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APPLICATION OF THE GRAPHICAL UNITARY GROUP APPROACH
TO THE ENERGY SECOND DERIVATIVE FOR CI WAVE FUNCTIONS
VIA THE COUPLED PERTURBED CI EQUATIONS

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by

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Abstract

Analytic derivatives of the potential energy for Self-Consistent-Field(SCF) wave functions have been developed in recent years and found to be useful tools. The first derivative for configuration interaction(CI) wave functions is also available. This work details the extension of analytic methods to energy second derivatives for CI wave functions.

The principle extension required for second derivatives is evaluation of the first order change in the CI wave function with respect to a nuclear perturbation. The shape driven graphical unitary group approach (SDGUGA) direct CI program was adapted to evaluate this term via the

coupled-perturbed CI equations. Several iterative schemes are compared for use in solving these equations. The pilot program makes no use of molecular symmetry but the timing results show that utilization of molecular symmetry is desirable. The principles for defining and solving a set of symmetry adapted equations are discussed.

Evaluation of the second derivative also requires the solution of the second order coupled-perturbed Hartree-Fock equations to obtain the correction to the molecular orbitals due to the nuclear perturbation. This process takes a consistently higher percentage of the computation time than for the first order equations alone and a strategy for its reduction is discussed.

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1 INTRODUCTION

One of the most active areas of research in ab initio theoretical chemistry in the last fifteen years has been the development of analytic derivative techniques for the nuclear parameters of electronic potential energy surfaces [1-19]. The increased power of computer technology and advances in methodology for evaluation of the electronic energy expressions have worked hand in hand to widen the range of molecules amenable to theoretical investigation. Since the electronic energy expression is developed within the Born-Oppenheimer approximation, the nuclear coordinates are also variational parameters that often must be optimized in order to obtain chemically reliable results. Derivative techniques have made it possible to address this optimization problem in a systematic fashion.

While larger molecules are being studied the range of questions which theoretical methods can answer reliably is also being expanded. One of the areas of chemistry where ab initio molecular orbital theory plays an important role is in the investigation of chemically unstable species, electronically excited states, transition states for chemical reactions, and exotic conformations that act as intermediates or test bonding concepts. Also species that have never been characterized experimentally but which would be expected to undergo interesting chemistry. In many of these species the intuitive concepts, such as bond type and hybridization, which can be used to predict qualitative

geometrical parameters in known molecules are insufficient or not applicable. Thus the theoretical methods must be unbiased by preconceptions. Derivatives provide an objective approach through the location of stationary points on the potential energy surface. These nuclear conformations are of potential chemical interest encompassing both stable molecular conformations and transition states along reaction pathways.

For small molecules an acceptable method of evaluating a gradient is by fitting a low order polynomial through a few points on the surface where only one coordinate has been varied. This method becomes unwieldy as the size of the molecule being studied increases and the method is subject to the numerical uncertainty of any such approximation. The development of analytic methods for evaluating the gradient of all cartesian degrees of freedom in a molecule[1-5] in the late 60's and early 70's has provided a method far superior in accuracy and far more economical computationally.

Second derivatives, by adding knowledge of the curvature, can aid in molecular structure determination but provide equally valuable information by giving unique characterization of the various types of stationary points encountered on a multi-dimensional potential energy surface. The calculation of second derivatives by central differences of analytic gradients has allowed systematic determination of reaction pathways and the possibility of "proving" a

transition state by verifying that only the reaction coordinate is a maximum on the potential energy surface[3,20,21]. In addition, the second derivatives give systematically reliable results for the fundamental vibrational frequencies of molecules[1,22,23]. The more recent development of methods for evaluating the second derivatives via analytic formulas[6-13] has been found to improve the accuracy and decrease the computational time required to obtain the second derivatives[12,13].

The results described above were obtained for Hartree-Fock or Self-Consistent-Field (SCF) wave functions. SCF is computationally simple and can be applied to an ever increasing family of molecules[24]. However, its simplicity often means that the method is insufficient to make an accurate determination of many chemical properties, notably reaction barriers[25] and dissociation energies[26]. The largest effect that is missing from SCF is the instantaneous electron repulsion which leads to correlated electron motions and is thus called the correlation effect[27]. The magnitude of the energy correction is small, about 0.5% of the total for water[28], but the differential effect is often crucial to the chemistry. The added theoretical and computational complexity in determining correlated wave functions has slowed development of derivative techniques. This work details implementation of analytic second derivative formulas for one class of correlated wave function, configuration interaction.

The configuration interaction (CI) method has been one of the best studied of correlation methods and is one of the most used methods for actual calculations. The Graphical Unitary Group Approach (GUGA) has been one of the most systematically developed strategies for evaluation of CI wave functions and has provided a framework for full implementation of the direct CI method[29]. Allied with this is the method's facile ability to determine the one and two particle density matrices which are an integral part of the derivative formalism described here.

Earlier work by Brooks and co-workers[14] has established the feasibility of calculating analytic gradients for CI wave functions within the GUGA framework. Two novel procedures are required for the extension to second derivatives, the second order coupled-perturbed Hartree-Fock and the first order coupled perturbed configuration interaction equations. Gerratt and Mills[8] proposed coupled perturbed Hartree-Fock for the solution of the first order correction to the SCF wave function, and Pople and co-workers[11] cast it in a form suitable for solving problems of arbitrary size. The extension to second order is mainly an algebraic extension, first successfully implemented by Osamura and Yamaguchi[30]. An interesting suggestion by Handy[31] showed that the solution of the full set of second order equations could be avoided, and its implementation will be discussed.

The coupled perturbed CI equations determine the first order correction to the CI expansion due to a nuclear perturbation. For the first derivative it is easily shown that the first order correction makes no contribution. For second derivatives, however, it does contribute and requires the solution of a set of linear equations the length of the CI expansion. The work presented here adapts a formalism first proposed by Osamura and co-workers[17] for the solution of the first order CPMCHF equations. The equations are the CI equivalent of the CPHF and are thus termed the coupled perturbed CI (CPCI) equations. A derivation of these equations is presented and a practical implementation using a variant of the direct CI method is detailed. This includes discussion of the convergence properties of a number of iterative methods and a proposal for symmetry adaptation of the equations.

The method has been applied to a number of test cases and was verified by comparison with finite difference results. The timings for the steps of the two approaches to determination of second derivatives are examined and compared with theoretical orders for the processes. The utility of the method will be discussed especially as applied to larger molecules.

2 CHARACTERISTICS OF CI AND THE GRAPHICAL UNITARY GROUP APPROACH

The work presented here uses the unitary group approach for the evaluation of matrix elements and to generate the list of configurations that are used. The discussion of the implementation will use the graphical representation as an aid in understanding the problem. The unitary group approach (UGA) and its graphical representation (GUGA) have been discussed by many authors[32-41] so only a short outline will be presented here. Emphasis will be made on those aspects of a GUGA direct CI program which have bearing on the solution of the CPCI equations.

2.1 Considerations for a Direct CPCI Formalism

CI is one of the most general methods that has been applied to the correlation problem. The wave function is expanded in a set of spin-space adapted configurations. Straightforward application of the variational principle allows the expansion coefficients to be determined by solution of the secular problem in the space of the configuration state functions. Determination of the first order corrections to the CI wave function can make use of the methodology for CI to a large extent. The differences that arise are considered here.

The spin-space adapted configurations of the CI expansion are products of a set of molecular orbitals. In the standard approach these orbitals are required to be an orthonormal set since this choice greatly reduces the complexity of the matrix element evaluation[41]. One common choice is the set of orbitals that satisfy the SCF condition augmented by the canonical orthogonal set of orbitals generated in the diagonalization of the Fock matrix. Many alternatives have been used including the natural orbitals[43,44], improved virtual orbitals[45], and orbitals from a multiconfiguration SCF (MCSCF) in a smaller space. In calculations where only the energy is to be determined each of these sets is acceptable and has advantages in terms of lowering the total energy or improving some other physical characteristic.

The situation is changed somewhat if the derivatives of the energy are to be calculated. Since the orbital basis is implicitly dependent on the nuclear geometry its variation on nuclear perturbations must be considered. Since the orbital set is held fixed in the CI method it is a non-variational parameter and its derivative, like those of the basis functions, must be evaluated at each order. Thus the orbital basis chosen must allow definition of the correction due to nuclear perturbation. The only case previously developed is for the SCF wave function [8,16,17] and MCSCF wave functions are under current development[18,46].

Vital to any CI method is the evaluation of the spin-coupling coefficients between the expansion configurations. While the general solution to spin-coupling problems is known and can be expressed in many equivalent forms[47] care must be exercised that the resulting formalism is sufficiently general. Naturally the same must be true for CPCI but of greater importance is the fact that for orthonormal bases the spin-coupling coefficients are independent of the nuclear degrees of freedom[48]. This means that any method which works for CI can be adapted for the evaluation of the first order wave function.

Another consideration is the fact that the CI expansion is relatively slow to converge[49]. The exact solution to Schrodinger's equation requires the use of a full CI expansion, the size of which is given by Weyl's formula[36],

$$\frac{N}{\text{FCI}} = \frac{2S+1}{n+1} \binom{n+1}{N/2-S} \binom{n+1}{n-N/2+S+1} \quad (2.1.1)$$

where n is the number of molecular orbitals in the basis set, S is the total spin and N is the number of electrons. In general the CI method is used with truncated expansions, often defined by the number of replacements from some reference configuration, e.g. single and double replacements from an SCF configuration (SDCI). Even then it is not unusual for small molecules, tri- or tetratomics, to require tens or hundreds of thousands of configurations to achieve a physically accurate description. For CI second derivatives to be a useful method it must be possible to determine the first order wave function for long expansions.

In the CI problem this limitation was overcome by the use of the direct CI method, first proposed by Roos[50]. The direct CI method makes use of iterative methods[51] for the extraction of the lowest eigenvalues and eigenvectors, notably using Davidsons algorithm[52]. Davidson's algorithm is an iterative procedure which requires storage only for a set of trial vectors and their products with the hamiltonian matrix. For the first order correction to the CI wave function a similar direct process, this time for the

solution of a large set of linear equations will be desirable. Pople and co-workers[11] have shown that such an iterative scheme is possible in their evaluation of the first order correction to the SCF wave function.

The last aspect of CI which requires modification for treatment of the CPCI method is the utilization of molecular symmetry. Most small molecules in their equilibrium geometry have some elements of spatial symmetry[53]. The totally symmetric nature of the hamiltonian means that the configuration space can be put into block diagonal form. This result follows because only those configuration pairs where the direct product of the electronic wave function symmetries contains the totally symmetric representation will be non-zero. Often the point group symmetry of a molecule is isomorphic to a non-degenerate abelian group and only those electronic states of the same symmetry will interact. This results in a significant reduction in the size of the secular problem to be solved and is built into most state of the art CI algorithms.

