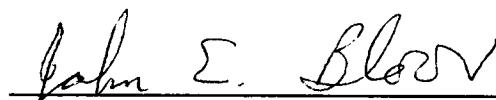
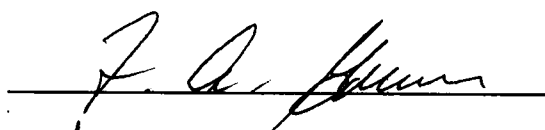
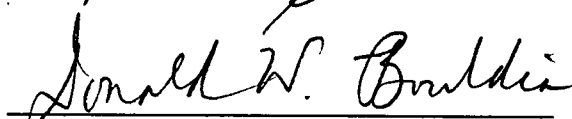


To the Graduate Council:

I am submitting herewith a dissertation written by Peter Chien-Nan Yih entitled "Ab Initio Calculations of Dipole Polarizabilities for Nonlinear Optics Applications." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


John E. Bloor, Major Professor

We have read this thesis and
recommend its acceptance:


Accepted for the Council:


Associate Vice Chancellor
and Dean of The Graduate School

AB INITIO CALCULATION
OF DIPOLE POLARIZABILITIES
FOR NONLINEAR OPTICS APPLICATIONS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Peter Chien-Nan Yih
December 1995

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ABSTRACT

In the field of photonics, the analog of electronics, which describes the technology of using photons to acquire, store, transmit, and process information, molecules with large dipole polarizabilities and hyperpolarizabilities are of interest. Ab initio calculations of dipole polarizabilities (DP) and hyperpolarizabilities (DH) of systems of model molecules enhances greatly the development process of new materials and ultimately the fabrication of devices which implement photonics. Ab initio calculations at the Hartree Fock (HF) self-consistent field (SCF) level and at the second-order Moller Plesset Perturbation Theory level (MP2) using the Hondo 8 (H8) and Gaussian 90 (G90) computer codes are performed to calculate accurate values of the dipole moment (DM), dipole polarizabilities (DP), first and second dipole hyperpolarizabilities (DH) for a series of small polyatomic molecules. These are the following: AH_3 ($A = N, P, As$), formamide, benzene, pyridine, pyrrole, AH_2 ($A = S, Se, Te$), AH_4 , A_2H_4 , and A_2H_2 ($A = C, Si, Ge$). The pyrrole calculations show how the effective core potential (ECP) could be used to produce reasonably accurate results. Accurate HF SCF calculations using very large basis sets are used as reference results, which are used to develop much smaller basis sets without significant loss in accuracy of results. It was found that the MP2 calculations produced significant changes in the results. Typically, the DP increases by 10-20%, the second DH (γ tensors) increases 20-40%, and the first DH (β tensors) changes by 100%, and sometimes changes in sign. For example, a H_2Te [11s10p8d1f / 4s2p2d] basis set calculation β_{yyz} changes from 21.88 (HF) to -6.38 (MP2).

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LIST OF SYMBOLS

AO	atomic orbital
bfs	basis functions
bs	basis set
bss	basis sets
CAS	University of Tennessee Department of Computing and Administrative Systems
CASSCF	complete active space self-consistent field
CC	coupled cluster
CI	configuration interaction
CID	doublet excitation configuration interaction
CIS	singlet excitation configuration interaction
CISD	singlet and doublet configuration interaction
CPHF	coupled perturbed Hartree Fock
CPU	central processor unit
DH	dipole hyperpolarizability
DM	dipole moment
DP	dipole polarizability
DZ	double zeta
ECP	effective core potential
FFM	finite field method
G90	Gaussian 90 (ab initio program)
G92	Gaussian 92 (ab initio program)
GTO	Gaussian type orbital
GVB-PP	generalized valence bond - perfect pair

H8 Hondo-8 (ab initio program)
HF Hartree Fock
IO input / output
JCL job control language
LCAO linear combination of atomic orbitals
LDF local density functional
MBPT many body perturbation theory
MCSCF multiconfiguration self consistent field
MO molecular orbital
MPPT Moller Plesset perturbation theory
MP2 second order Moller Plesset perturbation theory
NLO non-linear optical
pf polarization function
pfs polarization functions
PPP point to point protocol (a remote network link)
QCI quadratic configuration interaction
QCISD quadratic singlet and doublet excitation configuration interaction
R6000 IBM Risc 6000
RAM random access memory
RHF spin restricted closed-shell Hartree Fock
RHS right hand side
rf reduction factor
ROHF spin restricted open-shell Hartree Fock
S2 Sun Sparc 2
SCF self consistent field
SLIP serial line internet protocol

STO	Slater type orbital
TZV	triple zeta valence
UHF	spin unrestricted open-shell Hartree Fock
UPS	uninterruptable power supply
WF	wavefunction

CHAPTER I

AB INITIO CALCULATION METHODS

Introduction

Photonics, the analog of electronics, describes the technology of using photons instead of electrons to acquire, store, transmit, and process information [1]. Some major advantages of photonics over electronics are as follows: increased storage capacity, increased transmission bandwidth or capacity of throughput, increased speed of change or switching of information, an increased power density limit, possibility of three-dimensional connectivity, signals free from electromagnetic field interference, and security from unwanted detection of signals. In the context of photonics, some useful nonlinear optical phenomena are: the ability to alter the frequency of light, to amplify one source of light with another, to switch it, or to alter light's transmission characteristics through a medium as a function of its intensity. The great potential of implementing these functions of photonics through suitable materials and devices is the driving force for current fundamental and experimental research in the area of nonlinear optics [1].

One area of research within the field of nonlinear optics, is the ab initio calculation of dipole polarizabilities (DP), and dipole hyperpolarizabilities (DH) of certain model molecules. This area of research is the scope of this current dissertation. These calculations are done at the Hartree Fock (HF) level as well as at the second-order Moller Plesset Perturbation Theory (MPPT) level (MP2) (i.e., extension to the HF method [4, 6, 7] to include correlation effects). Basis set choice is also another important factor in the calculation of DP and DH. The background needed to understand these ab initio calculation methods, which are investigated in this dissertation, are discussed below.

Hartree Fock (HF) Method

One characteristic of the ab initio HF method is that all the integrals are calculated explicitly by the computer. Since the Schrodinger wave equation can be solved exactly only for atomic hydrogen, for other atoms and polyatomic molecules which are multi-electronic in nature, approximations must be made to obtain the solution. These assumptions and approximations which are used to arrive at the HF method are discussed below. Since the ab initio HF method is well known, only the fundamental details will be given [2, 3].

1. The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation states that: since the motion of the nuclei of atoms in a polyatomic molecule is much slower than electronic motion, therefore the nuclei are considered to be fixed, with respect to electronic motion. The Hamiltonian can be written (equation 1.1) as:

$$\mathbf{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} \quad (1.1)$$

where the A, B indices run over nuclei, and i, j indices run over electrons. The values Z_A , and Z_B are nuclear charges in atomic units, r_{iA} is an electron to nucleus distance, r_{ij} is an electron to electron distance, and R_{AB} is a nucleus to nucleus distance.

2. The Non-Relativistic and Time-Independent Assumptions

As the magnitude of the kinetic energy of an electron increases, the velocity of the electrons approaches c , the velocity of light, and relativistic effects become important. Practically this occurs for core level electrons of atoms or atoms within molecules belonging to the fourth row or below of the periodic chart (i.e., elements heavier than those of the fourth row). In terms of quantum mechanics, such an atom or molecule is modeled by the Dirac equation rather than the Schrodinger equation. In the limit of c approaching zero the Dirac equation becomes the Schrodinger equation.

For the purposes of the work performed within the scope of this dissertation the relativistic effect will be neglected, even though some of the molecules contain somewhat heavy elements.

Another assumption that is made is that the systems are in a steady state; that is the system is not time dependent. In terms of quantum mechanics, the partial derivative with respect to time of the wavefunction is zero.

3. The Hartree Fock Approximation

Electrons are fermions and thus obey Fermi-Dirac statistics; that is no two electrons can occupy the same state. This gives rise to an antisymmetrization requirement of any two electrons which interchange both spatial and spin coordinates. The total wavefunction Ψ can be given in terms of individual electronic wavefunctions ϕ_i for each i th electron and the spin functions α and β by the Slater determinant in equation 1.2 as:

$$\Psi(1, 2, 3 \dots 2n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) \alpha(1) & \phi_2(1) \beta(1) & \dots & \phi_n(1) \beta(1) \\ \phi_1(2) \alpha(2) & \phi_2(2) \beta(2) & \dots & \phi_n(2) \beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(2n) \alpha(2n) & \phi_2(2n) \beta(2n) & \dots & \phi_n(2n) \beta(2n) \end{vmatrix} \quad (1.2)$$

Each ϕ_i of the solution wavefunction gives rise to a minimization of the total energy of the system, and this minimal total energy is given by the equation 1.3 as follows:

$$E = \frac{\int \Psi^*(1, 2, 3 \dots 2n) H \Psi(1, 2, 3 \dots 2n) d\tau_1 d\tau_2 \dots d\tau_{2n}}{\int \Psi^* \Psi d\tau} \quad (1.3)$$

To obtain this minimal energy the variational principle is applied, and a series of one electron equations in terms of $\phi_i(n)$ are obtained (equations 1.4.1 and 1.4.2):

$$\mathbf{F} \left| \phi_i(n) \right\rangle = \epsilon_i \left| \phi_i(n) \right\rangle, \quad (1.4.1)$$

$$\text{or } \mathbf{F} \left| \phi_i(n) \right\rangle = \left[H_1 + \sum_{j \neq i} (2J_j - K_j) \right] \left| \phi_i(n) \right\rangle = \epsilon_i \left| \phi_i(n) \right\rangle, \quad (1.4.2)$$

where in equation 1.5 :

$$H_1 = \left[-\frac{1}{2} \nabla^2(n) - \sum_A \frac{Z_A}{r_{nA}} \right], \quad (1.5)$$

is called the one-electron contribution to the Fock operator $\mathbf{F}$ and consists of the kinetic energy of the electron n plus the Coulombic attraction of electron n to nucleus A . For the two electron part of equation 1.4.2, we have:

$$J_j(n) = \int \frac{d\tau_j \phi_j^*(m) \phi_j(m)}{r_{ij}}, \quad (1.6)$$

where $J_j(n)$ in equation 1.6 is the Coulomb integral consisting of the Coulombic repulsion potential between electron n and electron m , where $n \neq m$, and:

$$K_j(n) = \int \frac{d\tau_j \phi_j^*(m) \phi_i(m)}{r_{ij}}, \quad (1.7)$$

in equation 1.7 is the exchange integral. The exchange integral gives the energy difference between exchange of electron n and m , where $n \neq m$.

4. The Roothaan LCAO Treatment

In polyatomic molecules, a molecular orbital (MO) is constructed usually as a linear combination of atomic orbitals. This gives rise to the linear combination of atomic orbitals (LCAO) approximation. In equation 1.8, this linear combination is given as:

$$\phi_i = \sum_{\mu} c_{\mu i} \chi_{\mu} \quad , \quad (1.8)$$

where ϕ_i is the MO, $c_{\mu i}$ is the coefficient, and χ_{μ} is the atomic orbital. The set $\{ \chi_{\mu} \}$ should be a complete set if the LCAO expression is correct. In practice the number of AOs is severely curtailed. Next equation 1.8 is inserted into the Fock equation 1.4.2, and applying the variational principle to give the Roothaan equations 1.9 below:

$$\sum_{\mu\nu} (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) c_{\mu i} = 0 \quad , \quad (1.9)$$

where:

$$S_{\mu\nu} = \int \chi_{\mu}(n) \chi_{\nu}(n) d\tau_n \quad , \quad (1.10)$$

in equation 1.10, the expression $S_{\mu\nu}$ is called the overlap integral, ϵ_i is the energy of the electron associated with ϕ_i .

The matrix element $F_{\mu\nu}$ is given by equation 1.11.2 below:

$$F_{\mu\nu} = H_{\mu\nu} + G_{\lambda\sigma} , \quad (1.11.1)$$

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right] , \quad (1.11.2)$$

where:

$$H_{\mu\nu} = \int \left[\chi_{\mu}(n) \left[-\frac{1}{2} \nabla_n^2 \right] \chi_{\nu}(n) + \sum_A \frac{\chi_{\mu}(n) \chi_{\nu}(n)}{r_{An}} \right] d\tau_n , \quad (1.12)$$

in equation 1.12 are the one electron terms, and:

$$J_{\mu\nu} = (\mu\nu | \lambda\sigma) , \quad (1.13.1)$$

$$J_{\mu\nu} = \int \chi_{\mu}(n) \chi_{\nu}(n) \chi_{\lambda}(m) \chi_{\sigma}(m) d\tau_n d\tau_m , \quad (1.13.2)$$

equation 1.13.1 and 1.13.2 are the two electron Coulomb integral terms, and:

$$K_{\mu\nu} = (\mu\lambda | \nu\sigma) , \quad (1.14.1)$$

$$K_{\mu\nu} = \int \chi_{\mu}(n) \chi_{\lambda}(n) \chi_{\nu}(m) \chi_{\sigma}(m) d\tau_n d\tau_m , \quad (1.14.2)$$

equation 1.14.1 and 1.14.2 are the two electron exchange integral terms. The expression $P_{\lambda\sigma}$ is the one electron density matrix given by equation 1.15 below:

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occ.}} c_{\lambda i} c_{\sigma i} , \quad (1.15)$$

where occ. is the abbreviation for over all occupied MOs. In the general case there is no closed form solution to the Roothaan equations since the system is nonlinear in terms of $c_{\lambda i}$. The solution is obtained by the self-consistent field (SCF) process.

5. The SCF Process

The SCF process as outlined below is performed until the AO coefficients are converged to a predetermined accuracy:

- a. The molecule problem is specified by its nuclear coordinates $\{ R_A \}$, atomic numbers of its constituent atoms $\{ Z_A \}$, and a basis set $\{ \phi_A \}$.
- b. Next all required molecular integrals are calculated: $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu | \lambda\sigma)$.
- c. The overlap matrix S is diagonalized to obtain a transformation matrix X .
- d. A guess of the density matrix P is made.
- e. The two electron integrals $(\mu\lambda | \nu\sigma)$ and the matrix G are calculated.
- f. The Fock matrix is formed: $F = H^{\text{core}} + G$.
- g. The Fock matrix is transformed: $F' = X^\dagger F X$.
- h. The matrix F' is diagonalized to obtain C' and ϵ .
- i. The matrix C is calculated: $C = X C'$.
- j. A new P is calculated from C by equation 1.15.
- k. A comparison is made between the new P with the old P to see if convergence is met within the preset tolerance. If the density matrix has not converged the calculation is redone from step e onwards until convergence is achieved.
- l. Other quantities of interest such as: dipole moments, DP, DH, and multipole moments can then be calculated from the resultant solution.

Analytical Calculation of Dipole Polarizabilities and Hyperpolarizabilities

1. Basic Definitions

In order to understand how to calculate dipole polarizabilities (DP) and dipole hyperpolarizabilities (DH), we must first examine the dependence of the energy of a molecule to an applied electric field $\mathcal{E}$. The energy of a molecule is given by the Schrodinger's equation, which can be written as equation 1.16:

$$E(\mathcal{E}) = \langle \Psi(\mathcal{E}) | H(\mathcal{E}) | \Psi(\mathcal{E}) \rangle, \quad (1.16)$$

where $\mathcal{E}$ is the applied electric field, E is the energy, and H is the Hamiltonian, which is dependent on the applied electric field.

Next, we take the n cross partial derivatives of the energy with respect to electric fields $\mathcal{E}_i$, and write the field dependent energy as a Taylor series expansion [9], in equation 1.17.1:

$$E = E^{(0)} - \mu_i^{(0)} \mathcal{E}_i - \frac{1}{2} \alpha_{ij} \mathcal{E}_i \mathcal{E}_j - \frac{1}{6} \beta_{ijk} \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k - \frac{1}{24} \gamma_{ijkl} \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k \mathcal{E}_l, \quad (1.17.1)$$

where $\mu_i^{(0)}$ is the zeroth order dipole moment in the i th direction, α_{ij} is the ij th dipole polarizability, β_{ijk} is the ijk th first dipole hyperpolarizability, and γ_{ijkl} is the $ijkl$ th second dipole hyperpolarizability.

In relating theoretical work to experimental work, it is important to note that an expression given by Bloembergen [8] is often used to define nonlinear optical properties (NLO), equation 1.17.2 :

$$E = E^{(0)} - \mu_i^{(0)} \epsilon_i - \frac{1}{2} \alpha_{ij} \epsilon_i \epsilon_j - \frac{1}{3} \beta_{ijk} \epsilon_i \epsilon_j \epsilon_k - \frac{1}{4} \gamma_{ijkl} \epsilon_i \epsilon_j \epsilon_k \epsilon_l, \quad (1.17.2)$$

in which the definitions for μ , α , β , γ are the same as given previously. It is this second definition, equation (1.17.2), that experimentalists use to extract polarizability tensors from their measurements.

An alternative interpretation of the dipole polarizabilities is in terms of the spatial distribution of charge density of a molecule contributing to electric field dependence. The dipole moment can be defined as an expectation value in equation 1.18:

$$\mu(\epsilon) = \left\langle \Psi(\epsilon) \left| \sum_i q_i \cdot r_i \right| \Psi(\epsilon) \right\rangle, \quad (1.18)$$

where the index i runs over all electrons and nuclei.

The charge density is then expanded in a Taylor's series (equation 1.19):

$$\rho(r, E) = \rho^{(0)}(r) - \rho^{(1)}(r) \epsilon - \frac{1}{2} \rho^{(2)}(r) \epsilon \epsilon - \frac{1}{6} \rho^{(3)}(r) \epsilon \epsilon \epsilon \dots, \quad (1.19)$$

where we have the zeroth-, first-, second- and third-order derivatives of the charge density ρ . The dipole moment, DP, first and second dipole hyperpolarizabilities, DH, can then be obtained from equations 1.20 through 1.23.

The dipole moment along the zth direction can be obtained by the integral of equation 1.20 to give:

$$\mu_z(E) = \int z \rho(r, E) dr^3 , \quad (1.20)$$

and the expressions for the z-axis component of α , β , and γ , are given below in equations 1.21 through 1.23:

$$\alpha_{zz} = \int z \rho(r)^{(1)} dr^3 , \quad (1.21)$$

$$\beta_{zzz} = \frac{1}{2} \int z \rho(r)^{(2)} dr^3 , \quad (1.22)$$

$$\text{and } \gamma_{zzzz} = \frac{1}{6} \int z \rho(r)^{(3)} dr^3 , \quad (1.23)$$

where $\rho(r)^{(1)}$, $\rho(r)^{(2)}$, $\rho(r)^{(3)}$ are the first, second, and third derivatives of ρ with respect to the electric field along the z-axis respectively [10]. These definitions of μ , α , β , and γ (equations 1.20 through 1.22) can be applied in the Coupled Perturbed Hartree Fock method of calculation of μ , α , β , and γ . From equations 1.17.1 and 1.17.2, it is clear that the derivatives of μ with respect to $\mathcal{E}$, the electric field, give α , β , and γ .

2. Coupled Perturbed Hartree Fock Theory

Standard computer codes, such as Hondo 8 (H8) are available for the calculation of DP, and first and second DH properties. The H8 code applies the Coupled Perturbed Hartree Fock (CPHF) theory to calculate the DP, and first and second DH as follows. In the CPHF method, the analytical derivatives of the total electronic contribution to the dipole moment are taken [4]. The dipole moment is given in equation 1.24 as follows:

$$\mu_{\text{tot}} = \sum_{p,q} D_{pq} \langle p | \mu_b | q \rangle , \quad (1.24)$$

where D_{pq} is the density matrix given in equation 1.15, μ_b is the dipole moment operator found on the right-hand side (RHS) of equation 1.18, and p, q are indices of occupied MOs. The partial derivative of equation 1.24 with respect to the variable a is given as:

$$\frac{\partial}{\partial a} \mu_{\text{tot}} = \sum_{p,q} D_{pq} \langle p | \mu_b | q \rangle^a + D_{pq}^a \langle p | \mu_b | q \rangle , \quad (1.25)$$

where the a superscript denotes the partial derivative with respect to a . For DP and DH calculations, a is the electric field. The calculation of the second term on the RHS of equation 1.25, which involves the derivative of the density matrix, requires the use of coupled perturbed Hartree Fock theory (CPHF). In this treatment the perturbed orbital is expressed as a linear combination of the original orbitals:

$$\phi_i^a = \sum_j U_{ji}^a \phi_j , \quad (1.26)$$

where U_{ji}^a are the coupling coefficients.

These coupling coefficients U_{ji}^a are determined by solving the simultaneous equations:

$$\sum_{kl} A_{ij,kl} U_{kl} = B_{ij} \quad , \quad (1.27.1)$$

where the matrix A is given by:

$$A_{ij,kl} = (\epsilon_j - \epsilon_i) \delta_{ik} \delta_{jl} - (4 \langle ij | kl \rangle - \langle ik | jl \rangle - \langle il | jk \rangle) , \quad (1.27.2)$$

where δ is the Kronecker delta, and the matrix B is defined by:

$$B_{ij}^a = \epsilon_{ij}^a - \epsilon_j S_{ij}^a - \sum_{kl}^{\text{occ}} S_{kl}^a (2 \langle ij | kl \rangle - \langle ik | jl \rangle) , \quad (1.27.3)$$

where S^a is the derivative of the overlap matrix and ϵ^a is given:

$$\epsilon_{pq}^a = h_{pq}^a + \sum_{rs} D_{rs} (2 \langle pq | rs \rangle^a - \langle pr | qs \rangle^a) , \quad (1.27.4)$$

$$\epsilon_{ij}^a = \sum_{pq} C_{pi} C_{qj} \epsilon_{pq}^a , \quad (1.27.5)$$

where the indices i,j,k,l denote MOs and the indices p, q, r, and s denote atomic orbitals (AO). The quantity ϵ^a is transformed from the AO basis into the MO basis. The expression in equation 1.27.4 has the same structure as the Fock operator (equation 1.11.2) but is constructed in terms of derivatives with respect to $\underline{a}$ (i.e., $\mathbf{h}^a$ and $\langle pq | rs \rangle^a$). This is the $\underline{a}$ derivative analog of equation 1.11.2.

A matrix equation can be used to express the operation:

$$\epsilon^a = \mathbf{h}^a + \mathbf{g}^a * \mathbf{D} , \quad (1.28)$$

where the second term on the RHS denotes contraction of the two electron integrals with the density matrix, which is a matrix product.

Once these matrix equations are solved, the perturbed density matrix can be calculated:

$$D_{ij}^a = U_{ij}^a f_i + U_{ij}^a f_j , \quad (1.29)$$

where i, j are MO indices, and f_i, f_j are occupation numbers of the i, j th MO (zero or two), and a again denotes a derivative with respect to a .

Since the calculation of the DP and first and second DH take much more time than the SCF process, say by a factor of ten, the H8 computer code has implemented these DP and DH calculations in an as efficient manner as possible. Some of the techniques will be briefly outlined here. One step which consumes most of the central processor unit (CPU) time required is the calculation of derivatives two electron integrals.

An efficient way to calculate these derivatives is to use the sum over products of simpler integrals:

$$\langle pq | rs \rangle = \sum_i I_x(u_i) I_y(u_i) I_z(u_i) w_i , \quad (1.30)$$

where the I integrals exploit the shell structure of MOs (i.e., $P = \{ p_x, p_y, p_z \}$).

In the same manner, the derivative of the two-electron integrals may be calculated:

$$\frac{\partial}{\partial \epsilon_x} \langle pq | rs \rangle = \sum_i I'_x(u_i) I_y(u_i) I_z(u_i) w_i , \quad (1.31)$$

where the integral I'_x is also expressed as a linear combination of I . Another improvement is to exploit symmetry considerations of the molecule. Due to symmetry, certain matrix elements are either symmetrical or antisymmetrical, giving a + or - sign in front of an integral already calculated. Other elements simply cancel and give a zero result.

3. Finite-Field Method

The Finite-field method (FFM) were first used to calculate the DP by Cohen and Roothaan in 1965 of atoms [24]. Soon thereafter the FFM was applied to molecules by McLean and Yoshimino [25]. This method is now used in the G90 code. At the HF level, both the analytical CPHF method of calculating DP and DH properties, and the numerical FFM method is available in the Gaussian 90 code (G90) [12], and at the MP2 level in G90 and later versions, only the FFM is available for the calculation of DP and DH properties. The FFM differs from the CPHF method in that, in the FFM an electric field is applied explicitly and numerical derivatives are taken rather than in the CPHF method in which the analytical calculation of the field dependence is performed.

In the FFM a small but finite electric field perturbation is added to the Hamiltonian of the system. An alternative expansion to that of equation 1.17.1 is an expansion of the dipole moment, say along the z axis in equation 1.32 below:

$$\mu_z = \mu_z^0 + \alpha_{zz} \mathcal{E}_z + \cdots + \left(\frac{1}{2}\right) A_{zzz} \mathcal{E}_{zz} + \cdots, \quad (1.32)$$

where μ_z is the dipole moment along the z axis, μ_z^0 is the permanent free-field moment, $\mathcal{E}_z$ is the fixed applied electric field, and A is an induced dipole moment term.

The polarizability is calculated as a finite difference in equation 1.33 below:

$$\alpha_{zz}(\mathcal{E}_z) = \frac{\mu_z - \mu_z^0}{\mathcal{E}_z}. \quad (1.33)$$

If the value of α_{zz} is calculated for several choices of $\mathcal{E}_z$, then it is possible to take the limit $\mathcal{E}_z \rightarrow 0$ and obtain the DP defined generally by equation 1.34 below (i.e., j = z):

$$\alpha_{ij} = \left. \frac{\partial \mu_i}{\partial \mathcal{E}_j} \right|_{\mathcal{E}_j = 0}. \quad (1.34)$$

A balance has to be made between the desire for numerical accuracy which requires large fields and, the need to use small fields to minimize error due to truncation in the series of equation 1.32. Error terms due to the next higher order can be removed by the use of electric field values of equal magnitude but of opposite signs. The FFM has the advantage over the fixed-charge method discussed below, in that the FFM does not have contamination of higher gradient components.

Equation 1.34 calculated by equation 1.33 is a numerical derivative used in the FFM, whereas equation 1.25 calculated by equations 1.26 through 1.29 in the CPHF method depends on equation 1.31 which is an analytical derivative.

4. Fixed-Charge Method

The fixed-charge method method is used by Maroulis and Thakkar [9, 37, 51, 57, 58, 70]. Since some of these DP and DH calculations are on some of the same molecules studied in this dissertation, to which the results in this dissertation are compared. This method will be briefly discussed here.

The dipole polarizabilities, hyperpolarizabilities, and second hyperpolarizabilities, which are derivatives of the energy with respect to an applied perturbing electric field, are calculated approximately by sum and difference terms of the perturbed energy value as a result of applying a small finite electric field due to fixed point charges [9]. The electric field is applied by the use of a hypothetical test charge in the presence of the molecule. Maroulis and Thakkar [9] give equations for calculating the DP, α , and the second DH, γ , for the case of a $D_{\infty h}$ molecule (in this case $\beta = 0$ due to symmetry).

The equations for α are given below in equations 1.35.1, 1.35.2 below:

$$\alpha_{zz} \cong \alpha_{zz} + (3C_{zz,zz} + 2E_{z,zzz}) R^{-2} =$$

$$\frac{R^4 [S_+ (2Q, R, 0) - 16 S_+ (Q, R, 0)]}{12 Q^2}, \quad (1.35.1)$$

and

$$\alpha_{xx} = \frac{R^4 \left[S_+ \left(2Q, R, \frac{\pi}{2} \right) - 16 S_+ \left(Q, R, \frac{\pi}{2} \right) \right]}{12 Q^2}, \quad (1.35.2)$$

where:

$$S_+ (Q, R, \theta) = E^1 (Q, R, \theta) + E^1 (-Q, R, \theta) - 2E^0, \quad (1.36.1)$$

and

$$S_- (Q, R, \theta) = E^1 (Q, R, \theta) - E^1 (-Q, R, \theta), \quad (1.36.2)$$

where C is the quadrupole polarizability tensor, E in equation 1.35.1 is the dipole-octapole polarizability tensor, Q is the applied charge, R and θ are the molecular frame coordinates, and in equation 1.36.1 and 1.36.2 the value E^1 is the perturbed energy and E^0 is the unperturbed energy or energy with no test charge present.

The second DH is given by equations 1.37.1, 1.37.2, and 1.37.3 below:

$$\gamma_{zzzz} = \frac{R^8 [4S_+(Q, R, 0) - S_+(2Q, R, 0)]}{Q^4}, \quad (1.37.1)$$

$$\gamma_{xxxx} = \frac{R^8 [4S_+(Q, R, \frac{\pi}{2}) - S_+(2Q, R, \frac{\pi}{2})]}{Q^4}, \quad (1.37.2)$$

and:

$$6\gamma_{xxzz} = \frac{4R^8 [4S_+(Q, R, \frac{\pi}{4}) - S_+(2Q, R, \frac{\pi}{4})]}{Q^4} - \gamma_{zzzz} - \gamma_{xxxx}. \quad (1.37.3)$$

The error terms in equation 1.35.1 and 1.35.2 due to C and E can be subtracted explicitly if the values are known or the test charge can be placed at a R large enough to make the C and E terms insignificant. Dipole polarizability, DH, and second DH values for other molecules of other symmetries are calculated in a similar fashion. The application of the test charge, and subsequent calculations can be performed in a systematic fashion [9].

Electron Correlation Effect

One short coming of the HF theory is the neglect of the electron correlation effect (ECE). The electron correlation effect is the influence of an electron of one spin on other electrons of opposite spin in a given molecular system. This is not accounted in a central or mean field approach such as that of HF. In order to achieve higher accuracy in the calculation of DP, DH, and second DH values, electron correlation must be included.

Two common methods used to include the ECE are the Moller Plesset perturbation theory (MPPT) and the many body perturbation theory (MBPT). These two methods include electron correlation by a perturbational expansion of the energy of the molecular system. The MBPT uses many body terms in the expansion, and MPPT uses spin unrestricted HF calculation of excited states. The MBPT method is used in calculation of correlated NLO properties by Sadlej [40, 47, 48, 61] and Sekino and Bartlett [65]. The second-order MPPT (MP2) method is found in G90 [12] and later versions, and is used to calculate correlated DP, and first DH values in the work of this current dissertation. The framework of the MPPT will be described briefly.

Moller Plesset Perturbation Theory

The Moller Plesset perturbation theory (MPPT) is a method of including correlation effects by means of perturbation theory. This method is used in work in this dissertation performed using the G90 and G92 programs at the MP2 level, which is explained below. The MPPT method requires much less computational resources than other methods used to include correlation effects, perhaps with exception of recent local density functional methods [64]. A comparison of the results of this dissertation with some very recent results obtained by other methods indicate that the use of MPPT at the MP2 level accounts for most of the correlation effect in the calculation of NLO properties. This is very important since electron correlation is essential in determining the magnitude of NLO properties.

