.24 and III.5.26 as well as a modified III.5.24 where $k \rightarrow j$ yields

$$V_{\mu\nu}^{a_k a_j} = < \mu_A^{kj} \mid \sum_{C \neq A} V_c \mid \nu_B > - < \mu_A \mid V_A \mid \nu_B^{kj} >$$

(III.5.28)

Similarly,

$$V_{\mu\nu}^{a_k b_j} = < \mu_A^k \mid \sum_C V_c \mid \nu_B^j > + < \mu_A^k \mid V_B^j \mid \nu_B > + < \mu_A \mid V_B^k \mid \nu_B^j >$$

Using equation III.5.24 and modifying equation III.5.25 ($k \rightarrow j$),

$$V_{\mu\nu}^{a_k b_j} = \langle \mu_A^k \mid \sum_{C\neq A,B} V_c \mid \nu_B^j \rangle - \langle \mu_A^{kj} \mid V_B \mid \nu_B \rangle - \langle \mu_A \mid V_A \mid \nu_B^{kj} \rangle \tag{III.5.29}$$

The second derivative with respect to A_k and C_j is given by

$$V_{\mu\nu}^{a_k c_j} = \langle \mu_A^k \mid V_C^j \mid \nu_B \rangle$$

Using equation III.5.24, it reduces to

$$V_{\mu\nu}^{a_k c_j} = - \langle \mu_A^{kj} \mid V_C \mid \nu_B \rangle - \langle \mu_A^k \mid V_C \mid \nu_B^j \rangle \tag{III.5.30}$$

<u>Case 2 :</u>

$$V_{\mu\nu}^{a_k a_j} = \langle \mu_A^{kj} \mid \sum_C V_c \mid \nu_A \rangle + \langle \mu_A \mid \sum_C V_c \mid \nu_A^{kj} \rangle$$

$$+ \langle \mu_A^k \mid \sum_C V_c \mid \nu_A^j \rangle + \langle \mu_A^j \mid \sum_C V_c \mid \nu_A^k \rangle$$

$$+ \langle \mu_A^k \mid V_A^j \mid \nu_A \rangle + \langle \mu_A \mid V_A^k \mid \nu_A^j \rangle$$

$$+ \langle \mu_A^j \mid V_A^k \mid \nu_A \rangle + \langle \mu_A \mid V_A^j \mid \nu_A^k \rangle$$

$$+ \langle \mu_A \mid V_A^{kj} \mid \nu_A \rangle$$

Using equations III.5.24 to III.5.26, the above reduces to

$$V_{\mu\nu}^{a_k a_j} = \langle \mu_A^{kj} \mid \sum_{C\neq A} V_A \mid \nu_A \rangle + \langle \mu_A \mid \sum_{C\neq A} V_A \mid \nu_A^{kj} \rangle$$

$$+ < \mu_A^k \mid \sum_{C \neq A} V_c \mid \nu_A^j > + < \mu_A^j \mid \sum_{C \neq A} V_c \mid \nu_A^k >$$

(III.5.31)

The second derivative with respect to A_k and B_j is given by

$$V_{\mu\nu}^{a_k b_j} = < \mu_A^k \mid V_B^j \mid \nu_A > + < \mu_A \mid V_B^j \mid \nu_A^k >$$

This easily reduces to

$$V_{\mu\nu}^{a_k b_j} = - < \mu_A^{kj} \mid V_B \mid \nu_A > - < \mu_A^k \mid V_B \mid \nu_A^j >$$

$$- < \mu_A \mid V_B \mid \nu_A^{kj} > - < \mu_A^j \mid V_B \mid \nu_A^k > \qquad \text{(III.5.32)}$$

<u>Case 3:</u>

$$V_{\mu\nu}^{a_k a_j} = < \mu_C \mid V_A^{kj} \mid \nu_D >$$

This is reduced directly by equation III.5.26, yielding

$$V_{\mu\nu}^{a_k a_j} = < \mu_C^{kj} \mid V_A \mid \nu_D > + < \mu_C^k \mid V_A \mid \nu_D^j >$$

$$+ < \mu_C^j \mid V_A \mid \nu_D^k > + < \mu_C \mid V_A \mid \nu_D^{kj} > \qquad \text{(III.5.33)}$$

The derivative with respect to A_k and B_j is

$$V_{\mu\nu}^{a_k b_j} = 0 \ . \qquad \text{(III.5.34)}$$

Similar sets of equations can be derived for the third and fourth

derivatives of the NAI. Table III.5.1 lists the first and second derivative results already described above. Table III.5.2 contains the third derivatives, whereas Table III.5.3 contains the fourth derivatives. These tables are located at the end of the chapter.

The algorithm for the evaluation of the derivatives of the overlap, kinetic energy, and the nuclear attraction integrals is located in the appendix A.2.

III.6 DERIVATIVE TWO-ELECTRON REPULSION INTEGRALS

Derivatives of the ERI are much more straightforward than those of the NAI because the r_{12}^{-1} operator of the ERI is independent of nuclear coordinates. There are two general methods for taking the ERI derivatives; the first is the addition and subtraction of integral blocks introduced by Dupuis and King [32,50]; and the second is the differentiation of the quadrature formula first introduced by Saxe, Yamaguchi, and Schaefer [46], and later reintroduced by Schlegel, Binkley, and Pople[47]. Both methods take full advantage of translational invariance.

For the ERI, as for the NAI, it is advantegous to evaluate the derivatives of the integral with respect to all centers in the integral at one time. Although this requires more memory for the storage of intermediate arrays, many of the imtermediaries can be used repeatedly, saving the computational cost of recomputing them. It is thus necessary to know which derivatives need to be taken. Using the translational invariance relations of table III.2.2, the derivatives of one center of a multicenter ERI can always be neglected and calculated from the

derivatives with respect to the remaining centers. In the discussion that follows concerning the two general approaches to ERI derivatives, the use of translational invariance is neglected. It is brought back into the discussion when the actual method employed in the programs for the ERI dervative evaluation is discussed.

The first general ERI derivative method, that of Dupuis and King [32,50] uses the property that the first derivative of a cartesian gaussian G(a,A,n) is a linear combination of G(a,A,n+1) and G(a,A,n-1) where n is the angular momentum of the gaussian along the axis of the derivative. (See table III.3.1 for a list of the derivatives of gaussians). In this way, the first derivative with respect to the center **A** of a block of (pp|pp) integrals is a linear combination of (sp|pp) and (dp|pp) blocks of integrals. The second derivative is a combination of (pp|pp) and (fp|pp) blocks, and the third and fourth derivatives are combinations of (gp|pp), (dp|pp), (sp|pp) and (hp|pp), (fp|pp), (pp|pp) blocks, respectively. The major drawback of this method is that large amounts of storage can be required for the handling of these blocks.

The second method, that of differentiation of the quadrature formula, begins with the ERI as developed by Dupuis <u>et al</u>. (see references 32, 36, and 37 for details). It is given by

$$(\mu\nu|\rho\sigma) = \int_0^1 P_L(t) \exp\left(-pq/(p+q)\ \overline{PQ}^2\ t^2\right)\ dt \qquad \text{(III.6.1)}$$

where $P_L(t)$ is a polynomial of degree L in t^2. Note the similarity of the above equation to II.7.18. The ploynomial is split along each axes resulting in

$$(\mu\nu|\rho\sigma) = \int_0^1 I_x I_y I_z \exp\left(-pq/(p+q)\ \overline{PQ}^2\ t^2\right) dt \qquad \text{(III.6.2)}$$

The constants p and q as well as $\overline{PQ}^2$ are as defined in section II.7. Rys quadrature on III.6.2 yields

$$(\mu\nu|\rho\sigma) = \sum_{\gamma}^{N} w_\gamma\ I_x(t_\gamma)\ I_y(t_\gamma)\ I_z(t_\gamma) \qquad \text{(III.6.3)}$$

Saxe <u>et al.</u> [46] differentiated the equation III.6.2 resulting in

$$(\mu\nu|\rho\sigma)^{a_k} = \frac{\partial}{\partial A_k}(\mu\nu|\rho\sigma) = \int_0^1 \left\{ \frac{\partial}{\partial A_k} P_L(t) - t^2 P_L(t) \frac{\partial}{\partial A_k}\left(pq/(p+q)\ \overline{PQ}^2\right)\right\}$$

$$\times \exp\left(-pq/(p+q)\ \overline{PQ}^2\ t^2\right) dt \qquad \text{(III.6.4)}$$

The integrand still contains a polynomial in t^2, however, it is now of degree L+1. As a result, the integral can still be solved by Rys quadrature as the polynomial fits the quadrature requirements. (See section II.6 for a discussion of the requirements of Rys quadrature). For k equal to x, equation III.6.4 becomes

$$(\mu\nu|\rho\sigma)^{a_x} = \sum_{\gamma}^{N+1} w_\gamma\ \delta I_x(t_\gamma)\ I_y(t_\gamma)\ I_z(t_\gamma)$$

where

$$\delta I_x(t_\gamma) = \frac{\partial}{\partial A_x} I_x(t_\gamma) - t^2\ I_x(t_\gamma) \frac{\partial}{\partial A_x}\left(pq/(p+q)\ \overline{PQ}^2\right) \qquad \text{(III.6.5)}$$

This equation differs sightly from that of Saxe <u>et al.</u> in that an exponential of weighted positions, which in their notation is

$\exp(-G_x - G_y - G_z)$, has been incorporated into the definition of I_x, I_y, and I_z. This is done to make the notations of Dupuis, Saxe, and Schlegel match.

In order to find the δI_x for a given derivative integral, the recursion relations of Rys et al.[37] are themselves differentiated. This leads to a series of recursion relations much like those used for zeroth order integrals; except they are explicitly for derivatives. Second derivatives are found by differentiating equation III.6.4 a second time and differentiating the derivative recursion relations to obtain the necessary second derivative recurrence relations. Third and fourth derivatives would be found similarily. The drawback to this method is the complexity of the resulting recursion relations.

Schlegel, Binkley, and Pople[47] avoid the derivative recursion relations altogether by casting derivatives in terms of derivatives of the basic I_x, I_y, and I_z for a $(ss|ss)$ block of integrals. They begin with equation III.6.2 and differentiate leading to

$$(\mu\nu|\rho\sigma)^{a_x} = \sum_{\gamma}^{N+1} \left(\frac{\partial}{\partial A_x} I_x(t_\gamma) \right) I_y(t_\gamma)\, I_z(t_\gamma) \tag{III.6.6}$$

Noting that any gaussian can be made by the appropriate application of equation II.2.2 on the s-type gaussian, they obtained the solution for $\frac{\partial}{\partial A_x} I_x(0,0,0,0)$. In this notation, the indices of I_x are n, n', i, i' while those of I_y are l, l', j, j' and I_z are m, m', k, k' - the components of the total angular momentum of the four shells. The derivative of the $(ss|ss)$ block is proportional to

$$\frac{\partial}{\partial A_x} I_x(0,0,0,0) \propto (\alpha t^2 + \beta) I_x(0,0,0,0) \tag{III.6.7}$$

where α and β are constants and functions of A_x. The details of the differentiation are not important for this discussion, rather what is important is that the derivative of I_x is proportional to a function of A_x and the undifferentiated I_x. Using equation II.2.2 to make this general (any I_x can be created by the appropiate use of the M operators) yeilds,

$$\frac{\partial}{\partial A_x} I_x(n_A,n_B',i_C,i_D') = M^{n_{Ax}} M^{n_{Bx}'} M^{i_{Cx}} M^{i_{Dx}'} \frac{\partial}{\partial A_x} I_x(0,0,0,0) \tag{III.6.8}$$

Applying the above leads to the calculation of $I_x(n_A+1,n_B',i_C,i_D')$ and $I_x(n_A-1,n_B',i_C,i_D')$; these are one-dimensional integrals of higher and lower angular momentum functions. By means of reexamining the definition of $M^{n_{Ax}}$, Schlegel <u>et al.</u> [47] found that for Λ, a linear function of A_x, the $M^{n_{Ax}}$ operator obeys the following relation:

$$M^{n_{Ax}} \Lambda = \Lambda M^{n_{Ax}} + \lambda_{Ax}/2a \frac{\partial \Lambda}{\partial A_x} M^{n_{Ax}-1} \tag{III.6.9}$$

where a is the exponent of the gaussian on which $M^{n_{Ax}}$ operates. Since the derivative of $I_x(0,0,0,0)$ is proportional to a linear function of A_x, equation III.6.7 can be rewritten as

$$(\alpha t^2 + \beta) I_x = \Lambda I_x \tag{III.6.10}$$

Applying equation III.6.9 to III.6.10 to produce III.6.8 yields

$$\frac{\partial}{\partial A_x} I_x(n_A,n_B',i_c,i_D') = \Lambda\, I_x(n,n',i,i')$$

$$+ n/2a \frac{\partial \Lambda}{\partial A_x} I_x(n-1,n',i,i') + n'/2a \frac{\partial \Lambda}{\partial Bx} I_x(n,n'-1,i,i')$$

$$+ i/2a \frac{\partial \Lambda}{\partial C_x} I_x(n,n',i-1,i') + i'/2a \frac{\partial \Lambda}{\partial D_x} I_x(n,n',i,i'-1)$$

(III.6.11)

The result is that equation III.6.8 is now written without any angular momentum functions higher than the zeroth order ERI. Schlegel *et al.* [47] provide formulae for the evaluation of the first and second derivatives of I_x, I_y, and I_z. Equation III.6.11 implies that the limits of summation in the derivative integral evaluation need not increase (loops that depend on the angular momentum). The number of quadrature points does increase by one for each degree of differentation.

In the present series of derivative integral programs, the quadrature formulae are not differentiated. In light of the above discussion, this may seem surprising. The reason for this is that the integral algorithm of Saunders [22,38] lends itself to derivatives in a very straightforward way that avoids both the calculation of derivative recursion relations and the determination of the various derivative linear functions Λ of equation III.6.11.

As shown in appendix A.1, the Saunders algorithm loops over shells such that Jshell < Ishell, Kshell < Ishell, and Lshell < Kshell (or Jshell if Kshell is equal to Ishell). The result is that specific combinations of the nuclear centers will occur in the calculation of the ERI and its derivatives. By coupling this with the translational

invariance relations of Table III.2.2, it is easy to decide the derivative that is best produced through translational invariance. Table III.6.1 lists the various combinations of nuclear centers and the derivatives that are taken so as to use translational invariance to eliminate all the derivatives with respect to a particular center.

Consider the case of a four center integral where derivatives with respect to nuclear center D are being calculated from translational invariance. This represents the most difficult case of Table III.6.1. The zeroth-order ERI is given by equation II.7.22

$$(\mu\nu|\rho\sigma) = \sum_{\gamma}^{N} XX_{\gamma}^{*}\, XY_{\gamma}\, XZ_{\gamma} \qquad \text{(III.6.12)}$$

where

$$XX_{\gamma}^{*} = \sum_{t'} e_x(i,i',t')\, YX^{*}(t') \qquad \text{(III.6.13)}$$

$$YX^{*}(t') = \sum_{t} e_x(n,n',t)\, G_{t+t'}^{*}(\beta_{\gamma}, \overline{PQ}_x) \qquad \text{(III.6.14)}$$

The asterisk is used to signify that an additional factor of $(p+q)^{-1/2}w_{\gamma}$ has been incorporated in the generation of $G_{t+t'}$. XY, XZ and YY, YZ are defined similarily to the x-direction analog, however, the $(p+q)^{-1/2}w_{\gamma}$ is not included. See section II.7 for more details concerning these equations.

In the following, explicit formulae for the first and second derivatives of the atomic orbital integrals will be derived. Third and fourth derivatives are simply an extension of these two derivatives.

The first derivative with respect to a general nuclear center S, for the x direction, is given by:

Table III.6.1

Combinations of Centers and Derivatives for the ERI $(\mu\nu|\rho\sigma)$

notation: AAB indicates a third derivative that is a second derivative with respect to center A and a first derivative that is a first derivative with respect to center B.

Centers on which the orbitals are located				Translation invariance used to elminate all derivatives with respect to center	Degree of Derivative and the necessary derivatives			
μ	ν	ρ	σ		1	2	3	4
A	A	B	C	A	B,C	BB,CC, BC	BBB,CCC BBC,BCC	BBBB,CCCC,BBBC BBCC,BCCC
A	A	B	B	A	B	BB	BBB	BBBB
A	B	C	C	C	A,B	AA,BB, AB	AAA,BBB AAB,ABB	AAAA,BBBB,AAAB AABB,ABBB
A	B	B	C	B	A,C	AA,CC, AC	AAA,CCC AAC,ACC	AAAA,CCCC,AAAC AACC,ACCC

A	B	A	B	B	A	AA	AAA	AAAA
A	B	C	B	B	A,C	AA,CC	AAA,CCC	AAAA,CCCC,AAAC
						AC	AAC,ACC	AACC,ACCC
A	B	A	C	A	B,C	BB,CC	BBB,CCC	BBBB,CCCC,BBBC
						BC	BBC,BCC	BBCC,BCCC
A	A	A	A		all derivatives are zero			
A	B	C	D	D	A,B,C	AA,BB	AAA,BBB	AAAA,BBBB,CCCC
						CC,AB	CCC,AAC,	AAAB,AABB,ABBB
						AC	AAB,ABB	AAAC,AACC,ACCC
							BBC,BCC	BBBC,BBCC,BCCC

$$\frac{\partial}{\partial S_x} (\mu\nu|\rho\sigma) = \sum_{\gamma}^{N+1} \left(\frac{\partial}{\partial S_x} XX_{\gamma}^{*} \right) XY_{\gamma} \, XZ_{\gamma} \qquad \text{(III.6.15)}$$

For the case of S equal to A:

$$\frac{\partial}{\partial A_x} XX_{\gamma}^{*} = XXFA = \sum_{t'} e_x(i,i',t') \frac{\partial}{\partial A_x} YX_{\gamma}^{*}(t') \qquad \text{(III.6.16)}$$

where

$$\frac{\partial}{\partial A_x} YX_{\gamma}^{*}(t') = YXFA = 2a \sum_{t}^{t=n+1+n'} e_x(n+1,n',t) \, G_{t+t'}^{*}$$

$$- n \sum_{t}^{t=n+n'-1} e_x(n-1,n',t) \, G_{t+t'}^{*}$$

$$= 2a \; YXFA1 - n \; YXFA2 \qquad \text{(III.6.17)}$$

Note that this is the application of Table III.3.1 to the gaussian centered on nuclear center A. The acronyms, XXFA, YXFA, YXFA1, and YXFA2 are for the benefit of the derivative integral algorithm that appears in appendix A.3. The acronyms are meant to indicate precisely what derivatives are being taken: i.e., XXFA is the <u>XX</u> array <u>F</u>irst derivative with respect to center <u>A</u>, while YXFA1 is the <u>YX</u> array for the <u>F</u>irst derivative with respect to <u>A</u>, component number <u>1</u>. In all of the above equations, as in those that follow, if an index for the expansion coefficients is less than zero ($n-1 < 0$), then the entire summation is ignored.

For S equal to B, the result is:

$$\frac{\partial}{\partial B_x} XX_{\gamma}^{*} = XXFB = \sum_{t'} e_x(i,i',t') \frac{\partial}{\partial B_x} YX_{\gamma}^{*}(t') \qquad \text{(III.6.18)}$$

where

$$\frac{\partial}{\partial B_x} YX^*_\gamma (t') = YXFB = 2b \sum_{t}^{t=n+n'+1} e_x(n,n'+1,t)\ G^*_{t+t'}$$

$$- n' \sum_{t}^{t=n+n'-1} e_x(n,n'-1,t')\ G^*_{t+t'}$$

$$= 2b\ YXFB1 - n'\ YXFB2 \qquad \text{(III.6.19)}$$

For S equal to C, the result is very different:

$$\frac{\partial}{\partial C_x} XX^*_\gamma = XXFC = 2c \sum_{t'}^{t'=i+1+i'} e_x(i+1,i',t')\ YX^*(t')$$

$$- i \sum_{t'}^{t'=i-1+i'} e_x(i-1,i',t')\ YX^*(t')$$

$$= 2c\ XXFC1 - i\ XXFC2 \qquad \text{(III.6.20)}$$

Note that the $YX^*(t')$ has a larger index than that of equation III.6.13.