When the effect of a nuclear perturbation is evaluated the effective symmetry of the nuclear frame and the electronic wave function may be reduced. This allows configurations which formerly had no interaction with the reference to contribute. If no use of molecular symmetry is made these interactions are evaluated correctly but the number of resultant equations quickly becomes unmanageable and the number of insignificant operations, i.e.

multiplications by zero, becomes a dominant time consideration. If the derivatives of the nuclear frame are treated in a symmetry adapted manner the problem again becomes block diagonal and much more tractable.

2.2 The Graphical Unitary Group Approach

The unitary group provides a convenient framework for the evaluation of hamiltonian matrix elements by defining an ordered, spin-adapted basis set, the Gelfand-Tsetlin basis[32]. Early work by Jordan[33], Gelfand[32], Beidenharn[34], and Moshinsky[35] resulted in formulas applicable to arbitrary spin systems, and Paldus[36] specialized the UGA to the CI problem. Writing the hamiltonian in the notation of second quantization

$$H = \sum_{ij} h_{ij} X_{ij}^+ X_{ij} + \sum_{ijkl} (ij|kl) X_{ij}^+ X_{kl}^+ X_{ij} X_{kl} \quad (2.2.1)$$

the unitary group generators may be identified as

$$E_{ij} = X_{ij}^+ X_{ij} \quad (2.2.2a)$$

and the two electron term is a product of generators

$$e_{ijkl} = X_{ij}^+ X_{kl}^+ X_{ij} X_{kl} = E_{ij} E_{kl} - \delta_{ij} E_{kl} \quad (2.2.2b).$$

Non-zero matrix elements for the unitary group operators

$$\langle I | E_{ij} | J \rangle \neq 0 \quad (2.2.3)$$

obey the relation that $I > J$ if $i > j$, where I and J denote ordered Gelfand states.

In addition the following equivalences hold between operators[37]

$$E = E_{ij} + E_{ji} \quad (2.2.4a)$$

and

$$e_{ijkl} = e_{klij} + e_{jilk} + e_{lkji} \quad (2.2.4b).$$

Paldus[36] showed that the triangular tableau representation given by Gelfand and Tsetlin[32] could be replaced by a three column table, the Paldus table, when the spin system being described was restricted to electrons. The three columns, commonly labeled a,b and c, give the number of singlet coupled pairs of electrons, the number of unpaired electrons, and the number of unoccupied MO's respectively. As each orbital is coupled to its predecessors a new row of the table is generated. The method is limited to non-degenerate point groups so MO's are at most doubly occupied which in conjunction with the restrictions of Fermi statistics limits the possible changes in (a,b,c) to just four cases

case	a	b	c		
0	0	0	1	unoccupied	
1	0	1	0	spin increase	(2.2.5).
2	1	-1	1	spin decrease	
3	1	0	1	doubly occupied	

Some consideration of these cases shows that the following relations hold between a, b, and c,

$$a + b + c = i \quad (2.2.6)$$

$$2a + b = n \quad (2.2.7)$$

$$b_i = 2S_i$$

(2.2.8)

where n_{ei} is the number of electrons and S_i the total spin in the first i orbitals. A recent review of this material has been given by Paldus[37].

Shavitt[38] further compacted the notation by showing that the number of distinct rows in a Paldus table was much smaller than the number of configurations. A complete list of the Paldus tables could be given by compiling a list of the distinct rows and their interconnections, the distinct row table (DRT). An example of a DRT is given in Table I.

While the numerical form of the DRT is a very powerful computational realization of the unitary group it is Shavitt's proposal of a graphical representation that has allowed for many of the insights into the construction of matrix elements. The graphical equivalent of a DRT is formed by replacing each distinct row by a point on a graph. The points are labeled by the a and b indices and the orbital number, while the c value may be recovered by the use of eq.(2.2.6). The graph is defined by grouping rows with common a values together, increasing to the left. Next, within each group those rows with common b values are placed vertically, b increasing as the columns go to the left, and the orbital index is shown by a vertical displacement increasing from bottom to top.

Configurations are then defined by drawing segments to connect the rows which appeared in the Paldus table. The four cases are then seen to correspond to segments of different slope, the unoccupied orbital being vertical and cases 1 to 3 having ever decreasing slope. Superimposing all configurations, called walks, on the same graph completes what is commonly called a Shavitt graph. All configurations represent the same number of electrons coupled to the same total spin and if a vacuum row, (000), is included then all valid configurations (walks) start at the upper left and trace continuous paths until they meet at the lower right. Figure I shows a completed Shavitt graph.

The matrix elements take on a simple pictorial form in the graphical representation. The orbital indices on the generator designate levels of the graph between which the two walks may take separate paths, the range $R(E_{ij})$. Outside of this range they must coincide so that a closed loop on the graph is formed, with examples being shown in figure II. The numerical value of the matrix element is given by a product over the range of the loop,

$$\langle I | E_{ij} | J \rangle = \prod_{n=j}^i W(T_n, b_n) \quad (2.2.9a)$$

and

$$\langle I | e_{ijkl} | J \rangle = \prod_{S1} W(T_n, b_n) \left[\sum_{x=0}^1 \prod_{S2} W(T_x, b_n) \right] \quad (2.2.9b)$$

where W is a function of T_n , the segment pair forming the bra and ket walks at the n th level, and b_n , the b -value of the ket walk at the n th level. The ranges $S1$ and $S2$ are

given by

$$\begin{aligned} S_2 &= R(E_{ij}) \cup R(E_{kl}) \\ S_1 &= R(E_{ij}) \cap R(E_{kl}) - S_2 \end{aligned} \quad (2.2.10)$$

and the sum over x gives the possible spin recouplings. This form for the two electron term was first given by Shavitt and Paldus [39,40].

Once the matrix elements have been evaluated the graphical representation also suggests an easy route to determining the lexical indices. Shavitt[38] introduced a recursive algorithm for assigning weight factors to the segments so that the sequence number of a configuration is given by

$$I = \sum_n Y_n^j \quad (2.2.11)$$

where Y_n^j is the weight of the j th segment and n labels the orbital. These weights give a sequential numbering to the walks on the graph which preserves the lexical order. Graphically the lower of a pair of walks is the one which is on the left when the two walks separate, tracing from the top of the graph. Additionally the weighting process determines a set of counting indices for the rows that tell the number of paths to the bottom of the graph from that row, commonly called lower walks. The graphical representation of the UGA has been reviewed recently by Shavitt[41].

The unitary group does not take advantage of spatial point group symmetry in its original form but it can be built into the graphical representation. Shavitt[54] and Brooks[55] have each proposed modifications to the graph structure but Brooks' approach can be seen as an extreme form of Shavitt's. In each case a symmetry index is added to elements of the graph and the symmetry of a walk is given by the symmetry direct product over the partially occupied orbitals, cases 1 and 2. Each method is limited to utilization of real abelian point groups.

Shavitt's method allows separate sequential indexing of each symmetry block of the hamiltonian by adding a symmetry index to each arc and vertex. A completed loop is then paired with all appropriate head and tail symmetries that give the desired total symmetry. Brooks took advantage of the fact that in general eigenfunctions are sought for only one symmetry block. Thus a distinct row for each valid set of head, loop and tail can be created and the others discarded before the evaluation of the matrix elements. The merits of each of these strategies will be discussed in further detail for the symmetry adaptation of the CPCI equations.

The last aspect of the GUGA methodology that must be discussed is its utilization as a direct CI. The majority of CI calculations done are single and double replacements from one or a number of configurations. Roos[50] showed that for a closed shell singlet this means that the unique

matrix elements could be found analytically and the product

$$\sigma = HC \quad (2.2.12)$$

evaluated directly as opposed to forming and storing the hamiltonian. Siegbahn[29] showed that the unitary group provided a means of factoring the matrix elements for CISD from an arbitrary set of references. This is seen if the orbitals occupied in some reference are grouped together at the top of the graph, as shown in figure III, allowing eq.(2.2.9a) to be factored,

$$\langle I | E_{ij} | J \rangle = \prod_n^{\text{int}} W(T, b)_{nn} \prod_n^{\text{ext}} W(T, b)_{nn} \quad (2.2.13),$$

where int refers to the range of occupied or internal orbitals and ext to the unoccupied or external range of orbitals. The two electron term can require that two products over the internal space be kept but this poses no serious difficulty.

Consideration of the graph over the external orbital range shows a repetitive nature. This reflects the fact that it is possible to enumerate all the partial products over the external orbitals. For the internal space a general method such as the Loop Driven GUGA formalism of Brooks and Schaefer[55] is used. Recent improvements in the direct CI method have included elimination of the need to hold the complete CI vector and product in core[56], adaptation of the external space to a vector processor[57], and generalization of the configuration selection scheme[58].

2.3 CI Energy Expressions and Definitions

In the development of CI derivatives and the coupled perturbed CI equations the following definitions and conventions will be used. Indices denoting the orbital expansions will be lower case roman with i, j, k and l denoting the molecular orbitals and m, n, o and p the atomic orbitals. Similarly r and s will be used for sums over the MO basis introduced by the orbital corrections. The configuration space will be given by upper case romans $I, J, K, \dots$ and the nuclear coordinates will be denoted by lower case roman $a, b, \dots$.

The hamiltonian will be written as

$$H = \sum_{IJ} a_{ij} h_{ij} + \sum_{ijkl} b_{ijkl} (ij|kl) \quad (2.3.1)$$

where the second quantization operators have been replaced by

$$a_{ij} = \langle I | E_{ij} | J \rangle \quad (2.3.2a)$$

and

$$b_{ijkl} = \langle I | e_{ijkl} | J \rangle \quad (2.3.2b)$$

and the one and two electron molecular integrals are defined by

$$h_{ij} = \sum_{mn} C_m^i C_n^j h_{mn} \quad (2.3.3a)$$

and

$$(ij|kl) = \sum_{mnop} C_m^i C_n^j C_o^k C_p^l (mn|op) \quad (2.3.3b).$$

It will also be useful to express the CI energy in terms of

The symmetric one and two particle density matrices [59]

$$g_{ij} = \sum_{IJ} C_{Iij}^{+IJ} C_J \quad (2.3.4a)$$

$$G_{ijkl} = \sum_{IJ} C_{Iijkl}^{+IJ} C_J \quad (2.3.4b)$$

which unlike the unitary group operators carry the same permutational symmetry as the MO integrals

$$g_{ij} = g_{ji} \quad (2.3.5a)$$

$$G_{ijkl} = G_{jikl} = G_{ijlk} = G_{jilk} = G_{klij} = G_{lkij} = G_{klji} = G_{lkji} \quad (2.3.5b).$$

The energy, in terms of the density matrix, is

$$E = \sum_{ij} g_{ij} h_{ij} + \sum_{ijkl} G_{ijkl} (ij|kl) \quad (2.3.6)$$

or substituting eq.(2.3.3) and interchanging the AO and MO sums we arrive at

$$E = \sum_{mn} g_{mn} h_{mn} + \sum_{mnop} G_{mnop} (mn|op) \quad (2.3.7)$$

where the "back-transformed" density matrices,

$$g_{mn} = \sum_{ij} C_{mij}^{ij} C_n g_{ij} \quad (2.3.8a)$$

$$G_{mnop} = \sum_{ijkl} C_{mijkl}^{ijkl} C_n G_{ijkl} \quad (2.3.8b)$$

as proposed by Brooks and co-workers[14] have been used.