Other popular methods used for including correlation are the following: the multiconfigurational self-consistent field method (MCSCF) [4], the configuration interaction method (CI) [66], the coupled-cluster method (CC) [67, 68], the local density functional methods [7, 64]. These other methods are not discussed here, since they are fully described in the appropriate references.

The MPPT is a special case of the general Rayleigh-Schrodinger Perturbation Theory [3]. For a nondegenerate system with energy state E_n with associated wavefunction Ψ_n , where n is one of the states in the system, we can write the Schrodinger equation in equation 1.38 :

$$H \left| \Psi_n \right\rangle = E_n \left| \Psi_n \right\rangle , \quad (1.38)$$

where the Hamiltonian H is given by equation 1.39 :

$$H = H_0 + \lambda V , \quad (1.39)$$

where H_0 is the unperturbed Hartree Fock Hamiltonian and λ is the perturbation coefficient. Now the perturbed Energy E_n and the perturbed wavefunction Ψ_n can be expressed as a power series of perturbations in equation 1.40.1 and 1.40.2 :

$$\left| \Psi_n \right\rangle = \left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle + \lambda^2 \left| \psi_n^{(2)} \right\rangle + \dots , \quad (1.40.1)$$

and:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots , \quad (1.40.2)$$

where the number indicates the order of perturbation for state $n = 0, 1, 2, \dots$ up to the number of states in the system.

The first order perturbation energy is given by equation 1.41 below:

$$E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle, \quad (1.41)$$

where V is the same perturbation potential given in equation 1.39.

The second-order perturbation energy is given by equations 1.42.1 and 1.42.2 below:

$$E_n^{(2)} = \langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle, \quad (1.42.1)$$

or:

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_n^{(0)} | V | \psi_m^{(0)} \rangle|^2}{(E_n^{(0)} - E_m^{(0)})}. \quad (1.42.2)$$

The third-order perturbation energy is given by equations 1.43.1 and 1.43.2 below:

$$E_n^{(3)} = \langle \psi_n^{(0)} | V | \psi_n^{(2)} \rangle, \quad (1.43.1)$$

or:

$$E_n^{(3)} = \sum_{m,p \neq n} \frac{\langle \psi_n^{(0)} | V | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | V | \psi_p^{(0)} \rangle \langle \psi_p^{(0)} | V | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_p^{(0)})} - E_n^{(1)} \sum_{m \neq n} \frac{|\langle \psi_n^{(0)} | V | \psi_m^{(0)} \rangle|^2}{(E_n^{(0)} - E_m^{(0)})^2}. \quad (1.43.2)$$

The fourth-order perturbation energy expression can be written in a similar fashion. The perturbation potential V given in equation 1.39 represents the correlation energy contribution and can be given as a two-electron exchange type of interaction given by equation 1.44 below:

$$V = \sum_{i < j} \frac{1}{r_{ij}} - V^{\text{HF}}, \quad (1.44)$$

where r_{ij} is the distance between electron i and j and V^{HF} is the HF ground reference state potential. The Gaussian 90 program allows the DP, and the first DH, but not the second DH to be calculated at the MP2 level [12].

An ordering of successively more accurate MPPT energies up to fourth order can be given as follows [10] :

$$\text{MP2} = E_{\text{HF}} + E^{(2)}, \quad (1.45.1)$$

$$\text{MP3} = \text{MP2} + E^{(3)}, \quad (1.45.2)$$

$$\text{DQ-MP4} = \text{MP3} + E_{\text{DQR}}^{(4)}, \quad (1.45.3)$$

$$\text{SDQ-MP4} = \text{MP3} + E_{\text{SDQR}}^{(4)}, \quad (1.45.4)$$

$$\text{MP4} = \text{MP3} + E_{\text{SDTQR}}^{(4)}, \quad (1.45.5)$$

where the number refers to the level or order of the perturbation, and the subscripts: HF refers to the Hartree Fock (single determinant) ground reference state, R indicate the renormalization term, S, single excitations, D, double excitations, T, triple excitations, and Q quadruple excitations [9].

The perturbational order, n , is related to excited states generated by the number of electrons promoted into these excited states from the ground state. In other methods such as CI, CC, and MCSCF, these excited states are represented by determinants such as that of equation 1.2. For example, MP2 is related to inclusion of doubly excited states, or the promotion of two electrons into virtual orbitals or excited state orbitals. Equivalently third order is related to the promotion of three electrons, and fourth order is related to the promotion of four electrons.

Equations for average and anisotropic quantities

The previous work of NLO properties (Table 1.5, and 1.6), and the work of this dissertation characterizes the quality of the NLO properties in terms of average and anisotropic quantities. The study of the effect of basis set choice on NLO properties is based upon examining changes in the individual values, their average and also the anisotropy values.

The definition of the average dipole polarizabilities $\bar{\alpha}$, $\bar{\beta}$, and $\bar{\gamma}$ are given below in equations 1.46.1, 1.46.2, and 1.46.3:

$$\bar{\alpha} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (1.46.1),$$

$$\bar{\beta} = \left(\frac{3}{5}\right) (\beta_{xxz} + \beta_{yyz} + \beta_{zzz}) \quad (1.46.2), \text{ and}$$

$$\bar{\gamma} = \left(\frac{1}{5}\right) [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{xxzz})] \quad (1.46.3).$$

The anisotropies in a and b are given by equations 1.47.1 and 1.47.2 below:

$$\Delta\alpha = \frac{\sqrt{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2}}{\sqrt{2}} \quad (1.47.1), \text{ and}$$

$$\Delta\beta = \beta_{zzz} - \frac{3}{2}(\beta_{xxz} + \beta_{yyz}) \quad (1.47.2).$$

These equations are used to calculate the corresponding quantities reported in the tables of the results reported in later chapters of this dissertation.

Basis Set Choice

A primary consideration in an ab initio calculation of a molecule is the basis set. There is always a trade-off balance between completeness of basis set versus computing resources (disk space required and CPU time). A linear increase in the number of basis functions corresponds to approximately an exponential increase in computing resources required. The selection of the best basis set for accurate calculation of DP and DH properties requires both intuition and scientific expertise.

1. Basis Set Notation

The Slater-type orbital (STO) is defined as follows in equation 1.48.1 :

$$\Psi = A r^{n-1} e^{-\zeta r}, \quad (1.48.1)$$

where A is a coefficient, r is the radial distance measure and ζ is an orbital exponent or screening parameter, and n is the principle quantum number [13]. The choice of the Slater exponent zeta, ζ , is important for an optimal calculation using a truncated STO basis set.

In early work by Slater, it was suggested that an expression (equation 1.48.2):

$$\zeta = \frac{(Z - s)}{n^*}, \quad (1.48.2)$$

be used. In this expression Z is the actual charge of the nucleus to which the STO is associated, s is a screening constant, and n^* is an effective quantum number. The values of s and n^* are chosen based upon empirical considerations.

Clementi and his coworkers [14], for a series of atoms, varied the STO exponent zeta, ζ , until the lowest total energy was found [14]. A comparison of Clementi's results with the Slater rule of equation 1.48.2 shows striking similarity.

The Gaussian-type orbital (GTO) is defined as follows in equation 1.49 :

$$\Psi = B r^n e^{-\alpha r^2}, \quad (1.49)$$

where B is a coefficient and a is the exponent of the Gaussian, and n is the analogy of the principle quantum number in the STO case, except it takes values of 1, 1+2, 1+4, ...

Two desirable properties of basis set functions are fast convergence for truncated basis sets and ease of evaluation on a digital computer. Slater type orbitals have fast convergence and the property of a proper cusp behavior at the nucleus of the atom to which the orbital is associated, but also have the major disadvantage of difficulty of evaluation. For nonlinear polyatomic molecules, the multi-center exchange type integrals which employ STOs are extremely difficult to evaluate.

GTO functions do not have the proper cusp behavior (which the STO functions have) and have slower convergence in that for each STO used in a calculation to provide a certain degree of accuracy, many more GTOs are required to provide a similar degree of accuracy of the calculation. Despite this requirement of many more GTOs per equivalent STO, GTOs are used predominantly in modern ab initio calculations, because GTO calculations require at least an order of magnitude less CPU time for computation than an equivalent calculation using STOs if the STO calculation is possible.

A contracted Gaussian basis function is defined in equation 1.50 :

$$\phi_{\mu} = \sum_{i=1}^N d_{i\mu} e^{-\alpha_{i\mu} f^2 r^2}, \quad (1.50)$$

where N is the number of **primitive functions**, also called the **degree-of-contraction**, each $d_{i\mu}$ is a **contraction coefficient**, each α_i is a **Gaussian exponent**, and f is a **scale factor** for the basis function [12]. A **shell** is defined to be a set of basis functions $\{ \phi_{\mu} \}$ with shared or equal exponents (i.e., the 2sp shell in the 6-31G has six s and six p primitives with equal s and p exponents whose coefficients are normalized together (p. 28)). Both the Hondo 8 (H8) [11] and the Gaussian 90 (G90) [12] programs (and later versions) support five types of shells: s, p, sp, d, and f.

Gaussian basis set types commonly used fall into three categories:

1. **Minimal Basis Set**
2. **Double Zeta (DZ) Basis set**
3. **Extended Basis Set.**

Although in most cases Gaussian basis functions are actually used in the computations performed, the terminology used for these three categories of basis sets is in terms of STOs or contracted Gaussians. The **minimal** basis set uses a number of GTOs to approximate the equivalent calculation in which one STO is used for each AO which makes up the MOs in the molecule. About six GTOs are required to approximate one STO in a minimal basis set calculation.

A **double zeta** basis set uses a number of GTOs to approximate the equivalent calculation in which two STOs (i.e., two ζ 's) are used for each AO which makes up the MOs in the molecule. An **extended** basis set uses more GTOs than that of a double zeta basis set and provides more accuracy than a calculation of double zeta quality.

Also, within each of these classes of basis sets, extra basis functions are added. These are termed polarization functions (pfs) and are required to improve the accuracy or quality of the calculation to within realistic limits. The addition of polarization functions improves both the calculation of optimized geometries and greatly the quality of molecular properties. In fact, in contrast to much earlier work in the literature, it has in recent years become clear that accurate calculations of properties of any type require the use of multiple polarization function sets (pfs) [56].

2. Contracted Basis Sets

In most ab initio codes, the CPU time required for calculation of one- and two-electron integrals in the single-determinant HF process is roughly proportional to the fourth power of the number of Gaussian primitives [20]. In post HF correlation methods such as MP2 the CPU time dependence on the number of basis functions is steeper than the fourth power [20]. Other post HF SCF processes, however, depend more upon the number of basis functions (i.e., contractions) than upon the number of Gaussian primitives [20]. Ideally the best results would be obtained if all the coefficients of a Gaussian expansion were allowed to vary in the HF SCF process for a MO calculation, but the use of **contracted basis functions** requires far less CPU time than the use of uncontracted primitive functions. Also convergence becomes very difficult for large sets of uncontracted primitives. Another important consideration (in non-direct SCF calculations) is the requirement of large disk storage of one and two electron integrals during the HF SCF process, and the arguments for saving CPU time by using contracted basis functions apply also to diminished disk storage requirements. The direct SCF method is discussed in a later section in this chapter. Often, the real limitation on how large of a molecule and how large a basis set which could be used is determined by available disk storage requirements at a particular installation.

In the next three sections a summary of the contracted basis sets and the use of polarization and diffuse functions relevant to the later chapters of this work is given. Further details of basis sets can be found in recent reviews by Labanowski [20], and by Feller, Boyle, and Davidson [28]. Other basis sets used in the work of this dissertation include those found in a book by Csizmadia et al. [5], and those recently reported by Binning and Curtiss [26]. An outstanding feature of these articles describing basis sets is how few studies they are able to report on the molecular properties of polyatomic molecules, in which the larger basis sets are used for calculations involving the heavier elements (i.e., $Z > 18$).

A. Notation of Basis Set Contraction

A general basis of a certain level: minimal basis, DZ basis, TZ or extended is the starting point for construction of a contracted basis set. The primitive Gaussian functions of the general basis set is grouped according to shell type (i.e., s, p, sp, d, f, ...), and several contracted functions form a shell, and each of these shells are named according to l, the angular momentum quantum number. Parentheses, " () ", are used to denote the primitive basis functions of the general basis set, separated by a comma, " , ", for functions of different l. Square brackets, " [] ", are used to denote contracted basis functions, and a comma used to separate l-types. In later chapters the commas are left out for the sake of brevity. In molecular basis sets a slash, " / ", is used to separate the functions of the different atoms. Thus an example of a basis set contraction for a basis set for water is given as follows: (10s, 5p, 1d / 5s, 1p) $\rightarrow$ [4s, 2p, 1d / 2s, 1p]. This example denotes a contraction of the oxygen atom basis of (10s, 5p, 1d) $\rightarrow$ [4s, 2p, 1d], and a contraction of the hydrogen atom basis of (5s, 1p) $\rightarrow$ [2s, 1p].

B. A Silicon Basis Contraction Example

Gordon [21] gives an example of the 66-31G basis set for the silicon atom, which is given below in Table 1.1.

Table 1.1 66-31G basis set for silicon.

Type	Exponent	s - Coefficient	p - Coefficient
1 S	1.61921e4		
	2.43609e3	1.48559e-2	
	5.56001e2	7.25689e-2	
	1.56813e2	2.45655e-1	
	5.01692e1	4.86060e-1	
	1.70300e1	3.25720e-1	
2 SP	2.93350e2	-2.82991e-3	4.43334e-3
	7.01173e1	-3.60737e-2	3.24402e-2
	2.24301e1	-1.16808e-1	1.33719e-1
	8.19425	9.35768e-2	3.26780e-1
	3.14768	6.01705e-1	4.51139e-1
	1.21515	4.22207e-1	2.64105e-1
3 SP	1.65370	-2.40600e-1	-1.51774e-2
	5.40760e-1	7.37953e-2	2.75139e-2
	2.04406e-1	1.04094	7.83008e-1
3 SP	7.23837e-2	1.00000	1.00000

The above basis set has a contraction of (16s, 10p) $\rightarrow$ [4s, 3p] or (6631, 631). In the SP sets of contracted functions the s and p type have share exponents given in column 2.

C. Polarization and Diffuse Functions

Polarization functions are functions which have a higher l value than those of the normally occupied atomic orbitals for the ground state atom basis set. Thus according to this definition for lithium, p functions are not considered polarization functions, and for sulphur, d functions would be considered polarization functions. For Li and Be if p functions are not included even in a minimal basis set calculation, the results would be extremely poor. The exponents of polarization functions can be estimated from correlated atomic calculations [20], but in practice they are either derived by established rules of thumb, or for the inner ones by optimizing the energy of small molecules, such as those given by Feller, Boyle, and Davidson [28].

Polarization functions are important in adequate representation of the chemical bond. By definition polarization functions are diffuse functions with very small exponents (say less than 0.10). These are important for correct description of anions, weak bonds (i.e., hydrogen bonds), and for the calculation of properties (i.e., **dipole moments, DP, and DH**). Usually, polarization functions are specified in the basis set as uncontracted functions with a coefficient of exactly one.

3. Commonly Used Basis Sets

Some of the most commonly used basis sets, which are internally stored in G90 (for atoms with $Z = 1$ to $Z = 18$) are: STO-3G, 3-21G, 4-31G, 6-31G, TZV, D95, and variations on these. The STO-3G basis set consists of three GTOs fitted to each STO of a minimal basis set. The 3-21G, 4-31G, and 6-31G basis sets are called split valence, in that the first or left-most number indicate the number of GTO primitives used for core orbitals (i.e., $1s$ for the first row, and $2s, 2p$ for the second row of the periodic chart), and the next numbers indicate the number of primitive within each **contracted** or linear combination set as given by equation 1.48 for the valence orbitals.

For example, the 6-31G basis set has six primitives for each core orbital and two valence contracted functions with three and one primitive respectively for the valence orbitals.

The D95 basis set was developed by Dunning [15] and consists of the contraction of a 9s, 5p large optimized atomic basis set developed by Huzinaga [16]. This double zeta basis set splits the valence into two contracted functions.

The TZV basis set contains contracted functions which provide triple zeta quality for valence orbitals (i.e., the valence shell AOs are split into three contracted functions).

When one considers heavier atoms with a $Z > 18$, i.e., those of the second row and beyond in the periodic chart, there are not many basis sets from which one can choose. Huzinaga has developed the MIDI basis set for heavy atoms [23], and a few other basis sets for heavy atoms are tabulated in a book by Csizmadia et al. [5]. Some of these are used in this present work.

However, Binning and Curtiss have very recently developed basis sets for elements of the fourth row [26] of equal quality to the 6-31G basis set for lighter atoms, and this set supplemented by pfs is used extensively in the present work as discussed in the following chapters.

4. Basis Sets for Dipole Polarizability and Dipole Hyperpolarizability Calculations

Of the basis sets mentioned in section 3, the 3-21G, 4-31G, 6-31G, and TZV are among the starting point basis sets used in the present work. If DP and DH calculations are performed using these basis sets, the results would be very poor. Accurate results of properties such as DP and DH require basis sets which represent electron density in diffuse regions with higher angular momentum values, say p or d type, or even f types. Thus the basis sets mentioned in section 3 are only a starting point for the calculation of NLO properties such as the DP and DH. The addition of one or more p or d type diffuse polarization functions is absolutely essential [19].

The following procedure is the strategy used in the present work to derive a suitable basis set for calculation of DP and DH properties (from this point forward the terms polarization function, diffuse function, and diffuse polarization function will be used interchangeably, with abbreviation pf)...

1. A suitable contracted basis set is chosen as the starting point.
2. Each shell is extended by at least one diffuse set of pfs.

The pfs added for step 2 is chosen by an even-tempered sequence [28], i.e., the exponent relationship for an even-tempered sequence is given by equation 1.51 :

$$\alpha_i = \alpha_0 \beta^i, \quad (1.51)$$

where β is a reduction factor (rf) usually taken to be 0.4, and the i th function with exponent α_i is added, where α_0 was the most diffuse exponent of the shell in the original basis set of step 1. Thus the first added function of a shell starts by scaling the smallest existing exponent (i.e., the smallest exponent of the shell in the basis set chosen in step 1).

Let us say that we have a hypothetical basis set with the smallest exponent of type s, p, d as follows: $\alpha_s = 1.0$, $\alpha_p = 1.0$, $\alpha_d = 1.0$, then if we extend the s, p, and d type by four functions each using an rf of 0.4 we would add the following functions with exponent α and coefficient C:

$\alpha_{s1} = 0.4$	$C_{s1} = 1.0$	$\alpha_{p1} = 0.4$	$C_{p1} = 1.0$
$\alpha_{s2} = 0.16$	$C_{s2} = 1.0$	$\alpha_{p2} = 0.16$	$C_{p2} = 1.0$
$\alpha_{s3} = 0.064$	$C_{s3} = 1.0$	$\alpha_{p3} = 0.064$	$C_{p3} = 1.0$
$\alpha_{s4} = 0.0256$	$C_{s4} = 1.0$	$\alpha_{p4} = 0.0256$	$C_{p4} = 1.0$

$\alpha_{d1} = 0.4$	$C_{d1} = 1.0$
$\alpha_{d2} = 0.16$	$C_{d2} = 1.0$
$\alpha_{d3} = 0.064$	$C_{d3} = 1.0$
$\alpha_{d4} = 0.0256$	$C_{d4} = 1.0$

Addition of each pf is expensive in terms of computational resources (CPU time, and disk storage space), and therefore each function must be carefully chosen.

The addition of each p pf adds 3 functions per atom, each d pf either adds five or six functions per atom, and each f pf either adds seven or 10 functions per atom [11, 12].

The following notation will be used in this dissertation to denote pfs: either nL , where n is the number of pf sets and L is the type of pf, i.e., 3d pf sets, or $L(e_1, e_2, e_3, \dots)$, where L again is the type of pf and $e_1, e_2, e_3, \dots$ are the exponents, i.e., $p(0.9, 0.13, 0.02)$.

For example if a d pf is added to the hydrogen of NH_3 , fifteen basis functions are added to the basis set, and a tradeoff between the number of additional pfs used and the degree of accuracy of the calculated property desired is made for each molecule. By common sense, when addition of another pf does not change the calculated property desired more than a specified accuracy, then the basis set is considered to be saturated with respect to that property. Once a basis set has been determined, it is hoped that one can use it on the same atom in other molecules.

For NLO properties, from practical experience one might expect that some of the deeper (i.e., larger exponent) pfs although they are important for the dipole moment (DM), they can often be left out without affecting the calculated NLO properties. However, there have been very few previous systematic studies concerning the bs requirements for calculating DH, so the derivation of an adequate bs for calculation of DP and DH requires repeated calculational trials to determine the best suited bs.

Two methods which have been used to develop bss for NLO property calculations are the following: the polarized basis set method of Sadlej [45, 47, 48] (used for calculation of DMs and DP), and the Dykstra ELP method for DMs and DPs. The pfs proposed in the latter method, the Dykstra ELP (for electrical properties) are used extensively in the present work.

Dykstra ELP Polarization functions

A set of polarization functions (pfs) which has been used in previous work by Dykstra [19, 36], and also used in the present work of this dissertation are given in Table 1.2. These are a compact set of polarization functions (pfs) which gave reasonably good results for the calculation of the DM (μ), the DP, and the DH. Dykstra [19, 36] developed these pfs as a compromise between size and accuracy in results of low order multipole polarizabilities of small, first row molecules. The name ELP designates a electrical properties basis set. They have only been used previously at the HF level.

Dykstra [19] used, as his initial set, a triple zeta quality basis set, and augmented these by the pfs given in Table 1.2. One feature of these pfs is uniformity from element to element. A nonuniformity in atomic basis functions of a heteronuclear molecule creates an imbalance in the basis set, which degrades the quality of the calculated results. Another feature of the ELP pfs is that the l-type sets are balanced. Diffuse functions, which are important to the accuracy of these electrical properties, are present in the ELP pfs.

Sadlej's Basis Set Polarization Method

The **basis set polarization method** (BSPM) was developed by Sadlej [61] to produce basis sets used to obtain highly correlated DM and DP values for small hydrides. Several of the results of Sadlej's calculations [40, 47, 48, 61] are used for comparison purposes in this dissertation. Sadlej used the MBPT method up to fourth order to obtain his correlated results for the DM and DP properties.

Table 1.2 Dykstra Polarization functions:

Atom	S	P	D
Carbon	0.05	0.03	0.9
		0.005	0.13
			0.02
Nitrogen	0.06	0.04	0.9
		0.006	0.13
			0.02
Hydrogen	0.06	0.9	
		0.1	
Oxygen	0.06	0.05	0.9
		0.007	0.13
			0.02

The BSPM is based on the assumption that the dependence of the basis set functions on the relevant external perturbation is known (i.e., by application of an electric field). Optimal DPs are those that give the maximum mean DP. If this assumption is true, according to Sadlej [61] the polarization functions (pfs) for a given initial basis set can be determined.

The BSPM starts with the initial unperturbed set of basis functions:

$$\{ \chi_m^{(0)} \}, \quad (1.52)$$

where m is a index of the basis function. Then the polarized basis set is constructed from:

$$\left\{ \chi_m^{(0)}, \frac{\partial \chi_m}{\partial \lambda} \right\}, \quad (1.53)$$

where the additional basis functions are the derivative of the original basis functions with respect to λ the perturbation (i.e., the electric field). According to Sadlej [61], higher order derivatives for HF SCF calculation of electrical properties, such as DPs, are not necessary, whereas for correlated properties, higher order derivatives may be necessary up to the order of the correlation. Sadlej gives the following relation for the derivative of the basis functions:

$$\left(\frac{\partial \chi^l}{\partial F_\sigma} \right)_{F=0} = \alpha^{+0.5} \chi^{l-1}(0) + \alpha^{-0.5} \chi^{l+1}(0), \quad (1.54)$$

where F_σ is the electric field in direction $\sigma = x, y, \text{ or } z$, α is the Gaussian exponent, and l is the angular momentum of the basis function (bf) χ . The first term of the right hand side (RHS) is not necessary since other bfs of angular momentum $l-1$ are already in the basis set, and is therefore redundant.

Sadlej [61] also uses the even-tempered sequence method described earlier in this chapter (p. 25) to select pfs, which are added to the initial basis set, and then equation 1.56 of the BSPM is used to derive pfs which did not exist in the initial basis set. An example of Sadlej's polarization basis set [61] for nitrogen is given in Table 1.3. Sadlej used as his initial set the (7s, 4p) $\rightarrow$ [2s, 4p] double zeta basis set of van Duijneveldt [69].

The first s pf on nitrogen has an exponent of 0.73961, which is a rf of about 0.2 from the exponent 3.579794, and the next two s pfs have a rf of about 0.3. The two added p pfs have a rf of about 0.3, i.e., they form an even-tempered set.

Since there were no d pfs in the original basis set, the BSPM equation 1.52 was used to derive the d pf sets (i.e., the coefficient of the d pf is $\alpha^{-0.5}$ of the p coefficient). The first d pf has exponent 1.750842, which is the same as the next to last p bf in the original basis set. The coefficient of this pf is calculated as follows:

$$0.22477 = \frac{1}{\sqrt{1.750842}} 0.297420 ,$$

where the reciprocal square root of the exponent is used to determine the new coefficient.

The next d pf has exponent 0.560511 and the coefficient is calculated as follows:

$$0.65956 = \frac{1}{\sqrt{0.560511}} 0.493796 .$$

Table 1.3 Sadlej's nitrogen polarized basis set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
8104.0716	8.02d-04	26.868987	1.4478d-02
1216.0215	6.174d-03	5.991227	9.1156d-02
277.23428	3.1233d-02	1.750842	2.9742d-01
76.904023	1.15198d-01	0.560511	4.93796d-01
25.874419	2.96951d-01		
9.346767	4.47349d-01	0.175948	1.0000000d+00
3.579794	2.45003d-01		
		0.955231	1.0000000d+00
0.739610	1.0000000d+00		
		D	
		<u>Exponent</u>	<u>Coefficient</u>
0.222617	1.0000000d+00	1.7508	2.2477d-01
0.067006	1.0000000d+00	0.5605	6.5956d-01
		0.1759	8.7136d-01
		0.0552	7.0422d-01

The coefficients of the next two d pf sets, do not follow the relation of equation 1.52, but are rather derived from the SCF HF eigenvectors of the nearest ion.

The following steps are a summary of how Sadlej [61] derives his polarization basis set:

1. The given primitive Gaussian basis set should be contracted to the minimal acceptable size. A double zeta quality contracted basis is a reasonable choice.
2. The initial basis set should be extended by at least one diffuse function in each shell. These exponents can be derived from an even-tempered sequence.
3. The polarization functions are to be generated only for the outer most occupied shell of the given atom. The contraction coefficient in equation 1.52 should be determined from the SCF HF eigenvectors of the nearest negative ion.
4. Several primitive Gaussian functions with high exponents can be removed from the pf. At least two primitive polarization Gaussian functions should be retained. Four primitive polarization Gaussian functions should be retained for calculations including electron correlation.
5. A pf comprising of four primitive Gaussian functions should be decontracted into two contracted functions according to the scheme $(4 \rightarrow 2 + 2)$. No decontraction is necessary for pfs with only two primitive Gaussian functions.

Finally, Sadlej uses many body perturbation theory (MBPT) up to fourth order to include correlation in the calculation of the DM and DP properties. Sadlej does not calculate the DH. Sadlej's calculation results [40, 45, 47, 48, 61] of the DM and DP properties include MBPT up to the fourth order. Sadlej's correlated results are very relevant to the work described here because of the relatively small change in the results he finds on taking the computation past second order. For example, in the case of PH_3 (see Table 3.7), Sadlej calculated: $\mu = 0.2439$ a.u. and $\bar{\alpha} = 30.64$ in the MBPT(2) case, and $\mu = 0.2264$ a.u. and $\bar{\alpha} = 30.29$ in the SDQ-MBPT(4) case, giving a net change of -7.73% for μ , and -1.16% for $\bar{\alpha}$ [45].

Sekino and Bartlett's method

Recently (since much of the work described in the dissertation was completed) Sekino and Bartlett [65] reported calculations of NLO and DM properties of some small hydrides as indicated on page 43. In these calculations, Bartlett and Sekino used the basis set of Sadlej and also included correlation to second order using their MBPT and the coupled cluster (CC) methods. The CC calculations include the singlet / doublet excitation (CCSD), and the singlet / doublet / triplet excitation (CCSD(T)). The HF and correlated results of Sekino and Bartlett [65] are also compared with the results in later chapters for this dissertation. The work of Sadlej [45], and that of Sekino and Bartlett [65] are of paramount importance in assessing the role of correlation for NLO properties and the DM.

Feller, Boyle, and Davidson's polarization functions

Feller, Boyle, and Davidson [28] used energy optimized even-tempered sets of pfs in calculation of one-electron properties on a series of molecules. These exponents were optimized with respect to the total energy of the molecule. Feller, Boyle and Davidson performed their calculations at the HF SCF level as well by including electron correlation using the configuration interaction (CI) method. These pfs for NH_3 , PH_3 , and H_2S used by Feller, Boyle and Davidson are given in Table 1.4. Some of these pf sets were used in calculations performed in this dissertation. Their use turned out to be very important since in some molecules it became obvious that they must be included for the calculation of the DM and DP, contrary to the assumption made by Sadlej and others that in calculating properties which depend on the outer regions of electron density, that is is not necessary to describe the inner regions very accurately.

Table 1.4 Feller, Boyle, and Davidson's pfs

NH ₃	N-	d(2.74,0.94,0.32,0.11)	f(1.40,0.50)
	H-	p(4.15,1.06,0.27,0.07)	d(2.27,0.56)
PH ₃	P-	d(2.34,0.94,0.38,0.15)	
	H-	p(3.93,0.93,0.29)	d(2.27,0.56)
H ₂ S	S-	d(2.34,0.94,0.38,0.15)	f(1.40,0.50)
	H-	p(4.15,1.06,0.27,0.07)	d(2.27,0.56)

Maroulis' Choice of pfs

Maroulis who has also reported calculations of DP and DH of small molecules [70] outlines his method for choice of pfs in his paper on HCl calculations at the HF, MP2, MP3, and MP4 [70]. His method of pf exponent choice will be outlined below:

Diffuse functions with exponents chosen to form a geometric progression with the two most diffuse functions of the same symmetry in the substrate are added.

Polarization functions with exponents optimal for the energy of the free molecule or the energy of the molecule in the presence of a distant electric charge are added.

Polarization functions with exponents to maximize the mean quadrupole polarizability.

The third type of pfs were used by Maroulis [70] because he calculated quadrupole polarizabilities which are by far more sensitive to very diffuse pfs compared to DPs and DHs calculated in this present work.

