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DERIVATIVE METHODS FOR VARIOUS TYPES OF
CONFIGURATION INTERACTION WAVE FUNCTIONS
IN AB INITIO ELECTRONIC STRUCTURE THEORY**

T.J. Lee
(Ph.D. Thesis)

November 1986

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THE DEVELOPMENT AND APPLICATION OF ENERGY DERIVATIVE
METHODS FOR VARIOUS TYPES OF CONFIGURATION INTERACTION
WAVE FUNCTIONS IN AB INITIO ELECTRONIC STRUCTURE THEORY

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November 1986

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TIMOTHY J. LEE

ABSTRACT

Formulae are derived for the configuration interaction (CI) energy gradient where the CI is based upon a two-configuration self-consistent-field (TCSCF) reference wave function. The method presented is general enough to allow extension to multi-configuration self-consistent-field (MCSCF) reference wave functions with only modest effort. A derivation of the analytic CI energy second derivative is presented in Chapter III. The formulae given in this chapter are valid for general restricted Hartree-Fock (GRHF) reference wave functions. The third, and final, development topic studied is the analytic energy gradient for the externally contracted configuration interaction correlation method.

The formulations presented here are directed at obtaining the most efficient computational algorithm possible. The first two new developments have been implemented and compare very favorably with the finite differences technique. The externally contracted CI analytic gradient is formulated in a computationally efficient way, but has not yet been implemented.

A general discussion about the most efficient gradient technique for any conventional type of electron correlation procedure is presented. Also, the advantages of using derivative theory in the computation of static molecular

properties are enumerated.

Chapter V contains several chemical applications of the methods described earlier. Among these examples are the prediction of the infrared spectrum of HCNH^+ , NNOH^+ , C_2H_3^+ , C_2H_2^+ and HSOH . Theoretical predictions of the radiative decay lifetimes of the excited bending levels of CH_2^- are contrasted with the recently measured values. The last application concerns the effects of including triple and quadruple excitations in the CI expansion and allows the general structure of the CI Hamiltonian matrix to be deduced.

Finally, the author presents his views on the field of *ab initio* quantum chemistry and the direction in which it is headed.

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Firstly, I want to thank my family for all the support and help they have given me during my life, but especially these last four years. It is to you that I dedicate this thesis, because without your support it would have been so much more difficult.

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I have learned quite well that without friends life loses some of its meaning and so I want to thank Richard Remington and Dr. Yukio Yamaguchi for their patience and help in getting through the "Gould" old days. It is clear to me that no one else can really understand those times.

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Cheryn Gliebe has also made my graduate career much easier by always knowing where to go and/or what to do! Cheryn was always willing to listen as well, and for this I thank her. However, a word of advice to the beginning graduate student - if you do not know, then ask Cheryn.

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I think I could take up the argument where I left off,
and by following it closely awhile,
perhaps I could prove to your satisfaction,
either that you never existed at all,
or that you are dead now,
and consequently don't need

Mark Twain

Answers to Correspondents

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I. INTRODUCTION

To begin this thesis I wish to quote Robert S. Mulliken from his Nobel Prize Acceptance Lecture¹, "I would like to emphasize strongly my belief that the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand," and I could not agree more.

The development and implementation of analytic derivative methods in *ab initio* quantum chemistry has, without question, been one of the single most important advances in the history of the field. Without the use of analytic derivative methods it is virtually impossible (if not impractical) to locate precisely and characterize the stationary points on a multi-dimensional potential energy surface (PES). Moreover, the stationary points of a PES define or decide the chemistry and/or physics of the molecular system in question (at least for that one particular surface).

In all honesty, not all arguments in favor of analytic derivative methods are valid. For example, in supporting analytic derivative methods, many people quote the following statement made by D. R. Hartree², "The differentiation of a function specified only by a table of values ... is a notoriously unsatisfactory process, particularly if higher derivatives than the first are required." When quoted, this statement is generally intended to mean that derivatives of a function obtained in this way are numerically unstable. The differentiation of a function using only a table of suitable values will be correct provided the values contain enough accurate significant digits and are well distributed. We see this problem arise even in analytic derivative methods where we must converge the self-consistent-field (SCF) wave function more precisely (or "harder") for a second derivative analysis than for a gradient or a simple energy.

However, I do believe that the great advantage of analytic derivative methods

are their efficiency and their simplicity. Many quantum chemists who work in the development of analytic derivative methods have praised the efficiency of these methods in great detail. Furthermore, Chapters II through IV also consider the efficiency of analytic methods and so this discussion will be left until later.

Analytic derivative methods also make it easier to teach the computer (i.e., write a program) to obtain the quantities of interest. For example, if the harmonic vibrational frequencies of a molecule are needed, it is much easier to start the analysis with a force constant matrix than with a table of energy values or a set of analytic gradients. This is a rather oversimplified example but the important realization that formulae and algorithms are much simpler when one begins with the second derivative matrix is present.

Another, more recent use of derivative methods in *ab initio* quantum chemistry is the quick and easy evaluation of many molecular properties. The best example of this rather recent phenomenon is the use of dipole derivatives in determining the infrared intensities of a molecule. In the double harmonic approximation (i.e., truncating the potential expansion at quadratic terms and the dipole moment expansion at linear terms), the infrared intensity is proportional to the square of the dipole derivatives in a normal coordinate system. The dipole derivative is related to an energy second derivative and so is similar to, though usually not as complicated as, the computation of a force constant matrix. The first successful matrix isolation of cyclopropenylidene provides a good example of the usefulness of theoretical infrared intensities^{3,4}. As is discussed in Chapter II, virtually all molecular properties can be expressed as an energy derivative in some way and it is generally preferable to compute them as an energy derivative rather than as an expectation value.

Analytic derivative methods already exist for many types of SCF wave functions, so the next question one might ask is why go through all the effort of programming these analytic methods for different, more complicated, types of wave

functions? The answer is really included in the question itself. The reason that the configuration interaction (CI) or multi-reference self-consistent-field (MCSCF) techniques are more complicated is because they are more rigorous and involve less of an approximation than SCF or Hartree-Fock (HF) theory. So, the predictions one makes with these more complicated methods should also be more accurate and the examples presented in Chapter V bear out this conclusion.

Each chapter has its own introduction and so it would be redundant to go into too many details of the various chapters here. The next three chapters deal with the development and implementation of various analytic derivative methods which I have worked on in my time here at Berkeley. Chapter II presents an efficient formulation of two configuration self-consistent-field configuration interaction (TCSCF-CI) energy gradients. While the actual formulae are limited to TCSCF reference wave functions, the extension of the method to more general MCSCF wave functions is straightforward. This method has been implemented and a few applications are reported in Chapter V. Configuration interaction energy second derivatives based on any general open shell restricted Hartree-Fock (RHF) SCF wave function are developed and the implementation detailed in Chapter III. An application of this method is also reported in Chapter V. The multi-reference contracted CI (MRCCI) gradient method outlined in Chapter IV is still in the development stages and so has not yet been implemented. It is important to note that although the gradient method described in Chapter IV has not yet been implemented, the formulae are of a programmable nature. In other words, they are detailed and considerably expanded. The reason this is an important point is that if the derivations are ever to be of any use then they must be programmed to run on a computer, hence they should be formulated in this manner. This point is pursued further in the final chapter which gives the authors view of the future of *ab initio* quantum chemistry. Finally, several examples of the use of analytic derivative methods for correlated

wave functions are presented in Chapter V.

Before proceeding, a few additional definitions of terminology are needed. A two configuration SCF (TCSCF) procedure is a subset of the more general MCSCF method. A CI based upon MCSCF (TCSCF) molecular orbitals is abbreviated as MCSCF-CI (TCSCF-CI). A CI based upon SCF molecular orbitals is termed a SCF-CI or more commonly as just a CI.

II. THEORY FOR CONFIGURATION INTERACTION ENERGY FIRST DERIVATIVES BASED ON A TWO-CONFIGURATION SELF-CONSISTENT-FIELD WAVE FUNCTION

A. Introduction

For many molecular systems a single Slater determinant wave function gives an unrealistic description of the electronic structure and bonding. Restricted Hartree-Fock (RHF) wave functions also fail to properly describe certain molecular processes such as the dissociation of a homonuclear diatomic molecule into its two atomic components. An effective method for overcoming this inherent limitation has been known for several years now. In 1966 Das and Wahl⁵ introduced the first applications of the multiconfiguration self-consistent-field (MCSCF) procedure when they presented two-configuration self-consistent-field (TCSCF) descriptions of the dissociation of the H_2 , Li_2 and F_2 molecules. They also reported MCSCF calculations involving three configurations for the H_2 and Li_2 species⁵. However, even with a MCSCF wave function many molecular processes and properties are not described very well. For example, Dupuis, Lester, Lengsfeld and Liu⁶ demonstrated that although their MC4 calculations adequately describe the dissociative process $H_2CO \rightarrow CO + H_2$, a single and double replacement (with respect to the MCSCF valence orbitals) configuration interaction (MRCISD or MCSCF-CI) calculation was needed to more accurately determine the classical barrier height of the transition state. Dupuis and co-workers did show, however, that a large enough MCSCF (their MC10 results) eventually included the major portion of the correlation energy effect on the barrier height, but this procedure is not an alternative when larger systems are investigated. Englebrecht and Liu⁷ have demonstrated the usefulness of the MCSCF-CI approach in their investigation of the lowest 3B_2 and 3A_2 states of CO_2 where a nuclear framework having C_{2v} symmetry was only attained with MCSCF-CI

wave functions.

In the examples cited above, which is not designed to be an exhaustive list of published MCSCF-CI results, the MCSCF procedure improves upon the SCF results but it does not always include enough of the total electron correlation energy to obtain reliable results. However, the MCSCF procedure provides a very good zeroth order wave function from which dynamical electron correlation can be included, or in other words, from which a MCSCF-CI wave function can be determined. A major limitation of the MCSCF-CI procedure is the expense of locating stationary points on the Born-Oppenheimer potential energy surface. For molecular systems with more than a few independent nuclear degrees of freedom the only viable means of converging precisely on a stationary point is with the use of analytic energy gradients. Formulations for the analytic evaluation of MCSCF-CI energy gradients have been presented several times before⁸⁻¹² and the implementation of one of these methods was reported by Page and co-workers. However, all of these procedures are very expensive due to the necessity of transforming the derivative integrals into the molecular orbital basis in order to solve the coupled perturbed MCSCF (CPMCSCF) equations. In a recent article, though, Rice and Amos¹³ outlined a procedure which avoids the transformation of the derivative integrals and greatly reduces the computational effort required in determining the MCSCF-CI energy gradients analytically.

Another important point is the realization that there exist many chemical systems for which a TCSCF wave function provides a good zeroth order description, such as many singlet diradicals ($\tilde{a}^1A_1$ CH₂ being the prototype) and many strained organic molecules, such as bicyclobutene¹⁴. Furthermore, the TCSCF procedure is sufficiently simple to be performed in the atomic orbital (or symmetry orbital) basis, thus avoiding the costly transformation into the molecular orbital basis. Therefore, the extension of CI gradients to include TCSCF reference wave functions is an ex-

tremely useful one.

The following section contains a formulation of the TCSCF-CI energy first derivative. The derivation given below avoids transforming the derivative integrals and represents the most efficient implementation of any type of MCSCF-CI energy gradient to date. Section C contains a few computational considerations and a flow diagram of the implemented method. Applications of the method are reported in Chapter V.

B. Formulation of TCSCF-CI Gradients

The theory for CI gradient techniques has been given several times¹⁵⁻¹⁸, and the notation used here follows most closely that of Rice, Amos, Handy, Lee and Schaefer¹⁸ (RAHLS). The letters i,j,k,l,r and s will refer to molecular orbitals. The atomic orbital basis will be indicated by the indices μ, ν, ρ and σ . Nuclear perturbation coordinates are given by the letters a and b . Since the TCSCF-CI gradient is an extension of the SCF-CI gradient, a review of the relevant equations is presented before discussing the use of a TCSCF reference function.

The first derivative of the CI energy with respect to a nuclear degree of freedom as given by Brooks and co-workers¹⁵ is

$$E_{CI}^a = \sum_{ij} Q_{ij} h_{ij}^a + \sum_{ijkl} G_{ijkl} (ij|kl)^a + 2 \sum_{ij} U_{ij}^a X_{ji} \quad \text{II-(1)}$$

where h_{ij}^a and $(ij|kl)^a$ are the one and two electron derivative integrals transformed into the molecular orbital basis. It will be shown that this transformation of derivative integrals into the molecular orbital (MO) basis is unnecessary for TCSCF-CI gradients just as it is unnecessary for SCF-CI gradients. Q_{ij} and G_{ijkl} are the reduced one and two particle density matrices respectively and X_{ji} is the CI Lagrangian defined by

$$X_{ji} = \sum_r Q_{jr} h_{ir} + 2 \sum_{rkl} G_{jrkl} (ir|kl) \quad \text{II-(2)}$$

The density matrices are given by

$$Q_{ij} = \sum_I C_I C_J A_{ij}^{IJ} \quad \text{II-(3)}$$

$$G_{ijkl} = \sum_I C_I C_J B_{ijkl}^{IJ} \quad \text{II-(4)}$$

and are defined such that they have the full integral symmetry. The A_{ij}^{IJ} and B_{ijkl}^{IJ}

are the spin-adapted graphical unitary group coupling coefficients. The U_{ij}^a appearing in equation II-(1) are elements of the molecular orbital change matrices which, for an SCF reference function, are obtained by solving the coupled perturbed Hartree-Fock (CPHF) equations first introduced for nuclear perturbations by Gerratt and Mills¹⁹. These are defined (through first order) such that the changes in a molecular orbital on movement of nuclei are given by

$$\phi_i \rightarrow \phi_i + \sum_r U_{ri}^a \phi_r + \sum_\mu C_\mu^i \phi_\mu^a \quad \text{II-(5)}$$

RAHLS recently demonstrated that the CPHF contribution to the SCF-CI gradient may be rewritten in a form in which the Z-vector method of Handy and Schaefer²⁰ can be utilized. Their expression for the CI gradient is general (i.e., is correct for any kind of reference function) and is given by

$$E_{CI}^a = \sum_{ij} Q_{ij} h_{ij}^a + \sum_{ijkl} G_{ijkl} (ij|kl)^a + \sum_{i>j}^{c\text{inr}} (X_{ji} - X_{ij}) T_{ij}^a - \sum_{ij} X_{ij} S_{ij}^a, \quad \text{II-(6)}$$

where the T_{ij}^a are defined by

$$T_{ij}^a = (U_{ij}^a - U_{ji}^a), \quad \text{II-(7)}$$

or

$$U_{ij}^a = \frac{1}{2}(T_{ij}^a - S_{ij}^a), \quad \text{II-(8)}$$

and the S_{ij}^a are the derivative overlap integrals transformed into the MO basis. The relationships in equations II-(7) and II-(8) arise from differentiating the orthonormality condition

$$S_{ij} = \sum_{\mu\nu} C_\mu^i C_\nu^j S_{\mu\nu} = \delta_{ij}. \quad \text{II-(9)}$$

which gives

$$U_{ij}^a + U_{ji}^a = -S_{ij}^a \quad . \quad \text{II-(10)}$$

The letters c_{inr} in equation II-(6) refer to the CI non-redundant pairs of molecular orbitals. The SCF, or in this case TCSCF, non-redundant pairs are a subset of the CI non-redundant pairs, and the two spaces may be equivalent. This topic will be discussed in more detail later. Knowing that the CPHF equations which determine the T_{ij}^a are

$$A T^a = B^a \quad , \quad \text{II-(11)}$$

RAHLS showed that by defining Z to be the solution to

$$A^T Z = \Delta X \quad , \quad \text{II-(12)}$$

the CPHF contribution to equation II-(6) is given by

$$Z^T B^a \quad . \quad \text{II-(13)}$$

In equation II-(12) ΔX is taken from equation II-(6),

$$\Delta X_{ij} = (X_{ij} - X_{ji}) \quad . \quad \text{II-(14)}$$

Thus, only one set of CPHF equations need to be solved rather than N equations where N is equal to $3 \times$ the number of nuclei.

Before delving any further into the CI energy first derivative expression a few comments about how the CPHF equations derive are necessary. Initially the CPHF equations (for RHF SCF wave functions) were derived for closed shell SCF wave functions by taking derivatives (with respect to nuclear coordinates) of the variational condition of the SCF procedure. This condition is that the Fock matrix elements ϵ_{ij} , where i refers to a doubly occupied molecular orbital and j indicates an

unoccupied molecular orbital, be identically zero. Alternatively, one can view this derivation as simply requiring the variational condition to be true to first order when expanding the molecular orbitals and the atomic orbital one and two electron integrals in terms of the nuclear coordinates about the reference geometry (i.e., the geometry for which the SCF wave function was determined). In truth, the generalized CPHF equations²¹ are much more useful and, in the MO basis, require essentially the same degree of computational effort as the closed shell CPHF equations. To derive the generalized CPHF equations one simply takes derivatives of the variational condition for a general open shell RHF SCF wave function which is

$$\epsilon_{ij} = \epsilon_{ji} \quad \text{II-(15)}$$

where ϵ is defined by the expression

$$\epsilon_{ij} = f_i h_{ij} + \sum_k^{\text{occ}} [\alpha_{ik}(ij|kk) + \beta_{ik}(ik|jk)] \quad \text{II-(16)}$$

In the variational condition above, i and j must belong to different shells of the SCF, since if i and j are in the same scf shell then equation II-(15) is automatically satisfied. For example, if a triplet calculation (with only two open shell molecular orbitals) is performed, then there are three different shells present in the SCF; the doubly occupied orbitals, the singly occupied orbitals and the unoccupied molecular orbitals. Additionally, for an open shell singlet calculation (with only two open shell molecular orbitals) there are four shells in the SCF; the doubly occupied orbitals, the first open shell molecular orbital, the second open shell molecular orbital and the unoccupied orbitals. The f , α and β appearing in equation II-(16) are coupling coefficients and are defined by the particular type of calculation being performed. For a closed shell SCF determination $f_i = 1$ for i a doubly occupied molecular orbital, and zero for an unoccupied orbital; $\alpha_{ij} = 2$ for i and j both doubly occu-

pied and zero otherwise; and $\beta_{ij} = -1$ for i and j doubly occupied and zero otherwise. These parameters are given below (equations II-(25) and II-(26)) for a TCSCF wave function.

A TCSCF wave function may be defined in the following manner²²

$$\Psi_{\text{TCSCF}} = C_1 \Psi_1 + C_2 \Psi_2 \quad \text{II-(17)}$$

where

$$\Psi_1 = A(\phi_1^2 \dots \phi_m^2 \phi_n^0) \quad \text{II-(18)}$$

$$\Psi_2 = A(\phi_1^2 \dots \phi_m^0 \phi_n^2) \quad \text{II-(19)}$$

Note the relationship between the special orbital m and C_1 and also that of special orbital n and C_2 .

E_{TCSCF} (the electronic energy of the system) is then straightforwardly evaluated as

$$E_{\text{TCSCF}} = \sum_{IJ} C_I C_J H_{IJ} \quad , \quad \text{II-(20)}$$

where the Hamiltonian matrix elements are given by

$$\begin{aligned} H_{11} = & 2 \sum_i^{\text{do}} h_{ii} + \sum_{ij}^{\text{do}} [2(ii|jj) - (ij|ij)] + 2h_{mm} \\ & + 2 \sum_i^{\text{do}} [2(mm|ii) - (mi|mi)] + (mm|mm) \end{aligned} \quad \text{II-(21)}$$

$$\begin{aligned} H_{22} = & 2 \sum_i^{\text{do}} h_{ii} + \sum_{ij}^{\text{do}} [2(ii|jj) - (ij|ij)] + 2h_{nn} \\ & + 2 \sum_i^{\text{do}} [2(nn|ii) - (ni|ni)] + (nn|nn) \end{aligned} \quad \text{II-(22)}$$

$$H_{12} = (mn|mn) \quad \text{II-(23)}$$

Alternatively, the TCSCF energy may be given by

$$E_{\text{TCSCF}} = \sum_i^{\text{occ}} [f_i h_{ii} + \epsilon_{ii}] \quad , \quad \text{II-(24)}$$

where ϵ_{ii} is defined in equation II-(16). Thus, it is necessary to define the f , α and β parameters for a singlet TCSCF wave function. For the doubly occupied space these parameters have already been defined. The changes for the variable occupancy space are

$$\begin{aligned} f_m = \alpha_{mm} = C_1^2, \quad f_n = \alpha_{nn} = C_2^2 \quad , \\ \alpha_{mn} = \beta_{mm} = \beta_{nn} = \alpha_{nm} = 0 \quad , \quad \beta_{mn} = \beta_{nm} = C_1 C_2 \end{aligned} \quad \text{II-(25)}$$

and

$$\begin{aligned} \alpha_{im} = \alpha_{mi} = 2C_1^2 \\ \beta_{im} = \beta_{mi} = -C_1^2 \\ \alpha_{in} = \alpha_{ni} = 2C_2^2 \quad \text{for } i = \text{do} \\ \beta_{in} = \beta_{ni} = -C_2^2 \end{aligned} \quad \text{II-(26)}$$

When the reference wave function is determined via a TCSCF procedure, then instead of solving one set of CPHF-like equations it is necessary to solve one set of coupled perturbed TCSCF (CPTCSCF) equations. The form of the CPTCSCF equations has been reported previously by Yamaguchi, Osamura and Schaefer²²

$$\begin{pmatrix} A^{11} & A^{21T} \\ A^{21} & A^{22} \end{pmatrix} \begin{pmatrix} U^a \\ \frac{\partial C_I}{\partial a} \end{pmatrix} = \begin{pmatrix} B_0^{a1} \\ B_0^{a2} \end{pmatrix} \quad , \quad \text{II-(27)}$$

where the following definitions have been made

$$\begin{aligned} A_{ij,kl}^{11} = & 2(\alpha_{il} - \alpha_{jl} - \alpha_{ik} + \alpha_{jk})(ij|kl) \\ & + (\beta_{il} - \beta_{jl} - \beta_{ik} + \beta_{jk})[(ik|jl) + (il|jk)] \\ & + (\epsilon_{jl} - \xi_{jl}^i)\delta_{ik} + (\epsilon_{ik} - \xi_{ik}^i)\delta_{jl} \\ & - (\epsilon_{il} - \xi_{il}^i)\delta_{jk} - (\epsilon_{jk} - \xi_{jk}^i)\delta_{il} \end{aligned} \quad \text{II-(28)}$$

$$A_{I,ij}^{21} = 2 \sum_J C_J (\epsilon_{ij}^{IJ} - \epsilon_{ji}^{IJ}) = A_{ij,I}^{12} \quad \text{II-(29)}$$

$$A_{I,I}^{22} = -(1/2) [H_{II} - \delta_{II} E_{\text{TCSCF}} + C_I C_I] \quad \text{II-(30)}$$

$$\begin{aligned} B_{0ij}^{a1} = & \epsilon_{ji}^a - \epsilon_{ij}^a + \sum_{k>l}^{\text{alocc}} S_{kl}^a \{ 2(\alpha_{ik} - \alpha_{jk})(ij|kl) \\ & + (\beta_{ik} - \beta_{jk})[(ik|jl) + (il|jk)] \\ & + (\epsilon_{il} - \xi_{il}^i)\delta_{jk} - (\epsilon_{jl} - \xi_{jl}^j)\delta_{ik} \} \\ & + \sum_k^{\text{occ}} S_{kk}^a [(\alpha_{ik} - \alpha_{jk})(ij|kk) + (\beta_{ik} - \beta_{jk})(ik|jk)] \end{aligned} \quad \text{II-(31)}$$

and

$$B_{0I}^{a2} = (1/2) \sum_J C_J H_{IJ}^a - (1/2) C_I E^a - \sum_J C_J [2 \sum_{i>j}^{\text{all}} S_{ij}^a \epsilon_{ij}^{IJ} + \sum_i^{\text{all}} S_{ii}^a \epsilon_{ii}^{IJ}] \quad \text{II-(32)}$$

The CPTCSCF equations can be reformulated to suit our needs as

$$\begin{pmatrix} A^{11} & 2A^{21\top} \\ 2A^{21} & 4A^{22} \end{pmatrix} \begin{pmatrix} \mathbf{T}^a \\ \frac{\partial C_I}{\partial \mathbf{a}} \end{pmatrix} = \begin{pmatrix} \mathbf{B}^{a1} \\ \mathbf{B}^{a2} \end{pmatrix}, \quad \text{II-(33)}$$

where

$$\begin{aligned} B_{ij}^{a1} = & 2 \epsilon_{ji}^a - 2 \epsilon_{ij}^a + \sum_{rs}^{\text{all}} S_{rs}^a \{ 2(\alpha_{is} - \alpha_{js})(ij|rs) \\ & + (\beta_{is} - \beta_{js})[(ir|js) + (is|jr)] \\ & + (\epsilon_{ir} - \xi_{ir}^j)\delta_{js} - (\epsilon_{jr} - \xi_{jr}^i)\delta_{is} \} \end{aligned} \quad \text{II-(34)}$$

and

$$B_I^{a2} = 4 B_{0I}^{a2} + 2 \sum_{i>j}^{\text{tcnr}} S_{ij}^a A_{I,ij}^{21} \quad \text{II-(35)}$$

The expression in equation II-(34) is identical to that given by RAHLS for the CPHF contribution in SCF-CI gradients. In equation II-(35) tcnr refers to TCSCF non-redundant pairs which are

$i = \text{d.o.} ; j = \text{special 1 (m), special 2 (n) or unoccupied}$
 $i = \text{special 1 (m)} ; j = \text{special 2 (n) or unoccupied}$
 $i = \text{special 2 (n)} ; j = \text{unoccupied}$

Special refers to the two molecular orbitals with variable occupation in a TCSCF. A more detailed discussion of independent (non-redundant) pairs is presented later.

One difference between solving a set of CPTCSCF-like equations rather than one set of CPHF-like equations for a SCF-CI gradient is that although the derivative of the configuration interaction coefficients appear in equation II-(33), according to equation II-(6) they give no direct contribution to the TCSCF-CI energy gradient. Therefore, the corresponding elements of ΔX appearing in equation II-(12) must be set equal to zero.

Many of the terms appearing in equations II-(28) through II-(35) have not yet been defined²²:

$$\xi_{ij}^k = f_k h_{ij} + \sum_l^{\text{occ}} [\alpha_{kl}(ij|ll) + \beta_{kl}(il|jl)] \quad \text{II-(36)}$$

$$\epsilon_{ik}^{11} = h_{ik} + \sum_j^{\text{do}} [2(ik|jj) - (ij|kj)] + 2(ik|mm) - (im|km) , \quad \text{II-(37)}$$

for $k = \text{all}$, $i = \text{doubly occupied (do) and special orbital m}$;

$$\epsilon_{ik}^{22} = h_{ik} + \sum_j^{\text{do}} [2(ik|jj) - (ij|kj)] + 2(ik|nn) - (in|kn) , \quad \text{II-(38)}$$

for $k = \text{all}$, $i = \text{do and special orbital n}$;

$$\epsilon_{mi}^{12} = \epsilon_{mi}^{21} = (1/2) (in | mn) \quad \text{II-(39)}$$

$$\epsilon_{ni}^{12} = \epsilon_{ni}^{21} = (1/2) (im | nm) \quad \text{II-(40)}$$

for $i = \text{all}$. All ϵ^{IJ} matrix elements not explicitly defined in equations II-(37) through II-(40) are zero. The H_{IJ}^a are defined similar to the H_{IJ} except with derivative integrals transformed into the molecular orbital basis. Analogously, ϵ^a is defined just as ϵ but with MO derivative integrals. The E_{TCSCF} appearing in equation II-(30) is the TCSCF energy less the nuclear contribution and E^a appearing in equation II-(32) is given by

$$E^a = 2 \sum_i^{\text{occ}} f_i h_{ii}^a + \sum_{ij}^{\text{occ}} [\alpha_{ij}(ii | jj)^a + \beta_{ij}(ij | ij)^a] - 2 \sum_{ij}^{\text{occ}} \epsilon_{ij} S_{ij}^a \quad \text{II-(41)}$$

Since the variational condition of an SCF or TCSCF directly affects only independent elements of the Fock matrix the CPHF or CPTCSCF equations are only defined over this region. Thus, in order to obtain an equation for the remaining U_{ij}^a (i.e., where i and j are in the same (TC) SCF shell), a matrix ϵ' is constructed, where

$$\epsilon'_{ij} = h_{ij} + \sum_k^{\text{occ}} f_k [2(ij | kk) - (ik | jk)] \quad \text{II-(42)}$$

and i and j belong to the same (TC) SCF shell. These sub-blocks are then diagonalized in order to obtain a convenient set of uniquely defined molecular orbitals within a given (TC) SCF shell. Now, by taking derivatives of this expression, an equation for the remaining U_{ij}^a is obtained. It should be realized that the definition of the ϵ' matrix is somewhat arbitrary and a few other workers¹⁸ in the field use different definitions.

The distinction between CI non-redundant (cincr) and SCF non-redundant (or for our purposes TCSCF non-redundant; tcnr) pairs was recently discussed in detail

by RAHLS and is especially important for our purposes. Whether using a TCSCF or an SCF reference, the distinction between the different types of independent or non-redundant pairs is really the same. For the reference wave function (i.e., the SCF or TCSCF wave function), an independent pair of molecular orbitals is defined to be one for which any mixing of the two orbitals would change the SCF, TCSCF or MCSCF energy. In other words, the relationship between these orbitals, either directly (as in a general MCSCF, where virtually every pair of orbitals may be an independent pair) or indirectly (as in an SCF or certain types of MCSCF's where it is really groups of orbitals which are related to other groups of orbitals) is defined by the procedure, or more succinctly the variational condition of the system. Another way to visualize the non-redundant pairs of molecular orbitals is to realize which pairs are redundant and the remaining pairs will be the non-redundant. The redundant pairs of MO's are simply defined to be those for which unitary rotations between the two molecular orbitals will not affect the SCF or TCSCF energy. For example, in a closed shell SCF calculation any unitary transformation between doubly occupied (unoccupied) orbitals will not change the SCF energy and so any pair of orbitals ij where i and j are both doubly occupied (both unoccupied) is a redundant pair. Thus, the independent pairs are any ij pair where i is doubly occupied and j is unoccupied.

The independent pairs of molecular orbitals in a TCSCF-CI or SCF-CI are defined to be those for which any mixing of the two would result in a different TCSCF-CI or SCF-CI energy. Clearly, the TCSCF or SCF non-redundant pairs are necessarily a subset of the TCSCF-CI or SCF-CI non-redundant pairs. However, the number of CI independent pairs will expand if orbitals in common shells in the SCF or TCSCF procedure are treated differently in the CI procedure. Probably the most common example of this situation is the use of frozen core and frozen virtual orbitals in the CI. As stated previously, any unitary transformation of doubly occupied

orbitals in an SCF will leave the SCF energy unaffected, but if frozen core orbitals are used to reduce the size of the CI expansion, then any mixing of the core orbital with any active doubly occupied orbital will necessarily change the SCF-CI energy. Another often used method which will result in expanding the list of CI independent pairs is performing a multireference CI procedure with SCF orbitals or alternatively, performing an MCSCF-CI and not using all the MCSCF configurations as references.

RAHLS showed how to include this additional contribution to the SCF-CI gradient without the numerical problems of past formalisms. The contribution to the TCSCF-CI gradient due to these additional CI non-redundant pairs ($acnr = cinr - tcnr$) can be included in a similar fashion. This $acnr$ contribution takes the form (recall equation II-(6))

$$\sum_{i>j}^{cinr} (X_{ji} - X_{ij}) T_{ij}^a = \sum_{i>j}^{tcnr} \Delta X_{ji} T_{ij}^a + \sum_{i>j}^{acnr} \Delta X_{ji} T_{ij}^a \quad \text{II-(43)}$$

$$\begin{aligned} &= \sum_{i>j}^{acnr} (X_{ji} - X_{ij}) \frac{1}{\epsilon'_{ii} - \epsilon'_{jj}} \left\{ B'_{ij}^a - \sum_{r>l} A'_{ij,rl} T_{rl}^a \right. \\ &\quad - 4C_1 [2(ij|mm) - (im|jm)] \frac{\partial C_1}{\partial a} \\ &\quad \left. - 4C_2 [2(ij|nn) - (in|jn)] \frac{\partial C_2}{\partial a} \right\} + \sum_{i>j}^{tcnr} \Delta X_{ji} T_{ij}^a \end{aligned} \quad \text{II-(44)}$$

where the following definitions have been made

$$B'_{ij}^a = -2(\epsilon'_{ij})^a + \sum_{rl}^{all} S_{rl}^a \{ f_l [4(ij|rl) - (ir|jl) - (il|jr)] + \delta_{il} \epsilon'_{jr} + \delta_{jl} \epsilon'_{ir} \} \quad \text{II-(45)}$$

and

$$\begin{aligned} A'_{ij,rl} &= (f_l - f_r) [4(ij|rl) - (ir|jl) - (il|jr)] \\ &\quad + \delta_{il} \epsilon'_{jr} + \delta_{jl} \epsilon'_{ir} - \delta_{ir} \epsilon'_{jl} - \delta_{jr} \epsilon'_{il} \end{aligned} \quad \text{II-(46)}$$

Note that $(\epsilon'_{ij})^a$ is defined as ϵ'_{ij} except with derivative integrals transformed into the MO basis. It should be emphasized that for equations II-(43) through II-(46) the ij pair refers to a TCSCF redundant pair but a CI non-redundant pair.