Two other definitions which will prove useful are the lagrangian matrix

$$\epsilon_{ir} = \sum_j g_{ij} h_{rj} + 2 \sum_{jkl} G_{ijkl} (rj|ki) \quad (2.3.9)$$

And the Y-matrix defined by Osamura and co-workers[17]

$$Y_{irjs} = g_{ij} h_{rs} + 2 \sum_{kl} [G_{ijkl}(rs|kl) + 2G_{ikjl}(rk|sl)] \quad (2.3.10).$$

3 THEORY OF CI ENERGY DERIVATIVES

3.1 General Aspects of Derivatives

Before embarking on derivation of the explicit formulas for the derivatives some simplifications can be made on general considerations. In the Born-Oppenheimer approximation the nuclear energy is treated classically so its contribution will not be included explicitly. Beginning with the electronic part of the CI energy expressed as an expectation value,

$$E = \sum_{IJ} C_I^+ H_{IJ} C_J \quad (3.1.1).$$

Formal differentiation with respect to nuclear coordinate a and application of the chain rule gives the CI derivative as,

$$\frac{\partial E}{\partial a} = \sum_{IJ} \left[\frac{\partial C_I^+}{\partial a} H_{IJ} C_J + C_I^+ \frac{\partial H_{IJ}}{\partial a} C_J + C_I^+ H_{IJ} \frac{\partial C_J}{\partial a} \right] \quad (3.1.2).$$

this equation can be simplified if we recall that the CI expansion is an eigenvector of the hermitian hamiltonian matrix so the CI energy can be factored out yielding

$$E = \sum_I C_I^+ \left[\frac{\partial C_I}{\partial a} + \sum_J \left(\frac{\partial C_J}{\partial a} H_{IJ} - H_{IJ} \frac{\partial C_J}{\partial a} \right) C_J \right] \quad (3.1.3).$$

Comparing this expression with what is obtained by differentiating the normalization condition for the CI wave function,

$$\frac{\partial}{\partial a} \sum_I C_I^+ C_I = \sum_I \left[\frac{\partial C_I^+}{\partial a} C_I + C_I^+ \frac{\partial C_I}{\partial a} \right] = 0 \quad (3.1.4)$$

the first term goes to zero leaving

$$E^a = \sum_{IJ} C_I^+ \frac{\partial H}{\partial a} C_J \quad (3.1.5)$$

as the only term that needs to be explicitly evaluated.

An important fact to note is that this argument only requires that we begin with a normalizable eigenfunction of the hamiltonian. Thus we can obtain a formal expression for the second derivative directly from eq.(3.1.5) by differentiating

$$\frac{\partial E^a}{\partial b} = E^{ab} = \sum_{IJ} \left[\frac{\partial C_I^+}{\partial b} \frac{\partial H}{\partial a} C_J + C_I^+ \frac{\partial^2 H}{\partial b \partial a} C_J + C_I^+ \frac{\partial H}{\partial a} \frac{\partial C_J}{\partial b} \right] \quad (3.1.6).$$

Inspection of this expression shows the origin of the two novel terms that arise in the CI second derivative. The hamiltonian is dependent on the MO expansion which is a non-variational parameter with respect to the CI energy. Thus to evaluate the second derivative of the CI hamiltonian requires the second order change in the MO expansion which is given by the second order CPHF. The first and third terms contain the derivative of the CI expansion coefficients along with the derivative of the hamiltonian. Since, in general, the derivative of the hamiltonian does not commute with the hamiltonian the CI vector cannot be a

simultaneous eigensolution and these terms cannot be simplified as in eq. (3.1.3).

A number of identities concerning derivatives will also prove useful. The derivatives of the hamiltonian will require the derivatives of MO integrals which are given by

$$h_{ij}^a = h_{ij}^a + \sum_r (U_{ir}^a h_{rj}^a + U_{jr}^a h_{ir}^a) \quad (3.1.7a)$$

$$(ij|kl)^a = (ij|kl)^a + \sum_r [U_{ir}^a (rj|kl) + U_{jr}^a (ir|kl) + U_{kr}^a (ij|rl) + U_{lr}^a (ij|kr)] \quad (3.1.7b)$$

where h_{ij}^a and $(ij|kl)^a$ are the AO derivative integrals transformed to the MO basis as in eq.(2.3.3). U^a is the first order correction to the SCF wave function defined by Gerratt and Mills[8] as

$$\frac{\partial C}{\partial a} = \sum_r U_{ir}^a C_{r m}^i \quad (3.1.8).$$

The extension to the second order correction will be defined by,

$$\frac{\partial^2 C}{\partial b \partial a} = \sum_r U_{ir}^{ab} C_{r m}^{i} \quad (3.1.9)$$

which has been evaluated by Osamura and Yamaguchi[30].

3.2 The CI Gradient Expression

The energy first derivatives for CI wave functions have been derived by Brooks and co-workers[14] in the GUGA formalism and by Pople and co-workers[15] for the special case of a doubles wave function. Some of the important terms for the second derivative appear here in a simpler fashion than for second derivatives so the derivation will be given briefly. Substituting the hamiltonian from equation (2.3.1) into equation (3.1.5) and using the fact that the coupling coefficients are independent of the geometry gives,

$$E^a = \sum_{IJ} C_I^+ \left[\sum_{ij} a_{ij}^{IJ} h_{ij}^a + \sum_{ijkl} b_{ijkl}^{IJ} (ij|kl)^a \right] C_J \quad (3.2.1)$$

then using eq.(3.1.7) and eq.(2.3.4)

$$E^a = \sum_{ij} g_{ij}^a [h_{ij}^a + \sum_r (U_{ir}^a h_{rj} + U_{jr}^a h_{ir})] + \sum_{ijkl} G_{ijkl} [(ij|kl)^a + \sum_r (U_{ir}^a (rj|kl) + U_{jr}^a (ir|kl) + U_{kr}^a (ij|rl) + U_{lr}^a (ij|kr))] \quad (3.2.2).$$

this simplifies by separating terms involving the derivative integrals from the terms giving the orbital correction and using eq.(2.3.5) as follows

$$\sum_{ijkl} G_{ijkl} U_{rk}^a (ij|rl) = \sum_{ijkl} G_{ijkl} U_{klij}^a (kl|rj) \quad (3.2.3a)$$

$$= \sum_{ijkl} G_{ijkl} U_{ijkl}^a (rj|kl) \quad (3.2.3b)$$

allows U^a to be factored out. Making the analogous

rearrangement on the other terms yields

$$E^a = \sum_{ij} g_{ij}^a h_{ij}^a + \sum_{ijkl} G_{ijkl}^a (ij|kl) + 2 \sum_{ir} U_{ir}^a \epsilon_{ir} \quad (3.2.4)$$

using eq.(2.3.9) in the last term.

The only remaining step is probably the most important computationally. The integral transformation step is of order n^5 , where n is the number of basis functions, which would need to be repeated for each nuclear degree of freedom for the derivative integrals. Brooks and co-workers[14] showed that this step could be avoided by defining the "back-transformed" density matrix of eq.(2.3.8). This is also an n^5 step but it only needs to be performed once and allows the final expression to be written

$$E^a = \sum_{mn} g_{mn}^a h_{mn}^a + \sum_{mnop} G_{mnop}^a (mn|op) + 2 \sum_{ir} U_{ir}^a \epsilon_{ir} \quad (3.2.5).$$

A couple of properties of this formalism should be noted for later use in evaluating the effectiveness of the analytic second derivatives. First it is general in the sense that no restriction has been made on the type of CI expansion used. Brooks' initial program was limited to closed shell singlet states by the CPHF solution but recent work has extended this to most of open-shell SCF cases [16],[17] and MCSCF-multi reference cases[46]. Further the wave function can be evaluated in full symmetry since only the density matrix must be combined with the derivative integrals. This requires only a sort step on the density

matrix before Dupuis' petite list formalism[4],[12] for derivative integrals may be used. The amount to which analytic second derivatives can be simplified and retain these two attributes will determine their utility.

3.3 The CI Hessian Expression

In principle the derivation could proceed directly from equation (3.2.5) by differentiating with respect to a second coordinate but this would entail defining derivatives of the CPHF expansion, a step best avoided. Instead begin with equation (3.1.6) and as with the gradient replace the hamiltonian using equation (2.3.1) and differentiate

$$\begin{aligned}
 E^{ab} = & \sum_{IJ} \frac{\partial C}{\partial b} \frac{1}{I} \left[\sum_{ij} a_{ij} \frac{\partial h}{\partial a} \right]_{ij} + \sum_{ijkl} b_{ijkl}^{IJ} \frac{\partial (ij|kl)}{\partial a} \frac{C}{J} \\
 & + \sum_{IJ} C \frac{1}{I} \left[\sum_{ij} a_{ij} \frac{\partial^2 h}{\partial b \partial a} \right]_{ij} + \sum_{ijkl} b_{ijkl}^{IJ} \frac{\partial^2 (ij|kl)}{\partial b \partial a} \frac{C}{J} \quad (3.3.1). \\
 & + \sum_{IJ} C \frac{1}{I} \left[\sum_{ij} a_{ij} \frac{\partial h}{\partial a} \right]_{ij} + \sum_{ijkl} b_{ijkl}^{IJ} \frac{\partial (ij|kl)}{\partial a} \frac{\partial C}{\partial b} \frac{C}{J}
 \end{aligned}$$

A fundamental difference from equation (3.2.1) is that only the second term can be expressed in terms of density matrices, the step which gave most of the simplifications found for the gradient. The first and third term may be compactly expressed by defining a hamiltonian made from derivative integrals,

$$H^{ab} = \sum_{IJ} a_{ij}^{IJ} \frac{\partial h}{\partial a} \frac{1}{ij} + \sum_{ijkl} b_{ijkl}^{IJ} \frac{\partial (ij|kl)}{\partial a} \frac{1}{ijkl} \quad (3.3.2)$$

and contraction of the CI vector on this matrix,

$$B_I^{ab} = \sum_{IJ} H_{IJ}^{ab} C_J \quad (3.3.3).$$

While this term requires the transformation step that was

avoided for the gradient it will be shown that it is necessary and that the inclusion of the orbital contribution is also advantageous.