Survey of Previous Work of Dipole Moments, Dipole Polarizabilities and Hyperpolarizabilities

Previous calculations of the dipole moment, dipole polarizabilities, and first and second dipole hyperpolarizabilities are summarized on p. 43. The symbol legend below the table give the references to the indicated calculations.

Sekino and Bartlett [65] report the NLO and DM properties of H₂, N₂, CO, CO₂, C₂H₄, HF, H₂O, NH₃, and H₂S, and include MBPT(2), CCSD and CCSD(T) treatments of correlation.

The ELP method of Dykstra et al. [19] which was discussed on p. 30 (Chapter I). The bs is summarized in Table 1.2 of this dissertation.

Feller et al. [28] have calculated dipole moments and quadrupole moments at the SCF and CI levels for: H₂O, CO, N₂, H₂S, NH₃, PH₃, HCl, and HF.

Jordan et al. [52] have calculated DP for C_2H_4 at the SCF and MP2 levels. Maroulis et al. [9, 37, 51, 57, 58] have calculated dipole moments, DPs and DHs by the fixed charge method of molecules discussed previously (p. 13) in Chapter I of this dissertation.

Prasad et al. [49, 62] reported calculations on the DMs, DPs, and DHs using the finite field method discussed briefly in Chapter I of this dissertation.

Prasad and Dupuis calculated the DPs and DHs of CHF_3 , $CHCl_3$, $CHBr_3$, and CHI_3 using the ECP method and the CPHF method [73].

Recently Hammond and Rice [71] have calculated NLO and DM properties of HCL at the HF and MBPT(2), CCSD, and CCSD(T) levels.

Sadlej et al. [45, 47, 48, 52, 61] have developed the basis set polarization method to determine the basis set for dipole moment and DP calculations at the SCF level and also with many body perturbation theory (MBPT).

Recently, Shelton and Rice [92] published a review of DH and second DH results for polyatomic molecules. This review contains results for some molecules that are not listed in this dissertation, and thus it can be used as a reference of NLO properties.

Spackman [46] has calculated DMs and DPs for H_2S , SiH_4 , C_2H_2 , and C_2H_4 using a small set of optimized pfs, which is even smaller than the ELP set of Dykstra [19]. A comparison of these results will show that these calculations are not very accurate. even for the DM and DP.

Overview

Table 1.5 shows that apart from benzene and pyridine, very few large molecules have been investigated, and, even for small hydrides, the only substantial study of the DHs is the work of Sekino and Bartlett [65] on the hydrides HF, H_2O , H_2S , and NH_3 . In fact their work on H_2S is the only study of the DHs of a polyatomic molecule containing an element with an atomic number greater than ten.

Table 1.5 Previous Work Summary

Molecule	μ	α	β	γ
F ₂	-----	B, M	-----	B, M
N ₂	-----	B, M	-----	B, M
HF	B, F, S	B, S	B	B
HCl	F, M, R, S	M, R, S	R	R
HBr	S	S		
HI	S	S		
LiH	D	D	D	
HCN	D	D	D	
CO	B, D, F	B, D	B, D	B
H ₂ O	B, D, F, S	B, D, S	B, D	B, D
H ₂ S	B, F, S	B, F, S	B	B
H ₂ Se	S	S		
H ₂ Te	S	S		
NH ₃	B, D, F, M, S	B, D, M, S	B	B
PH ₃	F, S	S		
AsH ₃	S	S		
SbH ₃	S	S		
CH ₄	-----	D, S	D	
C ₂ H ₂	-----	D, M, P, S2	-----	M, P
C ₂ H ₄	-----	B, D, M, J, P, S2	-----	B, P
GeH ₄	S	S		
SiH ₄	S	S, S2		
SnH ₄	S	S		

Table 1.5 (Continued)

Molecule	μ	α	β	γ
N ₂ H ₂	D	D	D	
H ₂ O ₂	D, M	D, M	D, M	D, M
Benzene	-----	P, H	-----	P
Pyridine	H	H		
H ₂ CO				
CHF ₃		D2	D2	D2
CHCl ₃		D2	D2	D2
CHBr ₃		D2	D2	D2
CHI ₃		D2	D2	D2

B - Sekino and Bartlett [65]

D - Dykstra et al. [19]

D2 - Karna and Dupuis [100]

F - Feller, Boyle, and Davidson [28]

H - Hinchliffe and Soscun [94, 95]

J - Jordan et al. [52]

M - Maroulis et al. [9, 37, 51, 57, 58, 70]

P - Prasad et al. [49, 62]

R - B.L. Hammond, J.E. Rice [71]

S - Sadlej et al. [45, 47, 48, 61]

S2 - Spackman et al. [46]

In order to rectify this situation, a systematic investigation of the change in the NLO properties of the hydrides of elements of Group V and VI, as the atomic number of the central atom was increased, was investigated. Also, it was decided to investigate the effect of including electron correlation, since Sekino and Bartlett in their early calculation on HF [72] had found that the effect of electron correlation was quite substantial on NLO properties.

Initially, very large basis sets, consistent with the available computational facilities, were employed to try to provide for the first time bs converged accurate ab initio values of the NLO and DM (Chapters III, and V - VIII). Then for some of the molecules the effect of reducing the basis set was investigated. In the case of nitrogen compounds, a relatively small basis set was derived from comparison with the accurate results of large basis set calculations in the case of ammonia to calculate the NLO properties of formamide, pyridine, and pyrrole (Chapter IV). In the case of pyridine and formamide both the effect of correlation and the effect of using an effective core potential were investigated (see Chapter IV). The new work presented in this dissertation is described in Chapters III through VIII of this dissertation as outlined below.

Plan of Dissertation

Chapter II contains a description of the hardware and software used and experience of using the computer systems described.

Chapter III reports and discusses results for ammonia, phosphine, and arsine.

Chapter IV reports and discusses results for formamide, pyridine, benzene, and pyrrole.

Chapter V reports and discusses the results for H_2S , H_2Se , and H_2Te .

Chapter VI reports and discusses the results for CH_4 , SiH_4 , and GeH_4 .

Chapter VII reports and discusses the results for C_2H_4 , Si_2H_4 , and Ge_2H_4 .

Chapter VIII reports and discusses the results C_2H_2 , Si_2H_2 , and Ge_2H_2 .

Chapter IX contains a summary and conclusions of the Dissertation.

CHAPTER II

DESCRIPTION OF THE HARDWARE AND SOFTWARE USED

As mentioned in the previous chapter, the computer codes used in the calculations of this dissertation consists of the Gaussian 90 (G90) program [12], the Gaussian 92 (G92) program [82], and the Hondo-8 (H8) program [11]. Three computers are currently used to perform the DP and DH calculations, the University of Tennessee Department of Computing and Administrative Systems (CAS) IBM 3090-400 with 256 Mb physical memory and about 3000 cylinders of 3390 disk storage per calculation and a limit of 24 hours of CPU time per job running the MVS / TSO operating system, a Sun Sparc 2 (S2) with 48 Mb of physical memory and about 3.9 Gb of disk storage with no limit on CPU time owned by CAS, and an IBM RISC 6000 model 320h (R6000) with 16 Mb physical memory and about 1 Gb of disk storage and unlimited CPU time, shared by the research groups of Drs. J.E. Bloor, S. Alexandratos, and D. Baker. The R6000 runs under the IBM AIX 3.2.3 version of Unix with the MIT X11R5 windowing system and the OSF Motif (version 1.2) widget set / window manager. It also has Adobe Display Postscript capability. This R6000 also has IBM accelerated 3-D graphics on a 20 inch 8-bit color monitor. The S2 runs under the Solaris 2.4 operating system. These three systems can be accessed remotely by the University of Tennessee TCP / IP optical fiber network, which is connected to Suranet for off-site access. Currently the University of Tennessee uses Class B IP addresses with a prefix of 128.169, and a subnet mask for Unix hosts of 255.255.252.0. This network is accessed remotely through a point to point protocol (PPP) link at 38.4k baud plus compression.

Currently the G90 program is compiled with the IBM VS Fortran version 2.4 on the 3090 system. The G92 program is compiled with the current level of the Sun Fortran compiler. The H8 program is compiled with IBM VS Fortran version 2.5 on the 3090 system and with IBM xlf Fortran version 2.4 on the RISC 6000 system, and with the current level of the Sun Fortran compiler. The JCL used to install the H8 on the 3090 is given in Appendix A. The H8 source files were copied to the 3090 using ftp from the R6000 to TSO on the 3090 into a partitioned data set which is compiled into an online load module by the JCL of Appendix A.

The G90 program was installed by Mr. Lonnie Gowan of CAS manually on a module by module basis under TSO. The source code for G90 was purchased from Gaussian Inc. on 6250BPI IBM SL reel tape.

The source code for H8 was supplied by Michel Dupuis of IBM, Kingston, NY, one of the authors of H8, on a DC6150 tape in uncompressed tar format for the R6000. During compilation of H8 the optimization and vectorization switches were set according to the H8 documentation [11] on both IBM systems. This was the first installation of H8 on a R6000 machine outside of IBM facilities. This H8 code has also been converted to run on Sun Sparc processors the Solaris 2.4 operating system. Minor code modifications were made for the Sun compilations of H8.

Job entry for the 3090 was accomplished by RJE on an IBM 3081 running the VM / SP CMS operating system from an IBM PS2 / 60, a Macintosh Iivx, and an IBM AT. The IBM PS2 / 60 has 1Mb physical memory, 40Mb fixed disk running IBM PC DOS 4.0, with TCP / IP capability using the Clarkson packet driver for an Unger Bass ethernet card. The Macintosh Iivx has 8Mb physical memory, 250Mb fixed disk running Apple Macintosh System 7.5.1, using modem PPP connection to the CAS network with Versaterm 5.0.4 and University of Michigan Merit PPP software.

The capabilities of the G90, G92 and H8 programs are discussed at length in their corresponding documentation [12, 11], however the general features of these codes are summarized below.

The Gaussian 92 Program

The G92 program is a further development of the Gaussian 70, Gaussian 76, Gaussian 80, Gaussian 82, Gaussian 86, Gaussian 88, and Gaussian 90 programs [29,30,31,32,33,34,83]. The current version of G92 includes the MINDO3, MNDO, and AM1 semi-empirical methods derived from the MOPAC program of J.J. P. Stewart [59,77,78]. The GVB code of F.W. Bobrowicz is also included with some performance improvements.

The summary of the changes between G92 and G90 taken from the documentation [82] is summarized below:

New Methods in G92:

Analytical MP2 second derivatives for closed and open shell, using semi-direct methods.

Self-Consistent Reaction Field.

All correlation calculations (except complex SCF and MP2) can now be done using the direct, in-core, and semi-direct methods.

Coupled Cluster energy calculations with both single and double substitutions (CCSD) and with non-iterative triples (CCSD(T)).

MP5 and QCISD(TQ).

Analytical CASSCF second derivatives, allowing frequencies and force constants at that level.

Brueckner Doubles correlation energy computations complete with triples and quadruples energy contributions: BD, BD(T), and BD(TQ).

Fast fully automated generation of electrostatic potential derived charges via the Merz-Singh-Kollman, CHELP, or CHELPG schemes.

PM3 and PM3MM semi-empirical models.

New Features in G92:

Direct and in-core GVB and CASSCF.

AO, direct and in-core SCF stability testing.

Geometry optimizations can be performed in cartesian coordinates or in mixed internal and cartesian coordinates.

Parallel processing of all key steps of SCF energy, gradient, and frequency calculations, and parallelization of the most costly phases of CI, MP4, QCI, CC, and BD calculations.

CIS and correlated gradients can be done with core electrons frozen.

Saddle points of order greater than one can be optimized.

Molecular orbitals and electrostatic potentials can be evaluated over 3d grids and stored in the same format as electron densities.

The FormChk utility permits generation of a formatted interface file for communication with visualization systems.

Automated generation of a PROAIMS/AIMPAC data file.

Extra overlay cards in non-standard route format can be added to a standard route.

Skip=OvNNN and Skip=M options allow further customization of a parse generated route.

The defaults file can be used to site-customize amount of memory allocated and number of processors which can be used for a single job.

Bug Fixes and Minor Changes in G92:

IRC calculations can now be restarted after successful termination.

The temperature and pressure can now be specified for the thermochemical analysis done during frequency calculations.

Functional Differences between G92 and G90:

Common blocks on checkpoint files has different lengths.

The default for all electron correlation methods is always frozen-core.

Since analytical second derivatives are available for MP2 as well as HF, the CalcFC option now requests analytical second derivatives at the first point of an optimization using the specified methods.

Freq=ReadIsotopes requires different input.

CIS SCF=Direct requests direct SCF, followed by a semi-direct integral transformation and a CIS calculation using the MO integrals.

The Gaussian 90 Program

The summary of the capabilities of G90 taken from the documentation [12] is summarized below:

Calculation of one- and two-electron integrals over s, p, d, and f contracted Gaussian functions. The basis functions can be either cartesian Gaussians or pure angular momentum functions, and a variety of basis sets are stored internally are available for use. Integrals can be stored in physical memory, externally on disk, or recomputed directly (Direct SCF including first and second derivatives), and Direct SCF MP2.

SCF calculations can be performed for the following types of systems:

- RHF - restricted closed-shell,
- UHF - unrestricted open-shell,
- ROHF - open-shell restricted HF,
- and multiconfigurational Generalized Valence Bond-Perfect Pairing (GVB-PP).

General MCSCF and complete active space SCF (CASSCF) are available.

Excited state energy calculations using single-excitation CI can be performed.

Evaluation of various one-electron properties of SCF, MP2, CI and QCI energies and wavefunctions, including Mulliken population analysis, multipole moments, and electrostatic fields can be performed.

Semi-empirical calculations using CNDO, INDO, MINDO/3, MNDO, and AMI model Hamiltonians can be performed.

Automated geometry optimization to a minima or saddle points, and numerical differentiation of wavefunctions to produce vibrational force constants, **electric dipole polarizabilities**, and dipole derivatives, and following of reaction paths can be calculated.

Correlation energy calculations using Moller-Plesset perturbation theory at second, third, or fourth order can be performed. MP2 uses a semi-direct method.

Correlation energy calculations using configuration interaction of the type: CI - single excitation, CID - double excitation, and CISD - all single and double excitations can be performed.

Correlation energy calculations using coupled cluster theory of the type: CCD - double substitutions, and QCISD - with quadratic configuration with single and double substitutions can be performed.

Analytic computation of the nuclear coordinate gradient of the RHF, UHF, ROHF, GVB-PP, CASSCF, MP2, CID, CISD, QCISD, and excited state CIS energies can be performed.

Harmonic vibrational analysis can be performed.

Calculation of intensities for vibrational level transitions at the HF, MP2, CI, and QCI levels can be performed.

Testing the SCF wave functions for stability under release of constraints can be performed.

The current version of G90 contains about 203,000 lines of Fortran source code, 20,000 lines of VMS operating system interface source code, and 12,000 lines of Trace/Unix operating system interface code. About 27% of the source code are comments.

Its current limitations are summarized in Appendix I of the documentation [12]. The current version of G90 is limited to 400 centers including real existing, ghost, and dummy atoms. The maximum number of variables for geometry optimization is unlimited for Berny and EnOnly optimizations, and is limited to 50 variables for Murtaugh-Sargent and Opt=EF optimizations, and is limited to 30 variables for Fletcher-Powell optimizations, and is limited to 10 variables for Opt=(EF, EnOnly) optimizations. Basis limitations of the G90 code are manifest in two manners: first, the limitations of the integral evaluation code of the number of primitive Gaussians and how they are combined as AO basis functions, and second, the dimensioning limits of the energy evaluation codes.

The maximum limitations of the integral evaluation code is as follows: 6000 primitive shells, 2000 primitive d-shells, 2000 primitive f-shells, and 2000 contracted shells, and maximum degree of contraction of 10. The current G90 supports s, sp, p, d, and f type shells. Note, a spd shell can be specified as a sp shell and a d shell. The final aspect of the limitation of the integral evaluation code manifests itself in the manner which the integral labels are packed, that is- the manner in which the two-electron integrals are stored and written out to disk.

The standard storage mode uses an eight bit label for the quantities $(\mu\nu | \lambda\sigma)$, the two-electron integrals (equation 1.14.1), in the VAX, Trace / Unix, and IBM environments thus limiting the calculations to a maximum of 255 basis functions, and a 16-bit label in the Cray COS environment limiting the calculations to a maximum of 65535 basis functions.

In the Raffenetti mode of storage (default for HF or GVB, including first and second derivative), the two linearized suffixes $(\mu\nu)$ and $(\lambda\sigma)$ are packed into a machine word, where $(\mu\nu) = (\mu(\mu - 1) / 2 + \nu)$. This gives a limitation of 361 basis functions on a 32 bit machine.

The effective core potential (ECP) feature discussed in Chapter I is available in G90, and is used in larger calculations, which would not have been possible due to the basis function storage limitations mentioned above. The ECP feature is also found in the H8 code discussed below.

As far as SCF and post-SCF processes there are only a few other restrictions. Complex HF calculations are limited to 180 basis functions, and complex MP2 calculations are limited to $O(N^3)$ words of main physical memory, where N is the number of basis functions. The GVB code is limited to 100 paired orbitals. The SCF=DM (steepest descent) is limited to 255 basis functions, although this can be avoided by using Direct-SCF, method described briefly in Chapter I.

The Hondo-8 Program

The current version of the Hondo-8 program has the following available features listed below:

1. Single configuration SCF wavefunctions of the following types can be calculated:
RHF - closed shell,
UHF - spin unrestricted,
ROHF - spin restricted open shell,
GVB - generalized valence bond,
MCSCF - multiconfiguration SCF, and
CI - configuration interaction.
2. The electron correlation correction to the energy of closed shell RHF wavefunctions can be calculated by means of Moller-Plesset perturbation theory at the second, third, and fourth order (with or without triple excitations) levels.
3. The effective core potential (ECP) approximation can be used.
4. Optimization of molecular geometries using the gradient of the energy with respect to nuclear coordinates is possible with all except the CI and MP wavefunction methods. Optimization can be carried out in cartesian space or in internal coordinate space, with the possibility of fixing certain cartesian or internal coordinates in the optimization.
5. The force constant matrix in cartesian space, and the vibrational spectrum, including infrared and Raman intensities, can be calculated with all except the CI and MP wavefunction methods.
6. Calculation of the dipole moment and polarizability derivatives with respect to the nuclear coordinates is possible, for use with a previously available force constant matrix. The force constant matrix can be transformed into the internal coordinate basis.
7. Transition state structures can be determined with all except the CI and MP wavefunction methods by taking advantage of the energy gradients.
8. The "Intrinsic Reaction Coordinate" (IRC) pathway can be determined with all except the CI and MP wavefunction methods by taking advantage of the energy gradients.
9. Molecular energies for several points on a potential energy surface can be calculated in a single run.
10. Non-gradient optimization of basis function exponents is possible. The H8 source code can be modified to carry out optimization of other non-linear parameters, for example contraction coefficients and geometrical parameters.
11. The minimum energy point on the crossing seam surface between two potential energy surfaces can be determined with RHF, UHF, ROHF, GVB, and MCSCF wavefunctions - all wavefunctions for which the program can compute analytical energy gradients.

12. The ubiquitous "electronic coupling matrix element" V_{ab} , for example, found in the electron transfer formalism can be calculated using RHF and UHF wavefunctions.

13. The following electronic properties can be calculated from the wavefunctions: (post SCF)

- a. dipole moment
- b. quadrupole moment
- c. octupole moment
- d. Mulliken population analysis
- e. valency and bond order analysis
- f. spin density at the nuclei
- g. electrostatic field at the nuclei
- h. electrostatic field gradient at the nuclei
- i. hyperfine interactions (Fermi contact term and anisotropic interaction)
- j. orbital localization
- k. electron and spin density maps
- l. electrostatic potential map
- m. dipole polarizabilities and hyperpolarizabilities
- n. frequency dependent polarizabilities and hyperpolarizabilities.

14. The potential due to finite point charges for a classical representation of an environment, or a uniform electric field can be incorporated into the one-electron Hamiltonian.

The H8 program can use: s, p, sp, d, spd, f, and g types of Gaussian basis function. When the ECP approximation is used (described briefly in Chapter I), if the energy gradient is requested, the g type wavefunction may not be used.

The current code can handle up to 128 atoms, 512 shells for a total of 2048 unique Gaussian exponential functions. This current version of H8 is limited to 255 basis functions using canonical electron repulsion integrals, and 360 basis functions when supermatrix integrals are used under non-direct SCF. This limitation is similar to that of G90. When direct-SCF is used up to 1024 basis functions can be used for word oriented machines under the RHF and UHF option only. The H8 program working area memory can be specified by the value in the variable MEMSCM in the common block /SCM/ at compilation time, with each unit value equal to 8 byte words. Thus if 500,000 is specified, then 4Mb of working area plus the 6Mb (Hondo-8 code size) is the required to run the program (i.e., 10Mb).

Hondo-8 Strategy for Polarizability and Hyperpolarizability Calculation

The coupled perturbed Hartree-Fock theory (CPHF) outlined on page 9 of Chapter I, for non frequency dependency has been extended to frequency dependent nonlinear optical property calculations [35] in H8. Although frequency dependency of NLO properties is treated in H8, it is not used in the scope of this dissertation, since it is a small effect in comparison to the magnitude of the NLO properties studied. The general CPHF formalism of treating NLO properties also applies in the non frequency dependent case. The following description outlines the calculation procedure that H8 uses to calculate α , β , and γ . In the current work, only zero frequency calculations of α , β , and γ are performed. To calculate the polarizability (α) the following steps are performed:

1. An initial guess for the Fock matrix along direction a is made:

$$F^a = \mu^a. \quad (2.1)$$

2. The matrices G^a , the two-electron part of the Fock matrix, U^a , the transformation matrix, C^a , the coefficient matrix, and D^a , the density matrix are calculated.
3. A new F^a is calculated from G^a , and H^a the one-electron part of the Fock matrix.
4. Convergence of U^a is tested against a threshold value.

The steps 2 through 4 are iterated until convergence is reached. The tensor α_{ab} is calculated from minus the trace of the product $H^a D^a(\omega)$. The values U^a and G^a are stored for the β and γ calculations. Note that the a superscript, and later the b,c,d superscripts denote derivatives in tensor directions a, b, c, and d. To calculate the first hyperpolarizability, β , the following steps are performed:

1. An initial guess of F^{bc} is calculated from the constant part of D^{bc} .

Similar steps to 2 through 4 are iterated until convergence of U^{bc} is achieved. The tensor β_{abc} is calculated from minus the trace of the product $H^a D^{bc}(\omega, \omega)$. The values ϵ_{bc} , the Lagrangian multipliers, along with the values: U^{bc} , G^{bc} , and D^{bc} are stored for γ calculations.

To calculate the second hyperpolarizability, γ , the following steps are performed:

1. An initial guess of F^{abc} is calculated from the constant part of D^{bcd} .

Similar steps to 2 through 4 are iterated until convergence of U^{bcd} is reached. The value g is calculated from minus the trace of the product $H^a D^{bcd}(\omega, \omega, \omega)$.

Direct SCF

One of the limitations of performing ab initio calculations is the large disk storage space requirement, primarily used to store the one and two electron integrals. An alternative method is the direct SCF method in which the one and two electron integrals are not stored, rather they are recalculated for instance of the integral that is required. The tradeoff is more CPU time required at a saving of disk storage space. In current computer technology, very fast CPU's are available, but the cost of disk storage is still at a premium. The direct SCF option is available in the Gaussian 90 code (G90), and is described in the G90 documentation [12]. This option of G90 was used in some of the calculations of this dissertation.

Effective Core Potential Method

There is usually a relatively large energy separation between the energies of core and valence orbitals, and due to this large energy difference, core and valence orbitals interact to a lesser degree than core orbitals with core orbitals and valence orbitals with valence orbitals. The effective core potential method (ECP) [75, 76] replaces the core orbitals of atomic centers of molecules with an effective or averaged potential, which is generated from atomic core orbitals. The G90 and H8 computer codes treat ECP operators as sums of products of polynomial radial functions, Gaussian radial functions and angular momentum projection operators on the various centers which the ECP method is specified [11,12]. The use of the ECP allows the calculations of larger molecules, or molecules with larger basis sets (i.e., the use of more polarization function sets (pfs)). ECP methods are used for some of the calculations of NLO properties described in Chapter IV.

Practical Experience of Using the R6000 and IBM 3090 and Sun Sparc 2 Systems

The nature of the calculation of dipole polarizabilities (DP) and dipole hyperpolarizabilities (DH) is such that very long CPU times are needed to complete a calculation. This presents problems in a practical computing environment. Currently the S2, the R6000 and the CAS IBM 3090 systems do not have uninterruptable power supplies (UPS), and thus a calculation that does not use a checkpoint / restart capability must be restarted from the beginning in the event of a power fault. Typical of calculations performed in this dissertation which required an unusually large amount of CPU time were: large basis set calculations (i.e., calculation IV / 3.3 on NH_3 , 162 basis functions), slowly converging calculations (i.e., calculations on H_2Se in Chapter V), and MP2 calculations (i.e., calculation V / 3.8 on NH_3) which required automatically applying an electric field up to thirteen times to calculate DP and DH quantities. The CAS IBM 3090 system is a time sharing systems running many batch jobs concurrently, and the calculation of DP and DH quantities using the H8 or G90 programs require a large amount of disk storage, a large amount of random access memory (RAM), and at least several hours of CPU time at a time. There is usually a large discrepancy between CPU time and latency time. Typically, latency times are three to ten times that of CPU time. The long latency times are probably due to: a.) the inefficiency of time shared memory paging, and b.) heavy usage by other users. Time shared memory paging is inefficient because input / output (IO) time is long compared to direct RAM access, and these large programs (H8, G92, and G90) may require a large amount of memory to be paged, and a thrashing back and forth effect of memory pages may result. The long latency times were a major problem in completion of the calculations performed in this dissertation because jobs were often canceled as the period for system preemption to perform system backup and system maintenance activities approached.

This is because at CAS, a frozen state model for system backup is used. This requires cancelling of all jobs running on the system at the time of backup, and not starting any new jobs several hours before preemption. Another problem with the use of a time shared mainframe system (i.e., the 3090 system) to perform large calculations, is that the amount of CPU time, and disk storage requirements must be requested at job submittal time within the job control language (JCL). In general, one does not know exactly how much CPU time or disk storage is required for a calculation, and only a guess can be made based on similar calculations from experience.

In the 3090 MVS environment, a job with a request of a large amount of CPU time, may sit in the execution queue for one to seven days before it begins execution depending on how much CPU time was requested. The net result was experienced all too frequently, was that a job after sitting in the queue several days, begins execution at a time that the requested disk space is not available and thus abends or stops. An additional shortfall of the MVS JCL, enforced on the user, is that it does not check for disk space availability before it starts execution, thus a job may stop due to a lack of required disk storage. It should be pointed out that hardware failure, a problem that plagues long runs on many machines, was not a serious problem since the current computer technology used for the IBM 3090 is very reliable, and hardware failure seldom occurs. However several of the longer computational jobs performed in the scope of this dissertation experienced disk failure on the 3090, which required the runs to be resubmitted. For example, a MP2 calculation on NH_3 (calculation V / 3.8, 113 basis functions) required about 30 hours of CPU, which had a latency + queue time of about three weeks. In order to minimize any delay due to queue wait time several restart jobs were enqueued simultaneously, so that all the enqueued jobs aged in the queue simultaneously and one job executed after the other.

If any one job failed, all subsequent runs failed, and the calculation must be started from the very beginning. Also if there is an error in any one job and fails, all subsequent jobs will also fail, since these multiple jobs are propagated from the same named checkpoint file. Another problem with the use of the G90 code on the IBM 3090 is with the direct SCF option. The program, depending on the size of the molecule / basis set, decides whether to do **all**, **part**, or **none** of the one and two electron integrals on the direct SCF or per instance calculation basis. Thus, at the submission of a job, the researcher is not certain how much CPU time or disk storage is required by the job. A wrong guess would result in the failure of the job.

Due to the inflexibilities of using the IBM 3090 mainframe system described in previous paragraphs, the use of a workstation dedicated entirely to the calculation of NLO properties was explored. The workstation chosen was an IBM RISC 6000 / 320h. The R6000 system provided much more flexibility in scheduling and usage. Job scheduling was done by mutual consent of the members of the research group which shared the use of the system at the time. Up to three modest size calculations could be started at the same time on the R6000 (i.e., each calculation would have about 330Mb of disk storage). Since CPU time on each job was not limited (i.e., 24 hour limit on the 3090) calculations could be performed on the R6000 that were not possible on the IBM 3090. One such calculation is I / 7.5, a Ge_2H_4 calculation which had slow converging β values to give the γ calculations, which took three weeks of CPU time and nearly all of the 1Gb disk. Such a calculation could not have been run on the CAS 3090 system. However the type of calculations which could be performed on the R6000 system was limited by the relatively small 1Gb disk (the largest disk possible, purchased with available funds at the time of the purchase).

There is a bug in the 3090 G90 code with respect to allocation of virtual memory, that limited the MP2 calculations to about 150 contracted basis functions or less. No matter how much memory the 3090 runs requested (up to 1024Mb), the G90 program was not able to utilize it properly. The G92 code running on the Sun S2 does not have this problem, and thus larger basis set calculations were able to be completed, but the S2 was based upon a 40Mhz second generation Sparc chip, so it was rather slow. For example for a MP2 calculation on a molecule of about 150 basis functions took almost four days to complete. The S2 had a large 3.9Gb disk, and thus more scratch space was available so that in principle larger calculations could be ideally be performed. However, experience has indicated that calculations taling over ten days have little chance of being brought to completion because of power outages, air condition failures, systems and / or operator intervention.

CHAPTER III

CALCULATION RESULTS FOR AMMONIA, PHOSPHINE, AND ARSINE

There is always a trade-off between the use of a basis set (bs) which includes many polarization functions (pfs), because they are needed to get the most accurate results and the need to limit the number of basis functions (bfs) because of limited computational resources. Throughout the development of ab initio work, the amount of available CPU time and disk storage have been and still are the two limiting factors which determine what calculations can be performed or not performed. In order to gain an understanding of the effect of limiting the bs, a series of calculations with particular emphasis on the number and type of polarization basis functions have been performed, on the series AH_3 , where $A = N, P, As$, [i.e., ammonia (NH_3), phosphine (PH_3), and arsine (AsH_3)]. This series is also used to investigate whether the same pfs can be used for hydrogen independent of the nature of the atom to which the hydrogen is attached.

In the process of determining a cost effective bs suitable for calculating acceptable β 's and γ 's several questions were posed:

What is the minimum set of pfs needed for the hydrogen atom?

What is the importance of adding f pfs to the N, P, or As atom?

What is the effect of correlation at the MP2 level?