RAHLS handled the acnr contribution by expanding the set of linear equations to be solved when obtaining the Z-vector, but it is not necessary to do so, and in fact it is preferable not to expand the set of linear equations. This can be accomplished by rewriting equation II-(44) as

$$\sum_{i>j}^{\text{cnr}} \Delta X_{ji} T_{ij}^a = \sum_{i>j}^{\text{acnr}} \frac{\Delta X_{ji} B'_{ij}{}^a}{\epsilon'_{ii} - \epsilon'_{jj}} + \sum_{r>l}^{\text{tcnr}} (\Delta X'_{lr} + \Delta X_{lr}) T_{rl}^a + \eta_1 \frac{\partial C_1}{\partial a} + \eta_2 \frac{\partial C_2}{\partial a} \quad \text{II-(47)}$$

where

$$\Delta X'_{lr} = \sum_{i>j}^{\text{acnr}} \frac{\Delta X_{ji} A'_{ij,rl}}{\epsilon'_{ii} - \epsilon'_{jj}} \quad \text{II-(48)}$$

$$\eta_1 = -4C_1 \sum_{i>j}^{\text{acnr}} \Delta X_{ji} \frac{[2(ij|mm) - (im|jm)]}{\epsilon'_{ii} - \epsilon'_{jj}} \quad \text{II-(49)}$$

$$\eta_2 = -4C_2 \sum_{i>j}^{\text{acnr}} \Delta X_{ji} \frac{[2(ij|nn) - (in|jn)]}{\epsilon'_{ii} - \epsilon'_{jj}} \quad \text{II-(50)}$$

Another important aspect to note is that now the derivatives of the (TCSCF) CI coefficients do give a direct contribution to the TCSCF-CI gradient. Thus, the expression for the TCSCF-CI gradient is (excluding nuclear repulsion terms)

$$E_{\text{TCSCF-CI}}^a = \sum_{ij} Q_{ij} h_{ij}^a + \sum_{ijkl} G_{ijkl} (ij|kl)^a + \sum_{i>j}^{\text{acnr}} \frac{\Delta X_{ji} B'_{ij}{}^a}{\epsilon'_{ii} - \epsilon'_{jj}} - \sum_{ij}^{\text{all}} S_{ij}^a X_{ij} \quad \text{II-(51)}$$

$$+ \sum_{i>j}^{\text{tcnr}} Z_{ij} B_{ij}^{a1} + \zeta_1 B_1^{a2} + \zeta_2 B_2^{a2}$$

where the one set of CPTCSCF-like equations to be solved have the form

$$\begin{pmatrix} A^{11} & 2A^{21T} \\ 2A^{21} & 4A^{22} \end{pmatrix} \begin{pmatrix} Z \\ \zeta \end{pmatrix} = \begin{pmatrix} \Delta X' + \Delta X \\ \eta \end{pmatrix} \quad \text{II-(52)}$$

Note that since the A matrix is symmetric we have not indicated the use of its transpose in equation II-(52) which is what is mathematically required as outlined by Handy and Schaefer²⁰. It is also worth noting that $Z_{ij} = -Z_{ji}$. Finally, by rearranging the summations in a few of the terms in equation II-(51) a final working equation for the TCSCF-CI energy gradient is obtained

$$E_{\text{TCSCF-CI}}^a = \sum_{ij} Q'_{ij} h_{ij}^a + \sum_{ijkl} G'_{ijkl} (ij|kl)^a + \sum_{ij} P_{ij} S_{ij}^a, \quad \text{II-(53)}$$

where the following definitions have been made

$$Q'_{ij} = Q_{ij} + \frac{v_{ij} \Delta X_{ji}}{\epsilon'_{jj} - \epsilon'_{ii}} + \omega_{ij} (f_j - f_i) Z_{ij} + 4\delta_{ij} \sum_I \zeta_I C_I (f_i^I - f_i) \quad \text{II-(54)}$$

$$\begin{aligned} P_{ij} = & -X_{ij} + \sum_{r>l}^{\text{acnr}} \frac{\Delta X_{lr}}{\epsilon'_{rr} - \epsilon'_{ll}} \{ f_j [4(ij|rl) - (ir|jl) - (il|jr)] + \delta_{rj} \epsilon'_{li} + \delta_{lj} \epsilon'_{ri} \} \\ & + \sum_{r>l}^{\text{tcnr}} Z_{rl} \{ 2(\alpha_{rj} - \alpha_{lj})(ij|rl) + (\beta_{rj} - \beta_{lj})[(ir|jl) + (il|jr)] \\ & + (\epsilon_{ri} - \xi_{ri}^I) \delta_{lj} - (\epsilon_{li} - \xi_{li}^I) \delta_{rj} \} + 4\theta_{ij} \epsilon_{ij} \sum_I \zeta_I C_I - 2 \sum_{II} \zeta_{II} C_{II} (\epsilon_{ij}^{II} + \epsilon_{ji}^{II}) \end{aligned} \quad \text{II-(55)}$$

$$\begin{aligned} G'_{ijkl} = & G_{ijkl} + \frac{2v_{ij} \Delta X_{ij} f_k \delta_{kl}}{\epsilon'_{ii} - \epsilon'_{jj}} - \frac{v_{ik} \Delta X_{ik} f_j \delta_{jl}}{\epsilon'_{ii} - \epsilon'_{kk}} \\ & + 2 \sum_I \zeta_I C_I [(\alpha_{ik}^I - \alpha_{ik}) \delta_{ij} \delta_{kl} + (\beta_{ij}^I - \beta_{ij}) \delta_{ik} \delta_{jl}] \\ & + 2 \sum_{I \neq J} \zeta_I C_J \delta_{im} \delta_{jn} \delta_{km} \delta_{ln} + \omega_{ij} Z_{ij} (\alpha_{jk} - \alpha_{ik}) \delta_{kl} + \sigma_{ik} Z_{ik} (\beta_{kj} - \beta_{ij}) \delta_{jl} \end{aligned} \quad \text{II-(56)}$$

$$\begin{aligned}\theta_{ij} &= 1 & i \text{ and } j \text{ occupied} \\ \theta_{ij} &= 0 & \text{otherwise}\end{aligned}\tag{II-57}$$

$$\begin{aligned}v_{ij} &= 1 & i \text{ and } j \text{ acnr} \\ v_{ij} &= 0 & \text{otherwise}\end{aligned}\tag{II-58}$$

$$\begin{aligned}\omega_{ij} &= 1 & i \text{ and } j \text{ tcnr} \\ \omega_{ij} &= 0 & \text{otherwise}\end{aligned}\tag{II-59}$$

$$f_i^I = \text{the value of } f_i \text{ in configuration I.}\tag{II-60}$$

Note that the values of f_i , α_{ij}^I and β_{ij}^I are simply the values of the standard parameters (i.e., without the superscript) in the configuration I. For example, $f_m^1 = 1 = f_n^2$ and $f_m^2 = 0 = f_n^1$. Also note that the definitions in equations II-(54) through II-(60) are for the unsymmetrized Q' , G' and P matrices. Finally we have,

$$E_{\text{TCSCF-CI}}^a = \sum_{\mu\nu} Q'_{\mu\nu} h_{\mu\nu}^a + \sum_{\mu\nu\rho\sigma} G'_{\mu\nu\rho\sigma} (\mu\nu | \rho\sigma)^a + \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu}^a\tag{II-61}$$

Back transforming Q' , P and G' into the atomic orbital basis allows the entire TCSCF-CI gradient to be evaluated as the derivative integrals are determined. This procedure avoids writing out to disk or transforming any derivative integrals, and also avoids the costly formation of the ϵ^a matrix. Furthermore, this procedure is easily generalized to the MCSCF-CI gradient. It is important to note that it is computationally more efficient to form Q' , P and G' in the MO basis and then back transform to the atomic orbital basis rather than back transforming Q and G and adding in the remaining contributions to Q' and G' due to Z , ζ and ΔX by separately back transforming these other quantities. The latter procedure essentially incorporates two n^5 (n is the number of atomic or molecular orbitals) back transformation steps whereas the former procedure has only one n^5 step since forming the extra contribution to G' in the MO basis is only of n^4 cost.

C. Computational Considerations and Concluding Remarks

The implementation of the TCSCF-CI energy gradient was not too difficult since the SCF-CI first derivative (based on the Z-vector) had already been implemented at Berkeley. The major difference lies in solving one set of CPTCSCF-like equations rather than one set of CPHF equations. This step was accomplished by modifying a generalized CPHF program.

Figure II-1 contains a flow diagram of the SCF-CI analytic energy second derivative, the first portion of which (as marked on the diagram) describes the procedure for an SCF-CI analytic energy gradient. The flow diagram is appropriate for a TCSCF-CI gradient if one notes the appropriate changes (i.e., TCSCF in place of SCF and CPTCSCF-like equations rather than CPHF-like equations when solving for the Z-vector). As expected, the atomic orbital (AO) integrals are evaluated first. The TCSCF procedure is performed followed by a transformation of the AO integrals into the MO basis. The two-reference CI procedure is now performed with the construction of the reduced one and two particle density matrices following. At this point the CI Lagrangian matrix, X , is formed whereby Z and ζ are determined via equation II-(52). The matrices Q' , G' and P are now formed and written to disk. It is important at this point to realize that not a single step of the procedure has involved any type of derivative integral. In other words, derivative integrals have not been written to peripheral storage or transformed into the MO basis. Finally, the Q' , G' and P matrices are "back transformed" into the AO basis and multiplied by the derivative integrals as they are formed. One very important point to remember, is that the present density matrix based method is not limited to TCSCF-CISD expansions, but inherits the flexibility of the GUGA CI program. Thus, the only limitations are computational resources. This point will be mentioned again in Chapter V, where harmonic vibrational frequencies incorporating CISDTQ wave functions are reported.

At this point it is important to understand the significance of the $Z;\zeta$ vector. If one were to use this vector to 1) rotate the molecular orbitals ; 2) perform another CI ; 3) form another $Z;\zeta$ vector and so forth ... then eventually a stationary set of molecular orbitals would be obtained. This set of MO's would correspond to the MCSCF orbitals of the TCSCF-CI configuration space. So, in other words, the first $Z;\zeta$ vector is the first order correction of the TCSCF-CI towards its MCSCF. This is an important point for several reasons but most important when considering the determination of a molecular property based upon the TCSCF-CI wave function. For example, there has been a long running debate on the best method to evaluate the dipole moment of a molecule when using a truncated SCF-CI (or TCSCF-CI) wave function. Many people favor an expectation value

$$\mu_f = \sum_{ij} Q_{ij} h_{ij}^f \quad , \quad \text{II-(62)}$$

where the h_{ij}^f represent the dipole moment integrals (this formula also assumes that electric field independent basis sets are being used which are far and away the most commonly used bases). Note that the above equation assumes the convention

$$h_{ij}^f = - \sum_{\mu\nu} C_{\mu}^i C_{\nu}^j \langle \mu | f | \nu \rangle \quad . \quad \text{II-(63)}$$

Others view the dipole moment as an energy derivative²³ (derivative of E_{CI} with respect to an external electric field and evaluated at the zero of the external field). This interpretation results in the following formula for a component of the dipole moment

$$\mu_f = \sum_{ij} Q'_{ij} h_{ij}^f \quad , \quad \text{II-(64)}$$

where Q' was defined in equation II-(54). So, as we see, the only difference

between these two approaches (for truncated CI expansions) is the addition of the $Z;\zeta$ contribution. Hence, since we now realize that $Z;\zeta$ corresponds to the first order correction towards the larger MCSCF, it is only sensible to include this contribution. The present argument has a much better theoretical foundation than one used previously for favoring the energy derivative method, which was that a dipole moment is measured by applying an external electric field at several strengths and then extrapolating to the zero of the external field, since in the limit of a full CI, the two theoretical approaches will give the identical result.

III. THEORY FOR CONFIGURATION INTERACTION ENERGY SECOND DERIVATIVES BASED ON ANY RESTRICTED HARTREE-FOCK REFERENCE FUNCTION

A. Introduction

The analytic evaluation of energy second derivatives has been one of the major successes of *ab initio* quantum chemistry in the past decade. The principal uses of the energy second derivative with respect to nuclear perturbations have been (1) the prediction of harmonic frequencies and normal modes and (2) the rapid location of stationary points on a multidimensional potential energy surface. The literature of the past few years is full^{24,25} of examples.

The first analytic second derivative method developed was for closed shell restricted Hartree-Fock (RHF) and general unrestricted²⁶ Hartree-Fock (UHF) wave functions. Analytic second derivative methods for high spin open shell²⁷ and general open shell²⁸ RHF wave functions (GRHF) soon followed. The delay for the GRHF method was due to the necessity of solving the more complicated generalized coupled perturbed Hartree-Fock (GRCPHF) equations²⁸ rather than the closed shell coupled perturbed Hartree-Fock (CPHF) equations¹⁹, which are based on a single Fock operator.

Beyond the self-consistent-field (SCF) level of theory Yamaguchi, Osamura, Fitzgerald and Schaefer²⁹ reported the first evaluation of two-configuration SCF (TCSCF) second derivatives, Camp and co-workers³⁰ reported complete active space SCF (CASSCF) second derivatives and Hoffmann and co-workers³¹ were the first to report general multiconfiguration SCF (MCSCF) second derivatives. Not long thereafter, Page, Saxe, Adams and Lengsfeld¹¹ reported the implementation of their MCSCF second derivative method. The first implementation of an analytic second derivative method for a nonfully optimized wave function (i.e., not a subset of an

MCSCF wave function) was by Fox and co-workers³² for configuration interaction (CI) wave functions. Fox and co-workers³² were also the first to overcome a major obstacle in obtaining the first order CI wave function via the coupled perturbed configuration interaction (CPCI) equations. More recently Handy and co-workers^{33,34} reported analytic second derivatives of second order Moller-Plesset perturbation theory (MP2) energies based on closed shell references.

The purpose of this research is to report a more efficient evaluation of analytic energy second derivatives for CI wave functions. Since the paper by Fox and co-workers³² there have been many advances in the theoretical methods used in *ab initio* derivative theory. Most notably, the exploitation of translational and rotational invariance as outlined by Page, Saxe, Adams and Lengsfeld³⁵ (PSAL) greatly reduces the necessary work. The translational-rotational invariance relationships given by PSAL may be conveniently used to great advantage in the analytic CI second derivative procedure outlined below.

Another major improvement reported here is the use of the Z-vector method of Handy and Schaefer²⁰ in order to avoid the explicit solution of the second order²¹ CPHF equations. The implementation of the Z-vector for CI second derivatives is similar to that reported for CI gradients¹⁸, but inevitably more complicated.

Lastly, a more efficient algorithm by which the Y matrix contribution (as defined by Fox and co-workers) may be included, has been devised and implemented. The new algorithm avoids the explicit formation of the Y matrix, which is an n^6 process where n is the number of molecular orbitals.

The largest analytic CI second derivative reported by Fox and co-workers³² was double zeta H_2CO (24 basis functions) which yields 8385 configurations in the CI expansion. The present method is capable of handling very large basis sets and CI expansions and this point is demonstrated with the application to hydrogen thioperoxide reported in Chapter V. The primary limitation is the available compu-

tational resources since no large matrices are required to be held in main memory. To illustrate, the present system of codes could most likely handle basis sets as large as 100 contracted Gaussian functions and 10^6 CSF's on the new IBM 3090.

B. CI Analytic Second Derivative Expression

Firstly, for ease in reading, a few notes about the notation used [for equations III-(1) through III-(41)] in this section are needed. The indices i, j, k, l, r and s always refer to molecular orbitals, whereas μ, ν, ρ and σ always refer to atomic orbitals and a, b refer to nuclear coordinates. The total number of nuclear degrees of freedom ($3 \times$ the number of atoms) is denoted by N and the total number of molecular orbitals is given by n . For the purposes of a timing analysis of each term, the number of atomic orbitals is assumed to be equivalent to the number of molecular orbitals.

Fox and co-workers derived an expression for the CI analytic second derivative. It is obtained from a formal differentiation of the energy expression,

$$\begin{aligned}
 E_{CI}^{ab} = \frac{\partial^2 E_{CI}}{\partial a \partial b} = & \sum_{ij} Q_{ij} h_{ij}^{ab} + \sum_{ijkl} G_{ijkl} (ij | kl)^{ab} \\
 & + 2 \sum_{ij} U_{ij}^{ab} X_{ji} + \sum_{ij} (U_{ij}^a X_{ji}^b + U_{ij}^b X_{ji}^a) \\
 & + 2 \sum_{ij} \sum_{rs} U_{ri}^a U_{sj}^b Y_{risj} + 2 \sum_I \frac{\partial C_I}{\partial a} B_I^b.
 \end{aligned} \tag{III-1}$$

All terms occurring in equation III-(1) are now defined:

(i) Q_{ij} and G_{ijkl} are the molecular orbital one and two particle density matrices for the CI wave function. They were previously defined as

$$Q_{ij} = \sum_I C_I C_J A_{ij}^{IJ} \tag{III-2}$$

and

$$G_{ijkl} = \sum_I C_I C_J B_{ijkl}^{IJ} \tag{III-3}$$

where C_I ($I = 1, 2, \dots, M$) are the CI coefficients and A_{ij}^{IJ} and B_{ijkl}^{IJ} are the unitary group matrix element coupling coefficients. The density matrices are easily obtained

from the unitary group CI program³⁶ developed by Saxe, Fox, Handy and Schaefer.

(ii) h_{ij}^{ab} and $(ij|kl)^{ab}$ are the second derivative integrals transformed into the molecular orbital basis, i.e.,

$$h_{ij}^{ab} = \sum_{\mu\nu} C_{\mu}^i C_{\nu}^j h_{\mu\nu}^{ab} , \quad \text{III-(4)}$$

$$(ij|kl)^{ab} = \sum_{\mu\nu\rho\sigma} C_{\mu}^i C_{\nu}^j C_{\rho}^k C_{\sigma}^l (\mu\nu|\rho\sigma)^{ab} , \quad \text{III-(5)}$$

where the C_{μ}^i , C_{ν}^j correspond to the coefficients in the SCF wave function. As explained later, these integrals are never explicitly evaluated in the MO basis.

(iii) U_n^a and U_n^{ab} are solutions of the first and second order CPHF equations. These are defined such that the changes in a molecular orbital on movement of nuclei are given by

$$\begin{aligned} \phi_i \rightarrow \phi_i + (\sum_r U_n^a \phi_r + \phi_i^a) \delta_a + (\sum_r U_n^b \phi_r + \phi_i^b) \delta_b \\ + (\sum_r U_n^{ab} \phi_r + \phi_i^{ab}) \delta_a \delta_b , \end{aligned} \quad \text{III-(6)}$$

where ϕ_i^a , ϕ_i^{ab} denote orbitals evaluated in terms of differentiated basis functions.

(iv) X_{ij} is the CI Lagrangian which is defined by

$$X_{ij} = \sum_r Q_{ir} h_{rj} + 2 \sum_{rkl} G_{irkl} (jr|kl) . \quad \text{III-(7)}$$

X_{ij}^a is determined by the same expression as equation III-(7) but evaluated with molecular orbital derivative integrals.

(v) The Y matrix elements, Y_{risj} , have been defined by Osamura¹⁷ and co-workers:

$$Y_{risj} = Q_{ij} h_{rs} + 2 \sum_{kl} [G_{ijkl} (rs|kl) + 2G_{ikjl} (rk|sl)] . \quad \text{III-(8)}$$

(vi) $\partial C_I / \partial a$ is the solution of the coupled-perturbed CI equations (CPCI) which were written by Fox and co-workers as

$$\sum_J (H_{IJ} - E^0 \delta_{IJ} + C_I C_J) \frac{\partial C_J}{\partial a} = B_I^{0a} \quad , \quad \text{III-(9)}$$

$$B_I^{0a} = -\sum_J (H_{IJ}^{(a)} - E^{0a} \delta_{IJ}) C_J \quad . \quad \text{III-(10)}$$

Here H_{IJ} are the secular matrix elements for two configuration state functions (CSF's) Φ_I and Φ_J , and are defined in terms of the matrix element coupling coefficients:

$$\langle \Phi_I | H | \Phi_J \rangle = H_{IJ} = \sum_{ij} A_{ij}^{IJ} h_{ij} + \sum_{ijkl} B_{ijkl}^{IJ} (ij | kl) \quad . \quad \text{III-(11)}$$

In equation III-(9) E^0 is the CI energy less the nuclear repulsion contribution and E^{0a} is the CI gradient less the nuclear contribution. For our purposes E^{0a} can be defined in two ways:

$$E^{0a} = \sum_{ij} Q_{ij} h_{ij}^a + \sum_{ijkl} G_{ijkl} (ij | kl)^a + 2 \sum_{ij} U_{ij}^a X_{ji} \quad \text{III-(12)}$$

or

$$E^{0a} = \sum_{IJ} C_I C_J H_{IJ}^{(a)} \quad \text{III-(13)}$$

where $H_{IJ}^{(a)}$ is evaluated in the same manner as equation III-(11) but with fully differentiated molecular orbital integrals, $h_{ij}^{(a)}$ and $(ij | kl)^{(a)}$. These are given by

$$h_{ij}^{(a)} = h_{ij}^a + \sum_r (U_r^a h_{rj} + U_r^a h_{ri}) \quad \text{III-(14)}$$

and

$$(ij|kl)^{(a)} = (ij|kl)^a + \sum_r [U_n^a(rj|kl) + U_{nj}^a(ir|kl) + U_{rk}^a(ij|rl) + U_n^a(ij|kr)] \quad \text{III-(15)}$$

(vii) Finally, the vector which multiplies the solution of the CPCI equations in equation III-(1), B_I^a is expressed as

$$B_I^a = \sum_J H_{IJ}^{(a)} C_J = E^{0a} C_I - B_I^{0a} \quad \text{III-(16)}$$

where B_I^{0a} was given in equation III-(10).

Handy and Schaefer²⁰ have shown how that the second order CPHF equations need not be solved explicitly. Therefore, at this stage the theory presented here departs from that of Fox and co-workers.

The second order CPHF equations may be written as

$$AT^{ab} = B^{ab} \quad \text{III-(17)}$$

where

$$T_{ij}^{ab} = U_{ij}^{ab} - U_{ji}^{ab} \quad \text{III-(18)}$$

When using the Z-vector approach it is more appropriate to write the CPHF equation (for any order) in terms of the purely antisymmetric T rather than U . Also, if ij refer to a dependent pair of orbitals (a dependent pair is defined to be one for which an orthonormal transformation of ϕ_i, ϕ_j leaves the CI energy unaffected; see Chapter II for a more detailed discussion of CI dependent and independent pairs) then the CI energy derivatives will be invariant to rotations U_{ij}^{ab}, U_{ji}^{ab} . The only constraint on U_{ij}^{ab}, U_{ji}^{ab} comes from twice differentiating the orthonormality condition, which gives

$$U_{ij}^{ab} + U_{ji}^{ab} = -\xi_{ij}^{ab} \quad \text{III-(19)}$$

where

$$\xi_{ij}^{ab} = S_{ij}^{ab} + \sum_r (U_{ir}^a U_{jr}^b + U_{ir}^b U_{jr}^a - S_{ir}^a S_{jr}^b - S_{ir}^b S_{jr}^a) , \quad \text{III-(20)}$$

$$S_{ij}^{ab} = \sum_{\mu\nu} C_{\mu}^i C_{\nu}^j S_{\mu\nu}^{ab} . \quad \text{III-(21)}$$

Hence it is not necessary to explicitly solve for U_{ij}^{ab} when ij is a dependent pair but let

$$U_{ij}^{ab} = U_{ji}^{ab} = -\frac{1}{2} \xi_{ij}^{ab} \quad \text{III-(22)}$$

Thus the antisymmetric T_{ij}^{ab} is set to zero for ij a dependent pair.

The second order CPHF equations in the form

$$AU^{ab} = B^{ab} \quad \text{III-(23)}$$

have been presented by Osamura, Yamaguchi and Schaefer²¹. However, when using equation III-(17), the B^{ab} matrix is different and its elements are given by

$$\begin{aligned} B_{ij}^{ab} = & 2\varepsilon_{ji}^{ab} - 2\varepsilon_{ij}^{ab} + \sum_r \sum_k^{\text{alocc}} [R_{jirk} - R_{ijrk} + \delta_{kj}(\varepsilon_{ir} - \zeta_{ir}^j) \\ & + \delta_{ki}(\zeta_{jr}^i - \varepsilon_{jr})] \xi_{rk}^{ab} + 2 \sum_r^{\text{all}} (U_{ri}^a \varepsilon_{jr}^b + U_{ri}^b \varepsilon_{jr}^a - U_{rj}^a \varepsilon_{ir}^b - U_{rj}^b \varepsilon_{ir}^a \\ & + U_{rj}^a \zeta_{ir}^{jb} + U_{rj}^b \zeta_{ir}^{ja} - U_{ri}^a \zeta_{jr}^{ib} - U_{ri}^b \zeta_{jr}^{ia}) \\ & + 2 \sum_{rs}^{\text{all}} (U_{ri}^a U_{sj}^b + U_{ri}^b U_{sj}^a) (\zeta_{sr}^j - \zeta_{rs}^i) \\ & + 2 \sum_{rs}^{\text{alocc}} \sum_k^{\text{alocc}} (U_{rk}^a U_{sj}^b + U_{rk}^b U_{sj}^a) (R_{rkis}^i - R_{sirk}^i) \\ & + 2 \sum_{rs}^{\text{alocc}} \sum_k^{\text{alocc}} (U_{rk}^a U_{si}^b + U_{rk}^b U_{si}^a) (R_{sjrk}^i - R_{rkjs}^i) \\ & + 2 \sum_{rs}^{\text{alocc}} \sum_k^{\text{alocc}} U_{rk}^a U_{sk}^b (R_{ijrs}^k - R_{jirs}^k) \end{aligned} \quad \text{III-(24)}$$

$$+ 2 \sum_r \sum_k^{\text{allocc}} [U_{rk}^a (R_{ijrk}^b - R_{jirk}^b) + U_{rk}^a (R_{ijrk}^a - R_{jirk}^a)]$$

This expression for B^{ab} is derived by twice differentiating the variational RHF SCF condition:

$$\epsilon_{ij} = \epsilon_{ji} \quad , \quad i > j, \quad \text{SCF independent pair.} \quad \text{III-(25)}$$

Here ϵ_{ij} denotes the SCF Lagrangian, which for the GRHF wave function is defined

$$\epsilon_{ij} = f_i h_{ij} + \sum_k^{\text{occ}} [\alpha_{ik} (ij | kk) + \beta_{ik} (ik | jk)] \quad \text{III-(26)}$$

with f , α and β being the usual GRHF parameters (see Table II-1 for the values of these quantities for some typical GRHF wave functions). The various terms introduced in equation III-(24) are

$$R_{jirk} = 2\alpha_{ik} (ij | rk) + \beta_{ik} [(jr | ik) + (jk | ir)], \quad \text{III-(27)}$$

$$R_{jirs}^k = 2\alpha_{ik} (ij | rs) + \beta_{ik} [(jr | is) + (js | ir)], \quad \text{III-(28)}$$

$$\zeta_{ir}^j = f_j h_{ir} + \sum_k^{\text{occ}} [\alpha_{jk} (ir | kk) + \beta_{jk} (ik | rk)] \quad \text{III-(29)}$$

ϵ_{ij}^b , ζ_{ir}^{kb} and R_{jirk}^b are defined as ϵ_{ij} , ζ_{ir}^k and R_{jirk} but with molecular orbital derivative integrals h_{ij}^b and $(ij | kl)^b$ replacing the corresponding ordinary integrals.

The second order CPHF contribution to the CI second derivative, the third term in equation III-(1), is then evaluated as follows:

$$2 \sum_{ij} U_{ij}^{ab} X_{ji} = - \sum_{ij}^{\text{all}} \zeta_{ij}^{ab} X_{ji} + \sum_{i>j}^{\text{ip}} T_{ij}^{ab} (X_{ji} - X_{ij}), \quad \text{III-(30)}$$

where the substitution

$$U_{ij}^{ab} = \frac{1}{2}(T_{ij}^{ab} - \xi_{ij}^{ab}) \quad \text{III-(31)}$$

has been made. Note that the summation in the second term of equation III-(30) is only over SCF independent (or non-redundant) pairs (ip). Using the CPHF equation III-(17) for T^{ab} this term may be rewritten

$$\sum_{i>j}^{ip} Z_{ij} B_{ij}^{ab} \quad , \quad \text{III-(32)}$$

where Z_{ij} is defined to be the solution of the simultaneous equations:

$$\sum_{k>l}^{ip} A_{ijkl} Z_{kl} = X_{ji} - X_{ij}, \quad i>j, \quad \text{SCF independent pairs.} \quad \text{III-(33)}$$

The A matrix is defined by

$$\begin{aligned} A_{ijkl} = & R_{jikl} - R_{ijkl} - R_{jilk} + R_{ijlk} \\ & + \delta_{jl}(\epsilon_{ik} - \zeta_{ik}^i) + \delta_{il}(\zeta_{jk}^i - \epsilon_{jk}) \\ & - \delta_{jk}(\epsilon_{il} - \zeta_{il}^i) - \delta_{ik}(\zeta_{jl}^i - \epsilon_{jl}) \quad . \end{aligned} \quad \text{III-(34)}$$

This completes the working expression for the evaluation of the analytic CI energy second derivative. In the next section the computational requirements of each individual term as it contributes to the analytic CI Hessian is discussed in detail.

C. Computational Considerations

Figure II-1 is a flow chart of the CI second derivative procedure with the term (s) that each program evaluates (if any) in parentheses. The initial part of the calculation involves computation of the atomic orbital integrals; an SCF calculation; a four-index transformation of the atomic orbital integrals into the molecular orbital basis followed by a CI energy calculation. At this point, the one and two particle density matrices are determined with the subsequent evaluation of the CI Lagrangian via equation III-(33). The one and two particle density matrices are back transformed into the atomic orbital basis; these are not, however, the Q and G matrices defined previously, but are modified one and two particle density matrices defined below.

For convenience all of the terms contributing to the CI second derivative are regrouped and labeled according to the type of term and where each is evaluated. In brackets, on the right, is the equation from which each term arose:

Group (A)

$$\sum_{ij} Q_{ij} h_{ij}^{ab} + \sum_{ijkl} G_{ijkl} (ij | kl)^{ab} , \quad [\text{III-(1)}]$$

$$2 \sum_{i>j}^{ip} Z_{ij} (\epsilon_{ji}^{ab} - \epsilon_{ij}^{ab}) , \quad [\text{III-(24),(32)}]$$

$$\sum_{i>j}^{ip} Z_{ij} \sum_r \sum_k^{\text{all occ}} [R_{jirk} - R_{ijrk} + \delta_{kj} (\epsilon_{ir} - \zeta_{ir}^j) + \delta_{ki} (\zeta_{jr}^i - \epsilon_{jr})] S_{rk}^{ab} \quad [\text{III-(24),(32)}]$$

$$- \sum_{ij}^{\text{all}} S_{ij}^{ab} X_{ji} \quad [\text{III-(30)}]$$

By modifying the molecular orbital density matrices to include the Z-vector contribution, the first two terms of (A) become

$$\sum_{ij} Q'_{ij} h_{ij}^{ab} + \sum_{ijkl} G'_{ijkl} (ij | kl)^{ab} \quad \text{III-(35)}$$

The last two terms of (A) may be evaluated in a similar manner:

$$\sum_{ij}^{\text{all}} P_{ij} S_{ij}^{ab} \quad \text{III-(36)}$$

by defining

$$P_{ij} = W_{ij} - X_{ji} \quad , \quad \text{III-(37)}$$

$$W_{ij} = \sum_{r>k}^{\text{ip}} Z_{rk} [R_{krj} - R_{rkj} + \delta_{jk}(\epsilon_{ri} - \zeta_{ri}^k) + \delta_{rj}(\zeta_{ki}^r - \epsilon_{ki})], \quad j \text{ occupied}, \quad \text{III-(38)}$$

$$W_{ij} = 0, \quad j \text{ unoccupied.}$$

Group (A) is then evaluated when the second derivative integrals are determined by back transforming Q' , G' and P into the atomic orbital basis. The back transformation of G' is an n^5 process while the evaluation of second derivative atomic orbital integrals is of the order $N^2 n^4$.

The first order CPHF equation

$$AU^a = B^a \quad \text{III-(39)}$$

must now be solved for the independent U^a . The elements of A are as given in equation III-(34) and an element of B^a is given by

$$B_{ij}^a = \epsilon_{ji}^a - \epsilon_{ij}^a + \sum_r \sum_k^{\text{all occ}} [R_{jirk} - R_{ijrk} + \delta_{jk}(\epsilon_{ir} - \zeta_{ir}^j) + \delta_{ki}(\zeta_{jr}^i - \epsilon_{jr})] S_{rk}^a \quad \text{III-(40)}$$

The solutions of these equations, U^a , are now used to evaluate the following group

of terms:

Group (B)

$$2 \sum_{ij} \sum_{rs}^{\text{all}} U_{ri}^a U_{sj}^a Y_{risj} \quad , \quad \text{[III-(1)]}$$

$$2 \sum_{i>j}^{\text{ip}} Z_{ij} \left[\sum_{rs}^{\text{allocc}} \sum_k (U_{rk}^a U_{sj}^b + U_{rk}^b U_{sj}^a) (R_{rkis}^i - R_{sirk}) \right. \\ \left. + \sum_{rs}^{\text{allocc}} \sum_k (U_{rk}^a U_{si}^b + U_{rk}^b U_{si}^a) (R_{sjrk} - R_{rkjs}^i) \right] \quad , \quad \text{[III-(24),(32)]}$$

$$2 \sum_{i>j}^{\text{ip}} Z_{ij} \sum_{rs}^{\text{allocc}} \sum_k U_{rk}^a U_{sk}^b (R_{ijrs}^k - R_{jirs}^i) \quad \text{[III-(24),(32)]}$$

$$2 \sum_{i>j}^{\text{ip}} Z_{ij} \sum_{rs}^{\text{all}} (U_{ri}^a U_{sj}^b + U_{ri}^b U_{sj}^a) (\zeta_{sr}^j - \zeta_{rs}^i) \quad \text{[III-(24),(32)]}$$

$$\sum_{rk}^{\text{all}} [W_{rk} - X_{rk}] \sum_s^{\text{all}} [U_{rs}^a U_{ks}^b + U_{rs}^b U_{ks}^a \\ - S_{rs}^a S_{ks}^b - S_{rs}^b S_{ks}^a] \quad . \quad \text{[III-(20),(24),(30),(32)]}$$

It is evident that the first term of (B) is most efficiently programmed if the Y matrix is never explicitly formed (which is an n^6 process). To illustrate, consider a four-index term of Y [equation III-(8)].

$$\sum_{ij} \sum_{rs} U_{ri}^a U_{sj}^b \sum_{kl} G_{ikjl}(rk|sl) \quad . \quad \text{III-(41)}$$

This is most efficiently done as

Do k

Do l

read kl square of I (integrals)

read kl square of G (density matrix)

```

Do b
  Do j
    Do r
      Do s
        
$$I'_{rj}^{klb} = I'_{rj}^{klb} + I_{rs}^{kl} * U_{sj}^b$$

      End s
    End r
  End j
  Do r
    Do i
      Do j
        
$$Y'_{ir}^{klb} = Y'_{ir}^{klb} + G_{ij}^{kl} * I'_{rj}^{klb}$$

      End j
    End i
  End r
  Do a
    Do r
      Do i
        
$$F^{ab} = F^{ab} + Y'_{ir}^{klb} * U_{ri}^a$$

      End i
    End r
  End a
End b
End l
End k

```

As can be seen, this is now an Nn^5 process, which for large basis sets and/or

a small number of atoms can be much less than n^6 . For example, for the DZP HSOH case illustrated in Chapter V, the number of basis functions n is 50 and N is only 12. This procedure requires two sorts of integrals and the two particle density matrix but this is not very expensive even for large basis sets. The remainder of the terms in (B) are all less expensive being of the order Nn^4 or less.

The remaining terms which contribute to the analytic CI second derivative all require the molecular orbital derivative integrals:

Group (C)

$$2 \sum_{i>j}^{ip} Z_{ij} \sum_r (U_{ri}^a \epsilon_{jr}^b + U_{ri}^b \epsilon_{jr}^a - U_{rj}^a \epsilon_{ir}^b - U_{rj}^b \epsilon_{ir}^a + U_{rj}^a \zeta_{ir}^{jb} + U_{rj}^b \zeta_{ir}^{ja} - U_{ri}^a \zeta_{jr}^{ib} - U_{ri}^b \zeta_{jr}^{ia}) , \quad [\text{III-(24),(32)}]$$

$$2 \sum_{i>j}^{ip} Z_{ij} \sum_r \sum_k^{\text{all occ}} [U_{rk}^a (R_{ijrk}^b - R_{jirk}^b) + U_{rk}^b (R_{ijrk}^a - R_{jirk}^a)] , \quad [\text{III-(24),(32)}]$$

$$2 \sum_{ij} (U_{ij}^a X_{ji}^b + U_{ij}^b X_{ji}^a) . \quad [\text{III-(1)}]$$

The evaluation of the first two terms requires $N^2 n^4$ processes while the last is limited by Nn^5 because the formation of the derivative Lagrangian is an n^5 process.