Substitution of B^e and the density matrices from equation (2.3.4) into the second derivative expression yields

$$E^{ab} = 2 \sum_I \frac{\partial C}{\partial b \partial I} B^e_I + \sum_{ij} g_{ij} \frac{\partial^2 h}{\partial b \partial a \partial ij} + \sum_{ijkl} G_{ijkl} \frac{\partial^2 (ij|kl)}{\partial b \partial a} \quad (3.3.4).$$

To obtain the working formulas the second derivatives of the MO integrals must be evaluated. Treating the one electron term in detail we begin by differentiating equation (2.3.3a) which yields

$$\begin{aligned} \frac{\partial^2 h}{\partial b \partial a \partial ij} = & \sum_{mn} \left[\frac{\partial^2 C}{\partial b \partial a} C^i_m C^j_n + \frac{\partial C}{\partial b} C^i_m \frac{\partial C}{\partial a} C^j_n + \frac{\partial C}{\partial a} C^i_m \frac{\partial C}{\partial b} C^j_n + C^i_m \frac{\partial^2 C}{\partial b \partial a} C^j_n \right] h_{mn} \\ & + \sum_{mn} \left[\frac{\partial C}{\partial b} C^i_m C^j_n + C^i_m \frac{\partial C}{\partial b} C^j_n \right] \frac{\partial h}{\partial a \partial mn} \\ & + \sum_{mn} \left[\frac{\partial C}{\partial a} C^i_m C^j_n + C^i_m \frac{\partial C}{\partial a} C^j_n \right] \frac{\partial h}{\partial b \partial mn} + \sum_{mn} C^i_m C^j_n \frac{\partial^2 h}{\partial b \partial a \partial mn} \end{aligned} \quad (3.3.5a)$$

Substituting the CPHF identities from eqs. (3.1.8-9) and extending the MO definition to second derivative integrals gives

$$\begin{aligned} = & h^{ab}_{ij} + \sum_r \left[U^{ba}_{ir} h^{ab}_{rj} + U^{ba}_{jr} h^{ab}_{ir} + U^{ab}_{ir} h^{ba}_{rj} + U^{ab}_{jr} h^{ba}_{ir} \right] \\ & + \sum_r \left[U^{ab}_{ir} h^{ba}_{rj} + U^{ab}_{jr} h^{ba}_{ir} \right] + \sum_{rs} \left[U^{ab}_{ir} U^{ba}_{js} h^{rs} + U^{ba}_{ir} U^{ab}_{js} h^{sr} \right] \end{aligned} \quad (3.3.5b).$$

Differentiation with respect to the nuclear coordinates does

not affect the interchange symmetry of the MO indices so contraction with the density matrix simplifies the one electron term to

$$\sum_{ij} g_{ij} \frac{\partial^2 h}{\partial b \partial a} = \sum_{ij} g_{ij} h_{ij}^{ab} + 2 \sum_{ir} (U_{ir}^{b a} h_{rj}^{a b} + U_{ir}^{a b} h_{rj}^{b a}) + \sum_{ijrs} (U_{ir}^{a b} U_{js}^{b a} + U_{ir}^{b a} U_{js}^{a b}) g_{ijrs} h_{ijrs} \quad (3.3.6).$$

Similar treatment of the two electron integrals yields

$$\begin{aligned} \frac{\partial^2 (ij|kl)}{\partial b \partial a} &= (ij|kl)^{ab} \\ &+ \sum_r [U_{ir}^{b a} (rj|kl) + U_{jr}^{a b} (ir|kl) + U_{kr}^{a b} (ij|rl) + U_{lr}^{a b} (ij|kr)] \\ &+ \sum_r [U_{ir}^{a b} (rj|kl) + U_{jr}^{b a} (ir|kl) + U_{kr}^{b a} (ij|rl) + U_{lr}^{b a} (ij|kr)] \\ &+ \sum_r [U_{ir}^{ab} (rj|kl) + U_{jr}^{ab} (ir|kl) + U_{kr}^{ab} (ij|rl) + U_{lr}^{ab} (ij|kr)] \\ &+ \sum_{rs} [(U_{ir}^{a b} U_{js}^{b a} + U_{ir}^{b a} U_{js}^{a b}) (rs|kl) + (U_{kr}^{a b} U_{ls}^{b a} + U_{kr}^{b a} U_{ls}^{a b}) (ij|rs)] \\ &+ \sum_{rs} [(U_{ir}^{a b} U_{ks}^{b a} + U_{ir}^{b a} U_{ks}^{a b}) (rj|sl) + (U_{ir}^{a b} U_{ls}^{b a} + U_{ir}^{b a} U_{ls}^{a b}) (rj|ks)] \\ &+ (U_{jr}^{a b} U_{ks}^{b a} + U_{jr}^{b a} U_{ks}^{a b}) (ir|sl) + (U_{jr}^{a b} U_{ls}^{b a} + U_{jr}^{b a} U_{ls}^{a b}) (ir|ks)] \end{aligned} \quad (3.3.7).$$

This simplifies on contraction with the two particle density matrix in a manner analagous to the gradient case for the first four terms but the last two terms have been grouped to indicate that two types survive. The final sum is

$$\begin{aligned}
\sum_{ijkl} G_{ijkl} \frac{\partial^2 (ij|kl)}{\partial \bar{b} \partial a} &= \sum_{ijkl} G_{ijkl} (ij|kl)^{ab} \\
&+ 4 \sum_{ijklr} U_{ir}^{ab} (rj|kl) + 4 \sum_{ijklr} [U_{ir}^a (rj|kl)^b + U_{ir}^b (rj|kl)^a] \\
&+ \sum_{ijrs} (U_{ir}^a U_{js}^b + U_{ir}^b U_{js}^a) (2 \sum_{kl} [G_{ijkl} (rs|kl) + 2 G_{ikjl} (rk|sl)])
\end{aligned} \quad (3.3.8)$$

Combination of (3.3.4), (3.3.6) and (3.3.8) followed by the substitution of the lagrangian, the derivative lagrangian

$$\epsilon_{ir}^a = \sum_j g_{ij}^a h_{rj}^a + 2 \sum_{jkl} G_{ijkl} (rj|kl)^a \quad (3.3.9)$$

and the Y-matrix from eq.(2.3.10) gives the second

derivative equivalent of eq.(3.2.4). Next the

"back-transformed" density matrices can be used to avoid transformation of the second derivative integrals making the working equation

$$\begin{aligned}
E^{ab} &= \sum_{mn} g_{mn}^{ab} h_{mn}^{ab} + \sum_{mnop} G_{mnop} (mn|op)^{ab} \\
&+ 2 \sum_{ir} [U_{ir}^{ab} \epsilon_{ir}^{ab} + U_{ir}^a U_{ir}^b \epsilon_{ir}^{ba} + U_{ir}^b U_{ir}^a \epsilon_{ir}^{ab}] \\
&+ \sum_{irjs} [U_{ir}^a U_{js}^b + U_{ir}^b U_{js}^a] Y_{irjs} \\
&+ 2 \sum_I \frac{\partial^2 C^B}{\partial \bar{b} \partial I} \epsilon_I^A
\end{aligned} \quad (3.3.10)$$

3.4 The Coupled-Perturbed CI Equations

The CPHF procedure is well suited to the determination of the first order correction to the SCF wave function because it allows expression of the wave function change in terms of the unperturbed MO basis. Direct determination of the first order wave function would mean that partially transformed integrals would need to appear explicitly. In addition the use of the molecular orbital set as an orthonormal expansion set poses no computational difficulties since it is available through the SCF procedure.

The first order correction to the CI wave function differs on both of these counts. The CI wave function is not normally used as the basis for any higher order calculation and choosing the eigenvectors of the CI hamiltonian as a basis is simply not feasible for general CI calculations. Most methods now in use extract only the lowest eigenvalue and eigenvector with the ability of obtaining a few higher roots of the secular equation if desired. A practical method for determination of the first order CI wave function must have the same ability.

An expression for the determination of the first order wave function can be found by differentiation of the secular equation,

$$\frac{\partial}{\partial a} (H-E_0) C = 0 \quad (3.4.1a)$$

$$(H-E_0) \frac{\partial}{\partial a} C = (H-E_0) C \quad (3.4.1b)$$

which in principle yields the desired solution. Some consideration, however, shows that the system of equations is singular. This follows since E is an eigenvalue of H making at least one eigenvalue of $(H-EI)$ zero and thus the determinant must go to zero.

This singularity could be avoided, in principle, by removing the offending row of the matrix and fixing that element of the first order wave function to zero. This has a disadvantageous effect on the adaptation of a direct CI program in that the resultant matrix is non-square which is an unnecessary complication.

An approach that does not cause this difficulty was proposed by Lengsfeld[60] for MCSCF optimization. Zero can always be added to an equation without changing the solution. An appropriate form for zero can be seen by considering the projection operator for the reference state,

$$P = CC^+ \quad (3.4.2)$$

which when it operates on the corresponding first order wave function yields zero,

$$P \frac{\partial C}{\partial a} = C(C^+ \frac{\partial C}{\partial a}) = 0 \quad (3.4.3)$$

since the first order wave function must be orthogonal to the zeroth order wave function.

We can verify that addition of zero in this form has no other effects by showing that the original equation lies entirely in the conjugate space. The projector for the conjugate space,

$$Q=1-P \quad (3.4.4)$$

operating on eq.(3.4.1b) yields

$$Q(H - E_0) \frac{\partial C}{\partial a} = -Q(H - E_0) C \quad (3.4.5a)$$

$$[(H - E_0) - C(H - E_0)C] \frac{\partial C}{\partial a} = -(H - E_0)C + C(C(H - E_0)C) \quad (3.4.5b)$$

$$[(H - E_0) - C(H - E_0)C] \frac{\partial C}{\partial a} = -(H - E_0)C + C(H - E_0)C \quad (3.4.5c)$$

by use of eq.(3.1.5) and the hermiticity of the hamiltonian, which is identical to our starting point. Thus we can rewrite eq.(3.4.1) as

$$(H - E_0 + CC) \frac{\partial C}{\partial a} = -(H - E_0)C \quad (3.4.6)$$

which is non-singular.

An alternative derivation which was given by Osamura[17] which shows more clearly the identification as a coupled perturbed CI method. Beginning with a formal definition of the CI wave function as a Taylor expansion with respect to a nuclear perturbation,

$$C_I^0 = C_I^0 + \lambda \sum_{K \neq 0} \frac{a_K}{K} C_I^K + \dots \quad (3.4.7)$$

where the superscript indexes the eigenstate and $K=0$ defines the reference state. Similarly the hamiltonian and the energy are expanded,

$$H = H + \lambda H^a + \dots \quad (3.4.8)$$

$$E = E + \lambda E^a + \dots \quad (3.4.9).$$

Substitution into the secular equation and collection of

terms to first order in λ yields

$$\sum_J \left(H_{IJ} C_I^0 + H_{IJ} \sum_{K \neq 0} V_{KJ} C_K^0 - E_0 C_J^0 - E_0 \sum_{K \neq 0} V_{KJ} C_K^0 \right) = 0 \quad (3.4.10).$$

grouping like terms and left multiplying by C_I^{L+} gives

$$\sum_{K \neq 0} \left(\sum_{IJ} C_I^{L+} (H_{IJ} - E_0 \delta_{IJ}) C_J^K \right) V_{KJ}^a = - \sum_{IJ} C_I^{L+} C_J^K (H_{IJ} - E_0 \delta_{IJ}) C_J^0 \quad (3.4.11).$$

Using the fact that C^K is the K -th eigenvector the elements of V^a can be found easily as

$$V_{L0}^a = (E_0 - E_L) \sum_{IJ} C_I^{L+} C_J^K (H_{IJ} - E_0 \delta_{IJ}) C_J^0 / (E_L - E_0) \quad (3.4.12).$$

however the determination of the complete eigenspectrum is not possible for a general CI.