The second derivative with respect to S_x of equation III.6.12 is given by:

$$\frac{\partial^2}{\partial S_x \partial S_x} (\mu\nu|\rho\sigma) = \sum_{\gamma}^{N+2} \left(\frac{\partial}{\partial S_x \partial S_x} XX^*_\gamma \right) XY_\gamma\ XZ_\gamma \qquad \text{(III.6.21)}$$

For S equal to A, equation III.6.21 yields:

$$\frac{\partial^2}{\partial A_x \partial A_x} XX^*_\gamma = XXSA = \sum_{t'} e_x(i,i',t') \frac{\partial^2}{\partial A_x \partial A_x} YX^*(t') \qquad \text{(III.6.22)}$$

where

$$\frac{\partial^2}{\partial A_x \partial A_x} YX^*_\gamma(t') = YXSA = 4a^2 \sum_t^{t=n+2+n'} e_x(n+2,n',t)\, G^*_{t+t'}$$

$$- 2a(2n+1) \sum_t^{t=n+n'} e_x(n,n',t)\, G^*_{t+t'} + n(n-1) \sum_t^{t=n-2+n'} e_x(n-2,n',t)\, G^*_{t+t'}$$

$$= 4a^2\, YXSA1 - 2a(2n+1)\, YX + n(n-1)\, YXSA2$$

(III.6.23)

For S equal to B:

$$\frac{\partial^2}{\partial B_x \partial B_x} XX^*_\gamma = \sum_{t'} e_x(i,i',t') \frac{\partial^2}{\partial B_x \partial B_x} YX^*(t')$$

where the result can be directly written down in analogy to equation III.6.23

$$\frac{\partial^2}{\partial B_x \partial B_x} YX^*(t') = YXSB = 4b^2\, YXSB1 - 2b(2n'+1)\, YX + n'(n'-1)\, YXSB2$$

(III.6.24)

For S equal to C:

$$\frac{\partial^2}{\partial C_x \partial C_x} XX^*_\gamma = XXSC = 4c^2 \sum_{t'}^{t'=i+2+i'} e_x(i+2,i',t')\, YX^*(t')$$

$$- 2c(2i+1) \sum_{t'}^{t'=i+i'} e_x(i,i',t')\, YX^*(t') + i(i-1) \sum_{t'}^{t'=i-2+i'} e_x(i-2,i',t')\, YX^*(t')$$

$$= 4c^2\, XXAC1 - 2c(2i+1)\, XX + i(i-1)\, XXSC2$$

(III.6.25)

The evaluation of the second derivative also leads to mixed center derivatives. Using the general nuclear centers **S**, and **T**, the second

derivative is given by:

$$\frac{\partial^2}{\partial S_x \partial T_x} (\mu\nu|\rho\sigma) = \sum_{\gamma}^{N+2} \left(\frac{\partial^2}{\partial S_x \partial T_x} XX_{\gamma}^{*} \right) XY_{\gamma}\, XZ_{\gamma} \qquad \text{(III.6.26)}$$

Table III.6.1 indicates that three cases of mixed center derivatives are needed; S equal to A and T equal to B; S equal to A and T equal to C; and S equal to B and T equal to C. For the first case, S equal to A and T equal to B, equation III.6.26 yields

$$\frac{\partial^2}{\partial A_x \partial B_x} XX_{\gamma}^{*} = XXSAB = \sum_{t'} e_x(i,i',t') \frac{\partial^2}{\partial A_x \partial B_x} YX_{\gamma}^{*} \qquad \text{(III.6.27)}$$

where

$$\frac{\partial^2}{\partial A_x \partial B_x} YX_{\gamma}^{*}(t') = 4ab \sum_{t}^{t=n+n'+2} e_x(n+1,n'+1,t)\, G_{t+t'}^{*}$$

$$- 2an' \sum_{t}^{t=n+n'} e_x(n+1,n'-1,t)\, G_{t+t'}^{*} - 2bn \sum_{t}^{t=n+n'} e_x(n-1,n'+1,t)\, G_{t+t'}^{*}$$

$$+ nn' \sum_{t}^{t=n+n'-2} e_x(n-1,n'-1,t)\, G_{t+t'}^{*}$$

$$= 4ab\ YXSAB1 - 2an'\ YXSAB2 - 2bn\ YXSAB3 + nn'\ YXSAB4 \qquad \text{(III.6.28)}$$

For the second case, S equal to A and T equal to C, the derivative is given by

$$\frac{\partial^2}{\partial A_x \partial C_x} XX_{\gamma}^{*} = XXSAC = 2c \sum_{t'}^{t'=i+i'+1} e_x(i+1,i',t) \frac{\partial}{\partial A_x} YX_{\gamma}^{*}(t')$$

$$- i \sum_{t'}^{t'=i+i'-1} e_x(i,i'-1,t') \frac{\partial}{\partial A_x} YX_{\gamma}^{*}(t')$$

$$= 2c \sum_{t'} e_x(i+1,i',t')\ \mathrm{YXFA} - i \sum_{t'} e_x(i-1,i',t')\ \mathrm{YXFA} \tag{III.6.29}$$

where YXFA is as defined by equation III.6.17. This reduces to

$$\mathrm{XXSAC} = 2c\ \mathrm{XXSAC1} - i\ \mathrm{XXSAC2} \tag{III.6.30}$$

Finally, for S equal to B and T equal to C:

$$\frac{\partial^2}{\partial B_x \partial C_x} XX_\gamma^* = \mathrm{XXSBC} = 2c \sum_{t'} e_x(i+1,i',t')\ \mathrm{YXFB}$$

$$- i \sum_{t'} e_x(i-1,i,t')\ \mathrm{YXFB}$$

$$= 2c\ \mathrm{XXSBC1} - i\ \mathrm{XXBC2} \tag{III.6.31}$$

The extension of these formulae to third and fourth derivatives is straightforward. Table III.6.1 shows the necessary combinations of derivatives needed to completely ignore the derivatives with respect to one center, and build it later through translational invariance.

In all of these formulae, for each degree of differentiation the summation limits of t and t' increase. This means that the limits of the indices of the expansion coefficients and the G arrays must increase. Producing these expansion coefficients of higher indices requires little computational effort as the coefficients are generated through an efficient recursion relationship based on Hermite Polynomials, equation II.3.8. By requiring G arrays of higher index, additional Rys roots and weights are needed. This requirement is common

to all derivative integral packages that are based on Rys quadrature. (See equations III.6.5 and III.6.6). As the G arrays are generated through a simple recursion relation, equation II.6.28, the calculation of elements of the G array of larger indices is trivial. This method completely eliminates the need for differentiating the recurrence relations, as is necessary in the method of Saxe et al., as well as the need with differentiating the Λ functions, as is necessary with the method of Schlegel et al.

The method used here is related to the method of Dupuis et al. in that the integrals of differentiated gaussians are evaluated, however, instead of working with entire blocks of integrals, as does Dupuis et al., sums and differences of one-dimensional integrals are evaluated. This does not require more storage space. The second derivative of a (pp|pp) block of integrals (one degree of freedom), will only require the amount of storage space necessary to store a zeroth order (pp|pp) block.

The amount of necessary storage space is complicated by the evaluation of all the derivatives of a block of integrals at once. If an integral block over N+1 centers has IMEM members, then the second derivative block taking derivatives with respect to N centers has IMEM*(N3N)*(N3N+1)/2 members where N3N equals the number of derivative centers N multiplied by three. This amount includes all second derivatives; mixed center and same center derivatives. The sizes for first, third, and fourth derivatives are found similarly (Table III.1.1). This type of storage requirement is common to all derivative programs that evaluate all derivatives at once. It will only become serious for cases of high derivatives on blocks of large angular

momentum functions where each function is on a separate center. This problem can be overcome by solving the first, second, and third derivatives at one time, and then rerunning the derivative integral program for the fourth derivatives.

The algorithm for the simultaneous evaluation of first and second derivatives of the ERI is given in appendix A.3. Many of the terms used are defined in appendix A.1; the remaining correspond to terms used throughout the past two chapters. Restrictions of the loops are the same as those given for the zeroth order ERI in appendix A.1 unless stated otherwise.

Table III.2.2

The Use of Translation Invariance to Calculate Derivatives of One Center in a Multicentered Integral

notation: a, b, c, d represent nuclear centers

k, j, i, h represent cartesian coordinates

a^k represents the derivative with respect to center a with cartesian coordinate k

One Center Integrals: I(a)

all derivatives are zero

Two Center Integrals: I(a,b)

solving for derivatives with respect to b

First derivative: $b^k = - a^k$

Second derivatives: $val = a^k a^j$

$b^k a^j = - val$

$b^k b^j = val$

Third derivatives:

$$val = a^k a^j a^i$$

$$b^k a^j a^i = - val$$

$$b^k b^j a^i = val$$

$$b^k b^j b^i = - val$$

Fourth derivatives:

$$val = a^k a^j a^i a^h$$

$$b^k a^j a^i a^h = - val$$

$$b^k b^j a^i a^h = val$$

$$b^k b^j b^i a^h = - val$$

$$b^k b^j b^i b^h = val$$

Three Center Integrals: I(a,b,c)

solving for derivatives with respect to c

First derivative:

$$c^k = - a^k - b^k$$

Second derivatives:

$$c^k a^j = - a^k a^j - a^j b^k$$

$$c^k c^j = a^k a^j + b^k b^j + a^j b^k + a^k b^j$$

Third derivatives:

$$c^k a^j a^i = - a^k a^j a^i - a^j a^i b^k$$

$$c^k a^j b^i = - a^k a^j b^i - a^j b^k b^i$$

$$c^k c^j a^i = a^k a^j a^i + a^i b^k b^j + a^j a^i b^k + a^k a^j b^j$$

$$c^k c^j c^i = - a^k a^j a^i - b^k b^j b^i - a^k a^j b^i - a^k a^i b^j$$
$$- a^j a^i b^k - a^k b^j b^i - a^i b^k b^j - a^j b^k b^i$$

Fourth derivatives:

$$c^k a^j a^i a^h = - a^k a^j a^i a^h - a^j a^i a^h b^k$$

$$c^k c^j a^i a^h = a^k a^j a^i a^h + a^i a^h b^k b^j + a^j a^i a^h b^k + a^k a^i a^h b^j$$

$$c^k c^j c^i a^h = - a^k a^j a^i a^h - a^h b^k b^j b^i - a^k a^j a^h b^i - a^k a^i a^h b^j$$
$$- a^k a^h b^j b^i - a^i a^h b^k b^j - a^j a^i a^h b^k - a^j a^h b^k b^i$$

$$c^k c^j c^i c^h = a^k a^j a^i a^h + b^k b^j b^i b^h + a^k a^j a^i b^h + a^k b^j b^i b^h$$
$$+ a^k a^j a^h b^i + a^i b^k b^j b^h + a^k a^i a^h b^j + a^h b^k b^j b^i$$
$$+ a^j a^i a^h b^k + a^j b^k b^i b^h + a^k a^j b^i b^h + a^k a^i b^j b^h$$
$$+ a^k a^h b^j b^i + a^i a^h b^k b^j + a^j a^h b^k b^i + a^j a^i b^k b^h$$

$$c^k a^j a^i b^h = - a^k a^j a^i b^h - a^j a^i b^k b^h$$

$$c^k c^j a^i b^h = a^k a^j a^i b^h + a^i b^k b^j b^h + a^j a^i b^k b^h + a^k a^i b^j b^h$$

Four Center Integrals : I(a,b,c,d)

solving for derivatives with respect to center d

First derivative: $d^k = - a^k - b^k - c^k$

Second derivatives:

$$d^k a^j = - a^k a^j - a^j b^k - a^j c^k$$

$$d^k d^j = a^k a^j + b^k b^j + c^k c^j + a^k b^j + a^j b^k + a^k c^j + a^j c^k + b^k c^j + b^j c^k$$

Third derivatives:

$$d^k a^j a^i = - a^k a^j a^i - a^j a^i b^k - a^j a^i c^k$$

$$d^k a^j b^i = - a^k a^j b^i - a^j b^k b^i - a^j b^i c^k$$

$$\begin{aligned} d^k d^j a^i = {} & a^k a^j a^i + a^i b^k b^j + a^i c^k c^j + a^k a^i b^j + a^j a^i b^k + a^k a^i c^j \\ & + a^j a^i c^k + a^i b^k c^j + a^i b^j c^k \end{aligned}$$

$$\begin{aligned} d^k d^j d^i = {} & - a^k a^j a^i - b^k b^j b^i - c^k c^j c^i - a^k a^i b^j - a^j a^i b^k - a^k a^j b^i \\ & - a^i b^k b^j - a^k b^j b^i - a^j b^k b^i - a^k a^j c^i - a^k a^i c^j - a^j a^i c^k \\ & - a^i c^k c^j - a^k c^j c^i - a^j c^k c^i - b^k b^i c^j - b^j b^i c^k - b^k b^j c^i \\ & - b^i c^k c^j - b^k c^j c^i - b^j c^k c^i - a^i b^k c^j - a^i b^j c^k - a^k b^i c^j \\ & - a^j b^i c^k - a^k b^j c^i - a^j b^k c^i \end{aligned}$$

Fourth derivative:

$$d^k a^j a^i a^h = - a^k a^j a^i a^h - a^j a^i a^h b^k - a^j a^i a^h c^k$$

$$\begin{aligned} d^k d^j a^i a^h = {} & a^k a^j a^i a^h + a^i a^h b^k b^j + a^i a^h c^k c^j + a^k a^i a^h b^j + a^j a^i a^h b^k \\ & + a^k a^i a^h c^j + a^j a^i a^h c^k + a^i a^h b^k c^j + a^i a^h b^j c^k \end{aligned}$$

$$\begin{aligned} d^k d^j d^i a^h = {} & - a^k a^j a^i a^h - a^h b^k b^j b^i - a^h c^k c^j c^i - a^k a^i a^h b^j \\ & - a^j a^i a^h b^k - a^k a^j a^h b^i - a^i a^h b^k b^j - a^k a^h b^j b^i - a^j a^h b^k b^i \end{aligned}$$

$$- a^k a^j a^h c^i - a^k a^i a^h c^j - a^j a^i a^h c^k - a^i a^h c^k c^j - a^k a^h c^j c^i$$
$$- a^j a^h c^k c^i - a^h b^k b^i c^j - a^h b^j b^i c^k - a^h b^k b^j c^i - a^h b^i c^k c^j$$
$$- a^h b^k c^j c^i - a^h b^j c^k c^i - a^i a^h b^k c^j - a^i a^h b^j c^k - a^k a^h b^i c^j$$
$$- a^j a^h b^i c^k - a^k a^h b^j c^i - a^j a^h b^k c^i$$

$$d^k d^j d^i d^h = a^k a^j a^i a^h + a^k a^j a^i b^h + a^k a^j a^i c^h + a^h b^k b^j b^i$$
$$+ b^k b^j b^i b^h + b^k b^j b^i c^h + a^h c^k c^j c^i + b^h c^k c^j c^i + c^k c^j c^i c^h$$
$$+ a^k a^i a^h b^j + a^k a^i b^j b^h + a^k a^i b^j c^h + a^j a^i a^h b^k + a^j a^i b^k b^h$$
$$+ a^j a^i b^k c^h + a^k a^j a^h b^i + a^k a^j b^i b^h + a^k a^j b^i c^h + a^i a^h b^k b^j$$
$$+ a^i b^k b^j b^h + a^i b^k b^j c^h + a^k a^h b^j b^i + a^k b^j b^i b^h + a^k b^j b^i c^h$$
$$+ a^j a^h b^k b^i + a^j b^k b^i b^h + a^j b^k b^i c^h + a^k a^j a^h c^i + a^k a^j b^h c^i$$
$$+ a^k a^j c^i c^h + a^k a^i a^h c^j + a^k a^i b^h c^j + a^k a^i c^j c^h + a^j a^i a^h c^k$$
$$+ a^j a^i b^h c^k + a^j a^i c^k c^h + a^i a^h c^k c^j + a^i b^h c^k c^j + a^i c^k c^j c^h$$
$$+ a^k a^h c^j c^i + a^k b^h c^j c^i + a^k c^j c^i c^h + a^j a^h c^k c^i + a^j b^h c^k c^i$$
$$+ a^j c^k c^i c^h + a^h b^k b^i c^j + b^k b^i b^h c^j + b^k b^i c^j c^h + a^h b^k b^j c^i$$
$$+ b^k b^j b^h c^i + b^k b^j c^i c^h + a^h b^j b^i c^k + b^j b^i b^h c^k + b^j b^i c^k c^h$$
$$+ a^h b^i c^k c^j + b^i b^h c^k c^j + b^i c^k c^j c^h + a^h b^k c^j c^i + b^k b^h c^j c^i$$
$$+ b^k c^j c^i c^h + a^h b^j c^k c^i + b^j b^h c^k c^i + b^j c^k c^i c^h + a^i a^h b^k c^j$$
$$+ a^i b^k b^h c^j + a^i b^k c^j c^h + a^i a^h b^j c^k + a^i b^j b^h c^k + a^i b^j c^k c^h$$
$$+ a^k a^h b^i c^j + a^k b^i b^h c^j + a^k b^i c^j c^h + a^j a^h b^i c^k + a^j b^i b^h c^k$$
$$+ a^j b^i c^k c^h + a^k a^h b^j c^i + a^k b^j b^h c^i + a^k b^j c^i c^h + a^j a^h b^k c^i$$
$$+ a^j b^k b^h c^i + a^j b^k c^i c^h$$

$$d^k d^j a^i b^h = a^k a^j a^i b^h + a^i b^k b^j b^h + a^i b^h c^k c^j + a^k a^i b^j b^h$$
$$+ a^k a^i c^j c^h + a^j a^i b^k b^h + a^i b^k b^h c^j + a^j a^i b^h b^k + a^i b^j b^h c^k$$

$$d^k a^j b^i c^h = - a^k a^j b^i c^h - a^j b^k b^j c^h - a^j b^i c^k c^h$$

$$d^k a^j b^i b^h = - a^k a^j b^i b^h - a^j b^k b^j b^h - a^j b^i b^h c^k$$

Table III.5.1

First and Second Derivatives of the NAI Using Translational Invariance

First Derivatives

Translational Invariance Relation:

$$< \mu_A \mid V_c^k \mid \nu_B > = - < \mu_A^k \mid V_c \mid \nu_B > - < \mu_A \mid V_c \mid \nu_B^k >$$

<u>Case 1: χ_μ on A and χ_ν on B</u>

$$V_{\mu\nu}^{a_k} = < \mu_A^k \mid \sum_{c \neq A} V_c \mid \nu_B > - < \mu_A \mid V_A \mid \nu_B^k >$$

$$V_{\mu\nu}^{b_k} = < \mu_A \mid \sum_{c \neq B} V_c \mid \nu_B^k > - < \mu_A^k \mid V_B \mid \nu_B >$$

$$V_{\mu\nu}^{c_k} = - < \mu_A^k \mid V_C \mid \nu_B > - < \mu_A \mid V_C \mid \nu_B^k >$$

<u>Case 2: χ_μ and χ_ν on A</u>

$$V_{\mu\nu}^{a_k} = < \mu_A^k \mid \sum_{c \neq A} V_c \mid \nu_B > + < \mu_A \mid \sum_{c \neq A} V_c \mid \nu_A^k >$$

$$V_{\mu\nu}^{c_k} = - < \mu_A^k \mid V_C \mid \nu_A > - < \mu_A \mid V_C \mid \nu_A^k >$$

Case 3: χ_μ on C and χ_ν on D

$$V_{\mu\nu}^{a_k} = - < \mu_C^k \mid V_A \mid \nu_D > - < \mu_C \mid V_A \mid \nu_D^k >$$

Second Derivatives

Translational Invariance Relations:

$$< \mu_A \mid V_C^{kj} \mid \nu_B > = < \mu_A^{kj} \mid V_C \mid \nu_B > + < \mu_A^k \mid V_C \mid \nu_B^j >$$

$$+ < \mu_A^j \mid V_C \mid \nu_B^k > + < \mu_A \mid V_C \mid \nu_B^{kj} >$$

$$< \mu_A^k \mid V_C^j \mid \nu_B > = - < \mu_A^{kj} \mid V_C \mid \nu_B > - < \mu_A^k \mid V_C \mid \nu_B^j >$$

$$< \mu_A \mid V_C^j \mid \nu_B^k > = - < \mu_A^j \mid V_C \mid \nu_B^k > - < \mu_A \mid V_C \mid \nu_B^{kj} >$$

Case 1:

$$V_{\mu\nu}^{a_k a_j} = < \mu_A^{kj} \mid \sum_{c \neq A} V_A \mid \nu_B > + < \mu_A \mid V_A \mid \nu_B^{kj} >$$

$$V_{\mu\nu}^{a_k b_j} = < \mu_A^k \mid \sum_{c \neq A,B} V_c \mid \nu_B^j > - < \mu_A^{kj} \mid V_B \mid \nu_B >$$

$$- < \mu_A \mid V_A \mid \nu_B^{kj} >$$

$$V_{\mu\nu}^{a_k c_j} = - < \mu_A^{kj} \mid V_C \mid \nu_B > - < \mu_A^k \mid V_C \mid \nu_B^j >$$

$$V_{\mu\nu}^{c_k c_j} = \langle \mu_A^{kj} \mid V_C \mid \nu_B \rangle + \langle \mu_A^{k} \mid V_C \mid \nu_B^{j} \rangle$$

$$+ \langle \mu_A^{j} \mid V_C \mid \nu_B^{k} \rangle + \langle \mu_A \mid V_C \mid \nu_B^{kj} \rangle$$