All that remains is the contribution from the solution of the CPCI equations which, for a singles and doubles CI (CISD is an n^6 process) is an Nn^6 process and thus the time limiting step. However, before the CPCI equations can be solved the fully differentiated integral list [equations III-(14) and (15)] must be formed. This process is somewhat less expensive than a transformation, but of the same order of magnitude (i.e., n^5 for each perturbation and so Nn^5 overall):

Group (D)

$$2 \sum_I \frac{\partial C_I}{\partial b} B_I^a \quad . \quad \text{[III-(1),(10),(16)]}$$

B_I^a is straightforwardly obtained from the SDGUGA CI program using the fully differentiated integrals. The CPCI equations are solved iteratively according to the method of Pople and co-workers. In the present implementation the CPCI equations are solved for each perturbation separately, though there may be some argument for solving them simultaneously. Further investigations into the best approach for solving the CPCI equations are in progress.

By examining equation III-(1) and Figure III-1 it can be seen that the exploitation of translational and rotational invariance via the method outlined by Page, Saxe, Adams and Lengsfeld (PSAL) is easily accomplished by simply restricting a and b .

PSAL showed that by formulating a set of linear equations

$$\sum_{j=1}^6 L_{j,r_i} F_{j,k} = -b_i^k, \quad i = 1 - 6, \quad \text{III-(42)}$$

with

$$b_i^k = \sum_{j=7}^N L_{j,r_i} F_{j,k} + \sum_{j=1}^N \tau_{j,r_i}^k g_j \quad \text{III-(43)}$$

(note that $N = 3 \times \text{number of atoms}$) the remaining 6 (5 for a linear molecule) rows and columns of the second derivative matrix F may be obtained from the other $N - 6$. The L_{j,r_i} is the first derivative of the Cartesian coordinate j with respect to the translation-rotation displacement coordinate r_i evaluated at $r_i = 0$. If one chooses the three directions along the lab fixed axis frame as the translations, and rotations about these axes as the rotations, the L matrix for each atom becomes

$$\begin{array}{cccccc}
 1 & 0 & 0 & 0 & +z & -y \\
 0 & 1 & 0 & -z & 0 & +x \\
 0 & 0 & 1 & +y & -x & 0
 \end{array} \quad \text{III-(44)}$$

where x , y and z are the Cartesian coordinates for that particular atom. The τ_{j,r_i}^k appearing in equation III-(43) is defined by

$$\tau_{j,r_i}^k = \frac{\partial L_{j,r_i}}{\partial x_k} \quad \text{III-(45)}$$

Using the convention given above the three τ matrices for a given atom would be

$$\begin{array}{ccc}
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 \\
 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
 \end{array} \quad \text{III-(46)}$$

Finally, the g appearing in equation III-(43) is the Cartesian gradient vector which would be zero if the calculation is performed at a stationary point. It is interesting to note that for the convention of choosing the displacement coordinates r_i described above, the higher order $\tau_{j,r_i}^{k,l}$ defined by PSAL would be identically zero. Care must be taken in choosing the six nuclear perturbations so that they are linearly independent. This is easily accomplished by making sure that the symmetries of the Cartesian coordinates for which the matrix elements are explicitly determined span the space of the symmetries of the vibrations of the molecule. For most molecules the six coordinates may be chosen as the three components of one atom, two of another and one of a third atom as suggested by PSAL. However, for very small molecules, such as symmetric triatomics, any combination of the above suggestion will not work. For example, in the symmetric triatomic case the six coordinates may be chosen as; the x and y coordinates on the central atom, and the x and z coordinates on the two symmetry related atoms. Note that C_{2v} symmetry has been assumed with the molecule in the yz plane and the z -axis being the C_2 axis.

Translational-rotational relationships for properties other than the energy also exist and may be very useful. For example, six (or five) components of the dipole derivatives ($\partial\mu_x/\partial x_j$) can be determined from the other N-6 by solving the set of equations

$$\sum_{j=1}^6 L_{j,i} \frac{\partial\mu_x}{\partial x_j} = -b_i^x, \quad i = 1 - 6 \quad \text{III-(47)}$$

where

$$b_i^x = \sum_7^N L_{j,i} \frac{\partial\mu_x}{\partial x_j} - \frac{\partial\mu_x}{\partial r_i} . \quad \text{III-(48)}$$

The $\partial\mu_x/\partial r_i$ matrix elements are given by

$$\begin{array}{cccccc} q & 0 & 0 & 0 & +\mu_z & -\mu_y \\ 0 & q & 0 & -\mu_z & 0 & +\mu_x \\ 0 & 0 & q & +\mu_y & -\mu_x & 0 \end{array} \quad \text{III-(49)}$$

where q is the charge of the molecule. Note, however, that if one uses the above equations in conjunction with finite differences of dipole moments evaluated at perturbed geometries (which is what we generally do since we are also interested in the second derivative matrix) and the dipole moment is always evaluated with respect to the center of mass then the appropriate $\partial\mu_x/\partial r_i$ matrix elements are given by

$$\begin{array}{cccccc} 0 & 0 & 0 & 0 & +\mu_z & -\mu_y \\ 0 & 0 & 0 & -\mu_z & 0 & +\mu_x \\ 0 & 0 & 0 & +\mu_y & -\mu_x & 0 \end{array} \quad \text{III-(50)}$$

Applications of the analytic CI second derivative method are reported in Chapter V.

D. Conclusions and Future Considerations

A scheme for the analytic determination of CI energy second derivatives which incorporates three significant improvements over the pioneering research of Fox and co-workers has been presented. These are the use of the Z-vector method to avoid solving the second order CPHF equations, the use of translational-rotational invariance and the more efficient evaluation of the $\mathbf{Y}$ matrix contribution. Furthermore, the incorporation of atom symmetry is straightforwardly achieved within the present framework by simply forming only symmetry unique rows and columns of the force constant matrix and then generating the symmetry related rows and columns via the molecular point group operations.

Symmetry blocking the CPCI equations is not so easily accomplished, and further work along these lines is in progress. In order to symmetry block the CPCI equations it is clear that symmetry adapted derivative integrals must be used, i.e. each of the five indices labelling a derivative two electron integral must belong to an irreducible representation of the molecular point group. In other words, symmetrized nuclear perturbations (coordinates) must be used. It is not important to use symmetry orbitals rather than atomic orbitals since the derivative integrals are transformed into the molecular orbital basis and each of the molecular orbitals belongs to an irreducible representation. However, difficulties still remain. Of minor concern is the fact that either the CPCI contribution arising from the symmetry blocked CPCI equations will have to be transformed from symmetrized nuclear coordinates to the standard cartesian coordinates before being added to the force constant matrix or, conversely, all contributions to the Hessian must be evaluated for the symmetrized nuclear coordinates. A major difficulty, however, does exist. The GUGA set of CI programs would have to be modified to handle each of the symmetry blocks of the Hamiltonian matrix separately, and to form matrix elements between CSF's belonging to different irreducible representations

when fully differentiated integrals are used (i.e., for B^a when a is not totally symmetric).

A possible alternative to symmetry blocking the CPCI equations would be to use the molecular point group symmetry for all the steps up to and including the evaluation of the first and second derivative integrals. The remaining part of the CI second derivative, including the CPCI, could then be evaluated in C_1 symmetry, i.e., no symmetry. There are practical advantages to this approach in that a large programming effort is avoided and yet the geometry of a molecule could be optimized using molecular symmetry (the GUGA CI program is able to handle D_{2h} and subgroups) and then the CI second derivative evaluated without reconverging the CI wave function in C_1 symmetry. Furthermore, the molecular point group symmetry may be used to advantage in the evaluation of the Y matrix contribution. The only difficulty here is mapping the symmetry CI vector into a no symmetry list. However, this problem may be much more easily overcome than the difficulties in symmetry blocking the CPCI equations. In summary, the best approach would be the initial implementation of the DRT mapping array (to take a symmetry CI vector to a C_1 symmetry list) before considering the more complicated symmetry blocking of the CPCI equations.

Several other points also require comment. The use of translational-rotational invariance effectively reduced the cpu time of the HSOH test case reported in Chapter V by a factor of 2. Since this test case represents one of the larger CI expansions for which CI force constants have been determined it is evident that the incorporation of translational-rotational invariance into the analytic CI second derivative is indeed important. Moreover, the CPCI equations need not be solved very accurately in order to obtain harmonic frequencies correct to within 1 cm^{-1} . This is an important consideration because the solution of the CPCI equations is very expensive. Preliminary tests with the DIIS method of converging the CPCI

equations are encouraging.

There are really two time limiting steps in the present analytic CI second derivative procedure. In most cases the CPCI will be the time limiting step. However, because the shape-driven algorithm (of the graphical unitary group approach) has been implemented into the CPCI procedure, it is possible that the Y matrix contribution can become the time limiting step. For example, Lee and Schaefer recently reported CISD results for two isomers of $C_2H_3^+$. Only a 29 800 configuration singles and doubles CI expansion was obtained even though the basis set consisted of 100 contracted Gaussian functions. Thus, the efficient evaluation of this contribution is exceedingly important.

Finally, there are two unrelated points which are worthy of mention. It should be realized that the analytic CI second derivative method presented here is not restricted to CISD expansions, but inherits the flexibility of the shape-driven graphical unitary group approach. Also, the RHF SCF reference wave function is not restricted to closed shell cases, but can be any GRHF wave function. Thus, the primary limitation is the available computational resources.

Secondly, in the initial implementation of the present CI second derivative method and the analytic MP2 energy second derivative³³, a simple program was used in debugging the out-of-core versions. That is, a basic, completely in core, hard dimensioned program for the entire CI or MP2 second derivative procedure was constructed, specifically for the H_2 (DZ basis) and the H_2O (minimum basis) molecules. Given the capabilities of today's computers, programs of this sort are easily manageable and are extremely useful for debugging purposes.

IV. THEORY FOR EXTERNALLY CONTRACTED CONFIGURATION INTERACTION ENERGY GRADIENTS

A. Introduction

As quantum chemists extend their *ab initio* methods to larger systems it is certain that if the determination of a wave function which includes dynamical electron correlation is desired, then more approximate *but still accurate* methods must be employed. This conclusion results from two important points. Firstly, as the molecular system in question becomes larger or simply contains one or more transition metal atoms, the SCF approximation becomes less satisfactory and some form of MCSCF will be required in order to obtain a reasonable zeroth order wave function. This, in turn, will require a multireference correlation procedure which is a non-trivial complication. Secondly, as the number of electrons in a molecular system and the number of basis functions needed to adequately describe the molecule increase, the computational requirements of a CISD, CCSD or any similar procedure will grow rapidly so as to make the calculation either impossible or impractical. Therefore, the power of the CCI approach lies in its ability to handle problems of chemical interest which could not be attempted otherwise.

The externally contracted CI developed by Siegbahn³⁷ has been the most extensively used CCI method to date. Siegbahn has reported potential curves for several states of the N_2 molecule, all of which yield bond lengths deviating from experiment by 0.005 Å or less. Pettersson, Langhoff and Chong³⁸ have recently reported a study of the electric dipole moment function of the ClO molecule. They also obtained a very good bond length using Siegbahn's MRCCI method. Another very encouraging study was recently completed by Rohlfing and Hay³⁹ where they report an equilibrium structure for the FOOF molecule which is in much closer agreement to experiment than any previously obtained. F_2O_2 has proven to be one

of the more difficult small molecular systems to be studied by quantum chemists. Again, the method used by Rohlfing and Hay to obtain the best results was the multi-reference externally contracted CI.

It is worthy of note that an internally contracted CI method has been discussed by Meyer⁴⁰, Siegbahn^{41,42}, and Werner and Reinsch⁴³ (WR). WR have reported the implementation of their MCSCF self-consistent electron pairs (SCEP) method⁴³ and Werner, Rosmus, Reinsch⁴⁴⁻⁴⁷ and co-workers have reported equilibrium structures for several diatomic molecules, generally in excellent agreement with experiment.

It is not the purpose here to investigate the pros and cons of the CCI approach nor to decide exactly which CCI approach is superior. It is evident that a multi-reference CCI (MRCCI) approach is suitable for many chemical problems and so a method to quickly and efficiently locate stationary points on a many dimensional potential energy surface and then characterize the stationary point via the force constant matrix would be very useful. It is for these reasons that a formulation of the MRCCI energy gradient which should be useful in the implementation of such a procedure is presented.

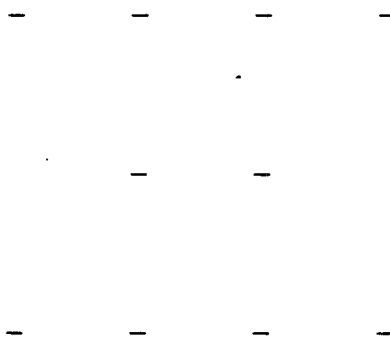
Since the externally contracted CI approach of Siegbahn³⁷ has been the most popular MRCCI method to date for use on polyatomic systems, the MRCCI energy gradient based on the externally contracted CI is presented here. However, the general approach and methods can be applied to the internally contracted CI of Werner and Reinsch⁴³ or similar methods. The following section contains a detailed derivation of the MRCCI energy gradient. As is always the case, the actual computational implementation of a procedure requires much thought as to appropriate intermediate products, loop structures and various other aspects. Section C contains a discussion which emphasizes the specific terms of the MRCCI gradient that will be the cpu intensive steps and general proposals for their efficient evaluation are suggested. No

claims are made as to the most efficient algorithm since the MRCCI energy first derivative is exceedingly complicated and it has been this author's experience that the most efficient procedure is almost never the first one to be tried. Some final remarks and general conclusions about gradient methods for correlated wave functions are also included at the end of Section C.

B. Formulation of the MRCCI Energy Gradient

Before presenting the CCI energy derivative expression, a few comments about notation are necessary. The notation used follows most closely that of Siegbahn³⁷ and that proposed by Taylor⁴⁸. The letters i,j,k,l,m and n will be used to indicate quantities in the molecular orbital (MO) basis, whereas r,s,p and q represent the use of the atomic orbital (AO) basis. The Greek letters μ , ν and ρ label configuration state functions (CSF's) in the CCI and are subject to one further restriction explained later. The capital letters I and J are used to denote CSF's in the valence MCSCF reference function. Finally, the letters a and b represent external molecular orbitals in a particular CSF in the CCI expansion.

The externally contracted CI can be visualized from the following diagram.



Let the upper part of the diagram represent the external space molecular orbitals and the lower six orbitals represent the CCI internal space. Then, let us assume that there are 4 electrons in this system. The MCSCF reference function will consist of all possible CSF's which can be generated with the restriction that all 4 electrons be in the lower four molecular orbitals (Note that each MO can accommodate two electrons). Hence, the CCI internal space and the reference MCSCF are not required to span the same space. The externally contracted CI is obtained by contracting CSF's with different internal electron configurations but the same external electron

configuration. Furthermore, only CSF's with at most two external orbitals are allowed. A more precise, mathematical definition will now be given.

The uncontracted CI wave function can be represented as

$$\Psi_{CI} = \sum_{\mu} C_{\mu} \Phi_{\mu} + \sum_{\nu} C_{\nu} \sum_a C_{\nu}^a \Phi_{\nu}^a + \sum_{\rho} C_{\rho} \sum_{ab} C_{\rho}^{ab} \Phi_{\rho}^{ab} \quad \text{IV-(1)}$$

where it should be realized that μ , ν and ρ label n , $n-1$ and $n-2$ internal electron configurations respectively. The basis for partitioning the wave function in this manner is seen by simply representing the CI coefficient of a CSF as a product of two terms

$$C_{\nu}^{\text{true}} = C_{\nu} C_{\nu}^a \quad \text{IV-(2)}$$

$$C_{\rho}^{\text{true}} = C_{\rho} C_{\rho}^{ab} \quad \text{IV-(3)}$$

where only one of the two terms is labelled by the external orbital(s). Then, in the externally contracted CI approach, the C_{ν}^a and C_{ρ}^{ab} are approximated via perturbation theory by

$$C_{\nu}^a = \frac{\langle 0 | H | \Phi_{\nu}^a \rangle}{E_0 - \langle \Phi_{\nu}^a | H | \Phi_{\nu}^a \rangle} \quad \text{IV-(4)}$$

and

$$C_{\rho}^{ab} = \frac{\langle 0 | H | \Phi_{\rho}^{ab} \rangle}{E_0 - \langle \Phi_{\rho}^{ab} | H | \Phi_{\rho}^{ab} \rangle} \quad \text{IV-(5)}$$

where H is the exact non-relativistic electronic Hamiltonian. The size of the variational CI procedure is then reduced by contracting over the external orbitals a and b to form a much smaller expansion

$$\Psi_{\text{CCI}} = \sum_{\mu} C_{\mu} \Phi_{\mu} + \sum_{\nu} C_{\nu} \Phi_{\nu} + \sum_{\rho} C_{\rho} \Phi_{\rho} \quad \text{IV-(6)}$$

where

$$\Phi_{\nu} = \sum_a C_{\nu}^a \Phi_{\nu}^a \quad \text{IV-(7)}$$

$$\Phi_{\rho} = \sum_{ab} C_{\rho}^{ab} \Phi_{\rho}^{ab} \quad \text{IV-(8)}$$

Hence, IV-(6) represents the externally contracted configuration interaction wave function. In actual practice, Hamiltonian matrix elements for the expanded CI are formed once and summed, but viewing the CCI wave function as given in equation IV-(6) is accurate as well as conceptually simple. It should be noted that the reference function $|0\rangle$ in equation IV-(5) is in general determined via an MCSCF procedure,

$$|0\rangle = \sum_I C_I |\Phi_I\rangle, \quad \text{IV-(9)}$$

and the Φ_I are valence CSF's. E_0 is given by

$$E_0 = \sum_{IJ} C_I H_{IJ} C_J, \quad \text{IV-(10)}$$

where

$$H_{IJ} = \sum_{ij} A_{ij}^{IJ} h_{ij} + \sum_{ijkl} B_{ijkl}^{IJ} (ij|kl). \quad \text{IV-(11)}$$

In equation IV-(11) the A_{ij}^{IJ} and B_{ijkl}^{IJ} are the standard spin-adapted coupling coefficients and h_{ij} and $(ij|kl)$ are one and two electron molecular orbital integrals, respectively. Accordingly, the matrix elements shown in equations IV-(4) and IV-(5) are given by

$$H_{0v}^a = \langle 0 | H | \Phi_v^a \rangle = \sum_I C_I \langle \Phi_I | H | \Phi_v^a \rangle = \sum_I C_I H_{Iv}^a \quad \text{IV-(12)}$$

where

$$H_{Iv}^a = \langle \Phi_I | H | \Phi_v^a \rangle = \sum_{ij} A_{ij}^{I,va} h_{ij} + \sum_{ijkl} B_{ijkl}^{I,va} (ij|kl) \quad \text{IV-(13)}$$

The CCI energy is given by

$$\begin{aligned} E_{\text{CCI}} = & \sum_{\mu\mu'} C_\mu H_{\mu\mu'} C_{\mu'} + \sum_{\mu\nu} C_\mu H_{\mu\nu} C_\nu + \sum_{\nu\mu'} C_\nu H_{\nu\mu'} C_{\mu'} \\ & + \sum_{\nu\nu'} C_\nu H_{\nu\nu'} C_{\nu'} + \sum_{\mu\rho'} C_\mu H_{\mu\rho'} C_{\rho'} + \sum_{\nu\rho'} C_\nu H_{\nu\rho'} C_{\rho'} \\ & + \sum_{\rho\mu'} C_\rho H_{\rho\mu'} C_{\mu'} + \sum_{\rho\nu'} C_\rho H_{\rho\nu'} C_{\nu'} + \sum_{\rho\rho'} C_\rho H_{\rho\rho'} C_{\rho'} \end{aligned} \quad \text{IV-(14)}$$

A few typical Hamiltonian matrix elements are given below

$$H_{\mu\mu'} = \langle \Phi_\mu | H | \Phi_{\mu'} \rangle \quad \text{IV-(15)}$$

$$= \sum_{ij} A_{ij}^{\mu,\mu'} h_{ij} + \sum_{ijkl} B_{ijkl}^{\mu,\mu'} (ij|kl) \quad \text{IV-(16)}$$

$$H_{\nu\mu'} = \sum_a C_v^a \langle \Phi_v^a | H | \Phi_{\mu'} \rangle \quad \text{IV-(17)}$$

$$= \sum_a C_v^a [\sum_{ij} A_{ij}^{va,\mu'} h_{ij} + \sum_{ijkl} B_{ijkl}^{va,\mu'} (ij|kl)] \quad \text{IV-(18)}$$

$$H_{\nu\nu'} = \sum_{aa'} C_v^a \langle \Phi_v^a | H | \Phi_{\nu'}^{a'} \rangle C_{\nu'}^{a'} \quad \text{IV-(19)}$$

$$= \sum_{aa'} C_v^a C_{\nu'}^{a'} [\sum_{ij} A_{ij}^{va,\nu'a'} h_{ij} + \sum_{ijkl} B_{ijkl}^{va,\nu'a'} (ij|kl)]. \quad \text{IV-(20)}$$

By using the symmetry of the Hamiltonian matrix and the fact that $\mu, \mu' ; \nu,$

v' ; and ρ, ρ' span the same space, equation IV-(14) can be rewritten as

$$E_{CCI} = \sum_{\mu\mu'} C_{\mu} H_{\mu\mu'} C_{\mu'} + 2 \sum_{\mu v'} C_{\mu} H_{\mu v'} C_{v'} + \sum_{vv'} C_{v} H_{vv'} C_{v'} \\ + 2 \sum_{\mu\rho'} C_{\mu} H_{\mu\rho'} C_{\rho'} + 2 \sum_{v\rho'} C_{v} H_{v\rho'} C_{\rho'} + \sum_{\rho\rho'} C_{\rho} H_{\rho\rho'} C_{\rho'} \quad \text{IV-(21)}$$

Differentiating equation IV-(21) with respect to a nuclear perturbation x , leads to an expression for the CCI energy gradient

$$E_{CCI}^x = \sum_{\mu\mu'} C_{\mu} H_{\mu\mu'}^{(x)} C_{\mu'} + 2 \sum_{\mu v'} C_{\mu} H_{\mu v'}^{(x)} C_{v'} + \sum_{vv'} C_{v} H_{vv'}^{(x)} C_{v'} \\ + 2 \sum_{\mu\rho'} C_{\mu} H_{\mu\rho'}^{(x)} C_{\rho'} + 2 \sum_{v\rho'} C_{v} H_{v\rho'}^{(x)} C_{\rho'} + \sum_{\rho\rho'} C_{\rho} H_{\rho\rho'}^{(x)} C_{\rho'} \quad \text{IV-(22)}$$

where derivatives of the CI coefficients C_{μ} , C_v , and C_{ρ} do not contribute since the CCI energy has been variationally optimized with respect to these parameters. The (x) superscript is used to indicate that fully differentiated MO integrals are used. The fully differentiated one and two electron integrals are given by

$$h_{ij}^{(x)} = h_{ij}^x + \sum_k [U_{ki}^x h_{kj} + U_{kj}^x h_{ki}] \quad \text{IV-(23)}$$

$$(ij|kl)^{(x)} = (ij|kl)^x + \sum_m [U_{mi}^x (mj|kl) + U_{mj}^x (im|kl) \\ + U_{mk}^x (ij|ml) + U_{ml}^x (ij|km)] \quad \text{IV-(24)}$$

where h_{ij}^x and $(ij|kl)^x$ are one and two electron derivative integrals transformed into the MO basis.

$$h_{ij}^x = \sum_{rs} C_r^i C_s^j h_{rs}^x \quad \text{IV-(25)}$$

$$h_{rs}^x = \frac{\partial \langle \chi_r | h | \chi_s \rangle}{\partial x} \quad \text{IV-(26)}$$

$$(ij|kl)^x = \sum_{rspq} C_r^i C_s^j C_p^k C_q^l (rs|pq)^x \quad \text{IV-(27)}$$

χ_r and χ_s are atomic orbital basis functions and the $U_{\mathbf{K}}^x$ are the solutions to the CPMCSCF equations, for an MCSCF reference function. A derivative Hamiltonian matrix element, $H_{\mu\mu}^{(x)}$, is simply given by

$$H_{\mu\mu}^{(x)} = \sum_{ij} A_{ij}^{\mu\mu'} h_{ij}^{(x)} + \sum_{ijkl} B_{ijkl}^{\mu\mu'} (ij|kl)^{(x)}. \quad \text{IV-(28)}$$

Since the coupling coefficients are independent of the perturbation x , the remaining derivative Hamiltonian matrix elements in which only coupling coefficients and integrals appear can be written in a similar fashion. The difficult part, and unique to the E_{CCI} gradient, is evaluating the derivative of a Hamiltonian matrix element that also depends on C_v^a or C_p^{ab} . Since these coefficients are not allowed to vary in the variational CCI calculation, they give a non-zero contribution to the gradient. However, their contribution need not be explicitly formed. By rearranging summations, several density matrix-like objects can be formed which precludes the necessity of writing to disk or transforming any derivative integrals. Furthermore, since the C_v^a and C_p^{ab} were formed from a well defined, non-variational procedure, it is not necessary to solve a set of CPCI-like equations for their contribution, but rather just explicitly differentiate equations IV-(4) and IV-(5). One set of CPMCSCF-like equations will need to be solved in order to obtain the contribution due to C_I^x and U^x , similar to the MCSCF-CI energy gradient.

Before proceeding any further, expressions for all the derivative Hamiltonian matrix elements appearing in equation IV-(22) (except for that given by equation IV-(28)) are presented in equations IV-(29) through IV-(33).

$$H_{\mu\nu}^{(x)} = \sum_{a'} [C_v^{a'} \{H_{\mu\nu}^{a'}\}^{(x)} + \{C_v^{a'}\}^{(x)} H_{\mu\nu}^{a'}] \quad \text{IV-(29)}$$

$$H_{vv}^{(x)} = \sum_{a,a'} [C_v^a C_v^{a'} \{H_{vv}^{a,a'}\}^{(x)} + C_v^a \{C_v^{a'}\}^{(x)} H_{vv}^{a,a'} + \{C_v^a\}^{(x)} C_v^{a'} H_{vv}^{a,a'}] \quad \text{IV-(30)}$$

$$H_{\mu\rho}^{(x)} = \sum_{a,b'} [C_{\rho}^{a,b'} \{H_{\mu\rho}^{a,b'}\}^{(x)} + \{C_{\rho}^{a,b'}\}^{(x)} H_{\mu\rho}^{a,b'}] \quad \text{IV-(31)}$$

$$H_{vp}^{(x)} = \sum_{a,a'} [C_v^a C_{\rho'}^{a'} \{H_{vp}^{a,a'}\}^{(x)} + C_v^a \{C_{\rho'}^{a'}\}^{(x)} H_{vp}^{a,a'} + \{C_v^a\}^{(x)} C_{\rho'}^{a'} H_{vp}^{a,a'}] \quad \text{IV-(32)}$$

$$H_{pp}^{(x)} = \sum_{ab,a'b'} [C_{\rho}^{ab} C_{\rho'}^{a'b'} \{H_{pp}^{ab,a'b'}\}^{(x)} + C_{\rho}^{ab} \{C_{\rho'}^{a'b'}\}^{(x)} H_{pp}^{ab,a'b'} + \{C_{\rho}^{ab}\}^{(x)} C_{\rho'}^{a'b'} H_{pp}^{ab,a'b'}] \quad \text{IV-(33)}$$

All of the derivative Hamiltonian matrix elements appearing on the right hand side (rhs) of equations IV-(29) through IV-(33) depend only on coupling coefficients and derivative integrals and so can be written in a fashion similar to equation IV-(28). A more enlightening form for E_{CCI}^X can be obtained by substituting the expressions given in equations IV-(29) through IV-(33) into equation IV-(22) and performing a little algebra.

$$\begin{aligned} E_{CCI}^X = & [\sum_{\mu\mu'} C_{\mu} C_{\mu'} H_{\mu\mu'}^{(x)} + 2 \sum_{\mu\nu'} C_{\mu} C_{\nu'} \sum_{a'} C_{\nu'}^{a'} \{H_{\mu\nu'}^{a,a'}\}^{(x)} \\ & + \sum_{\nu\nu'} C_{\nu} C_{\nu'} \sum_{aa'} C_{\nu}^a C_{\nu'}^{a'} \{H_{\nu\nu'}^{a,a'}\}^{(x)} + 2 \sum_{\mu\rho'} C_{\mu} C_{\rho'} \sum_{a'b'} C_{\rho'}^{a'b'} \{H_{\mu\rho'}^{a,b'}\}^{(x)} \\ & + 2 \sum_{\nu\rho'} C_{\nu} C_{\rho'} \sum_{aa'b'} C_{\nu}^a C_{\rho'}^{a'b'} \{H_{\nu\rho'}^{a,a'b'}\}^{(x)} \\ & + \sum_{\rho\rho'} C_{\rho} C_{\rho'} \sum_{aba'b'} C_{\rho}^{ab} C_{\rho'}^{a'b'} \{H_{\rho\rho'}^{ab,a'b'}\}^{(x)}] \\ & + [2 \sum_{\mu\nu'} C_{\mu} C_{\nu'} \sum_{a'} H_{\mu\nu'}^{a'} \{C_{\nu'}^{a'}\}^{(x)} + 2 \sum_{\nu\nu'} C_{\nu} C_{\nu'} \sum_{aa'} C_{\nu}^a H_{\nu\nu'}^{a,a'} \{C_{\nu'}^{a'}\}^{(x)} \\ & + 2 \sum_{\mu\rho'} C_{\mu} C_{\rho'} \sum_{a'b'} H_{\mu\rho'}^{a'b'} \{C_{\rho'}^{a'b'}\}^{(x)} + 2 \sum_{\nu\rho'} C_{\nu} C_{\rho'} \sum_{aa'b'} [C_{\nu}^a \{C_{\rho'}^{a'b'}\}^{(x)} \\ & + C_{\rho'}^{a'b'} \{C_{\nu}^a\}^{(x)}] H_{\nu\rho'}^{a,a'b'} + 2 \sum_{\rho\rho'} C_{\rho} C_{\rho'} \sum_{aba'b'} C_{\rho}^{ab} H_{\rho\rho'}^{ab,a'b'} \{C_{\rho'}^{a'b'}\}^{(x)}] \end{aligned} \quad \text{IV-(34)}$$

The first bracketed term in equation IV-(34) involves only derivative Hamiltonian matrix elements whereas the second deals with derivatives of the coefficients determined via equations IV-(4) and IV-(5). For convenience, let us concern ourselves only with the first bracketed term presently.