To remove this dependence from the solution we note that by defining V^a to be zero we could add a term $\delta_{K0} \delta_{L0}$ in eq.(3.4.11) and remove the restriction on K .

$$\sum_K \left(\sum_{IJ} C_I^{L+} (H_{IJ} - E_0 \delta_{IJ}) C_J^K + \delta_{K0} \delta_{L0} \right) V_{KJ}^a = - \sum_{IJ} C_I^{L+} C_J^K (H_{IJ} - E_0 \delta_{IJ}) C_J^0 \quad (3.4.13)$$

Multiplying on the left with the matrix of eigenvectors

$$\begin{aligned} \sum_{KL} \sum_{IJ} [C_I^{L+} C_J^K (H_{IJ} - E_0 \delta_{IJ}) + C_I^{L+} \delta_{K0} \delta_{L0}] V_{KJ}^a \\ = - \sum_{IJ} \sum_L C_I^{L+} C_J^K (H_{IJ} - E_0 \delta_{IJ}) C_J^0 \end{aligned} \quad (3.4.14)$$

and using the fact that the eigenvectors form a unitary matrix so the rows as well as the columns form orthonormal sets yields,

$$\begin{aligned}
& \sum_K \sum_{IJ} \delta_{MI} (H_{IJ} - E \delta_{IJ}) C_J^K + C_M^0 \delta_{K0} V_K^a \\
& = - \sum_{IJ} \delta_{IM} (H_{IJ} - E \delta_{IJ}) C_J^0 \quad (3.4.15).
\end{aligned}$$

Next insertion of the identity $\sum_N C_N^{K+} C_N^K$ on the right hand side yields

$$\begin{aligned}
& \sum_{IJ} (\delta_{MI} \delta_{JN} (H_{IJ} - E \delta_{IJ}) + C_M^0 C_N^0) \sum_K V_K^a C_N^K \\
& = - \sum_{IJ} \delta_{IM} (H_{IJ} - E \delta_{IJ}) C_J^0 \quad (3.4.16).
\end{aligned}$$

Recognizing the definition of the first order wave function from eq.(3.4.7) yields the final result in agreement with eq.(3.4.6). Again the fact that a term orthogonal to the final solution could be added to the equations without changing them allowed the singularity to be removed.

4 IMPLEMENTATION

Explicit dependence on the nuclear parameters enters through the integrals over the atomic orbital basis. The evaluation of these integrals after differentiation with respect to one or more nuclear coordinates has been treated by many authors[4,11-13] and will not be treated here other than to state that the derivative integrals are taken from the program by Saxe, Yamaguchi and Schaefer[13]. The use of these integrals in the molecular orbital basis is novel and some aspects will be discussed.

The wave function is implicitly dependent on the nuclear coordinates and the treatment of these terms will be covered in some detail. The first order CPHF solutions have been quite well studied and it is accepted that they can be solved in a stable and economical fashion using iterative methods. The extension to second order has been studied by Osamura and Yamaguchi[30] and will not be discussed as such but recently Handy[31] suggested a novel approach to determining the second order CPHF contribution to the CI second derivative. Analysis of this proposal and the dependence of the second order CPHF on derivative integrals will be examined.

Determination of an efficient method for the solution of the CPCI equations will be important. The number of configurations is much larger than the number of independent orbital parameters and the characteristics of the hessian have not been studied to determine suitability for iterative solution. In addition, neglect of molecular symmetry has much more serious consequences for the CPCI equations than for the corresponding CPHF equations. Thus an algorithm for symmetry adapted CPCI will be proposed.

4.1 MO Derivative Integrals

The difficulty with derivative integrals over the molecular orbital basis does not lie in the transformation required to obtain them. The four index transformation procedure has been well studied[61,62,63] and can be accomplished in a straightforward manner. However, for a molecule with M atoms and n basis functions the transformation step is of order $3M^5n$ which will grow to be an important computational consideration. Thus the choice of writing the equations involving derivative integrals in the MO basis must be examined. If the optimal procedure involves making the transformation, further questions concerning integral storage and evaluation of the orbital perturbation contribution must be raised.

Three terms in eq.(3.3.1) are strongly dependent on the derivative integrals, the derivative lagrangian, the contraction of the derivative hamiltonian and the second order CPHF. The efficiency of the overall process will be limited by the slowest step and economy measures in others may not be vital. Further any alternative formulation must not greatly increase the already substantial storage requirements.

The second order CPHF equations will be discussed again in the next section and their dependence on the MO derivative integrals given in eq.(4.2.2b). Osamura and co-workers have shown that the four index transformation of the atomic integrals can be avoided for first order CPHF. Instead a two index transformation on the expansion vectors of the iterative solution procedure is performed. The same approach can be applied to the second order equations with the derivative integrals⁵[30] avoiding the full 3M*n transformation step. The computational savings depends on the number of iterations required and the efficiency of the four index transformation.

Similarly a reformulation of the derivative lagrangian that would take advantage of the "back-transformed" density matrices could be sought. The problem with such an approach is that the lagrangian construction is of the same order as the transformation,⁵ n . This means that the overall reduction will be a small and constant factor.

The derivative hamiltonian is quite another matter. Restricting our attention to just the derivative integral contribution we define

$$H_{IJ}^a = \sum_{ij} a_{ij}^{IJ} h_{ij}^a + \sum_{ijkl} b_{ijkl}^{IJ} (ij|kl)^a \quad (4.1.1)$$

by analogy to eq.(3.3.3). A "back-transformation" step analogous to eq.(3.2.1) could be defined but it would be ill advised. The spin-coupling coefficients are sparse in the

orthonormal MO basis but "back-transformation" into the nonorthogonal AO basis would destroy this sparsity increasing the processing time for this step. In addition, the number of coefficients that arise in the MO basis would be overwhelming in most calculations.

Since the order of the derivative hamiltonian contraction goes as $3M^6n$, for a singles and doubles CI, efficient evaluation of B_a justifies the effort of transforming the derivative integrals. Further, once the derivative integrals have been transformed, alternative formulations for the CPHF and derivative lagrangian have no special merit for use in the CI equations. The AOCPHF formalism has been tested however, and is a viable alternative for higher SCF derivatives.

Treatment of the orbital perturbation correction proposed in eq.(3.1.7) is of order $3M^5n$. In the evaluation of the first order correction to the MCSCF wave function (CPMCHF) [17] Osamura proposed the use of a generalization of the lagrangian, the "bare" lagrangian

$$\epsilon_{ir}^{IJ} = \sum_j a_{ij}^{IJ} h_{rj} + \sum_{jkl} b_{ijlk}^{IJ} (r_j | kl) \quad (4.1.2)$$

for the equivalent of this term. For actual applications Hoffmann and co-workers[65] modified this by contraction with the CI vector to form the symmetric "half-bare" lagrangian,

$$\frac{I}{T} = \sum_J \left[\epsilon_{ir}^{IJ} + \epsilon_{ir}^{JI} \right] C_J \quad (4.1.3).$$

Formation of the symmetric "half-bare" lagrangian is of order N^5 but it only needs to be evaluated once and the final contribution is calculated by

$$\frac{\partial}{\partial I} B = \sum_J^H \frac{a}{IJ} C_J + \sum_{ir}^U \frac{a}{ir} \frac{I}{ir} T_{ir} \quad (4.1.4)$$

which is of order $3M^2N^2$, where N is the length of the CI expansion.

The choice between this form and eq.(3.3.3) is predicated on two factors, the size of the CI expansion and the nature of the final contraction. For an MCSCF wave function the CI expansion is typically limited to a few thousand configurations and the quality of the wave function is improved by optimization of the orbital expansion. This restriction means that the "half-bare" lagrangian may be held on a large scale storage device. In addition, this term arises in the wave function optimization and use of the "half-bare" lagrangian allows the imposition of restrictions on the orbital summations which arise in CPMCHF.

For a general CI wave function we have postulated that the configuration expansion is very long making storage of the "half-bare" lagrangian impossible and in the CI formalism restricted summations do not arise. Expression of the derivative integrals so as to include the orbital

perturbation has the added benefit of allowing the time consuming contraction against the CI expansion to be processed in one pass through a modified direct CI program.

The algorithm for processing small molecules is to transform the 3M sets of derivative integrals, evaluate the 3M derivative lagrangians and then add in the orbital contribution before evaluating B^0 . As the size of the molecular basis or the number of atoms increases this algorithm breaks down because the two electron integral list, the length of which goes as n^4 , cannot be stored for all 3M degrees of freedom simultaneously. This does not pose a restriction on the utility of the method but the processing sequence must be modified so that only one set of derivative integrals needs to be stored. This restriction will be discussed further with respect to the terms which are affected.

4.2 Evaluation of the Second Order CPHF Contribution

The second order CPHF equations are found by extending the expansion of the hamiltonian, wave function and energy to second order in a nuclear perturbation. Osamura and Yamaguchi have made this extension and solved the resultant equations[30] so the second order correction to the SCF wave function was taken as a given for this work. An alternative to the explicit solution of the second order CPHF equations for closed shell singlets is discussed here but the equations have been solved for more general cases.

The second order CPHF equations for a closed shell singlet are

$$(e_i - e_j) U_{ij}^{ab} - \sum_k^{\text{occ}} \sum_l^{\text{vir}} A_{kl,ij}^{ab} U_{kl}^{ab} = B_{0,ij}^{ab} \quad (4.2.1a).$$

the terms on the left hand side are the hessian

$$A_{kl,ij}^{ab} = 4(ij|kl) - (ik|jl) - (il|jk) \quad (4.2.1b)$$

and the eigenvalues of the SCF Fock matrix, e_i . The right

hand side is given by

$$\begin{aligned}
 B_{0,ij}^{ab} = & \epsilon_{ij}^{ab} - S_{ij}^{ab} e_j - \sum_{kl}^{occ} \epsilon_{kl}^{ab} [2(ij|kl) - (ik|jl)] \\
 & + \sum_m^{all} \sum_k^{occ} U_{mk}^a [4(ij|mk) - (im|jk) - (ik|jm)] \\
 & + \sum_m^{all} \sum_k^{occ} U_{mk}^b [4(ij|mk) - (im|jk) - (ik|jm)] \\
 & + U_{ji}^a e_j^{(b)} + U_{ji}^b e_j^{(a)} + U_{ij}^a e_i^{(b)} + U_{ij}^b e_i^{(a)} \quad (4.2.1c) \\
 & - \sum_m^{all} [U_{im}^a U_{mj}^b + U_{im}^b U_{mj}^a] e_i \\
 & - \sum_m^{all} [U_{jm}^a U_{mi}^b + U_{jm}^b U_{mi}^a] e_j \\
 & - \sum_m^{all} [U_{mi}^a U_{mj}^b + U_{mi}^b U_{mj}^a] e_m \\
 & + \sum_{mn}^{all} \sum_k^{occ} (U_{mk}^a U_{nk}^b + U_{mk}^b U_{nk}^a) [2(ij|mn) - (im|jn)]
 \end{aligned}$$

where $e_j^{(a)}$ is a diagonal element from a Fock matrix formed from true derivative integrals[11]. The form of eq.(4.2.1) is exactly the same as for first order CPHF and the hessian is exactly the same. The computationally expensive step is construction of the right hand side which takes $O(n^4)$ multiplications for each of the $3M(3M+1)/2$ unique terms.