Calculations were performed on each of the three molecules to determine the answers to the three questions above.

Ammonia

One of the starting point bss for the nitrogen atom in ammonia is taken from Table 7.73.2 in the book of bss compiled by Csizmadia et al. [5]. This [7s4p] bs was developed by Lie and Clementi [85] (Table B.1 of this dissertation). This bs for the nitrogen atom is of triple zeta quality or better. Alternative starting point bss also investigated for the nitrogen atom are the [5s3p] triple zeta valence (TZV) bs (Table B.2), the 6-31G bs [86,87], and the 3-21G bs [82]. The reason that the smaller 6-31G and 3-21G bss are used, is that the ammonia calculations are used as prototype calculations for larger molecules discussed later in this dissertation, and the experience gained from the ammonia calculations is expected to aid in the selection of a good set of pfs for these larger molecules.

One set of d pfs, which is used in ammonia calculations, was the nitrogen energy optimized 4d pfs of Fellers and Davidson [28], which consist of the d(2.74, 0.94, 0.32, 0.11) polarization function (pf) sets. Another set of pfs which is used for ammonia is that of Dykstra [36], that is- the nitrogen s(0.06), p(0.04, 0.006), d(0.9, 0.13, 0.02), and the hydrogen s(0.06), and p(0.9, 0.1) pf sets. For the nitrogen atom, various p pfs and d pfs were added to these sets used, and the best set was determined from repeated trials of actual calculations in which pfs were added until no further improvement (to within 10%) in the desired dipole polarizability (DP) and dipole hyperpolarizability (DH) properties were obtained.

The starting point bss used for hydrogen were: the contracted 1s bs developed by Ditchfield, Hehre, and Pople [84] which is tabulated in T1.42.1 of Csizmadia [5] (Table B.9), the TZV bs (Table B.10), the H8 6-31G bs (Table B.11), and the 3-21G bs (Table B.12). Various combinations of p pfs and d pfs were added to the hydrogen in order to determine the optimal sets.

The first calculation performed is calculation IV / 3.3, and is based upon the TZV bs for nitrogen (Table B.2), i.e., a (11s6p) $\rightarrow$ [5s3p] contracted bs, and the TZV, [3s], bs for hydrogen. This reference calculation for ammonia, column IV of Table 3.3, (the notation hereafter for each calculation will be denoted as column X / Table Y, i.e., IV / 3.3) consists of a 162 bfs with a nitrogen TZV [5s3p] bs augmented by the s(0.06), p(0.0536, 0.02144, 0.01072), and d(2.74, 0.94, 0.32, 0.11, 0.042, 0.016) pf sets and hydrogen TZV [3s] bs augmented by the s(0.06), p(1.0, 0.5, 0.25, 0.125), and d(0.5, 0.25, 0.125) sets of pfs of the three hydrogens, where the numbers inside the parentheses denote the value of the Gaussian exponents. The resultant bs is a [6s6p6d / 4s4p3d] bs. This calculation contains the most complete set of pfs and thus serves as a reference for other smaller bs calculations. Calculation IV / 3.3 gave $\mu = 0.6362$ a.u. compared to an experimental value of Marshall and Muentert [63] of $\mu = 0.5789$ a.u. (IV / 3.1) (Table 3.1) (a difference of +9.99%). The DM of IV / 3.3 is also similar to Feller, Boyle and Davidson's [28] HF result (I / 3.1), and Feller, Boyle, and Davidson's CI results [28] (II and III / 3.1) are between their HF result and the experimental result. Calculation IV / 3.3 also gave $\bar{\alpha} = 12.96$ a.u. compared to an experimental value [89,90,91] of $\bar{\alpha} = 14.80$ a.u. (V / 3.2) (Table 3.2) (a difference of -12.43%). Spackman's HF results [46] (I / 3.2) when compared to our reference IV / 3.3: μ differs by +15.7%, and $\Delta\alpha$ differs by -89%. These differences are probably due to the relatively small bs [46]. Sadlej's HF results (III / 3.1) agree well with the reference (IV / 3.3), which is also in comparatively good agreement with the published results of G. Maroulis [37] (I / 3.3) which consists of a (11s7p3d1f/6s2p1d) $\rightarrow$ [6s4p3d1f/4s2p1d] calculation with 94 contracted bfs. Thus comparison of the reference calculation IV / 3.3 with the results of Maroulis (I / 3.3) gave the results: β_{zzz} differs by +9.75%, $\bar{\beta}$ differs by +3.02%, $\Delta\beta$ differs by -12.60%, and $\bar{\gamma}$ differs by -3.02%. Maroulis chose his pf exponents by energy optimization (Chapter I, p. 41).

Table 3.1 Feller, Boyle and Davidson Results and Experimental Result of ammonia

	I ^a	II ^b	III ^c	IV ^d
μ (A.U.)	0.6359	0.6118	0.6130	0.5789
μ (Deb.)	1.6163	1.5551	1.5581	1.4714

- Feller, Boyle and Davidson's HF result [10s8p4d/6s4p1d] **130bfs** [28]
- Feller, Boyle and Davidson's SD-CI result [10s8p4d/6s4p1d] **130bfs** [28]
- Feller, Boyle and Davidson's MRSD-CI result [10s8p4d/6s4p1d] **130bfs** [28]
- Marshall and Muentner's experimental result [63]

Table 3.2 Spackman's and Sadlej's Results of ammonia

	I ^a	II ^b	III ^c	IV ^d	ve
μ (A.U.)	0.7372	0.6817	0.6369	0.5802	0.5789
μ (Deb.)	1.8737	1.7328	1.6189	1.4747	1.4714
a_{xx}	12.48	13.74	12.75	13.76	14.15
a_{zz}	12.54	15.53	13.28	15.66	16.09
$\bar{\alpha}$	12.50	14.33	12.93	14.39	14.80
$\Delta\alpha$	0.055	1.80	0.53	1.90	1.94

- Spackman's HF results **34bfs** [46]
- Spackman's MP2 results **34bfs** [46]
- Sadlej's HF results [5s3p2d / 3s2p] **53bfs** [61]
- Sadlej's MBPT(4) results [5s3p2d / 3s2p] **53bfs** [61]
- Marshall and Muentner's experimental results [63,89,90,91]

Table 3.3 NH₃ Reference Comparison

	I ^a	II ^b	III ^c	IV ^d	ve
μ (A.U.)	0.6406	0.6422	0.6369	0.6362	0.6345
μ (Deb.)	1.6283	1.6323	1.6188	1.6170	1.6127
α_{xx}	12.75	12.65	12.77	12.78	12.77
α_{zz}	13.27	13.19	13.35	13.32	13.30
$\bar{\alpha}$	12.92	12.83	12.96	12.96	12.94
$\Delta\alpha$	0.52	0.55	0.58	0.54	0.53
β_{xxx}	-8.77	-9.13	-----	-8.67	-8.65
β_{xxz}	7.21	7.80	7.00	7.34	7.56
β_{zzz}	11.71	9.80	11.10	10.67	10.58
β	15.68	15.24	15.06	15.21	15.42
$\Delta\beta$	-9.92	-13.60	-9.90	-11.35	-12.10
γ_{xxxx}	1232	1070	1200.00	1264.63	1294.47
γ_{xxxz}	-106	-119.9	-----	-67.81	-70.65
γ_{xxyy}	412	356.6	-----	421.54	431.48
γ_{xxzz}	1077	1070	1100.00	1081.35	1113.57
γ_{zzzz}	4319	4261	4500.00	4588.33	4610.90
γ	2383	2278.84	2400.00	2457.21	2503.60

- a. Maroulis [6s4p3d1f / 4s2p1d] **94 bfs** [37]
- b. Dykstra [6s5p3d / 4s2p] ELP bs **69 bfs** [36]
- c. Sekino and Bartlett HF SCF results [5s3p2d / 3s2p1d] **71 bfs** [65]
- d. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.01072), d(2.74, 0.94, 0.32, 0.11, 0.042, 0.016) H-(TZV) + s(0.06),p(1.0, 0.5, 0.25, 0.125), d(0.5, 0.25, 0.125) **162 bfs** [6s6p6d / 4s4p3d]
- f. N-(T7.73.2) + s(0.070547),p(0.0536, 0.02144), d(2.74, 0.94, 0.32, 0.11, 0.037) H-(T1.42.1) + p(0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625) **149 bfs** [8s6p4d / 1s4p3d]

The smaller Dykstra ELP calculation [36] which is reported in II / 3.3 compares reasonably with the reference calculation of IV / 3.3 for most of the NLO properties but differs considerably for others, i.e., $\bar{\beta}$ differs by -2.43%, but $\Delta\beta$ differs by +25.73%, and $\bar{\gamma}$ differs by -7.26%.

Recently a HF SCF calculation was reported by Sekino and Bartlett [65] (III / 3.3) which used a bs very similar to that of Sadlej [61], which not only gave results for μ and α like that of the reference, but also gave results for β and γ which were close to that of Maroulis [37] (I / 3.3). Comparing the reference IV / 3.3 to Sadlej's HF results [61] (III / 3.1) gave similar results.

Another calculation V / 3.3 used the T7.73.2 nitrogen basis (Table B.1) was also performed. This nitrogen bs consists of a (13s8p) $\rightarrow$ [7s4p] contracted bs, which is larger than the TZV bs for nitrogen. The hydrogen bs is used is that of the T1.42.1 [1s] bs (Table B.9). The nitrogen s pf is derived from the outermost s(0.0141093) basis function of the T7.73.2 bs, with a rf of 0.2, and the p pf sets are derived from the outermost p(0.1346) basis function, with a rf of 0.4, and the extra d(0.037) pf is derived from the Davidson d(0.11) pf with a rf of 0.35. This calculation produced results very similar to the reference calculation IV / 3.3. The only substantial difference is for $\Delta\beta$ which differs by +6.60%. The general similarity between the larger calculations reported in Table 3.3 supports the idea that at least at the HF SCF level results for the biggest calculations represent converged limit results.

1. TZV calculations

A. Table 3.4 Results - TZV calculations (NH_3) - Study of nitrogen p pfs

In Table 3.4 are the results of a series of calculations using the TZV bs, using the Dykstra ELP set of pfs (reported in Chapter I, Table 1.2). These pfs were developed by Dykstra as a reasonable compromise of a compact set of pfs to produce good DP and DH results, and later we will make an attempt to still further reduce the Dykstra ELP set of pfs.

Table 3.4 NH₃ TZV Results - Study of nitrogen p pfs

	I ^a	II ^b	III ^c	IV ^d	ve	VI ^f
μ (A.U.)	0.6428	0.6430	0.6430	0.6430	0.6430	0.6430
μ (Deb.)	1.6340	1.6343	1.6343	1.6345	1.6343	1.6342
α_{xx}	12.72	12.63	12.63	12.72	12.72	12.64
α_{zz}	13.21	13.21	13.22	13.21	13.22	13.22
$\bar{\alpha}$	12.88	12.83	12.83	12.88	12.89	12.83
$\Delta\alpha$	0.49	0.58	0.59	0.49	0.50	0.58
β_{xxx}	-8.78	-9.83	-9.83	-8.09	-8.84	-9.74
β_{xxz}	7.55	6.48	6.48	7.73	7.54	6.31
β_{zzz}	10.21	9.09	8.95	9.79	9.25	8.51
$\bar{\beta}$	15.19	13.23	13.15	15.15	14.60	12.68
$\Delta\beta$	-12.44	-10.35	-10.49	-13.40	-13.37	-10.42
γ_{xxxx}	1219.77	1083.64	1083.72	1219.65	1207.64	1045.02
γ_{xxxz}	-71.17	-118.55	-118.09	-68.25	-68.94	-112.17
γ_{xxyy}	406.58	361.21	361.23	406.54	402.54	348.33
γ_{xxzz}	1086.71	1024.14	1023.97	1100.06	1096.10	1010.00
γ_{zzzz}	4364.08	4259.59	4243.42	4433.81	4413.07	4173.51
γ	2392.72	2249.16	2245.84	2417.29	2403.57	2200.05

- a. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.00858), d(0.9, 0.13, 0.02)
H-(TZV) + p(0.9, 0.1), d(0.1) **87 bfs** [6s6p3d / 3s2p1d]
- b. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.00858), d(0.9, 0.13, 0.02)
H-(TZV) + p(0.9, 0.1) **69 bfs** [6s6p3d / 3s2p]
- c. N-(TZV) + s(0.06),p(0.0536, 0.02144), d(0.9, 0.13, 0.02)
H-(TZV) + p(0.9, 0.1) **66 bfs** [6s5p3d / 3s2p]
- d. N-(TZV) + s(0.06),p(0.04, 0.006), d(0.9, 0.13, 0.02)
H-(TZV) + p(0.9, 0.1), d(0.1) **84 bfs** [6s5p3d / 3s2p1d]
- e. N-(TZV) + s(0.06),p(0.04), d(0.9, 0.13, 0.02)
H-(TZV) + p(0.9, 0.1), d(0.1) **81 bfs** [6s4p3d / 3s2p1d]
- f. N-(TZV) + s(0.06),p(0.04), d(0.9, 0.13, 0.02)
H-(TZV) + p(0.9, 0.1) **63 bfs** [6s4p3d / 3s2p]

Calculation I / 3.4 consists of a [5s3p / 3s] contracted bs, with the nitrogen bs augmented by the s(0.06), p(0.0536, 0.02144, 0.008576) pfs and the Dykstra 3d(0.9, 0.13, 0.02) pfs, and the hydrogen bs augmented by the 2p(0.9, 0.1), and d(0.1) pf sets. As in IV / 3.3, these nitrogen p pfs are derived by using a rf of 1 / 2.5. The results of I / 3.4 are similar to the reference IV / 3.3 except for $\Delta\beta$ which differs by +9.60%. In II / 3.4 the d(0.1) pf set is removed from the hydrogen bs, which produced considerably different β values, that is: β_{xxx} differs by +13.38%, β_{xxz} differs by -11.71%, β_{zzz} differs by -14.80%, $\bar{\beta}$ differs by -13.01%, $\Delta\beta$ differs by -7.58%, and $\bar{\gamma}$ differs by -8.40%, when compared to IV / 3.3. In III / 3.4, the diffuse p(0.00858) pf set of nitrogen is removed, and there is very little change from II / 3.4.

In IV / 3.4, the nitrogen Dykstra p(0.04, 0.006) pf sets are used. This calculation (IV / 3.4) can be visualized as collapsing the two nitrogen p pfs of exponent 0.0536, and 0.02144 into one p pf of exponent 0.04, i.e., an intermediate value between 0.0536 and 0.02144, plus a diffuse p(0.006) pf. The results of this calculation IV / 3.4 changed very little compared to calculation I / 3.4, except for $\Delta\beta$ which differs by +7.71%. In calculation V / 3.4 the nitrogen p(0.006) pf is removed and produced results very similar to the III / 3.4. Calculation VI / 3.4 compared to the I / 3.4 gave the results: $\bar{\beta}$ differs by -3.88%, and $\Delta\beta$ differs by +7.48%. Thus the d(0.1) pf set on hydrogen is needed for accurate β and γ values.

A comparison of III / 3.4 to II / 3.4 showed that the nitrogen p(0.00858) pf is not needed and a comparison of V / 3.4 to IV / 3.4 showed that the Dykstra nitrogen p(0.006) pf is also not needed for NLO properties under the consideration that there are adequate pf sets of the hydrogen.

From this series of calculations (Table 3.4), it is concluded that the Dykstra ELP bs [36] although a good compromise which uses a small number of bfs only produces qualitative values of α , β , and γ . The results could be considerably improved by the use of at least one d(0.1) pf set on the hydrogens. A comparison of VI / 3.4 to III / 3.4 also shows that the nitrogen p(0.04) pf is a good substitute for the p(0.0536,0.02144) pf sets.

B. Tables 3.5 and 3.6 Results - Additional TZV calculations (NH_3) - Study of nitrogen p,d,f pfs

A series of calculations were performed (Table 3.5 and 3.6) to better understand the effects of p, d, and f pfs of the nitrogen of ammonia. Calculation I / 3.5 has the same nitrogen bs of IV / 3.3, except for a much smaller set of pfs, namely the p(0.9,0.1), and d(0.1) pf sets are used on hydrogen. This calculation (I / 3.5) produced similar results to IV / 3.3. Calculation II / 3.5 (102 bfs) used the same bs as in I / 3.5 except the nitrogen d(2.74) pf was removed. The changes are very small for all properties considered. Calculation III / 3.5 has the next inner d(0.94) pf set removed. This removal, when compared to the results of I / 3.5, shows a considerable change (+15.1%) in β_{zzz} .

Calculation IV / 3.5 had the d(0.10) pf of hydrogen removed, and when compared to III / 3.5 shows considerable change in the β tensor ($\bar{\beta}$ differs by -8.09%, and $\Delta\beta$ differs by +9.94%). The implication of this finding is that the use of the larger nitrogen 5d pf sets (Table 3.5) versus the 3d pf sets (Table 3.4) does reduce the importance of the d(0.10) pf set of hydrogen, although even for the larger set of pfs on nitrogen this produces significant changes.

In calculation V / 3.5 the nitrogen p(0.01072) pf is removed, and there were no significant changes. In calculation VI / 3.5 the nitrogen outermost d(0.016) pf is removed. In both calculations there are no significant changes in the results. Calculation I / 3.6 had 2f(0.25,0.125) pf sets added to the nitrogen bs, which produced a $\bar{\beta}$ which differs by +8.55%.

Table 3.5 NH_3 TZV Results - Study of nitrogen p and d pfs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	0.6351	0.6371	0.6578	0.6564	0.6564	0.6564
μ (Deb.)	1.6143	1.6194	1.7618	1.6685	1.6685	1.6685
α_{xx}	12.77	12.76	12.74	12.71	12.70	12.70
α_{zz}	13.27	13.26	13.26	13.27	13.27	13.27
$\bar{\alpha}$	12.94	12.93	12.92	12.89	12.89	12.89
$\Delta\alpha$	0.50	0.50	0.52	0.56	0.57	0.57
β_{xxx}	-9.04	-9.08	-9.24	-9.06	-9.13	-9.06
β_{xxz}	7.49	7.51	7.51	7.29	7.29	7.14
β_{zzz}	10.22	10.37	11.76	10.03	10.06	9.89
β	15.12	15.23	16.07	14.77	14.78	14.50
$\Delta\beta$	-12.25	-12.16	-10.77	-11.84	-11.81	-11.53
γ_{xxxx}	1289.75	1293.11	1301.55	1212.82	1214.94	1186.18
γ_{xxxz}	-57.87	-57.84	-61.02	-92.56	-93.15	-99.07
γ_{xxyy}	429.91	431.03	433.84	404.27	4.4097	395.39
γ_{xxzz}	1115.97	1117.67	1136.62	1106.57	1114.23	1097.26
γ_{zzzz}	4507.94	4519.76	4612.49	4549.35	4587.46	4550.77
γ	2482.23	2487.75	2525.95	2441.96	2456.84	2420.58

- a. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.01072), d(2.740.94,0.32,0.11,0.042, 0.016) H-(TZV) + s(0.06),p(0.9, 0.1), d(0.1) 108 bfs [6s6p6d / 4s2p1d]
- b. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.01072), d(0.94,0.32,0.11,0.042, 0.016) H-(TZV) + s(0.06),p(0.9, 0.1), d(0.1) 102 bfs [6s6p5d / 4s2p1d]
- c. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.01072), d(0.32, 0.11, 0.042, 0.016) H-(TZV) + s(0.06),p(0.9, 0.1), d(0.1) 96 bfs [6s6p4d / 4s2p1d]
- d. N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.01072), d(0.32, 0.11, 0.042, 0.016) H-(TZV) + s(0.06),p(0.9, 0.1) 78 bfs [6s6p4d / 4s2p]
- e. N-(TZV) + s(0.06),p(0.0536, 0.02144), d(0.32, 0.11, 0.042, 0.016) H-(TZV) + s(0.06),p(0.9, 0.1) 75 bfs [6s5p4d / 4s2p]
- f. N-(TZV) + s(0.06),p(0.0536, 0.02144), d(0.32, 0.11, 0.042) H-(TZV) + s(0.06),p(0.9, 0.1) 69 bfs [6s5p3d / 4s2p]

Table 3.6 NH₃ TZV Results - nitrogen f pfs

	Ia
μ (A.U.)	0.6581
μ (Deb.)	1.6726
α_{xx}	12.75
α_{zz}	13.28
$\bar{\alpha}$	12.93
$\Delta\alpha$	0.53
β_{xxx}	-9.01
β_{xxz}	7.58
β_{zzz}	11.07
β	15.74
$\Delta\beta$	-11.67
γ_{xxxx}	1257.15
γ_{xxxz}	-80.67
γ_{xxyy}	419.04
γ_{xxzz}	1110.03
γ_{zzzz}	4598.55
$\bar{\gamma}$	2478.21

- a. N-(TZV) + s(0.06),p(0.0536, 0.02144), d(0.32,0.11,0.042,0.016), f(0.25,0.125)
H-(TZV) + s(0.06),p(0.9, 0.1) **95** bfs [6s5p4d2f / 4s2p]

These calculations (Table 3.5) show that removal of the nitrogen inner d pfs do not produce any significant changes, and removal of the outer d pfs also do not produce any significant changes in the results. The addition of f pfs (Table 3.6) produces a change in β values.

2. Table 3.7 Results - Calculations based on N [7s4p] bs (NH_3) - Further study of nitrogen d pfs

Another set of calculations (Table 3.7) was performed on ammonia starting with the larger (13s8p) $\rightarrow$ [7s4p] bs developed by Lie and Clementi [85], which is tabulated in T7.73.2 of Csizmadia book [5] (Table B.1 of this dissertation). The energy optimized 4d pf sets reported by Feller, Boyle and Davidson [28] are used in the nitrogen bs in I / 3.7 and II / 3.7. Another nitrogen d pf set used in III / 3.7 through VI / 3.7 were generated from the Feller, Boyle, and Davidson d(2.741) pf using a rf of 0.5. Two nitrogen p pfs were generated from the most diffuse p valence bf using a rf of 0.5. The hydrogen bs is augmented by the 3p(0.5, 0.25, 0.10) and 3d(0.5, 0.25, 0.10) pf sets. The first hydrogen p and d pfs used the initial exponent of 0.5, and with a rf of 1/2.0 the others were generated. The Dykstra hydrogen p(0.9,0.1) pfs are used as well as the d(0.1) pf are used in Table 3.7 as designated in the footnotes.

Calculation I / 3.7 which had 140 bfs gave results which were practically identical to those of IV / 3.3. A comparison of I / 3.7 to IV / 3.3 indicated that the p(0.10) set of hydrogen was equivalent to the p(0.125, 0.0625) pf sets, and the d(0.1) pf set was equivalent to the d(0.125, 0.0625) pf sets. Calculation II / 3.7 has only one d (0.10) pf set of the hydrogens, but compared to I / 3.7 produced only insignificant changes (i.e., the hydrogen inner d(0.5, 0.25) pf sets are not very important for ammonia).

The next three calculations III / 3.7, IV / 3.7, and V / 3.7 form a series where the inner d pfs of nitrogen were removed systematically to study their effects on DP and DH properties.

Table 3.7 NH₃ T7.73.2 Results

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	0.6348	0.6339	0.6331	0.6336	0.6378	0.6303
μ (Deb.)	1.6134	1.6113	1.6091	1.6106	1.6210	1.6021
α_{xx}	12.77	12.77	12.74	12.74	12.74	12.70
α_{zz}	13.30	13.28	13.26	13.26	13.25	13.21
$\bar{\alpha}$	12.95	12.94	12.91	12.91	12.91	12.87
$\Delta\alpha$	0.53	0.51	0.52	0.52	0.51	0.51
β_{xxx}	-8.92	-8.74	-8.73	-8.71	-8.83	-8.58
β_{xxz}	7.32	7.22	7.15	7.15	7.19	7.25
β_{zzz}	10.73	10.55	10.71	10.78	11.01	8.47
β	15.22	14.99	15.01	15.05	15.23	13.78
$\Delta\beta$	-11.23	-11.11	-10.74	-10.67	-10.56	-13.28
γ_{xxxx}	1249.25	1248.55	1267.95	1267.56	1275.90	1200.13
γ_{xxxz}	-67.46	-62.91	-68.42	-68.45	-70.46	-49.86
γ_{xxyy}	416.41	416.18	422.64	422.51	425.29	400.04
γ_{xxzz}	1096.77	1099.42	1099.96	1100.31	1105.55	1092.75
γ_{zzzz}	4535.08	4484.78	4529.09	4532.63	4542.50	4416.15
γ	2450.69	2442.38	2462.02	2462.80	2473.42	2397.49

- a. N-(T7.73.2) + s(0.070547), p(0.047132, 0.023566), d(2.741, 0.941, 0.32, 0.11, 0.037), H-(T1.42.1) + p(0.5, 0.25,0.10), d(0.5,0.25,0.10) **140 bfs** [8s6p5d / 1s3p3d]
- b. N-(T7.73.2) + s(0.070547), p(0.047132, 0.023566), d(2.741,0.941, 0.32, 0.11, 0.037), H-(T1.42.1) + p(0.5, 0.25,0.10), d(0.10) **104 bfs** [8s6p5d / 1s3p1d]
- c. N-(T7.73.2) + s(0.070547), p(0.047132, 0.023566),d(2.741, 1.3705, 0.685, 0.3425, 0.17125, 0.0856, 0.0428,0.0214) H-(T1.42.1) + p(0.9, 0.1), d(0.10) **113 bfs** [8s6p8d / 1s2p1d]
- d. N-(T7.73.2) + s(0.070547), p(0.047132, 0.023566), d(1.3705, 0.685, 0.3425, 0.17125, 0.0856, 0.0428, 0.0214) H-(T1.42.1) + p(0.9, 0.1), d(0.10) **107 bfs** [8s6p8d / 1s2p1d]
- e. N-(T7.73.2) + s(0.070547), p(0.047132, 0.023566), d(0.685, 0.3425, 0.17125, 0.0856, 0.0428, 0.0214) H-(T1.42.1) + p(0.9, 0.1) d(0.10) **101 bfs** [8s6p8d / 1s2p1d]
- f. N-(T7.73.2) + s(0.070547), p(0.047132, 0.023566), d(2.741, 1.3705, 0.685, 0.3425, 0.17125, 0.0856, 0.0428, 0.0214) H-(T1.42.1) + p(0.9, 0.1) **95 bfs** [8s6p8d / 1s2p1d]

Calculation III / 3.7 has 8d pf sets starting with the Davidson d(2.741) pf, and subsequent pfs were generated using a rf of 0.5 (note that the d pf set used in the earlier calculations have a rf of about 0.35). Calculation IV / 3.7 has the d(2.741) pf set of nitrogen removed, and the calculation V / 3.7 has the d(1.3705) pf of nitrogen removed as well. A comparison of calculations III / 3.7 through V / 3.7 with the reference calculation IV / 3.3 does not show any significant difference (i.e., the nitrogen inner d pf sets are not very important, when the hydrogens have a good set of pfs (i.e., p(0.9,0.1), d(0.1))). These calculations III / 3.7 through V / 3.7 showed the same effect (i.e., no noticeable change) as in I / 3.5 through III / 3.5.

Calculation VI / 3.7 has no d pfs of hydrogen. Compared to III / 3.7 this gave the results: β_{zzz} differs by -20.91%, β differs by -9.52%, and $\Delta\beta$ differs by +30.49%. This showed again the importance of the d(0.10) pf of the hydrogen for accurate calculations of the first DH (β) even when a very large set of pfs are used on nitrogen.

3. Table 3.8 Results - 6-31G calculations (NH_3)

The 6-31G bs is much more compact than the TZV bs, and if it is adequate for DP and DH properties, the use of it would enable larger molecules to be studied than if the TZV bs is used. It requires in comparison to the 3-21G bs about the same amount of disk storage, but since there are more coefficients to optimize than the 3-21G bs, using it requires more CPU time than 3-21G bs calculations.

Several calculations in Table 3.8 were performed to explore the quality of μ , DP, and DH results of calculations using the 6-31G bs, the importance of f type pfs of nitrogen and the importance of correlation at the MP2 level.

Table 3.8 NH₃ 6-31G Results and MP2 Results

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	0.6438	0.6408	0.6410	0.6610	0.6013	0.5991
μ (Deb.)	1.6363	1.6288	1.6293	1.6801	1.5284	1.5227
α_{xx}	12.85	12.74	12.75	13.75	13.59	13.77
α_{zz}	13.26	13.30	13.30	15.54	15.40	15.83
$\bar{\alpha}$	12.99	12.93	12.94	14.35	14.19	14.46
$\Delta\alpha$	0.41	0.56	0.55	1.79	1.81	2.06
β_{xxx}	-9.18	-9.07	-9.13	-7.55	-6.62	-----
β_{xxz}	7.61	8.12	8.68	7.45	7.88	8.10
β_{zzz}	11.98	10.36	10.08	28.48	32.00	37.80
β	16.32	15.96	16.46	26.03	28.66	32.40
$\Delta\beta$	-10.85	-14.00	-15.96	+6.13	+8.36	13.50
γ_{xxxx}	1269.14	1233.21	1244.45	-----	-----	1800.00
γ_{xxxz}	-82.92	-90.94	-95.60	-----	-----	-----
γ_{xxyy}	423.04	411.06	414.81	-----	-----	-----
γ_{xxzz}	1139.57	1088.18	1103.77	-----	-----	1900.00
γ_{zzzz}	4448.70	4642.75	4635.83	-----	-----	8000.00
$\bar{\gamma}$	2478.27	2456.81	2473.88	-----	-----	4100.00

- a. N-(6-31G) + p(0.05), d(0.9, 0.13, 0.02)
H-(6-31G) + p(0.9, 0.1), d(0.1) **72 bfs** [3s3p3d / 2s2p1d]
- b. N-(6-31G) + s(0.06),p(0.03), d(0.9, 0.13, 0.02), f(0.125)
H-(6-31G) + p(0.9, 0.1), d(0.1) **83 bfs** [4s3p3d1f / 2s2p1d]
- c. N-(6-31G) + s(0.06),p(0.03), d(0.9, 0.13, 0.02), f(0.25, 0.125)
H-(6-31G) + p(0.9, 0.1), d(0.1) **93 bfs** [4s3p3d2f / 2s2p1d]
- d. N-(6-31G) + p(0.05), d(0.9, 0.13, 0.02), f(0.25, 0.125)
H-(6-31G) + p(0.9, 0.1), d(0.1) **92 bfs MP2** [3s3p3d2f / 2s2p1d]
- e. N-(T7.73.2) + s(0.070547), p(0.047132,0.023566), d(2.741, 1.3705, 0.685, 0.3425, 0.17125, 0.0856, 0.0428, 0.0214), H-(T1.42.1) + p(0.9, 0.1), d(0.1)
113 bfs MP2 [6s5p8d / 1s2p1d]
- f. MBPT(2) calculation from Reference [65] [5s3p2d / 3s2p]

Calculation I / 3.8 used the 6-31G bs augmented by the p(0.05) pf, the Dykstra d pfs for nitrogen, and the p(0.9, 0.1), d(0.1) pf sets for hydrogen. Compared to IV / 3.3 the individual b values change very little (β_{xxx} differs by +5.88%, β_{xxz} differs by +3.68%, β_{zzz} differs by +2.28%), and there are no significant changes in any of the other values.