Substituting an expression involving only coupling coefficients and derivative integrals for the derivative Hamiltonian matrix elements and rearranging the summations somewhat, yields the following equation for the first bracketed term

$$[E_{CCl}^x]^1 = \sum_{ij} g_{ij} h_{ij}^{(x)} + \sum_{ijkl} G_{ijkl} (ij | kl)^{(x)} \quad \text{IV-(35)}$$

where the following definitions have been made

$$\begin{aligned} g_{ij} = & \sum_{\mu\mu'} C_{\mu} C_{\mu'} A_{ij}^{\mu\mu'} + 2 \sum_{\mu\nu'} C_{\mu} C_{\nu'} \sum_{a'} C_{\nu'}^{a'} A_{ij}^{\mu,\nu'a'} \\ & + \sum_{\nu\nu'} C_{\nu} C_{\nu'} \sum_{aa'} C_{\nu}^a C_{\nu'}^{a'} A_{ij}^{\nu a,\nu'a'} \\ & + 2 \sum_{\mu\rho'} C_{\mu} C_{\rho'} \sum_{a'b'} C_{\rho'}^{a'b'} A_{ij}^{\mu,\rho'a'b'} \\ & + 2 \sum_{\nu\rho'} C_{\nu} C_{\rho'} \sum_{aa'b'} C_{\nu}^a C_{\rho'}^{a'b'} A_{ij}^{\nu a,\rho'a'b'} \\ & + \sum_{\rho\rho'} C_{\rho} C_{\rho'} \sum_{aba'b'} C_{\rho}^{ab} C_{\rho'}^{a'b'} A_{ij}^{\rho ab,\rho'a'b'} \end{aligned} \quad \text{IV-(36)}$$

$$\begin{aligned} G_{ijkl} = & \sum_{\mu\mu'} C_{\mu} C_{\mu'} B_{ijkl}^{\mu\mu'} + 2 \sum_{\mu\nu'} C_{\mu} C_{\nu'} \sum_{a'} C_{\nu'}^{a'} B_{ijkl}^{\mu,\nu'a'} \\ & + \sum_{\nu\nu'} C_{\nu} C_{\nu'} \sum_{aa'} C_{\nu}^a C_{\nu'}^{a'} B_{ijkl}^{\nu a,\nu'a'} \\ & + 2 \sum_{\mu\rho'} C_{\mu} C_{\rho'} \sum_{a'b'} C_{\rho'}^{a'b'} B_{ijkl}^{\mu,\rho'a'b'} \\ & + 2 \sum_{\nu\rho'} C_{\nu} C_{\rho'} \sum_{aa'b'} C_{\nu}^a C_{\rho'}^{a'b'} B_{ijkl}^{\nu a,\rho'a'b'} \\ & + \sum_{\rho\rho'} C_{\rho} C_{\rho'} \sum_{aba'b'} C_{\rho}^{ab} C_{\rho'}^{a'b'} B_{ijkl}^{\rho ab,\rho'a'b'} \end{aligned} \quad \text{IV-(37)}$$

The g_{ij} and G_{ijkl} can be viewed as the reduced one and two particle density matrices of the MRCCI wave function, since it is easily shown that

$$E_{CCI} = \sum_{ij} g_{ij} h_{ij} + \sum_{ijkl} G_{ijkl} (ij | kl) \quad \text{IV-(38)}$$

Turning now to the second bracketed term in equation IV-(34), it is apparent that $[E_{CCI}^x]^2$ can be represented by

$$[E_{CCI}^x]^2 = \sum_{ij} \frac{\partial g_{ij}}{\partial x} h_{ij} + \sum_{ijkl} \frac{\partial G_{ijkl}}{\partial x} (ij | kl) \quad \text{IV-(39)}$$

However, an equation involving derivative integrals will be much more useful from a computational point of view and so expressions for $\{C_v^a\}^{(x)}$ and $\{C_p^{ab}\}^{(x)}$ are needed. Symbolically representing equations IV-(4) and IV-(5) as

$$Z(x) = 0 \quad \text{for } x = x_0, \quad \text{IV-(40)}$$

and expanding $Z(x)$ as a power series about x_0 , we obtain

$$Z(x) = Z(x_0) + \left(\frac{\partial Z(x)}{\partial x}\right)_{x_0} (x - x_0) + \dots \quad \text{IV-(41)}$$

Therefore, in order that equation IV-(40) be true to first order

$$\left(\frac{\partial Z(x)}{\partial x}\right)_{x_0} = 0 \quad \text{IV-(42)}$$

must hold. Thus, differentiating equations IV-(4) and IV-(5) with respect to a nuclear perturbation x yields the following identities for $\{C_v^a\}^{(x)}$ and $\{C_p^{ab}\}^{(x)}$

$$\{C_v^a\}^{(x)} = \frac{\{H_{0v}^a\}^{(x)}}{(E_0 - H_{vv}^{a,a})} - \frac{C_v^a}{(E_0 - H_{vv}^{a,a})} (E_0^x - \{H_{vv}^{a,a}\}^{(x)}) \quad \text{IV-(43)}$$

$$\begin{aligned} \{C_p^{ab}\}^{(x)} = & \frac{\{H_{0p}^{ab}\}^{(x)}}{(E_0 - H_{pp}^{ab,ab})} \\ & - \frac{C_p^{ab}}{(E_0 - H_{pp}^{ab,ab})} (E_0^x - \{H_{pp}^{ab,ab}\}^{(x)}) \end{aligned} \quad \text{IV-(44)}$$

Note that the rhs of equations IV-(43) and IV-(44) are in terms of derivative Hamiltonian matrix elements and E_0^x only. Representing E_0^x as

$$E_0^x = \sum_I C_I C_J H_{IJ}^{(x)} \quad \text{IV-(45)}$$

and substituting these expressions into the second bracketed term in equation IV-(34) and making a few definitions we obtain

$$[E_{CCI}^x]^2 = \sum_{ij} [q_{ij} + p_{ij} + d_{ij}] h_{ij}^{(x)} + \sum_{ijkl} [Q_{ijkl} + P_{ijkl} + D_{ijkl}] (ij|kl)^{(x)} + \sum_I C_I^x \eta_I \quad \text{IV-(46)}$$

where

$$q_{ij} = \alpha \omega_{ij} \quad \text{IV-(47)}$$

$$Q_{ijkl} = \alpha \Omega_{ijkl} \quad \text{IV-(48)}$$

$$\begin{aligned} \alpha = & -[2 \sum_{\mu\nu'} C_\mu C_{\nu'} \sum_{a'} H_{\mu\nu'}^{a'} \Lambda_{\nu'}^{a'} C_{\nu'}^{a'} \\ & + 2 \sum_{\nu\nu'} C_\nu C_{\nu'} \sum_{aa'} C_\nu^a H_{\nu\nu'}^{aa'} \Lambda_{\nu'}^{a'} C_{\nu'}^{a'} \\ & + 2 \sum_{\mu\rho'} C_\mu C_{\rho'} \sum_{a'b'} H_{\mu\rho'}^{a'b'} \Lambda_{\rho'}^{a'b'} C_{\rho'}^{a'b'} \\ & + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_\nu^a H_{\nu\rho'}^{aa'b'} \Lambda_{\rho'}^{a'b'} C_{\rho'}^{a'b'} \\ & + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_{\rho'}^{a'b'} H_{\nu\rho'}^{aa'b'} \Lambda_{\nu}^a C_{\nu}^a \\ & + 2 \sum_{\rho\rho'} C_\rho C_{\rho'} \sum_{aba'b'} C_\rho^{ab} H_{\rho\rho'}^{ab,a'b'} \Lambda_{\rho'}^{a'b'} C_{\rho'}^{a'b'}] \end{aligned} \quad \text{IV-(49)}$$

$$\omega_{ij} = \sum_I C_I C_J A_{ij}^{IJ} \quad \text{IV-(50)}$$

$$\Omega_{ijkl} = \sum_I C_I C_J B_{ijkl}^{IJ} \quad \text{IV-(51)}$$

$$p_{ij} = 2 \sum_{\mu\nu'} C_\mu C_{\nu'} \sum_{a'} H_{\mu\nu'}^{a'} \Lambda_{\nu'}^{a'} C_{\nu'}^{a'} A_{ij}^{v'a',v'a'}$$

$$\begin{aligned}
& + 2 \sum_{\nu\nu'} C_\nu C_{\nu'} \sum_{aa'} C_\nu^a H_{\nu\nu'}^{a,a'} \Lambda_{\nu'}^{a'} C_{\nu'}^{a'} A_{ij}^{\nu'a',\nu'a'} \\
& + 2 \sum_{\mu\rho'} C_\mu C_{\rho'} \sum_{a'b'} H_{\mu\rho'}^{a'b'} \Lambda_{\rho'}^{a'b'} C_{\rho'}^{a'b'} A_{ij}^{\rho'a'b',\rho'a'b'} \\
& + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_\nu^a H_{\nu\rho'}^{a,a'b'} \Lambda_{\rho'}^{a'b'} C_{\rho'}^{a'b'} A_{ij}^{\rho'a'b',\rho'a'b'} \\
& + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_{\rho'}^{a'b'} H_{\nu\rho'}^{a,a'b'} \Lambda_\nu^a C_\nu^a A_{ij}^{\nu'a',\nu'a'} \\
& + 2 \sum_{\rho\rho'} C_\rho C_{\rho'} \sum_{aba'b'} C_\rho^{ab} H_{\rho\rho'}^{ab,a'b'} \Lambda_{\rho'}^{a'b'} C_{\rho'}^{a'b'} A_{ij}^{\rho'a'b',\rho'a'b'}
\end{aligned} \tag{IV-52}$$

$$\begin{aligned}
d_{ij} = & 2 \sum_{\mu\nu'} C_\mu C_{\nu'} \sum_{a'} H_{\mu\nu'}^{a'} \Lambda_{\nu'}^{a'} \sum_I C_I A_{ij}^{I,\nu'a'} \\
& + 2 \sum_{\nu\nu'} C_\nu C_{\nu'} \sum_{aa'} C_\nu^a H_{\nu\nu'}^{a,a'} \Lambda_{\nu'}^{a'} \sum_I C_I A_{ij}^{I,\nu'a'} \\
& + 2 \sum_{\mu\rho'} C_\mu C_{\rho'} \sum_{a'b'} H_{\mu\rho'}^{a'b'} \Lambda_{\rho'}^{a'b'} \sum_I C_I A_{ij}^{I,\rho'a'b'} \\
& + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_\nu^a H_{\nu\rho'}^{a,a'b'} \Lambda_{\rho'}^{a'b'} \sum_I C_I A_{ij}^{I,\rho'a'b'} \\
& + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_{\rho'}^{a'b'} H_{\nu\rho'}^{a,a'b'} \Lambda_\nu^a \sum_I C_I A_{ij}^{I,\nu'a'} \\
& + 2 \sum_{\rho\rho'} C_\rho C_{\rho'} \sum_{aba'b'} C_\rho^{ab} H_{\rho\rho'}^{ab,a'b'} \Lambda_{\rho'}^{a'b'} \sum_I C_I A_{ij}^{I,\rho'a'b'}
\end{aligned} \tag{IV-53}$$

$$\begin{aligned}
\eta_I = & 2 \sum_{\mu\nu'} C_\mu C_{\nu'} \sum_{a'} H_{\mu\nu'}^{a'} \Lambda_{\nu'}^{a'} H_{I\nu'}^{a'} \\
& + 2 \sum_{\nu\nu'} C_\nu C_{\nu'} \sum_{aa'} C_\nu^a H_{\nu\nu'}^{a,a'} \Lambda_{\nu'}^{a'} H_{I\nu'}^{a'} \\
& + 2 \sum_{\mu\rho'} C_\mu C_{\rho'} \sum_{a'b'} H_{\mu\rho'}^{a'b'} \Lambda_{\rho'}^{a'b'} H_{I\rho'}^{a'b'} \\
& + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_\nu^a H_{\nu\rho'}^{a,a'b'} \Lambda_{\rho'}^{a'b'} H_{I\rho'}^{a'b'} \\
& + 2 \sum_{\nu\rho'} C_\nu C_{\rho'} \sum_{aa'b'} C_{\rho'}^{a'b'} H_{\nu\rho'}^{a,a'b'} \Lambda_\nu^a H_{I\nu}^a \\
& + 2 \sum_{\rho\rho'} C_\rho C_{\rho'} \sum_{aba'b'} C_\rho^{ab} H_{\rho\rho'}^{ab,a'b'} \Lambda_{\rho'}^{a'b'} H_{I\rho'}^{a'b'}
\end{aligned} \tag{IV-54}$$

$$\Lambda_\nu^a = \frac{1}{E_0 - H_{\nu\nu}^{a,a}} \tag{IV-55}$$

P_{ijkl} and D_{ijkl} are defined as p_{ij} and d_{ij} respectively, except with B_{ijkl} replacing A_{ij} , and the Λ_ρ^{ab} are defined in an analogous fashion to Λ_ν^a . Note that q_{ij} and Q_{ijkl} derive from the second term of equations IV-(43) and IV-(44); p_{ij} and P_{ijkl} derive from the

third term and d_{ij} , D_{ij} and η_I derive from the first term.

A very compact expression for E_{CCI}^x is obtained by combining equations IV-(35) and IV-(46)

$$E_{CCI}^x = \sum_{ij} \gamma_{ij} h_{ij}^{(x)} + \sum_{ijkl} \Gamma_{ijkl} (ij | kl)^{(x)} + \sum_I C_I^x \eta_I \quad \text{IV-(56)}$$

where

$$\gamma_{ij} = g_{ij} + q_{ij} + p_{ij} + d_{ij} \quad \text{IV-(57)}$$

$$\Gamma_{ijkl} = G_{ijkl} + Q_{ijkl} + P_{ijkl} + D_{ijkl} \quad \text{IV-(58)}$$

It is true that the γ and Γ matrices do not have the full symmetry of the analogous one and two electron integral matrices. However, as in SCF-CI energy gradients, they can be symmetrized or forced to have the full integral symmetry since the quantities they multiply (fully differentiated derivative integrals) do have this symmetry. This is an important simplification for two reasons. Firstly, the additional symmetry can be used to advantage in the actual construction of the γ and Γ matrices since fewer matrix elements need be stored. Secondly, equation IV-(56) can be rewritten in a form which is computationally more efficient.

$$E_{CCI}^x = \sum_{ij} \gamma_{ij} h_{ij}^x + \sum_{ijkl} \Gamma_{ijkl} (ij | kl)^x + 2 \sum_{ij} U_{ij}^x X_{ji} + \sum_I C_I^x \eta_I \quad \text{IV-(59)}$$

where

$$X_{ji} = \sum_m \gamma_{mj} h_{im} + 2 \sum_{mkl} \Gamma_{jmkl} (im | kl) \quad \text{IV-(60)}$$

Note the similarity between equation IV-(59) and the expression for the TCSCF-CI energy gradient, equation II-(51). The contribution due to U^x or C^x in equation IV-(59) can now be included in a fashion similar to the TCSCF-CI case. Namely, the

exchange theorem of Handy and Schaefer is used to set up one set of CPMSCF-like equations to solve for the Z_{ij} and ζ_I . The additional contributions to γ and Γ are then constructed and added, to yield a final expression for the CCI energy gradient

$$E_{CCI}^x = \sum_{ij} \gamma'_{ij} h_{ij}^x + \sum_{ijkl} \Gamma'_{ijkl} (ij|kl)^x + \sum_{ij} v_{ij} S_{ij}^x \quad \text{IV-(61)}$$

$$E_{CCI}^x = \sum_{rs} \gamma'_{rs} h_{rs}^x + \sum_{rspq} \Gamma'_{rspq} (rs|pq)^x + \sum_{rs} v_{rs} S_{rs}^x \quad \text{IV-(62)}$$

Equation IV-(62) has been included to emphasize that once the γ' , Γ' and v matrices have been constructed in the MO basis, they are back transformed into the AO basis where they can be multiplied by the AO derivative integrals as they are constructed. Hence, it is not necessary to write to disk or transform any derivative integrals. Furthermore, the CCI gradient cast in the present form is clearly less costly than the uncontracted CI gradient, although the *most efficient* computational approach is not easily recognized. In Section IV-C considerations for an efficient implementation are discussed.

C. Implementational Considerations and General Conclusions

The most cpu intensive step of the CCI energy gradient, with the possible exception of the derivative integrals, will be the construction of the γ and Γ' matrices. The difficult task then, is to construct the G (g), Q (q), P (p) and D (d) matrices and the η vector, where possible, simultaneously. One could easily write formula, based on equations IV-(36),(37),(47)-(55), which would reduce the number of uncontracted CI steps to three. This is largely due to the similarity of Q (q) and P (p).

However, it is probable that further improvements could be made and in truth, any efficient procedure for externally contracted CI gradients must take advantage of the factorization of the coupling coefficients A and B into internal and external parts when constructing the γ and Γ' matrices. The MRCCI energy determination already exploits this simplification. Unfortunately, there is not the time, presently, for me to undertake such a project, since the subject is quite complicated.

Currently, the worst case scenerio would have the MRCCI gradient take approximately 3 times longer than the MRCCI energy. This will most certainly be improved upon with further insights into the efficient evaluation of γ and Γ' . However, even at this stage the analytic MRCCI energy gradient would seem to be very worthwhile, both from a computational viewpoint and an applications viewpoint.

The results of Chapters II and IV do allow a general conclusion to be made about the most efficient method for the evaluation of the energy gradient based on a conventional form of correlated wave function (i.e., CI, Moller-Plesset perturbation theory, coupled cluster theory or any similar procedure). Specifically, the following general set of equations will always be traversed:

$$E^x = \sum_{ij} Q_{ij} h_{ij}^{(x)} + \sum_{ijkl} G_{ijkl} (ij | kl)^{(x)} \quad \text{IV-(63)}$$

$$E^x = \sum_{ij} Q_{ij} h_{ij}^x + \sum_{ijkl} G_{ijkl} (ij | kl)^x + \sum_{ij} U_{ij}^x X_{ji} \quad \text{IV-(64)}$$

$$E^x = \sum_{ij} Q'_{ij} h_{ij}^x + \sum_{ijkl} G'_{ijkl} (ij | kl)^x + \sum_{ij} P_{ij} S_{ij}^x \quad \text{IV-(65)}$$

$$E^x = \sum_{\mu\nu} Q'_{\mu\nu} h_{\mu\nu}^x + \sum_{\mu\nu\rho\sigma} G'_{\mu\nu\rho\sigma} (\mu\nu | \rho\sigma)^x + \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu}^x \quad \text{IV-(66)}$$

where μ , ν , ρ and σ indicate the use of the atomic orbital basis. Equations IV-(63) through IV-(66) assume that a single configuration reference function is used, although with a multi-configuration reference function these equations will be only slightly modified as in equation IV-(56) or II-(51). It is important to note that although the detailed formula for the Q and G matrices will inevitably be determined by the specific type of correlation procedure, the properties of these matrices will be the same independent of the correlation technique used. In other words, Q and G may be forced to have the full integral symmetry and the X matrix will define the correlation independent pairs of molecular orbitals (i.e., $X_{ij} \neq X_{ji}$ for a correlation independent pair). Several researchers have contributed to the establishment of these properties for SCF-CI and MCSCF-CI energy gradients. The work of Pople and co-workers and Handy and co-workers have clearly established these properties for MP2 energy gradients. Analytic CCSD energy gradients may also be represented by equations IV-(63) through IV-(66) as demonstrated by Bartlett and co-workers and Scheiner and co-workers.

The basic reason that equation IV-(66) represents the most efficient formulation possible is really quite simple. Firstly, derivative integrals are not required to be stored or transformed. This is clearly a very important consideration, since in the limit of a large number of atoms, the transformation of all sets of derivative integrals will indeed be very expensive.

Also, the formation of the G matrix will necessarily require the same order of

magnitude of cpu time as the energy itself and need only be performed *once*. The additional contributions to G' will always be n^4 (in the MO basis and excluding the formation of X), and so are not expensive. Thus, once the G' matrix is formed only one n^5 step remains (back transformation of G' into the AO basis) and the determination of the AO derivative integrals.

Lastly, experience with MP2 and CI analytic energy second derivatives has demonstrated that the Q' , G' and P matrices will always be dotted against the highest order derivative integrals, i.e., for a CI third derivative Q' , G' and P will multiply the atomic orbital third derivative one electron, two electron and overlap integrals, respectively.

II. CHEMICAL APPLICATIONS

A. General Introduction and Computational Details

Presented in this chapter are several applications of the derivative methods outlined in Chapters II and III. The individual sections are grouped so that the content is internally consistent though each section may represent more than a single project. The single criterion used in selecting the projects to be included in this chapter was that they use some form of correlated derivative technique. The projects chosen, I believe, represent a good sampling of the work I have performed. They also exhibit the power and usefulness of analytic derivative methods for correlated wave functions in *ab initio* quantum chemistry.

Since I have spent a good deal of effort in predicting band centers of polyatomic cations, four have been included here. Protonated HCN and protonated nitrous oxide have been included because the theoretical predictions made using the correlated derivative methods were experimentally shown to be exceedingly accurate. Protonated acetylene and the acetylene radical cation have been included because the systems are quite interesting, especially considering that they are predicted to have band centers right on top of one another. Protonated acetylene is interesting for another reason too, in that it has many large amplitude motions due to the nature (flatness) of its potential energy surface. This molecule exhibits the need of better ways of treating what I term as "equilibrium dynamics." In other words, general methods for going beyond the harmonic oscillator approximation for polyatomic systems with many anharmonic or large amplitude modes need to be developed.

The study on the HSOH molecule is included because it represents the first example where it became clear that analytic CI second derivative methods are cost effective. Hydrogen thioperoxide is also of chemical interest and these aspects are

discussed.

I find the study on CH_2^- extremely interesting. The original problem itself is really quite complex but in the end the ultimate goal was simply to theoretically predict the radiative decay lifetimes of the bending levels of CH_2^- . In truth, I believe that I learned as much working on this project as any other study with which I was involved in my graduate years.

Finally, the higher excitation study on HF and N_2 is presented. This study is quite unique in its presentation of results from so many different types of electron correlation methods. From the results presented, one is able to deduce a fairly accurate picture of the structure of the electronic Hamiltonian matrix and this will no doubt be very useful in the future when one is deciding the direction which his research should follow.

Before beginning with the first section a few computational details will be given. Unless otherwise specified, all basis sets used for H and all first row atoms are Dunning's⁴⁹ double zeta (DZ) contraction of Hunzinaga's⁵⁰ primitive set. The s functions on H have been scaled by 1.2, i.e., all primitive Gaussian orbital exponents were multiplied by 1.44. For the standard DZ plus polarization (DZ+P) basis sets the polarization exponents are $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{N}) = 0.80$ and in most cases $\alpha_p(\text{H}) = 1.0$. For the acetylene and protonated acetylene results the value $\alpha_p(\text{H}) = 0.75$ was used. For sulfur, the Dunning and Hay⁵¹ DZ basis was augmented with one set of polarization functions [$\alpha_d(\text{S}) = 0.50$] to give the DZ+P basis.

All CI calculations were performed with the shape driven graphical unitary group CI program³⁶. The analytic CI gradient¹⁸ and analytic CI second derivative methods were used where noted.

B. Molecular Structure and Infrared Spectrum of Protonated HCN, HCNH^+ and Protonated Nitrous Oxide, NNOH^+ and ONNH^+

1. HCNH^+

During the past few years the infrared spectra of a number of polyatomic molecular ions, including HCO^+ , HN_2^+ , H_3O^+ , and NH_4^+ , have been observed⁵²⁻⁵⁶ at high resolution using the velocity-modulated absorption spectroscopy technique developed by Saykally and co-workers⁵⁷. In the cases of the larger molecules H_3O^+ and NH_4^+ , the spectroscopic identification was assisted by reliable theoretical^{58,59} predictions. It is apparent that the spectroscopic tools developed by Saykally⁵⁷ and by Oka⁶⁰ are applicable to a broad range of positive ions, and new experimental results should be forthcoming shortly. In their paper, Crofton and Oka⁵⁵ specifically identify CH_5^+ , HCNH^+ , and C_2H_3^+ as important targets and call for theoretical predictions of the IR spectra of these species. Of these, the CH_5^+ ion has already been studied⁶¹ by Frisch and Pople. The present theoretical report⁶² concerns HCNH^+ , protonated HCN.

The theoretical approach adopted here was to predict the harmonic vibrational frequencies of HCNH^+ using two well-calibrated methods. Both the SCF and CISD methods were used in conjunction with a DZ+P basis set. The CI wave functions included all single and double excitations relative to the Hartree-Fock reference configuration, with the exception that the core orbitals (two lowest occupied and two highest virtual SCF orbitals) were deleted.

At the SCF level of theory, analytic first and second derivative methods were used to determine gradients and force constants. At the CI level, analytic gradients were used in the geometry search, while force constants were evaluated via finite differences of analytic gradients. The latter procedure requires gradient calculations in C_s symmetry, where 7813 configurations are included in each CI wave function.

The DZ+P SCF predictions are summarized in Table V-(1), along with the geometrical structures in Figure V-(1). The total energy at this level of theory is -93.17698 hartrees and the equilibrium dipole moment (with respect to the center of mass) is 0.59 D. It is well known that the DZ+P SCF harmonic vibrational frequencies for such a small molecule will be considerably higher than the observed (anharmonic) fundamentals. Therefore the DZ+P SCF frequencies have been scaled down using precisely analogous predictions^{59,63} for the isoelectronic HCN and HNC molecules, for which the fundamentals have been observed⁶⁴⁻⁶⁶ in the laboratory. Note that this procedure does not provide an estimate for the HCNH^+ degenerate bending mode ν_5 , since the analogous fundamental ν_2 of the isolated HNC molecule has not been observed.

Infrared intensities are also predicted in Table V-(1). The two fundamentals most readily observed in Saykally's experiment are the N-H and C-H stretching frequencies. Note further, that the stronger (of the two) N-H stretch is comparable to the O-H stretch recently observed for H_3O^+ . The C-H vibration is predicted to give rise to a somewhat weaker absorption. It may be that the N-H stretch is a better candidate for immediate observation. This qualitative prediction is confirmed at the DZ+P CI level of theory.

CI harmonic vibrational frequencies are also given in Table V-(1), and these are expected to be significantly closer to the exact (unknown) values. In a survey of five closed-shell molecules, Yamaguchi⁵⁹ found the DZ+P CI harmonic frequencies to lie 3.5% higher than the experimental harmonic frequencies on average. Even so, the remaining errors and required correction for anharmonicity necessitates an estimation procedure analogous to that described above for the DZ+P SCF method. The results of this semiempirical scheme are given in Table V-(1) and are encouragingly close to the SCF estimates. The final predicted ν_1 (N-H stretch) is 3474 cm^{-1} , only 19 cm^{-1} higher than the SCF based value. The value $\nu_1(\text{N-H}) = 3474\text{ cm}^{-1}$ is

also readily distinguishable from the strong absorption $\nu_3(\text{N-H}) = 3343 \text{ cm}^{-1}$ observed recently by the Oka and Saykally groups for NH_4^+ . Direct comparison with the analogous calculations for NH_4^+ gives 132 cm^{-1} (DZ+P SCF) and 122 cm^{-1} (DZ+P CI) for the predicted difference between $\nu_1(\text{HCNH}^+)$ and $\nu_3(\text{NH}_4^+)$.

The DZ+P CI equilibrium geometry total energy for HCNH^+ is -93.44627 hartrees and the dipole moment μ (evaluated as an energy derivative) is predicted to be 0.34 D relative to the center of mass. This dipole moment is somewhat larger than the value $\mu = 0.23 \text{ D}$ predicted⁶⁷ by Haese and Woods, and hence improves the expectation of observing HCNH^+ in the microwave region, and subsequently in interstellar space.

Not long after the completion of the just described research Altman, Crofton and Oka⁶⁸, using these theoretical predictions as a guide, were able to experimentally observe the C-H and N-H stretching fundamental frequencies at 3188 cm^{-1} and 3474 cm^{-1} , respectively. From Table V-(1), we see that the estimated DZ+P CISD fundamentals are at 3201 cm^{-1} and 3474 cm^{-1} for the C-H and N-H stretches, respectively, and are in excellent agreement with the high resolution infrared experiments.

Also, the millimeter and submillimeter spectrum of HCNH^+ was observed⁶⁹ in the laboratory. Almost simultaneously, the microwave spectrum of HCNH^+ was detected⁷⁰ in interstellar space, though its ^{14}N quadrupole coupling constant was too small⁷¹ to allow resolution of the fine structure.

2. NNOH^+ and ONNH^+

The first high-resolution spectroscopic observation of protonated nitrous oxide (N_2O) has recently been reported⁷² by Amano. The band origin of the ν_1 fundamental is $3330.9107 \text{ cm}^{-1}$. With this sort of resolution, the reader may wonder what contribution theory might possibly make to the problem. However, despite the awe-

some precision of Amano's spectroscopic measurements, one fundamental question remains unanswered from his important laboratory study.

What is the shape of the HN_2O^+ molecule? From the observed A rotational constant, Amano concluded that the molecule is bent and that the angle $\theta(\text{HON})$ or $\theta(\text{HNN})$ is about 112° . But it was not possible to determine whether the molecule is O-protonated or N-protonated from the spectroscopic data. Amano does cite a recent paper by McMahon and Kebarle⁷³, who note a strong correlation for a series of molecules between proton affinity and oxygen 1s ionization potentials. McMahon and Kebarle state "The only points included in the plot not falling on or near the correlation line are those for CO and N_2O . The lack of correlation for CO is a result of the fact that the most favorable protonation of CO is on carbon rather than oxygen. The data for N_2O would suggest a similar interpretation, i.e., N_2O must be a nitrogen, rather than an oxygen base giving rise to ONNH^+ rather than NNOH^+ as the most stable structure." A more naive argument leading to the same conclusion is that the proton affinity of NH_3 (205 kcal/mol) is significantly greater⁷⁴ than that of H_2O (165 kcal/mol).

This research presents an interpretation of the Amano experiments⁷² based on *ab initio* molecular orbital theory. Equilibrium geometries, energetics, and vibrational frequencies have been predicted for both the oxygen-protonated and nitrogen-protonated structures. Initially, the DZ+P SCF level of theory was utilized.

The DZ+P SCF predictions for protonated nitrous oxide are summarized in Figure V-(2) and Table V-(2). The predicted rotational constant A *immediately shows that the observed species is oxygen-protonated nitrous oxide*. The A constant for the nitrogen-protonated structure is nearly twice the observed value, while the DZ+P SCF prediction for NNOH^+ is just 4.8% higher. Note that the identification of the oxygen-protonated species is not consistent with the abovementioned arguments of McMahon and Kebarle⁷³ or with that based on the fact that the proton

affinity of ammonia is notably greater than that of water.

Generally, a comparison between the theoretical and experimental values of ν_1 would be sufficient to distinguish between the two structures. From Table V-(2) it may be concluded that such a distinction is not possible at the DZ+P SCF level of theory. For water and the hydronium^{52,58} ion (H_3O^+) DZ+P SCF *harmonic* O-H stretching frequencies are about 12% above the experimental *anharmonic* O-H stretching frequencies. However, the predicted O-H harmonic frequency for NNOH^+ is 16% above the observed fundamental. This agreement is not sufficiently consistent with earlier comparisons to identify NNOH^+ as the observed species.

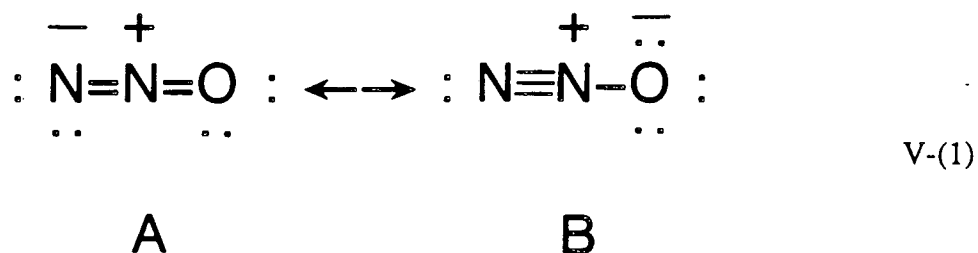
It is of course possible that the ONNH^+ species might be *excluded* by a comparison of the theoretical N-H harmonic vibrational frequency with Amano's observed⁷² fundamental. For NH_4^+ the DZ+P SCF⁵⁹ harmonic frequency ω_3 is 3737 cm^{-1} , or 11.8% above the observed^{55,56} fundamental $\nu_3 = 3343\text{ cm}^{-1}$. However, for ONNH^+ , the DZ+P SCF harmonic stretch is 8.8% above Amano's $\nu_1 = 3331\text{ cm}^{-1}$. So in fact, the ONNH^+ ω_1 fits the observed ν_1 slightly better than the NNOH^+ harmonic frequency at the DZ+P SCF level of theory. Fortunately, the great disparity in rotational constants resolves the problem in favor of the NNOH^+ structure.

The effects of electron correlation were variationally considered by means of configuration interaction. Specifically, all valence shell single and double excitations were included in the CI (i.e., CISD). For C_s symmetry there are a total of 25 839 configurations. CISD equilibrium geometries were optimized using analytic CI gradient methods, and harmonic vibrational frequencies were evaluated at the correlated level via finite differences of analytic gradients. The latter procedure requires the determination of some points under C_1 symmetry (no elements of symmetry except the identity), where the CI includes 49 141 configurations. Dipole moment derivatives were determined via finite differences of CI dipole moments, the latter being defined²³ as an energy derivative.

The DZ+P CISD theoretical predications are included in Table V-(2) and Figure V-(2). These higher-level theoretical results confirm the SCF prediction that the NNOH^+ structure is indeed the one observed by Amano. In fact, the predicted rotational constants are perhaps a bit closer to experiment than might be expected from this level of theory. In particular, the DZ+P CISD value of the A constant, 627 900 MHz, is only 0.3% higher than Amano's spectroscopic value. The absolute errors, approximately 100 MHz, are even smaller for the B and C rotational constants.

The correlated (CISD) geometrical structures are qualitatively similar to the SCF predictions. However, there are some non-trivial geometrical shifts for the higher energy ONNH^+ isomer. There the N-N distance increases by 0.030 Å and the N-O distance by 0.024 Å, when correlation effects are considered. Also, the HNN angle is seen to decrease by 4.3° in going from SCF to CISD. Such a large correlation effect on bond angle was not found^{75,76} for the isoelectronic isomers HNCO and HCNO .

A final comparison from Figure V-(2) may be made between the $\text{NNOH}^+/\text{ONNH}^+$ structures and that of the parent neutral N_2O molecule. The simple resonance hybrid picture of nitrous oxide is:



As a proton approaches the nitrogen end of N_2O , the left-hand valence structure will be favored over the right, and the resulting ONNH^+ valence structure will be



Taking structures (1A) and (2) literally, one would conclude that the major structural shift upon nitrogen protonation should be a lengthening of the N=N double bond. In (1A) this distance is shortened due to the attraction of the formal plus and minus charges on the adjacent nitrogen atoms. In (2) the negative charge is removed. Inspection of Figure V-(2) shows that the N=N distance is indeed predicted to increase upon nitrogen-protonation, by 0.023 Å (DZ+P SCF) or by 0.025 Å (DZ+P CISD).

Analogous reasoning suggests that as a proton approaches N₂O from the oxygen side, resonance structure (1B) will be favored over (1A) giving



for the qualitative valence bond description of the electronic structure. Simple logic then suggests that the N-O single bond distance for (3) should be longer than that for the neutral N₂O molecule. Theory confirms this simple prediction, with the N-O distance increase upon oxygen-protonation being 0.087 Å (DZ+P SCF) or 0.089 Å (DZ+P CISD). It is certainly encouraging that such a qualitative, traditional picture gives the correct trend for these structural results.

Finally, the harmonic vibrational frequencies predicted at the DZ+P CISD level of theory are considered. Table V-(2) shows, as expected, that both X-H stretching frequencies decrease when electron correlation is explicitly considered. However, the decreases (50 cm⁻¹ = 1.4% for ONNH⁺; and 136 cm⁻¹ = 3.6% for NNOH⁺) are even smaller than expected. The CI harmonic frequency for the oxygen-protonated species is 3729 cm⁻¹, or 11.9% above the observed fundamental. This large deviation (3.5% is a more typical error for this level of theory⁵⁹) reconfirms the earlier statement that the theoretical rotational constants are absolutely vital in the identification of the observed NNOH⁺ isomer. It also suggests that a larger basis

set or a more complete description of correlation effects is required for a satisfactory treatment of the IR spectrum of NNOH^+ .

The above considerations warranted additional SCF structures and vibrational frequencies to be determined using the DZ basis set augmented by two sets of polarization functions (DZ+2P). Polarization function orbital exponents were $\alpha_d(\text{N}, \text{O}) = 1.5, 0.35$ and $\alpha_p(\text{H}) = 1.4, 0.25$. Total energies at the predicted equilibrium geometries were $-183.938\,46$ (ONNH^+) and $-183.975\,41$ hartree (NNOH^+). For the former structure, the use of two sets of polarization functions decreases the HNN bond angle by 3.8° , from 135.4° (DZ+P) to 131.6° (DZ+2P). The predicted X-H stretching frequencies are 3592 cm^{-1} (ONNH^+) and 3844 cm^{-1} (NNOH^+), corresponding to reductions of 31 and 21 cm^{-1} , respectively, compared to the DZ+P SCF predictions. The DZ+2P X-H stretching frequencies are thus 7.8% and 15.4% above Amano's observed fundamental. It is clear that this extension of the basis set does not provide a satisfactory theoretical prediction of the O-H stretching frequency.

The harmonic vibrational frequencies of nitrous oxide itself are predicted to be $2589, 1358$ and 668 cm^{-1} (DZ+P SCF) and $2402, 1352$ and 606 cm^{-1} (DZ+P CISD). These predictions are 16.4%, 5.7% and 13.4% (DZ+P CISD) higher than the observed⁷⁷ fundamentals.

Every level of theory considered here indicates that the oxygen-protonated structure lies energetically lower than the nitrogen-protonated species. The energy difference between the two structures is predicted to be 24.6 kcal/mol (DZ+P SCF), 14.2 kcal/mol (DZ+P CISD), 11.5 kcal/mol (unlinked cluster⁷⁸ corrected DZ+P CISD), and 23.3 kcal/mol (DZ+2P SCF). These results are of course consistent with the identification of the oxygen-protonated structure as the observed species.

C. Structures, Vibrational Frequencies and Infrared Intensities from Explicitly Correlated Wave Functions for the Classical and Nonclassical Forms of Protonated Acetylene, $C_2H_3^+$ and the Acetylene Radical Cation, $C_2H_2^+$

1. $C_2H_3^+$

In 1984 Raine and Schaefer⁷⁹ (RS), at the encouragement of Crofton and Oka⁵⁵ reported theoretical predictions of the vibrational frequencies and infrared intensities of the classical and nonclassical isomers of protonated acetylene. Based on successful analogous predictions for protonated ammonia^{55,56,59} and protonated water^{52,58}, RS used a relatively simple *ab initio* theoretical method, the SCF method employing a standard DZ+P basis set.

From the scaled harmonic vibrational frequencies, it appeared possible to make a clear distinction between the two isomers. Specifically RS stated that "If only one of the structures is present in the experiment, it should be possible to differentiate between the two. Working in the IR region, looking at the C-H stretches, the intensities indicate that only one fundamental (3148 cm^{-1}) would be observed for the nonclassical, bridged structure. The classical structure, on the other hand, would possibly exhibit three fundamental C-H stretches." However, RS also cautioned that "On the basis of energetics it is possible that both structures will be present, so the high resolution vibrational spectroscopy might not aid in the determination of the unique low energy structure." In 1985, Oka and co-workers⁸⁰ believed that they had indeed observed protonated acetylene. However, the experimental spectrum was very complicated, and a simple analysis was not possible. Moreover, the predictions of RS were not of much help in attempting to unravel this intricate spectrum.

The most obvious potential source of error in the theoretical work of RS is the use of an inadequately complete level of theory. Methods suitable for NH_4^+ ,

H_3O^+ , and most recently protonated carbon dioxide⁸¹ might not be as successful for the C_2H_3^+ system. Therefore, two significantly higher levels of theory are applied to the C_2H_3^+ problem in this research. The other likely source of difficulty is the presence of two structurally dissimilar isomers lying very close together energetically and separated by only a small barrier. The importance of this consideration is, unfortunately, much more difficult to assess.