Since the hessian is the same as for the first order equations the iterative method proposed by Pople and co-workers[11] offers a route to the solution of these equations, regardless of size. The drawback to this approach is that as the number of right hand sides increases the efficacy of iterative methods over determination of the inverse decreases. In addition should convergence difficulties arise a large number of iterative steps could be required, further decreasing the utility of this approach.

Hardy[31] noted that since the energy second derivative has such a simple dependence on the second order CPHF direct determination of this contribution might be a competitive alternative. The second order contribution can be expressed schematically as

$$U = \begin{matrix} ab & -1 & ab \\ A & B & \\ & 0 & \end{matrix} \quad (4.2.2)$$

then the contribution in eq.(3.3.10) is

$$U = \begin{matrix} ab & ab & -1 & ab \\ B & A & \epsilon & B \\ & 0 & & 0 \end{matrix} Z \quad (4.2.3)$$

where the Z vector can be found by

$$A Z = \epsilon \quad (4.2.4).$$

Since there is only one Z vector the advantages of an iterative method are regained and convergence difficulties should be more easily dealt with. A rigorous treatment of eqs.(4.2.2-4) follows.

The first step is to restrict eq.(4.2.3) to the linearly independent elements of U^{ab} by the second order orthonormality constraint

$$U_{ij}^{ab} + S_{ij}^{ab} + U_{ji}^{ab} = 0 \quad (4.2.5)$$

where

$$S_{ij}^{ab} = S_{ij}^{ab} + \sum_s [U_{is}^{ab} U_{js}^{ab} + U_{js}^{ab} U_{is}^{ab} - S_{is}^{ab} S_{js}^{ab} - S_{js}^{ab} S_{is}^{ab}] \quad (4.2.6).$$

Breaking the sum in eq.(4.2.3) into triangular ranges and adding zero in the form

$$\epsilon_{ri} U_{ir}^{ab} - \epsilon_{ri} U_{ir}^{ab}$$

yields

$$\sum_{ir} \epsilon_{ir} U_{ir}^{ab} = \sum_{i>r} [(\epsilon_{ir} - \epsilon_{ri}) U_{ir}^{ab} + \epsilon_{ri} (U_{ri}^{ab} + U_{ri}^{ab})] + \sum_i \epsilon_{ii} U_{ii}^{ab} \quad (4.2.7).$$

Using eq.(4.2.5) only the anti-symmetric part of the lagrangian remains explicitly dependent on U^{ab} .

The remaining term is still not completely independent since the energy is invariant to rotations among the occupied or virtual orbitals. These dependent elements of U^{ab} are given by

$$U_{ir}^{ab} = B_{0,ir}^{ab} / (\epsilon_r - \epsilon_i) - \sum_k^{\text{occ}} \sum_l^{\text{vir}} A_{kl,ir}^{ab} U_{kl}^{ab} / (\epsilon_r - \epsilon_i) \quad (4.2.8).$$

Substitution into eq.(4.2.7) yields

$$\begin{aligned} \sum_{ir} \epsilon_{ir} U_{ir}^{ab} &= \sum_{i>r} (\epsilon_{ir} - \epsilon_{ri}) B_{0,ir}^{ab} / (\epsilon_r - \epsilon_i) - \sum_{i>r} \epsilon_{ri} S_{ri}^{ab} \\ &\quad - 1/2 \sum_i \epsilon_{ii} S_{ii}^{ab} + \sum_l^{\text{occ}} \sum_r^{\text{vir}} \bar{X}_{lr} U_{lr}^{ab} \end{aligned} \quad (4.2.9)$$

where

$$\bar{X}_{ir} = \epsilon_{ir} - \epsilon_{ri} - \sum_{k>1}^{dep} A_{ir,kl} / (\epsilon_{ir} - \epsilon_{kl}) \quad (4.2.10)$$

The CPHF equation can now be solved formally as

$$U_{ir}^{ab} = \sum_k^{doc} \sum_l^{vir} [(\epsilon_{ir} - \epsilon_{kl}) \delta_{kl,ir} + A_{ir,kl}] B_{0,kl}^{-1} \quad (4.2.11)$$

and substituted into eq.(4.2.9). This makes the definition of the Z vector,

$$\sum_k^{doc} \sum_l^{vir} [(\epsilon_{ir} - \epsilon_{kl}) \delta_{kl,ir} + A_{ir,kl}] Z_{kl,ir} = \bar{X}_{ir} \quad (4.2.12)$$

which is solved by a modified first order CPHF program. The dependent blocks of Z can be defined as $(\epsilon_{ir} - \epsilon_{ri}) / (\epsilon_{ir} - \epsilon_{ri})$ making the final expression

$$\sum_{ir} \epsilon_{ir} U_{ir}^{ab} = \sum_{i>r} Z_{ir}^{ab} B_{0,ir}^{-1} - \sum_{i>r} \epsilon_{ri} S_{ir}^{ab} - 1/2 \sum_{ii} \epsilon_{ii} S_{ii}^{ab} \quad (4.2.13)$$

The accurate determination of the Z vector should be easier than the solution of the original equations but it will not result in computational savings unless the time limiting construction of $B_{0,ir}^{ab}$ can be improved. Expanding $B_{0,ir}^{ab}$ using eq.(4.2.1c) and reversing the order of summation in the derivative integral term allows

$$Z_{mk}^a = \sum_{i>r} Z_{ir}^a [4(ir|mk)^a - (im|rk)^a - (ik|rm)^a] \quad (4.2.14)$$

to be defined. This term is of order n^4 but only needs to be done $3M$ times followed by $3M*(3M-1)/2$ steps of order n^2 which will result in substantial savings as the number of

atoms increases. In addition this step can be performed for each set of MO derivative integrals in turn so the storage problem is avoided. Similar treatment of the terms dependent on the two electron integrals also aids in reducing the effort in the evaluation of the second order CPHF contribution.

4.3 Iterative Solution of the Coupled Perturbed CI Equations

The first order correction to the CI wave function is solved through a set of equations assumed to be so large that direct methods are impractical. Iterative methods offer an extendable approach and they have been shown to provide a practical path to the solution of a pair of related problems, the CI secular equation[52] and the CPHF equations[11]. Since the CI secular equation is an important time step in a CI energy determination we know that this set of equations must be handled with care.

The CPCI equation can be rewritten by defining

$$A = (H - E1 + CC)^T = (H' + D + CC)^T \quad (4.3.1)$$

where H' is the CI hamiltonian with the diagonal elements set to zero and D is a matrix of the diagonal elements of H less the reference energy. The iterative sequence is defined by

$$\sigma_i^i = H'B^i + DB^i + \beta_i^i C^i \quad (4.3.2)$$

where $\beta_i^i = C^T B^i$.

This term is evaluated with an adapted version of the SDGUGA direct CI program[56]. The modified diagonal elements are easily computed because the CI program normally calculates these once and stores them. Thus given the modified diagonals only two vectors, or fractions thereof, must be held in core at any time. Similarly by calculating

for each trial vector and updating the product vector only two vectors need to be held. The CI program was written to evaluate the first term with only fractions of the trial and product vectors held in core so the CPCI can be solved for any size of system limited only by available computation facilities.

The right hand side of eq.(3.4.6) can also be viewed as an iteration of a direct CI and a modification of order N but with the MO integrals replaced by their derivative counterparts. To accomplish this define,

$$B_{0,I}^a = \sum_J (H_{IJ}^a - E_0 \delta_{IJ}) C_J = B_I^a - E_0 C_I \quad (4.3.3)$$

which requires a larger change to the CI algorithm. It is neither practical nor productive to hold more than one set of derivative integrals simultaneously. Thus each degree of freedom is treated as a single iteration of the CI requiring the evaluation of the diagonal elements each time. Further this iteration process should be incorporated into the transformation procedure to reduce the storage for derivative integrals. Because both B_0^a and B^a are required later the scalar modification is done after storing the initial product.

The use of derivative integrals makes one important difference in that the reduced symmetry introduces coupling between configurations of different symmetry. Since the CI hamiltonian can be reduced to just those configurations that

interact by symmetry the configuration list must now be expanded. Thus in eq.(4.3.3) I runs over the full no symmetry configuration list while J can be restricted to just those configurations with the same symmetry as the reference.

The CPCI equations can now be given in the shorthand form,

$$\begin{matrix} a & a \\ AC & -B \\ & 0 \end{matrix} = 0 \quad (4.3.4)$$

which will be solved by expanding C^a in a set of trial vectors

$$C^a = \sum_i^m \alpha_i^a B^i \quad (4.3.5)$$

reducing the problem to the determination of α_i^a . Pople and co-workers[11] proposed one method which can be derived in the same manner as used by Weber, Lacroix, and Wanner[66] for Davidson's diagonalization algorithm. Equation (4.3.4) is equivalent to the statement that the scalar product of the left hand side with an arbitrary vector is zero. Choosing arbitrary vectors from the expansion set and substituting eqs.(4.3.2,5) gives

$$\begin{matrix} j & i & a & j & a \\ B & \sigma & \alpha & - B & B \\ & & i & & 0 \end{matrix} = 0 \quad (4.3.6)$$

which is a set of linear equations of order m, $m \ll N$, and can be solved by a direct method. To generate the set of trial vectors Pople proposed Schmidt-orthonormalization of the Krylov sequence[67],

$$\mathbf{B}^{m+1} = \sigma^m - \sum_i \langle \mathbf{B}^i | \sigma^m \rangle \mathbf{B}^i / \langle \mathbf{B}^i | \mathbf{B}^i \rangle \quad (4.3.7),$$

using Dirac notation for the inner product. The Krylov sequence spans the space of a divisor of the characteristic polynomial so it is converged when a linearly dependent vector is generated. Since A is closely related to the CI hamiltonian which is diagonally dominant a good approximation is to take $\mathbf{B} = \mathbf{B}_0$.