In calculations II / 3.8 and III / 3.8 the addition to f pfs of the nitrogen has a considerable effect even at the HF SCF level (i.e., when calculation III / 3.8 is compared to the I / 3.8 it is found that: β_{xxz} differs by +14.06%, β_{zzz} differs by -15.86%, and $\Delta\beta$ differs by +41.10%).

The next calculation IV / 3.8 introduced electron correlation by performing MP2, second order Moller-Plesset perturbation theory, using the G90 program. There are considerable changes compared to calculation IV / 3.3: μ differs by +3.90%, α_{xx} differs by +7.59%, α_{zz} differs by +16.67%, β_{xxx} differs by -12.92%, and β_{zzz} differs by +166.92%, so that $\Delta\beta$ changes its sign and $\bar{\beta}$ is increased by 58% (γ calculations are not available in G90).

This calculation at the time it was performed was the first to show that correlation, calculated at the MP2 level is very important. Another MP2 calculation V / 3.8 was performed, using the larger bs of III / 3.7 (based upon the T7.73.2 nitrogen bs). The results of V / 3.8 also show a big change compared to calculation IV / 3.3, that is: μ differs by -5.49%, α_{xx} differs by +6.33%, α_{zz} differs by +15.62%, β_{xxx} differs by -23.64%, β_{xxz} differs by +7.36%, and β_{zzz} differs by +199.91%. The results of V / 3.8 compared to experimental values [46] gave the results: μ differs by +3.96%, and $\bar{\alpha}$ differs by -4.12%. These two MP2 calculations IV / 3.8 and V / 3.8 compare quite well with the experimental DM and DP values [63,89,90,91] (V / 3.2) as well as with Sadlej's MBPT(4) results [61] (IV / 3.2) and Spackman's MP2 results [46] (II / 3.4).

Recently Sekino and Bartlett [65] performed a second order many body perturbation theory (MBPT(2)) calculation similar to that reported by Sadlej [61], who however only reported μ and α values. The results of this calculation are given in VI / 3.8. These results compares well with the MP2 results of IV / 3.8 and V / 3.8, although β_{zzz} of V / 3.8 differs by 15.34% from VI / 3.8 resulting in a considerable $\Delta\beta$. If the reference HF SCF reference calculation IV / 3.3 is compared with the correlated results of VI / 3.8, the $\bar{\gamma}$ is also affected considerably by electron correlation (i.e., a -40.1% difference).

These results showed the great importance of electron correlation to NLO properties, especially for the first DH (β), which is increased almost two fold, and the second DH (γ) is also affected, but to a lesser degree.

4. Table 3.9 Results - 3-21G calculations (NH_3)

The 3-21G bs is a compact bs, which has been in the past often used for relatively large molecules in ab initio calculations. The question is whether the smaller 3-21G set is capable of producing results similar to that of larger bss described earlier. With this in mind, several calculations using various pf sets of nitrogen and hydrogen for ammonia built upon the 3-21G bs were performed and the results are presented in Table 3.9.

Calculation I / 3.9 consists of the p(0.04), d(0.9, 0.13, 0.02) pfs of nitrogen, and p(0.9, 0.1), d(0.1) of hydrogen added to the 3-21G bss. The results of I / 3.9 gave very good values for the dipole moment, α 's, and γ 's (i.e., $\bar{\gamma}$ differs only by -0.65% from the reference IV / 3.3), however β_{zzz} differs by +35.70%, $\bar{\beta}$ differs by +15.56%, and $\Delta\beta$ differs by -8.27% from calculation IV / 3.3. Since it was hoped that the 3-21G bs could be used for calculations of larger molecules, using ammonia as a prototype the effect of reducing the number of hydrogen pfs was investigated. In II / 3.9, the hydrogen d(0.1) pf set is removed which caused: β_{zzz} to differ by -7.52%.

Table 3.9 NH₃ 3-21G Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	0.6453	0.6448	0.6457	0.6430	0.7319	0.8589
μ (Deb.)	1.6402	1.6390	1.6412	1.6344	1.8603	2.2596
α_{xx}	12.81	12.75	12.63	12.61	12.57	11.24
α_{zz}	13.21	12.81	12.74	13.54	12.44	11.37
$\bar{\alpha}$	12.94	12.77	12.67	12.92	12.53	11.28
$\Delta\alpha$	0.40	0.06	0.11	0.93	-0.13	0.13
β_{xxx}	-8.87	-10.72	-10.92	-9.00	-11.05	-13.83
β_{xxz}	7.86	8.90	9.08	5.83	8.58	4.00
β_{zzz}	14.48	12.77	14.75	-0.70	20.46	15.47
β	18.12	18.34	19.75	6.58	22.57	14.08
$\Delta\beta$	-9.10	-13.93	-12.49	-18.19	-5.28	+3.47
γ_{xxxx}	1261.46	1043.01	1028.75	870.94	1032.06	1116.89
γ_{xxxz}	-83.39	-131.32	-134.29	-77.72	-146.12	-31.00
γ_{xxyy}	420.48	347.66	342.91	290.31	344.01	372.29
γ_{xxzz}	1125.98	997.24	985.89	1249.23	1027.53	1620.19
γ_{zzzz}	4338.29	3547.09	3540.33	5730.93	3861.78	8157.48
γ	2441.22	2063.48	2045.44	2610.07	2144.80	3523.32

- a. N-(3-21G) + p(0.04), d(0.9, 0.13, 0.02)
H-(3-21G) + p(0.9, 0.1), d(0.1) **72 bfs** [3s3p3d / 2s2p1d]
- b. N-(3-21G) + p(0.04), d(0.9, 0.13, 0.02)
H-(3-21G) + p(0.9, 0.1) **54 bfs** [3s3p3d / 2s2p]
- c. N-(3-21G) + p(0.04), d(0.9, 0.13, 0.02)
H-(3-21G) + p(0.1) **45 bfs** [3s3p3d / 2s1p]
- d. N-(3-21G) + p(0.04), d(0.9, 0.13, 0.02)
H-(3-21G) **36 bfs** [3s3p3d / 2s]
- e. N-(3-21G) + p(0.04), d(0.13, 0.02)
H-(3-21G) + p(0.1) **39 bfs** [3s3p2d / 2s1p]
- f. N-(3-21G) + p(0.05), d(0.05)
H-(3-21G) **24 bfs** [3s3p1d / 2s]

In III / 3.9, the p(0.9) pf sets of hydrogen are removed. A comparison of III / 3.9 to II / 3.9, showed only small changes in the dipole moment and α 's (i.e., $\bar{\alpha}$ differs by -0.78%), but $\bar{\beta}$ differs by +7.69%, and $\Delta\beta$ differs by -10.33%. Further removal of the p(0.1) pf set on hydrogen in calculation IV / 3.9 gave good values for the dipole moment $\mu = 0.6430$ a.u. and the α 's by comparison to that of I / 3.9 (the calculation with a 2p1d set on hydrogen), that is: $\bar{\alpha}$ differs by -0.15%, but $\Delta\alpha$ differs by +132.50%, β_{xxz} differs by -25.82%, β_{zzz} differs by -104.58%, and $\bar{\gamma}$ differs by +6.92%. These results clearly show the need for the p(0.1) pf set on the hydrogen.

The removal of the innermost d(0.90) set of nitrogen starting from III / 3.9 produced the results of V / 3.9 which show a large change in μ (i.e., +13.35% compared to III / 3.9). Again these are unsatisfactory results.

In calculation VI / 3.9, with 24 bfs, one p(0.05) and one d(0.05) pf set of nitrogen is left (i.e., these two pfs are used by Dupuis et al. on carbon for many hydrocarbon calculations [35]). This calculation produced the results: $\bar{\alpha}$ differs by -12.82%, β_{xxx} differs by +55.90%, β_{xxz} differs by -49.11%, β_{zzz} differs by +6.87%, and $\bar{\gamma}$ differs by +44.32% (compared to I / 3.9).

The use of an additional d(0.13) pf set of nitrogen in calculation V / 3.9 produced better results for $\bar{\gamma}$ (differs by +8.89%), but still produced poor estimates of β 's, that is: β_{xxx} differs by +5.98%, β_{xxz} differs by -30.02%, and β_{zzz} differs by -77.90% (compared to I / 3.9).

In calculation I / 3.10 (Table 3.10) the p(0.05), and d(0.13,0.05) pfs are used on the nitrogen, and no pfs are used on the hydrogen. The results of I / 3.10 show that the DM, and DP values are similar to those of V / 3.9, however the first and second DH did not compare as well as those of V / 3.9. This shows the importance of the hydrogen pfs.

Table 3.10 NH₃ 3-21G Results - no hydrogen p and d pfs

	1a
μ (A.U.)	0.7325
μ (Deb.)	1.8618
α_{xx}	12.50
α_{zz}	13.18
$\bar{\alpha}$	12.73
$\Delta\alpha$	0.68
β_{xxx}	-9.40
β_{xxz}	5.50
β_{zzz}	3.20
β	8.52
$\Delta\beta$	-13.30
γ_{xxxx}	866.16
γ_{xxxz}	-81.83
γ_{xxyy}	288.72
γ_{xxzz}	1272.53
γ_{zzzz}	5890.85
γ	2658.15

a. N-(3-21G) + p(0.05), d(0.13, 0.05)
 H-(3-21G) 30 bfs

[3s3p1d / 2s]

Thus the 3-21G bs produced fairly good values for the dipole moment, α 's, and $\bar{\gamma}$, but poor values for the β 's. Also the effect of the removal of pf sets from the nitrogen and hydrogen is magnified when the smaller 3-21G starting point bs is used, compared to the larger 6-31G and TZV and T7.73.2 nitrogen bss. Thus when the 3-21G bs is used, a careful choice of pf sets must be used, and the results may still not be satisfactory. Whenever possible one should employ the more reliable 6-31G bs as a starting point.

Phosphine

As in the case of ammonia, a series of calculations were performed to gain knowledge concerning the pf / bs dependencies of the dipole moment, DP and DH properties. As a starting point bs for phosphorus, the Dunning [7s5p] contracted bs [84] tabulated in T15.16.1 in the book by Csizmadia et al. [5] (see Table B.3) is used. This consists of a (11s6p) primitive Gaussian bs from Huzinaga [83] contracted to a [7s5p] bs. Since within the last decade the 6-31G bs proposed by Hehre et al. [86] has become the most widely used bs for ab initio calculations of polyatomic molecules, it is also used here in another series of calculations as a starting point bs for calculation of NLO properties.

The results of the DM for the two reference calculations I / 3.13 and II / 3.13 which are at the HF SCF level differ by only 1.5% from the results of a very large bs calculation by Feller, Boyle and Davidson [28] (see Table 3.11). However these results are 7.6% smaller than the HF SCF result reported by Sadlej [45] (Table 3.12). As discussed in Chapter I (p. 33) of this dissertation, the major reason for the development of the BSPM by Sadlej is to develop a moderate sized bs suitable for accurate calculation of the DM and DP. This discrepancy (i.e., 7.6%) caused us considerable concern. It was finally resolved, at least to our satisfaction, by analysis of the results produced by the 6-31G bs calculations reported in Table 3.16. As will be discussed later, the results of Table 3.11 are not entirely satisfactory compared to the reference calculations I / 3.13 and II / 3.13.

Table 3.11 Feller, Boyle, and Davidson's and Experimental Results of phosphine

	I ^a	II ^b	III ^c	IV ^d
μ (A.U.)	0.2638	0.2390	0.2353	0.227
μ (Deb.)	0.6705	0.6075	0.5981	0.5570

- a. Feller, Boyle, and Davidson's HF result [12s10p4d/6s3p] **111bfs** [28]
- b. Feller, Boyle, and Davidson's SD-CI result [12s10p4d/6s3p] **111bfs** [28]
- c. Feller, Boyle, and Davidson's MRSD-CI result [12s10p4d/6s3p] **111bfs** [28]
- d. Hilger and Strandberg's experimental result [64,79, 80, 81]

Table 3.12 Sadlej's Results of phosphine

	I ^a	II ^b	III ^c
μ (A.U.)	0.2815	0.2439	0.2264
μ (Deb.)	0.7155	0.6199	0.5754
a_{xx}	29.58	30.06	29.78
a_{zz}	30.59	31.79	31.32
$\bar{\alpha}$	29.92	30.64	30.29
$\Delta\alpha$	1.01	1.73	1.54

- a. Sadlej's HF results [7s5p2d/3s2p] **61bfs** [45]
- b. Sadlej's MBPT(2) results [7s5p2d/3s2p] **61bfs** [45]
- c. Sadlej's SDQ-MBPT results [7s5p2d/3s2p] **61bfs** [45]

In particular, it was noticed that on removal of the two innermost $d(2.34, 0.936)$ pf sets on phosphorus, the DM increases by 6.3%, which is about the same increase needed for Sadlej's calculation I / 3.12 to match our reference calculation I / 3.13. Examination of the bs used by Sadlej [45] showed that the highest d pf exponent is only 0.5979, i.e., the d pf set is deficient in inner d pfs, which Feller, Boyle and Davidson [28] have shown to be significant in a variational calculation of the energy.

The presence of the inner d pfs is important also for the calculation of the DP (α). A number of workers has pointed out that one way of optimizing the exponents in the pf is by maximizing the DP [46]. However in the work described in this dissertation we have found that on a number of occasions, upon increasing the number of bfs the DP decreased. It is now evident from these results that the optimization of the pf exponents by maximizing the DP can only be done if a full set of pfs is present, otherwise spuriously large DP values can be obtained.

Thus the value of $\bar{\alpha} = 29.92$ given by Sadlej is probably higher than our reference calculation I / 3.13 value of $\bar{\alpha} = 29.83$ due to Sadlej's omission of the two inner d pf sets of phosphorus rather than any deficiency in the reference calculation. The omission allows the outer d pf orbitals to have a greater electron density than they otherwise would have. Since the DH (β tensor) is also very sensitive to the electron density furthest from the nucleus, this also could result in spurious values for this property.

1. Dunning [7s5p] bs calculations (PH_3) - study of phosphorus pfs

A. Table 3.13 Results

Calculation I / 3.13 (Table 3.13) is the reference calculation for phosphine at the HF level, and uses a [8s8p6d / 2s4p3d] bs of 164 basis functions. The hydrogen bs is augmented with the $p(0.50, 0.25, 0.125, 0.0625)$ and the $d(0.25, 0.125, 0.0625)$ pfs. Comparing I / 3.13 to Sadlej's HF results [45] (I / 3.12) gave the following: μ differs by -7.4%, $\bar{\alpha}$ differs by -0.3%.

Table 3.13 PH₃ Dunning [7s5p] Results - large bs calculations

	I ^a	II ^b	III ^c	IV ^d	ve	VI ^f
μ (A.U.)	0.2608	0.2595	0.2604	0.2605	0.2606	0.2575
μ (Deb.)	0.6630	0.6597	0.6620	0.6620	0.6624	0.6546
α_{xx}	29.48	29.48	29.48	29.48	29.49	29.40
α_{zz}	30.52	30.51	30.44	30.44	30.42	30.40
$\bar{\alpha}$	29.83	29.52	29.80	29.80	29.78	29.73
$\Delta\alpha$	1.04	1.03	0.96	0.96	0.93	1.00
β_{xxx}	-13.71	-13.18	-14.22	-14.20	-14.11	-13.12
β_{xxz}	4.44	5.52	4.44	4.47	4.84	6.07
β_{zzz}	31.36	30.94	31.23	31.09	31.58	29.86
β	24.14	25.19	24.07	24.02	24.76	25.20
$\Delta\beta$	18.04	14.38	17.91	17.68	17.06	11.65
γ_{xxxx}	4698.39	4415.58	4501.56	4493.64	4305.80	4134.16
γ_{xxxz}	272.93	294.36	336.28	332.03	270.19	265.57
γ_{xxyy}	1566.14	1471.82	1500.50	1497.85	1435.24	1378.04
γ_{xxzz}	3277.56	3309.11	3200.16	3203.14	3045.92	2959.67
γ_{zzzz}	12503.17	11705.33	12087.70	12103.73	11716.27	11193.00
γ	7628.49	7343.31	7378.49	7380.45	7076.40	6811.21

- a. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.94, 0.38, 0.15, 0.075, 0.0375), H-(6-31G) + p(0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625) **164 bfs** [8s8p6d / 2s4p3d]
- b. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.94, 0.38, 0.15, 0.075, 0.0375), H-(6-31G) + p(1.0, 0.5, 0.25, 0.125, 0.0625), d(0.5, 0.25) **152 bfs** [8s8p6d / 2s5p2d]
- c. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.936, 0.3744, 0.1498, 0.0599, 0.02396), H-(6-31G) + p(0.9, 0.1), d(0.1) **110 bfs** [8s8p6d / 2s2p1d]
- d. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094), d(2.34, 0.936, 0.3744, 0.1498, 0.0599, 0.02396), H-(6-31G) + p(0.9, 0.1), d(0.1) **107 bfs** [8s7p6d / 2s2p1d]
- e. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599, 0.02396), H-(6-31G) + p(0.9, 0.1), d(0.1) **104 bfs** [8s6p6d / 2s2p1d]
- f. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.936, 0.3744, 0.1498, 0.0599), H-(6-31G) + p(0.9, 0.1), d(0.1) **101 bfs** [8s8p5d / 2s2p1d]

Comparing I / 3.13 to the HF limit result in Table 3.11 [28] (I / 3.11) shows: μ differs only by -1.3%. Comparing I / 3.13 to Hilger and Strindberg's experimental result (IV / 3.11) [64,79,80,81] shows: μ to differ by +14.89%. Calculation I / 3.13 was close to the upper limit of our computational capability, but probably represents a converged bs result anyway.

However in order to determine whether the use of pf sets on the hydrogen with an exponent higher than 0.5 could have an effect on NLO properties a compromise was made in II / 3.13 by the addition of a p(1.0) pf set and the removal of the d(0.125, 0.0625) pf sets on hydrogen. The only significant change when compared to I / 3.13 was for β_{xxz} which increased by +24.32%, and as a result a reduction in $\Delta\beta$ by 20.30%. The large number of pfs used on the hydrogen bs in I / 3.13 and II / 3.13 were responsible for the greatest part of the very large amount of CPU time used in these two calculations.

Calculation III / 3.13, which used a much smaller bs (i.e., p(0.9, 0.1), and d(0.1) pfs on hydrogen, the Dykstra ELP set [36]), gave very similar results at a fraction of the CPU time, and therefore the bs used in this calculation is a viable option to use in the rest of the study of how the in NLO properties change as the result of bs changes.

First, the effect of reducing the number of p pfs on phosphorus was investigated in IV / 3.13 and V / 3.13. In IV / 3.13 the phosphorus p(0.01047) pf is removed, and in V / 3.13 the p(0.02094) pf is removed as well. The results of these calculations showed only small differences in the β values. In fact, the largest change was in $\bar{\gamma}$, which was reduced by only 4.1% in V / 3.13 compared to III / 3.13. In VI / 3.13, the phosphorus outermost d(0.0239) pf is removed from the bs of III / 3.13. The largest change is in β_{xxz} (+36.7%), which then caused a change of +4.7% in $\bar{\beta}$, and a change of -35% in $\Delta\beta$. There is also a change of -7.7% in $\bar{\gamma}$ (compared to III / 3.13), which are still acceptable results.

B. Table 3.14 - Study of hydrogen pfs

In Table 3.14, the effect of changing the hydrogen pfs was studied. Prior to the work on water [44] and phosphacetyne [88] published from this research group, very little attention had been paid to the need for multiple pfs on the attached hydrogen for NLO properties, but this previous work showed that for acceptable results, at least one d pf is needed, and at least two p pfs, one with a diffuse exponent and one with an exponent close to the value used in energy optimized calculations in the H_2 molecule are needed. The results of the calculations in Table 3.14 support this conclusion.

In I / 3.14, 5d pfs are used on phosphorus, and the 2p1d pfs are used on the hydrogen. This was the same bs as V / 3.13 except the phosphorus outermost d(0.02396) pf is removed. The results are very similar to VI / 3.13 which also has 5d pfs on phosphorus as well as two more diffuse p pfs on phosphorus.

In II / 3.14, one diffuse s(0.06) pf set on hydrogen is added, and this only produced small changes in the NLO properties (i.e., less than 2%). However, the addition of this s(0.06) hydrogen pf introduced linear dependencies into the bs and caused convergence problems in the calculation of NLO properties. To avoid this problem only the contracted 1s bs (Appendix B.9) is used for the remainder of the calculations in Table 3.14.

In III / 3.14, the hydrogen inner p(0.9) pf set is removed, causing a reduction in μ of 6.67%, which is a very significant change for the DM, and $\bar{\gamma}$ is reduced by 4.17% (compared to II / 3.14). For the DH values: β_{xxx} differs by -11.35%, β_{xxz} differs by +32.17%, β_{zzz} differs by -5.44%, and accordingly: $\bar{\beta}$ differs by +3.30%, and $\Delta\beta$ differs by -36.79% (all comparing III / 3.14 to II / 3.14). Thus the hydrogen p(0.9) pf set or a inner pf set of similar exponent is needed for accurate NLO properties.

Table 3.14 PH₃ Dunning [7s5p] Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	V ^e	VI ^f
μ (A.U.)	0.2606	0.2607	0.2433	0.2524	0.2477	0.2260
μ (Deb.)	0.6623	0.6625	0.6184	0.6417	0.6297	0.5745
α_{xx}	29.44	29.44	29.24	29.24	29.19	28.70
α_{zz}	30.40	30.40	30.15	30.31	30.13	29.74
$\bar{\alpha}$	29.76	29.76	29.54	29.60	29.50	29.05
$\Delta\alpha$	0.96	0.96	0.91	1.07	0.94	1.04
β_{xxx}	-14.06	-14.62	-12.96	-13.09	-9.87	-9.14
β_{xxz}	5.01	4.88	6.45	6.25	9.06	10.93
β_{zzz}	31.36	32.20	30.45	34.24	33.75	35.35
$\bar{\beta}$	24.83	25.18	26.01	28.04	31.12	34.33
$\Delta\beta$	16.33	17.56	11.10	15.49	6.57	2.56
γ_{xxxx}	4197.20	4307.72	4035.22	4682.30	4494.57	4577.98
γ_{xxxz}	267.96	304.23	231.51	280.50	312.93	282.83
γ_{xxyy}	1399.03	1435.87	1345.05	1527.42	1498.16	1525.98
γ_{xxzz}	2937.88	2977.53	2883.58	3178.72	3136.43	3227.60
γ_{zzzz}	11224.28	11262.76	10920.00	11922.00	11168.27	10860.03
$\bar{\gamma}$	6833.65	6932.01	6642.97	7371.34	7139.91	7195.67

- a. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599),
H-(6-31G) + p(0.9, 0.1), d(0.1) **98 bfs** [8s6p5d / 2s2p1d]
- b. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599),
H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) **101 bfs** [8s6p5d / 3s2p1d]
- c. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599),
H-(T1.42.1) + p(0.1), d(0.1) **86 bfs** [8s6p5d / 1s1p1d]
- d. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599),
H-(T1.42.1) + p(0.9, 0.1), d(0.0625) **95 bfs** [8s6p5d / 1s2p1d]
- e. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599),
H-(T1.42.1) + p(0.9, 0.0625), d(0.1) **95 bfs** [8s6p5d / 1s2p1d]
- f. P-(T15.16.1) + s(0.0626), p(0.04188), d(2.34, 0.936, 0.3744, 0.1498, 0.0599),
H-(T1.42.1) + p(0.9, 0.0625) **77 bfs** [8s6p5d / 1s2p]

In IV / 3.14 a hydrogen d(0.0625) pf set replaced the d(0.10) pf set. In comparing IV / 3.14 to the reference I / 3.13, it is seen that although $\bar{\gamma}$ differs by -3.37%, an improvement, β_{xxx} differs by -4.52%, β_{xxz} differs by +40.77%, β_{zzz} differs by +9.18%, so that $\bar{\beta}$ differs by +16.16%, and $\Delta\beta$ differs by -14.14%. These are substantial differences. In V / 3.14 the hydrogen outermost p(0.10) pf set is replaced by a p(0.0625) pf set, and when compared to the reference I / 3.13, the μ and α results are similar, and there is a slight improvement in $\bar{\gamma}$, but there are still substantial differences in β values. In VI / 3.14, the hydrogen d pf set is removed altogether from the set used in V / 3.14. This caused a change of -8.8% in μ and a change of -61% in $\Delta\beta$ due to a large change in β_{zzz} , and the other values are about the same. Thus the d(0.10) pf set on hydrogen is important for accuracy in both the DM and NLO properties.

C. Table 3.15 - Effects of phosphorus f pfs and MP2

In Table 3.15, the result of adding a phosphorus f pf to the bs used in III / 3.13, and the also the effect of including electron correlation (MP2) is reported. In I / 3.15 a phosphorus f(0.125) pf is added to the bs of III / 3.13, and when compared to III / 3.13, there are no substantial changes in the NLO properties. In II / 3.15, the same bs is used for a MP2 calculation. The inclusion of correlation caused the DM to be 0.31% higher than the experimental value of 0.227 a.u. [64,79,80,81], and the DP values are practically the same as Sadlej's MBPT(2) results [45]. From the HF limit to MP2, there are large changes in the DH (II / 3.10 to I / 3.10): $\bar{\beta}$ differs by -51.46%, and $\Delta\beta$ differs by -168.74%. When II / 3.10 is compared to Sadlej's MBPT(2) (II / 3.12) [45] results: Sadlej's DM value is 7% higher, but the DP values are similar. Sadlej's SDQ-MBPT(4) (III / 3.12) [45] results are very similar to those of II / 3.10. The DM of II / 3.10 is also comparable to the CI results of Feller, Boyle and Davidson (II / 3.11 and III / 3.11) [28].

Table 3.15 PH₃ Dunning [7s5p] Results - effect of phosphorus f pfs and MP2

	Ia	IIb
μ (A.U.)	0.2607	0.2279
μ (Deb.)	0.6627	0.5793
α_{xx}	29.48	30.04
α_{zz}	30.48	31.90
$\bar{\alpha}$	29.81	30.66
$\Delta\alpha$	1.00	1.86
β_{xxx}	-14.34	-11.78
β_{xxz}	4.43	6.30
β_{zzz}	30.98	6.74
β	23.90	11.60
$\Delta\beta$	17.69	-12.16
γ_{xxxx}	4502.41	-----
γ_{xxxz}	342.01	-----
γ_{xxyy}	1500.79	-----
γ_{xxzz}	3184.67	-----
γ_{zzzz}	12206.19	-----
$\bar{\gamma}$	7390.25	-----

- a. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.936, 0.3744, 0.1498, 0.0599, 0.02396), f(0.125),
H-(6-31G) + p(0.9, 0.1), d(0.1) 120 bfs [8s8p6d1f / 2s2p1d]
- b. P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.936, 0.3744, 0.1498, 0.0599, 0.02396), f(0.125),
H-(6-31G) + p(0.9, 0.1), d(0.1) 120 bfs MP2 [8s8p6d1f / 2s2p1d]

The conclusion to be reached from these calculations based upon the Dunning [7s5p] phosphorus basis set (tables 3.13, 3.14, and 3.15) is that at least for PH₃, accurate NLO properties and the DM can be obtained using the Dunning [7s5p] bs augmented by a 1s1p6d set of pfs on phosphorus, and a hydrogen 1s bs augmented by the p(0.9,0.1) d(0.1) pf sets. The diffuse phosphorus p(0.02094, 0.01047) pfs were found not to be important, however, the phosphorus 6d was slightly better than 5d (i.e., the d(0.02396) pf made small differences). On the hydrogen, the p(0.9, 0.1) pf sets are important. The p(0.1) is better than the p(0.0625) pf set, and the d(0.1) is better than the d(0.0625) pf set for accurate NLO properties.

3. Split valence 6-31G bs calculations

A. Table 3.16 Results

The 6-31G* bs [87], i.e., the standard split valence bs augmented by one d(0.55) pf bs has in recent years become the bs of choice for the calculations of molecules containing more than four heavy atoms. It is also regarded by many [56] as the smallest bs which is meaningful with respect to including electron correlation. It is thus important to establish the validity of this bs for calculating NLO properties. Table 3.16 and the results in the following section summarizes the most important results obtained using various combinations of pfs with the 6-31G bs for PH₃ in our work. In the first calculation I / 3.16 the Dunning [7s5p] phosphorus bs is replaced by the 6-31G bs. When compared to I / 3.13, there are substantial changes, specifically: β_{xxx} differs by -6.64%, β_{xxz} differs by +16.67%, β_{zzz} differs by -4.56%, and $\Delta\beta$ differs by -20.23%, but $\bar{\gamma}$ only differs by -3.39%, and the changes in : μ , $\bar{\alpha}$, $\Delta\alpha$, $\bar{\beta}$, and $\bar{\gamma}$ are minor compared to the reference (I / 3.13).