The first step in the present research was to construct configuration interaction wave functions with the standard DZ+P basis set (note that $\alpha_p(\text{H}) = 0.75$ was used in this study). The CI included all single and double excitations, with the restriction that the core-like (carbon 1s) orbitals were not involved in the CI. That is, the two lowest occupied SCF molecular orbitals were constrained to be doubly occupied in all configurations, and the two highest virtual orbitals were deleted from the CI procedure. In this way there are 5208 CSF's for the classical and 5034 CSF's for the nonclassical structures of C_2H_3^+ . As Figure V-(3) shows both isomers have C_{2v} symmetry.

At the DZ+P CISD level of theory the classical and nonclassical structures were vigorously optimized using analytic CI gradient methods. Then all Cartesian force constants were determined by finite differences of analytic CI gradients. In the latter procedure, geometries as low in symmetry as point group C_1 must be considered, and this necessarily involves larger CI wave functions. Specifically in C_1 symmetry the classical and nonclassical C_2H_3^+ structures require 18 336 configurations for a CI treatment consistent with that described above for the C_{2v} stationary points. Harmonic vibrational frequencies were determined from the Cartesian force constants in the standard⁸² manner.

CI wave functions involving all *triple excitations* were also determined with the DZ+P basis set for both structures. This provides a good idea of the importance of this first class of higher excitations in a precise variational treatment. With two

frozen core and two deleted virtual molecular orbitals, the CISDT wave functions included 213 780 and 212 462 configurations, respectively, for the classical and nonclassical structures.

In light of the lack of obvious agreement between the DZ+P SCF predictions of RS and the observations of Oka, it was also considered necessary to make some predictions with a basis set significantly larger than DZ+P. The larger basis chosen has previously been used by Lee and Schaefer⁸³ and may be labeled TZ+diffuse+2P. For the carbon atom, this basis set begins with the (12s7p) primitive Gaussian basis of van Duijneveldt⁸⁴ and contracts this basis [7s4p]. Similarly van Duijneveldt's hydrogen (6s) basis is contracted to [3s]. To the above basis sets diffuse functions were added, namely $\alpha_s(\text{C}) = 0.039\ 906$, $\alpha_p(\text{C}) = 0.030\ 237$, and $\alpha_s(\text{H}) = 0.030\ 155$. Finally, polarization functions were added, with orbital exponents $\alpha_p(\text{H}) = 0.25$ and 1.4 and $\alpha_d(\text{C}) = 0.35$ and 1.5 .

The final designation for this relatively large basis set is C(13s8p2d/8s5p2d), H(7s2p/4s2p), and full details (e.g., contraction coefficients) are given in Table I of reference 83. Quite a number of significant papers have appeared⁸⁵⁻¹⁰⁷ dealing with the energy difference between classical and nonclassical C_2H_3^+ , but none have employed a basis set as complete as the present. CISD wave functions of the type described above have also been determined with this large basis set, and include (in C_{2v} symmetry) 29 800 configurations (classical) and 28 545 configurations (nonclassical), respectively.

Before presenting the theoretical predictions for C_2H_3^+ , it is well to consider the parent acetylene molecule, for which much unimpeachable experimental data exist. The C-C equilibrium bond distance is known¹⁰⁸ to be $1.203\ \text{\AA}$, a value with which the large basis SCF ($1.179\ \text{\AA}$) and DZ+P CI ($1.213\ \text{\AA}$) predictions agree satisfactorily. For the C-H distance theory predicts $1.054\ \text{\AA}$ (large basis SCF) and $1.062\ \text{\AA}$ (DZ+P CI) vs the experimental¹⁰⁸ $1.061\ \text{\AA}$. The differences between CI and ex-

periment are 0.010 Å (C=C) and 0.001 Å (C-H), suggesting that theory is doing a reasonable job in reproducing the true structure.

Theoretical harmonic and experimental anharmonic vibrational frequencies for C_2H_2 and C_2D_2 are compared in Table V-(3). It should be noted that for the family of molecules CH_4 , HCN , H_2O , and H_2CO , the DZ+P CI harmonic frequencies averaged 3.5% above the "observed" harmonic⁵⁹ frequencies. For C_2H_2 , the differences between theoretical harmonic and observed anharmonic frequencies are 199 cm^{-1} or 5.9% (σ_g), 98 cm^{-1} or 4.9% (σ_g), 189 cm^{-1} or 5.7% (σ_u), -1 cm^{-1} or -0.1% (π_g), and 30 cm^{-1} or 4.1% (π_u). For the C-H stretches the differences of 5.9% and 5.7% are encouragingly consistent.

The basis set dependence of the harmonic frequencies at the SCF level of theory may also be seen in Table V-(3). The differences between the DZ+P SCF and large basis SCF frequencies are 15 (σ_g), -2 (σ_g), 18 (σ_u), -6 (π_g), and 10 cm^{-1} (π_u), respectively. Thus one sees, at least at the SCF level, that the doubling of the basis set produces only minor changes in the predicted vibrational frequencies.

Also given in Table V-(3) are IR intensities¹⁰⁹ for acetylene at three levels of theory. It is encouraging that these results also show little dependence of basis set within the confines of single-configuration Hartree-Fock theory. In each case, the effect of electron correlation is to reduce by 15%-20% the predicted IR intensity. Thus the DZ+P CI intensities are expected to be within perhaps 20% of the exact double harmonic approximation values, and to be useful in assigning IR spectra.

The only shift in vibrational frequency ordering in Table V-(3) occurs for the degenerate bending modes of C_2D_2 . There the π_g mode is higher at the large basis SCF level of theory. In contrast the DZ+P CI method correctly predicts the π_g mode to lie lower by 49 cm^{-1} . The experimental difference is 32 cm^{-1} .

Particularly encouraging in Table V-(3) is the close agreement between theory and experiment for the IR intensities of C_2H_2 . The 1985 paper by Amos already

showed qualitative agreement at the SCF level of theory. Table V-(3) shows that CI, even with the relatively modest DZ+P basis, significantly improves the agreement with experiment. In fact the agreement between CI and experiment in Table V-(3) is to within 10%, perhaps partly fortuitous in light of the seriousness of the double harmonic approximation adopted in our theoretical approach.

Although not the primary focus of this research, historically the greatest interest in the $C_2H_3^+$ problem has abided with the classical-nonclassical energy difference. The highest level of theory previously applied to this problem appears in the work of Raghavachari, Whiteside, Pople, and Schleyer¹⁰⁵ (RWPS). RWPS determined the two $C_2H_3^+$ structures using second-order perturbation theory and the 6-31G* basis set. The 6-31G* basis set is quite similar to the standard DZ+P basis, except that the former does not include a polarization function (p functions) on the three hydrogen atoms and is to some extent deficient in the core/valence region (i.e., the s,p set for a first row atom is deficient) which, for highly accurate *ab initio* calculations, has lead to erroneous conclusions such as the importance of diffuse functions in determining the proton affinities of neutral molecules. With these MP2/6-31G* structures, RWPS reported single point energies from fourth-order perturbation theory exclusive of triple excitations (MP4SDQ) with a larger 6-311G** basis set. In this manner, they predicted the nonclassical structure to lie energetically 3 kcal/mol below the classical structure. Another previous study that must be cited is the research of Weber, Yoshimine, and McLean⁹¹⁻⁹⁴ (WYM), who used a DZ+P CI approach in some respects similar to that reported here. WYM predicted *ab initio* the classical structure to lie 0.01 kcal/mol lower, and estimated the nonclassical (bridged) structure to ultimately lie 1-2 kcal/mol lower. Finally, the 1980 work of Kohler and Lischka⁹⁹ based their estimate that the nonclassical structure lies 3.5-4.0 kcal/mol lower on their CEPA treatment of the problem.

Energetic results from this research are presented in Table V-(4). The large

(TZ+diffuse+2P) basis set SCF method predicts the classical structure to lie lower in energy by $-0.006\,767$ hartrees = -4.98 kcal/mol. Except for the lack of f functions, the large basis SCF energies should approach the Hartee-Fock limits rather closely.

The DZ+P CISD energy difference between the classical and nonclassical structures of C_2H_3^+ is $0.000\,896$ hartrees = 0.56 kcal/mol, with the nonclassical structure lying lower. It is possible to estimate the importance of higher than double excitations (namely unlinked clusters) using a simple approximation⁷⁸ introduced by Davidson. In this way the Davidson corrected DZ+P CI energy difference is $0.000\,964$ hartrees = 0.60 kcal/mol, very similar to the straight CISD prediction with the same basis set.

The largest CI expansions considered were CISDT wave functions constructed from the DZ+P basis set. The classical-nonclassical energy difference obtained in this way is $0.001\,076$ hartrees = 0.68 kcal/mol. This result is consistent with the prediction from the Davidson-corrected CISD treatment in that higher excitations slightly favor the nonclassical structure. The lowering of the total energies due to triple excitations is substantial, about 0.009 hartrees.

The lowest energy wave functions, of course, are the CISD wave functions constructed from the large basis set. The absolute energies are about 0.04 hartrees below the DZ+P CISD results. Equilibrium geometries were not determined at the large basis CI level of theory. However, as Table V-(4) shows, the large basis CI treatments were carried out at both the large basis SCF and DZ+P CI stationary point geometries. Perhaps surprisingly, the former geometries yield lower large basis CISD energies. However, the energy differences are not great, as the energy surfaces are relatively flat in this region. Conversely the Davidson-corrected energies are lower with the DZ+P CISD geometries than with the large basis SCF structures. Actually, as Figures V-(3) and V-(4) show, the two sets of structures are similar and should yield similar energetic predictions.

At the large basis SCF geometries, the classical-nonclassical energy difference with the large basis CI method is 0.000 824 hartrees = 0.52 kcal/mol. The analogous Davidson-corrected energy difference is 0.000 544 hartrees = 0.34 kcal/mol. At the DZ+P CI stationary point geometries, the large basis CI energy difference is 0.001 072 hartrees = 0.67 kcal/mol. The analogous Davidson-corrected energy difference between the classical and nonclassical structures is 0.001 184 hartrees = 0.74 kcal/mol.

It is appropriate to consider the effect of zero-point vibrational energy (ZPVE) on the energy difference ΔE (classical-nonclassical). Within the harmonic approximation, the ZPVE's at the DZ+P CI level of theory are 22.36 (classical) and 21.98 kcal/mol (nonclassical). This small difference of 0.47 kcal/mol was anticipated due to the fact that the classical structure has three (high frequency) C-H stretches, while one of these is shifted lower due to the bridging proton in the nonclassical structure.

The standard correction for finite temperature¹¹⁰ (298 K) is 0.39 kcal/mol for the classical structure but 0.57 for the nonclassical. It is seen that this correction amounts to 0.18 kcal/mol, in the opposite direction to the ZPVE correction. The sum of the two corrections lowers the nonclassical structure by $0.47 - 0.18 = 0.29$ kcal/mol.

The best strictly *ab initio* estimate of ΔE (classical-nonclassical) for $C_2H_3^+$ is obtained by adding the above 0.29 kcal/mol correction to the 0.68 kcal/mol difference from CISDT. In this manner ΔE is predicted to be 0.97 kcal/mol. Based on experience, a proper variational treatment of all quadruple excitations might increase this ΔE value by perhaps 0.5 kcal/mol. Such a predicted energy difference is slightly less than the best previous^{91,95,99,105} theoretical estimates.

Figure V-(3) compares the DZ+P SCF and DZ+P CI molecular structures for $C_2H_3^+$. In general this figure shows that electron correlation has little effect on the predicted equilibrium geometries - as was discussed above for the parent neutral ace-

tylene molecule. The largest single difference occurs for the C-C bond distance of the nonclassical structure. There CI increases the C-C separation by 0.021 Å relative to the SCF prediction. But there are no qualitative changes in either of the two structures of protonated acetylene.

Figure V-(4) presents the large basis set SCF structures, which should be compared with the DZ+P SCF geometrical parameters, given in parentheses in Figure V-(3). Recall from the earlier discussion that the large basis set has slightly more than twice as many functions as the standard DZ+P set. Nevertheless, the DZ+P SCF and large basis SCF structures are very similar, with the four distinct bond angles differing by no more than 0.2 degrees. The differences in bond distances are a bit larger in percentage terms, but still minor. All bond distances are decreased, as expected, in going from the DZ+P to much larger TZ+diffuse+2P set. The differences range from 0.004 to 0.012 Å. This minor basis set dependence supports the belief that, in general, DZ+P CISD structures should be quite reliable for neutrals and positively charged species.

Also included in Table V-(4) are dipole moments evaluated with respect to the center of mass. These dipole moments are seen to be relatively insensitive to the level of theory applied. For the CI dipole moments, the results are also relatively insensitive to the theoretical method of evaluation, be it as a simple expectation value, or via a more elaborate energy derivative²³ method. In every case the nonclassical structure dipole moment (approximately 1.25 D) is larger than that predicted (approximately 0.75 D) for the classical structure. This result implies that, should the classical and nonclassical $C_2H_3^+$ microwave (pure rotational) spectra be separable, the latter is predicted to be the more intense for high temperatures. At low temperatures the population differences of the two forms will dominate the pure rotational spectrum intensities.

The rotational constants for the DZ+P CISD optimum structures are 9.29,

1.08, and 0.97 cm^{-1} for the classical structure and 13.79, 1.13, and 1.04 cm^{-1} for the nonclassical structure. Therefore, since the classical conformer has an *A*-axis dipole moment and the nonclassical form has a *B*-axis dipole moment, the pure rotational spectra of the two species may be separable. However, this conclusion assumes negligible coupling of molecular rotations with other nuclear motions.

The predicted IR spectra of the classical and nonclassical structures of protonated acetylene are given in Table V-(5). The first point to be made in this regard is that both structures are minima at every level of theory considered. This is consistent with the conclusion of Weber, Yoshimine, and McLean^{91,94} that the two structures represent distinct minima separated by a small barrier.

In their earlier paper, RS⁷⁹ concentrated their discussion on the C-H stretching frequencies, in the anticipation that they would be observed first in the laboratory. And this is indeed the region of the vibrational spectrum in which Oka and co-workers⁸⁰ have been working. The IR intensities associated with the harmonic vibrational frequencies are qualitatively similar to those of RS. That is, for the classical structure, all three C-H stretches are predicted to be very strong, with CISD intensities of 125 (3179 cm^{-1}), 235 (2954 cm^{-1}), and 171 km/mol (3040 cm^{-1}), respectively. However, for the bridged or nonclassical structure, there are only two C-H stretches predicted to lie above 2500 cm^{-1} , and the normal mode predicted at 3254 cm^{-1} has a very small intensity. The only readily observable C-H stretch should be the fundamental estimated at 3155 cm^{-1} , having an enormous intensity, 396 km/mol.

The "estimated" fundamentals in Tables V-(5) and V-(6) were obtained by scaling the *ab initio* results by factors derived from comparison between theory and experiment for acetylene. For example, the two C-H stretches of C_2H_2 at the large basis SCF level of theory lie 8.5% and 8.0%, respectively, above experiment. The scale factor for the large basis SCF frequencies was thus taken to be 8.3%, the aver-

age of the two differences. In like manner, the DZ+P CI harmonic frequencies are an average 5.8% above the observed fundamentals, and this factor was used to make the estimates in Table V-(5).

For the nonclassical structure the three estimates for the intense C-H stretching frequency are 3148 (RS, DZ+P SCF), 3149 (large basis SCF), and 3155 cm^{-1} (DZ+P CI), respectively. The insensitivity to theoretical method is striking. For the classical structure, the three analogous estimates for the highest C-H stretch are 3174, 3169, and 3179 cm^{-1} , respectively. For the middle C-H stretch (b_1 symmetry) of the classical structure, the three estimates are 3026, 3036, and 3040 cm^{-1} , respectively. And for the lowest classical structure C-H stretch, the theoretically based estimates are 2935, 2953, and 2954 cm^{-1} , respectively. It is apparent that a rather consistent view of the IR spectrum emerges from this research.

The C-C stretching frequencies may be estimated in an analogous manner, and these results are likewise included in Table V-(5). For the nonclassical structure, the C-C vibration is estimated at 1899, 1892, and 1905 cm^{-1} , respectively. Table V-(5) also shows that this normal mode has a relatively weak IR intensity. Of medium intensity (63 km/mol at the DZ+P CI level of theory) is the C-C stretch for the classical structure. This fundamental is estimated at 1622 (DZ+P SCF), 1625 (large basis SCF), and 1670 cm^{-1} (DZ+P CI), respectively. This is the only example for which a significant difference occurs between the three estimation procedures. Of course, in the absence of other considerations, we favor the CI-based estimate of 1670 cm^{-1} .

Table V-(6) shows the present theoretical predictions for the perdeuterated forms of the vinyl cation. All procedures employed were identical to those described above for C_2H_3^+ . Deuteration does provide at least one significant change in the predicted IR spectrum apart from the inevitable fact that the C-D frequencies are much lower than their C-H counterparts. Specifically, the highest C-D stretch

for the classical structure now has a relatively low intensity (19 km/mol), quite unlike the value predicted (125 km/mol) for $C_2H_3^+$. In addition, there is a reversal in the a_1 frequency ordering of the nonclassical $C_2D_3^+$ C=C stretch (1856 SCF, 1769 CI) with the central deuterium stretch (1777 SCF, 1793 CI) going from large basis SCF to DZ+P CISD.

For the $C_2H_3^+$ system, the infrared spectra predicted here are quite similar to those reported⁷⁹ earlier at a much lower level of theory. This seems puzzling, since the earlier predictions were not at all helpful⁸⁰ in analyzing the recently observed IR spectrum. This work greatly lessens the probability that the previous theoretical study was inadequate in terms of its treatment of the molecular electronic structure.

A much more difficult consideration to assess is the restriction of the current research to the harmonic approximation. For ordinary stable molecules such as H_3O^+ such procedures have been tested and found satisfactory. But the $C_2H_3^+$ system has two potential minima, rather different structurally, and yet separated by a small energy barrier, perhaps 2 kcal/mol or even less. While beyond the scope of this research, it is clear that there is a genuine need for the development of methods to properly solve the vibrational Schrodinger equation for multinuclear systems with several loose or anharmonic degrees of freedom.

2. $C_2H_2^+$

After the above research on the two isomers of protonated acetylene was completed, the possibility that it was the acetylene radical cation, $C_2H_2^+$, which Oka and his co-workers had observed rather than protonated acetylene was considered. Thus, the following discussion concerns the acetylene radical cation, a promising candidate to become the first odd-electron molecular ion of more than three atoms to be observed via high resolution infrared spectroscopic techniques.

With one major exception, the theoretical methods used here are analogous to

those employed for the $C_2H_3^+$ study. The DZ+P CISD wave functions consisted of 2029 configurations in D_{2h} symmetry. CISD harmonic vibrational frequencies were obtained via finite differences of analytic CI gradients. This involves some gradients of C_s symmetry, for which there are 7534 configurations. The dipole moments (which were obtained at perturbed geometries in order to determine dipole derivatives), were evaluated as energy derivatives²³ and with respect to the center of mass.

In addition to the the SCF and CISD theoretical treatments, a multi-configuration self-consistent-field approach has been used. The present MCSCF method, called CASSCF (complete active space SCF) in the important paper by Roos, Taylor, and Siegbahn¹¹¹, consists of a full CI in the space of carbon and hydrogen valence atomic orbitals. Specifically, the SCF ground electronic configuration for $C_2H_2^+$ is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 \quad X \quad {}^2\Pi_u \quad V-(4)$$

and the other two unoccupied valence MO's are $1\pi_g$ and $3\sigma_u$. For $C_2H_2^+$, the CASSCF holds the $1\sigma_g$ and $1\sigma_u$ orbitals doubly occupied and includes a full CI within the $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $1\pi_u$, $1\pi_g$, $3\sigma_u$, $4\sigma_g$, and $4\sigma_u$ orbitals. Since the π orbitals are doubly degenerate, the CASSCF is a 9 electron, 10 orbital full CI. For D_{2h} structures, these CASSCF wave functions include 3460 configurations. For the C_s structures which are examined to determine the Cartesian force constants via finite differences of analytic gradients, there are 13 608 configurations in the CASSCF. The actual MCSCF method used in this research is The actual MCSCF method¹¹² used in this research is that of Werner and Knowles.

$C_2H_2^+$ is a Renner-Teller molecule, i.e., the degeneracy of the $X \quad {}^2\Pi_u$ electronic ground state is split by nuclear deviations from linearity. Following the analysis of Lee, Fox, Schaefer, and Pitzer¹¹³, $C_2H_2^+$ has a Type (A) Renner-Teller

potential energy hypersurface. That is, both components of the ${}^2\Pi_u$ state increase in energy as the molecule is bent - and the harmonic frequencies for the two components are different. In Table V-(7), which summarizes the results, both sets of harmonic bending frequencies are given. Since the main purpose of this research is to characterize the stretching modes of $C_2H_2^+$, the bending modes are not treated beyond the standard methods. A precise treatment of these bending vibrational degrees of freedom will clearly require that one go beyond the Born-Oppenheimer and harmonic approximations. The interested reader is referred to the work of Petelin and Kiselev¹¹⁴ for details of the coupling of the vibrational angular momenta with the electronic orbital angular momenta (which is the Renner-Teller effect) for X_2Y_2 molecules.

The best opportunity for observing the high resolution IR spectrum of $C_2H_2^+$ probably lies with the σ_u asymmetric C-H stretching frequency which is the region of the spectrum where Oka and co-workers are investigating. Both the SCF and CI levels of theory suggest that this fundamental has a high IR intensity, about 400 km/mol. For neutral acetylene, the comparable SCF C-H stretching frequency is predicted to lie 282 cm^{-1} above the observed fundamental. Subtracting this amount from the $C_2H_2^+$ prediction gives a rough estimate of 3147 cm^{-1} for the radical cation fundamental. The comparable CISD offset for neutral acetylene is 189 cm^{-1} , which subtracted from the 3340 cm^{-1} result (DZ+P CISD) yields 3151 cm^{-1} . In the previous $C_2H_3^+$ study the C-H stretching modes were scaled, using the theoretical harmonic and experimentally observed (fundamental) frequencies of acetylene to determine the scaling factor. Performing the analogous adjustment here yields a predicted $\nu_3(C_2H_2^+) = 3152\text{ cm}^{-1}$ (DZ+P SCF) and 3156 cm^{-1} (DZ+P CISD), respectively.

The agreement between the different estimates is good, but the absence of any comparisons between theory and experiment for radical cation vibrational

frequencies requires one to be very cautious about these empirically adjusted predictions. It should be noted that Reutt, Wang, Pollard, Trevor, Lee and Shirley¹¹⁵ recently reported an improved photoelectron spectrum of C_2H_2^+ and C_2D_2^+ . The only data which they report and which may be compared with the theoretical predictions reported here is the ν_2 fundamental frequency for which they obtain 1829 cm^{-1} . The harmonic *ab initio* values are 2051 cm^{-1} , 1812 cm^{-1} and 1907 cm^{-1} for the DZ+P SCF, MCSCF and CISD levels of theory respectively. Errors of this type for SCF and CISD are quite common and so theory and experiment are in agreement here.

As a final closing comment, it is interesting to note the closeness of the estimated σ_u (approximately 3150 cm^{-1} ; C_2H_2^+) band center with that of the high intensity mode of the nonclassical form of protonated acetylene (approximately 3152 cm^{-1} ; C_2H_3^+). Remember also, that the nonclassical form is the lower energy form of the two isomers, though they are very close in energy and separated by a small barrier. Since the proton affinity of C_2H_3^+ is predicted to be 162 kcal/mol , it is quite likely that Oka and his co-workers are actually observing both C_2H_2^+ and C_2H_3^+ . However, the C_2H_3^+ is probably extremely difficult to analyze.

D. The Infrared Spectrum of Hydrogen Thioperoxide and its Isotopomers

Hydrogen thioperoxide, HSOH, has been studied via *ab initio* techniques only a few times¹¹⁶⁻¹²⁰ previously. The basis sets used in the past have generally been rather small with the split valence 3-21G* basis being the largest for which a full geometry optimization¹¹⁹ was performed. Wallmeier and Kutzelnigg¹¹⁸ did use a DZ+P basis but only optimized five of the six nuclear degrees of freedom. A structure fully optimized at a correlated level of theory has never been reported for thioperoxide. Furthermore, *ab initio* predictions of the harmonic vibrational frequencies and IR intensities of HSOH have never been reported. A theoretical study of HSOH is of interest for several reasons, two of which are given here.

Thioperoxide is the simplest molecule which may exhibit a classical S-O single bond. The S-O bond in most simple compounds (e.g., SO, SO₂, HSO) definitely exhibits multiple bond characteristics. The single bond nature of the S-O bond in thioperoxide is supported by the comparison of Wallmeier and Kutzelnigg's results¹¹⁸ (1.686 Å) with the experimentally known¹²¹ results for HSO (1.494 Å). A full geometry optimization of HSOH at the CI level of theory will help to clarify this point.

Thioperoxide is also potentially of interest in atmospheric chemistry, especially where there are high sulfur concentrations (e.g., where sulfur containing coals are burned). It has been shown that the closely related HSO radical is of importance in the oxidation of sulfur containing compounds^{122,123} and so may play a role in atmospheric processes just as the HO₂ radical^{124,125} does. Therefore, it is also likely that thioperoxide will exist in the atmosphere.

Many species closely related to HSOH have been structurally characterized via spectroscopic information (HOO¹²⁶, HSO¹²¹, HSSH¹²⁷, HOOH¹²⁸) and so *ab initio* predictions of the harmonic vibrational frequencies and IR intensities of

thioperoxide should greatly aid in its spectroscopic identification.

Using a DZ+P basis, the HSOH structure was fully optimized at both the SCF and CI levels of theory. All configurations resulting from single and double excitations from the Hartree-Fock reference wave function were included in the CI expansion leading to 116 403 configuration state functions.

Figure V-(5) presents the optimum structures obtained in the present work and Table V-(8) compares these structures with those obtained in previous theoretical work. All of the structures shown in Table V-(8) are in general agreement. The explicit inclusion of electron correlation effects via CISD causes a slight lengthening of bonds and closing of bond angles. Electron correlation does not greatly affect the torsional angle, increasing it by only 0.6° .

The analytic CISD harmonic vibrational frequencies and IR intensities for HSOH, DSOH, HSOD, and DSOD are presented in Table V-(9). The analytic evaluation of vibrational frequencies was tested by finite differences of analytic gradients. The "double harmonic" approximation was utilized in determining the IR intensities and the dipole derivatives were determined by taking finite differences of dipole moments evaluated at perturbed geometries. The CI dipole moment is evaluated as an energy derivative. The analytic evaluation of dipole derivatives for CI wave functions is currently being undertaken.

For comparison with CISD results, Table V-(10) contains harmonic vibrational frequencies and IR intensities for HSOH and its isotopomers obtained at the SCF level of approximation. As expected, correlation has the effect of lowering the harmonic frequencies and IR intensities. Yamaguchi and Schaefer⁵⁹ have demonstrated that CISD harmonic frequencies are generally about 3% to 5% above the "experimental harmonic" frequencies when using a DZ+P basis. It is well established now that the SCF approximation tends to overestimate these quantities by about 10% to 15%. Of course these generalizations are qualified since extensive

comparisons between theory and experiment for the harmonic frequency of a torsional motion have not been made. This mode is probably very anharmonic as well.

The CISD harmonic frequencies bear the expected relationship to the SCF values based on the equilibrium structures at the two different levels of theory. The CISD stretching modes are 174 cm^{-1} (O-H), 55 cm^{-1} (S-H), and 64 cm^{-1} (S-O) below the SCF predictions. The two bending harmonic frequencies decrease by 45 cm^{-1} (HOS) and 57 cm^{-1} (HSO). As is expected, the CISD torsional harmonic frequency (489 cm^{-1}) is almost identical to the SCF based value (496 cm^{-1}), since Hartree-Fock theory does quite well for internal rotation barriers as a rule.

The HSOH IR intensities generally decrease in going from SCF predictions to the CISD values although the S-H stretch IR intensity is slightly increased. Not surprisingly, the torsional mode IR intensity is not strongly affected by the inclusion of electron correlation.

Comparing the CISD predicted S-O stretching frequency of 808 cm^{-1} with the experimentally known harmonic frequency of diatomic SO (1124 cm^{-1}) yields further support for the presence of a S-O single bond in hydrogen thioperoxide. It is also interesting to note that the HSOH CISD S-O bond length ($1.686\text{ \AA}$) is the same as that obtained by Wallmeier and Kutzelnigg at a lower level of theory.

Also pertinent to the present study is the comparison of central processor unit (CPU) time between the analytic CI second derivative procedure and the finite difference of analytic gradients technique. Table V-(11) contains such a comparison. Using the analytic second derivative method outlined in Chapter III resulted in a net savings of 44% of the CPU time required for the finite difference procedure. Note also that the minimum number of finite difference points were used in this comparison.

E. Radiative Decay Lifetimes of the Bending Levels of CH_2^-

1. Introduction and Theoretical Approach

Recently the presence and radiative decay of vibrationally excited CH_2^- , generated in a hot cathode discharge of methane, was established¹²⁹ by measuring the time dependent photodetachment from excited states of CH_2^- as it radiatively relaxed in a high vacuum ion trap. The time dependence of the photodetachment was found to be consistent with an electron affinity of 5250 cm^{-1} (0.65 eV) for ground state X $^3\text{B}_1$ methylene. The radiative decay lifetimes of the first three excited bending vibrations of CH_2^- were also tentatively assigned. The main goal of the CH_2^- work was to demonstrate the existence of vibrationally excited ($v_2 \neq 0$) CH_2^- when created in a discharge. Hot bands are a potential problem^{130,131} in the photoelectron and photodetachment spectroscopy of negative ions created by discharge, sputter and other high temperature ion sources. The interpretation of the first photoelectron spectrum of the methylene anion proved to be particularly difficult¹³² because the standard techniques used to identify hot bands failed to do so. It is now well established^{129,133,134}, though, that hot bands were present in the photoelectron spectrum as first suggested¹³⁵ by Harding and Goddard.

In this research the radiative decay lifetimes of the v_2 bending vibrations of X $^2\text{B}_1$ CH_2^- are examined theoretically using *ab initio* quantum chemical techniques. Predictions of the $v_2 = 1, 2, 3$, and 4 lifetimes are compared with a more refined analysis of the experimental data of Okumura, Yeh, Normand, van den Biesen, Bustamente and Lee¹²⁹ (OYNVBL), which also includes additional data not reported earlier.

Because the CH_2^- bending vibration is a large amplitude motion, a large part of the potential and dipole moment surfaces are sampled. Such calculations are relatively difficult, and have not been systematically investigated. Bunker and

Langhoff¹³⁶ have presented transition moment matrix elements of vibrational transitions, for $X\ ^3B_1\ CH_2$ and $\tilde{a}\ ^1A_1\ CH_2$. These were determined from *ab initio* electronic structure calculations coupled with semi-rigid-bender¹³⁷ (SRB) vibrational wave functions. The goal of the present study is to determine the radiative decay lifetimes of the bending mode in CH_2^- with qualitative and semi-quantitative accuracy. Since it is believed that the ν_2 fundamental and combinations thereof are reasonably far removed from the ν_1 and ν_3 fundamentals (and combinations) it is a reasonable approximation to ignore their coupling. Therefore, the SRB model Hamiltonian of Bunker and Landsberg¹³⁷ is a useful method for obtaining the bending vibrational wave functions. Equally important is the existence of an empirically derived SRB potential function^{138,139} for CH_2^- . This will enable the purely *ab initio* radiative decay lifetimes to be compared with those obtained by coupling the empirical potential and the *ab initio* dipole moment function.

It is a well known fact that highly accurate *ab initio* predictions for anions are difficult, requiring extremely large basis sets coupled with highly correlated wave functions. In a recent study Lee and Schaefer⁸³ demonstrated that even at the self-consistent-field level of theory rather large basis sets are necessary in order to "converge" many molecular properties. Thus, it was necessary first to determine the size and type (i.e., how many s, p and d functions) of basis set needed at the configuration interaction level of theory. Though it is not the purpose of this research to detail the results of the basis set study as that will be done in a later publication¹⁴⁰, an indication of the sensitivity to the basis of several geometrical properties will be given.

Of course many studies of polyatomic anionic species have involved the use of correlated wave functions but none have explicitly investigated the basis set dependence on all the properties of interest here, namely geometrical structure, surface shape and most importantly, the shape of the dipole moment surface. It is noteworthy that Werner, Rosmus and co-workers^{46,47,141} have theoretically

investigated OH^- , C_2^- , NH^- , and CH^- and Botschwina¹⁴²⁻¹⁴⁴ has studied CN^- , CCH^- and NH_2^- . Werner, Rosmus and Reinsch⁴⁷ demonstrated the need of a MCSCF reference wave function for diatomics, but this undoubtedly is due in large part to the inadequate description of the dissociation process which plague many restricted Hartree-Fock (RHF) SCF wave functions. For the type of molecular motion which is being studied here, specifically the bending mode in a symmetric, non-linear triatomic, the SCF wave function should give a good zeroth order description. The one possible exception to this may be when the HCH angle is very small (i.e., $\text{CH}_2^- \rightarrow \text{C}^- + \text{H}_2$). However, no evidence was found for the deterioration of the single configuration reference function as the bond angle decreased. Further support for this argument can be found in a recent study on the effects of triple and quadruple excitations on the harmonic vibrational frequencies of several molecules¹⁴⁵, where it was found that these higher excitations contributed very little to bending harmonic frequencies.

In Botschwina's study¹⁴² of NH_2^- he did not include the dipole moment or the IR intensities. Also, though the final basis is rather large, only one basis set is used for CCH^- and NH_2^- and two for CN^- . Thus it is difficult to deduce any basis set dependencies.

It is also of interest to note the recent work of Adler-Golden, Langhoff, Bauschlicher, and Carney¹⁴⁶ (ALBC) on the ozone molecule. Although O_3 is not an anion, ALBC's work is relevant because of their success in reproducing the experimental IR intensities, which depend upon the same transition moment matrix elements as vibrational radiative decay lifetimes. Using a CASSCF wave function to compute the dipole moment function, ALBC obtained IR intensities in reasonable quantitative agreement with experiment for fundamentals, hot bands and combination bands. ALBC computed the energy and dipole moment for more than 200 points of the CASSCF Born-Oppenheimer potential energy surface and then used a variational

approach to solve for the vibrational wave functions.

The reader should realize that CH_2^- is a Renner-Teller molecule similar to the carefully studied NH_2 molecule. The barrier to linearity is on the order of 10 000 cm^{-1} , and in this study only the vibrational levels up to approximately 5 000 cm^{-1} above the lower state ($^2\text{B}_1$) minimum are under consideration. Furthermore, only $J = 0$ states are being considered. OYNVBL's experiment cannot distinguish between the different rotational effects and the experimental results presented here represent a Boltzman average of these effects. With these restrictions the theoretical analysis is considerably simplified because if $J \neq 0$, a correct theory must involve both the $^2\text{B}_1$ and $^2\text{A}_1$ surfaces. However, if the similarity between CH_2^- and NH_2 is realized then one would expect the Renner-Teller couplings to be small for small v quantum numbers and $J \neq 0$.