<u>Case 2:</u>

$$V_{\mu\nu}^{a_k a_j} = \langle \mu_A^{kj} \mid \sum_{c \neq A} V_c \mid \nu_A \rangle + \langle \mu_A \mid \sum_{c \neq A} V_c \mid \nu_A^{kj} \rangle$$

$$+ \langle \mu_A^{k} \mid \sum_{c \neq A} V_c \mid \nu_A^{j} \rangle + \langle \mu_A^{j} \mid \sum_{c \neq A} V_c \mid \nu_A^{k} \rangle$$

$$V_{\mu\nu}^{a_k c_j} = - \langle \mu_A^{kj} \mid V_C \mid \nu_A \rangle - \langle \mu_A^{k} \mid V_C \mid \nu_A^{j} \rangle$$

$$- \langle \mu_A^{j} \mid V_C \mid \nu_A^{k} \rangle - \langle \mu_A \mid V_C \mid \nu_A^{kj} \rangle$$

$$V_{\mu\nu}^{c_k c_j} = - V_{\mu\nu}^{a_k c_j}$$

<u>Case 3:</u>

$$V_{\mu\nu}^{a_k a_j} = \langle \mu_C^{kj} \mid V_A \mid \nu_D \rangle + \langle \mu_C^{k} \mid V_A \mid \nu_D^{j} \rangle$$

$$+ \langle \mu_C^{j} \mid V_A \mid \nu_D^{k} \rangle + \langle \mu_C \mid V_A \mid \nu_D^{kj} \rangle$$

$$V_{\mu\nu}^{a_k b_j} = 0$$

Table III.5.2

Third Derivatives of the NAI Using Translational Invariance

Translational Invariance Relations:

$$< \mu_A \mid V_C^{kji} \mid \nu_B > = - < \mu_A^{kji} \mid V_C \mid \nu_B > - < \mu_A^{kj} \mid V_C \mid \nu_B^i >$$

$$- < \mu_A^{ki} \mid V_C \mid \nu_B^j > - < \mu_A^k \mid V_C \mid \nu_B^{ji} >$$

$$- < \mu_A^{ji} \mid V_C \mid \nu_B^k > - < \mu_A^j \mid V_C \mid \nu_B^{ki} >$$

$$- < \mu_A^i \mid V_C \mid \nu_B^{kj} > - < \mu_A \mid V_C \mid \nu_B^{kji} >$$

$$< \mu_A^{kj} \mid V_C^i \mid \nu_B > = - < \mu_A^{kji} \mid V_C \mid \nu_B > - < \mu_A^{kj} \mid V_C \mid \nu_B^i >$$

$$< \mu_A^k \mid V_C^i \mid \nu_B^j > = - < \mu_A^{ik} \mid V_C \mid \nu_B^j > - < \mu_A^k \mid V_C \mid \nu_B^{ij} >$$

$$< \mu_A^j \mid V_C^i \mid \nu_B^k > = - < \mu_A^{ij} \mid V_C \mid \nu_B^k > - < \mu_A^j \mid V_C \mid \nu_B^{ik} >$$

$$< \mu_A \mid V_C^i \mid \nu_B^{kj} > = - < \mu_A \mid V_C \mid \nu_B^{kji} > - < \mu_A^i \mid V_C \mid \nu_B^{kj} >$$

<u>Case 1:</u>

$$V_{\mu\nu}^{a_k a_j a_i} = < \mu_A^{kji} \mid \sum_{c \neq A} V_c \mid \nu_B > - < \mu_A \mid V_A \mid \nu_B^{kji} >$$

$$V_{\mu\nu}^{a_k a_j b_i} = \langle \mu_A^{kj} \mid \sum_{c \neq A,B} V_c \mid \nu_B^{i} \rangle - \langle \mu_A^{kji} \mid V_B \mid \nu_B \rangle$$

$$+ \langle \mu_A \mid V_A \mid \nu_B^{kji} \rangle$$

$$V_{\mu\nu}^{a_k b_j b_i} = \langle \mu_A^{k} \mid \sum_{c \neq A,B} V_c \mid \nu_B^{ji} \rangle - \langle \mu_A \mid V_A \mid \nu_B^{kji} \rangle$$

$$+ \langle \mu_A^{kji} \mid V_B \mid \nu_B \rangle$$

$$V_{\mu\nu}^{a_k a_j c_i} = - \langle \mu_A^{kji} \mid V_C \mid \nu_B \rangle - \langle \mu_A^{kj} \mid V_C \mid \nu_B^{i} \rangle$$

$$V_{\mu\nu}^{a_k c_j c_i} = \langle \mu_A^{kji} \mid V_C \mid \nu_B \rangle + \langle \mu_A^{kj} \mid V_C \mid \nu_B^{i} \rangle$$

$$+ \langle \mu_A^{ki} \mid V_C \mid \nu_B^{j} \rangle + \langle \mu_A^{k} \mid V_C \mid \nu_B^{ji} \rangle$$

$$V_{\mu\nu}^{c_k c_j c_i} = - \langle \mu_A^{kji} \mid V_C \mid \nu_B \rangle - \langle \mu_A^{kj} \mid V_C \mid \nu_B^{i} \rangle$$

$$- \langle \mu_A^{ki} \mid V_C \mid \nu_B^{j} \rangle - \langle \mu_A^{k} \mid V_C \mid \nu_B^{ji} \rangle$$

$$- \langle \mu_A^{ji} \mid V_C \mid \nu_B^{k} \rangle - \langle \mu_A^{j} \mid V_C \mid \nu_B^{ki} \rangle$$

$$- \langle \mu_A^{i} \mid V_C \mid \nu_B^{kj} \rangle - \langle \mu_A \mid V_C \mid \nu_B^{kji} \rangle$$

$$V_{\mu\nu}^{a_k b_j c_i} = - \langle \mu_A^{ki} \mid V_C \mid \nu_B^{j} \rangle - \langle \mu_A^{k} \mid V_C \mid \nu_B^{ji} \rangle$$

Case 2:

$$V_{\mu\nu}^{a_k a_j a_i} = \langle \mu_A^{kji} \mid \sum_{c\neq A} V_c \mid \nu_A \rangle + \langle \mu_A \mid \sum_{c\neq A} V_c \mid \nu_A^{kji} \rangle$$

$$+ \langle \mu_A^{kj} \mid \sum_{c\neq A} V_c \mid \nu_A^{i} \rangle + \langle \mu_A^{i} \mid \sum_{c\neq A} V_c \mid \nu_A^{kj} \rangle$$

$$+ \langle \mu_A^{ki} \mid \sum_{c\neq A} V_c \mid \nu_A^{j} \rangle + \langle \mu_A^{k} \mid \sum_{c\neq A} V_c \mid \nu_A^{ji} \rangle$$

$$+ \langle \mu_A^{ji} \mid \sum_{c\neq A} V_c \mid \nu_A^{k} \rangle + \langle \mu_A^{j} \mid \sum_{c\neq A} V_c \mid \nu_A^{ki} \rangle$$

$$V_{\mu\nu}^{a_k a_j c_i} = - \langle \mu_A^{kji} \mid V_C \mid \nu_A \rangle - \langle \mu_A^{kj} \mid V_C \mid \nu_A^{i} \rangle$$

$$- \langle \mu_A^{ki} \mid V_C \mid \nu_A^{j} \rangle - \langle \mu_A^{k} \mid V_C \mid \nu_A^{ji} \rangle$$

$$- \langle \mu_A^{ji} \mid V_C \mid \nu_A^{k} \rangle - \langle \mu_A^{j} \mid V_C \mid \nu_A^{ki} \rangle$$

$$- \langle \mu_A^{i} \mid V_C \mid \nu_A^{kj} \rangle - \langle \mu_A \mid V_C \mid \nu_A^{kji} \rangle$$

$$V_{\mu\nu}^{a_k c_j c_i} = - V_{\mu\nu}^{a_k a_j c_i}$$

$$V_{\mu\nu}^{c_k c_j c_i} = V_{\mu\nu}^{a_k a_j c_i}$$

Case 3:

$$V_{\mu\nu}^{a_k a_j a_i} = - \langle \mu_C^{kji} \mid V_A \mid \nu_D \rangle - \langle \mu_C^{kj} \mid V_A \mid \nu_D^{i} \rangle$$

$$- \langle \mu_C^{ki} \mid V_A \mid \nu_D^{j} \rangle - \langle \mu_C^{k} \mid V_A \mid \nu_D^{ji} \rangle$$

$$- \langle \mu_C^{ji} \mid V_A \mid \nu_D^{k} \rangle - \langle \mu_C^{j} \mid V_A \mid \nu_D^{ki} \rangle$$

$$- \langle \mu_C^{i} \mid V_A \mid \nu_D^{kj} \rangle - \langle \mu_C \mid V_A \mid \nu_D^{kji} \rangle$$

$$V_{\mu\nu}^{a_k a_j b_i} = 0$$

$$V_{\mu\nu}^{a_k b_j b_i} = 0$$

Table III.5.3

Fourth Derivatives of the NAI Using Translational Invariance

Translational Invariance Relations:

$$< \mu_A \mid V_C^{kjih} \mid \nu_B > = < \mu_A^{kjih} \mid V_C \mid \nu_B > + < \mu_A^{kji} \mid V_C \mid \nu_B^h >$$

$$+ < \mu_A^{kjh} \mid V_C \mid \nu_B^i > + < \mu_A^{kj} \mid V_C \mid \nu_B^{hi} >$$

$$+ < \mu_A^{kih} \mid V_C \mid \nu_B^j > + < \mu_A^{ki} \mid V_C \mid \nu_B^{hj} >$$

$$+ < \mu_A^{kh} \mid V_C \mid \nu_B^{ji} > + < \mu_A^k \mid V_C \mid \nu_B^{jih} >$$

$$+ < \mu_A^{jih} \mid V_C \mid \nu_B^k > + < \mu_A^{ji} \mid V_C \mid \nu_B^{kh} >$$

$$+ < \mu_A^{jh} \mid V_C \mid \nu_B^{ki} > + < \mu_A^j \mid V_C \mid \nu_B^{kih} >$$

$$+ < \mu_A^{ih} \mid V_C \mid \nu_B^{kj} > + < \mu_A^i \mid V_C \mid \nu_B^{kjh} >$$

$$+ < \mu_A^h \mid V_C \mid \nu_B^{kji} > + < \mu_A \mid V_C \mid \nu_B^{kjih} >$$

$$< \mu_A^{kji} \mid V_C^h \mid \nu_B > = - < \mu_A^{kjih} \mid V_C \mid \nu_B > - < \mu_A^{kji} \mid V_C \mid \nu_B^h >$$

$$< \mu_A^{kj} \mid V_C^h \mid \nu_B^i > = - < \mu_A^{kjh} \mid V_C \mid \nu_B^i > - < \mu_A^{kj} \mid V_C \mid \nu_B^{hi} >$$

$$< \mu_A^{ki} \mid V_C^h \mid \nu_B^j > = - < \mu_A^{kih} \mid V_C \mid \nu_B^j > - < \mu_A^{ki} \mid V_C \mid \nu_B^{hj} >$$

$$< \mu_A^k \mid V_C^h \mid \nu_B^{ji} > = - < \mu_A^{kh} \mid V_C \mid \nu_B^{ji} > - < \mu_A^k \mid V_C \mid \nu_B^{jih} >$$

$$< \mu_A^{ji} \mid V_C^h \mid \nu_B^k > = - < \mu_A^{jih} \mid V_C \mid \nu_B^k > - < \mu_A^{ji} \mid V_C \mid \nu_B^{kh} >$$

$$< \mu_A^j \mid V_C^h \mid \nu_B^{ki} > = - < \mu_A^{jh} \mid V_C \mid \nu_B^{ki} > - < \mu_A^j \mid V_C \mid \nu_B^{kih} >$$

$$< \mu_A^i \mid V_C^h \mid \nu_B^{kj} > = - < \mu_A^{ih} \mid V_C \mid \nu_B^{kj} > - < \mu_A^i \mid V_C \mid \nu_B^{kjh} >$$

$$< \mu_A \mid V_C^h \mid \nu_B^{kji} > = - < \mu_A^h \mid V_C \mid \nu_B^{kji} > - < \mu_A \mid V_C \mid \nu_B^{kjih} >$$

<u>Case 1:</u>

$$V_{\mu\nu}^{a_k a_j a_i a_h} = < \mu_A^{kjih} \mid \sum_{c \neq A} V_c \mid \nu_B > + < \mu_A \mid V_A \mid \nu_B^{kjih} >$$

$$V_{\mu\nu}^{a_k a_j a_i b_h} = < \mu_A^{kji} \mid \sum_{c \neq A,B} V_c \mid \nu_B^h > - < \mu_A^{kjih} \mid V_B \mid \nu_B >$$

$$- < \mu_A \mid V_A \mid \nu_B^{kjih} >$$

$$V_{\mu\nu}^{a_k a_j b_i b_h} = < \mu_A^{kj} \mid \sum_{c \neq A,B} V_c \mid \nu_B^{ih} > + < \mu_A^{kjih} \mid V_B \mid \nu_B >$$

$$+ < \mu_A \mid V_A \mid \nu_B^{kjih} >$$

$$V_{\mu\nu}^{a_k b_j b_i b_h} = < \mu_A^k \mid \sum_{c \neq A,B} V_c \mid \nu_B^{jih} > - < \mu_A \mid V_A \mid \nu_B^{kjih} >$$

$$- < \mu_A^{kjih} \mid V_B \mid \nu_B >$$

$$V_{\mu\nu}^{a_k a_j a_i c_h} = - < \mu_A^{kjih} \mid V_C \mid \nu_B > - < \mu_A^{kji} \mid V_C \mid \nu_B^h >$$

$$V_{\mu\nu}^{a_k a_j c_i c_h} = < \mu_A^{kjih} \mid V_C \mid \nu_B > + < \mu_A^{kji} \mid V_C \mid \nu_B^h >$$

$$+ < \mu_A^{kjh} \mid V_C \mid \nu_B^i > + < \mu_A^{kj} \mid V_C \mid \nu_B^{hi} >$$

$$V_{\mu\nu}^{a_k c_j c_i c_h} = -< \mu_A^{kjih} \mid V_C \mid \nu_B > - < \mu_A^{kji} \mid V_C \mid \nu_B^h >$$

$$- < \mu_A^{kjh} \mid V_C \mid \nu_B^i > - < \mu_A^{kj} \mid V_C \mid \nu_B^{hi} >$$

$$- < \mu_A^{kih} \mid V_C \mid \nu_B^j > - < \mu_A^{ki} \mid V_C \mid \nu_B^{hj} >$$

$$- < \mu_A^{kh} \mid V_C \mid \nu_B^{ji} > - < \mu_A^k \mid V_C \mid \nu_B^{jih} >$$

$$V_{\mu\nu}^{c_k c_j c_i c_h} = < \mu_A^{kjih} \mid V_C \mid \nu_B > + < \mu_A^{kji} \mid V_C \mid \nu_B^h >$$

$$+ < \mu_A^{kjh} \mid V_C \mid \nu_B^i > + < \mu_A^{kj} \mid V_C \mid \nu_B^{hi} >$$

$$+ < \mu_A^{kih} \mid V_C \mid \nu_B^j > + < \mu_A^{ki} \mid V_C \mid \nu_B^{hj} >$$

$$+ < \mu_A^{kh} \mid V_C \mid \nu_B^{ji} > + < \mu_A^k \mid V_C \mid \nu_B^{jih} >$$

$$+ < \mu_A^{jih} \mid V_C \mid \nu_B^k > + < \mu_A^{ji} \mid V_C \mid \nu_B^{kh} >$$

$$+ < \mu_A^{jh} \mid V_C \mid \nu_B^{ki} > + < \mu_A^j \mid V_C \mid \nu_B^{kih} >$$

$$+ < \mu_A^{ih} \mid V_C \mid \nu_B^{kj} > + < \mu_A^{i} \mid V_C \mid \nu_B^{kjh} >$$

$$+ < \mu_A^{h} \mid V_C \mid \nu_B^{kji} > + < \mu_A \mid V_C \mid \nu_B^{kjih} >$$

$$V_{\mu\nu}^{a_k a_j b_i c_h} = - < \mu_A^{kjh} \mid V_C \mid \nu_B^{i} > - < \mu_A^{kj} \mid V_C \mid \nu_B^{ih} >$$

$$V_{\mu\nu}^{a_k b_j b_i c_h} = - < \mu_A^{kh} \mid V_C \mid \nu_B^{ji} > - < \mu_A^{k} \mid V_C \mid \nu_B^{jih} >$$

$$V_{\mu\nu}^{a_k b_j c_i c_h} = < \mu_A^{kih} \mid V_C \mid \nu_B^{j} > + < \mu_A^{ki} \mid V_C \mid \nu_B^{jh} >$$

$$+ < \mu_A^{kh} \mid V_C \mid \nu_B^{ji} > + < \mu_A^{k} \mid V_C \mid \nu_B^{jih} >$$

<u>Case 2:</u>

$$V_{\mu\nu}^{a_k a_j a_i a_h} = < \mu_A^{kjih} \mid \sum_{c \neq A} V_c \mid \nu_A > + < \mu_A^{kji} \mid \sum_{c \neq A} V_c \mid \nu_A^{h} >$$

$$+ < \mu_A^{h} \mid \sum_{c \neq A} V_c \mid \nu_A^{kji} > + < \mu_A \mid \sum_{c \neq A} V_c \mid \nu_A^{kjih} >$$

$$+ < \mu_A^{kjh} \mid \sum_{c \neq A} V_c \mid \nu_A^{i} > + < \mu_A^{kj} \mid \sum_{c \neq A} V_c \mid \nu_A^{ih} >$$

$$+ < \mu_A^{ih} \mid \sum_{c \neq A} V_c \mid \nu_A^{kj} > + < \mu_A^{i} \mid \sum_{c \neq A} V_c \mid \nu_A^{kjh} >$$

$$+ < \mu_A^{kih} \mid \sum_{c \neq A} V_c \mid \nu_A^{j} > + < \mu_A^{ki} \mid \sum_{c \neq A} V_c \mid \nu_A^{jh} >$$

$$+ < \mu_A^{kh} \mid \sum_{c \neq A} V_c \mid \nu_A^{ji} > + < \mu_A^{k} \mid \sum_{c \neq A} V_c \mid \nu_A^{jih} >$$

$$+ < \mu_A^{jih} \mid \sum_{c \neq A} V_c \mid \nu_A^{k} > + < \mu_A^{ji} \mid \sum_{c \neq A} V_c \mid \nu_A^{kh} >$$

$$+ \langle \mu_A^{jh} \mid \sum_{c \neq A} V_c \mid \nu_A^{ki} \rangle + \langle \mu_A^{j} \mid \sum_{c \neq A} V_c \mid \nu_A^{kih} \rangle$$

$$V_{\mu\nu}^{a_k a_j a_i c_h} = - \langle \mu_A^{kjih} \mid V_C \mid \nu_A \rangle - \langle \mu_A^{kji} \mid V_C \mid \nu_A^{h} \rangle$$

$$- \langle \mu_A^{kjh} \mid V_C \mid \nu_A^{i} \rangle - \langle \mu_A^{kj} \mid V_C \mid \nu_A^{hi} \rangle$$

$$- \langle \mu_A^{kih} \mid V_C \mid \nu_A^{j} \rangle - \langle \mu_A^{ki} \mid V_C \mid \nu_A^{hj} \rangle$$

$$- \langle \mu_A^{kh} \mid V_C \mid \nu_A^{ji} \rangle - \langle \mu_A^{k} \mid V_C \mid \nu_A^{jih} \rangle$$

$$- \langle \mu_A^{jih} \mid V_C \mid \nu_A^{k} \rangle - \langle \mu_A^{ji} \mid V_C \mid \nu_A^{kh} \rangle$$

$$- \langle \mu_A^{jh} \mid V_C \mid \nu_A^{ki} \rangle - \langle \mu_A^{j} \mid V_C \mid \nu_A^{kih} \rangle$$

$$- \langle \mu_A^{ih} \mid V_C \mid \nu_A^{kj} \rangle - \langle \mu_A^{i} \mid V_C \mid \nu_A^{kjh} \rangle$$

$$- \langle \mu_A^{h} \mid V_C \mid \nu_A^{kji} \rangle - \langle \mu_A \mid V_C \mid \nu_A^{kjih} \rangle$$

$$V_{\mu\nu}^{a_k a_j c_i c_h} = - V_{\mu\nu}^{a_k a_j a_i c_h}$$

$$V_{\mu\nu}^{a_k c_j c_i c_h} = V_{\mu\nu}^{a_k a_j a_i c_h}$$

$$V_{\mu\nu}^{c_k c_j c_i c_h} = - V_{\mu\nu}^{a_k a_j a_i c_h}$$

Case 3:

$$V_{\mu\nu}^{a_k a_j a_i a_h} = \langle \mu_C^{kjih} \mid V_A \mid \nu_D \rangle + \langle \mu_C^{kji} \mid V_A \mid \nu_D^{h} \rangle$$

$$+ \langle \mu_C^{kjh} \mid V_A \mid \nu_D^{i} \rangle + \langle \mu_C^{kj} \mid V_A \mid \nu_D^{hi} \rangle$$

$$+ \langle \mu_C^{kih} \mid V_A \mid \nu_D^{j} \rangle + \langle \mu_C^{ki} \mid V_A \mid \nu_D^{hj} \rangle$$

$$+ \langle \mu_C^{kh} \mid V_A \mid \nu_D^{ji} \rangle + \langle \mu_C^{k} \mid V_A \mid \nu_D^{jih} \rangle$$

$$+ \langle \mu_C^{jih} \mid V_A \mid \nu_D^{k} \rangle + \langle \mu_C^{ji} \mid V_A \mid \nu_D^{kh} \rangle$$

$$+ \langle \mu_C^{jh} \mid V_A \mid \nu_D^{ki} \rangle + \langle \mu_C^{j} \mid V_A \mid \nu_D^{kih} \rangle$$

$$+ \langle \mu_C^{ih} \mid V_A \mid \nu_D^{kj} \rangle + \langle \mu_C^{i} \mid V_A \mid \nu_D^{kjh} \rangle$$

$$+ \langle \mu_C^{h} \mid V_A \mid \nu_D^{kji} \rangle + \langle \mu_C \mid V_A \mid \nu_D^{kjih} \rangle$$

$$V_{\mu\nu}^{a_k a_j a_i b_h} = 0$$

$$V_{\mu\nu}^{a_k a_j b_i b_h} = 0$$

$$V_{\mu\nu}^{a_k b_j b_i b_h} = 0$$

IV DERIVATIVE ENERGY EQUATIONS

IV.1 INTRODUCTION

In the previous chapter the derivatives of atomic orbital integrals were presented without specific reference to the nature of the wave function for which the derivatives of the energy were being calculated. As such, the derivative integral algorithms are valid for any arbitrary wave function. In this chapter, however, the discussion of the derivative energy equations is limited to Hartree-Fock closed-shell wave functions.