Table 3.16 PH₃ 6-31G Results - Study of phosphorus d pfs

	Ia	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	0.2624	0.2789	0.2791	0.2793	0.2790	0.2793
μ (Deb.)	0.6670	0.7089	0.7094	0.7098	0.7091	0.7099
α_{xx}	29.47	29.56	29.53	29.52	29.51	29.54
α_{zz}	30.44	30.43	30.38	30.37	30.27	30.39
$\bar{\alpha}$	29.79	29.85	29.81	29.80	29.76	29.82
$\Delta\alpha$	0.97	0.87	0.85	0.85	0.76	0.85
β_{xxx}	-12.80	-13.19	-13.47	-13.35	-12.90	-13.17
β_{xxz}	5.18	4.30	4.81	4.98	4.29	5.01
β_{zzz}	29.93	28.06	29.98	29.37	26.64	29.17
$\bar{\beta}$	24.17	22.00	23.76	23.60	21.13	23.51
$\Delta\beta$	14.39	15.16	15.55	14.43	13.77	14.14
γ_{xxxx}	4429.46	4480.85	4211.74	0.4132	3979.95	4143.15
γ_{xxxz}	303.03	301.42	277.88	237.05	300.05	259.58
γ_{xxyy}	1476.45	1498.59	1403.89	1377.32	1326.64	1381.02
γ_{xxzz}	3187.17	3200.06	2941.58	2899.62	2712.42	2943.91
γ_{zzzz}	12286.21	12211.95	11157.49	11128.64	9495.59	11072.88
$\bar{\gamma}$	7369.34	7392.21	6831.01	6749.16	6191.68	6779.36

- a. P-(6-31G) + s(0.0626), p(0.04188, 0.02094,0.01047),
d(2.34, 0.936, 0.3744, 0.1498, 0.0599, 0.02396),
H-(6-31G) + p(0.9, 0.1), d(0.1) **101 bfs** [5s6p6d / 2s2p1d]
- b. P-(6-31G) + s(0.0626), p(0.04188, 0.02094,0.01047),
d(0.3744, 0.1498, 0.0599, 0.02396),
H-(6-31G) + p(0.9, 0.1), d(0.1) **89 bfs** [5s6p4d / 2s2p1d]
- c. P-(6-31G) + s(0.0626), p(0.04188, 0.02094,0.01047),
d(0.3744, 0.1498, 0.0599),
H-(6-31G) + p(0.9, 0.1), d(0.1) **83 bfs** [5s6p3d / 2s2p1d]
- d. P-(6-31G) + s(0.0626), p(0.04188), d(0.3744, 0.1498, 0.0599),
H-(6-31G) + p(0.9, 0.1), d(0.1) **77 bfs** [5s4p3d / 2s2p1d]
- e. P-(6-31G) + s(0.0626), d(0.3744, 0.1498, 0.0599),
H-(6-31G) + p(0.9, 0.1), d(0.1) **74 bfs** [5s3p3d / 2s2p1d]
- f. P-(6-31G) + s(0.0626), p(0.03), d(0.3744, 0.1498, 0.0599),
H-(6-31G) + p(0.9, 0.1), d(0.1) **77 bfs** [5s4p3d / 2s2p1d]

In II / 3.16, the phosphorus inner d(2.34, 0.936) pfs are removed, and comparing it to I / 3.16: μ differs by +6.29%, $\Delta\alpha$ differs by -10.31%, and β_{xxz} differs by -16.99%. Nevertheless, this change brought the β values closer to those of I / 3.13. This is an example where better β values are obtained fortuitously as the result of using a smaller bs, due to cancelling out of opposing differences. However, if one is interested in the DM or the anisotropy of the DP ($\Delta\alpha$), these calculations show it is essential to include the inner d pfs on phosphorus.

In III / 3.16, the outermost phosphorus d(0.02396) pf is removed. This resulted in only small changes, except for $\bar{\gamma}$ which differs by -7.59% (compared to II / 3.16). In IV / 3.16 the two outermost phosphorus p(0.02094, 0.01047) pfs are removed. The results are very similar to III / 3.16. Just as in the progression III / 3.13, IV / 3.13, and V / 3.13, these results show that the removal of the two phosphorus p pfs does not effect NLO properties. However these 6-31G results are still poorer than those of Table 3.13. In V / 3.16 the last phosphorus p(0.04188) pf is removed. This had a considerable effect, when compared to the reference I / 3.13: $\Delta\alpha$ differs by -26.92%, β_{zzz} differs by -15.05%, and $\bar{\gamma}$ differs by -18.83%. Thus at least one diffuse phosphorus p pf is essential for NLO properties. In VI / 3.16, the phosphorus p(0.04188) pf of IV / 3.16 is replaced by a p(0.03) pf, and the results are very similar to IV / 3.16. This shows that precisely optimizing the diffuse exponents would probably not lead to any significant improvement.

B. Table 3.17 Results

In I / 3.17 (Table 3.17), a phosphorus f(0.125) pf is added to the bs of VI / 3.16, without producing any significant changes in the DM and NLO properties. In II / 3.17, the same set of Dykstra 3d pfs (Chapter I p.34) as was used for nitrogen are used on the phosphorus with a 6-31G bs, and when compared to I / 3.13, the results in general are not acceptable. In particular, the very small β_{xxz} value gave rise to a $\bar{\beta}$ which differs by -47.47%, and a $\Delta\beta$ which differs by +9.09%.

Table 3.17 PH₃ 6-31G Results - further study of phosphorus d pfs

	I ^a	II ^b	III ^c	IV ^d	V ^e
μ (A.U.)	0.2791	0.2735	0.2707	0.3494	0.3494
μ (Deb.)	0.7094	0.6951	0.6882	0.8880	0.8882
α_{xx}	29.54	29.41	29.51	29.59	29.64
α_{zz}	30.41	30.03	30.37	29.83	29.84
$\bar{\alpha}$	29.83	29.62	29.80	29.67	29.71
$\Delta\alpha$	0.87	0.62	0.86	0.24	0.20
β_{xxx}	-13.30	-15.44	-12.81	-15.00	-15.23
β_{xxz}	5.00	0.29	5.61	3.40	3.32
β_{zzz}	28.14	20.55	30.24	26.96	25.73
$\bar{\beta}$	22.88	12.68	24.88	20.26	19.42
$\Delta\beta$	13.14	19.68	13.41	16.76	15.77
γ_{xxxx}	4219.60	4243.81	4267.33	4088.65	4342.68
γ_{xxxz}	268.04	253.97	279.28	380.18	344.80
γ_{xxyy}	1406.50	1414.58	1422.41	1362.87	1447.54
γ_{xxzz}	2948.21	2893.07	3067.70	2954.39	3205.73
γ_{zzzz}	11192.20	11031.03	11625.85	10644.49	12103.42
$\bar{\gamma}$	6847.44	6784.01	7055.22	6673.01	7301.35

- a. P-(6-31G) + s(0.06), p(0.03), d(0.3744,0.1498,0.0599), f(0.125)
H-(6-31G) + p(0.90, 0.10), d(0.10) **87 bfs** [5s4p3d1f / 2s2p1d]
- b. P-(6-31G) + s(0.06), p(0.03), d(0.9,0.13,0.02)
H-(6-31G) + p(0.90, 0.10), d(0.10) **77 bfs** [5s4p3d / 2s2p1d]
- c. P-(6-31G) + s(0.06), p(0.03), d(0.55, 0.15, 0.05)
H-(6-31G) + p(0.90, 0.10), d(0.10) **77 bfs** [5s4p3d / 2s2p1d]
- d. P-(6-31G) + s(0.06), p(0.03), d(0.0599)
H-(6-31G) + p(0.90, 0.10), d(0.10) **65 bfs** [5s4p1d / 2s2p1d]
- e. P-(6-31G) + s(0.06), p(0.03), d(0.04)
H-(6-31G) + p(0.90, 0.10), d(0.10) **65 bfs** [5s4p1d / 2s2p1d]

This calculation shows that any attempt to transfer the pf functions from one row of the periodic table to another is fraught with danger, even though Dykstra showed it could be reasonable to use the same pfs across a row.

Since in the 6-31G* bs, a d(0.55) pf is normally used, the phosphorus d(0.55,0.15,0.05) pfs are used in III / 3.17. Here rf of 0.27 and 0.33 are used to generate the two extra pfs. When these results are compared to I / 3.13, major changes are seen: $\Delta\alpha$ differs by -17.3%, and $\Delta\beta$ differs by -25.7%. The other properties did not differ significantly from the reference (I / 3.13).

In IV / 3.17, an attempt was made to replace the 3d pfs of III / 3.17 with one outer d(0.0599) pf on phosphorus. The results compared to the reference (I / 3.13) shows that: μ differs by + 33.97%, $\Delta\alpha$ differs by -76.92%, $\bar{\beta}$ differs by -16.07%, $\Delta\beta$ differs by -7.09%, and $\bar{\gamma}$ differs by -12.53%. In V / 3.17, a phosphorus d(0.04) pf replaced the d(0.0599) pf of IV / 3.12. When compared to I / 3.13 this change gave even worst results. These two calculations IV / 3.17 and V / 3.17 took considerably less CPU time than I / 3.13, and in that light, these results are almost acceptable for the NLO properties, but the DMs are very poor. This demonstrates the principle that as long as diffuse pfs of each type (i.e., p and d) are present, qualitatively acceptable NLO properties will probably be obtained. However the results of IV / 3.17 and V / 3.17 show that the β tensor and the γ tensor changes may be in different directions (i.e., + and -), and using a small set of pfs, it is not possible to get accurate values of β and γ simultaneously. It is also obvious that accurate anisotropic values $\Delta\alpha$ and $\Delta\beta$ are much more difficult to get than the individual tensor values α and β .

The conclusion from these calculations is that almost any bs of double zeta quality can be used as a starting point bs for NLO properties calculations as long as there is at least one diffuse phosphorus p pf with an exponent between 0.02 and 0.05, and a set of 3d pfs from the range of 0.6 to 0.02 (satisfactory results can be obtained without optimizing of the individual exponents). Pf sets on the hydrogen similar to the 2p1d pf sets used in the majority of these calculations are needed to obtain satisfactory NLO results. Careful optimizing of individual exponents is not required to obtain results within 10% of "accurate values."

Arsine

Several calculations performed by Sadlej [47] on arsine are presented in Table 3.18. An experimental result for the DM is also given. Our calculations will be compared to these results.

1. Table 3.19 Results - Study of arsenic bs (AsH_3)

The calculations of arsine in this table are based upon the recently developed Curtiss / Binning [26] bs for arsenic (Table B.4) extended by various combinations of pfs on arsenic and hydrogen. This bs consists of a 14s11p5d primitive set contracted to a [6s3p1d] bs. The reference calculation for arsine, I / 3.19, consists of 184 bfs with a [7s7p6d / 1s5p4d] bs. For the hydrogen bs, the five sets of p pfs were chosen starting with an exponent of 1.0 and a reduction factor (rf) of 0.5, and the four sets of d pfs were chosen starting with an exponent of 0.5 and a rf of 0.5. The calculations summarized in Table 3.19 and the following section were performed in order to determine how this very large basis set could be made more practical and economical without significant loss in accuracy of the NLO molecular properties of interest.

Table 3.18 Sadlej's Results of arsine

	I ^a	II ^b	III ^c	IV ^d
μ (A.U.)	0.1588	0.1200	0.1014	0.0850
μ (Deb.)	0.4036	0.3050	0.2577	0.2161
a_{xx}	34.29	34.82	34.71	-----
a_{zz}	35.36	36.66	36.53	-----
$\bar{\alpha}$	34.65	35.43	35.32	-----
$\Delta\alpha$	1.07	1.84	1.82	-----

- Sadlej's HF results [9s7p4d/3s2p] **81bfs** [47]
- Sadlej's MBPT(2) results [9s7p4d/3s2p] **81bfs** [47]
- Sadlej's SDQ-MBPT results [9s7p4d/3s2p] **81bfs** [47]
- Di Lonardo, Fusina, Trombetti's experimental result [93]

Table 3.19 AsH₃ Binning / Curtiss Results - large bs calculations

	Ia	IIb	IIIc	IVd	Ve
μ (A.U.)	0.1674	0.1699	0.1653	0.1645	0.1667
μ (Deb.)	0.4255	0.4319	0.4200	0.4205	0.4236
α_{xx}	34.34	34.37	34.33	34.28	34.29
α_{zz}	35.29	35.33	35.29	35.22	35.26
$\bar{\alpha}$	34.66	34.69	34.65	34.59	34.62
$\Delta\alpha$	0.95	0.96	0.96	0.94	0.97
β_{xxx}	-16.13	-15.97	-16.10	-15.83	-15.70
β_{xxz}	5.38	4.50	5.23	4.84	5.46
β_{zzz}	38.36	38.70	39.04	37.43	37.76
β	29.47	28.62	29.70	28.27	29.21
$\Delta\beta$	22.22	25.20	23.35	22.91	21.38
γ_{xxxx}	6138.50	6181.39	5787.86	6082.86	6121.94
γ_{xxxz}	335.10	385.00	391.57	351.74	357.71
γ_{xxyy}	2046.15	2060.44	1929.27	2027.60	2040.65
γ_{xxzz}	4060.31	4104.74	4135.19	4072.90	4099.12
γ_{zzzz}	15447.52	15390.43	14452.09	15150.31	15188.31
γ	9611.60	9658.61	9285.42	9532.56	9582.00

- a. As-(BC) + s(0.0569), p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) + p(1, 0.5, 0.25, 0.125, 0.0625), d(0.5, 0.25, 0.125, 0.0625) **184 bfs**
[7s7p6d / 1s5p4d]
- b. As-(BC) + p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) + p(1, 0.5, 0.25, 0.125, 0.0625), d(0.125, 0.0625) **147 bfs**
[6s7p6d / 1s5p2d]
- c. As-(BC) + p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) + p(1, 0.5, 0.25, 0.125, 0.0625), d(0.5, 0.25) **147 bfs**
[6s7p6d / 1s4p2d]
- d. As-(BC) + s(0.0569),p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) + p(1, 0.125), d(0.0625) **103 bfs**
[7s7p6d / 1s2p1d]
- e. As-(BC) + p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) + p(0.5, 0.25, 0.0625), d(0.0625) **111 bfs**
[6s7p6d / 1s3p1d]

In II / 3.19 and III / 3.19, both use 147 basis functions, the 4d pf sets on hydrogen are reduced to 2d with different exponents in each of the two calculations. Calculation II / 3.19 which uses the hydrogen d(0.125, 0.0625) pf sets gives results very similar to I / 3.19 except that: β_{xxz} differs by -16.36%, which leads to the result: $\Delta\beta$ differs by +13.4%. The results of III / 3.19 were obtained using the hydrogen d(0.5, 0.25) pf sets, and are very similar to I / 3.19. Thus the d(0.5, 0.25) pf sets are considerably better than the d(0.125, 0.0625) pf sets for hydrogen, for β values but slightly poorer for γ values, for the arsenic bs used. This is an unexpected result based upon previous experience as usually the more diffuse pfs of the hydrogen are more important than the less diffuse ones.

Calculation IV / 3.19 used only the p(1.0, 0.125) and d(0.0625) pf sets on the hydrogen and resulted only in a minor change in the β 's compared to I / 3.19, that is: β_{xxx} differs by -5.40%, β_{xxz} differs by +6.77%, β_{zzz} differs by -7.30%, $\bar{\beta}$ differs by -4.07%, $\Delta\beta$ differs by +3.10%. Calculation V / 3.19 uses the hydrogen p(0.5,0.25,0.0625), and d(0.0625) pf sets, and gives very similar results to I / 3.19 (i.e., less than 4% difference in NLO properties).

2. Table 3.20 Results - Further Study of arsenic bs (AsH_3)

The calculations of Table 3.20 were performed to see what further reduction in the number of bfs could be made without loss in accuracy of NLO properties.

In I / 3.20 it is shown that the presence of the diffuse s pfs do play a significant role in the calculation of the β values. A comparison of I / 3.20 with I / 3.19 gave the result: β_{xxz} differs by +8.55%. There are no significant changes in the other values.

Nevertheless for computational stability reasons (i.e., to avoid convergence problems due to linear dependencies) these diffuse s pfs were omitted in subsequent calculations as noted in the bs descriptions in the footnotes of Table 3.20 or explicitly stated in the text here. In the next four calculations the effect of removal of arsenic p and d pfs is studied. In II / 3.20, the outermost arsenic d(0.01258) pf is removed.

Table 3.20 AsH₃ Binning / Curtiss Results - further study of arsenic bs

	Ia	IIb	IIIc	IVd	Ve
μ (A.U.)	0.1642	0.1640	0.1641	0.1640	0.1876
μ (Deb.)	0.4174	0.4168	0.4170	0.4167	0.4769
α_{xx}	34.18	34.17	34.17	34.16	34.18
α_{zz}	35.17	35.17	35.16	35.15	35.19
$\bar{\alpha}$	34.51	34.50	34.50	34.49	34.52
$\Delta\alpha$	0.99	1.00	0.99	0.99	1.01
β_{xxx}	-16.40	-16.50	-16.46	-15.92	-19.17
β_{xxz}	5.84	5.91	5.86	5.70	4.07
β_{zzz}	39.44	39.61	39.66	38.66	33.44
β	30.67	30.85	30.83	30.04	24.95
$\Delta\beta$	21.92	21.88	22.08	21.56	21.23
γ_{xxxx}	6266.69	6241.85	6241.33	6157.79	6249.07
γ_{xxxz}	376.99	376.01	372.83	407.09	336.85
γ_{xxyy}	2088.88	2080.60	2080.43	2052.56	2083.01
γ_{xxzz}	4129.48	4130.22	4140.01	4121.14	4194.90
γ_{zzzz}	15291.35	15329.00	15359.53	14995.44	15991.58
$\bar{\gamma}$	9704.07	9698.95	9712.61	9580.13	9887.07

- a. As-(BC) + s(0.055), p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) +s(0.045), p(0.5, 0.0625), d(0.0625) **106 bfs** [7s7p6d / 2s2p1d]
- b. As-(BC) + s(0.055), p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5, 0.0625), d(0.0625) **100 bfs** [7s7p5d / 2s2p1d]
- c. As-(BC) + s(0.055),p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) + s(0.045),p(0.5,0.0625), d(0.0625) **97 bfs** [7s6p5d / 2s2p1d]
- d. As-(BC) + s(0.055), p(0.0534), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5, 0.0625), d(0.0625) **94 bfs** [7s5p5d / 2s2p1d]
- e. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5, 0.0625), d(0.0625) **91 bfs** [7s6p4d / 2s2p1d]

A comparison of II / 3.20 with I / 3.20 show no significant changes. In III / 3.20 the outermost arsenic p(0.01335) pf is removed, and again there are no significant changes. Since there are no significant changes, these two pfs may be safely omitted. In IV, the arsenic p(0.0267) pf is removed, and again there are no significant changes. In V / 3.20, the arsenic d(0.49135) pf is removed, and compared to IV / 3.20 gave the results: μ differs by +14.4%, β_{xxx} differs by +20.4%, β_{xxz} differs by -28.6%, β_{zzz} differs by -13.5%, $\bar{\beta}$ differs by -16.9%. The other values do not differ significantly. This is a most unexpected change since usually the changes in NLO properties are associated with the more diffuse pfs. This result demonstrates again that great care must be exercised in the choice of pfs, and that there should be a smooth transition between the inner pfs optimized variationally on the energy and the outer pfs chosen to produce accurate NLO properties.

The sensitivity to the inner arsenic d pf also explains the difference of +5.4% in the DM of the reference calculation (I / 3.19 $\mu = 0.1674$ a.u.) to Sadlej's [47] HF SCF result (I / 3.18 $\mu = 0.1588$ a.u.), although the DP values are almost identical.

Two calculations were performed with the bs of I / 3.20 augmented first by an arsenic f(0.125), and then in the second calculation an arsenic f(0.25). Although the results of these calculations are not reported here, there are only minimal changes in the NLO properties for both calculations (i.e., less than 5% difference compared to I / 3.20). Although the arsenic f pfs do not cause any significant changes in the NLO properties at the HF SCF level, these pfs could be important when electron correlation is included (i.e., MP2 calculations).

3. Table 3.21 MP2 Results (AsH_3)

In Table 3.21 two MP2 calculations of arsine are presented. In I / 3.21 a [6s7p6d1f / 1s2p1d] 112 bfs basis is used. The results of I / 3.21 of μ , $\Delta\alpha$, and β values are significantly different than those of I / 3.19 at the HF SCF level. When I / 3.21 is compared to Sadlej's MBPT(2) results [47] (II / 3.18), μ differs by +17.7%, but the $\bar{\alpha}$ and $\Delta\alpha$ values are very similar. In calculation II / 3.21 a [7s6p5d / 2s2p1d] 97 bfs basis is used. This gave a slightly smaller DM value, and when compared to Sadlej's MBPT(2) results [47] (II / 3.18), μ differs by +11.6%. Even Sadlej's SDQ-MBPT(4) calculation [47] (III / 3.18) gave a DM that is 19.3% too large compared to the experimental result of Di Lonardo, Fusina, and Trombetti [93].

In going from HF SCF to MP2 the $\bar{\alpha}$ result changes very little, however $\Delta\alpha$ almost doubles in value. The DM and DH or β values also change significantly. The changes in the DM from I / 3.19 to I / 3.21 or II / 21 is not as large as Sadlej's HF SCF calculation I / 3.18 to his MBPT(2) calculation II / 3.18. This suggests that I / 3.21 and II / 3.21 are only qualitatively useful, in that they demonstrate large changes in the $\Delta\alpha$ and β values, the bs choice for MP2 calculations needed to get accurate DM and DH values needs further investigation, which will have to wait until an improvement of the available computational facilities.

Table 3.21 AsH₃ Binning / Curtiss Results - MP2

	I ^a	II ^b
μ (A.U.)	0.1412	0.1339
μ (Deb.)	0.3589	0.4828
α_{xx}	34.85	34.65
α_{zz}	36.66	36.49
$\bar{\alpha}$	35.45	35.26
$\Delta\alpha$	1.81	1.84
β_{xxx}	-12.61	-13.66
β_{xxz}	7.16	6.48
β_{zzz}	10.63	10.34
$\bar{\beta}$	14.97	13.98
$\Delta\beta$	-10.85	-9.10
γ_{xxxx}	-----	-----
γ_{xxxz}	-----	-----
γ_{xxyy}	-----	-----
γ_{xxzz}	-----	-----
γ_{zzzz}	-----	-----
$\bar{\gamma}$	-----	-----

- a. As-(BC) + p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), f(0.125), H-(T1.42.1) +p(0.5, 0.0625), d(0.0625)
112 bfs MP2 [6s7p6d1f / 1s2p1d]
- b. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5, 0.0625), d(0.0625)
97 bfs MP2 [6s6p5d / 2s2p1d]

4. Table 3.22 Results - Study of hydrogen bs (AsH_3)

The variation of the β tensor values with changes in the number and type of pfs on the hydrogen atom of arsine seems to be unusually large. Since the relative importance of the p and d pfs on the attached hydrogen of polyatomic molecules has been largely neglected, apart from the work in our group [44], an investigation of their role in determining NLO properties for arsine was investigated. The results of this study are summarized in Table 3.22 and the following section. In these two tables the effect of adding various combinations of hydrogen pfs to a [7s6p5d / 2s] bs is studied.

In I / 3.22, there are no p or d pfs on the hydrogen. The results of I / 3.22 are considerably different from the reference I / 3.19, that is: μ differs by -46.8%, β_{xxz} differs by +194.4%, β_{zzz} differs by +94.3%, $\bar{\beta}$ differs by +116.3%, $\Delta\beta$ differs by +21.6%, and $\bar{\gamma}$ differs by -15.6% (note: that the DP values are acceptable). This therefore is one of the many cases we have studied where a bs pf set which is adequate for the DP could be useless for calculating DHs. In II / 3.22 the addition of a hydrogen p(0.5) pf set gave considerably improved DM results, that is: μ differs by -13.0%, but β_{xxz} differs by +123.2%, β_{zzz} differs by +70.6%, $\bar{\beta}$ differs by +82.1%, $\Delta\beta$ differs by +32.4%, and $\bar{\gamma}$ differs by -14.6% (i.e., the DH values are still poor). In III / 3.22, a diffuse hydrogen p(0.0625) pf set is used in place of the p(0.5) pf set of II / 3.22. A comparison of III / 3.22 to I / 3.19 gave poorer agreement of the DM, but improved β and γ values: μ differs by -26.2%, β_{xxx} differs by -22.3%, β_{xxz} differs by +84.0%, β_{zzz} differs by +25.9%, and $\bar{\gamma}$ differs by -3.7%. In IV / 3.22 the two hydrogen p(0.5, 0.0625) pf sets are used, which produced a better DM (differs by -3.8% from I / 3.19), and the quality of the β and γ tensor values are similar to those of III / 3.22, and the DP values are still good. The effect here is not additive.

Table 3.22 AsH₃ Binning / Curtiss Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	0.0891	0.1456	0.1236	0.1610	0.1409	0.1309
μ (Deb.)	0.2266	0.3700	0.3141	0.4092	0.3581	0.3327
α_{xx}	32.64	33.39	33.48	33.98	33.81	33.63
α_{zz}	33.58	34.49	34.35	35.07	34.64	34.44
$\bar{\alpha}$	32.95	33.76	33.77	34.34	34.09	33.90
$\Delta\alpha$	0.94	1.10	0.87	1.09	0.83	0.81
β_{xxx}	-16.44	-18.09	-12.53	-13.57	-8.49	-16.59
β_{xxz}	15.84	12.01	9.90	8.42	13.04	7.01
β_{zzz}	74.53	65.43	42.04	37.81	43.66	45.29
β	63.73	53.67	37.10	32.79	41.84	35.59
$\Delta\beta$	27.01	29.40	12.34	12.55	4.54	24.26
γ_{xxxx}	4787.59	4814.48	5865.55	5819.39	5709.75	6325.72
γ_{xxxz}	732.67	916.76	450.10	439.42	502.78	343.47
γ_{xxyy}	1595.85	1604.81	1955.15	1939.78	1903.22	2108.54
γ_{xxzz}	3439.92	3494.61	4140.63	4184.68	3957.96	4098.36
γ_{zzzz}	14040.37	14210.94	14068.35	14417.39	14848.50	15050.58
γ	8113.38	8205.59	9254.44	9334.89	9181.25	9662.49

- a. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045) **61 bfs** [7s6p5d / 2s]
- b. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5) **70 bfs** [7s6p5d / 2s1p]
- c. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.0625) **70 bfs** [7s6p5d / 2s1p]
- d. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5, 0.0625) **79 bfs** [7s6p5d / 2s2p]
- e. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), d(0.125) **79 bfs** [7s6p5d / 2s1d]
- f. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), d(0.0625) **79 bfs** [7s6p5d / 2s1d]

In V / 3.22, a hydrogen d(0.125) pf set is added to the bs of I / 3.22. The effect is considerable, especially on the β values. The improvement in the DM value is similar to that II / 3.22, in which a hydrogen p(0.5) pf set is used. In VI / 3.22, a hydrogen d(0.0625) pf set is used instead of the d(0.125) pf set of V / 3.22. The improvement in the DM value from I / 3.22 is still considerable, and the β values are closer to the reference I / 3.19 (i.e., β_{zzz} differs by +18.1%, $\bar{\beta}$ differs by +20.8%, $\Delta\beta$ differs by +9.2%). Thus the addition of at least one p pf set and one d pf set is important to get reasonable values of the DM and NLO properties. If only one p pf set is used the 0.0625 exponent is better than 0.5, and if only one d pf set is used the 0.0625 exponent is better than 0.125.

5. Table 3.23 Results - Study of multiple pfs on hydrogen (AsH_3)

In I / 3.23 (Table 3.23), the effect of adding a hydrogen p(0.0625) and a d(0.0625) pf set to the bs of I / 3.22 (bs with no added pfs on hydrogen) was investigated. The DM and DP values are still too low compared to I / 3.19, while the β values are similar to those of VI / 3.22 which has one hydrogen d(0.0625) pf set added. The $\bar{\gamma}$ value of I / 3.23 is within 1% of that of the reference I / 3.19. In II / 3.23 a hydrogen inner p(0.5) pf set is added to the bs of I / 3.23. As expected, the DM and DP values are very similar to those of the reference I / 3.19, while the β and γ values are also reasonable (compared to I / 3.19), however β_{xxz} is still 8.9% too high. This series of calculations I / 3.22 through VI / 3.22, I / 3.23, and II / 3.23 clearly show the need for multiple hydrogen pfs of both the p and d type, and also that the effect of the pfs is unfortunately not additive. In order to get a better understanding of the differences in the β values noticed in the large bs calculations of Table 3.19, the effect of using multiple hydrogen d pfs was next attempted.

Table 3.23 AsH₃ Binning / Curtiss Results - further study of hydrogen pfs

	Ia	IIb	IIIc	IVd	Ve
μ (A.U.)	0.1368	0.1641	0.1679	0.1642	0.1666
μ (Deb.)	0.3477	0.4170	0.4268	0.4174	0.4233
α_{xx}	33.77	34.17	34.29	34.19	34.28
α_{zz}	34.61	35.16	35.26	35.15	35.24
$\bar{\alpha}$	34.05	34.50	34.61	34.51	34.60
$\Delta\alpha$	0.84	0.99	0.97	0.96	0.96
β_{xxx}	-15.75	-16.46	-16.81	-16.05	-16.78
β_{xxz}	7.31	5.86	4.66	5.27	4.98
β_{zzz}	42.96	39.66	40.10	39.31	40.25
β	34.55	30.82	29.65	29.91	30.13
$\Delta\beta$	21.03	22.08	26.12	23.50	25.31
γ_{xxxx}	6179.15	6241.26	6186.71	6210.61	6194.32
γ_{xxxz}	329.47	372.82	416.15	399.92	388.83
γ_{xxyy}	2059.70	2080.40	2062.22	2070.19	2064.76
γ_{xxzz}	4036.41	4139.95	4125.30	4124.44	4084.99
γ_{zzzz}	15002.69	15359.36	15633.43	15404.38	15321.69
γ	9525.19	9712.49	9726.49	9692.74	9635.95

- a. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.0625), d(0.0625) **88 bfs**
[7s6p5d / 2s1p1d]
- b. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5,0.0625), d(0.0625) **97 bfs**
[7s6p5d / 2s2p1d]
- c. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5,0.0625), d(0.125,0.0625) **115 bfs**
[7s6p5d / 2s2p2d]
- d. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5,0.0625), d(0.25,0.0625) **115 bfs**
[7s6p5d / 2s2p2d]
- e. As-(BC) + s(0.055), p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +s(0.045), p(0.5,0.0625), d(0.25,0.125,0.0625) **133 bfs**
[7s6p5d / 2s2p3d]

This study with both multiple p and d pf sets present was expected to require large amounts of CPU time but also convergence difficulties had to be handled. There are three places in NLO properties calculations, where convergence difficulties can occur. The first is in the convergence of the total energy in the SCF cycles, second is in the calculation of the DP values, and third is in the convergence of the β values used to calculate the γ values as explained in Chapter 1, pp. 11-13. Any one of these problems causes the calculation to stop. The results of this study are summarized in III / 3.23 through V / 3.23 and in Table 3.24. In III / 3.23 a hydrogen d(0.25) pf set is added to the bs of II / 3.23. There are small changes in the DM and DP values. These changes are however insignificant compared to a 20.5% drop in the β_{xxz} value (compared to II / 3.23). In IV / 3.23, a hydrogen d(0.25) pf set is used instead of the d(0.125) pf set of III / 3.23. This gave a β_{xxz} value 10% smaller than that of II / 3.23. In V / 3.23, the two d(0.25, 0.125) pf sets are used. The β result was close that of IV / 3.23 (i.e., only when one hydrogen d(0.25) pf set was present). Thus, the large effect of adding the d(0.125) pf set was nullified.

Calculations III / 3.23, IV / 3.23, and V / 3.23 imply that the low value (β_{xxz} of 4.50) seen in the large bs calculation II / 3.19 (147 bfs) is an artifact caused by the use of only two d pf sets (i.e., d(0.125, 0.0625)), in comparison to the very large reference I / 3.19 (184 bfs).