All of the basis sets employed in this study embody the same starting point which is the TZ+diffuse basis described previously⁸³ for the C_2H_3^+ study (Chapter V, section C). The smallest basis investigated contained two sets of polarization functions ($\alpha_d(\text{C}) = 1.5$ and 0.35; $\alpha_p(\text{H}) = 1.4$ and 0.25) on both C and H. This basis is designated [8s5p2d/4s2p] and is labeled TZ+diffuse+2P as it was previously. The second basis investigated had another set of diffuse sp functions added ($\alpha_s(\text{C}) = 0.015\ 545$; $\alpha_p(\text{C}) = 0.011\ 808$; $\alpha_s(\text{H}) = 0.010\ 310$) and is labeled TZ+2diffuse+2P. The third basis set can be designated TZ+diffuse+3P' where now there are three sets of polarization functions on C ($\alpha_d(\text{C}) = 2.25, 0.75, 0.25$). Later it was found preferable to incorporate a set of more diffuse polarization functions into the C basis and so the TZ+diffuse+3P basis consists of $\alpha_d(\text{C}) = 0.75, 0.25, 0.083$ for the carbon d functions. The final two bases were arrived at by adding yet another set of polarization functions to the carbon atomic basis. The basis labeled TZ+diffuse+4P' has an additional C d function with an exponent $\alpha_d = 2.25$ whereas the basis labeled

TZ+diffuse+4P has a more diffuse polarization function, $\alpha_d(C) = 0.028$. The CI's included all configurations resulting from single and double replacements from the SCF reference wave function and hence are classified CISD. The CI dipole moment was evaluated with respect to the center of mass as an energy²³ derivative.

To give an idea of the basis set dependence Table V-(12) contains the CISD equilibrium geometry, and Table V-(13) gives the CISD dipole moment of CH_2^- for several basis sets. The results depicted in Tables V-(12) and V-(13) demonstrate the need of very diffuse polarization functions for anions at the CISD level of theory. This is especially true for the dipole moment where the TZ+diffuse+3P' value (1.97 D) is reduced to 1.72 D with the TZ+diffuse+3P basis set. Since the TZ+diffuse+4P dipole moment is only 0.03 D less than the TZ+diffuse+3P value, the dipole moment function was determined initially with the TZ+diffuse+3P basis, and later with the TZ+diffuse+4P basis set.

In the SRB model¹³⁷ the effective bending potential and the bond length as a function of the supplement to the bond angle are required. The supplement is defined as $\rho = \pi - \alpha$ where α is the bond angle. The dipole moment function must also be a function of ρ . Therefore, the procedure we used was to optimize the C-H bond length (i.e., until $\delta E_{CI}/\delta r_{C-H} = 0$) at specific bond angles. The potential, bond length and dipole moment were then fit to a Taylor series expansion about linearity (at linearity $\rho = 0$). Because of the symmetry about linearity, only even powers of ρ appear in the potential and bond length functions and only odd powers of ρ appear in the dipole moment function. These functions (derived from the TZ+diffuse+3P basis) are given in equations V-(5) through V-(7) with the units being cm^{-1} , Å and D respectively.

$$V(\rho) = -13951 \rho^2 + 6733.1 \rho^4 - 1555.7 \rho^6 + 238.95 \rho^8 - 16.101 \rho^{10} \quad \text{V-(5)}$$

$$r_{C-H}(\rho) = 1.081844 + 0.0230140\rho^2 - 0.000506\rho^4 \quad V-(6)$$

$$\begin{aligned} \mu(\rho) = & 3.033421\rho - 1.914737\rho^3 + 0.893442\rho^5 - 0.295384\rho^7 \\ & + 0.062339\rho^9 - 0.007390\rho^{11} + 0.000372\rho^{13} \end{aligned} \quad V-(7)$$

The potential and dipole moment functions were least squares fit from 18 points with α , the bond angle ranging from 60 to 148. The bond length function used only 13 points even though the bond was optimized for each angle α . Only 13 points were used here in order to minimize the variance of the fit. However, the bending energy levels as well as the transition moment matrix elements were quite insensitive to the bond length function used as long as it had the form of equation V-(6). These functions are shown in Figures V-(6) through V-(8). Also depicted in Figures V-(6) and V-(7) are the potential and dipole moment functions obtained with the TZ+diffuse+4P basis. These calculations were performed at the TZ+diffuse+3P geometries. The explicit forms of the functions are

$$V(\rho) = -14042\rho^2 + 6870.5\rho^4 - 1637.08\rho^6 + 259.97\rho^8 - 18.050\rho^{10} \quad V-(8)$$

$$\begin{aligned} \mu(\rho) = & 3.336752\rho - 2.715518\rho^3 + 1.748393\rho^5 - 0.793873\rho^7 \\ & + 0.225337\rho^9 - 0.035182\rho^{11} + 0.00228163\rho^{13} \end{aligned} \quad V-(9)$$

Asymmetric geometries were not considered for the following reasons. As noted previously, Bunker and Langhoff¹³⁶ have reported transition moment matrix elements for $\tilde{a}^1A_1$ CH₂ using an empirically derived SRB potential with an *ab initio* dipole moment function. Their dipole moment function has the form

$$\mu_b = \rho \sin(cp) + q \sin^2(cp) + \mu'_a S_1 \quad V-(10)$$

$$\mu_a = \mu'_a S_3 \quad V-(11)$$

where $S_1 = \Delta r_i = r_i - r_e$. Equation V-(11) deals with asymmetric geometries and as

noted we did not consider these. The last term in equation V-(10) allows for the change in the dipole moment with respect to changes in the bond length, and hence has more flexibility than our functional form. However, if this term is neglected the radiative decay lifetimes of $\tilde{a}^1A_1$ CH₂ change by only +3, +1 and -4 milliseconds for the $v_2 = 1, 2$ and 3 levels respectively. Thus, there was no compelling reason to incorporate a like term into the CH₂⁻ dipole moment function. Furthermore, it was very difficult to fit a function of the form present in equation V-(10) and so a Taylor series expansion, which was much easier to fit, was used. Figure V-(7) is a plot of the CISD dipole curves obtained from the TZ+diffuse+3P basis and TZ+diffuse+4P basis sets.

The determination of a radiative decay lifetime is rather straightforward and has been briefly reviewed by McKellar¹³³ and co-workers. The radiative decay lifetime of the $v_2 = i$ vibrational state is given by

$$\tau_i = 1/\sum_j A_{ij} \quad \text{V-(12)}$$

where the Einstein A_{ij} coefficient is given by

$$A_{ij}/s^{-1} = \frac{64\pi^4}{3hc^3} (\omega_{ij}/\text{cm}^{-1})^3 |\langle i | \mu/D | j \rangle|^2 \quad \text{V-(13)}$$

$$= 3.14 \times 10^{-7} (\omega_{ij}/\text{cm}^{-1})^3 |\langle i | \mu/D | j \rangle|^2 \quad \text{V-(14)}$$

Here ω_{ij} is the difference of the vibrational levels $|i\rangle$ and $|j\rangle$, where $|j\rangle$ are the vibrational levels below $|i\rangle$. In the model used here the $|i\rangle$ and $|j\rangle$ are the SRB wave functions.

Table V-(14) contains the experimentally determined radiative decay lifetimes while the purely *ab initio* radiative decay lifetimes along with those obtained with

the two SRB potentials of Sears and Bunker^{138,139} coupled with the *ab initio* dipole moment function are given in Table V-(15). As can be seen, there are not large differences between the sets of theoretical values. The results of Table V-(15) indicate that the *ab initio* potential function is quite adequate and that the radiative decay lifetimes are very sensitive to the dipole moment function. Further support for the high quality of the *ab initio* potential is presented in Table V-(16) where the SRB vibrational energy levels for the various potential functions are given. The theoretical potentials agree with the empirically derived potentials reasonably well, especially in the lower levels.

The transition moment matrix elements and Einstein A coefficients used in determining the radiative decay lifetimes are listed in Tables V-(17) and V-(18), respectively. As is expected, the absolute value of the transition moment matrix elements is largest for adjacent vibrational levels.

Not quite so easily predicted is the relationship of the Einstein A coefficients with Δv_2 . For the $i=3, 4$ levels the Einstein A_{ij} coefficient is largest for $\Delta v_2 = 2$. Also interesting to note is that although the radiative decay lifetimes derived from the empirical potentials are very similar, the individual Einstein A coefficients are somewhat different and in fact the most recent potential agrees much better with the *ab initio* results.

One way of testing the qualitative reliability of the theoretical decay lifetimes would be to determine the τ_i lifetimes incorporating the double harmonic approximation (i.e., using mechanical and electrical harmonicity which means truncating the potential at quadratic terms and the dipole moment function at linear terms). Harmonic vibrational frequency and IR intensity determinations for small molecules are becoming quite common, even at the CISD level of theory. Using the TZ+diffuse+3P basis the harmonic frequencies of CH_2^- are $\omega_1 = 2782 \text{ cm}^{-1}$, $\omega_2 = 1314 \text{ cm}^{-1}$ and $\omega_3 = 2841 \text{ cm}^{-1}$ with the corresponding IR intensities being 633

km/mol, 12 km/mol and 363 km/mol respectively. Using the *ab initio* dipole derivatives the radiative decay lifetimes of the first excited vibrational state are found to be $\tau_1 = 1.6$ ms, 385 ms and 2.7 ms for the ν_1 , ν_2 and ν_3 modes respectively. The ν_2 value is qualitatively similar to the value obtained with the SRB bending wave functions with this basis, 574 ms.

2. Discussion

There are few calculations of vibrational intensities or lifetimes for polyatomic ions whose accuracy can be verified by experiment. Theoretical values of the $v = 1$ lifetimes of CH^- agree to within 10% of the experimental value obtained by Okumura, Yeh, Normand and Lee¹⁴⁷, but the strong C-H bond means that CH^- can be approximated by a harmonic oscillator quite reliably. A method such as the semi-rigid bender model used here should be more accurate than using the harmonic oscillator approximation.

The longest experimental lifetime agrees reasonably well with the best theoretical prediction of the $\nu_2 = 1$ lifetime of 431 ms. However, the experimental values for the $\nu_2 = 2$, and $\nu_3 = 3$ (70 ms and 14 ms) levels are significantly smaller than the theoretical values of 207 ms and 108 ms. Thus, the experimental lifetimes obtained from a fit with a three exponential model do not agree with theory.

The five- to seven- fold decrease in the experimental lifetimes with vibrational quantum number seems anomalously large. The theoretical lifetimes decrease by only a factor of about two for each additional quantum in the bending mode. It is quite possible that an additional component with an intermediate lifetime is present in the experiment but cannot be extracted from the data due to the signal-to-noise ratio. OYNVBL have commented that examination of their data reveals that there are not enough data points between 150 and 300 ms to preclude the existence of such a component.

The discrepancy between the results of the fit and theory indicate that four exponentials may be necessary in fitting the data. OYNVBL have tried this and find that an unconstrained fit (eight parameters) of the data to a sum of four exponentials does not yield a unique result. However, the trend in the theoretical results suggest that a geometric progression for the four lifetimes may be assumed and such a fit (for a certain range of ratios) does yield a unique result. OYNVBL performed several fits holding the ratio τ_i/τ_{i+1} constant. They find that the range of lifetimes is large, and the lowest value of τ_i/τ_{i+1} which allows a fit of the data is 3.0, with the lifetimes being 15 ms, 45 ms, 135 ms, and 405 ms. The $v_2 = 1$ lifetime agrees with the *ab initio* value, and the $v_2 = 2$ lifetime is somewhat closer to the theoretical result, but the two smaller lifetimes are still significantly less than theory. Therefore, the lifetimes extracted from the data using a four component model with constant ratio τ_i/τ_{i+1} still do not completely agree with the theoretical results. Furthermore, the ratio $\tau_i/\tau_{i+1} = 2.5$ gives a fit one standard error worse than the best fit, with lifetimes of 19 ms, 47 ms, 118 ms, and 296 ms. Thus, the experimental data cannot be fit with the theoretical ratio τ_i/τ_{i+1} of approximately two for a geometric progression of four lifetimes. The two major difficulties in relating the experimental data with the theoretical results are, firstly, that at the shortest times ($\tau < 30$ ms), where the experimental data is most reliable and the theory most uncertain, experiment definitely obtains a lifetime around 15 ms and the theory does not yield a value anywhere in this region. Secondly, at long lifetimes, where the theory should be most reliable, the experiment is very uncertain due to the poor signal-to-noise ratio.

OYNVBL did find that if the theoretical values for τ_i for $i = 1, 2$, and 3 are used, along with a fourth decay that is allowed to vary, the data can be fit with the $\tau_4 = 15$ ms. This result implies that the theoretical results would be consistent with experiment if one postulates an alternative relaxation mechanism giving rise to a fast

decay. Next, possible sources for this alternative mechanism are considered.

OYNVBL considered the possibility that the fast decay component could be the result of an experimental artifact, but they discounted this possibility for several reasons. If the *ab initio* results are extended to include the $v_2 = 5$ state a lifetime of 40 ms is obtained with the TZ+diffuse+4P data. This value is somewhat longer than the observed lifetime. In addition, two objections might be raised to this possible explanation of the 15 ms experimental lifetime. Firstly, even at a vibrational temperature of 2500 K, only 1.5% of the total population is expected to be in this level. Secondly, $v_2 = 5$ lies well above the threshold for electron detachment, and is therefore only metastable to electron loss.

Thus far contributions from the excited states $v_1 = 1$ and $v_3 = 1$ have been neglected. Based on isotope shifts and the Teller-Redlich rule, Leopold¹³⁴ *et al.* estimate that the CH_2^- vibrational frequencies for v_1 and v_3 are 2580 cm^{-1} and 2635 cm^{-1} respectively. The theoretical harmonic values reported here (2782 cm^{-1} and 2841 cm^{-1} respectively) are in reasonable agreement with these estimates, with both theoretical values being 7.8% higher. Bunker and Langhoff¹³⁶ have calculated the stretching transition moments for the neutral $\tilde{a}^1\text{A}_1\text{ CH}_2$, in the double harmonic approximation. These yield radiative lifetimes of approximately 15 and 28 ms for v_1 and v_3 respectively. These lifetimes match the fast component observed, however, performing the analogous calculation for CH_2^- (using the TZ+diffuse+3P basis results) yields lifetimes of 1.6 ms and 2.7 ms respectively for the v_1 and v_3 modes. Also, these excited states are expected to have very small relative cross sections for photodetachment. The small change in the C-H bond length ($1.116\text{ \AA}$ for $^2\text{B}_1\text{ CH}_2^-$ and $1.08\text{ \AA}$ for $^3\text{B}_1\text{ CH}_2$) results in very poor Franck-Condon factors for transitions of the stretches with $\Delta v \neq 0$. No such transitions have been reported in any of the photoelectron spectra published to date. Furthermore, OYNVBL observed that the fast component possessed a large relative cross section, with the transition seemingly

saturated at the intensities used in the experiment. Thus, it is difficult to reconcile the observed cross section with the expected poor Franck-Condon overlap, and the fact that the *ab initio* estimated lifetimes of the stretches are not consistent with the experimental observations either.

In the theoretical approach used, the possibility of a Fermi-resonance was not considered. Because the stretching modes have relatively large transition moments, the strong coupling of a stretching mode with a bending level $v_2 = n$ could greatly reduce the lifetime of the latter. The $v_2 = 1$ frequency of 2580 cm^{-1} estimated by Leopold *et al.* is very close to the v_2 level at 2584 cm^{-1} obtained from the best *ab initio* potential, but the actual frequencies are not known well enough to make any firm conclusions.

Another possibility is that the OYNVBL are observing vibrational autodetachment of highly excited rovibrational states with energies above the electron detachment threshold. The $v_2 = 4$ state, for instance, lies very close to the electron continuum. In order for the electron of a vibrationally excited anion to detach, the mechanism must involve a breakdown of the Born-Oppenheimer approximation. Very little is known about such vibrational autodetachment rates. The fast component decays at a rate that is four to seven orders of magnitude slower than the NH^- rotational autodetachment rates observed by Neumark, Lykke, Andersen, and Lineberger¹⁴⁸, and three orders of magnitude slower than the SF_6^- autodetachment¹⁴⁹ rates. These experiments are sensitive to fast processes, and cannot measure long decays. Thus, long-lived autodetaching states may have been present but unobserved in the earlier experiments. However, rovibrational states of CH_2^- that are metastable to detachment may not be long-lived. There is a crossing of the CH_2 anion and neutral potential energy curves possibly near $v_2 = 0$ of the neutral. The propensity rules of Simons¹⁵⁰ indicate that such a crossing would result in rapid electron detachment from any anion states above the detachment threshold.

None of these possibilities is entirely satisfactory. Thus, the identity of a component with $\tau = 14$ ms remains unclear, and the discrepancy between the *ab initio* results and the experimental data is unresolved.

F. The Effects of Triple and Quadruple Excitations on Variational Procedures for the Quantum Mechanical Prediction of Vibrational Frequencies and Infrared Intensities

1. Introduction

In applying configuration interaction theory, wave functions have generally been truncated in some way because the cost of performing a full CI is exorbitant, even for very small molecules with small basis sets. Furthermore, this cost grows wildly for relatively small basis set augmentations. Although, new technology¹⁵¹⁻¹⁵³ (specifically for full CI calculations) has recently been developed which greatly reduces this computational cost, it is still much too large except for small molecules¹⁵⁴⁻¹⁵⁹ (e.g., CH₂ and H₂O) with modest DZ+P basis sets, and even these calculations must be performed on a state of the art super-computer such as the Cray-2.

The most common type of truncation is to allow all configurations which are either a single or a double substitution from a given single determinant reference or, possibly, a small group of reference configurations. Naturally, it would be interesting to know the limitations of this approximation and in what particular instances a singles and doubles CI is a useful tool and when it is not. Despite the high computational cost, a few quantum chemists¹⁵⁴⁻¹⁵⁹ have investigated the importance of higher than double excitations, but only on the effect of the total energy. It is well established now, that as a single reference deteriorates a SCF-CISD procedure becomes less and less reliable. But what are the consequences of neglecting these higher excitations upon other molecular properties, especially at the equilibrium stationary point? No one has ever investigated this question. The results presented here are part of such an investigation. The equilibrium structures, vibrational frequencies, infrared intensities and dipole moments of HF, CO, N₂, H₂O, ¹A₁ CH₂,

3B_1 CH₂, and NH₃ have recently been studied at the CISD, CISDT (CISD + *triples*), and CISDTQ (CISDT + *quadruples*) levels of theory by Lee, Remington, Yamaguchi and Schaefer. Here, the CISD, CISDT, and CISDTQ results for HF and N₂ with both DZ and standard DZ+P basis sets are presented in Tables V-(19) through V-(26). Also presented are analogous results at the CID, CIDQ, and CISDQ levels of theory. Coupled cluster singles and doubles (CCSD) energies, optimum structures and harmonic vibrational frequencies are also given (for both basis sets and both molecules). The CCSD method used was the recently implemented closed shell formalism¹⁶⁰ of Scuseria, Scheiner, Lee, Rice and Schaefer. Two reference CISD (TCSCF-CISD) results for HF are compared with the single reference CISDTQ quantities and for N₂, the higher excitation CI values are contrasted with MP2, MP4(SDQ), and MP4(SDTQ) results which are given in Table V-(27). A discussion of these interesting results follows.

2. Discussion of Results

There are several very interesting conclusions which can be drawn from the information in Tables V-(19) through V-(27). Perhaps the most striking point, is the fact that the DZ+P results almost mimic the DZ results. This conclusion alone is well worth the cost and effort which went into this study. For example, the decrease in the harmonic frequency for DZ HF is 9 (CISD-CISDT), and 47 cm⁻¹ (CISDT-CISDTQ), respectively as triple and quadruple excitations are included in the CI expansion. The analogous results for DZ+P HF are 11 (CISD-CISDT) and 48 cm⁻¹ (CISDT-CISDTQ). For DZ N₂ these values are 31 (CISD-CISDT) and 118 cm⁻¹ (CISDT-CISDTQ), while for DZ+P N₂ they are 35 (CISD-CISDT) and 113 cm⁻¹ (CISDT-CISDTQ). So, as we see the effect of higher than double excitations is rather similar for both the DZ and DZ+P basis sets. This result is particularly surprising when one considers the recent full CI results of Bauschlicher, Taylor and

co-workers. These workers found that as the bonds of a given molecule were stretched, and the reference wave function became progressively worse, the larger basis set (especially those which included polarization functions) tended to mimic the full CI surface better than the smaller basis. A simple interpretation of these results would be that in the previous studies the flexibility of the basis set had a compensating effect for the deterioration of the SCF reference wave function. The reason this effect was not exhibited in the vibrational frequencies was simply that the molecular geometry never strays very far from equilibrium or in other words, the reference wave function is strongly dominant in all calculations reported here.

Another quite interesting result is the fact that the TCSCF-CISD results for HF are nearly identical to the CISDTQ values. The TCSCF for HF is a σ to σ^* (bonding to antibonding) transition and thus, allows HF to dissociate properly. The TCSCF-CISD wave function does contain some configurations which are quadruple excitations relative to the single dominant Hartree-Fock reference, but very few. The TCSCF-CISD has only 1015 configurations (DZ+P HF) whereas the CISDTQ contains 48 963 CSF's (DZ+P HF)!! Therefore, at least for many small molecules, *virtually all* the important quadruply excited configurations may be included in a CISD procedure by using a multi-reference wave function which correlates two orbitals (a bonding and antibonding molecular orbital) for every *bonding pair* of electrons. This statement is certainly not true for all small molecules. However, it should be true for many systems and is at the very least a good starting point for a multireference CI procedure. Note also that the $E_{\text{TCSCF-CI+D}}$ values are determined via the multi-reference analog of Davidson's correction for unlinked clusters of quadruple excitations.

If one compares the CID, CIDQ, and CISDQ vibrational frequencies (for both HF and N₂) in the tables, it becomes readily evident that the effects of the singly, triply, and quadruply excited configurations are to a very large extent additive with

the HF frequency being more closely additive than the N_2 value. These results lead directly to the conclusion that the most important off diagonal or coupling matrix elements in the Hamiltonian matrix are between the doubly excited configurations and the other configurations. This is not really a surprising conclusion. However, it does lead to another view of the properties of the full CI matrix. Specifically, at least for a system with one strongly dominant reference determinant, higher than quadruple excitations will change CISDTQ results very little since it is not possible for configurations higher than quadruply excited ones to directly couple with the doubly excited configurations. For chemical systems which require a multireference description, this could be extended to state that any configurations which are more than a quadruple excitation from *all* of the *important* reference configurations are of only minimal importance.

Combining the last two points, it is evident that a more precise definition of *all of the important* CSF's in a CI procedure can be made. Generally, highly accurate descriptions of chemical systems may be made by including all singly and doubly excited CSF's from all the important reference configurations. In other words, perform a MCSCF in order to obtain a good zeroth order reference wave function which embodies the majority of the non dynamical correlation energy of the molecular system. Then perform a singles and doubles CI from this reference function to take account of the dynamical correlation energy of the chemical system. In this way only the important CSF's are included in the CI procedure and the many which are only of minimal importance have been weeded out of the CI expansion. As with all generalizations, there are exceptions and the just stated general conclusion is no different. For chemical systems where the electron correlation energy converges very slowly with respect to excitation level the procedure suggested above will not be adequate, but then the only known adequate procedure would be to perform a full CI or something close to it. The infamous $F + H_2$, and the FOOF molecule are

good examples of this exception.

The importance of triply excited configurations for multiply bonded species has been noted by several authors. These previous studies have always been limited to Moller-Plesset perturbation theory energetics. The harmonic vibrational frequencies for HF and N₂ listed in the tables indicate that the triply excited CSF's are much more important in N₂ than they are in HF. In fact, in HF the single excitations are much more important than are the triple excitations. For example, inclusion of the single excitations causes the harmonic frequency of HF to decrease by 28 (DZ;CID-CISD or 32 DZ;CIDQ-CISDQ) and 17 cm⁻¹ (DZ+P;CID-CISD or 20 DZ+P;CIDQ-CISDQ), respectively, whereas triple excitations cause the frequency to decrease by only 9 (DZ;CISD-CISDT or 9 DZ;CISDQ-CISDTQ) and 11 cm⁻¹ (DZ+P;CISD-CISDT or 11 DZ+P;CISDQ-CISDTQ), respectively. For N₂ it is more difficult to define exactly what effect each excitation level is producing because there is stronger coupling between the singles and triples, and the triples and quadruples, though, as stated earlier, this coupling is comparatively still quite small. It may be concluded with certainty though, that the triple excitations are only marginally more important than the singly excited CSF's.

After examining the data, it is quite evident that for both HF and N₂ the quadruple excitations are more important than are either the single or triple excitations. In fact, the quadruply excited configurations are more important than the combined single and triple configurations, though not by much for HF.

The CCSD results agree most closely with the CIDQ results for N₂ and are between the CISDQ and CIDQ results for HF but are closer to the CISDQ values. Initially, one would probably think that CCSD should be closest to CISDQ since CCSD includes singles, doubles and the term which has been stated as the major contribution to the quadruples (this term corresponds to the product of doubles in coupled cluster theory). This assumption seems to be reasonably valid for HF but

not quite so true for N_2 . For lack of any other data on CCSD frequencies, I must conclude that the agreement between CCSD and CIDQ for N_2 is fortuitous and probably a result of the somewhat larger contribution higher excitations make to N_2 (specifically the contributions to the quadruples which are not present in CCSD).

The Moller-Plesset (MP) harmonic frequencies for N_2 do not effectively mimic the CI results and in fact are somewhat erratic. The MP4(SDQ) harmonic frequency (2289 cm^{-1}) is similar to the CISDTQ value (2296 cm^{-1}). However, the MP4(SDTQ) result is shifted strongly downward to 2145 cm^{-1} . Thus, the similarity between the CISDTQ and MP4(SDQ) values is most likely fortuitous. As the MP4 results demonstrate, Moller-Plesset perturbation theory does not seem to be a good method to use for N_2 , probably because of the multiple bond nature of N_2 . This conclusion has been reached by many before.

The IR intensity and dipole moment of HF have not been commented on until now. It is evident that higher excitations do not play a large role in either of these quantities, though it is also evident that electron correlation through singles and doubles is important. It is interesting to note the decrease in the CPHF contribution to the dipole moment when singles are included. Some quantum chemist have argued that the singles essentially allow relaxation of the molecular orbitals and hence conclude that the dipole moment of a molecule calculated as an expectation value would be accurate if singles were included in the CI expansion. The limited number of results presented here support that view, but the author cautions that if dipole surfaces, dipole derivatives or just very accurate dipole moments are desired then it is best to determine it as an energy derivative (see Chapter II for a detailed explanation of this point).

I. FUTURE CONSIDERATIONS AND CONCLUDING REMARKS

Reflecting back upon the quote which begins this thesis and accepting the many accomplishments of computational chemistry which have been achieved since, it is clear that the sentiment which Mulliken expressed in 1967 is even more true today in 1986. In the last 15 years, *ab initio* quantum chemistry has progressed to the point where it can actually challenge and overturn the interpretation of experiments. There are many examples in the literature where theory has preceded experiment and the list grows longer every year. Moreover, there is little doubt that the introduction and implementation of derivative methods in *ab initio* quantum chemistry has been a large part of this success.

Even more important is the fact that today, so many studies are performed with both theoretical and experimental input; with the two approaches complementing one another. This type of collaboration will undoubtedly prosper and become more of a standard practice than it is currently, because, as many scientists have learned, theory and experiment working together can accomplish much more than either can independently.

But where is the basic science of quantum chemistry headed? Based on my limited experience in *ab initio* quantum chemistry, it seems evident that the field will progress in two general directions. Firstly, considerably more accurate methods will be developed and will continue to be applied to rather small molecules, since it would be too costly to apply them to large systems. The methods which will be developed for the determination of highly accurate energies and wave functions will be quite varied. I believe, for two reasons, that there will be a major effort in coupled cluster techniques in the next few years. As was illustrated by the results presented in the higher excitations section, CCSD contains a larger fraction of the total correlation energy than does CISD. Both are n^6 processes, although, CCSD is

more expensive due to a larger prefactor. However, CCSD is significantly less costly than CISDTQ which is an n^{10} procedure.

The other appealing property which truncations in coupled cluster theory exhibit is that they are size extensive, which means that if one performed a CCSD calculation on two non-interacting water molecules (i.e., separated by a large distance) then the correlation energy determined would be twice the correlation energy of a single water molecule. Truncations in CI theory do not in general have this property and this is a severe limitation if one wants to accurately obtain the enthalpy of a reaction involving many relatively small molecules (e.g., an $[n]$ paracyclophane homodesmotic reaction¹⁶¹). What is normally done when using CISD expansions is to perform a calculation with the (2) molecules of interest at infinite (1000 bohr) separation and then use this result instead of the sum of their individual CISD energies. Obviously, this is a less viable approach when many small systems are involved because the "super-molecule" will become too large.

The other "conventional" type of electronic structure method which will be investigated vigorously in the coming years is MCSCF-CISD. The ability to easily accommodate a MCSCF wave function as the reference is the biggest advantage that CI has over all of the other correlation techniques. Furthermore, the MCSCF-CISD results presented here and those obtained by Bauschlicher, Taylor and co-workers¹⁵⁶⁻¹⁵⁹ are extremely encouraging. However, it is not clear that the same quality of wave function may be obtained with larger systems. Probably the best approach to obtain MCSCF-CI wave functions is to form as large an MCSCF as possible within the valence space (i.e., CASSCF if possible and if not, then through all quintuples or all quadruples) and then perform a CISD from these molecular orbitals using as references all the important configurations in the MCSCF. This approach seems to be computationally the most feasible and also still very general so that the MCSCF space will not bias the results one obtains.

The more unconventional electronic structure methods probably will not be used or developed to a large extent in the future. The one possible exception may be quantum Monte Carlo, since this method has the potential to greatly benefit from certain types of massively parallel computers. However, too much is still unknown in this area to arrive at any definite conclusions.

Given the advanced computational facilities which have become available in the last few years and the willingness of *ab initio* quantum chemists to "take advantage" of these situations, it seems clear that a great number of quantum chemists will begin to work on "equilibrium dynamics." With the computers now available, generating a high quality surface for small or medium sized molecules is neither difficult nor expensive, and equally important, high resolution spectroscopists are performing more studies on small to medium sized molecules which have large amplitude motions (e.g., $C_2H_3^+$) and so interest in this area is high.

There are, of course, other areas which quantum chemists have already begun to investigate, such as the use of effective core potentials (or relativistic effects) in order to reduce the number of electrons which must be treated, consequently reducing the number of atomic basis functions which must be included. These areas will certainly continue to receive a great deal of attention.

The second area of major emphasis will be on applying our conventional methods to larger systems. Here at Berkeley, we have already begun studies^{161,162} on such systems. As the chemical system under investigation becomes larger, at some point the spacing between the various electronic states becomes smaller and at that time several problems will appear. For example, it has been shown¹⁶³ that the crossing of electronic states which belong to different irreducible representations of the molecular point group may cause a singularity in the CPHF equations or any similar set of equations (e.g., CPMSCF). Furthermore, the non dynamical electron correlation energy should increase dramatically. However, the point at which these

problems begin to appear (i.e., the size of the chemical system) is not known very well. Hence, investigations will help us to learn the limitations of conventional quantum chemical methods.

Whatever the directions *ab initio* quantum chemistry follows in the upcoming years, it is apparent that its success is inherently tied to the computer, just as much of current spectroscopy is linked to the laser. A current state of the art suite of quantum chemical programs consists of roughly one half million lines of fortran code. Thus, to support a competitive research group it is vital that 1) a stable computing environment be maintained and 2) continuity in the group (with respect to expertise in exactly how the programs operate) be sustained.