This limitation is not severe, as the closed-shell molecule represents perhaps the largest class of polyatomic molecules for which detailed experimental anharmonic constants are available for comparison (e.g., H_2O, NH_3, HCN, H_2CO). The potential use of these derivative energy equations is not limited by restricting the discussion to a single determinant (non-correlated) wave function. The studies of Pulay et al. [17,51,52] that evaluate higher than second order force constants through finite differences of energy gradients show that cubic and quartic force constants do not change significantly in the transition from a Hartree-Fock wave function to a correlated wave function. This is in direct opposition to the results for quadratic force contsants which are found to change significatntly in going from the Hartree-Fock wave function to the correlated wave function [53]. The single determinant wave function therefore represents an important class of

wave functions for the analytic evaluation of cubic and quartic force constants.

In this chapter, the derivative energy equations with respect to nuclear perturbations for first, second, and third derivatives of the Hartree-Fock closed-shell electronic wave function will be derived. All formulae will be derived within the molecular orbital basis. It is important to recognize that this is not the first set of derivations of the energy derivatives. The contributions of the many researchers in the calculation of the first derivative have been collected and summarized by Pulay [41,54]. The second derivative, being a more recent development, is best reviewed through the original papers. These include the works of Gerratt and Mills [55], Thomsen and Swanstrøm [40,56], Pople, Krishnan, Schegel, and Binkley [42], Takata, Dupuis and King [50], and Saxe, Yamaguchi, and Schaefer [46]. Third derivative equations were first developed by Moccia in 1970 [57], and more recently by Pulay [16] and Simons and Jørgensen [58].

The first derivative energy equation derived in this chapter matches those previously published, while the second derivative differs in its form from previous derivations. The difference is that the second derivative presented here is symmetric in its permutation of the derivative degrees of freedom. As the third derivative formulae presented in this chapter are derived within the molecular orbital framework, they differ radically from the results of Moccia [57] and Pulay [16] whose equations are in the atomic orbital basis. It is believed that the present equations based in the molecular orbital basis are inherently computationally more tractable. Like the second derivative, the third derivative is presented in a highly symmetric form

where all terms have a permutation of derivative degrees of freedom.

All the derivative energy formulae presented in this chapter are derived for a non-orthogonal finite basis set. This is the type of basis set most commonly used in quantum chemistry. Recently, however, Jørgensen and Simons [59] have advocated the use of symmetry orthogonalized atomic orbitals. They have presented specific equations for the first and second derivatives of the energy with respect to nuclear perturbations for a variety of wave functions [59], and very general equations for third and fourth derivatives [58]. Within the symmetry orthogonalized atomic orbital formalism, all geometrical data is concentrated within the integrals and none is present in the molecular orbital coefficients. This is in contrast to the traditional approach where both the integrals and the molecular orbital coefficients display a geometrical dependence. Jørgensen and Simons can thus avoid the solution of the coupled-perturbed Hartree-Fock (CPHF) equations. It appears that this will reduce the total computational effort. A closer look reveals that although computational effort is reduced in one area (no CPHF), it is greatly expanded in another (the derivative integrals). This does not seem to be a distinct advantage.

All derivatives in this chapter are for nuclear perturbations within the Born-Oppenheimer approximation. Naturally this includes derivatives of the nuclear repulsion energy. Since these can be derived in a straightforward manner they are not presented here. All of the derivative energy equations have been coded and tested by finite differences of the energies and of energy derivatives. Unfortunately, the fourth derivative of the Hartree-Fock electronic energy has yet to be completely tested and hence is not included in this chapter. The

results of the calculation of the cubic force constants of the water molecule are presented in chapter V.

As will soon become apparent, the indices of the various matrices in the energy equations are very important and must be handled with extreme care. The convention employed thoughout this chapter is as follows: i, j, and k correspond to doubly occupied molecular orbitals; m, r, and s correspond to all molecular orbitals, both occupied and unoccupied (virtual); and q corresponds to virtual orbitals. Greek subscripts are used to label atomic orbitals, as was done in chapters II and III.

IV.2 FIRST DERIVATIVE

In the molecular orbital (MO) basis, the Hartree-Fock closed shell electronic energy is given by

$$E = 2 \sum_{i}^{do} h_{ii} + \sum_{i}^{do} \sum_{j}^{do} [\, 2(ii|jj) - (ij|ij) \,] \tag{IV.2.1}$$

where the summations are over all doubly occupied molecular orbitals. The MO integrals, h_{ii} and $(ii|jj)$ are the transformed one-electron and two-electron atomic orbital integrals of chapter II. For the one-electron atomic orbital integrals the transformation is a two index transformation given by

$$h_{ii} = \sum_{\mu}^{all} \sum_{\nu}^{all} C_{\mu}^{i} C_{\nu}^{i} h_{\mu\nu} \tag{IV.2.2}$$

The two-electron transformation is similar, however, the transformation

is over four indices, not two. In the discussion that follows of the derivative energy equations, it is often more convenient to work in terms of the Fock matrix. The Fock matrix follows from the Fock operator defined by Roothaan [18]:

$$\varepsilon_{im} = h_{im} + \sum_{j}^{do} [\ 2(im|jj) - (ij|mj)\ ] \tag{IV.2.3}$$

Once a self-consistent set of molecular orbitals are achieved, then the Fock matrix is diagonal. The elements of the Fock matrix are the lagrangian multipliers which are the molecular orbital energies. The total electronic energy in terms of the lagrangian multipliers is

$$E = \sum_{i}^{do} (\ h_{ii} + \varepsilon_{ii}\ ) \tag{IV.2.4}$$

The first derivative of equation IV.2.1 with respect to a nuclear coordinate a (note that this convention differs slightly from that used in chapter III in that the cartesian coordinate k is assumed to be incorporated into the nuclear coordinate a) is given by

$$\frac{\partial}{\partial a} E = 2 \sum_{i}^{do} \frac{\partial}{\partial a} h_{ii} + \sum_{i}^{do} \sum_{j}^{do} \frac{\partial}{\partial a} [\ 2(ii|jj) - (ij|ij)\ ] \tag{IV.2.5}$$

The one-electron derivative is given by

$$\frac{\partial}{\partial a} h_{ii} = \sum_{\mu}^{all} \sum_{\nu}^{all} \{ (\frac{\partial}{\partial a} C_{\mu}^{i}) C_{\nu}^{i} h_{\mu\nu} + C_{\mu}^{i} (\frac{\partial}{\partial a} C_{\nu}^{i}) h_{\mu\nu}$$

$$+ C_{\mu}^{i} C_{\nu}^{i} (\frac{\partial}{\partial a} h_{\mu\nu}) \} \tag{IV.2.6}$$

The first and second terms of IV.2.6 contain the first order change of the molecular orbital coefficients, while the third term is a transformation of a derivative atomic orbital integral.

The first order change of the molecular orbital coefficients has been given by Gerratt and Mills [55] as

$$\frac{\partial}{\partial a} C_{\mu}^{i} = \sum_{m}^{all} U_{mi}^{a} C_{\mu}^{m} \qquad \text{(IV.2.7)}$$

Using this notation, the one-electron derivative is rewritten as

$$\frac{\partial}{\partial a} h_{ii} = \sum_{\mu}^{all} \sum_{\nu}^{all} \Big(\sum_{m}^{all} U_{mi}^{a} C_{\mu}^{m} C_{\nu}^{i} h_{\mu\nu} + \sum_{m}^{all} C_{\mu}^{i} U_{mi}^{a} C_{\nu}^{m} h_{\mu\nu}$$

$$+ C_{\mu}^{i} C_{\nu}^{i} h_{\mu\nu}^{a} \Big)$$

$$= \sum_{m}^{all} U_{mi}^{a} h_{mi} + \sum_{m}^{all} U_{mi}^{a} h_{im} + h_{ii}^{a} \qquad \text{(IV.2.8)}$$

Since the one-electron integrals, h_{im} and h_{mi}, are symmetric, equation IV.2.8 reduces to

$$\frac{\partial}{\partial a} h_{ii} = 2 \sum_{m}^{all} U_{mi}^{a} h_{im} + h_{ii}^{a} \qquad \text{(IV.2.9)}$$

Applying the same steps that were used to obtain the derivative of the one-electron integrals, the derivative of the two-electron integrals is given by

$$\frac{\partial}{\partial a} [\ 2(ii|jj) - (ij|ij)\ ] = 4 \sum_{m}^{all} \Big(U_{mi}^{a} (mi|jj) + U_{mj}^{a} (ii|mj) \Big)$$

$$- 2 \sum_{m}^{all} (U^{a}_{mi} (mj|ij) + U^{a}_{mj} (im|ij)) + 2(ii|jj)^{a} - (ij|ij)^{a}$$

$$= 2(ii|jj)^{a} - (ij|ij)^{a} + 2 \sum_{m}^{all} U^{a}_{mi} [2(mi|jj) - (mj|ij)]$$

$$+ 2 \sum_{m}^{all} U^{a}_{mj} [2(ii|mj) - (im|ij)] \qquad \text{(IV.2.10)}$$

Since i and j run over the same set of orbitals (doubly occupied), the terms involving the U^{a} can be combined giving

$$\frac{\partial}{\partial a} [2(ii|jj) - (ij|ij)] = 2(ii|jj)^{a} - (ij|ij)^{a}$$

$$+ 4 \sum_{m}^{all} U^{a}_{mi} [2(mi|jj) - (mj|ij)] \qquad \text{(IV.2.11)}$$

The total first derivative of the electronic energy is the sum of equations IV.2.9 and IV.2.11.

$$\frac{\partial}{\partial a} E = 2 \sum_{i}^{do} h^{a}_{ii} + \sum_{i}^{do} \sum_{j}^{do} \{ 2(ii|jj)^{a} - (ij|ij)^{a} \}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} U^{a}_{mi} \{ h^{a}_{im} + \sum_{j}^{do} 2(mi|jj) - (mj|ij) \}$$

(IV.2.12)

Using the Fock matrix formalism of equation IV.2.3, the total first derivative is further reduced to

$$\frac{\partial}{\partial a} E = 2 \sum_{i}^{do} h^{a}_{ii} + \sum_{i}^{do} \sum_{j}^{do} 2(ii|jj)^{a} - (ij|ij)^{a} \qquad \text{(a)}$$

$$+ \quad 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{a} \, \varepsilon_{im} \qquad \text{(b)}$$

(IV.2.13)

As the Fock matrix is diagonal for a converged wave function (the condition of self-consistency), the first derivative is rewritten as

$$\frac{\partial}{\partial a} E = E^{a'} + 4 \sum_{i}^{do} U_{ii}^{a} \, \varepsilon_{ii} \qquad \text{(IV.2.14)}$$

where $E^{a'}$ is the derivative atomic orbital contribution to the gradient, given by line (a) of IV.2.13.

To obtain U_{ii}^{a}, the orthonormality condition

$$\sum_{\mu}^{all} \sum_{\nu}^{all} C_{\mu}^{r} \, S_{\mu\nu} \, C_{\nu}^{s} = \delta_{rs} \qquad \text{(IV.2.15)}$$

is directly differentiated for r equal to s equal to i. The result, upon performing the transformation to molecular orbitals, is

$$\sum_{m}^{all} U_{mi}^{a} \, S_{mi} + S_{ii}^{a} + \sum_{m}^{all} U_{mi}^{a} \, S_{im} = 0$$

(IV.2.16)

This can be reduced by using two properties of the overlap matrix. First, the overlap matrix is symmetric, and as a result IV.2.16 rearranges to give

$$S_{ii}^{a} = - 2 \sum_{m}^{all} U_{mi}^{a} \, S_{mi} \qquad \text{(IV.2.17)}$$

Second, the overlap matrix is a unit matrix and thus the sum on the right of IV.2.17 reduces to a single term leaving

$$S^a_{ii} = -2\, U^a_{ii} \qquad \text{(IV.2.18)}$$

Substituting this into the gradient of the electronic energy yields

$$\frac{\partial}{\partial a} E = E^{a'} - 2 \sum_i^{do} S^a_{ii}\, \epsilon_{ii} \qquad \text{(IV.2.19)}$$

This result is in accordance to Wigner's theorem of perturbations, namely, that the wave function of nth order is sufficient to produce properties of the 2n+1 order [60].

IV.4.2.1 COMPUTATIONAL REMARKS

Since the first derivative of the electronic energy has no explicit CPHF response, it can be calculated within the derivative atomic orbital integral programs described in chapter III. The one-electron term of $E^{a'}$ can be calculated by performing the two index transformation of the derivative atomic orbital integrals given by equation IV.2.2 and then summing down the diagonal. It can also be found by multiplying by a density matrix factor and summing over all atomic orbitals. The density factor is defined by

$$D_{\mu\nu} = \sum_i^{do} C^i_\mu\, C^i_\nu \qquad \text{(IV.2.20)}$$

so that

$$2 \sum_i^{do} h_{ii} = 2 \sum_\mu^{all} \sum_\nu^{all} D_{\mu\nu}\, h_{\mu\nu} \qquad \text{(IV.2.21)}$$

We use the density matrix factor method.

As the two-electron integrals are calculated in blocks, the density factor for the two-electron contribution to $E^{a'}$ is also calculated in blocks. If all the values of the block of density factors fall below a given threshold, then the entire block of derivative integrals need not be calculated. As only the unique two-electron integrals and their derivatives are evaluated ($(\mu\nu|\rho\sigma) = (\rho\sigma|\mu\nu) = (\nu\mu|\rho\sigma)$ etc.), the density factor takes on the following form:

$$D_{\mu\nu\rho\sigma} = \left(16\, D_{\mu\nu}\, D_{\rho\sigma} - 4\, D_{\mu\rho}\, D_{\nu\sigma} - 4\, D_{\mu\sigma}\, D_{\nu\rho} \right) f_{\mu\nu}\, f_{\rho\sigma}\, f_{\mu\rho,\nu\sigma} \tag{IV.2.22}$$

where

$$f_{\mu\nu} = 1/2 \text{ if } \mu = \nu$$
$$= 1 \text{ otherwise}$$

$$f_{\rho\sigma} = 1/2 \text{ if } \rho = \sigma$$
$$= 1 \text{ otherwise}$$

$$f_{\mu\rho,\nu\sigma} = 1/2 \text{ if } \mu = \rho \text{ and } \nu = \sigma$$
$$= 1 \text{ otherwise}$$

The MO derivative overlap matrix multiplied by the lagrangian multiplier can be calculated in the atomic orbital basis by using the atomic orbital lagrangian given by

$$\omega_{\mu\nu} = \sum_{i}^{do} C_{\mu}^{i}\; C_{\nu}^{i}\; \varepsilon_{ii} \tag{IV.2.23}$$

Thus the term is given by

$$\sum_{i}^{do} S_{ii}^{a} \, \epsilon_{ii} = \sum_{\mu}^{all} \sum_{\nu}^{all} S_{\mu\nu} \, \omega_{\mu\nu} \qquad \text{(IV.2.24)}$$

The computational procedure is outlined below:

(1) Evaluate the Hartree-Fock equations and obtain a well-converged SCF wave function.

(2) Calculate the one-electron derivative contributions to $E^{a'}$ and evaluate the overlap contribution using equation IV.2.24.

(3) Calculate the density factor for two-electron integrals. If all the density factors are below a given threshold, then the entire block of integrals is ignored. Evaluate the block of derivative integrals and calculate its contribution to $E^{a'}$ by multiplying the derivative integrals by the appropriate $D_{\mu\nu\rho\sigma}$.

(4) Sum the contributions to $E^{a'}$ together and add the overlap contribution.

IV.3 SECOND DERIVATIVE

The second derivative of the electronic energy for the Hartree-Fock closed-shell wave function is obtained by taking the second derivative of equation IV.2.13 with respect to a nuclear coordinate b.

$$\frac{\partial^2}{\partial a \partial b} E = 2 \sum_{i}^{do} \frac{\partial}{\partial b} h_{ii}^{a} + \sum_{i}^{do} \sum_{j}^{do} \frac{\partial}{\partial b} \left(2(ii|jj)^{a} - (ij|ij)^{a} \right)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \left\{ \left(\frac{\partial}{\partial b} U_{mi}^{a} \right) \epsilon_{im} + U_{mi}^{a} \left(\frac{\partial}{\partial b} \epsilon_{im} \right) \right\} \qquad \text{(IV.3.1)}$$

The first two terms are reduced by the same steps that obtained equations IV.2.9 and IV.2.11, resulting in

$$\frac{\partial^2}{\partial a \partial b} E = 2 \sum_{i}^{do} h_{ii}^{ab} + \sum_{i}^{do} \sum_{j}^{do} \left(2(ii|jj)^{ab} - (ij|ij)^{ab} \right)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{b} \, \varepsilon_{im}^{a}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \left\{ \left(\frac{\partial}{\partial b} U_{mi}^{a} \right) \varepsilon_{im} + U_{mi}^{a} \left(\frac{\partial}{\partial b} \varepsilon_{im} \right) \right\} \tag{IV.3.2}$$

where ε_{im}^{a} is the derivative Fock matrix given by

$$\varepsilon_{im}^{a} = h_{im}^{a} + \sum_{j}^{do} \left(2(im|jj)^{a} - (ij|mj)^{a} \right) \tag{IV.3.3}$$

This matrix is not diagonal, in contrast to the Fock matrix given by equation IV.2.3.