Another approach to determining an iterative sequence is minimization of the residual error. Given an orthonormal set of trial vectors the residual is defined by

$$\sum_i \alpha_i \mathbf{B}_i - \mathbf{B}_0 = \mathbf{R} \quad (4.3.8).$$

Minimization of the norm of the residual can be accomplished by differentiation with respect to α yielding

$$\frac{\partial |\mathbf{R}|^2}{\partial \alpha} = \sum_j \langle \mathbf{B}_j | \mathbf{B}_j \rangle \alpha_j - \langle \mathbf{B}_j | \mathbf{B}_0 \rangle = 0 \quad (4.3.9)$$

which leads to a set of equations that are quadratic in A .

To expand the vector set the method of coordinate relaxation can be used. Consider correcting the J th element by adding the unit vector $\mathbf{e}_J$ as an expansion vector,

$$\mathbf{R}_{m+1,J} = \mathbf{R}_{m,J} - \alpha_{m+1,J} \mathbf{e}_J \quad (4.3.10).$$

Left multiplying by $\mathbf{e}_J^T$ and solving for α yields

$$\alpha_{m+1,J} = \mathbf{R}_{m,J}^T \mathbf{e}_J / \langle \mathbf{e}_J | \mathbf{e}_J \rangle \quad (4.3.11).$$

Computing this ratio for each element gives the analogue of Davidson's simultaneous relaxation method[52,66].

Both of these methods can be solved for all degrees of freedom with a common set of expansion vectors. This technique is not as effective as one might hope because solutions tend to come from orthogonal spaces, essentially blocked by molecular symmetry. Thus a separate expansion for each symmetry type would be as effective.

The dependence of the second derivative on the CPCI is quite simple, so as was proposed for the second order CPHF contribution it is possible to avoid explicit determination of the CPCI. This changes the task from stabilization of a long vector where the small components are expected to have negligible contribution to evaluation of a matrix where the change on each iteration is a direct measure of the error.

This approach starts from the CPCI contribution where substitution of the formal solution yields,

$$\begin{matrix} b & @ & b & -1 & @ & b & & -1 & @ \\ C & B & = & B & A & B & = & B & (D+A') & B \\ & & & 0 & & & & 0 & & \end{matrix} \quad (4.3.12)$$

where D is the matrix of diagonal elements and A' the off-diagonal matrix. If the norm of A' is less than unity the power series expansion

$$(D+A')^{-1} = D^{-1} \sum_{i=0}^{\infty} (-A'D^{-1})^i \quad (4.3.13)$$

will converge. The change on the i'th iteration is given by

the magnitude of

$$\Delta \begin{pmatrix} b \\ C \end{pmatrix} \begin{pmatrix} a \\ B \end{pmatrix} = \begin{pmatrix} b \\ 0 \end{pmatrix} D^{-1} (-A' D^{-1}) \begin{pmatrix} a \\ B \end{pmatrix} \quad (4.3.14)$$

summed over all pairs of nuclear coordinates.

This approach is more attractive if the term is written in a symmetric fashion with respect to a and b . The product of the derivative hamiltonian on the CI vector can be expressed as

$$\begin{pmatrix} a \\ B \end{pmatrix} = E \begin{pmatrix} a \\ C \end{pmatrix} + F \begin{pmatrix} a \\ F \end{pmatrix} \quad (4.3.15a)$$

where $F \begin{pmatrix} a \\ F \end{pmatrix}$ is constrained by

$$\sum_I C_I^T F_I \begin{pmatrix} a \\ F \end{pmatrix} = 0 \quad (4.3.15b),$$

note that $B \begin{pmatrix} a \\ 0 \end{pmatrix} = -F \begin{pmatrix} a \\ F \end{pmatrix}$. Substitution into eq.(4.3.12) yields

$$\begin{pmatrix} b \\ C \end{pmatrix} \begin{pmatrix} a \\ B \end{pmatrix} = -E \begin{pmatrix} a \\ F \end{pmatrix} (D+A')^{-1} \begin{pmatrix} b \\ C \end{pmatrix} + F \begin{pmatrix} b \\ F \end{pmatrix} (D+A')^{-1} \begin{pmatrix} a \\ F \end{pmatrix} \quad (4.3.16)$$

and the action of A^{-1} on C is found using

$$AC = (H - E1 + CC^T)C = (HC - EC) + C(CC^T)C = C \quad (4.3.17).$$

Multiplying eq.(4.3.17) from the left with A^{-1} yields

$$A^{-1} C = C \quad (4.3.18).$$

Substitution into eq.(4.3.16) and use of eq.(4.3.15b) gives

$$\begin{pmatrix} b \\ C \end{pmatrix} \begin{pmatrix} a \\ B \end{pmatrix} = F \begin{pmatrix} b \\ D \end{pmatrix} \sum_i (-1)^i (A D^{-1})^i \begin{pmatrix} a \\ F \end{pmatrix} \quad (4.3.19)$$

where the symmetry between a and b allows two terms of the expansion to be generated for each matrix multiplication.

The first two methods can be adapted to converge on the hessian contribution by interchanging the sums,

$$\sum_I C_{I I}^B \theta_I = \sum_I \alpha_i \sum_I B_{I I}^B \theta_I \quad (4.3.20).$$

For Pople's expansion this requires the otherwise unnecessary determination of α on every iteration but for the residual minimization it makes only a small change in the algorithm.

4.4 Symmetry adaptation of the CPCI equations

As was noted earlier the contraction of the CI vector on a hamiltonian constructed with derivative integrals introduces coupling between states of different electronic symmetry. Thus there are contributions to the second derivatives from more configurations than contribute to the energy. It is possible to identify which couplings occur simply on the basis of the symmetry properties of derivative integrals and take linear combinations which allow the CPCI equations to be block diagonalized. The use of such a blocking in the GUGA framework and the definition of the totally symmetric hessian will be discussed.

Differentiation of an integral with respect to a nuclear coordinate lowers the symmetry of the molecule by distinguishing otherwise equivalent basis functions. Dupuis and co-workers[4] have shown how to efficiently calculate derivative integrals by calculating entire shell blocks of integrals labeled by unique atom indices, the petite list. Not all of the integrals in a block are non-zero but use of the Rys polynomial quadrature method generates the entire block from a small number of common factors. Thus the cost of evaluating zeros is small compared to the cost of detecting them.

The symmetry of a differentiated gaussian basis function can be seen simply from the formula for a cartesian gaussian

$$g = X^{n_x} Y^{n_y} Z^{n_z} \exp(-\xi(X^2 + Y^2 + Z^2)) \quad (4.4.1)$$

where X, Y, and Z are the cartesian distances from the nucleus on which the function is centered. Differentiation with respect to the Y coordinate of this nucleus yields another gaussian

$$g = X^{n_x} (2\xi Y^{(n_y+1)} - n_y Y^{(n_y-1)}) Z^{n_z} \exp(-\xi(X^2 + Y^2 + Z^2)) \quad (4.4.2)$$

which differs only in the Y polynomial prefactor. Thus if g has an equivalent function, g', on a symmetrically related center those symmetry operations which force relations on Y will be lost. This reduces the effective symmetry to a subgroup of the symmetry of the undifferentiated basis functions.

While the basis functions do not carry the symmetry of the point group the block of integrals calculated using the Rys quadrature do. Dupuis and King showed[4] that the derivative integrals are related by linear combinations of the functions in the symmetry unique shell and a similar rotation of a vector along the direction of the differentiation. They used these relations to further show that a similar transformation could be effected on a skeleton gradient making it possible to deal with only the elements of the petite list.

For the purpose of CPCI a different approach will be more fruitful. Instead of differentiating with respect to single nuclear coordinates the derivatives can be defined with respect to symmetry adapted coordinates. The related atoms and unique shell labels will be the same as used by Dupuis but linear combinations of related derivatives will be taken. The symmetry adapted derivative integrals will carry one of the irreducible representations of the equilibrium symmetry group given by the symmetry direct product of the indices, and the necessary combinations will coincide with those required for a set of symmetrically equivalent p-functions.

This transformation to symmetry adapted derivative integrals simplifies the CPCI in the following manner. Using the GUGA representation of a matrix element the total symmetry of a each walk, Γ , can be factored into head, tail, and loop contributions,

$$\Gamma_w = \Gamma_h \times \Gamma_l \times \Gamma_t \quad (4.4.3).$$

To determine the symmetry of the integrals that correspond to this matrix element the product across the loop segments must be determined. The coincidence of the two walks outside the range of the loop forces the head and tail symmetries to match so the symmetry product of the two walks contains two factors of the totally symmetric representation leaving

$$\Gamma_w \times \Gamma_{w'} = \Gamma_l \times \Gamma_{l'} \quad (4.4.4).$$

This is the generalization of the fact that only configurations of one symmetry can contribute to the energy. More importantly in CPCI the symmetry of the configurations with non-zero coefficients is fixed so each set of symmetry adapted derivative integrals can couple the reference to only one other irreducible representation which thereby symmetry blocks B^a .

Comparison of the hessian, A , with the hamiltonian shows that it is totally symmetric. Thus once B^a is symmetry blocked only those degrees of freedom which carry the same irreducible representation will interact but unlike the zeroth order wave function each block must be evaluated. The optimum strategy would be to have each block of the hessian sequentially and independently numbered. Shavitt's algorithm[54] for treating symmetry can thus be used to good advantage in the CPCI solution. Brooks' method[55] is nicely streamlined for the treatment of each block but separate searches would be required for each irreducible representation. An implementation of Shavitt's method where part of the vector could be held on disc[56] could potentially update all of the trial vectors on one scan of the DRT.

Shavitt's algorithm is superior for evaluation of B^a as well. Evaluation of matrix elements between symmetry blocks using Brooks' algorithm would require comparison of DRT's containing different sets of rows. Thus loops could close except for symmetry which would have to be monitored and

verified. Shavitt's algorithm, on the other hand, generates the same loops for either CPCI or the evaluation of B^e and only the selection criteria for matching tail and head segments needs to be changed.

The second derivative matrix contribution formed this way is also defined over symmetry adapted derivatives. This requires either back transformation of the CPCI term or symmetry adaptation of the other terms. In either case this can be done on the molecular hessian and is thus not a computational problem. The use of symmetry adapted derivatives also allows the CPCI solution to be restricted to those degrees of freedom that retain the equilibrium symmetry. Often molecular geometries are first determined with higher symmetry than the global equilibrium will possess to speed computation. Once B^e is symmetry blocked any desired block can be solved and definition of a symmetry adapted gradient vector would be sufficient for geometry optimization.

5 TIMING AND ANALYSIS

The methods described have been implemented in a pilot program and tested on a number of molecules. The results have been verified by comparison with finite difference calculations which test the accuracy of the second derivative and give a quantitative measure of the efficiency of the method. Comparison of the iterative procedures used for the solution of the CPCI equations will be made and a partial assessment of the effect of symmetry adaptation will be made.