REFERENCES

1. R. S. Mulliken, *Science*, **157** (1967) 13.
2. D. R. Hartree, *Numerical Analysis*, Oxford University Press, Oxford, 1968.
3. T. J. Lee, A. Bunge and H. F. Schaefer, *J. Am. Chem. Soc.*, **107** (1985) 137.
4. H. P. Reisenauer, G. Maier, A. Reimann and R. W. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **23** (1984) 641.
5. G. Das and A. C. Wahl, *J. Chem. Phys.*, **44** (1966) 87.
6. M. Dupuis, W. A. Lester, B. H. Lengsfeld and B. Liu, *J. Chem. Phys.*, **79** (1983) 6167.
7. L. Engelbrecht and B. Liu, *J. Chem. Phys.*, **78** (1983) 3097.
8. Y. Osamura, Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **77** (1982) 383.
9. P. Jorgensen and J. Simons, *J. Chem. Phys.*, **79** (1983) 334.
10. A. Banerjee, J. O. Jensen, J. Simons and R. Shepard, *Chem. Phys.*, **87** (1984) 203.
11. M. Page, P. Saxe, G. F. Adams and B. H. Lengsfeld, *J. Chem. Phys.*, **81** (1984) 434.
12. R. S. Shepard, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, eds. J. Simons and P. Jorgensen, (Reidel, Dordrecht, 1986).
13. J. E. Rice and R. D. Amos, *Chem. Phys. Lett.*, **122** (1985) 585.
14. B. A. Hess, W. D. Allen, D. Michalska, L. J. Schaad and H. F. Schaefer, submitted to *J. Am. Chem. Soc.*
15. B. R. Brooks, W. D. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **72** (1980) 4652.
16. R. Krishnan, H. B. Schlegel and J. A. Pople, *J. Chem. Phys.*, **72** (1980) 4654.
17. Y. Osamura, Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **77** (1982) 383.
18. J. E. Rice, R. D. Amos, N. C. Handy, T. J. Lee and H. F. Schaefer, *J. Chem. Phys.*, **85** (1986) 963.
19. J. Gerratt and I. M. Mills, *J. Chem. Phys.*, **49** (1968) 1719.
20. N. C. Handy and H. F. Schaefer, *J. Chem. Phys.*, **81** (1984) 5031

21. Y. Osamura, Y. Yamaguchi and H. F. Schaefer, *Chem. Phys.*, **103** (1986) 227.
22. Y. Yamaguchi, Y. Osamura and H. F. Schaefer, *J. Amer. Chem. Soc.*, **105** (1983) 7506.
23. G. H. F. Diercksen, B. O. Roos and A. J. Sadlej, *Chem. Phys.*, **59** (1981) 29.
24. H. F. Schaefer and Y. Yamaguchi, *J. Mol. Struct.*, **135** (1986) 369.
25. For a recent review see B. A. Hess, L. J. Schaad, P. Carsky and R. Zahradnik,
Chem. Rev. (in press).
26. J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, *Int.*
J. Quantum Chem. Symp., **13** (1979) 225.
27. P. Saxe, Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **77** (1982) 5647.
28. Y. Osamura, Y. Yamaguchi, P. Saxe, M. A. Vincent, J. F. Gaw and H. F. Schaefer,
Chem. Phys., **72** (1982) 131.
29. Y. Yamaguchi, Y. Osamura, G. Fitzgerald and H. F. Schaefer, *J. Chem. Phys.*, **78** (1983) 1067.
30. R. N. Camp, H. F. King, J. W. McIver and D. Mullaly, *J. Chem. Phys.*, **79** (1983) 1088.
31. M. R. Hoffmann, D. J. Fox, J. F. Gaw, Y. Osamura, Y. Yamaguchi, R. S. Grev, G. Fitzgerald,
H. F. Schaefer, P. J. Knowles and N. C. Handy, *J. Chem. Phys.*, **80** (1984) 2660.
32. D. J. Fox, Y. Osamura, M. R. Hoffmann, J. F. Gaw, G. Fitzgerald, Y. Yamaguchi and
H. F. Schaefer, *Chem. Phys. Lett.*, **102** (1983) 17.
33. N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice, E. D. Simandiras, T. J. Lee, R. J. Harrison,
W. D. Laidig, G. Fitzgerald and R. J. Bartlett, *Geometrical Derivatives of Energy Surfaces*
and Molecular Properties, edited by P. Jorgensen and J. Simons (Reidel, Dordrecht, 1986).
34. N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice and E. D. Simandiras,
Chem. Phys. Lett., **120** (1985) 151.
35. M. Page, P. Saxe, G. F. Adams and B. H. Lengsfeld, *Chem. Phys. Lett.*, **104** (1984) 587.
36. P. Saxe, D. J. Fox, H. F. Schaefer and N. C. Handy, *J. Chem. Phys.*, **77** (1982) 5584.
37. P. E. M. Siegbahn, *Int. J. Quantum Chem.*, **23** (1983) 1869.
38. L. G. Pettersson, S. R. Langhoff and D. P. Chong, *J. Chem. Phys.*, **85** (1986) 2836.
39. C. M. Rohlfing and P. J. Hay, submitted to *J. Chem. Phys.*

40. W. Meyer, in *Modern Theoretical Chemistry*, H. H. Schaefer, Ed. (Plenum, New York, 1977), Vol. 3, Ch. 11.
41. P. E. M. Siegbahn, *Int. J. Quantum Chem.*, 18 (1980) 1229.
42. P. E. M. Siegbahn, in *Lecture Notes in Chemistry : The Unitary Group*, J. Hinze, Ed. (Springer, Berlin, 1981), p. 119.
43. H-J. Werner and E. A. Reinsch, *J. Chem. Phys.*, 76 (1982) 3144.
44. H-J. Werner, J. Kalcher and E. A. Reinsch, *J. Chem. Phys.*, 81 (1984) 2420.
45. H-J. Werner, P. Rosmus, W. Schatzl, W. Meyer, *J. Chem. Phys.*, 80 (1984) 831.
46. P. Rosmus and H-J. Werner, *J. Chem. Phys.*, 80 (1984) 5085.
47. H-J. Werner, P. Rosmus and E. A. Reinsch, *J. Chem. Phys.*, 79 (1983) 905.
48. P. Taylor, *J. Chem. Phys.*, 74 (1981) 1256.
49. T. H. Dunning, *J. Chem. Phys.*, 53 (1970) 2823.
50. S. Huzinaga, *J. Chem. Phys.*, 42 (1965) 1293.
51. T. H. Dunning and P. J. Hay, *Modern Theoretical Chemistry*, edited by H. F. Schaefer (Plenum, New York, 1977), Vol. 3, pp. 1-27.
52. C. S. Gudeman, M. H. Begemann, J. Pfaff and R. J. Saykally, *Phys. Rev. Lett.*, 50 (1983) 727.
53. C. S. Gudeman, M. H. Begemann, J. Pfaff and R. J. Saykally, *J. Chem. Phys.*, 78 (1983) 5837.
54. M. H. Begemann, C. S. Gudeman, J. Pfaff and R. J. Saykally, *Phys. Rev. Lett.*, 51 (1983) 554.
55. M. W. Crofton and T. Oka, *J. Chem. Phys.*, 79 (1983) 3157.
56. E. Schafer, M. H. Begemann, C. S. Gudeman and R. J. Saykally, *J. Chem. Phys.*, 79 (1983) 3159.
57. C. S. Gudeman and R. J. Saykally, *Annu. Rev. Phys. Chem.*, 35 (1984) 387.
58. M. E. Colvin, G. P. Raine, H. F. Schaefer and M. Dupuis, *J. Chem. Phys.*, 79 (1983) 1551.
59. Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, 73 (1980) 2310.
60. See also T. Oka, *Phys. Rev. Lett.*, 45 (1980) 531.
61. M. J. Frisch and J. A. Pople xxx
62. Note that HCNH^+ has already attracted considerable theoretical attention due to its

- hypothesized importance in interstellar space. See T. L. Allen, J. D. Goddard and H. F. Schaefer, *J. Chem. Phys.*, **73** (1980) 3255, and references therein.
63. W. D. Laidig, Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **80** (1984) 3069.
 64. G. Strey and I. M. Mills, *Mol. Phys.*, **26** (1973) 129.
 65. R. A. Creswell and A. G. Robiette, *Mol. Phys.*, **36** (1978) 869.
 66. A. G. Makai and R. L. Sams, *J. Chem. Phys.*, **75** (1981) 4178.
 67. N. N. Haese and R. C. Woods, *Chem. Phys. Lett.*, **61** (1979) 396 ;
see also P. S. Dardi and C. E. Dykstra, *Astrophys. J.*, **240** (1980) L171.
 68. R. S. Altman, M. W. Crofton and T. Oka, *J. Chem. Phys.*, **80** (1984) 3911.
 69. M. Bogey, C. Demuynck and J. L. Destombes, *J. Chem. Phys.*, **83** (1985) 3703.
 70. L. M. Ziurys and B. E. Turner, 17th International Symposium on Free Radicals and Other Transient Species, Granby, Colorado, August 1985; L. M. Ziurys and B. E. Turner, *Astrophys. J. Lett.* xxx
 71. G. E. Scuseria, T. J. Lee, R. J. Saykally and H. F. Schaefer, *J. Chem. Phys.*, **84** (1986) 5711.
 72. T. Amano, *Chem. Phys. Lett.*, **127** (1986) 101.
 73. T. B. McMahon and P. Kebarle, *J. Chem. Phys.*, **83** (1985) 3919.
 74. C. R. Moylan and J. I. Brauman, *Ann. Rev. Phys. Chem.*, **34** (1983) 187.
 75. A. D. McLean, G. H. Loew and D. S. Berkowitz, *J. Mol. Spectry.*, **72** (1978) 430.
 76. L. Farnell, R. H. Nobes and L. Radom, *J. Mol. Spectry.*, **9** (1982) 271.
 77. R. P. Grosso and T. K. McCubbin, *J. Mol. Spectry.*, **13** (1964) 240.
 78. S. R. Langhoff and E. R. Davidson, *Intern. J. Quantum. Chem.*, **8** (1974) 61.
 79. G. P. Raine and H. F. Schaefer, *J. Chem. Phys.*, **81** (1984) 4034.
 80. T. Oka (personal communication, October 1985).
 81. Theory - M. J. Frisch, H. F. Schaefer and J. S. Binkley, *J. Phys. Chem.*, **89** (1985) 2192.
Experiment - T. Amano and K. Tanaka, *J. Chem. Phys.*, **83** (1985) 3721.
 82. E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

83. T. J. Lee and H. F. Schaefer, *J. Chem. Phys.*, **83** (1985) 1784.
84. F. B. van Duijneveldt, IBM Technical Research Report No. RJ945.,
December 10, 1971, San Jose, California.
85. A. C. Hopkinson and I. G. Csizmadia, *Chem. Commun.*, (1971) 1291.
86. W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **93** (1971) 808.
87. A. C. Hopkinson, K. Yates and I. G. Csizmadia, *J. Chem. Phys.*, **55** (1971) 3835.
88. P. C. Hariharan, W. A. Lathan and J. A. Pople, *Chem. Phys. Lett.*, **14** (1972) 385.
89. B. Zurawski, R. Ahlrichs and W. Kutzelnigg, *Chem. Phys. Lett.*, **21** (1973) 309.
90. W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle and J. A. Pople,
Prog. Phys. Org. Chem., **11** (1974) 175.
91. J. Weber, M. Yoshimine and A. D. McLean, *J. Chem. Phys.*, **64** (1976) 4159.
92. J. A. Pople, *Int. J. Mass. Spectrom. Ion Phys.*, **19** (1976) 89.
93. D. Poppinger, *Chem. Phys.*, **12** (1976) 131.
94. J. Weber and A. D. McLean, *J. Amer. Chem. Soc.*, **98** (1976) 875.
95. N. C. Baird and K. F. Taylor, *J. Amer. Chem. Soc.*, **100** (1978) 1333.
96. A. Streitwieser and S. Alexandratos, *J. Amer. Chem. Soc.*, **100** (1978) 1979.
97. H. Lischka and H-J. Kohler, *J. Amer. Chem. Soc.*, **100** (1978) 5297.
98. R. A. Poirier, R. Daudel and I. G. Csizmadia, *Int. J. Quantum Chem.*, **18** (1980) 727.
99. H-J. Kohler and H. Lischka, *Theor. Chim Acta*, **54** (1980) 23.
100. Y. Apeloig, P. v. R. Schleyer and J. A. Pople, *J. Amer. Chem. Soc.*, **99** (1977) 1291.
101. Y. Apeloig, P. v. R. Schleyer and J. A. Pople, *J. Amer. Chem. Soc.*, **99** (1977) 5901.
102. Y. Apeloig and A. Stranger, *J. Org. Chem.*, **47** (1982) 1462.
103. J. E. Del Bene, M. J. Frisch, K. Raghavachari and J. A. Pople, *J. Phys. Chem.*, **86** (1982) 1529.
104. H. Mayr, R. Schneider, D. Wilhelm and P. v. R. Schleyer, *J. Org. Chem.*, **46** (1981) 5336.
105. K. Raghavachari, R. A. Whiteside, J. A. Pople and P. v. R. Schleyer,
J. Amer. Chem. Soc., **103** (1981) 5649.
106. E. Fois, A. Gamba, G. B. Suffriti, M. Simonetta, I. Szele and H. Zollinger,

- J. Phys. Chem., 86 (1982) 3722.
107. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
108. See page 164 of H. Callomon, E. Hirota, H. Kuchitsu, W. J. Lafferty, A. G. Maki and C. S. Pote, *Structure Data of Free Polyatomic Molecules* (Springer, Berlin, 1976).
109. Y. Yamaguchi, M. J. Frisch, J. F. Gaw, H. F. Schaefer and J. S. Binkley, *J. Chem. Phys.*, 84 (1986) 2262.
110. J. E. Del Bene, H. D. Mettee, M. J. Frisch, B. T. Luke and J. A. Pople, *J. Phys. Chem.*, 87 (1983) 17.
111. B. O. Roos, P. R. Taylor and P. E. M. Siegbahn, *Chem. Phys.*, 48 (1980) 157.
112. H-J. Werner and P. J. Knowles, *J. Chem. Phys.*, 82 (1985) 5053.
113. T. J. Lee, D. J. Fox, H. F. Schaefer and R. M. Pitzer, *J. Chem. Phys.*, 81 (1984) 356.
114. A. N. Petlin and A. A. Kiselev, *Int. J. Quantum Chem.*, 6 (1972) 701.
115. J. E. Reutt, L. S. Wang, J. E. Pollard, D. J. Trevor, Y. T. Lee and D. A. Shirley, *J. Chem. Phys.*, 84 (1986) 3022.
116. E. Magnusson, *J. Comput. Chem.*, 5 (1984) 612.
117. E. Magnusson, *J. Amer. Chem. Soc.*, 106 (1984) 1185.
118. H. Wallmeier and W. Kutzelnigg, *J. Amer. Chem. Soc.*, 101 (1979) 2084.
119. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed., edited by R. A. Whiteside, M. J. Frisch and J. A. Pople.
120. R. Latinen and T. Pakkanen, *J. Mol. Struct.*, 91 (1983) 337.
121. N. Ottashi, M. Kakimoto, S. Saito and E. Hirota, *J. Mol. Spectry.*, 84 (1980) 204.
122. J. R. Slagle, R. E. Graham and D. Gutman, *Int. J. Chem. Kinet.*, 8 (1976) 451.
123. S. Glavas and S. Toby, *J. Phys. Chem.*, 79 (1975) 779.
124. G. Fitzgerald, T. J. Lee, H. F. Schaefer and R. J. Bartlett, *J. Chem. Phys.*, 83 (1985) 6275.
125. See G. Fitzgerald and H. F. Schaefer, *J. Chem. Phys.*, 81 (1984) 362, and Refs. 2-26 therein.
126. K. G. Lubic, T. Amano, H. Uehara, K. Kawaguchi and E. Hirota,

- J. Chem. Phys., 81 (1984) 4826.
127. G. Winnewisser, M. Winnewisser and W. Gordy, J. Chem. Phys., 49 (1968) 3465.
 128. G. A. Khackkuruzov and I. Przhevalskii, Opt. Spectrosc., 36 (1974) 172.
 129. M. E. Okamura, L. I-C. Yeh, D. Normand, J. J. H. van den Biesen,
S. W. Bustamente and Y. T. Lee, Tetrahedron, 41 (1985) 1423.
 130. R. R. Corderman and W. C. Lineberger, Ann. Rev. Phys. Chem., 30 (1979) 347.
 131. B. K. Janousek and J. I. Brauman, Gas Phase Ion Chemistry , (edited by M. T. Bowers),
Vol. 2, p. 53 (Academic Press, New York, 1979).
 132. P. C. Engelking, R. R. Corderman, J. J. Wendoloski, G. B. Ellison, S. V. O'Neil and
W. C. Lineberger, J. Chem. Phys., 74 (1981) 5460.
 133. A. R. W. McKellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally and
S. R. Langhoff, J. Chem. Phys., 79 (1983) 5251.
 134. D. G. Leopold, K. K. Murray, A. E. Stevens Miller and W. C. Lineberger,
J. Chem. Phys., 83 (1985) 4849.
 135. L. B. Harding and W. A. Goddard, Chem. Phys. Lett., 55 (1983) 217.
 136. P. R. Bunker and S. R. Langhoff, L. Mol. Spectry., 102 (1983) 204.
 137. P. R. Bunker and B. M. Landsberg, J. Mol. Spectry., 67 (1977) 374.
 138. T. J. Sears and P. R. Bunker, J. Chem. Phys., 79 (1983) 5265.
- This SRB potential is derived from Ref. 132.
139. P. R. Bunker and T. J. Sears, J. Chem. Phys., 83 (1985) 4866.
- This SRB potential is derived from Ref. 134.
140. T. J. Lee, J. E. Rice and H. F. Schaefer, to be published.
 141. U. Manz, A. Zilch, P. Rosmus and H-J. Werner, J. Chem. Phys., 84 (1986) 1683.
 142. P. Botschwina, J. Mol. Spectry., 117 (1986) 173.
 143. P. Botschwina, Chem. Phys. Lett., 114 (1985) 58.
 144. P. Botschwina, Habilitationsschrift
 145. T. J. Lee, R. B. Remington, Y. Yamaguchi and H. F. Schaefer, J. Chem. Phys., to be published.

146. S. M. Adler-Golden, S. R. Langhoff, C. W. Bauschlicher, G. D. G. D. Carney,
J. Chem. Phys., 83 (1985) 255.
147. M. Okamura, L. I-C. Yeh, D. Normand and Y. T. Lee, J. Chem. Phys., 85 (1986) 1971.
148. D. N. Neumark, K. R. Lykke, T. Andersen and W. C. Lineberger,
J. Chem. Phys., 83 (1985) 4364.
149. J. E. Delmore and A. D. Appelhans, J. Chem. Phys., 84 (1986) 6238.
150. J. Simons, J. Amer. Chem. Soc., 103 (1981) 3971.
151. P. E. M. Siegbahn, Chem. Phys. Lett., 109 (1984) 417.
152. P. J. Knowles and N. C. Handy, Chem. Phys. Lett., 111 (1984) 315.
153. P. Saxe; 7th Annual West Coast Theoretical Chemistry Conference,
Santa Barbara, California, April 1986.
154. P. Saxe, H. F. Schaefer and N. C. Handy, Chem. Phys. Lett., 79 (1981) 202.
155. R. J. Harrison and N. C. Handy, Chem. Phys. Lett., 96 (1983) 386.
156. C. W. Bauschlicher, S. R. Langhoff, P. R. Taylor and H. Partridge,
submitted to Chem. Phys. Lett.
157. C. W. Bauschlicher, S. R. Langhoff, P. R. Taylor, N. C. Handy and P. J. Knowles,
J. Chem. Phys., 85 (1986) 1469.
158. C. W. Bauschlicher and P. R. Taylor, J. Chem. Phys., 85 (1986) 2779.
159. C. W. Bauschlicher, S. R. Langhoff, H. Partridge and P. R. Taylor,
J. Chem. Phys., 85 (1986) 3407.
160. G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice and H. F. Schaefer,
J. Chem. Phys., in press.
161. J. E. Rice, T. J. Lee, R. B. Remington, W. D. Allen, D. A. Clabo and H. F. Schaefer,
submitted to J. Am. Chem. Soc.
162. T. J. Lee, J. E. Rice, R. B. Remington and H. F. Schaefer, to be published.
163. N. C. Handy, T. J. Lee and W. H. Miller, Chem. Phys. Lett., 125 (1986) 12.

FIGURE CAPTIONS

Figure II-(1). Flow diagram of the analytic CI second derivative procedure. (a) Procedure required for the analytic evaluation of the CI gradient or TCSCF-CI gradient if a TCSCF is performed rather than a SCF and one set of CPTCSCF-like equations are solved rather than one set of CPHF-like equations.

Figure V-(1). Predicted equilibrium geometries for protonated HCN. Bond distances are in Å.

Figure V-(2). Theoretical predictions for the structures of nitrous oxide (N_2O) and protonated nitrous oxide. A double zeta plus polarization (DZ+P) basis set was used in conjunction with configuration interaction including single and double excitations (CISD). In parentheses are given DZ+P SCF predictions. All bond distances are in Å.

Figure V-(3). Theoretical equilibrium geometries for the classical and nonclassical isomers of protonated acetylene. Geometrical parameters are given first from CI wave functions and second, in parentheses, from SCF wave functions. A DZ+P basis set was used. All bond distances are in Å.

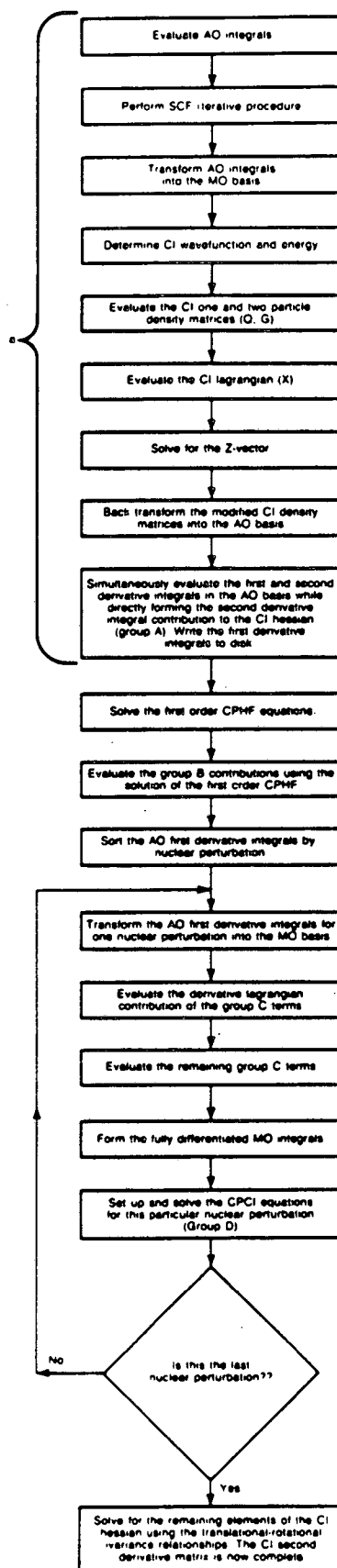
Figure V-(4). Theoretical equilibrium geometries for the classical and nonclassical structures C_2H_3^+ . The C(13s 8p 2d/8s 5p 2d), H(7s 2p/4s 2p) basis set, described in the text, was used in conjunction with the SCF level of theory. All bond distances are in Å.

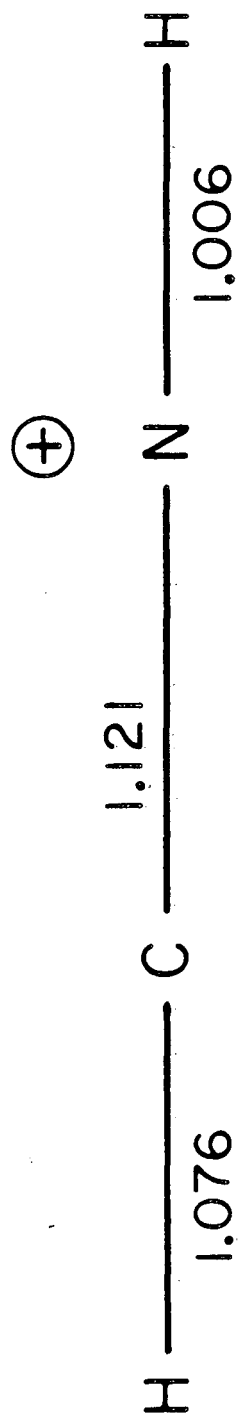
Figure V-(5). CISD and SCF predicted equilibrium structure for HSOH. Bond lengths are in Å and angles are in degrees.

Figure V-(6). *Ab initio* potential energy curves for CH_2^- . See text for details of the basis sets.

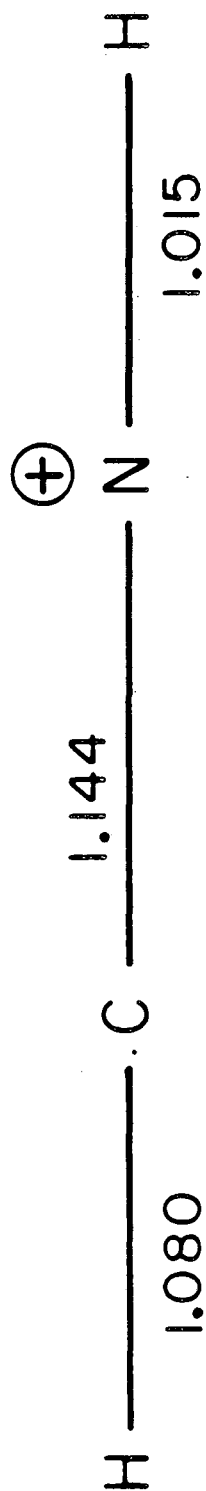
Figure V-(7). *Ab initio* dipole moment curves for the bending mode of CH_2^- . See text for details.

Figure V-(8). The *ab initio* optimum bond length of CH_2^- for various HCH angles. The TZ+diffuse+3P basis was used. See text for details of this basis.



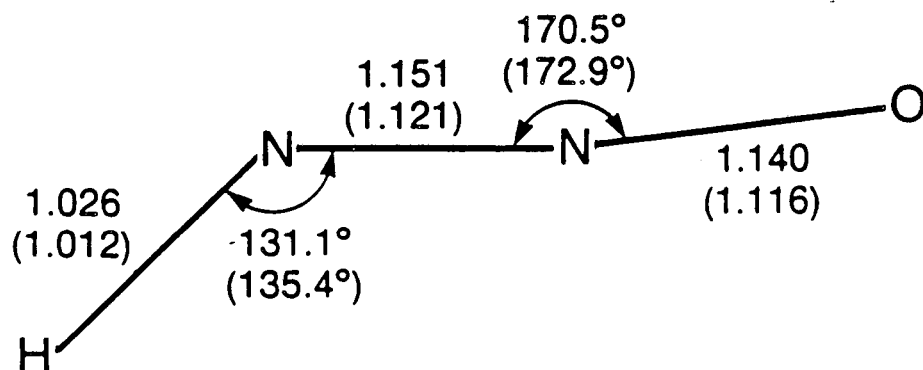
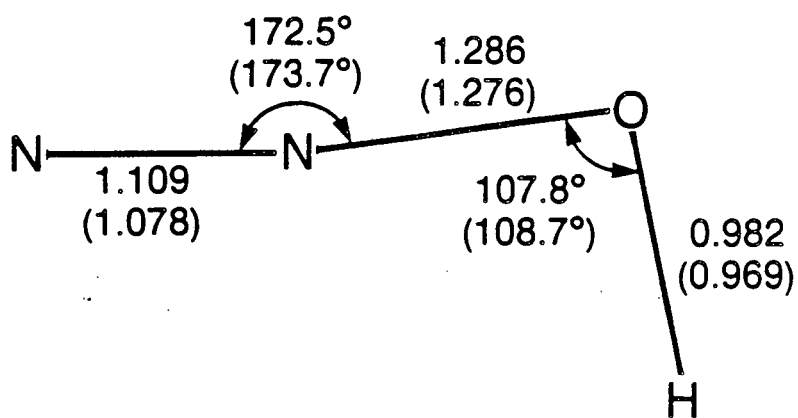
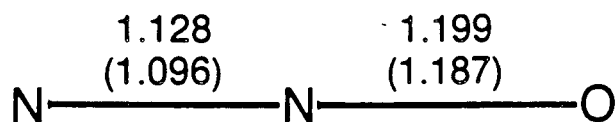


DZ + P SCF

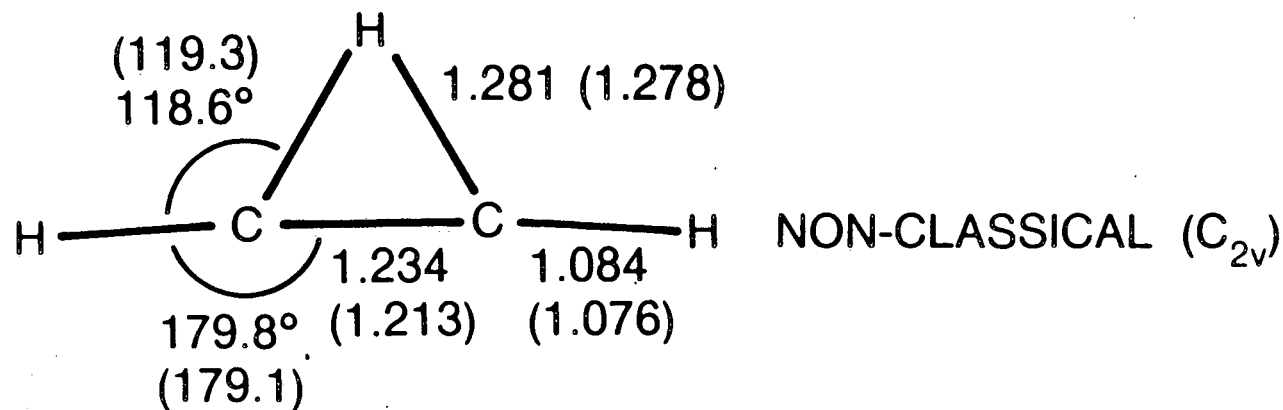
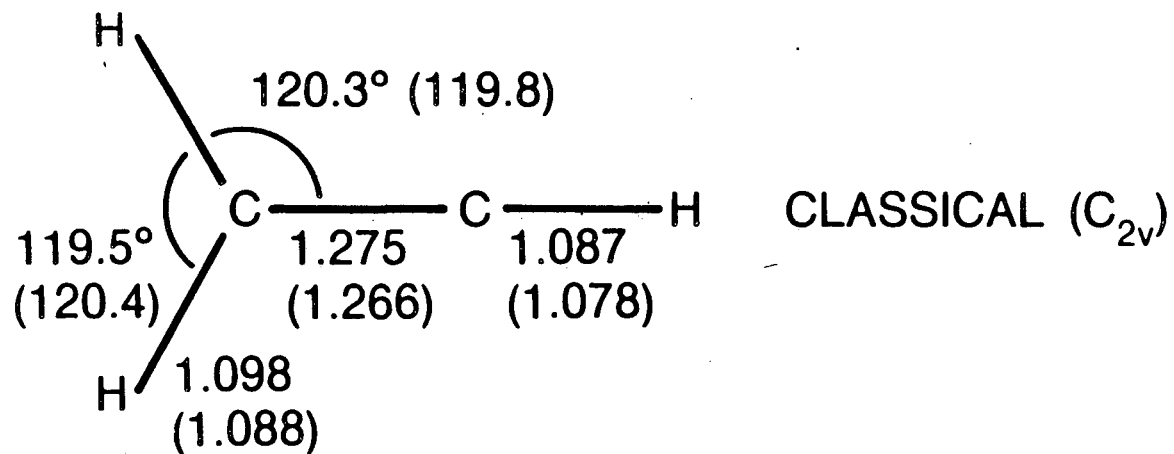


DZ + P CI

XBL 8311 - 4088

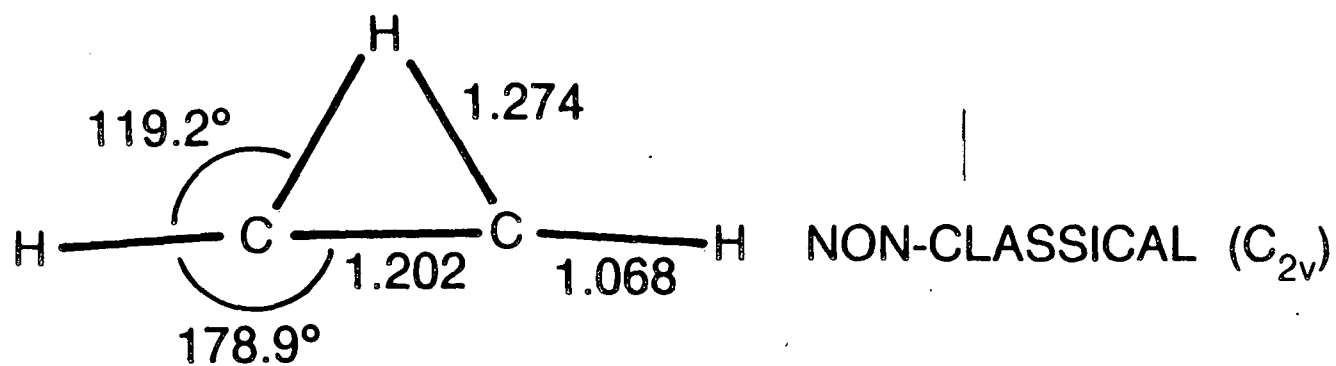
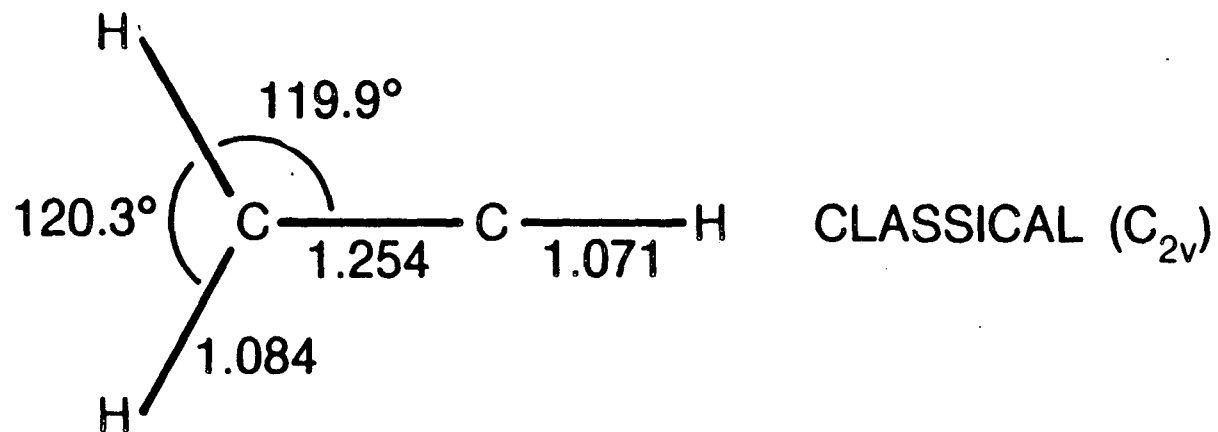


DZ + P CI (SCF)