The first of the final two terms of IV.3.2 is evaluated by noting that it is still restricted by the lagrangian multiplier ε_{im}. Knowing that ε_{im} is diagonal

$$\left(\frac{\partial}{\partial b} U_{mi}^{a} \right) \varepsilon_{im} = \left(-1/2 \frac{\partial}{\partial b} S_{ii}^{a} \right) \varepsilon_{ii}$$

$$= - \sum_{m}^{all} \left\{ U_{mi}^{b} S_{mi}^{a} - 1/2 \, S_{ii}^{ab} \right\} \varepsilon_{ii} \tag{IV.3.4}$$

The final term of equation IV.3.2 is the derivative of the Fock matrix, which is not equivalent to equation IV.3.3. It is obtained by direct differentiation of the Fock matrix

$$\frac{\partial}{\partial b}\,\varepsilon_{im} = \varepsilon_{im}^{(b)} = h_{im}^{b} + \sum_{j}^{do}\{\,2(im|jj)^{b} - (ij|mj)^{b}\,\}$$

$$+ \sum_{r}^{all} U_{ri}^{b}\,h_{rm} + \sum_{r}^{all} U_{rm}^{b}\,h_{ir} + \sum_{j}^{do}\sum_{r}^{all}\{\,U_{ri}^{b}\,[\,2(rm|jj) - (rj|mj)\,]$$

$$+ U_{rm}^{b}\,[\,2(ir|jj) - (ij|rj)\,]$$

$$+ U_{rj}^{b}\,[\,4(im|rj) - (ir|mj) - (ij|mr)\,]\,\}$$

$$= \varepsilon_{im}^{b} + \sum_{r}^{all} U_{ri}^{b}\,\varepsilon_{rm} + \sum_{r}^{all} U_{rm}^{b}\,\varepsilon_{ir}$$

$$+ \sum_{j}^{do}\sum_{r}^{all} U_{rj}^{b}\,[\,4(im|rj) - (ir|mj) - (ij|mr)\,] \qquad \text{(IV.3.5)}$$

The lagrangian multipliers, ε_{ir} and ε_{rm} are diagonal, and the sums over them reduce to a single term each. By defining

$$A_{im,rj} = 4(im|rj) - (ir|mj) - (ij|mr) \qquad \text{(IV.3.6)}$$

the derivative of the Fock matrix is finally reduced to

$$\varepsilon_{im}^{(b)} = \varepsilon_{im}^{b} + U_{mi}^{b}\,\varepsilon_{mm} + U_{im}^{b}\,\varepsilon_{ii} + \sum_{j}^{do}\sum_{r}^{all} U_{rj}^{a}\,A_{im,rj} \qquad \text{(IV.3.7)}$$

The derivative of the Fock matrix, $\varepsilon_{im}^{(b)}$, like the Fock matrix itself, is diagonal.

Substituting IV.3.4 and IV.3.7 into equation IV.3.2, the second derivative becomes

$$\frac{\partial^2}{\partial a \partial b} E = E^{ab'} + 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{b} \, \varepsilon_{im}^{a}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{b} \, S_{mi}^{a} \, \varepsilon_{ii} - 2 \sum_{i}^{do} S_{ii}^{ab} \, \varepsilon_{ii}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{a} \, \varepsilon_{im}^{b} + 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{a} \, U_{mi}^{b} \, \varepsilon_{mm}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{a} \, U_{im}^{b} \, \varepsilon_{ii}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} U_{mi}^{a} \, U_{rj}^{b} \, A_{im,rj} \qquad \text{(IV.3.8)}$$

where $E^{ab'}$ is the second derivative atomic orbital contribution, the first line of equation IV.3.2. Collecting like terms yields

$$\frac{\partial^2}{\partial a \partial b} E = E^{ab'} + 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} \, \varepsilon_{im}^{b} + U_{mi}^{b} \, \varepsilon_{im}^{a} \} \qquad \text{(a)}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{b} \, S_{mi}^{a} \, \varepsilon_{ii} - 2 \sum_{i}^{do} S_{ii}^{ab} \, \varepsilon_{ii} \qquad \text{(b)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} \, U_{mi}^{b} \, \varepsilon_{mm} + U_{mi}^{a} \, U_{im}^{b} \, \varepsilon_{ii} \} \qquad \text{(c)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} U_{mi}^{a} \, U_{rj}^{b} \, A_{im,rj} \qquad \text{(d)}$$

(IV.3.9)

The first order change in the molecular orbital coefficients, the U_{mi}^{a} and the U_{mi}^{b} in the above equation, are obtained through the coupled-perturbed Hartree-Fock (CPHF) equations of Gerratt and Mills [55]. This is done by finding solutions to the Fock equations at a perturbed geometry in terms of the solutions of the Fock equations at the

unperturbed geometry, i.e., the Fock equations are expanded in a taylor series. Pople and co-workers [42] have given an iterative solution to the CPHF equations which has been generally recognized [61] as the cornerstone of analytic derivative evaluation. Techniques in CPHF theory have been extended by the work of Osamura and co-workers: large molecular systems through the introduction of the atomic orbital-based CPHF [62]; and for general open/closed shell systems through a unified formalism [63].

The CPHF equation for closed-shell molecules [42] is

$$U^a_{rs} (\varepsilon_{ss} - \varepsilon_{rr}) - \sum_q^{vir} \sum_i^{do} U^a_{qi} A_{rs,qi} = B^a_{0,rs} \tag{IV.3.10}$$

where

$$B^a_{0,rs} = \varepsilon^a_{rs} - S^a_{rs} \varepsilon_{ss} - \sum_i^{do} \sum_j^{do} S^a_{ij} [2(rs|ij) - (ri|sj)] \tag{IV.3.11}$$

Expanding the orthonormality condition, equation IV.2.15, in a taylor series and collecting terms of first order in the expansion parameter yields

$$U^a_{mr} + U^a_{rm} + S^a_{mr} = 0 \tag{IV.3.12}$$

The importance of this term cannot be understated; it allows the reduction of both the second and third derivative expressions to simple symmetric forms.

Note that the second component of the term (c) of equation IV.3.9 can be rearranged using equation IV.3.12.

$$\sum_{i}^{do} \sum_{m}^{all} U_{mi}^{a} U_{im}^{b} \varepsilon_{ii} = \sum_{i}^{do} \sum_{m}^{all} \{ -U_{im}^{a} - S_{mi}^{a} \} U_{im}^{b} \varepsilon_{ii} \tag{IV.3.13}$$

When this is substituted back into equation IV.3.9, and similar terms combined, the second derivative is given by

$$\begin{aligned}
\frac{\partial^2}{\partial a \partial b} E = E^{ab'} &+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} \varepsilon_{im}^{b} + U_{mi}^{b} \varepsilon_{im}^{a} \} \\
&- 4 \sum_{i}^{do} \sum_{m}^{all} S_{mi}^{a} \{ U_{mi}^{b} + U_{im}^{b} \} \varepsilon_{ii} \\
- 2 \sum_{i}^{do} S_{ii}^{ab} \varepsilon_{ii} &+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} U_{mi}^{a} U_{rj}^{b} A_{im,rj} \\
&+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} U_{mi}^{b} \varepsilon_{mm} - U_{im}^{a} U_{im}^{b} \varepsilon_{ii} \}
\end{aligned} \tag{IV.3.14}$$

Using equation IV.3.12, the above reduces to the final form for the second derivative.

$$\begin{aligned}
\frac{\partial^2}{\partial a \partial b} E = E^{ab'} &+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} \varepsilon_{im}^{b} + U_{mi}^{b} \varepsilon_{im}^{a} \} && \text{(a)} \\
&- 2 \sum_{i}^{do} S_{ii}^{ab} \varepsilon_{ii} && \text{(b)} \\
&+ 4 \sum_{i}^{do} \sum_{m}^{all} S_{mi}^{a} S_{mi}^{b} \varepsilon_{ii} && \text{(c)} \\
&+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} U_{mi}^{a} U_{rj}^{b} A_{im,rj} && \text{(d)} \\
&+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} U_{mi}^{b} \varepsilon_{mm} - U_{im}^{a} U_{im}^{b} \varepsilon_{ii} \} && \text{(e)}
\end{aligned} \tag{IV.3.15}$$

IV.3.2 COMPUTATIONAL REMARKS

Unlike the first derivative, the second derivative to the electronic energy contains a CPHF response and can only be calculated by solving the CPHF equations of IV.3.10 and IV.3.11. Techiques for the solution of the CPHF equations include the iterative method of Pople et al. [42], the general open/closed shell formalism of Osamura et al. [62], and the atomic orbital-based solution of Osamura et al. [63].

The $E^{ab'}$ of equation IV.3.15 is calculated in the same manner as the $E^{a'}$ for first derivatives, except second derivative atomic orbital integrals are evaluated. Term (b) of IV.3.15 can also be calculated in the atomic orbital basis using the atomic orbital lagrangian of IV.2.23. In doing so (N3N) (N3N+1) /2 transformations of the second derivative atomic orbital overlap integrals to the MO basis are avoided where N is the number of atoms. Term (c) is not usually calculated in the atomic orbital basis as the first derivative overlap matrices are needed in the MO basis for the CPHF solution (equation IV.3.11).

The derivative Fock matrix, ε^a_{im}, can be partially formed in the atomic orbital basis within the derivative integral program. The contribution of each two-electron integral to the derivative Fock matrix can be empirically established and multiplied by a density factor to produce a half-transformed two-electron derivative Fock matrix.

$$T^a_{\mu\nu} = \sum_{\rho}^{\text{all}} \sum_{\sigma}^{\text{all}} \sum_{j}^{\text{do}} C^j_\rho C^j_\sigma \{ 2(\mu\nu|\rho\sigma)^a - (\mu\rho|\nu\sigma)^a \}$$

$$= \sum_{\rho}^{\text{all}} \sum_{\sigma}^{\text{all}} D_{\rho\sigma} \{ 2(\mu\nu|\rho\sigma)^a - (\mu\rho|\nu\sigma)^a \}$$

$$= \{ 2(\mu\nu|jj)^a - (\mu j|\nu j)^a \} \qquad \text{(IV.3.16)}$$

The $T^a_{\mu\nu}$ for each degree of freedom can then be transformed to the two-electron contribution for each derivative Fock matrix by a simple two index transformation. This avoids the necessity of a four index transformation that would occur N3N times; once for each unique degree of freedom. Instead, N3N two-index transformations must occur.

By using these techniques, the four index transformation of the first derivative two-electron integrals as well as the four index transformation of the second derivative two-electron integrals, and the two index transformation of the second derivative overlap matrix are completely avoided. The techniques will also cut down on the necessary storage space as the first derivative and second derivative two-electron integrals need never be stored.

The computational steps for the simultaneous calculation of first and second derivatives of the energy with respect to nuclear perturbations are as follows:

(1) Calculate a set of well-converged molecular orbital coefficients by solving the Hartree-Fock equations.

(2) Calculate the one-electron derivative contributions to $E^{a'}$ and $E^{ab'}$ and solve term (b) of IV.3.15 using the atomic orbital lagrangian. $S^a_{\mu\nu}$, and $h^a_{\mu\nu}$ must be stored externally.

(3) Calculate the density factor for the two-electron integrals. If all members of $D_{\mu\nu\rho\sigma}$ for the block of integrals fall below the

threshold, no derivative integrals are calculated. Otherwise both first and second derivative integrals are evaluated forming $E^{a'}$ and $E^{ab'}$. The half-transformed two-electron contribution to the derivative Fock matrix, $T^a_{\mu\nu}$ (equation IV.3.16) is also formed. $T^a_{\mu\nu}$ is stored externally as are $E^{a'}$, and $E^{ab'}$.

(4) The zeroth order integrals used in step (1) are transformed.

(5) $S^a_{\mu\nu}$, $h^a_{\mu\nu}$, and $T^a_{\mu\nu}$ are transformed and ϵ^a_{im} is formed.

(6) CPHF equations are solved (equations IV.3.10 and IV.3.11). U^a is stored externally.

(7) The remaining parts of equation IV.3.15 are evaluated.

IV.4 THIRD DERIVATIVES

Like the first and second derivatives, the third derivative is obtained by directly differentiating the closed-shell Hartree-Fock energy expression. Beginning with equation IV.3.15 and differentiating with respect to a nuclear coordinate c, the following expression is obtained:

$$\frac{\partial^3}{\partial a \partial b \partial c} E = 2 \sum_i^{do} \frac{\partial}{\partial c} h_{ii}^{ab} + \sum_i^{do} \sum_j^{do} \frac{\partial}{\partial c} \left(2(ii|jj)^{ab} - (ij|ij)^{ab} \right) \tag{a}$$

$$+ 4 \sum_i^{do} \sum_m^{all} \left\{ \left(\frac{\partial}{\partial c} U_{mi}^a \right) \varepsilon_{im}^b + U_{mi}^a \left(\frac{\partial}{\partial c} \varepsilon_{im}^b \right) + \left(\frac{\partial}{\partial c} U_{mi}^b \right) \varepsilon_{im}^a + U_{mi}^b \left(\frac{\partial}{\partial c} \varepsilon_{im}^a \right) \right\} \tag{b}$$

$$+ 4 \sum_i^{do} \sum_m^{all} \left\{ \left(\frac{\partial}{\partial c} S_{mi}^a \right) S_{mi}^b \varepsilon_{ii} + S_{mi}^a \left(\frac{\partial}{\partial c} S_{mi}^b \right) \varepsilon_{ii} + S_{mi}^a S_{mi}^b \left(\frac{\partial}{\partial c} \varepsilon_{ii} \right) \right\} \tag{c}$$

$$- 2 \sum_i^{do} \left\{ \left(\frac{\partial}{\partial c} S_{ii}^{ab} \right) \varepsilon_{ii} + S_{ii}^{ab} \left(\frac{\partial}{\partial c} \varepsilon_{ii} \right) \right\} \tag{d}$$

$$+ 4 \sum_i^{do} \sum_m^{all} \left\{ \left(\frac{\partial}{\partial c} U_{mi}^a \right) U_{mi}^b \varepsilon_{mm} + U_{mi}^a \left(\frac{\partial}{\partial c} U_{mi}^b \right) \varepsilon_{mm} + U_{mi}^a U_{mi}^b \left(\frac{\partial}{\partial c} \varepsilon_{mm} \right) \right.$$

$$\left. - \left(\frac{\partial}{\partial c} U_{im}^a \right) U_{im}^b \varepsilon_{ii} - U_{im}^a \left(\frac{\partial}{\partial c} U_{im}^b \right) \varepsilon_{ii} - U_{im}^a U_{im}^b \left(\frac{\partial}{\partial c} \varepsilon_{ii} \right) \right\} \tag{e}$$

$$+ 4 \sum_i^{do} \sum_m^{all} \sum_r^{all} \sum_j^{do} \left\{ \left(\frac{\partial}{\partial c} U_{mi}^a \right) U_{rj}^b A_{im,rj} + U_{mi}^a \left(\frac{\partial}{\partial c} U_{rj}^b \right) A_{im,rj} \right.$$

$$\left. + U_{mi}^a U_{rj}^b \left(\frac{\partial}{\partial c} A_{im,rj} \right) \right\} \tag{f}$$

(IV.4.1)

To obtain the simplest solution to the third derivative in the above equation, each group of terms (a) through (f), will be examined

and reduced to as simple a form as possible.

Beginning with term (a) which contains the derivatives of the second derivative MO integrals, note that it is analogous to the first terms found in the gradient and second derivative derivations. Its solution will involve third derivatives of the MO integrals, plus a first order change in the MO coefficients with respect to a nuclear perturbation c multiplied by the second derivative Fock matrix.

$$\text{IV.4.1 (a)} = 2 \sum_{i}^{do} h_{ii}^{abc} + \sum_{i}^{do} \sum_{j}^{do} [\, 2(ii|jj)^{abc} - (ij|ij)^{abc} \,]$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{c} \, \varepsilon_{im}^{ab}$$

$$= E^{abc'} + 4 \sum_{i}^{do} \sum_{m}^{all} U_{mi}^{c} \, \varepsilon_{im}^{ab} \qquad \text{(IV.4.2)}$$

The sums of the third derivative MO integrals are represented by $E^{abc'}$.

The next term in the equation IV.4.1, (b), contains both derivatives of U^a and U^b as well as derivatives of the derivative Fock matrix. To evaluate the derivative of U^a and U^b, we begin with the second derivatives of the MO coefficients. Using the first derivative given by equation IV.2.7

$$\frac{\partial^2}{\partial a \partial c} C_{\mu}^{i} = \frac{\partial}{\partial c} \left\{ \sum_{m}^{all} U_{mi}^{a} \, C_{\mu}^{m} \right\}$$

$$= \sum_{m}^{all} \left(\frac{\partial}{\partial c} U_{mi}^{a} \right) C_{\mu}^{m} + \sum_{m}^{all} \sum_{r}^{all} U_{mi}^{a} \, U_{rm}^{c} \, C_{\mu}^{r} \qquad \text{(IV.4.3)}$$

By analogy to the work of Gerratt and Mills [55], Osamura and Yamaguchi [64] defined

$$\frac{\partial^2}{\partial a \partial c} C_\mu^i = \sum_m^{all} U_{mi}^{ac} C_\mu^m \qquad \text{(IV.4.4)}$$

Substituting IV.4.4 into equation IV.4.3 yields

$$\sum_m^{all} U_{mi}^{ac} C_\mu^m = \sum_m^{all} \left(\frac{\partial}{\partial c} U_{mi}^a \right) C_\mu^m + \sum_m^{all} \sum_r^{all} U_{mi}^a U_{rm}^c C_\mu^r \qquad \text{(IV.4.5)}$$

In the last term both m and r run over all orbitals, and as a result the labels may be interchanged, yielding

$$\sum_m^{all} U_{mi}^{ac} C_\mu^m = \sum_m^{all} \left(\frac{\partial}{\partial c} U_{mi}^a \right) C_\mu^m + \sum_r^{all} \sum_m^{all} U_{ri}^a U_{mr}^c C_\mu^m \qquad \text{(IV.4.6)}$$

It is clear that for a specific value of m and i, the above yields

$$\frac{\partial}{\partial c} U_{mi}^a = U_{mi}^{ac} - \sum_r^{all} U_{ri}^a U_{mr}^c \qquad \text{(IV.4.7)}$$

The derivative of the derivative Fock matrix is given by a analogy to equation IV.3.7 as

$$\frac{\partial}{\partial c} \varepsilon_{im}^a = \varepsilon_{im}^{ac} + \sum_r^{all} U_{ri}^c \varepsilon_{rm}^a + \sum_r^{all} U_{rm}^c \varepsilon_{ir}^a$$

$$+ \sum_r^{all} \sum_j^{do} U_{rj}^c \left(4(im|rj)^a - (ir|mj)^a - (ij|mr)^a \right) \qquad \text{(IV.4.8)}$$

Note that unlike IV.3.7, the second and third terms of the above cannot be reduced to a single term each as ε_{rm}^a and ε_{ir}^a are not diagonal. However, with the introduction of a derivative A matrix, $A_{im,rj}^a$

$$A^{a}_{im,rj} = 4(im|rj)^{a} - (ir|mj)^{a} - (ij|mr)^{a}$$

(IV.4.9)

equation IV.4.8 can be given in a simpler form

$$\frac{\partial}{\partial c}\,\varepsilon^{a}_{im} = \varepsilon^{ac}_{im} + \sum_{r}^{all} U^{c}_{ri}\,\varepsilon^{a}_{rm} + \sum_{r}^{all} U^{a}_{rm}\,\varepsilon^{a}_{ir}$$

$$+ \sum_{r}^{all}\ \sum_{j}^{do} U^{c}_{rj}\,A^{a}_{im,rj}$$

(IV.4.10)

Terms (c) and (d) of equation IV.4.1 involve derivatives of the derivative overlap matrix and derivatives of the lagrangian multiplier. Straight differentiation of the derivative overlap matrix produces

$$\frac{\partial}{\partial c}\,S^{a}_{mi} = S^{ac}_{mi} + \sum_{r}^{all} U^{c}_{rm}\,S^{a}_{ri} + \sum_{r}^{all} U^{c}_{ri}\,S^{a}_{mr}$$

(IV.4.11)

$$\frac{\partial}{\partial c}\,S^{ab}_{mi} = S^{abc}_{mi} + \sum_{r}^{all} U^{c}_{rm}\,S^{ab}_{ri} + \sum_{r}^{all} U^{c}_{ri}\,S^{ab}_{mr}$$

(IV.4.12)

The remaining derivatives of the lagrangian multiplier in terms (c) and (d) are given by equation IV.3.7.

All the components of term (e) of IV.4.1 have been previously defined: the derivative of the U matrix by equation IV.4.7, and the derivatives of the lagrangian multiplier by IV.3.7. Term (e) points out the necessity of carefully keeping track of U matrix indices as the term contains both $U^{a}_{mi}\,U^{b}_{mi}$ and $U^{a}_{im}\,U^{b}_{im}$ and their derivatives. As shown by equation IV.3.12 these terms are not equivalent, and the inadvertent

switching of indices can be disastrous.