5.1 Description of Test Cases

The four demonstration molecules chosen were CH_2 , H_2O , CH_2O and H_5^+ . All molecules tested were closed shell singlets because of a limitation of the pilot program. Each molecule, except H_5^+ , was tested with two different basis sets to determine the dependence on the number of basis functions, n . Calculations were also performed both at stationary and at non-stationary points on the potential surface to eliminate fortuitous cancelations that might occur at stationary points.

The first three molecules employed the STO-3G basis[68] and the double zeta (DZ) contraction proposed by Dunning[69]. For H_5^+ only the DZ basis was used. The number of configurations in a singles plus doubles CI ranges from 66 to 8385 when no use of molecular symmetry is taken.

The finite difference times are compared for three different levels of symmetry utilization. Accurate finite difference results require the use of a two point differencing formula,

$$E_{ab} = \frac{\left(\frac{\partial E}{\partial a}\right)_{+b} - \left(\frac{\partial E}{\partial a}\right)_{-b}}{2\Delta b} \quad (5.1.1)$$

where the plus and minus denote positive and negative displacements along the b cartesian coordinate. This process thus requires 6M gradients. The most compatible way to obtain the timing comparisons is to do all displacements

with no symmetry. An intermediate level is to use symmetry when applicable but to do all 6M displacements. The actual method of choice is to do only displacements on unique centers and in unique directions, i.e. if the plus and minus displacements are related by a plane of symmetry only one need be done explicitly. These three approaches are labeled no symmetry, w/o symmetry, and w/ symmetry respectively.

5.2 Accuracy and Timing

The accuracy of the second derivatives is easiest to assess by comparing the fundamental vibrational frequencies that are predicted. The largest differences between the finite difference and the analytic frequencies are given in Table II. The only point where agreement is not satisfactory is for H_5^+ which is an extremely flat potential surface making finite difference methods hard to apply. An internal check involves the translation-rotation eigenvalues. Since the derivatives for all cartesian coordinates are evaluated, terms for the center of mass arise which should be rigorously zero. For finite difference methods it is hard to get these values below 10 wave numbers but this limit was surpassed in all cases by the analytic method.

Table II also displays the ratio of the total computation times for finite difference to analytic second derivatives. These results are encouraging in the sense that for all cases the analytic times are competitive with the finite difference result making full use of symmetry. If the more compatible no symmetry numbers are used the improvement on using analytic second derivatives ranges from 2 to 5 times. However, the trend is clear that as the size of the problem increases the advantage decreases.

In order to assess where further work needs to be done the most important time steps have been broken down in Tables III and IV. Direct comparison is only possible for the derivative integral contribution and here the advantage of the analytic formulation is clear. While the percentages probably overstate the case on the larger systems the analytic method gains in two respects. First most second derivative integrals are products of first derivative integrals making the number of additional integrals which must be calculated small. Secondly the number of formulae which can be solved in terms of translational invariance[3,6,12] is greater. Thus just as was found for SCF first and second derivatives analytic determination of the derivative integrals is a strong advantage for analytic methods.

The next area for comparison is the evaluation of the wave function perturbation. For the finite difference method most of this step is embodied in the evaluation of the SCF and CI wave functions at perturbed geometries. Since both of these processes have been well studied it is unlikely that the 40-50% spent on these calculations will change significantly. For the analytic approach these are precisely the procedures that are least optimized and the techniques described here should be a solution.

The nature of bent triatomic molecules can be exploited to test the importance of symmetry adaptation in the CPCI. The only non-zero first-order CI wave function corrections are for in plane coordinates so the wave function can be restricted to C_s symmetry. This reduces the number of configurations for DZ H O from 1081 to 673 and the time per iteration from 7 to 4 ² seconds. Full use of symmetry would lower this by a further factor of two making the overall reduction go as the order of the point group. For the cases tested to date this would make analytic second derivatives about a factor of two faster than finite differences.

5.3 CPCI Strategies

The three approaches to the solution of the CPCI equations have been programmed and the timing results appear in Table V. The row labeled "CPCI convergence" was obtained by full convergence of the residual minimization method. The next two rows are for direct determination of the second derivative contribution and the Pople method has yet to be cast in a form where it will converge. Convergence of the second derivative matrix was defined by the root mean square change in the second derivative matrix being less than 0.00005.

The direct determination approach is successful in that it reduces the time needed for an accurate second derivative. The use of the residual minimization would seem to be the recommended method. However, the fact that direct determination does not generalize to uses where the CPCI solution is explicitly needed and the relatively meager improvement in the timing suggests that a more fundamental reformulation is needed.

A second measure of the convergence properties is the number of iterations that are required per degree of freedom. Table VI shows this result for the methods that converged. The average number of iterations is 6.5 which compares favorably with Davidson's diagonalization algorithm which averages around 7 iterations for each root of the CI secular equation. This supports the conclusion that little

more is to be gained by improvements of a purely numerical nature.

5.4 Conclusion

This set of pilot programs demonstrates that analytic energy second derivatives of CI wave functions can be calculated reliably. The computational advantages over finite difference methods are not as great as for energy second derivatives of SCF wave functions. This is mainly due to the effort required to determine the first order correction to the CI wave function.

The most important extension to the method which needs to be implemented is the utilization of molecular symmetry. The CI method is most useful for small molecules which most often have some elements of spatial symmetry. The neglect of molecular symmetry increases the size of the CPCI equations to the point that finite difference approaches using symmetry are superior.

The CPCI equations can be solved by iterative methods and the convergence is similar to that achieved in Davidson's diagonalization algorithm. For small systems the use of a modified Krylov sequence is a viable alternative but for medium and large cases a method based on minimization of the residual error is superior. Stronger numerical methods exist if the matrix can be decomposed in part but this in general is impossible for CI wave functions.

While the final results are not in yet and these preliminary evaluations are not totally positive, analytic second derivatives at the CI level should be a useful tool. The ability to characterize surfaces without making displacements greatly simplifies the details of obtaining valid characteristics. The use for geometry optimization will not be great until some adaptation like restriction to the totally symmetric space is in place.

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Table 1. Sample Distinct Row Table.

Row a b			Number Lower Walks	Chaining Indices				Arc Weights			
1	2	1	75	1	2	3	4	0	20	40	55
Orbital 5 Basis Function 3 Alpha Occupied											
1	2	1	20	1	2	3	4	0	3	9	12
2	2	0	20	2	0	4	5	0	0	6	14
3	1	2	15	3	4	6	7	0	3	11	12
4	1	1	20	4	5	7	8	0	8	14	17
Orbital 4 Basis Function 1 Doubly Occupied											
1	2	1	3	0	1	0	2	0	0	0	1
3	1	2	3	0	2	0	4	0	0	0	2
4	1	1	8	2	3	4	5	0	2	5	6
5	1	0	6	3	0	5	6	0	0	3	5
6	0	3	1	0	4	0	0	0	0	0	0
7	0	2	3	4	5	0	0	0	1	0	0
8	0	1	3	5	6	0	0	0	2	0	0
Orbital 3 Basis Function 2 Doubly Occupied											
1	2	0	1	0	0	0	1	0	0	0	0
2	1	1	2	0	1	0	2	0	0	0	1
3	1	0	3	1	0	2	3	0	0	1	2
4	0	2	1	0	2	0	0	0	0	0	0
5	0	1	2	2	3	0	0	0	1	0	0
6	0	0	1	3	0	0	0	0	0	0	0
Orbital 2 Basis Function 4 Unoccupied											
1	1	0	1	0	0	0	1	0	0	0	0
2	0	1	1	0	1	0	0	0	0	0	0
3	0	0	1	1	0	0	0	0	0	0	0
Orbital 1 Basis Function 5 Unoccupied											
1	0	0	1	0	0	0	0	0	0	0	0

Table II. CI Second Derivatives Examples.

Molecule	Basis	Configs.	Largest Error	Largest Zero	Finite Difference/ Analytic Timings		
					No Symmetry	W/O Symmetry	W/ Symmetry
H ₂ O	STO-3G	66	0.2	2.2	5.4	5.0	2.9
CH ₂	STO-3G	91	0.1	2.6	5.1	5.0	2.8
H ₅ ⁺	DZ	153	6.4i	2.0	3.9	3.4	1.6
H ₂ CO	STO-3G	561	0.3	2.5	3.4	3.0	1.5
CH ₂	DZ	861	0.4	1.4	2.6	2.3	1.2
H ₂ O	DZ	1081	0.5	1.5	2.7	2.2	1.2
H ₂ CO	DZ	8385	0.2	3.3	2.1	1.4	0.7

Table III. Analytic Second Derivatives Timing Percentages.

	STO-3G H ₂ O	STO-3G CH ₂	DZ H ₅ ⁺	STO-3G H ₂ CO	DZ CH ₂	DZ H ₂ O	DZ H ₂ CO
SCF-CI	14.9	14.2	6.6	6.9	6.9	7.6	5.2
PDM [*]	4.6	4.6	1.4	1.1	2.7	2.5	1.2
DINTS	24.3	24.3	15.5	19.6	11.0	9.9	6.1
t-DINTS DLAG	6.0	6.0	20.9	9.9	21.0	18.7	21.0
CPHF1,2	15.4	15.4	27.8	16.2	16.6	16.9	15.7
CPCI	18.6	14.6	15.1	38.2	21.1	28.4	35.6

^{*}Includes the back-transformation and evaluation of the lagrangian.

Table IV. Finite Difference Timing Percentages.*

	STO-3G H ₂ O	STO-3G CH ₂	DZ H ₅ ⁺	STO-3G H ₂ CO	DZ CH ₂	DZ H ₂ O	DZ H ₂ CO
SCF-CI	51.2	51.6	41.3	42.8	38.5	51.1	46.9
PDM	12.2	12.2	13.6	6.2	14.5	14.6	20.6
DINTS	34.6	34.6	40.8	49.6	34.6	32.0	31.4
CPHF	1.9	1.9	4.2	1.4	2.2	2.2	2.4

*Breakdown corresponds with the W/ Symmetry column of Table II.

Table V. CPCI Timing Comparisons.*

Method	STO-3G CH ₂	DZ H ₅ ⁺	STO-3G H ₂ CO	DZ CH ₂	DZ H ₂ O
CPCI Convergence	28	59	610	223	334
Second Deriv. Convergence					
Residual Minimization	14	31	330	165	22
Krylov Sequence	18	19	665	204	349
Pople Expansion		- diverges -			

*Times are CPU seconds on a Harris 800 Computer

Table VI. CPCI Iterations per Degree of Freedom.*

Method	STO-3G CH ₂	DZ H ₅ ⁺	STO-3G H ₂ CO	DZ CH ₂	DZ H ₂ O
CPCI Convergence	5.1	6.5	7.2	6.5	6.9
Second Deriv. Convergence					
Residual Minimization	3.0	4.5	5.7	6.0	5.4
Krylov Sequence	4.9	6.0	11.3	9.8	10.1

*Translational degrees of freedom were excluded.

Figure II. Sample Loops.

Figure III. Direct CI DRT Organization.