6. Table 3.24 Results - Small bs calculations (AsH_3)

In an attempt to better understand these observations, further calculations were performed using various hydrogen p pfs based on a smaller [6s6p5d / 1s] contracted bs, and these results are summarized in Table 3.24.

In I / 3.24 (93 bfs), the same bs as that of II / 3.23 (97 bfs) is used except that the arsenic outer s pf and the hydrogen s pf set removed. The differences are relatively minor (i.e., β_{xxz} differs by + 6.8%).

Table 3.24 AsH₃ Binning / Curtiss Results small bs calculations

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	0.1639	0.1673	0.1499	0.1581	0.1599	0.1665
μ (Deb.)	0.4167	0.4252	0.3810	0.4018	0.4064	0.4232
α_{xx}	34.13	34.26	34.08	34.23	34.20	34.26
α_{zz}	35.15	35.22	34.96	35.12	35.10	35.24
$\bar{\alpha}$	34.47	34.58	34.37	34.53	34.50	34.59
$\Delta\alpha$	1.02	0.96	0.88	0.89	0.90	0.98
β_{xxx}	-15.65	-16.28	-13.90	-15.23	-16.34	-17.07
β_{xxz}	6.26	5.49	5.30	4.64	5.22	5.22
β_{zzz}	40.01	38.26	38.63	39.73	40.50	41.03
β	31.52	29.54	29.54	29.41	30.56	30.88
$\Delta\beta$	21.23	21.79	22.73	25.81	24.84	25.37
γ_{xxxx}	6161.25	6200.84	6080.57	6145.52	6128.95	6151.44
γ_{xxxz}	375.90	390.05	269.26	384.28	308.71	362.33
γ_{xxyy}	2053.71	2066.91	2026.82	2048.49	2042.96	2050.46
γ_{xxzz}	4165.89	4187.12	4059.06	4097.45	4040.92	4101.04
γ_{zzzz}	15365.00	15570.89	15082.35	15473.21	15443.51	15562.73
γ	9691.69	9770.97	9506.66	9650.20	9590.19	9674.12

- a. As-(BC) + p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +p(0.50,0.0625), d(0.0625) **93 bfs** [6s6p5d / 1s2p1d]
- b. As-(BC) + p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +p(0.5,0.125,0.0625), d(0.0625) **102 bfs** [6s6p5d / 1s3p1d]
- c. As-(BC) + p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +p(0.125,0.0625), d(0.0625) **93 bfs** [6s6p5d / 1s2p1d]
- d. As-(BC) + p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) +p(0.125,0.0625), d(0.125,0.0625) **111 bfs** [6s6p5d / 1s2p2d]
- e. As-(BC) + p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) + p(0.125,0.0625), d(0.25,0.125,0.0625) **129 bfs** [6s6p5d / 1s2p3d]
- f. As-(BC) + p(0.0534,0.0267), d(0.49135, 0.19654, 0.07862, 0.03145), H-(T1.42.1) + p(0.5,0.0625), d(0.25,0.125,0.0625) **129 bfs** [6s6p5d / 1s2p3d]

In II / 3.24, a hydrogen p(0.125) pf set is added to the bs of I / 3.24. Again the differences are small (i.e., β_{xxz} differs by +4.0%, and β_{xxz} differs by -12.3% compared to I / 3.24). Next an attempt was made to add a hydrogen p(0.125) pf set, however the calculation had severe convergence problems. Further investigation, lead to the discovery that dropping the hydrogen p(0.5) pf set allowed the calculation to complete. Thus in III / 3.24 (93 bfs), the hydrogen p(0.125, 0.0625) pf sets and the d(0.0625) pf set are used. Except for the expected drop in the DM and a sizeable change in the β_{xxx} value (14.7% lower compared to II / 3.24), the results are very similar to the larger 3p1d calculation II / 3.24 (102 bfs). In IV / 3.24, a hydrogen d(0.125) pf set is added to the bs of III / 3.24. This improved the DM value considerably, and β_{xxx} is improved (5.6% lower compared to the reference I / 3.19), and as expected β_{xxz} decreases by 12.5% (compared to III / 3.24). In V / 3.24, a third hydrogen d(0.25) pf set is added. The only significant change is an increase in β_{xxz} of 12.5%, bringing it to within 3% of that of the very large (184 bfs) reference I / 3.19. Finally, in VI / 3.24, a hydrogen p(0.5) pf set is used instead of the p(0.125) pf set of V / 3.24. The β_{xxz} value remains the same, but the β_{xxx} and β_{zzz} values increase slightly.

A comparison of this calculation (VI / 3.24) (129 bfs) with I / 3.24 (93 bfs), which only used one hydrogen d(0.0625) pf set, shows that the use of the extra 2d pf sets, which is very expensive (in terms of added CPU time), results in very little changes in the DM, DP, and second DH values. It does however, cause more significant changes in the very sensitive β tensor (i.e., β_{xxx} differs by +9.1%, β_{xxz} differs by -16.6%, β_{zzz} differs by +2.5%, $\bar{\beta}$ differs by -2.0%, and $\Delta\beta$ differs by +19.5%. These changes are caused by the two added hydrogen d pf sets, which cause a cancelling out effect on each other, emphasizing once again, that the effect of adding pfs on the hydrogen is almost never additive.

CHAPTER IV

CALCULATION RESULTS FOR FORMAMIDE, PYRIDINE, BENZENE, PYRROLE

There is great interest in the design and characterization of organic materials in the application of nonlinear optics (NLO). Calculation of NLO properties for molecules such as formamide, pyridine, benzene, and pyrrole, can serve as prototypes for future calculations on more complex organic materials. However ab initio calculations using the large basis sets described in Chapter III of this dissertation are not practical for the calculation of NLO properties of large organic molecules. Within a non empirical scheme however there is at least one methodology if employed bring calculations of large molecules within the realm of possibility and practicality. This is the ECP method:

1. The use of a small starting basis, especially for the description of bonding orbitals.
2. The replacement of the individual core orbitals by an effective core potential (ECP) as discussed in Chapter I of this dissertation.

In this chapter a description of the attempts to incorporate methods 1 and 2 for a number of nitrogen compounds is given. The implementation of this method within our large molecular structure codes like the Gaussian codes (G90, G92, ...) has only been recently achieved, and therefore will be left for future development, and not will included in the scope of this dissertation. The ECP method is duscussed briefly in Chapter II (p.56) of this dissertation. As an example of a small valence basis set, the standard 3-21G basis set of Pople et al. [29, 30, 31, 32, 33, 34] is used together with the ECPs proposed by Stevens, Basch and Krauss [74] stored in the H8 program. Previously, the only attempts to incorporate ECPs in the calculation of NLO properties was that of Dupuis et al. [100] on CHCl_3 , CHBr_3 , and CHI_3 .

Formamide

Formamide is an example of a medium sized molecule, which is important because it is a prototype of polypeptides and is used to study intermolecular interactions of proteins. Formamide is of interest in its enhancement of nonlinear optical parameters due to charge transfer (i.e., between NH₂ electron donor and the carbonyl group electron acceptor). All calculations were performed at the HF 6-31G optimized geometry.

The reference I / 4.1 (Table 4.1) was performed with a 3-21G basis set augmented by pfs on C, O, and N, each with one diffuse s, one p, and 3 d pfs using the Dykstra exponents [36] (see Table 3.1). The omission of the most diffuse p pf set (i.e., p(0.005)), which is included in the ELP set (Chapter I p.33), did not affect the calculated results, so they were omitted in all our calculations. In II / 4.1, the same pfs as in I / 4.1 are used except the ECP replaced the core orbitals. Compared to I / 4.1, it is seen that there are some large changes in the β tensor values (β_{xxy} differs by +33.6%, and β_{yyz} differs by -11.0%). However, the ECP calculation required 30% less CPU time than the full 3-21G calculation (II / 4.1 vs. I / 4.1). In calculation III / 4.1 the pf sets p(0.9, 0.1) are added to the hydrogen basis set, and when compared to II / 4.1 shows the following: β_{xxy} differs by +33.8%, and β_{yyz} differs by -6.7%.

Table 4.1 Formamide Results

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	1.6552	1.6500	1.6485	1.6402	1.7901	1.4754
μ (Deb.)	4.2070	4.1940	4.1900	4.1690	4.5500	3.7500
α_{xx}	25.51	25.73	25.90	26.01	21.60	28.93
α_{xz}	2.81	2.93	2.95	2.98	2.03	3.46
α_{yy}	18.04	18.41	18.51	18.41	14.06	20.03
α_{zz}	28.55	28.80	28.98	29.09	29.08	33.20
$\bar{\alpha}$	24.03	24.31	24.46	24.51	24.59	27.39
$\Delta\alpha$	9.37	9.25	9.32	9.52	13.01	11.64
β_{xxx}	39.61	41.40	41.63	45.31	60.79	66.74
β_{xxz}	17.51	18.80	19.63	21.04	28.31	23.17
β_{xyy}	5.54	7.40	9.91	9.09	12.72	0.122
β_{xzz}	7.95	8.07	7.65	7.67	8.76	12.18
β_{yzz}	17.78	15.82	14.83	15.10	20.78	28.55
β_{zzz}	-19.13	-18.91	-20.14	-19.75	-39.53	-16.48
$\bar{\beta}$	9.53	11.21	11.47	13.40	10.25	17.91
$\Delta\beta$	-71.66	-75.31	-79.03	-82.87	-124.46	-85.99
γ_{xxxx}	3546.21	3674.06	3772.09	4010.15	4259.45	-----
γ_{xxxz}	-348.86	-347.44	-273.43	-275.86	-378.66	-----
γ_{xxyy}	819.51	842.75	964.20	967.31	1291.58	-----
γ_{xxzz}	964.55	1016.26	1015.82	1076.51	1239.04	-----
γ_{yyyy}	2754.54	2767.67	k2748.32	2748.58	3448.36	-----
γ_{yyzz}	1172.05	1138.14	1163.38	1206.32	1494.45	-----
γ_{zzzz}	3666.34	3850.14	3343.98	3988.52	5514.68	-----
$\bar{\gamma}$	3175.86	3257.23	3343.98	3455.50	4254.53	-----

- a. C,N,O-(3-21G)+Dykstra 1s1p3d+1s, H-(3-21G)+ s(0.06) **102 bfs** [4s3p3d / 3s]
b. C,N,O-(ECP)+Dykstra 1p3d,p(0.04), H-(3-21G) + s(0.06) **99 bfs** [3s3p3d / 3s]
c. C,N,O-(ECP)+Dykstra 1p3d, H-(3-21G) + s(0.06), p(0.9, 0.1) **117 bfs**
[3s3p3d / 3s2p]
d. C,N,O-(ECP)+Dykstra 1p3d, H-(3-21G)+ s(0.06), p(0.9, 0.1), d(0.1)
135 bfs [3s3p3d / 3s2p1d]
e. C,N,O-(ECP)+C,N-[p(0.05), d(0.05)], H-(3-21G)+ s(0.06) **63 bfs** [3s3p1d / 3s]
f. C,N,O-(3-21G)+Dykstra 1s1p3d+1s, H-(3-21G)+ s(0.06), p(0.9, 0.1)
120 bfs MP2 [4s3p3d / 3s2p]

In calculation IV / 4.1, a d(0.1) pf set was added to the hydrogen basis set, to produce a +8.8% change in β_{xxx} (compared to III / 4.1). This suggests that the added computational resource expense of the addition of the d pf set does not result in any great improvement in the quality of β . In calculation V / 4.1 only one d(0.05) and one p(0.05) pf sets were used as suggested by Dupuis et al. [35]. This calculation V / 4.1 compared to I / 4.1 shows relatively large changes ($\bar{\alpha}$ differs by -10.2%, β_{xxx} differs by +51.3%, β_{xxz} differs by +61.7%, β_{zzz} differs by +106.6%, and $\bar{\gamma}$ differs by +73.6%). These large changes in the β values and $\bar{\gamma}$ (compared to I / 4.1), indicate that β and γ calculated by the use of such a limited set of pfs in the basis set may have only qualitative significance.

Finally a MP2 calculation using the basis set of III / 4.1 (120 bfs) was performed (VI / 4.1) to study the effects of correlation. The MP2 calculation VI / 4.1 gave results that were substantially different from the HF calculation III / 4.1, in that: μ differs by -10.50%, $\bar{\alpha}$ differs by -11.75%, β_{xxx} differs by +60.70%, β_{xxz} differs by +18.01%, β_{xyy} differs by -98.65%, β_{xzz} differs by +59.20%, β_{yyz} differs by +92.50%, and β_{zzz} differs by +41.70%. The MP2 calculation (VI / 4.1) gave some values (μ of 3.75 Debyes, and $\bar{\alpha}$ of 27.39 a.u.) which were in excellent with experimental values quoted by Waite et al. [38]. There are no experimental hyperpolarizabilities with which to compare the β results.

Benzene and Pyridine

1. Benzene Results

Benzene is a symmetric molecule (D_{6h} symmetry), and as the result the net dipole moment and the first hyperpolarizabilities (β 's) are zero. The effect of the destruction of this symmetry by replacing one carbon bonded to hydrogen with nitrogen (so introducing polarity and consequently non zero values of μ and β) is of considerable interest.

The results of such a substitution to benzene produces pyridine. Calculations of NLO properties of pyridine are summarized in Table 4.3. Calculations I / 4.2 (Table 4.2) of benzene and I / 4.3 of pyridine were performed with equal basis sets, that is- 3-21G basis set supplemented with a p(0.05) and a d(0.05) pf set on C and N. A similar calculation for benzene [41] and other conjugated hydrocarbons [42] have been reported in the literature. The results of benzene vs. pyridine (i.e., I / 4.2 and I / 4.3) predict a small drop in the average dipole polarizability ($\bar{\alpha}$) of 7.53% resulting from a reduction in the out of plane matrix element α_{yy} , and a drop in $\bar{\gamma}$ of 21.80%. Also the β values were substantial.

In II / 4.2, for benzene, the same basis set of I / 4.2 is used for a MP2 calculation, and the results show a slight increase in $\bar{\alpha}$ (i.e., 3%). When I / 4.2 is compared to a SCF calculation by Perrin, Prasad, Mougenot, and Dupuis [62], and II / 4.2 is compared to their MP2 calculation, the results are very similar (i.e., differ by less than 5%). When II / 4.2 is compared to Proutiere, and Camail's experimental results [96], $\bar{\alpha}$ differs by -5.7%. When the $\bar{\gamma}$ from I / 4.2 is compared to Zhao, Samoc, Singh, and Prasad's experimental result [62], it shows a +14.1% difference.

2. Pyridine Results

In calculation II / 4.3 (Table 4.3) of pyridine, a p(0.1) pf set was added to the hydrogen basis set of I / 4.3, causing a further drop in $\bar{\gamma}$ of 6.0%. Usually the changes in the first DHs are expected to be considerable, but in this case the only change is -13.2% for β_{zzz} . In III / 4.3 the Dykstra [36] 3d of set was used on carbon and nitrogen, and this produces a 5.2% increase in $\bar{\alpha}$, but μ drops by 15.6%. Calculation IV / 4.3, with 206 basis functions was performed with a p(0.9, 0.1) pf set on the hydrogen. This calculation (IV / 4.3) is close to the maximum size limit which the IBM 3090/400 G90 code can handle, and required three hours of CPU time.

Table 4.2 Benzene Results and quoted values

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^{f,g}
α_{xx}	73.83	73.66	74.21	76.02	77.51	79.15
α_{zz}	38.40	40.18	39.47	41.28	44.69	44.15
$\bar{\alpha}$	62.02	63.83	62.63	64.44	66.60	67.50
$\Delta\alpha$	35.43	35.48	34.74	34.74	32.81	35.00
γ_{xxxx}	14031.62	-----	14190	19332	-----	-----
γ_{xxyy}	4677.21	-----	4728	6402	-----	-----
γ_{xxzz}	6053.96	-----	6462	8688	-----	-----
γ_{zzzz}	11344.76	-----	12480	15708	-----	-----
γ	14595.70	-----	15228	20388	-----	12900

- a. C(3-21G)+p(0.05), d(0.05), H(3-21G) 120 bfs [3s3p1d / 2s]
- b. C(3-21G)+p(0.05), d(0.05), H(3-21G) 120 bfs MP2 [3s3p1d / 2s]
- c. Perrin, Prasad, Mougenot, and Dupuis' SCF results [62]
- d. Perrin, Prasad, Mougenot, and Dupuis' MP2 results [62]
- e. Hinchliffe, and Soscun's 631+G(3p,3d) HF results [94]
- f. Proutiere, and Camail's experiment DP results [96]
- g. Zhao, Samoc, Singh, Prasad's experimental $\bar{\gamma}$ result [62]

Table 4.3 Pyridine Results

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	1.10	1.10	0.95	0.94	1.09	-----
μ (Deb.)	2.80	2.79	2.40	2.39	2.77	-----
α_{xx}	71.28	72.35	74.82	75.46	73.14	76.9
α_{yy}	66.10	67.07	69.55	70.07	66.35	70.20
α_{zz}	34.67	36.54	40.72	40.83	40.21	37.10
$\bar{\alpha}$	57.35	58.65	61.69	62.13	57.86	61.40
$\Delta\alpha$	34.31	33.48	31.79	32.27	30.93	36.91
β_{xxz}	20.34	18.54	21.42	21.04	-----	-----
β_{yyz}	16.80	16.90	21.32	18.16	-----	-----
β_{zzz}	-10.35	-8.98	-14.53	-10.40	-----	-----
β	16.07	15.88	16.92	17.28	-----	-----
$\Delta\beta$	-66.06	-62.14	-78.63	-69.20	-----	-----
γ_{xxxx}	13204.36	11995.02	-----	-----	-----	-----
γ_{xxyy}	4811.09	4391.33	-----	-----	-----	-----
γ_{xxzz}	3839.71	3577.92	-----	-----	-----	-----
γ_{yyyy}	8824.67	9395.18	-----	-----	-----	-----
γ_{yyzz}	3875.57	3560.07	-----	-----	-----	-----
γ_{zzzz}	9993.13	9206.39	-----	-----	-----	-----
γ	11415.00	10731.00	-----	-----	-----	-----

- a. C,N-(3-21G)+p(0.05), d(0.05), H(3-21G) 118 bfs [3s3p1d / 2s]
b. C,N-(3-21G)+p(0.05), d(0.05), H(3-21G)+p(0.1) 133 bfs [3s3p1d / 2s1p]
c. C,N-(3-21G)+Dykstra 1s1p3d, H-(3-21G) + 2s 206 bfs [4s3p3d / 4s]
d. C,N-(3-21G)+Dykstra 1s1p3d, H-(3-21G)+p(0.9, 0.1) 226 bfs [3s3p3d / 2s2p]
e. Hinchliffe, and Soscun's 6311+G(3p,3d) results [95]
g. Mulder, and VanDijk's experimental results [39]

Comparing IV / 4.3 to I / 4.3 shows the following: $\bar{\alpha}$ differs by +5.6%, β_{xxz} differs by +5.3%, β_{yyz} differs by +28.4%, β_{zzz} differs by +40.4%. The polarizability values of IV / 4.2 agree well with Mulder, and Van Dijk's experimental results VI / 4.3 [39] (α_{xx} differs by -2.78%, α_{yy} differs by -0.93%, α_{zz} differs by +8.89%). This is in contrast to some semi-empirical values in the literature calculated using the MNDO method. For example a recent MNDO calculation [40] gave $\alpha_{xx} = 67.34$ a.u., $\alpha_{yy} = 59.85$ a.u., $\alpha_{zz} = 8.43$ a.u., and $\bar{\alpha} = 45.2$ a.u., i.e., the out of plane term α_{zz} to $\bar{\alpha}$ is grossly underestimated giving a very low $\bar{\alpha}$. Hinchliffe, and Soscun's very recent large bs 6311+G(3p,3d) calculation [95] reported in V / 4.3 is very similar to I / 4.3, except for α_{zz} that differs by +16%, which causes $\Delta\alpha$ to differ by -9.9%.

From the results in Table 4.2 for benzene and pyridine, and the previous discussion (Chapter III) on other molecular results, it is clear that good values of β and γ require careful choice of pfs. Current semi-empirical methods appear to yield unreliable results because their parameters do not take into account adequate diffuse pfs, and at best can only yield roughly qualitative correct results.

Pyrrole

Pyrrole is a molecule of interest because it is a fragment of polymers that are used as semiconductors, and these polymers have desirable nonlinear optical parameters [1]. Prior to this work, there has been no previous ab initio calculations of the NLO properties of pyrrole. Calculations of pyrrole are summarized in Table 4.4. The $\bar{\alpha}$ and $\bar{\gamma}$ of pyrrole and benzene are predicted to be similar in magnitude. The results for pyrrole show that by substituting a NH group for the C-C bond, there is no particular enhancement of NLO properties. Calculation I / 4.4 is the smallest basis set, in that - the 3-21G set is augmented by a p(0.05) and a d(0.05) pf set on the C and N atoms.

Table 4.4 Pyrrole Results

	I ^a	II ^b	III ^c	IV ^d
μ (A.U.)	0.7542	0.7310	0.7345	0.7423
μ (Deb.)	1.917	1.858	1.867	1.887
α_{xx}	57.33	60.91	61.97	63.21
α_{yy}	33.61	38.44	39.00	39.55
α_{zz}	56.04	59.26	60.43	60.59
$\bar{\alpha}$	48.99	52.87	53.80	54.45
$\Delta\alpha$	23.10	21.69	22.24	22.47
β_{xxz}	-28.88	-37.76	-40.24	-27.88
β_{yyz}	17.31	33.58	34.70	38.35
β_{zzz}	20.99	35.10	36.33	35.02
β	5.65	18.55	18.47	27.29
$\Delta\beta$	38.35	41.37	44.64	19.32
γ_{xxxx}	21322.58	18260.97	-----	-----
γ_{xxyy}	9864.56	10951.30	-----	-----
γ_{xxzz}	4257.78	3331.20	-----	-----
γ_{yyyy}	13030.68	17968.40	-----	-----
γ_{yyzz}	5859.08	5722.70	-----	-----
γ_{zzzz}	10007.97	7345.60	-----	-----
γ	16864.82	16717.10	-----	-----

- a. C,N-(3-21G)+p(0.05), d(0.05), H(3-21G) **100 bfs** [3s3p1d / 2s]
b. C,N-(3-21G)+Dykstra 1s1p3d, H(3-21G)+p(0.1) **180 bfs** [4s3p3d / 2s1p]
c. C,N-(3-21G)+Dykstra 1s1p3d, H(3-21G)+s(0.06),p(0.9, 0.1)
200 Basis Functions [4s3p3d / 3s2p]
d. C,N-(3-21G)+Dykstra 1s1p3d, H(3-21G)+p(0.1) **180 bfs MP2**
[4s3p3d / 2s1p]

In II / 4.4 the use of the Dykstra 3d pf sets on C and N produced a very noticeable change in the β values in comparison to I / 4.4 (β_{xxz} differs by +30.8%, β_{yyz} differs by +94%, β_{zzz} differs by +67.2%). However, in III / 4.4 the addition of the p(0.9, 0.1) pf sets to the hydrogen basis set does not produce much extra change (β_{yyz} differs by +6.57%). This small change in the β values indicates that the use of p(0.9, 0.1) pf sets with a considerable increase in computational complexity which results in more CPU time is not justified by the results. In IV / 4.4 the same bs of II / 4.4 was used in a MP2 calculation, and a comparison with II / 4.4 shows only small changes in the DM and DP, but as usual, substantial increase in the β_{yyz} value (i.e., 14.2%), which caused $\bar{\beta}$ to differ by +47.1%, and $\Delta\beta$ to differ by -53.3%.

These preliminary results show that even with small pf sets, fairly good results can be obtained. These ab initio results are for organic molecules, a great improvement over the semi-empirical methods. Even though these molecules are relatively small, better quality calculations cannot be performed with the present computational facilities available. To perform even similar calculations on larger molecules would require much faster computers, and much larger memories and disk storage facilities than are available to us at the present time.

CHAPTER V

CALCULATION RESULTS FOR H_2S , H_2SE , AND H_2TE

The first molecule on which our group investigated the relationships between the magnitude of the DM, DP, and DH and the size and type of pfs in the bs was the water molecule [44]. In this chapter this study has been extended to the other hydrides H_2X of Group VI, where $\text{X} = \text{S}, \text{Se}, \text{and Te}$. Particular attention has been paid to the possibility of using the knowledge gained concerning the bs used for water on the other molecules. Also since molecules containing Group VI elements, especially sulfur and selenium offer great potential as molecules whose NLO properties are of commercial value, an investigation of how small the bs may become for S, Se, and Te before the accuracy of calculated NLO properties deteriorates was performed.

Hydrogen Sulfide (H_2S)

This molecule has the distinction along with HCl [71] of being the only molecule containing a third period element for which ab initio calculations have been performed for the DH. There have been also a number of reports on the calculation of the DM [28,46,61,65], the DP [46,61,65], and the DH [65]. These values are reported in Tables 5.1, 5.2, and 5.3.

The bs used in the reference calculation for sulfur in H_2S is based on the triple zeta valence (TZV) bs. This is a (13s8p) -> [6s5p] bs stored internally in the Hondo 8 program [11]. This bs is augmented by a series of pf sets, and the hydrogen TZV, (6s) -> [3s] bs is augmented by pf sets as well.

Table 5.1 Feller, Boyle and Davidson Results and Experimental Result of H₂S

	I ^a	II ^b	III ^c	IV ^d
μ (A.U.)	0.4297	0.4139	0.4081	0.4010
μ (Deb.)	1.0922	1.0520	1.0373	1.0192

- Feller, Boyle and Davidson's HF result [10s3p2d/6s3p1d] **73bfs** [28]
- Feller, Boyle and Davidson's SD-CI result [10s3p2d/6s3p1d] **73bfs** [28]
- Feller, Boyle and Davidson's MRSD-CI result [10s3p2d/6s3p1d] **73bfs** [28]
- Hilger and Strandberg's experimental result [79]

Table 5.2 Spackman's and Sadlej's Results of H₂S

	I ^a	II ^b	III ^c	IV ^d	v ^e	VI ^f
μ (A.U.)	0.527	0.444	0.4367	0.4085	0.3897	0.383
μ (Deb.)	1.34	1.13	1.110	1.038	0.991	0.974
α_{xx}	21.55	24.28	23.69	24.21	24.16	25.92
α_{yy}	23.60	24.48	23.85	25.14	25.13	25.21
α_{zz}	22.48	23.71	23.39	24.20	24.16	25.30
$\bar{\alpha}$	22.54	24.16	23.64	24.52	24.48	24.66
$\Delta\alpha$	1.78	0.70	0.40	0.94	0.97	0.67

- Spackman's HF results **32bfs** [46]
- Spackman's MP2 results **32bfs** [46]
- Sadlej's HF results [6s3p1d / 3s2p] **39bfs** [61]
- Sadlej's MBPT(2) results [6s3p1d / 3s2p] **39bfs** [61]
- Sadlej's MBPT(4) results [6s3p1d / 3s2p] **39bfs** [61]
- Bogaard et al. experimental results [53,101]

Table 5.3 Sekino and Bartlett's H₂S Results

	I ^a	II ^b
μ (A.U.)	0.4384	0.4037
μ (Deb.)	1.114	1.026
α_{xx}	23.84	25.35
α_{yy}	23.76	24.41
α_{zz}	23.43	24.45
$\bar{\alpha}$	23.68	24.74
$\Delta\alpha$	0.37	0.92
β_{xxz}	-5.6	-5.5
β_{yyz}	9.9	9.2
β_{zzz}	-7.9	-0.2
β	-2.16	8.7
$\Delta\beta$	-14.35	-22.25
γ_{xxxx}	10900	14200
γ_{xxyy}	2400	3300
γ_{xxzz}	2600	3500
γ_{yyyy}	2600	3300
γ_{yyzz}	1200	1600
γ_{zzzz}	3900	5100
γ	6000	7800

- a. Sekino and Bartlett's SCF results [7s5p2d / 3s2p] **52bfs** [65]
- b. Sekino and Bartlett's MBPT(2) results [7s5p2d / 3s2p] **52bfs** [65]

1. Tables 5.4 and 5.5 Results

The reference calculation (I / 5.4) (Table 5.4) consists of a 143 bfs [6s7p7d / 4s4/3d] bs. This bs uses a sulfur s(0.05) pf, and 2p(0.045, 0.025) pfs constructed from the most diffuse valence bf with a rf of 0.5. The sulfur d pf set is based on the three energy optimized pf set of Feller et al. [28], d(2.34,0.94,0.38), augmented by four more d pfs constructed with a rf of 0.5. For the hydrogen, the TZV [3s] bs is augmented by four p and three d pfs. These pf sets were constructed with an initial exponent of p(1.0) with a rf of 0.5, and d(0.25) with a rf of also 0.5. This reference calculation produces a DM of 0.424 a.u., an $\bar{\alpha}$ of 23.77, a β_{xxz} of 5.57, β_{yyz} of 10.25, and a β_{zzz} of 6.89, and a $\bar{\gamma}$ of 6195.78 (all units in a.u.s). It is valuable at this point to compare the reference calculation with previous results. The DM is only 1.3% smaller than the HF value quoted by Feller et al. [28] (0.4297 a.u.), and is 3% smaller than the HF value quoted by Sadlej [61] (0.4367 a.u.). On the other hand, the DM result given by Spackman [46] differs by 30%, indicating that the bss used by Spackman are quite inadequate for the task for which they were used. The DPs are not too different from those reported by Sadlej [61], and his $\bar{\alpha}$ value (23.64 a.u.) is only 0.55% smaller than that of our reference calculation, while Spackman's value is 5.4% too small. The anisotropy of the DP ($\Delta\alpha$) is by far a more sensitive test of the bs than the individual DP tensor values. The $\Delta\alpha$ value calculated from Sadlej's HF result is 0.4, which compares reasonably with our reference value of 0.52. The $\Delta\alpha$ value calculated from Spackman's results is much too large (1.78). The $\Delta\alpha$ value reported by Sekino and Bartlett [65] is of course close to Sadlej's results, since they used primarily the same bs. Sekino and Bartlett [65] report three sets of results for the DH. The first set uses the bs recommended by Sadlej.