The only remaining undefined derivative in equation IV.4.1 occurs in term (f), the derivative of the A matrix. Direct differentiation yields

$$\frac{\partial}{\partial c} A_{im,rj} = 4(im|rj)^c - (ir|mj)^c - (ij|mr)^c$$

$$+ \sum_s^{all} U_{si}^c \{ 4(sm|rj) - (sr|mj) - (sj|mr) \}$$

$$+ \sum_s^{all} U_{sm}^c \{ 4(is|rj) - (ir|sj) - (ij|sr) \}$$

$$+ \sum_s^{all} U_{sr}^c \{ 4(im|sj) - (is|mj) - (ij|ms) \}$$

$$+ \sum_s^{all} U_{sj}^c \{ 4(im|rs) - (ir|ms) - (is|mr) \}$$

$$= A_{im,rj}^c + \sum_s^{all} \{ U_{si}^c A_{sm,rj} + U_{sm}^c A_{is,rj} + U_{sr}^c A_{im,sj}$$

$$+ U_{sj}^c A_{im,rs} \} \qquad \text{(IV.4.13)}$$

Substituting all of these reduced terms back into equation IV.4.1 and combining like terms results in (in a few terms, labels that run over the same set of orbitals have been interchanged)

$$\frac{\partial^3}{\partial a \partial b \partial c} E = E^{abc'} + 4 \sum_i^{do} \sum_m^{all} \{ U_{mi}^c \varepsilon_{im}^{ab} + U_{mi}^b \varepsilon_{im}^{ac}$$

$$+ U_{mi}^a \varepsilon_{im}^{bc} \} \qquad \text{(a)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \left(U_{mi}^{bc} - \sum_{r}^{all} U_{ri}^{b} U_{mr}^{c} \right) \{ \varepsilon_{im}^{a}$$

$$+ U_{mi}^{a} \varepsilon_{mm} + \sum_{r}^{all} \sum_{j}^{do} U_{rj}^{a} A_{im,rj} \} \qquad (b)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \left(U_{mi}^{ac} - \sum_{r}^{all} U_{ri}^{a} U_{mr}^{c} \right) \{ \varepsilon_{im}^{b}$$

$$+ U_{mi}^{b} \varepsilon_{mm} + \sum_{r}^{all} \sum_{j}^{do} U_{rj}^{b} A_{im,rj} \} \qquad (c)$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \left(U_{im}^{bc} - \sum_{r}^{all} U_{rm}^{b} U_{ir}^{c} \right) U_{im}^{a} \varepsilon_{ii} \qquad (d)$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \left(U_{im}^{ac} - \sum_{r}^{all} U_{rm}^{a} U_{ir}^{c} \right) U_{im}^{b} \varepsilon_{ii} \qquad (e)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{mi}^{a} U_{ri}^{c} \varepsilon_{rm}^{b} + U_{mi}^{a} U_{rm}^{c} \varepsilon_{ir}^{b}$$

$$+ U_{mi}^{b} U_{ri}^{c} \varepsilon_{rm}^{a} + U_{mi}^{b} U_{rm}^{c} \varepsilon_{ir}^{a} \} \qquad (f)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} \{ U_{mi}^{a} U_{rj}^{c} A_{im,rj}^{b}$$

$$+ U_{mi}^{b} U_{rj}^{c} A_{im,rj}^{a} + U_{mi}^{a} U_{rj}^{b} A_{im,rj}^{c} \} \qquad (g)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} \sum_{s}^{all} \{ U_{mi}^{a} U_{rj}^{b} U_{si}^{c} A_{sm,rj}$$

$$+ U_{mi}^{a} U_{rj}^{b} U_{sm}^{c} A_{is,rj} + U_{mi}^{a} U_{rj}^{b} U_{sr}^{c} A_{im,sj}$$

$$+ U_{mi}^{a} U_{rj}^{b} U_{sj}^{c} A_{im,rs} \} \qquad (h)$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U^{a}_{mi} U^{b}_{mi} \varepsilon^{(c)}_{mm} - U^{a}_{im} U^{b}_{im} \varepsilon^{(c)}_{ii}$$

$$+ S^{a}_{mi} S^{b}_{mi} \varepsilon^{(c)}_{ii} \} \qquad \text{(i)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ S^{ac}_{mi} S^{b}_{mi} + S^{a}_{mi} S^{bc}_{mi} \} \varepsilon_{ii} \qquad \text{(j)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U^{c}_{rm} S^{a}_{ri} S^{b}_{mi} + U^{c}_{ri} S^{a}_{mr} S^{b}_{mi}$$

$$+ U^{c}_{rm} S^{a}_{mi} S^{b}_{ri} + U^{c}_{ri} S^{a}_{mi} S^{b}_{mr} \} \varepsilon_{ii} \qquad \text{(k)}$$

$$- 2 \sum_{i}^{do} \{ S^{abc}_{ii} \varepsilon_{ii} + S^{ab}_{ii} \varepsilon^{(c)}_{ii} \} \qquad \text{(l)}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} U^{c}_{mi} S^{ab}_{mi} \varepsilon_{ii} \qquad \text{(m)}$$

(IV.4.14)

Again each term can be reduced. By adding and subtracting $\sum U^{b}_{sm} \varepsilon_{is}$ to IV.4.14 (b) and $\sum U^{a}_{rm} \varepsilon_{ir}$ to IV.4.14 (c), the respective terms simplify, yielding

$$\text{IV.4.14 (b)} = 4 \sum_{i}^{do} \sum_{m}^{all} \left(U^{bc}_{mi} - \sum_{r}^{all} U^{b}_{ri} U^{c}_{mr} \right) \{ \varepsilon^{(a)}_{im} - \sum_{s}^{all} U^{b}_{sm} \varepsilon_{is} \}$$

(IV.4.15)

$$\text{IV.4.14 (c)} = 4 \sum_{i}^{do} \sum_{m}^{all} \left(U^{ac}_{mi} - \sum_{r}^{all} U^{a}_{ri} U^{c}_{mr} \right) \{ \varepsilon^{(b)}_{im} - \sum_{s}^{all} U^{b}_{sm} \varepsilon_{is} \}$$

(IV.4.16)

Since $\varepsilon^{(a)}_{im}$ and $\varepsilon^{(b)}_{im}$ (the derivative of the orbital energy) and ε_{is} (the orbital energy) are diagonal, the above equations will reduce to an even

simpler form.

$$\text{IV.4.14 (b)} = 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{ii}^{bc} \, \varepsilon_{ii}^{(a)} - \sum_{r}^{all} U_{ri}^{b} \, U_{ir}^{c} \, \varepsilon_{ii}^{(a)}$$

$$- U_{mi}^{bc} \, U_{im}^{a} \, \varepsilon_{ii} + \sum_{r}^{all} U_{ri}^{b} \, U_{im}^{a} \, U_{mr}^{c} \, \varepsilon_{ii} \} \qquad \text{(a)}$$

$$\text{IV.4.14 (c)} = 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{ii}^{ac} \, \varepsilon_{ii}^{(b)} - \sum_{r}^{all} U_{ri}^{a} \, U_{ir}^{c} \, \varepsilon_{ii}^{(b)}$$

$$- U_{mi}^{ac} \, U_{im}^{b} \, \varepsilon_{ii} + \sum_{r}^{all} U_{ri}^{a} \, U_{mr}^{c} \, U_{im}^{b} \, \varepsilon_{ii} \} \qquad \text{(b)}$$

(IV.4.17)

As with the first order U^a matrix, the diagonal elements of U^{ac} have a special form. In expanding the orthonormality equation IV.2.15 to second order, Osamura and Yamaguchi [64] defined the following relationship in analogy to equation IV.3.12:

$$U_{mr}^{ac} + U_{rm}^{ac} + \xi_{mr}^{ac} = 0 \qquad \text{(IV.4.18)}$$

where

$$\xi_{mr}^{ac} = S_{mr}^{ac} + \sum_{s}^{all} \{ U_{ms}^{a} \, U_{rs}^{c} + U_{rs}^{a} \, U_{ms}^{c} - S_{ms}^{a} \, S_{rs}^{c} - S_{rs}^{a} \, S_{ms}^{c} \} \qquad \text{(IV.4.19)}$$

For a diagonal U^{ac}, equation IV.4.18 immediately yields

$$U_{ii}^{ac} = -1/2 \; \xi_{ii}^{ac} \qquad \text{(IV.4.20)}$$

Substituting this into IV.4.17 and adding the terms (a) and (b) together results in

$$\text{IV.4.14 (b+c)} = -2 \sum_{i}^{do} \sum_{m}^{all} \{ \xi_{ii}^{bc} \, \varepsilon_{ii}^{(a)} + \xi_{ii}^{ac} \, \varepsilon_{ii}^{(b)} \} \qquad \text{(a)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ - U_{mi}^{bc} \, U_{im}^{a} \, \varepsilon_{ii} - U_{mi}^{ac} \, U_{im}^{b} \, \varepsilon_{ii} \qquad \text{(b)}$$

$$+ \sum_{r}^{all} (- U_{ri}^{b} \, U_{ir}^{c} \, \varepsilon_{ii}^{(a)} - U_{ri}^{a} \, U_{ir}^{c} \, \varepsilon_{ii}^{(b)} \qquad \text{(c)}$$

$$+ U_{ri}^{b} \, U_{mr}^{c} \, U_{im}^{a} \, \varepsilon_{ii} + U_{ri}^{a} \, U_{mr}^{c} \, U_{im}^{b} \, \varepsilon_{ii}) \} \qquad \text{(d)}$$

(IV.4.21)

Note that within each to the terms (a), (b), and (c) of IV.4.21 the basic quantities are displayed with a permutation of the derivatives a and b. This is the type of symmetry desired for the final equation, only that the final equation should show the permutation for all three degrees of freedom a, b, and c.

Continuing the reduction of the terms in IV.4.14, terms (d) and (e) are expanded resulting in

$$\text{IV.4.14 (d+e)} = -4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{im}^{ac} \, U_{im}^{b} + U_{im}^{bc} \, U_{im}^{a}$$

$$- \sum_{r}^{all} (U_{rm}^{a} \, U_{ir}^{c} \, U_{im}^{b} + U_{rm}^{b} \, U_{ir}^{c} \, U_{im}^{a}) \} \, \varepsilon_{ii}$$

(IV.4.22)

Adding this to IV.4.21 yields

$$\text{IV.4.14 (b+c+d+e)} = -2 \sum_{i}^{do} \sum_{m}^{all} \{ \xi_{ii}^{bc} \, \varepsilon_{ii}^{(a)} + \xi_{ii}^{ac} \, \varepsilon_{ii}^{(b)} \} \qquad \text{(a)}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{im}^{a} (U_{im}^{bc} + U_{mi}^{bc}) \, \varepsilon_{ii} + U_{im}^{b} (U_{im}^{ac} + U_{mi}^{ac}) \, \varepsilon_{ii}$$

(b)

$$+ U^{b}_{mi}\, U^{c}_{im}\, \varepsilon^{(a)}_{ii} + U^{a}_{mi}\, U^{c}_{im}\, \varepsilon^{(b)}_{ii} - \sum_{r}^{all} (U^{b}_{ri}\, U^{c}_{mr}\, U^{a}_{im} \qquad \text{(c)}$$

$$+ U^{a}_{rm}\, U^{c}_{ir}\, U^{b}_{im} + U^{b}_{rm}\, U^{c}_{ir}\, U^{a}_{im})\, \varepsilon_{ii} \quad \} \qquad \text{(d)}$$

(IV.4.23)

where r has been replaced by m in term (c) of IV.4.21. Using equation IV.4.18, term (b) of IV.4.23 reduces to (without the summations)

$$\text{IV.4.23 (b)} = \{ U^{a}_{im}\, \xi^{bc}_{im} + U^{b}_{im}\, \xi^{ac}_{im} \}\, \varepsilon_{ii} \qquad \text{(IV.4.24)}$$

This eliminates the remaining second order CPHF term leaving the third derivative completely specified by the result of the first order CPHF equations. This is in accord with Wigner's perturbation theorem which states that an nth order wave function is sufficient to determine properties of order 2n+1 [60]. This result was first demonstrated for third derivatives of the Hartree-Fock wave functions by Moccia [57] in 1970, and more recently by Pulay [16].

Though reduced to the results of the first order CPHF equations, more terms must be collected before the final equation displays the desired symmetry. Returning to IV.4.14, terms (f) and (h) are combined, yielding

$$\text{IV.4.14 (f+h)} = 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U^{a}_{mi}\, U^{c}_{ri} (\varepsilon^{b}_{rm} + \sum_{s}^{all} \sum_{j}^{do} U^{b}_{sj}\, A_{rm,sj}) \qquad \text{(a)}$$

$$+ U^{a}_{mi}\, U^{c}_{rm} (\varepsilon^{b}_{ir} + \sum_{s}^{all} \sum_{j}^{do} U^{b}_{sj}\, A_{ir,sj}) \qquad \text{(b)}$$

$$+ U^{b}_{mi}\, U^{c}_{ri} (\varepsilon^{a}_{rm} + \sum_{s}^{all} \sum_{j}^{do} U^{a}_{sj}\, A_{js,mr}) \qquad \text{(c)}$$

$$+ U^{b}_{mi} U^{c}_{rm} \left(\varepsilon^{a}_{ir} + \sum_{s}^{all} \sum_{j}^{do} U^{a}_{sj} A_{js,ri} \right) \} \qquad \text{(d)}$$

(IV.4.25)

where appropriate interchanging of labels has occurred with term (h) in IV.4.14. Note that $A_{rm,sj}$ is equivalent to $A_{js,mr}$ and that $A_{ir,sj}$ is equivalent to $A_{js,ri}$. By the addition and subtraction of $\sum U^{b}_{sr} \varepsilon_{sm}$ and $\sum U^{b}_{sm} \varepsilon_{rs}$ to term (a) of the above, term (a) is recast in terms of the derivative orbital energy. Following a similar procedure for (b), (c), and (d) yields IV.4.25 in terms of the appropriate derivatives of the orbital energies

$$\text{IV.4.14 (f+h)} = 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U^{a}_{mi} U^{c}_{ri} \left(\varepsilon^{(b)}_{rm} - U^{b}_{mr} \varepsilon_{mm} - U^{b}_{rm} \varepsilon_{rr} \right) \qquad \text{(a)}$$

$$+ U^{a}_{mi} U^{c}_{rm} \left(\varepsilon^{(b)}_{ir} - U^{b}_{ri} \varepsilon_{rr} - U^{b}_{ir} \varepsilon_{ii} \right) \qquad \text{(b)}$$

$$+ U^{b}_{mi} U^{c}_{ri} \left(\varepsilon^{(a)}_{rm} - U^{a}_{mr} \varepsilon_{mm} - U^{a}_{rm} \varepsilon_{rr} \right) \qquad \text{(c)}$$

$$+ U^{b}_{mi} U^{c}_{rm} \left(\varepsilon^{(a)}_{ir} - U^{a}_{ri} \varepsilon_{rr} - U^{a}_{ir} \varepsilon_{ii} \right) \} \qquad \text{(d)}$$

(IV.4.26)

Use has been made of the diagonal property of the orbital energy in reducing sums of lagrangian multipliers to single terms in IV.4.26.

Equation IV.4.26, however, does not take advantage of the diagonal nature of the derivative of the orbital energies. Combining IV.4.26 with equation IV.4.23 and reducing the derivatives of the orbital energies to their diagonal form yields

$$\text{IV.4.14 (b+c+d+e+f+h)} = - 2 \sum_{i}^{do} \{ \xi^{bc}_{ii} \varepsilon^{(a)}_{ii} + \xi^{ac}_{ii} \varepsilon^{(b)}_{ii} \} \qquad \text{(a)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{im}^{a} \xi_{im}^{bc} + U_{im}^{b} \xi_{im}^{ac} \} \varepsilon_{ii} \qquad \text{(b)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{ir}^{c} (U_{rm}^{a} U_{im}^{b} + U_{im}^{a} U_{rm}^{b}) \} \varepsilon_{ii}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{mi}^{a} (U_{rm}^{b} U_{ri}^{c} + U_{ri}^{b} U_{rm}^{c}) \varepsilon_{rr} \qquad \text{(c)}$$

$$+ U_{mi}^{b} (U_{rm}^{a} U_{ri}^{c} + U_{ri}^{a} U_{rm}^{c}) \varepsilon_{rr} + U_{ri}^{c} (U_{mi}^{a} U_{mr}^{b} + U_{mr}^{a} U_{mi}^{b}) \varepsilon_{mm} \} \qquad \text{(d)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} U_{mi}^{c} \varepsilon_{mm}^{(b)} + U_{mi}^{b} U_{mi}^{c} \varepsilon_{mm}^{(a)} \} \qquad \text{(e)}$$

IV.4.27)

When IV.4.26 and IV.4.23 are combined note that the $\varepsilon_{ii}^{(a)}$ and $\varepsilon_{ii}^{(b)}$ terms of IV.4.23 (c) cancel with the $\varepsilon_{ir}^{(a)}$ and $\varepsilon_{ir}^{(b)}$ terms of IV.4.26 because of the diagonal character of the derivative of the orbital energy. Also, as both r and m run over the same set of orbitals, a U_{mr}^{c} component of term (c) of IV.4.23 cancels with the last component of term (d) of IV.4.26.

Interchanging labels m and r in the last component of term (d) in the above yields

$$\text{IV.4.27 (d)} = - 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{mi}^{a} (U_{rm}^{b} U_{rm}^{c} + U_{ri}^{b} U_{rm}^{c})$$

$$+ U_{mi}^{b} (U_{rm}^{a} U_{ri}^{c} + U_{ri}^{a} U_{rm}^{c}) + U_{mi}^{c} (U_{ri}^{a} U_{rm}^{b} + U_{rm}^{a} U_{rm}^{b}) \varepsilon_{rr}$$

(IV.4.28)

Returning to equation IV.4.14 and substituting equation IV.4.27 with a modified term (d) given by equation IV.4.28 results in a third derivative expression nearly displaying the desired symmetry.

$$\frac{\partial^3}{\partial a \partial b \partial c} E = E^{abc'} + 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{c} \, \varepsilon_{im}^{ab} + U_{mi}^{b} \, \varepsilon_{im}^{ac}$$

$$+ U_{mi}^{a} \, \varepsilon_{im}^{bc} \} \qquad \text{(a)}$$

$$- 2 \sum_{i}^{do} \{ \xi_{ii}^{bc} \, \varepsilon_{ii}^{(a)} + \xi_{ii}^{ac} \, \varepsilon_{ii}^{(b)} \} \qquad \text{(b)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{im}^{a} \, \xi_{im}^{bc} + U_{im}^{b} \, \xi_{im}^{ac} \} \, \varepsilon_{ii} \qquad \text{(c)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U_{mi}^{a} \, U_{mi}^{c} \, \varepsilon_{mm}^{(b)} + U_{mi}^{b} \, U_{mi}^{c} \, \varepsilon_{mm}^{(a)}$$

$$+ U_{mi}^{a} \, U_{mi}^{b} \, \varepsilon_{mm}^{(c)} \} \qquad \text{(d)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{ir}^{c} \, (U_{rm}^{a} \, U_{im}^{b} + U_{im}^{a} \, U_{rm}^{b}) \} \, \varepsilon_{ii}$$

$$\text{(e)}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{mi}^{a} \, (U_{rm}^{b} \, U_{ri}^{c} + U_{ri}^{b} \, U_{rm}^{c})$$

$$+ U_{mi}^{b} \, (U_{rm}^{a} \, U_{ri}^{c} + U_{ri}^{a} \, U_{rm}^{c}) + U_{mi}^{c} \, (U_{ri}^{a} \, U_{rm}^{b} + U_{rm}^{a} \, U_{ri}^{b}) \} \, \varepsilon_{rr}$$

$$\text{(f)}$$

$$+ \sum_{i}^{do} \sum_{m}^{all} \{ 4 \, (S_{mi}^{a} \, S_{mi}^{b} - U_{im}^{a} \, U_{im}^{b}) - 2 \, S_{ii}^{ab} \} \, \varepsilon_{ii}^{(c)}$$

$$\text{(g)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ S_{mi}^{ac} \, S_{mi}^{b} + S_{mi}^{a} \, S_{mi}^{bc} - U_{mi}^{c} \, S_{mi}^{ab} \} \, \varepsilon_{ii} \qquad \text{(h)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{rm}^{c} \, (S_{ri}^{a} \, S_{mi}^{b} + S_{mi}^{a} \, S_{ri}^{b})$$

$$+ U_{ri}^{c} \, (S_{mi}^{a} \, S_{mr}^{b} + S_{mr}^{a} \, S_{mi}^{b}) \} \, \varepsilon_{ii} \qquad \text{(i)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} \{ U_{mi}^{a} U_{rj}^{c} A_{im,rj}^{b} + U_{mi}^{b} U_{rj}^{c} A_{im,rj}^{a}$$

$$+ U_{mi}^{a} U_{rj}^{b} A_{im,rj}^{c} \} \qquad (j)$$

$$- 2 \sum_{i}^{do} S_{ii}^{abc} \varepsilon_{ii} \qquad (k)$$

(IV.4.29)

The symmetry of term (b) of equation IV.4.29 can be completed by reducing term (g). Going back to IV.4.19, term (g) is rewritten as

$$\text{IV.4.29 (g)} = - 2 \sum_{i}^{do} \xi_{ii}^{ab} \varepsilon_{ii}^{(c)} \qquad \text{(IV.4.30)}$$