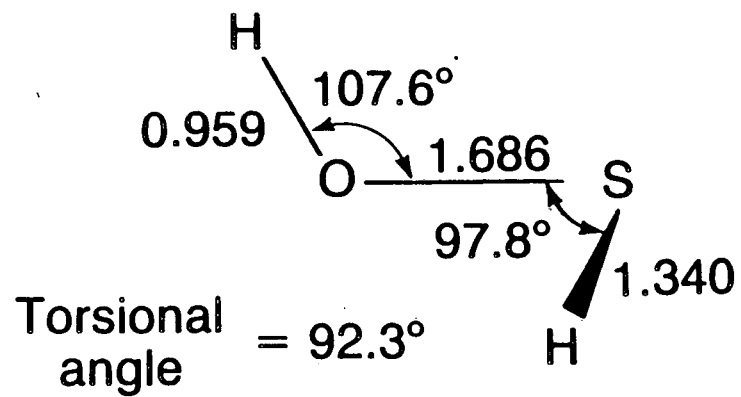


XBL 861-8601

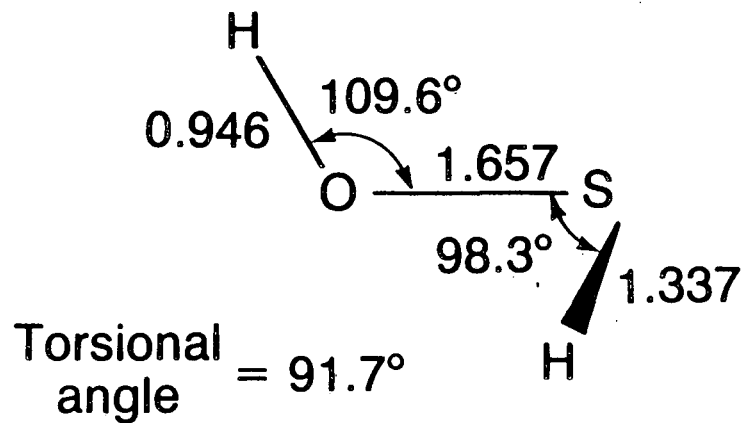
TZ + diffuse + 2P SCF



XBL 861-8602



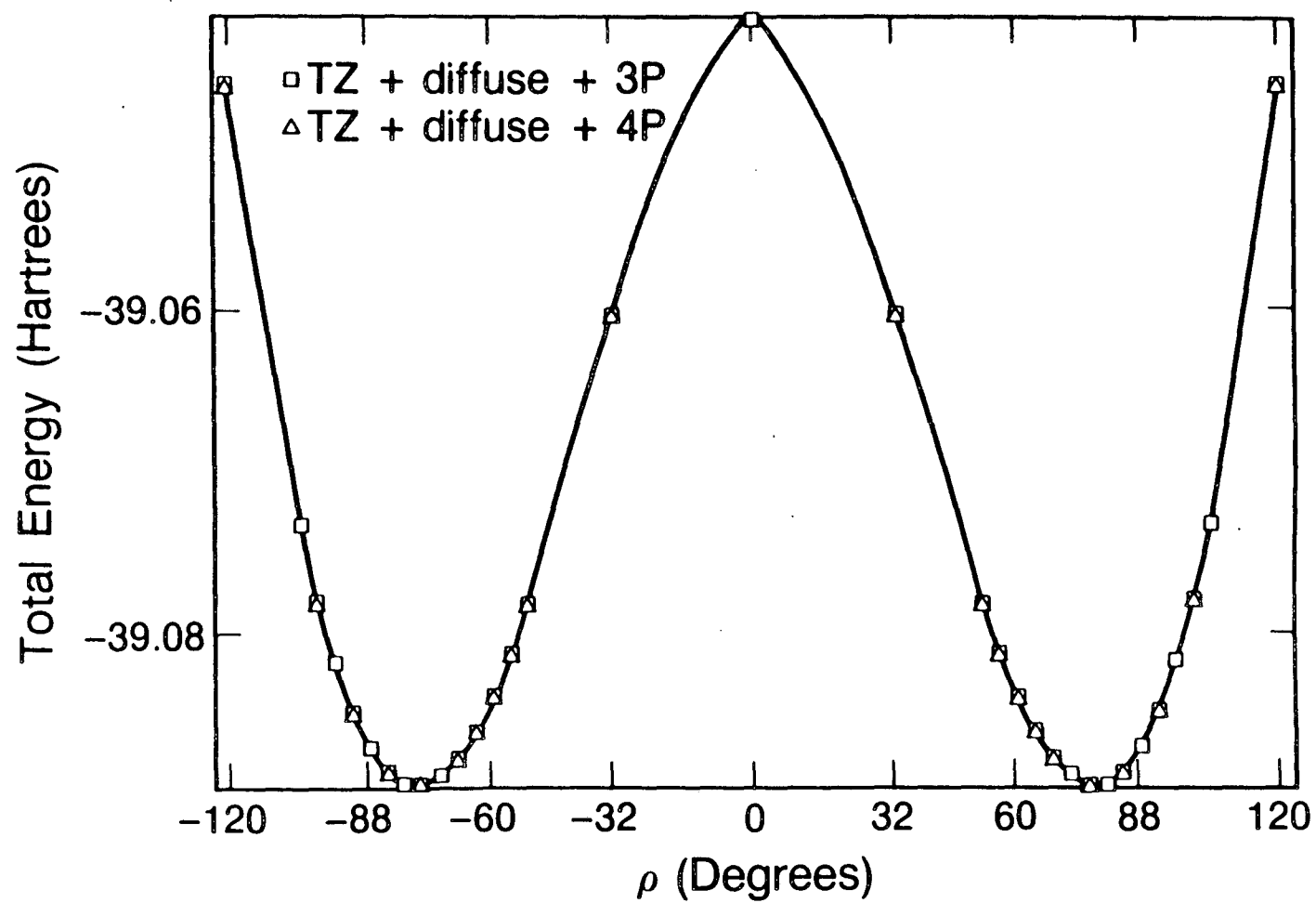
DZ + P CISD



DZ + P SCF

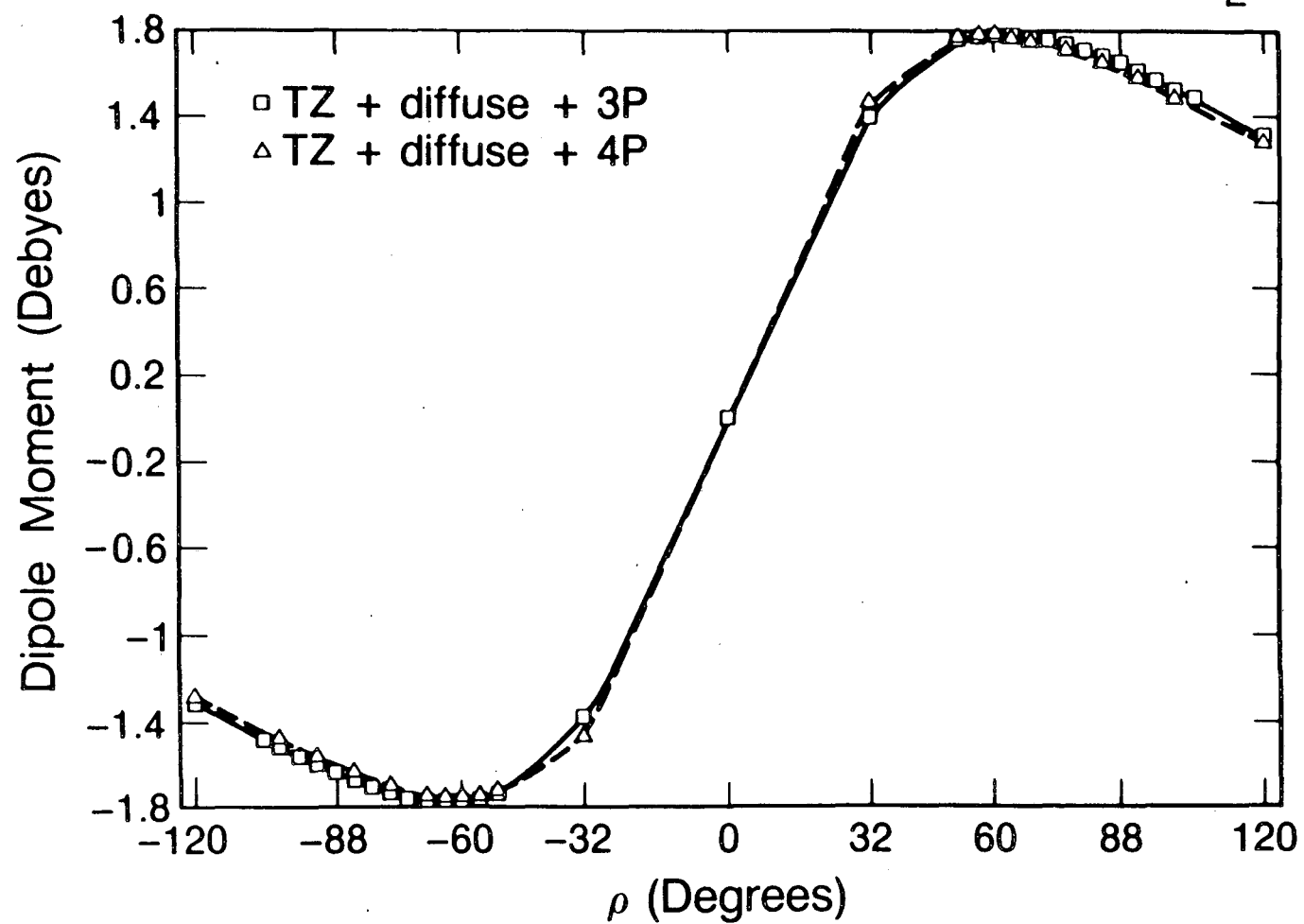
XBL 864-8717

POTENTIAL ENERGY FUNCTION OF CH_2^-



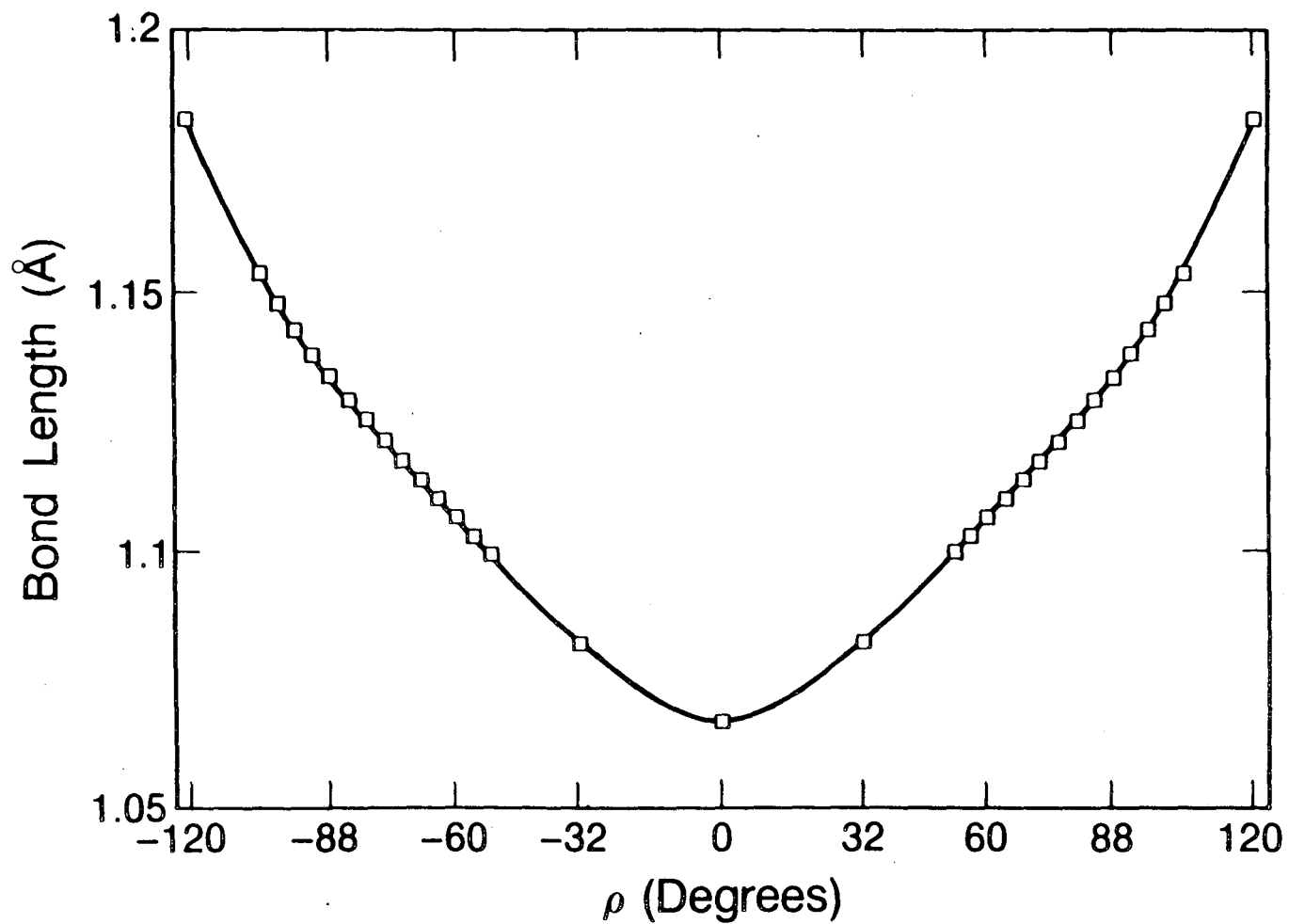
XBL 865-8773

DIPOLE MOMENT FUNCTION OF CH_2^-



XBL 865-8774

BOND LENGTH AS A FUNCTION OF ρ



XBL 865-8772

Table V-(1). Vibrational frequency and intensity predictions for HCNH^+ made at the double zeta plus polarization (DZ+P) self-consistent field (SCF) and configuration interaction (CI) levels of theory.

Normal mode description		DZ+P SCF	Estimated (cm^{-1})	Intensity (km/mole)
ν_1 (σ)	N-H stretch	3869	3455	541
ν_2 (σ)	C-H stretch	3501	3188	353
ν_3 (σ)	C-N stretch	2434	2132	62
ν_4 (π)	HCN bend	937	779	102
ν_5 (π)	HNC bend	799	...	308

Normal mode description		DZ+P CI	Estimated (cm^{-1})	Intensity (km/mole)
ν_1 (σ)	N-H stretch	3754	3474	475
ν_2 (σ)	C-H stretch	3423	3201	357
ν_3 (σ)	C-N stretch	2283	2161	39
ν_4 (π)	HCN bend	836	790	212
ν_5 (π)	HNC bend	700	...	186

Table V-(2) Theoretical and experimental rotational and vibrational spectroscopic parameters for protonated nitrous oxide. Infrared intensities are given in km/mole (in parentheses).

		⁺ HNNO		NNOH ⁺		Experiment
		DZ+P SCF	DZ+P CISD	DZ+P SCF	DZ+P CISD	
Total Energy (hartrees)		-183.92178	-184.37884	-183.96105	-184.40145	
Rotational Constants	A(MHz)	1 208 300	1 003 300	655 900	627 900	625 954
	B(MHz)	12 300	11 800	11 500	11 200	11 301
	C(MHz)	12 200	11 700	11 300	11 000	11 085
Dipole Moment (debye)		3.94	3.64	2.40	2.43	
Vibrational Frequencies	a' $\omega_1(\text{cm}^{-1})$	3623 (956)	3573 (757)	3865 (477)	3729 (418)	$\nu_1 = 3331$
	a' $\omega_2(\text{cm}^{-1})$	2590 (884)	2467 (205)	2787 (1)	2525 (3)	
	a' $\omega_3(\text{cm}^{-1})$	1610 (43)	1491 (149)	1532 (117)	1451 (114)	
	a' $\omega_4(\text{cm}^{-1})$	713 (56)	714 (249)	1072 (39)	1068 (53)	
	a' $\omega_5(\text{cm}^{-1})$	501 (465)	590 (144)	463 (15)	419 (14)	
	a'' $\omega_6(\text{cm}^{-1})$	681 (0)	617 (6)	517 (1)	470 (3)	

Table V-(3) Theoretical and experimental vibrational frequencies and IR intensities for acetylene and C_2D_2 . Intensities in km/mole are given below the vibrational frequencies in cm^{-1} . The observed fundamentals are from T. Shimanouchi, Tables of Molecular Vibrational Frequencies, NSRDS-NBS 39 (National Bureau of Standards, Washington, D.C., 1972). Experimental IR intensities were taken from the tabulation of R. D. Amos, Chem. Phys. Lett. 114, 10 (1985).

Method	TZ+diffuse+2P			Experiment
	DZ+P SCF	DZ+P CI	SCF	
<u>C₂H₂ Molecule</u>				
σ_g	3677	3573	3662	3374
	0	0	0	--
σ_g	2203	2072	2205	1974
	0	0	0	--
σ_u	3571	3478	3553	3289
	100.6	83.7	96.9	76 ^a ,70 ^b
π_g	767	611	773	612
	0	0	0	--
π_u	858	760	848	730
	225.5	188.3	230.9	194 ^a ,177 ^b

Table V-(3) (continued)

Method	DZ+P SCF	DZ+P CI	TZ+diffuse+2P SCF	Experiment
<u>C₂D₂ Molecule</u>				
σ_g	2958	2843	2950	2701
	0	0	0	--
σ_g	1937	1842	1936	1762
	0	0	0	--
σ_u	2622	2554	2609	2439
	54.2	45.1	52.2	
π_g	640	509	646	505
	0	0	0	--
π_u	630	558	623	537
	121.5	101.5	124.5	

^aW. M. A. Smit, A. J. van Straten, and T. Visser, J. Mol. Struct. 48, 177 (1978).

^bK. Kim and W. T. King, J. Mol. Struct. 57, 201 (1979).

Table V-(4) Total energies (in hartrees) and dipole moments (in debyes) for the classical and nonclassical forms of protonated acetylene, $C_2H_3^+$.

Basis Set	TZ+diffuse+2P	TZ+diffuse+2P	DZ+P
Method Used to Optimize Geometry	SCF	DZ+P CI	DZ+P CI
<u>Classical $C_2H_3^+$</u>			
E_{SCF}	-77.117154	-77.116036	-77.098871
E_{CISD}	-77.381839	-77.381346	-77.340344
$E_{CI+Davidson}$	-77.406873	-77.406952	-77.363074
E_{CISDT}	--	--	-77.349009
μ_{CISD}	0.68 ^b	0.69 ^b	0.75 ^a , 0.70 ^b
<u>Nonclassical $C_2H_3^+$</u>			
E_{SCF}	-77.110387	-77.108010	-77.090247
E_{CISD}	-77.382663	-77.382418	-77.341240
$E_{CI+Davidson}$	-77.407417	-77.408136	-77.364038
E_{CISDT}	--	--	-77.350085
μ_{CISD}	1.14 ^b	1.14 ^b	1.24, ^a 1.27 ^b

^aDipole moment evaluated as an energy derivative; see text for details.

^bDipole moment calculated as an expectation value.

Table V-(5) Vibrational frequencies (in cm^{-1}) and IR intensities (km/mole) for the classical and nonclassical forms of protonated acetylene.

Method Property	TZ+diffuse+2P SCF			DZ+P CISD		
	$\omega(\text{ab initio})$	$\nu(\text{estimated})$	Intensity	$\omega(\text{ab initio})$	$\nu(\text{estimated})$	Intensity
<u>Classical C_2H_3^+</u>						
a_1	3431	3169	166.9	3364	3179	125.4
a_1	3198	2953	185.1	3126	2954	234.8
a_1	1815	1625	30.5	1753	1670	63.2
a_1	1360		53.2	1254		67.6
b_1	3287	3036	151.3	3217	3040	171.1
b_1	1172		0.0	1106		0.5
b_1	460		20.7	345		36.0
b_2	1030		75.7	873		125.1
b_2	672		84.0	601		47.2
<u>Nonclassical C_2H_3^+</u>						
a_1	3528	3258	0.1	3443	3254	0.0
a_1	2456		80.0	2471		49.6
a_1	2113	1892	8.4	2000	1905	4.8
a_1	991		48.6	923		0.0
a_2	728		-0-	587		-0-
b_1	3410	3149	402.1	3339	3155	396.1
b_1	1333		4.8	1279		7.5
b_1	418		43.2	513		34.7
b_2	845		124.1	757		119.5

Table V-(6) Vibrational frequencies (in cm^{-1}) and IR intensities (km/mole) for the classical and nonclassical forms of C_2D_3^+ .

Method Property	TZ+diffuse+2P SCF			DZ+P CISD		
	$\omega(\text{ab initio})$	$\nu(\text{estimated})$	Intensity	$\omega(\text{ab initio})$	$\nu(\text{estimated})$	Intensity
<u>Classical C_2D_3^+</u>						
a_1	2611	2416	37.6	2558	2437	19.4
a_1	2327	2153	130.1	2274	2166	185.5
a_1	1684	1533	19.0	1631	1560	45.7
a_1	988			20.3	909	35.2
b_1	2442	2259	75.6	2390	2277	104.2
b_1	960			0.8	905	0.0
b_1	338			7.3	254	20.4
b_2	813			23.1	680	59.9
b_2	527			43.1	477	35.9
<u>Nonclassical C_2D_3^+</u>						
a_1	2848	2635	2.9	2748	2618	2.1
a_1	1856	1689	14.1	1793		16.9
a_1	1777		26.4	1769	1692	18.9
a_1	722		16.8	672		0.0
a_2	608		-0-	489		-0-
b_1	2505	2318	180.8	2453	2337	208.5
b_1	970		2.1	923		2.3
b_1	349		40.5	432		31.0
b_2	621		53.5	556		68.6

Table V-(7) Theoretical predictions for the acetylene radical cation $C_2H_2^+$. Infrared intensities (in km/mole) are given after the predicted vibrational frequencies in parentheses.

	Self-Consistent-Field (SCF)	Multi-Configuration Self-Consistent-Field (MCSCF)	Configuration Interaction (CISD)
Total Energy (hartrees)	-76.47068	-76.60021	-76.68820
$r_e(C-H)$, Å	1.075	1.096	1.082
$r_e(C-C)$, Å	1.234	1.273	1.259
Rotational Constants (cm^{-1})			
$C_2H_2^+$	1.131	1.069	1.094
$C_2D_2^+$	0.816	0.773	0.791
Vibrational Frequencies (cm^{-1})			
$C_2H_2^+$ $\omega_1(\sigma_g)$	3536(0)	3285(0)	3434(0)
$\omega_2(\sigma_g)$	2051(0)	1812(0)	1907(0)
$\omega_3(\sigma_u)$	3429(485)	3204(345)	3340(439)
$\omega_4(\pi_g)^b$	868(0)	741(0)	780(0)
$\omega_5(\pi_g)^a$	739(0)	505(0)	563(0)
$\omega_6(\pi_u)^b$	841(260)	710(208)	741(234)
$\omega_7(\pi_u)^a$	802(76)	697(64)	727(74)
$C_2D_2^+$ $\omega_1(\sigma_g)$	2822(0)	2586(0)	2706(0)
$\omega_2(\sigma_g)$	1818(0)	1629(0)	1712(0)
$\omega_3(\sigma_u)$	2518(227)	2352(186)	2452(237)
$\omega_4(\pi_g)^b$	723(0)	616(0)	649(0)
$\omega_5(\pi_g)^a$	616(0)	420(0)	468(0)
$\omega_6(\pi_u)^b$	618(106)	521(112)	544(126)
$\omega_7(\pi_u)^a$	589(22)	512(34)	534(40)

^aThese frequencies correspond to the energetically lower-lying component of the Renner-Teller pair of potential surfaces.

^bThese frequencies refer to the energetically higher-lying component of the Renner-Teller pair of potential surfaces.

Table V-(8) Theoretical predictions of the structure of thioperoxide, HSOH. A double zeta plus polarization (DZ+P) basis was used in conjunction with the SCF and CI levels of theory. Bond lengths are in angstroms and angles in degrees.

Molecular Parameter	DZ+P ^a SCF	3-21G ^{*b} SCF	DZ+P SCF	DZ+P CISD
Energy (hartrees)	-473.3143	-471.23374	-473.51765	-473.90803
r _{S-O}	1.686	1.661	1.657	1.686
r _{S-H}	1.337	1.329	1.337	1.340
r _{O-H}	0.949	0.969	0.946	0.959
<HOS	107.9	111.3	109.6	107.6
<HSO	100 ^c	99.6	98.3	97.8
torsional angle	94.3	91.1	91.7	92.3

^aTaken from Ref. 118. See footnote c.

^bTaken from Ref. 119.

^cThis parameter was not optimized.

Table V-(9) CISD predictions of the harmonic vibrational frequencies and IR intensities of thioperoxide and its deuterated isotopomers. The frequencies were obtained via the analytic CI second derivative matrix. Frequencies are in cm^{-1} and IR intensities are in km/mole .

Mode	Description	HSOH	DSOH	HSOD	DSOD
ω_1	O-H stretch	4005	4005	2918	2918
ω_2	S-H stretch	2770	1990	2770	1990
ω_3	HOS bend	1244	1244	913	913
ω_4	HSO bend	1064	775	1063	774
ω_5	S-O stretch	808	813	802	807
ω_6	Torsional motion	489	451	405	358
I_1		65.2	65.2	37.7	37.9
I_2		18.3	10.4	18.4	10.2
I_3		49.1	48.9	38.0	37.9
I_4		3.6	10.3	5.2	11.9
I_5		51.8	43.5	40.1	31.9
I_6		101.1	115.6	49.7	56.7

Table V-(10) SCF predictions of the harmonic vibrational frequencies and IR intensities of thioperoxide and its deuterated isotopomers. Frequencies are in cm^{-1} and IR intensities are in km/mole .

Mode Description		HSOH	DSOH	HSOD	DSOD
ω_1	O-H stretch	4179	4179	3045	3045
ω_2	S-H stretch	2825	2029	2825	2029
ω_3	HOS bend	1289	1289	952	953
ω_4	HSO bend	1121	819	1120	818
ω_5	S-O stretch	872	875	861	864
ω_6	Torsional motion	496	459	409	363
I_1		100.8	100.8	58.0	58.2
I_2		16.5	9.4	16.5	9.2
I_3		62.6	62.5	60.8	61.2
I_4		6.3	8.4	8.1	10.6
I_5		68.6	64.0	42.4	37.3
I_6		112.8	127.6	55.0	61.8

Table V-(11) Comparison of the CPU time required for the determination of the CI second derivative matrix. Analytic vs. finite-difference-of-analytic gradients. The times reported are in hours on an IBM 3081K.

	Analytic evaluation	Finite ^a difference of analytic gradients
Absolute	13.3	24.4
Percentage	56%	100%

^aNote that the minimum number (12) of gradient calculations was performed.

Table V-(12) CISD equilibrium geometries of CH_2^- using several basis sets. Bond lengths in Å and bond angles in degrees. See text for description of basis sets.

Basis Set	$r_{\text{C-H}}$	$\angle\text{HCH}$
TZ + diffuse + 2P	1.116	102.5
TZ + 2 diffuse + 2P	1.116	102.5
TZ + diffuse + 3P'	1.116	102.6
TZ + diffuse + 3P	1.122	102.5

Table V-(13) CISD total energies (Hartrees) and dipole moments (Debyes) of CH_2^- using several basis sets. Each dipole moment was evaluated as an energy derivative. See text for details concerning the basis sets.

Basis Set	Geometry of Calculation	E_{CISD}	μ
TZ + diffuse + 2P	Same method	-39.088974	1.98
TZ + 2 diffuse + 2P	Same method	-39.089076	2.00
TZ + diffuse + 3P'	Same method	-39.092463	1.97
TZ + diffuse + 3P	Same method	-39.089542	1.72
TZ + diffuse + 4P	TZ + diffuse + 3P	-39.089639	1.69
TZ + diffuse + 4P'	TZ + diffuse + 3P	-39.093362	1.76

Table V-(14) Experimental lifetimes derived from fits of the data with sums of exponentials.

Three Exponentials			Four Exponentials ^a	
v_2	Y_i	τ_i	Y_i	τ_i
1	2.6%	525 ms	3.1%	405 ms
2	3.2%	70	0.6%	135
3	3.0%	14	2.3%	45
4			2.8%	15

^a τ_i were constrained to a geometric progression, with ratio $\tau_i/\tau_{i+1} = 3.0$.

Table V-(15) Radiative decay lifetimes (milliseconds) of the bending vibrational states of CH_2 . The first column represents a purely ab initio value whereas the remaining columns coupled empirical potentials with an ab initio dipole moment function.^a

ν_2	<u>Ab Initio</u> ^b	Empirical ^c	Empirical ^d
1	431 (574)	471 (615)	491 (661)
2	207 (232)	231 (258)	231 (257)
3	118 (114)	134 (135)	129 (125)
4	68 (60)	82 (76)	75 (67)

^aValues in parentheses were obtained with the TZ + diffuse + 3P basis while the others incorporated the TZ + diffuse + 4P basis.

^bPurely ab initio values obtained with the appropriate basis. See text for details.

^cSee Ref. 138 for the first empirically derived SRB potential.

^dSee Ref. 139 for the second empirically derived SRB potential.

Table V-(16) Bending vibrational energy levels determined from the semi-rigid-bender (SRB) wavefunctions.
Units are cm^{-1} .

ν_2	<u>Ab Initio</u> ^a		Sears and Bunker ^b	Bunker and Sears ^c
	TZ + diffuse + 3P	TZ + diffuse + 4P		
0	638	638	591	604
1	1934	1933	1789	1835
2	3212	3210	2970	3043
3	4466	4465	4131	4227
4	5689	5689	5272	5382

^aThis work.

^bRef. 138.

^cRef. 139.

Table V-(17) Transition moment matrix elements between the bending vibrational levels. Semi-rigid-bender (SRB) vibrational wavefunctions were coupled with the TZ diffuse + 4P dipole moment function.^a The SRB wavefunctions were determined from both ab initio and empirically derived potential energy functions.

v_2	v_2'	<u>Ab Initio</u>	Empirical ^b	Empirical ^c
1	0	0.05835 (0.05050)	0.06277 (0.05493)	0.05908 (0.05090)
2	0	-0.01599 (-0.01890)	-0.01414 (-0.01758)	-0.01670 (-0.01981)
2	1	0.07271 (0.06057)	0.08226 (0.07051)	0.07436 (0.06170)
3	0	-0.00328 (-0.00335)	-0.00504 (-0.00554)	-0.00358 (-0.00367)
3	1	-0.03063 (-0.03569)	-0.02660 (-0.03205)	-0.03181 (-0.03711)
3	2	0.07561 (0.05839)	0.09301 (0.07634)	0.07854 (0.06057)
4	0	-0.00007 (-0.00001)	-0.00095 (-0.00068)	-0.00011 (0.00001)
4	1	-0.00614 (-0.00674)	-0.00950 (-0.01135)	-0.00666 (-0.00740)
4	2	-0.04873 (-0.05531)	-0.04147 (-0.04801)	-0.05034 (-0.05705)
4	3	0.06857 (0.04543)	0.09716 (0.07504)	0.07317 (0.04912)

^aValues in parentheses are due to the TZ + diffuse + 3P basis.

^bSee Ref. 138.

^cSee Ref. 139.

Table V-(18) Einstein A coefficients for the coupling of bending vibrational levels. The Semi-rigid-bender (SRB) bending vibrational wavefunctions were coupled with the TZ + diffuse + 4P dipole moment function.^a Both ab initio and empirical potential functions were used. Units are second⁻¹.

v_2	v_2'	<u>Ab Initio</u>	Empirical ^b	Empirical ^c
1	0	2.31969 (1.74133)	2.12396 (1.62650)	2.03709 (1.51203)
2	0	1.36463 (1.91045)	0.84336 (1.30459)	1.26854 (1.78534)
2	1	3.45704 (2.39981)	3.49127 (2.56480)	3.06030 (2.10721)
3	0	0.18950 (0.19707)	0.35379 (0.42703)	0.19078 (0.20053)
3	1	4.77557 (6.48085)	2.85097 (4.13962)	4.34464 (5.91491)
3	2	3.53832 (2.10750)	4.25278 (2.86484)	3.20985 (1.90933)
4	0	0.00022 (0.00000)	0.02924 (0.01493)	0.00042 (0.00000)
4	1	0.62710 (0.75423)	1.19563 (1.70773)	0.62006 (0.76694)
4	2	11.34029 (14.59012)	6.58413 (8.82556)	10.17250 (13.06543)
4	3	2.70566 (1.18553)	4.39718 (2.62302)	2.58848 (1.16645)

^aValues in parantheses are due to the TZ + diffuse + 3P basis.

^bSee Ref. 138 for the empirically derived SRB potential.

^cSee Ref. 139 for the empirically erived SRB potential.

Table V-(19). Optimum geometries, harmonic frequencies and infrared intensities for HF at various levels of electron correlation. Note that one core (doubly occupied orbital) and one frozen virtual orbital were present in all the calculations. A double zeta basis set was used.

	CISD	CISDT	CISDTQ	TCSCF-CISD
E(SCF)	-100.021205	-100.021179	-100.020995	-100.047554
E	-100.142171	-100.143254	-100.147871	-100.144463
E(CI+D)	-100.146263	---	---	-100.147018
# CSF'S (C2V)	111	501	1479	190
REF. COEF. 1	0.9830	0.9826	0.9809	0.9819
REF. COEF. 2				-0.0972
R-HF (ANG)	0.9464	0.9468	0.9499	0.9495
FREQ (1/CM)	3855	3846	3799	3802
INT (KM/MOL)	33.32	32.16	27.58	26.83
DIPOLE (DEBYE)	2.32	2.31	2.31	2.30

Table V-(20). Optimum geometries, harmonic frequencies and infrared intensities for HF at various levels of electron correlation using a double zeta basis set, with one core and one frozen virtual orbital.

	CID	CIDQ	CISDQ	CCSD
E(SCF)	-100.021269	-100.021103	-100.021020	-100.021051
E(CI)	-100.140938	-100.145802	-100.147152	-100.146419
E(CI+D)	-100.144800	---	---	
# CSF'S (C2V)	101	1079	1089	111
REF. COEF.	0.9837	0.9820	0.9811	
R-HF (ANG)	0.9451	0.9481	0.9495	0.9490
FREQ (1/CM)	3883	3840	3808	3816
INT (KM/MOL)	35.21	30.86	28.80	
DIPOLE (DEBYE)	2.32	2.32	2.31	

Table V-(21). Optimum geometries, harmonic frequencies and infrared intensities for HF at various levels of electron correlation using a double zeta plus polarisation basis set, with one core and one frozen virtual orbital.

	CISD	CISDT	CISDTQ	TCSCF-CISD
E(SCF)	-100.047761	-100.047739	-100.047616	-100.070808
E(CI)	-100.233574	-100.235710	-100.242307	-100.236219
E(CI+D)	-100.241244	---	---	-100.242199
# CSF'S (C2V)	552	6712	48963	1015
REF. COEF. 1	0.9791	0.9785	0.9763	0.9781
REF. COEF. 2				-0.0847
R-HF (ANG)	0.9184	0.9189	0.9217	0.9212
FREQ (1/CM)	4264	4253	4205	4207
INT (KM/MOL)	102.24	98.06	89.69	89.21
DIPOLE (DEBYE)	1.97	1.96	1.96	1.96

Table V-(22). Optimum geometries, harmonic frequencies and infrared intensities for HF at various levels of electron correlation using a double zeta plus polarisation basis set, with one core and one frozen virtual orbital.

	CID	CIDQ	CISDQ	CCSD
E(SCF)	-100.047789	-100.047680	-100.047640	-100.047660
E	-100.232224	-100.239047	-100.240543	-100.239732
E(CI+D)	-100.239557	---	---	
# CSF'S (C2V)	530	42781	42803	552
REF. COEF.	0.9800	0.9778	0.9769	
R-HF (ANG)	0.9176	0.9203	0.9211	0.9207
FREQ (1/CM)	4281	4237	4216	4224
INT (KM/MOL)	105.62	97.90	94.06	
DIPOLE (DEBYE)	1.97	1.97	1.96	

Table V-(23). Optimum geometries, harmonic frequencies and infrared intensities for N₂ at various levels of electron correlation using a double zeta basis set, with two core and two frozen virtual orbitals.

	CISD	CISDT	CISDTQ
E(SCF)	-108.874738	-108.874097	-108.871372
E(CI)	-109.085924	-109.092015	-109.111244
E(CI+D)	-109.103545	---	---
# CSF'S (D2H)	260	2733	19231
REF. COEF.	0.9574	0.9537	0.9414
R-NN (ANG)	1.1347	1.1378	1.1492
FREQ (1/CM)	2290	2259	2141

Table V-(24). Optimum geometries, harmonic frequencies and infrared intensities for N₂ at various levels of electron correlation using a double zeta basis set, with two core and two frozen virtual orbitals.

	CID	CIDQ	CISDQ	CCSD
E(SCF)	-108.875080	-108.872707	-108.872062	-108.872671
E	-109.083770	-109.103183	-109.105908	-109.103201
E(CI+D)	-109.100438	---	---	
# CSF'S (D2H)	251	16749	16758	260
REF. COEF.	0.9592	0.9477	0.9451	
R-NN (ANG)	1.1329	1.1440	1.1466	1.1441
FREQ (1/CM)	2310	2194	2165	2193

Table V-(25). Optimum geometries, harmonic frequencies and infrared intensities for N₂ at various levels of electron correlation using a double zeta plus polarisation basis set, with two core and two frozen virtual orbitals.

	CISD	CISDT	CISDTQ
E(SCF)	-108.956122	-108.955419	-108.952940
E(CI)	-109.244750	-109.254423	-109.278511
E(CI+D)	-109.271037	---	---
# CSF'S (D2H)	1002	23909	356457
REF. COEF.	0.9534	0.9482	0.9347
R-NN (ANG)	1.1123	1.1158	1.1264
FREQ (1/CM)	2444	2408	2296

Table V-(26). Optimum geometries, harmonic frequencies and infrared intensities for N₂ at various levels of electron correlation using a double zeta plus polarisation basis set, with two core and two frozen virtual orbitals.

	CID	CIDQ	CISDQ	CCSD
E(SCF)	-108.956412	-108.954432	-108.953890	-108.954288
E	-109.242252	-109.265874	-109.268994	-109.266866
E(CI+D)	-109.267319	---	---	
# CSF'S (D2H)	982	333530	333550	1002
REF. COEF.	0.9551	0.9431	0.9406	
R-NN (ANG)	1.1107	1.1203	1.1226	1.1210
FREQ (1/CM)	2462	2358	2332	2352

Table V-(27). Optimum geometries and harmonic frequencies for N₂ at various levels of Moller-Plesset perturbation theory. The polarization exponents for the TZ+2P basis are 1.5 and 0.5.

BASIS/METHOD	DZP/MP2	DZP/MP4 (SDQ)	DZP/MP4 (SDTQ)	DZP/MP2	TZ2P/MP2
FROZEN ORBITALS	2cor/0vir	2cor/0vir	2cor/0vir	0cor/0vir	0cor/0vir
TOTAL ENERGY (HARTREES)	-109.266574	-109.268531	-109.282847	-109.295108	-109.364122
R-NN (ANG)	1.140	1.124	1.135	1.139	1.113
FREQ (1/CM)	2108	2289	2145	2125	2175

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