The reduction of terms continues by using IV.3.12 to rewrite the third component of term (h)

$$\text{IV.4.28 (h)} = 4 \sum_{i}^{do} \sum_{m}^{all} \{ S_{mi}^{ac} S_{mi}^{b} + S_{mi}^{a} S_{mi}^{bc} + (U_{im}^{c} + S_{mi}^{c}) S_{mi}^{ab} \} \varepsilon_{ii}$$

$$= 4 \sum_{i}^{do} \sum_{m}^{all} \{ S_{mi}^{ac} S_{mi}^{b} + S_{mi}^{a} S_{mi}^{bc} + S_{mi}^{c} S_{mi}^{ab} \} \varepsilon_{ii} \qquad (a)$$

$$+ 4 \sum_{i}^{do} \sum_{r}^{all} U_{ir}^{c} S_{ri}^{ab} \varepsilon_{ii} \qquad (b)$$

(IV.4.31)

where the m in term (b) has been replaced by r. Combining term (b) of IV.4.31 with term (e) of IV.4.29 yields

$$\text{IV.4.31 (b)} + \text{IV.4.29 (e)} = 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} U_{ir}^{c} \{ S_{ri}^{ab} + U_{rm}^{a} U_{im}^{b}$$

$$+ U_{im}^{a} U_{rm}^{b} \} \varepsilon_{ii} \qquad \text{(IV.4.32)}$$

With the aid of IV.4.19, this can be recast as

$$\text{IV.4.32} = 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{ir}^{c} \, \xi_{ir}^{ab} \qquad \text{(a)}$$

$$+ U_{ir}^{c} (S_{mr}^{a} \, S_{ir}^{b} + S_{ir}^{a} \, S_{mr}^{b}) \} \, \varepsilon_{ii} \qquad \text{(b)}$$

(IV.4.33)

Term (a) of the above, upon replacing r with m combines with IV.4.29 (c) to complete the symmetry of that term. The second term, (b), combines with equation IV.4.29 (i) to produce

$$\text{IV.4.29 (i)} = 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U_{ir}^{c} (S_{mr}^{a} \, S_{ir}^{b} + S_{ir}^{a} \, S_{ir}^{b}) \qquad \text{(a)}$$

$$+ U_{ri}^{a} (S_{ri}^{a} \, S_{mr}^{b} + S_{mr}^{a} \, S_{ri}^{b}) + U_{rm}^{c} (S_{ri}^{a} \, S_{mi}^{b} + S_{mi}^{a} \, S_{ri}^{b}) \} \, \varepsilon_{ii} \qquad \text{(b)}$$

(IV.4.34)

Since the derivative overlap matrix is symmetric, term (a) and the first component of term (b) in the above can be combined. Using the orthonormality condition equation IV.3.12, equation IV.4.34 reduces to

$$\text{IV.4.34} = 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ -S_{ir}^{c} (S_{mr}^{a} \, S_{ir}^{b} + S_{ir}^{a} \, S_{mr}^{b})$$

$$+ U_{rm}^{c} (S_{ri}^{a} \, S_{mi}^{b} + S_{mi}^{a} \, S_{ri}^{b}) \} \, \varepsilon_{ii} \qquad \text{(IV.4.35)}$$

Expanding the U_{rm}^{c} term in the above with the orthonormality condition results in

$$\text{IV.4.34} = -4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ S^a_{mr} S^b_{ir} S^c_{ir} + S^a_{ir} S^b_{mr} S^c_{ir} \quad \text{(a)}$$

$$+ S^a_{ri} S^b_{mi} S^c_{rm} + S^a_{mi} S^b_{ri} S^c_{rm} \quad \text{(b)}$$

$$+ S^a_{ri} S^b_{mi} U^c_{mr} + S^a_{mi} S^b_{ri} U^c_{mr} \} \varepsilon_{ii} \quad \text{(c)}$$

(IV.4.36)

The first component of term (c) of the above may be rewritten with interchanged indices, r and m. Term (c) becomes

$$\text{IV.4.36 (c)} = - S^a_{mi} S^b_{ri} U^c_{rm} - S^a_{mi} S^b_{ri} U^c_{mr}$$

$$= - S^a_{mr} S^b_{ir} (U^c_{rm} + U^c_{mr})$$

$$= S^a_{mi} S^b_{ri} S^c_{rm} \qquad \text{(IV.4.37)}$$

Substituting this back into IV.4.36 results in

$$\text{IV.4.36} = -4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ S^a_{im} S^b_{ir} S^c_{mr} + S^a_{mr} S^b_{im} S^c_{ir}$$

$$+ S^a_{ir} S^b_{mr} S^c_{im} \} \varepsilon_{ii} \qquad \text{(IV.4.38)}$$

Including all of these latest terms in the third derivative energy equation IV.4.29, the final equation is obtained. Note that it displays the desired symmetry of permuting the derivative degrees of freedom for each term.

$$\frac{\partial^3}{\partial a \partial b \partial c} E = E^{abc'} + 4 \sum_{i}^{do} \sum_{m}^{all} \{ U^{c}_{mi} \, \varepsilon^{ab}_{im} + U^{b}_{mi} \, \varepsilon^{ac}_{im}$$

$$+ U^{a}_{mi} \, \varepsilon^{bc}_{im} \} \qquad \text{(a)}$$

$$- 2 \sum_{i}^{do} \xi^{bc}_{ii} \, \varepsilon^{(a)}_{ii} + \xi^{ac}_{ii} \, \varepsilon^{(b)}_{ii} + \xi^{ab}_{ii} \, \varepsilon^{(c)}_{ii} \} \qquad \text{(b)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U^{a}_{im} \, \xi^{bc}_{im} + U^{b}_{im} \, \xi^{ac}_{im} + U^{c}_{im} \, \xi^{ab}_{im} \} \, \varepsilon_{ii} \qquad \text{(c)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ U^{a}_{mi} \, U^{c}_{mi} \, \varepsilon^{(b)}_{mm} + U^{b}_{mi} \, U^{c}_{mi} \, \varepsilon^{(a)}_{mm}$$

$$+ U^{a}_{mi} \, U^{b}_{mi} \, \varepsilon^{(c)}_{mm} \} \qquad \text{(d)}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ U^{a}_{mi} (U^{b}_{rm} \, U^{c}_{ri} + U^{b}_{ri} \, U^{c}_{rm})$$

$$+ U^{b}_{mi} (U^{a}_{rm} \, U^{c}_{ri} + U^{a}_{ri} \, U^{c}_{rm}) + U^{c}_{mi} (U^{a}_{ri} \, U^{b}_{rm} + U^{a}_{rm} \, U^{b}_{ri}) \} \, \varepsilon_{rr} \qquad \text{(e)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} \{ U^{a}_{mi} \, U^{c}_{rj} \, A^{b}_{im,rj} + U^{b}_{mi} \, U^{c}_{rj} \, A^{a}_{im,rj}$$

$$+ U^{a}_{mi} \, U^{b}_{rj} \, A^{c}_{im,rj} \} \qquad \text{(f)}$$

$$+ 4 \sum_{i}^{do} \sum_{m}^{all} \{ S^{ac}_{mi} \, S^{b}_{mi} + S^{a}_{mi} \, S^{bc}_{mi} + S^{c}_{mi} \, S^{ab}_{mi} \} \, \varepsilon_{ii} \qquad \text{(g)}$$

$$- 4 \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \{ S^{a}_{im} \, S^{b}_{ir} \, S^{c}_{mr} + S^{a}_{mr} \, S^{b}_{im} \, S^{c}_{ir}$$

$$+ S^{a}_{ir} \, S^{b}_{mr} \, S^{c}_{im} \} \, \varepsilon_{ii} \qquad \text{(h)}$$

$$- 2 \sum_{i}^{do} S_{ii}^{abc} \quad \varepsilon_{ii} \qquad \text{(i)}$$

(IV.4.39)

IV.4.2 COMPUTATIONAL REMARKS

The most computationally expensive term of in IV.4.39 (other than the calculation of the third derivative integrals) is term (f). In this term, N3N sets of four-index transformations of the two-electron first derivative atomic orbital integrals are required so that the $A^{a}_{im,rj}$ matrices can be assembled. If there is enough central storage space in the computer, then all N3N derivative atomic orbital integrals can be simultaneously transformed and term (f) directly evaluated. If however, there is little central memory or the number of derivative integrals is simply too large, then a procedure much like that used in the atomic orbital basis CPHF solution of Osamura et al. [62], is best applied to the evaluation of term (f) of IV.4.39.

$$\sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} U^{a}_{mi} \, U^{b}_{rj} \, A^{c}_{im,rj}$$

$$= \sum_{i}^{do} \sum_{m}^{all} \sum_{r}^{all} \sum_{j}^{do} \sum_{\mu,\nu}^{all} \sum_{\rho,\sigma}^{all} U^{a}_{mi} \, U^{b}_{rj} \, \{ 4 \, C^{i}_{\mu} \, C^{m}_{\nu} \, C^{r}_{\rho} \, C^{j}_{\sigma} \, (\mu\nu|\rho\sigma)^{c}$$

$$- C^{i}_{\mu} \, C^{r}_{\rho} \, C^{m}_{\nu} \, C^{j}_{\sigma} \, (\mu\rho|\nu\sigma)^{c} - C^{i}_{\mu} \, C^{j}_{\rho} \, C^{m}_{\nu} \, C^{r}_{\sigma} \, (\mu\rho|\nu\sigma)^{c} \}$$

$$= \sum_{i}^{do} \sum_{m}^{all} \sum_{\mu,\nu}^{all} U^{a}_{mi} \, C^{i}_{\mu} \, C^{m}_{\nu} \, \{ \sum_{\rho,\sigma}^{all} \sum_{r}^{all} \sum_{j}^{do} U^{b}_{rj} \, (2 \, (C^{r}_{\rho} \, C^{j}_{\sigma} + C^{j}_{\rho} \, C^{r}_{\sigma}) \, (\mu\nu|\rho\sigma)^{c} -$$

$$- (C^{r}_{\rho} \, C^{j}_{\sigma} + C^{j}_{\rho} \, C^{r}_{\sigma}) \, (\mu\rho|\nu\sigma)^{c}) \} \qquad \text{(IV.4.40)}$$

By letting

$$P_{\rho\sigma} = \sum_{r}^{all} \sum_{j}^{do} U^{b}_{rj} \left(C^{r}_{\rho} C^{j}_{\sigma} + C^{j}_{\rho} C^{r}_{\sigma} \right) \qquad \text{(IV.4.41)}$$

equation IV.4.40 can be rewritten as

$$\text{IV.4.40} = \sum_{i}^{do} \sum_{m}^{all} \sum_{\mu,\nu}^{all} U^{a}_{mi} C^{i}_{\mu} C^{m}_{\nu} \sum_{\rho,\sigma}^{all} P_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma)^{c} - (\mu\rho|\nu\sigma)^{c} \right\} \qquad \text{(IV.4.42)}$$

The contribution of each derivative integral in the above is empirically known by the indicies of the integral. This is much like the production of $T^{a}_{\mu\nu}$ described in section IV.3.2. The multiplication of the integrals and $P_{\rho\sigma}$ can be thought of as forming a half-transformed $Q_{\mu\nu}$.

$$Q_{\mu\nu} = \sum_{\rho,\sigma}^{all} P_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma)^{c} - (\mu\rho|\nu\sigma)^{c} \right\} \qquad \text{(IV.4.43)}$$

The $Q_{\mu\nu}$ is then transformed by a two-index transformation and multiplied and summed over U^{a}.

$$\text{IV.4.40} = \sum_{i}^{do} \sum_{m}^{all} U^{a}_{mi} \left\{ \sum_{\mu}^{all} \sum_{\nu}^{all} C^{i}_{\mu} C^{m}_{\nu} Q_{\mu\nu} \right\} \qquad \text{(IV.4.44)}$$

As with the second derivative, the third derivative involves derivative Fock matrices - only this time both first and second derivatives. The first derivative half-transformed $T^{a}_{\mu\nu}$ is formed as in equation IV.3.16 and the second derivative is formed likewise. The $T^{a}_{\mu\nu}$ and $T^{ab}_{\mu\nu}$ are transformed by a two index transformation and added to h^{a}_{im} and h^{ab}_{im} to produce ε^{a}_{im} and ε^{ab}_{im} .

The computational steps are:

(1) Calculate the zeroth-order integrals and solve the SCF equations to obtain the unperturbed molecular orbital coefficients. This wave function must be well-converged.

(2) Calculate the one-electron contributions to $E^{a'}$, $E^{ab'}$, and $E^{abc'}$. Using the atomic orbital lagrangian, term (i) of equation IV.4.39 is evaluated. $h^a_{\mu\nu}$, $h^{ab}_{\mu\nu}$, $S^a_{\mu\nu}$, $S^{ab}_{\mu\nu}$ are stored externally.

(3) Calculate the density factor for the two-electron blocks of integrals. If all the density factors are below a given threshold, then the block of integrals is ignored. Otherwise evaluate the derivative two-electron integrals adding their contributions to $E^{a'}$, $E^{ab'}$ and $E^{abc'}$. The half-transformed $T^a_{\mu\nu}$ and $T^{ab}_{\mu\nu}$ are also calculated and stored externally. $(\mu\nu|\rho\sigma)^a$ must also be stored on an external device.

(4) Transform with a two index transformation: $h^a_{\mu\nu}$, $h^{ab}_{\mu\nu}$, $S^a_{\mu\nu}$, $S^{ab}_{\mu\nu}$, $T^a_{\mu\nu}$ and $T^{ab}_{\mu\nu}$.

(5) Solve the CPHF equations. The U^a matrices are stored on an external device. Form the ξ^{ab} and store them externally.

(7) Evaluate the remaining terms in IV.4.39. Use the techniques of equations IV.4.40-IV.4.44 for the production of the derivative A martix.

In the following chapter, the results of the application of chapters II, III, and IV on the water molecule will be discussed. The resulting second and third order cartesian force constants will be transformed to normal coordinate space, allowing the rotation-vibration interaction constant of chapter I to be calculated.

V RESULTS OF THE THIRD-ORDER FORCE CONSTANT CALCULATION

V.1 INTRODUCTUION

The calculation of the energy for an ab initio wave function is a calculation from first principles. The description of the force field, however, has often been clouded by the use of experimental data and approximate means to describe the field itself. This new development of analytic cubic force constants coupled with the previously developed analytic quadratic force constants returns the force field to first principles.

Previous theoretical force fields have generally approximated cubic and quartic force constants by sums and differences of energies and energy gradients calculated at experimental [17,52] or relaxed [13,65] geometries. In this manner, the quadratic and cubic force constants in terms of the gradient of the energy g_i are given by

$$F^{ij} = \{ g_i(\mathrm{ref} - \Delta q_j) - g_i(\mathrm{ref} + \Delta q_j) \} / 2\, \Delta_j$$

$$F^{ijj} = \{ 2\, g_i(\mathrm{ref}) - g_i(\mathrm{ref} + \Delta q_j) - g_i(\mathrm{ref} - \Delta q_j) \} / \Delta_j^2 \qquad \text{(V.1.1)}$$

where ref refers to the reference geometry, Δq_i the change in a particular internal coordinate q_i, and Δ_j the step size of coordinate j. The diagonal quartic force constants are calculated by either fitting energy points to a fourth-order polynomial (Schlegel et

al.[13]) or the quartic force constants of the morse oscillator are used to approximate the quartic stretching force constants (Pulay et al.[51]. Non-diagonal quartic force constants are not calculated. Note also that equation V.1.1 gives only the diagonal and semi-diagonal cubic force constants. It has been generally assumed that F^{ijk} with $i \neq j \neq k$ is small and can thus be neglected.

Although these methods have had success in reproducing the experimentally obtained force contstants [17,51,52,13,65,66], the calculation of analytic force constants reduces the errors inherent with the point difference methods given by equation V.1.1. Analytic methods also have the advantage that all the force constants are calculated. This avoids any systematic error due to the dropping of non-diagonal cubic and quartic force constants that may indeed be small, but too important to neglect.

Whether to use the theoretical minimum or the experimental minimum geometry in the theoretical calculation of the force constants has been an area debated by theoreticans for many years [41,54]. To date, most cubic and quartic force constant calculations have used experimental r_e structures. As these studies have been used primarily to supplement and expand experimental data, the use of the experimental r_e structure is reasonable. However, for analytic cubic force constants (and evidentually quartic), the role of the force constants will be to help define experimental data not necessarily to validiate it. This predictive role is possible because the analytic calculations are not restricted to molecular systems with straightforwardly defined internal coordinates as gradients along these coordinates are not needed. Instead, novel systems where there is little or no experimental data can

be readily calculated. In such cases, the use of the theoretical minimum is the only reasonable choice.

The most obvious omission in this study of the Hartree-Fock analytic force constants is the neglect of electron correlation. The effect of electron correlation on quadratic force constants is substantial [53], and most attempts to accurately describe potential surfaces have concentrated on the interplay between basis set size and correlation effects. The effects of electron correlation on cubic and quartic force constants has been investigated by many authors [17,12,52,67]. Pulay et al. [17,52] have shown that for NH_3, HF, HCN, and CH_4, the contribution of electron correlation to cubic and quartic force constants is small. Equally important is their finding that while the Hartree-Fock contribution to these force constants is sensitive to the nuclear reference frame, the electron correlation contribution is not. These findings are also supported by Rosenberg et al. [67] in their study of the water molecule. For weakly bonded systems, for example the HF dimer and HF trimer [68], neither the Hartree-Fock nor electron correlation contributions to the higher force constants are known. The analytic cubic force constant formalism presented in this work, however, will allow the Hartree-Fock question to be definitively answered.

Basis set size and the stability of cubic and quartic force constants has also been investigated by Pulay et al. [52]. They conclude that basis sets on the order of triple-zeta plus two polarization functions are necessary to correctly describe the core-core replusion they feel is responsible for the large Hartree-Fock contribution to the higher force constants. Unfortunately, time constraints have made it

impossible to address this question in the present study.

V.2 THE WATER MOLECULE

The water molecule was chosen as the test case for the analytic energy derivative formulae - the force constants - presented in chapter IV. The water molecule represents an ideal starting place for higher analytic force constants as there is much data, both experimental and theoretical, concerning its potential surface [69,67,70,71].

The water molecule was completely optimized with analytic gradients using the standard double-zeta (DZ) basis set of Huzinaga and Dunning [72,73]. The basis set for the oxygen atom is comprised of nine s-type gaussian primitives contracted to four s-type functions and five p-type gaussian primitives contracted to two p-type functions ([9s5p/4s2p]). For the hydrogens the basis set consisted of four s-type gaussian primitives contracted to two s-type functions ([4s/2s]) scaled by the standard factor of 1.2. The total number of atomic orbitals is thus fourteen. Although this is clearly not among the largest basis sets employed on the water molecule (see reference 69 for an excellent SCF study of the water molecule), it does represent a significant challenge to the derivative integral and derivative energy programs.

For a triatomic molecule, there are 9 unique first derivative degrees of freedom, 45 unique second derivative degrees of freedom, and 165 unique third derivative degrees of freedom. For H_2O, many of these unique degrees of freedom are equivalent; however, this will not be taken advantage of in the calculation. The water molecule quite clearly illustrates how the number of derivative two-electron integrals quickly

escalates. There are a total of 4013 two-electron charge distribution interactions for the C_1 water molecule. This is less than the number of interactions for the zero-order integrals because no derivative integrals are calculated if all the atomic orbitals are on the same nuclear center. When these 4013 interactions are multiplied by the total number of degrees of freedom for the H_2O molecule, the result is that a total of 878,847 derivative integrals must be evaluated. This includes all first, second, and third derivative integrals. As mentioned in chapters III and IV, only the first derivative two-electron integrals have to be stored externally. The second and third derivative two-electron integrals are multiplied by a density factor and summed, thus avoiding their storage. In the calculation of the quadratic and cubic force constants for H_2O, the computational steps outlined in section IV.4.2 were followed.

The analyatic force constants in cartesian coordinate representation were checked for accuracy by performing the appropriate lower-order analytic force constant calculation at displaced cartesian coordinates and then calculating the higher-order force constant with the appropriate two-point difference formula. All one- and two-electron derivative integrals were checked by finite differences of the appropriate lower-order integrals evaluated at displaced geometries. Table V.2.1 compares the computational time for calculating the third derivatives of the energy with respect to cartesian coordinates by finite differences of cartesian second derivatives and the analytic evaluation of the third derivatives. Although the version of the third derivative integral program used for this timing comparison has since been improved, the timings indicate that the analytic evaluation of

third derivatives is indeed computationally economical.

As explained in chapter I, the final force constants are given not with respect to cartesian coordinates but rather with respect to normal coordinates. The transformation to normal coordinate space (see section I.3) reduces the third-order force constant matrix from 165 elements to a mere 27 elements. The theoretical quadratic and cubic force constants in normal coordinate space are presented in table V.2.2. The corresponding experimental force constants reduced to normal coordinate space by Hoy, Mills, and Strey [15] are also presented in the table. Note that only the non-zero force constants are given.

The agreement between theory and experiment is excellent. Although the DZ basis set employed here does not have the flexibility that polarization functions would add, it nonetheless does a remarkable job describing the cubic stretching (deformation) constants. The poorest agreement occurs with the ϕ_{122} force constant. This type of deformation will be better described at the DZ plus polarization level as the bending coordinate is treated better at this level.

V.3 CONCLUSION

The results of this chapter indicate that for basis sets of moderate size the analytic evaluation of cubic force constants is an accurate and practical process for closed-shell Hartree-Fock wave functions. Although calculations for larger molecules with more sophisticated basis sets have yet to be performed, it is believed that the results of this chapter will directly extrapolate to these larger systems. The next step in analytic third derivatives is the evaluation

of third derivative energy equations for open-shell Hartree-Fock wave functions. As this will not require a new derivative integral program, it is expected that open-shell cubic force constants will be forthcoming shortly. Third derivatives of the multi-configurational wave functions, wave functions that treat the electron correlation problem, are also within reach.

To calculate the anharmonic constants presented in chapter I, the fourth-order force constants are needed. This requires a new derivative integral program. The design of the derivative integral algorithms presented in chapter III allow facile extension to fourth derivatives. The fourth derivative energy equations, although not presented here, are derived in a manner similar to the third-order equations. The success of analytic third derivatives virtually guarantees the success of analytic fourth derivatives. The completion of this step will allow the *ab initio* calculation of a rotation-vibration spectrum.

Table V.2.1

Timing Comparison of Third Derivatives from Finite Differences of Second Derivatives and Analytic Evaluation

A single second derivative calculation in C_1 symmetry	~1 minute
Number of necessary second derivative points to obtain the third derivative [a]	9
entire third derivative calculation	~9 minutes
analytic evaluation of third derivative: entire calculation	~7 minutes

Timings are on the Gould 32/87/80 mini-computer. The third derivative code has been substantially improved since this timing comparison was made.

[a] The second derivative code used for these calculations is the highly optimized code of Saxe and Yamaguchi. Details concerning their method may be found in reference 46.

Table V.2.2

Cubic and Harmonic Force Constants with Respect to Harmonic Normal Coordinates for H_2O in cm^{-1}

notation: mode 1 is the symmetric stretch, mode 2 is the bend, and mode 3 is the asymmetric stretch.

	Present Results	Experimental [15]
r_e	0.9513 Å	0.9572 Å
α_e	112.52 °	104.52 °
ϕ_{11}	4028.3	3832.0
ϕ_{22}	1710.6	1648.9
ϕ_{33}	4204.2	3942.5
ϕ_{111}	-1853.1	-1815.1
ϕ_{112}	107.3	106.2
ϕ_{122}	362.1	335.0
ϕ_{133}	-1873.6	-1855.8
ϕ_{222}	-404.4	-381.7
ϕ_{233}	294.1	277.6

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Appendices

A.1 THE MCMURCHIE AND DAVIDSON INTEGRAL EVALUATION ALGORITHM AND THE SAUNDERS INTEGRAL EVALUATION ALGORITHM

In the following section, both the McMurchie and Davidson and the Saunders alogrithm for the solution of the ERI are presented. Though the alogrithms are presented in a Fortran 77 like manner, liberties have been taken so that the algorithms match the equations presented in section II.7. Before the two algorithms are presented, a number of definitions are required:

(a) Nshell : the total number of shells

(b) Ishell, Jshell, Kshell, Lshell : the shell in question

(c) Ifns, Jfns, Kfns, Lfns : the set of primitives (functions) that make up a particular shell (a contraction set)

(d) a,b,c,d : the exponets of a particular primitive

(e) Tmax : $\lambda_A + \lambda_B$, the sum of the total angular momentums on Ishell and Jshell

(f) T'max : $\lambda_C + \lambda_D$

(g) Kfirst, Klast, Lfirst, Llast, Jfirst, Jlast, Ifirst, Ilast : the first and last members of the specified shell when all the members of all the shells are grouped in a list 1 to Norbitals

(h) Norbitals : total number of atomic orbitals

(i) Int : an array that for a given atomic orbital, contains the x, y, and z angular quantum numbers (the n, l, and m for that particular

orbital)

The McMurchie and Davidson algorithm is presented below:

```
For Ishell=1,Nshell
. For Jshell=1,Ishell
. . Tmax is computed
. . For Ifns
. . . For Jfns
. . . . p= a + b
. . . . generate the expansion coefficients
. . . . zero I
. . . . For Kshell=1,Ishell
. . . . . For Lshell=1,Kshell (or Jshell if Kshell=Ishell)
. . . . . T'max is computed   Maxt=T'max + Tmax
. . . . . For Kfns
. . . . . i,j,k angular quantum numbers
. . . . . For Lfns
. . . . . i',j',k' angular quantum numbers
. . . . . q = c + d
. . . . . generate the expansion coefficients
. . . . . compute F_j(z) and R(Maxt,Maxt,Maxt)
. . . . . For ρ= Kfirst, Klast
. . . . . For σ= Lfirst, Llast
. . . . . For v' = 1, T'max
. . . . . Dv'=e_z(k,k',v')
. . . . . For u' = 1, T'max
```

```
. . . . . . . . . . . . . . Du'=e_y(j,j',u')
. . . . . . . . . . . . . . For t'= 1, T'max
. . . . . . . . . . . . . . . Dt'=e_x(i,i',t')
. . . . . . . . . . . . . . . . For v = 1, Tmax
. . . . . . . . . . . . . . . . . . For u = 1, Tmax
. . . . . . . . . . . . . . . . . . . . For t = 1, Tmax
. . . . . . . . . . . . . . . . . . . . . . I(t,u,v,σ,ρ) =
                                            I(t,u,v,σ,ρ) +
                                            Dv'*Du'*Dt'*
                                            R(t+t',u+u',v+v')
. . . . . . . . . . . . . . . . . . . . end for
. . . . . . . . . . . . . . . . . . end for
. . . . . . . . . . . . . . . . end for
. . . . . . . . . . . . . . . end for
. . . . . . . . . . . . . . end for
. . . . . . . . . . . . end for
. . . . . . . . . . end for
. . . . . . . . end for
. . . . . . end for
. . . . . . For ρ= 1,Norbitals
. . . . . . . For σ= 1,Norbitals
. . . . . . . . For μ= Ifirst, Ilast
. . . . . . . . . Int(μ) n,l,m angular quantum numbers for the
                 Ishell
```

```
. . . . . . . . . For ν= Jfirst, Jlast
. . . . . . . . . . Int(ν) n',l',m' angular quantum numbers for
                    the Jshell
. . . . . . . . . . For v= 1,Tmax
. . . . . . . . . . . Dv=e_z(m,m',v)
. . . . . . . . . . . For u=1,Tmax
. . . . . . . . . . . . Du=e_y(l,l',u)
. . . . . . . . . . . . For t= 1,Tmax
. . . . . . . . . . . . . Dt=e_x(n,n',t)
. . . . . . . . . . . . . (μν|ρσ) = (μν|ρσ) +
                              Dt*Du*Dv*I(t,u,v,σ,ρ)
. . . . . . . . . . . . end for
. . . . . . . . . . . end for
. . . . . . . . . . end for
. . . . . . . . . end for
. . . . . . . . end for
. . . . . . . end for
. . . . . end for
. . . . end for
. . . end for
. . end for
. end for
end for
```

The Saunders alogrithm is given below:

```
For Ishell=1,Nshell
. λA is obtained
. For Jshell=1,Ishell
.   . λB is obtained
.   . Tmax is computed
.     Int array is produced for μ and ν orbitals
.   . For Ifns
.   .   . For Jfns
.   .   .   . p= a + b
.   .   .   . generate the expansion coefficients
.   .   .   . For Kshell=1,Ishell
.   .   .   .   . λC is obtained
.   .   .   .   . For Lshell=1,Kshell (or Jshell if Kshell=Ishell)
.   .   .   .   .   . λD is obtained
.   .   .   .   .   . T'max is computed   Maxt=T'max + Tmax
.   .   .   .   .   . Int array is produced for ρ and σ orbitals
.   .   .   .   .   . For Kfns
.   .   .   .   .   .   . For Lfns
.   .   .   .   .   .   .   . q = c + d
.   .   .   .   .   .   .   . generate the expansion coefficients
.   .   .   .   .   .   .   . compute  β  and find the Rys roots and weights
.   .   .   .   .   .   .   . calculate Gt, Gu, and Gv for t,u,v equal to maxt;
                               use the recursion relationships to fill out the G
                               arrays
.   .   .   .   .   .   .   . For Iroot = 1,Nroots
```

```
. . . . . For Ino = 0, λA
. . . . . For Jno = 0, λB
. . . . . IJ = Ino + Jno
. . . . . For kl = 0, λC + λD
. . . . . For t = 1,IJ
. . . . . tt'= kl + t, uu'= tt', and vv'=tt'
. . . . . YX(kl)=YX(kl) + ex(Ino,Jno,ij)
                          *Gtt'
. . . . . YY(kl)=YY(kl) + ey(Ino,Jno,ij)
                          *Guu'
. . . . . YZ(kl)=YZ(kl) + ez(Ino,Jno,ij)
                          *Gvv'
. . . . . end for
. . . . . end for
. . . . . For Kno = 0, λC
. . . . . For Lno = 0,λD
. . . . . KL=kno+lno, u'=tmx, and v'=tmx
. . . . . For t'= 0,KL
. . . . . XX(Lno,Kno,Jno,Ino)=
                XX(Lno, Kno,Jno,Ino) +
                ex(Kno,Lno,t')*YX(t')
. . . . . XY(Lno,Kno,Jno,Ino)=
                XY(Lno, Kno,Jno,Ino) +
                ey(Kno,Lno,t')*YY(t')
. . . . . XZ(Lno,Kno,Jno,Ino)=
                XZ(Lno, Kno,Jno,Ino) +
                ez(Kno,Lno,t')*YZ(t')
```

```
. . . . . . . . . . . . . . end for
. . . . . . . . . . . . . . end for
. . . . . . . . . . . . . end for
. . . . . . . . . . . . end for
. . . . . . . . . . . end for
. . . . . . . . . . . For μ = Ifirst, Ilast
. . . . . . . . . . . . Int(μ) produces n,l,m for μ orbital
. . . . . . . . . . . . For ν = Jfirst, Jlast
. . . . . . . . . . . . . Int(ν) produces n',l',m' for ν orbital
. . . . . . . . . . . . . For ρ = Kfirst, Klast
. . . . . . . . . . . . . . Int(ρ) produces i,j,k for ρ orbital
. . . . . . . . . . . . . . For σ = Lfirst, Llast
. . . . . . . . . . . . . . . Int(σ) produces i',j',k' for σ
                                orbital
. . . . . . . . . . . . . . . (μν|ρσ) = (μν|ρσ) +
                                XX(n,n',i,i')*XY(l,l',j',j')
                                *XZ(m,m',k,k')
. . . . . . . . . . . . . . . end for
. . . . . . . . . . . . . . end for
. . . . . . . . . . . . . end for
. . . . . . . . . . . end for
. . . . . . . . . . end for
. . . . . . . . . end for
. . . . . . . . end for
. . . . . . end for
. . . . . end for
. . . . end for
```

```
. . . end for
. . end for
. end for
end for
```

A.2 THE DERIVATIVE ONE-ELECTRON ALGORITHM

The following algorithm is for the evaluation of derivative one-electron integrals. Definitions of terms in the algorthim are at the beginning of appendix A.1. The algorithm is set up for fourth derivatives, but can be easily modified for a more restricted case. See sections III.3 through III.5 for details of the equations.

Loop over Ishell

Loop over Jshell $\leq$ Ishell

$t = \lambda_A + \lambda_B$

Loop over contractions on Ishell

Loop over contractions on Jshell

calculate the expansion coefficients where maximum angular momentum index is tmax=t+4 (because of 4 derivatives)

p=a+b

calculate β

calculate tmax Rys roots and weights and fill the G arrays where the maximum index is tmax

Loop over Ino = 0, λ_A

Loop over Jno = 0, λ_B

evaluate overlap and kinetic energy derivative integrals : $\langle \mu^n | \nu \rangle$ for n=1,4
$\langle \mu^n | T | \nu \rangle$ for n=1,4

expand about the two centers

Loop number of atoms V_c = 1, natoms

Loop over number of Rys roots Iroot=1,[t/2] + 1 + 4 (due to the fourth derivative)

Loop over Ino = 0, λ_A

Loop over Jno = 0, λ_B

evaluate derivative NAI integrals :

$\langle \mu^n | V_c | \nu \rangle$ for n=1,4

$\langle \mu | V_c | \nu^n \rangle$ for n=1,4

$\langle \mu^n | V_c | \nu^m \rangle$ for m=1,3 and n=1,3 such that n+m=4

expand about the two centers of Ishell and Jshell

use translational invariance to complete the derivative in accordance to table III.3.1-III.3.3

A.3 DERIVATIVE TWO-ELECTRON INTEGRAL ALGORITHM

The following algorithm is for the simultaneous evaluation of all first and second derivatives of a four center two-electron integral using translational invariance to calculate the derivatives on center D. Details concerning the acronyms may be found in section III.6. The extension to higher derivatives is accomplished by changing the appropriate limits of summation.

Loop over Ishell and Jshell

Loop over Kshell and Lshell (skip if all four shells are on the same center)

Loop over contractions on the four shells calculating the expansion coefficients where the maximum index is $\lambda + 2$

calculate the Rys roots and weights and fill the G arrays again the maximum index for the array is $\lambda_{max} + 2$

Loop over quadrature points Iroot=1,[t+t'/2] + 3

Loop over angular momentum on Ishell and Jshell (Ino=0,λ_A and Jno=0,λ_B, IJ variable that lables an Ino, Jno pair)

Loop over t'=$\lambda_C + \lambda_D + 2$

Loop over t = 0, Ino+Jno+2

If t < Ino+Jno : compute YX, YY, YZ

If t' < $\lambda_C + \lambda_D$

If t < Ino+Jno-2

compute YXSA2, YYSA2, YZSA2, YXSB2, YYSB2, YZSB2, YXSAB4, YYSAB4, YZSAB4

If t < Ino+Jno

compute YXSAB2, YYSAB2, YZSAB2, YXSAB3, YYSAB3,YZSAB3

compute YXSA1, YYSA1, YZSA1, YXSB1, YYSB1, YZSB1, YXSAB1, YYSAB1, YZSAB1

If t' < $\lambda_C + \lambda_D + 1$

If t < Ino+Jno-1

compute YXFA1, YYFA1, YZFA1, YXFB1, YYFB1 YZFB1

If t < Ino+Jno+1

compute YXFA2, YYFA2, YZFA2, YXFB2, YYFB2, YZFB2

If $t' < \lambda_C + \lambda_D + 1$

YX=YX, YY=YY, YZ=YZ

YXFA=2aYXFA1 - nYXFA2

YYFA=2aYYFA1 - nYYFA2

YZFA=2aYZFA1 - nYZFA2

YXFB=2bYXFB1 - n'YXFB2

YYFB=2bYYFB1 - n'YYFB2

YZFB=2bYZFB1 - n'YZFB2

If $t' < \lambda_C + \lambda_D + 2$

YXSA=4a^{2}YXSA1 - 2a(2n+1)YX + n(n-1)YXSA2

YYSA=4a^{2}YYSA1 - 2a(2n+1)YY + n(n-1)YYSA2

YZSA=4a^{2}YZSA1 - 2a(2n+1)YZ + n(n-1)YZSA2

YXSB=4b^{2}YXSB1 - 2b(2n'+1)YX + n'(n'-1)YXSB2

YYSB=4b^{2}YYSB1 - 2b(2n'+1)YY + n'(n'-1)YYSB2

YZSB=4b^{2}YZSB1 - 2b(2n'+1)YZ + n'(n'-1)YZSB2

YXSAB=4abYXSAB1 - 2an'YXSAB2 - 2bnYXSAB3 -
nn'YXSAB4

YYSAB=4abYYSAB1 - 2an'YYSAB2 - 2bnYYSAB3 -
nn'YYSAB4

YXSAB=4abYZSAB1 - 2an'YZSAB2 - 2bnYZSAB3 -
nn'YZSAB4

Loop over angular momentum on Kshell and Lshell
(Kno=0,λ_C, Lno=0,λ_D, KL is the variable that lables a
unique Kno, Lno pair)

Loop over t' = 0, Kno+Lno+2

If t' < Kno+Lno

compute XX, XY, XZ, XXFA, XYFA, XZFA, XXSA,
XYSA, XZSA, XXFB, XYFB, XZFB, XXSB, XYSB,
XZSB, XXSAB, XYSAB, XZSAB

If t' < Kno+Lno-2

compute XXSC2, XYSC2, XZSC2

If t' < Kno+Lno-1

compute XXFC2, XYFC2, XZFC2, XXAC2, XYAC2,

```
        XZAC2, XXBC2, XYBC2, XZBC2
    If t' < Kno+Lno+1
        compute XXFC1, XYFC1, XZFC1, XXAC1, XYAC1,
        XZAC1, XXBC1, XYBC1, XZBC1
    compute XXSC1, XYSC1, XZSC1
XXFA(IJ,KL)=XXFA
XYFA(IJ,KL)=XYFA
XZFA(IJ,KL)=XZFA
XXFB(IJ,KL)=XXFB
XYFB(IJ,KL)=XYFB
XZFB(IJ,KL)=XZFB
XXSA(IJ,KL)=XXSA
XYSA(IJ,KL)=XYSA
XZSA(IJ,KL)=XZSA
XXSB(IJ,KL)=XXSB
XYSB(IJ,KL)=XYSB
XZSB(IJ,KL)=XZSB
XXSAB(IJ,KL)=XXSAB
XYSAB(IJ,KL)=XYSAB
XZSAB(IJ,KL)=XZSAB
XXFC(IJ,KL)=2cXXFC1 - iXXFC2
XYFC(IJ,KL)=2cXYFC1 - iXYFC2
XYFC(IJ,KL)=2cXZFC1 - iXZFC2
XXSC(IJ,KL)=4c^2XXSC1 - 2c(2i+1)XX - i(i-1)XXFC2
XYSC(IJ,KL)=4c^2XYSC1 - 2c(2i+1)XY - i(i-1)XYFC2
XZSC(IJ,KL)=4c^2XZSC1 - 2c(2i+1)XZ - i(i-1)XZFC2
XXSAC(IJ,KL)=2cXXSAC1 - iXXSAC2
XYSAC(IJ,KL)=2cXYSAC1 - iXYSAC2
XZSAC(IJ,KL)=2cXZSAC1 - iXZSAC2
XXSBC(IJ,KL)=2cXXSBC1 - iXXSBC2
XYSBC(IJ,KL)=2cXYSBC1 - iXYSBC2
XZSBC(IJ,KL)=2cXZSBC1 - iXZSBC2
```

Expand about the four shells generating the appropriate IJ, and KL for the particular integral in question (Int array) only indicating one type of derivative for each direction

$(\mu\nu|\rho\sigma)^{a_x} = (\mu\nu|\rho\sigma)^{a_x}$ + XXFA(IJ,KL)*XY(IJ,KL)*XZ(IJ,KL)

$(\mu\nu|\rho\sigma)^{a_x a_x} = (\mu\nu|\rho\sigma)^{a_x a_x}$ +
XXSA(IJ,KL)*XY(IJ,KL)*XZ(IJ,KL)

$(\mu\nu|\rho\sigma)^{a_x a_y} = (\mu\nu|\rho\sigma)^{a_x a_y}$ +
XXFA(IJ,KL)*XYFA(IJ,KL)*XZ(IJ,KL)

$(\mu\nu|\rho\sigma)^{a_x b_x} = (\mu\nu|\rho\sigma)^{a_x b_x}$ +
XXSAB(IJ,KL)*XY(IJ,KL)*XZ(IJ,KL)

$(\mu\nu|\rho\sigma)^{a_x b_y} = (\mu\nu|\rho\sigma)^{a_x b_y}$ +
XXFA(IJ,KL)*XYFB(IJ,KL)*XZ(IJ,KL)

$(\mu\nu|\rho\sigma)^{a_x c_x} = (\mu\nu|\rho\sigma)^{a_x c_x}$ +
XXSAC(IJ,KL)*XY(IJ,KL)*XZ(IJ,KL)

$(\mu\nu|\rho\sigma)^{a_x c_y} = (\mu\nu|\rho\sigma)^{a_x c_y}$ +
XXFA(IJ,KL)*XYFC(IJ,KL)*XZ(IJ,KL)

.

.

.

use translational invariance relations of table III.2.2 to get the derivatives with respect to nuclear center D

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