Table 5.4 H₂S TZV Results - Study of sulfur bs

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	0.424	0.423	0.423	0.423	0.423	0.423
μ (Deb.)	1.078	1.076	1.076	1.076	1.076	1.076
α_{xx}	24.08	24.07	24.07	24.07	24.15	24.12
α_{yy}	23.75	23.74	23.74	23.74	23.70	23.67
α_{zz}	23.48	23.75	23.45	23.46	23.42	23.37
$\bar{\alpha}$	23.77	23.85	23.75	23.75	23.76	23.72
$\Delta\alpha$	0.52	0.33	0.54	0.53	0.64	0.65
$-\beta_{xxz}$	5.57	5.70	5.71	5.70	6.66	8.55
β_{yyz}	10.25	10.32	10.28	10.28	11.66	10.60
$-\beta_{zzz}$	6.89	6.83	7.03	6.87	10.23	14.80
$-\beta$	1.33	1.33	1.48	1.37	3.14	7.65
$-\Delta\beta$	13.91	13.76	13.89	13.74	17.73	17.88
γ_{xxxx}	11041.95	11041.73	11028.70	10980.32	10909.13	10177.90
γ_{xxyy}	2527.76	2569.67	2553.53	2560.59	2405.41	2240.50
γ_{xxzz}	2641.47	2678.24	2667.69	2652.78	2493.21	2384.63
γ_{yyyy}	2892.08	2896.60	2859.67	2892.79	2294.40	1820.67
γ_{yyzz}	1327.91	1326.77	1301.71	1324.87	1446.62	1102.42
γ_{zzzz}	4050.58	4075.39	4035.65	4070.45	3353.48	2901.22
γ	6195.78	6232.61	6193.97	6204.01	5849.50	5270.98

S1 $\equiv$ S(TZV) + p(0.045, 0.0225), d(2.34, 0.94, 0.38, 0.19, 0.095, 0.047, 0.0235)
[6s7p7d]

a. S1, H(TZV) + s(0.06), p(1.0, 0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
143 bfs [6s7p7d / 4s5p3d]

b. S1, H(TZV) + s(0.06), p(0.6, 0.2, 0.07), d(0.25, 0.125, 0.0625, 0.03125)
143 bfs [6s7p7d / 4s3p4d]

c. S1+ s(0.05), H(TZV) + s(0.06), p(0.6, 0.2, 0.07), d(0.25, 0.125, 0.0625)
132 bfs [6s7p7d / 4s3p3d]

d. S1 - d(0.0235), H(TZV) + s(0.06), p(0.6, 0.2, 0.07), d(0.25, 0.125, 0.0625, 0.03125) **137 bfs** [6s7p6d / 4s3p4d]

e. S1+ s(0.05), H(TZV) + p(0.6, 0.2, 0.07) **94 bfs** [6s7p7d / 3s3p]

f. S1+ s(0.05), H(TZV) + p(0.6, 0.2) **88 bfs** [6s7p7d / 4s2p]

The second set is the first set augmented with a hydrogen d(0.1) pf set, and with the third bs they attempted to improve the description of the lone pair functions by adding a set of non-atomic centered s and p pfs located in the lone pair direction. It can be seen by comparing these results with our reference calculation that the results of using the smallest bs (i.e., that proposed by Sadlej) for the calculation of the DM and DP, are fairly inadequate for calculating the DHs. The two larger sets are considerably improved, but are still not good enough for the β_{xxz} component. It also appears, if one accepts the reference calculation as the best calculation, that the use of non-atom centered pfs does not improve the results at the HF (SCF) level.

In II / 5.4 the 3p sets of p(0.6, 0.2, 0.07), which was found adequate for calculations of the water molecule [44] were used along with a extra d(0.03125) set on hydrogen. The results compared to I / 5.4 are very similar, that is: $\bar{\alpha}$ differs by - 0.04%, $\bar{\beta}$ differs by -2.3%, $\bar{\gamma}$ differs by -0.1%. Calculation III / 5.4 was performed with the d(0.03125) pf set on hydrogen removed from the bs used in II / 5.4, which also produces very little change. Calculation IV / 5.4 was performed with the d(0.0235) pf set on sulfur removed from II / 5.4, which also produces little change in the results. In V / 5.4 all the d pf sets on hydrogen are removed, although: $\bar{\alpha}$ differs only by -0.04%, β_{xxz} differs by +18%, β_{yyz} differs by +12.6%, β_{zzz} differs by +32.9%, $\bar{\gamma}$ differs by -6% (comparing V / 5.4 to I / 5.4). In VI / 5.4 the p(0.07) pf set on hydrogen is further removed. This removal introduced large changes ($\bar{\alpha}$ differs by -0.13%, β_{xxz} differs by +25.42%, β_{yyz} differs by -11.50%, β_{zzz} differs by +30.64%, $\bar{\gamma}$ differs by -10.99% (comparing VI / 5.4 to V / 5.4)). In I / 5.5 (Table 5.5), the p(0.6, 0.2, 0.07) pf set on hydrogen is used but a d(0.075) set instead of a d(0.0625) set (used in previous calculations) is used on the hydrogen, which produces little change ($\bar{\alpha}$ did not change, β_{xxz} differs by +5.8%, β_{yyz} differs by -3.6%, β_{zzz} differs by -3.5%, $\bar{\gamma}$ differs by -0.02% (comparing I / 5.5 to I / 5.4)).

Table 5.5 H₂S TZV Results - hydrogen d(0.075) pf

	I ^a
μ (A.U.)	0.423
μ (Deb.)	1.076
α_{xx}	24.14
α_{yy}	23.72
α_{zz}	23.43
$\bar{\alpha}$	23.76
$\Delta\alpha$	0.62
$-\beta_{xxz}$	5.89
β_{yyz}	9.88
$-\beta_{zzz}$	6.65
$-\beta$	1.60
$-\Delta\beta$	12.64
γ_{xxxx}	10941.05
γ_{xxyy}	2562.78
γ_{xxzz}	2665.29
γ_{yyyy}	2796.01
γ_{yyzz}	1297.07
γ_{zzzz}	3959.67
$\bar{\gamma}$	6149.40

S1 $\equiv$ S(TZV) + p(0.045, 0.0225), d(2.34, 0.94, 0.38, 0.19, 0.095, 0.047, 0.0235)
[6s7p7d]

a. S1 + s(0.05), H(TZV) + s(0.06), p(0.6, 0.2, 0.07), d(0.075)
108 bfs [7s7p7d / 4s3p1d]

Calculations V / 5.4, VI / 5.4, and I / 5.5, show the importance of the diffuse p(0.07) and d(0.075) pf sets on the hydrogen. Calculation I / 5.5 is probably an optimally minimal bs for the calculations of the properties of interest, since any further reduction results in poorer β and γ results. Some calculations with further reduced bss on both sulfur and hydrogen than that of I / 5.5 are presented in Table 5.6 (i.e., calculations I / 5.6 through V / 5.6).

2. Table 5.6 Results - H₂S more detailed investigation of sulfur and hydrogen pf sets

Calculation I / 5.6 (Table 5.6) was performed with the p(0.6) pf set on hydrogen removed, which produces the results: $\bar{\alpha}$ differs by -0.13%, β_{xxz} differs by +5.5%, β_{yyz} differs by -2.4%, β_{zzz} differs by +13.3%, $\bar{\gamma}$ differs by -1.6% (comparing I / 5.6 to I / 5.5). In II / 5.6 again the d(0.0237) on the sulfur is removed, which produces the results: β_{xxz} differs by -21.3%, β_{zzz} differs by -5.5%, $\bar{\gamma}$ differs by -2.6% (comparing II / 5.6 to I / 5.6). The change in β_{xxz} due to the removal of the d pf on sulfur compensates for change in β_{xxz} due to the removal of the p pf set (i.e., I / 5.6), thus β_{xxz} differs by -8.6% (comparing I / 5.6 to I / 5.4).

Calculations III / 5.6 and IV / 5.6 were performed to study the effect of removing successively the most diffuse p pf sets on the sulfur. In III / 5.6 the p(0.0225) pf set on sulfur is removed, which produces a change in β_{xxz} of +28% (comparing III / 5.6 to II / 5.6). Calculation IV had the further removal of the p(0.045) pf set on sulfur, which produces the results: β_{xxz} differs by +4%, β_{zzz} differs by -7.6%, $\bar{\gamma}$ differs by -19.6% (comparing IV / 5.6 to II / 5.6). In V / 5.6, the innermost and outermost d pfs on sulfur are removed to give a [6s6p5d / 3s2p1d] bs, which produces the results: β_{xxz} differs by -21.7%, β_{yyz} differs by -2.4%, β_{zzz} differs by -10.6%, $\bar{\gamma}$ differs by -1.1% (comparing V / 5.6 to III / 5.6). Note also the DM is influenced very little.

Table 5.6 H₂S TZV Results - Study of sulfur d pfs

	Ia	IIb	IIIc	IVd	Ve
μ (A.U.)	0.418	0.417	0.417	0.417	0.422
μ (Deb.)	1.061	1.061	1.060	1.060	1.073
α_{xx}	24.13	24.12	24.13	23.67	24.04
α_{yy}	23.69	23.68	23.67	23.65	23.66
α_{zz}	23.40	23.39	23.38	23.34	23.67
$\bar{\alpha}$	23.74	23.73	23.72	23.55	23.79
$\Delta\alpha$	0.63	0.64	0.64	0.32	0.38
$-\beta_{xxz}$	6.28	5.13	6.57	5.34	5.40
β_{yyz}	9.81	9.46	9.76	9.56	10.00
$-\beta_{zzz}$	7.29	7.27	7.32	6.72	6.62
$-\beta$	2.26	1.76	2.48	1.50	1.21
$-\Delta\beta$	12.58	13.77	12.10	13.05	13.53
γ_{xxxx}	11310.08	11049.91	11069.76	6995.63	10898.93
γ_{xxyy}	2490.84	2440.08	2427.95	2126.80	2395.94
γ_{xxzz}	2613.90	2562.50	2534.52	2188.63	2498.68
γ_{yyyy}	2684.25	2607.98	2528.66	2442.09	2528.22
γ_{yyzz}	1265.89	1229.21	1200.40	1155.43	1197.65
γ_{zzzz}	3853.87	3759.22	3679.57	3494.33	3676.24
$\bar{\gamma}$	6117.89	5976.22	5920.80	4774.80	5857.60

S1 $\equiv$ S(TZV) + p(0.045, 0.0225), d(2.34, 0.94, 0.38, 0.19, 0.0095, 0.047, 0.0235)
[6s7p7d]

- S1 + s(0.05), H(TZV) + p(0.2, 0.07), d(0.075) 100 bfs
- S1 + s(0.05) - d(0.0235), H(TZV) + p(0.2, 0.07), d(0.075) 94 bfs
- S1 - p(0.0235), H(TZV) + s(0.06), p(0.2, 0.07), d(0.075) 98 bfs
- S1 - p(0.047, 0.0235), H(TZV) + s(0.06), p(0.2, 0.07), d(0.075) 95 bfs
- S1 - p(0.0235) - d(2.34, 0.0235), H(TZV) + s(0.06), p(0.2, 0.07), d(0.075)
86 bfs

3. Table 5.7 Results - H₂S investigation of sulfur f pfs

The role of f type pf sets was studied in calculation I / 5.7 (Table 5.7) in which f(0.25, 0.125) pf sets are added to the bs used in I / 5.6. The changes are small but significant (μ differs by +1.7%, β_{zzz} differs by -11.4%, $\bar{\gamma}$ differs by +3% (comparing I / 5.7 to I / 5.6)). This same bs is used in a G90 calculation with MP2 correlation (II / 5.7). These results compare quite well with the results of the MBPT(2) calculation by Sadlej [45]

(IV / 5.2). There are substantial changes (β_{zzz} differs by -135%, $\bar{\beta}$ changes sign and differs by 141.2%, and $\Delta\beta$ differs by -42.4% (comparing II / 5.7 to I / 5.7). In III / 5.7, another MP2 calculation is reported. The outermost sulfur d(0.0235) pf is removed from II / 5.7. This introduces small but significant changes in β_{xxz} which substantially changes $\bar{\beta}$ and $\Delta\beta$ ($\bar{\beta}$ differs by +304.9%, and $\Delta\beta$ differs by +54.4%). This is unexpected and unfortunately raises a warning that just because a pf set is not important at the HF level, it does not mean that it will not be important when electron correlation is included. Note that the β tensor values of our MP2 calculations (I / 5.7 and II / 5.7) bracket the MBPT (2) results of Sekino and Bartlett [65] (II / 5.3), and the $\bar{\beta}$ values of both of our MP2 calculations differ greatly from that of Sekino and Bartlett even though his HF (SCF) results are similar to ours.

Table 5.7 H₂S TZV Results - MP2

	I ^a	II ^b	III ^c
μ (A.U.)	0.420	0.401	0.408
μ (Deb.)	1.067	1.020	1.037
α_{xx}	24.02	25.45	25.46
α_{yy}	23.72	24.37	24.32
α_{zz}	23.44	24.41	24.37
$\bar{\alpha}$	23.73	24.74	24.72
$\Delta\alpha$	0.50	1.06	1.12
$-\beta_{xxz}$	5.64	6.02	4.10
β_{yyz}	9.95	9.48	10.46
$-\beta_{zzz}$	6.78	2.44	2.24
$\bar{\beta}$	-1.48	0.61	2.47
$-\Delta\beta$	13.25	7.63	11.78
γ_{xxxx}	10885.88	-----	-----
γ_{xxyy}	2542.20	-----	-----
γ_{xxzz}	2656.87	-----	-----
γ_{yyyy}	2812.45	-----	-----
γ_{yyzz}	1292.03	-----	-----
γ_{zzzz}	3985.52	-----	-----
$\bar{\gamma}$	6133.21	-----	-----

S1 $\equiv$ S(TZV) + p(0.045, 0.0225), d(2.34, 0.94, 0.38, 0.19, 0.0095, 0.047, 0.0235)
[6s7p7d]

a. S1 + s(0.05)+f(0.25,0.125), H(TZV)+ p(0.2, 0.07), d(0.075)
120 bfs [7s7p7d2f / 3s2p1d]

b. S1 + s(0.05)+f(0.25,0.125), H(TZV)+ p(0.2, 0.07), d(0.075)
120 bfs MP2 [7s7p7d2f / 3s2p1d]

c. S1 + s(0.05) - d(0.0235)+f(0.25,0.125), H(TZV)+ p(0.2, 0.07), d(0.075)
114 bfs MP2 [7s7p6d2f / 3s2p1d]

Hydrogen Selenide (H_2Se)

The hydrogen selenide (H_2Se) calculations were based upon the Curtiss / Binning [26] bs which consists of a (14s11p5d) -> [6s4p1d] contracted bs of Triple Zeta quality or better. Various sets of additional pf basis functions on the selenium and hydrogen were used.

A great deal of difficulty was experienced in getting proper convergence for most of the H_2Se calculations. This problem was overcome in some cases by the use of a low damping factor at the expense of increased CPU time. However in many other calculations this problem was not overcome so that this section of the dissertation is not as complete as it might be. For example, the addition of selenium f pf sets with an exponent less than one causes the calculation not to converge.

1. Table 5.9 Results - Effects of the Selenium Basis Set

In Table 5.9, the largest calculation, calculation I (I / 5.9) consists of 174 bfs, and this calculation is our H_2Se reference calculation. The dipole moment of calculation I / 5.9 is 3.5% higher than the HF SCF value recently reported by Sadlej [47]. Although the dipole polarizability tensor values of calculation I / 5.9 follow the same trend of the values reported by Sadlej, the polarizability anisotropy factor, $\Delta\alpha$ is 30.5% smaller than that calculated from the DP values reported by Sadlej [47] (I / 5.8) (Table 5.8). Further work to understand this discrepancy is desirable, but since the approach used to create the bs used in I / 5.9 is based upon sound principles, which have produced successful results for other molecules, there is no reason to doubt the result obtained by us compared to the result of the smaller bs calculation performed by Sadlej [47] especially since in none of Sadlej's work is the anisotropy of the DP considered a desirable parameter to be used in assessing the validity of his work.

Table 5.8 Sadlej's Results of H_2Se

	I ^a	II ^b	III ^c	IV ^{d,e}
μ (A.U.)	0.3216	0.2783	0.2642	0.247
μ (Deb.)	0.8174	0.7073	0.6715	0.628
α_{xx}	30.16	30.70	30.51	-----
α_{yy}	30.63	32.12	31.98	-----
α_{zz}	29.93	30.78	30.60	-----
$\bar{\alpha}$	30.24	31.20	31.03	32.2
$\Delta\alpha$	0.62	1.38	1.43	-----

- a. Sadlej's HF results [9s7p4d / 3s2p] **72bfs** [47]
- b. Sadlej's MBPT(2) results [9s7p4d / 3s2p] **72bfs** [47]
- c. Sadlej's SDQ-MBPT(4) results [9s7p4d / 3s2p] **72bfs** [47]
- d. Mirri, Corbelli, and Forti's DM experimental result [102]
- e. Syrkin, and Dyatkina's DP experimental result [103]

Table 5.9 H₂Se Binning / Curtiss Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	0.3254	0.3255	0.3257	0.3256	0.3256	0.3264
μ (Deb.)	0.8271	0.8273	0.8280	0.8277	0.8277	0.8295
α_{xx}	30.35	30.35	30.34	30.33	30.35	30.33
α_{yy}	30.59	30.58	30.63	30.63	30.59	30.66
α_{zz}	30.09	30.09	30.08	30.07	30.07	30.08
$\bar{\alpha}$	30.35	30.34	30.35	30.35	30.34	30.36
$\Delta\alpha$	0.43	0.43	0.48	0.49	0.45	0.52
β_{xxz}	-11.22	-11.73	-12.02	-12.00	-11.97	-12.35
β_{yyz}	10.86	11.39	11.98	11.73	11.11	12.60
β_{zzz}	15.03	14.56	14.78	14.79	12.02	15.11
$\bar{\beta}$	8.80	8.53	8.84	8.71	6.70	9.22
$\Delta\beta$	15.57	15.07	14.84	15.20	13.31	14.74
γ_{xxxx}	4673.53	4618.71	4652.04	4650.00	4605.03	4601.25
γ_{xxyy}	4135.77	4141.20	4137.36	4143.57	4135.28	4182.64
γ_{xxzz}	2115.57	2083.68	2107.29	2111.22	2032.46	2102.25
γ_{yyyy}	18209.29	17854.37	18528.46	18623.03	18126.81	18512.58
γ_{yyzz}	4278.39	4277.31	4258.04	4262.46	4209.52	4299.17
γ_{zzzz}	6307.63	6273.50	6233.20	6241.61	5976.81	6195.48
γ	10049.98	9950.19	10083.82	10109.83	9892.63	10095.48

Se1 $\equiv$ Se(BC) + s(0.05), p(0.0492, 0.0196, 0.00784), d(0.5725, 0.28625, 0.14313, 0.07156, 0.03578, 0.01789) [7s7p7d]

- Se1, H-(TZV) + s(0.05), p(1.0, 0.5, 0.25, 0.125, 0.0625, 0.03125), d(0.5, 0.25, 0.125, 0.0625, 0.03125) 174 bfs [7s7p7d / 4s6p5d]
- Se1, H-(TZV) + p(1.0, 0.5, 0.25, 0.125, 0.0625), d(0.5, 0.25, 0.125, 0.0625) 154 bfs [7s7p7d / 4s5p4d]
- Se1, H-(TZV) + s(0.05), p(1.0, 0.125, 0.0625, 0.03125), d(0.125, 0.0625, 0.03125) 138 bfs [7s7p7d / 4s4p3d]
- Se1 - d(0.01789), H-(TZV) + s(0.05), p(1.0, 0.125, 0.0625, 0.03125), d(0.125, 0.0625, 0.03125) 132 bfs [7s7p6d / 4s4p3d]
- Se1 - d(0.03578, 0.01789), H-(TZV) + s(0.05), p(1.0, 0.125, 0.0625, 0.03125), d(0.125, 0.0625, 0.03125) 126 bfs [7s7p5d / 4s4p3d]
- Se1 - p(0.0196, 0.00784), H-(TZV) + s(0.05), p(1.0, 0.125, 0.0625, 0.03125), d(0.125, 0.0625, 0.03125) 132 bfs [7s5p7d / 4s4p3d]

In II / 5.9 the most diffuse p(0.03125) and d(0.03125) pf sets on the hydrogen are removed. The changes produced are minor (β_{xxz} differs by +4.5%, β_{yyz} differs by +4.8%, β_{zzz} differs by -3.1%, $\bar{\gamma}$ differs by -1.00% (compared to I / 5.9). In III / 5.9, the hydrogen p(0.5, 0.25) and d(0.5, 0.25) pf sets are removed, which gives the results: β_{xxz} differs by +7.1%, β_{yyz} differs by +10.3%, β_{zzz} differs by -1.7%, $\bar{\beta}$ differs by +0.5%, $\Delta\beta$ differs by -5%, and $\bar{\gamma}$ differs by +0.03% (comparing III / 5.9 to I / 5.9). These results are just about within the limits of acceptability and since the calculation converged smoothly and took considerably less CPU time than I / 5.9, it is used as a reference in the study of the effect of the hydrogen pf sets, which is given in Table 5.10. Calculation IV is the result of the removal of the outermost d(0.01789) pf set on selenium. This produces the following: β_{xxz} which differs by +7.1%, β_{yyz} which differs by +10.3%, β_{zzz} which differs by -1.7%, and $\bar{\gamma}$ which differs by +0.033% comparing IV / 5.9 to I / 5.9) (i.e., this diffuse d(0.01289) is not needed). In V / 5.9 the next outermost d(0.03578) pf set is removed on selenium. The changes are larger than in the previous calculation, although except for β_{zzz} which is reduced by 20%, they still are small (comparing V / 5.9 to I / 5.9). In VI / 5.6, the two outermost selenium p(0.01960, 0.00784) pf set is removed from the bs of III / 5.9. Again the changes are fairly minor. These results all indicate that the selenium bs used in the reference calculation can be reduced by at least one p pf set and one d pf set with virtually no degradation in the results, and if necessary two more pf sets (1p and 1d) could also be removed with only a small loss in accuracy.

2. Effects of the Hydrogen Basis Set

Calculations in Table 5.10 were performed to resolve the relationship between the β values and the pf sets used on the hydrogen bs. Calculation I / 5.10 uses a 7s7p5d bs on selenium and a 3p3d pf bs on the hydrogens, with the pfs and exponents as indicated in Table 5.10. In II / 5.8 the p(0.05) and d (0.05) pf sets are used instead of the p(0.0625) and d(0.0625) pf sets as the most diffuse pf sets on the hydrogen. This produces considerable changes, all of which make the calculation worse than the reference calculation IV / 5.9. The use of the more diffuse exponent of 0.05 instead of 0.0625 for the p and d pfs alone were performed. The results in each case (not reported) are poorer than when the 0.0625 exponent was used. In III / 5.10 the bs is that of I / 5.10, except the innermost selenium d(0.25) is removed. This removal produces only minor changes in all properties. However, like the bs of IV / 5.9, the middle p(0.125) pf set is removed. There are considerable changes in all three β tensor values (β_{xxz} differs by +11.3%, β_{yyz} differs by +9.9%, and β_{zzz} differs by -4.1%). Finally in V / 5.10 and VI / 5.10, two converged calculations containing selenium f pf set are reported. These calculations were performed with a f(1.0) pf set in V / 5.10, and a f(0.5) pf set in VI / 5.10. By comparing these calculations to III / 5.10, it can be seen that the addition of the f pf set can influence NLO properties results. The DM are changes only very slightly, and the DP and $\bar{\gamma}$ values are virtually unchanged. The changes in the β tensor values are small in V / 5.10 (i.e., β_{xxz} differs by +4.5%, β_{yyz} differs by +6.7%, and β_{zzz} differs by +1.6%, compared to I / 5.10), whereas the changes are much larger in VI / 5.10 (i.e., β_{xxz} differs by +16.2%, β_{yyz} differs by +14.09%, and β_{zzz} differs by -6.8%, compared to I / 5.10).

Attempts to obtain results of calculations using a selenium f pf set with other exponents both at the HF (SCF) level and the MP2 levels are in progress, and may be completed in future work.

Table 5.10 H₂Se Binning / Curtiss Results - further study of bs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	0.3271	0.3274	0.3257	0.3256	0.3218	0.3244
μ (Deb.)	0.8313	0.8321	0.8280	0.8277	0.8179	0.8246
α_{xx}	30.33	30.32	30.37	30.25	30.30	30.25
α_{yy}	30.70	30.17	30.70	29.98	30.67	30.02
α_{zz}	30.10	30.07	30.14	30.49	30.08	30.57
$\bar{\alpha}$	30.38	30.19	30.40	30.24	30.35	30.28
$\Delta\alpha$	0.52	0.22	0.49	0.44	0.52	0.48
β_{xxz}	-11.68	-12.25	-11.53	-12.83	-12.24	-13.57
β_{yyz}	11.57	9.38	11.03	12.12	12.35	13.20
β_{zzz}	15.43	14.21	15.86	15.21	15.67	14.38
$\bar{\beta}$	9.19	6.80	9.22	8.70	9.47	8.41
$\Delta\beta$	15.43	18.52	16.61	16.28	15.50	14.38
γ_{xxxx}	4441.47	4501.28	4497.61	4409.80	4519.49	4523.28
γ_{xxyy}	4068.94	3700.54	4120.32	3901.20	4129.54	4078.94
γ_{xxzz}	2030.51	2019.92	2062.48	2024.40	2059.71	2058.13
γ_{yyyy}	18267.08	13822.60	18298.57	16258.98	18222.55	17901.77
γ_{yyzz}	4288.04	3897.17	4365.64	4119.96	4388.58	4341.81
γ_{zzzz}	6121.07	6038.74	6231.54	3096.49	6220.21	6219.61
$\bar{\gamma}$	9920.92	8719.58	10024.92	9371.28	10023.58	9920.49

Se2 $\equiv$ Se(BC) + s(0.05), p(0.0492), d(0.5725, 0.28625, 0.14313, 0.07156, 0.03578)
[7s5p6d]

a. Se2, H-(TZV) + s(0.06), p(1.0, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
120 bfs [7s5p6d / 4s3p3d]

b. Se2, H-(TZV) + s(0.06), p(1.0, 0.125, 0.05), d(0.25, 0.125, 0.05)
120 bfs [7s5p6d / 4s3p3d]

c. Se2, H-(TZV) + s(0.06), p(1.0, 0.125, 0.0625), d(0.125, 0.0625)
108 bfs [7s5p6d / 4s3p2d]

d. Se2, H-(TZV) + s(0.06), p(1.0, 0.0625), d(0.125, 0.05)
102 bfs [7s5p6d / 4s2p2d]

e. Se2+f(1.0), H-(TZV) + s(0.06), p(1.0, 0.125, 0.05), d(0.125, 0.0625)
118 bfs [7s5p6d1f / 4s3p2d]

f. Se2+f(0.5), H-(TZV) + s(0.06), p(1.0, 0.125, 0.05), d(0.125, 0.0625)
118 bfs [7s5p6d1f / 4s3p2d]

Hydrogen Telluride (H_2Te)

There have been few previous calculations on tellurium molecules. The handbook of Gaussian bss [5] only lists two bss for tellurium. The larger one proposed by Huzinaga [104] consists of (18s14p8d) primitive Gaussians contracted to [16s12p8d] (i.e., only the deepest s and p bfs are contracted). Uncontracted bss or only slightly contracted bss are notorious for having convergence difficulties and since the addition of diffuse pfs needed for calculation of NLO properties would add to the computational difficulties, thus it was decided to adopt a slightly smaller (15s11p6d) bs contracted to [10s8p4d] reported in T52.1.1 in a book tabulated by Csizmadia [5] which is proposed by Stromberg, Gropen, and Wahlgren [97]. It should be noted here that the calculations of Sadlej on H_2Te , which appeared [48] while this work was in progress, were performed using the uncontracted Huzinaga bs which they, because of the wide experience in their theoretical research group at the University of Lund in Sweden, they were able to contract to a [10s8p4d] bs. As will be discussed later the addition of pfs to this bs yielded very similar results for the DP but not for the DM.

1. Table 5.12 Results

In the largest calculation I / 5.12 (Table 5.12) that was possible to perform, the original [10s8p4d] bs is supplemented by one extra s, three p, and four d pfs. The p pfs are generated from the outermost valence p Gaussian using a rf of 0.5 and the four d pfs using a rf of 0.4 from the outermost valence d Gaussian as indicated in the footnotes of Table 5.12. In the hydrogen bs the standard TZV bs is supplemented by pfs using a rf of 0.5 for both p and d pfs (as indicated in the footnote a of Table 5.12). The average DP, $\bar{\alpha}$, of this calculation (I / 5.12) is practically identical to that reported by Sadlej [48] for his spd bs (reported in I / 5.11) (Table 5.11) ($\bar{\alpha} = 43.31$). The DM however is slightly smaller (i.e., by 4.3%) than the spd calculation value of 0.1755 a.u. reported by Sadlej [48].

Table 5.11 Sadlej's Results of H_2Te

	I ^a	II ^b	III ^c
μ (A.U.)	0.1755	0.1095	0.1026
μ (Deb.)	0.4460	0.2783	0.2608
α_{xx}	43.29	43.09	43.03
α_{yy}	43.93	44.59	44.53
α_{zz}	42.72	43.25	42.96
$\bar{\alpha}$	43.31	43.64	43.51
$\Delta\alpha$	1.05	1.43	1.54

- a. Sadlej's HF results [11s9p6d / 3s2p] **92bfs** [48]
- b. Sadlej's MBPT(2) results [11s9p6d1f / 3s2p] **102bfs** [48]
- c. Sadlej's SDQ-MBPT(4) results [11s9p6d1f / 3s2p] **102bfs** [48]

Table 5.12 H₂Te T52.1.1 Results - large bs calculations

	I ^a	II ^b	III ^c	IV ^d	Ve
μ (A.U.)	0.168	0.169	0.169	0.156	0.146
μ (Deb.)	0.426	0.430	0.430	0.396	0.372
α_{xx}	43.35	43.38	43.37	43.25	42.58
α_{yy}	43.96	43.94	43.96	43.82	43.73
α_{zz}	42.80	42.84	42.82	42.73	41.90
$\bar{\alpha}$	43.37	43.39	43.38	43.27	42.74
$\Delta\alpha$	1.01	0.95	0.99	0.94	1.16
β_{xxz}	-6.60	-7.14	-6.64	-6.70	-11.18
β_{yyz}	22.35	19.60	22.09	19.13	38.90
β_{zzz}	48.29	47.39	48.81	47.79	78.93
$\bar{\beta}$	38.42	35.91	38.56	36.13	63.99
$\Delta\beta$	24.67	28.70	25.64	29.15	37.35
γ_{xxxx}	8813.56	8699.59	8711.54	8559.29	4804.84
γ_{xxyy}	8328.60	8349.06	8313.96	8229.14	7175.65
γ_{xxzz}	4095.19	4079.90	4089.50	4035.73	3097.19
γ_{yyyy}	36433.57	36469.86	36244.94	36590.50	32706.02
γ_{yyzz}	8632.70	8774.80	8765.84	8719.36	7646.80
γ_{zzzz}	12067.83	12007.35	12059.37	11872.66	7470.89
γ	19885.59	19916.90	19870.89	19798.2	16164.21

Te1 $\equiv$ Te(T52.1.1) + s(0.05), p(0.04950, 0.02475, 0.012375),
d(0.411034, 0.164414, 0.065760, 0.0329) [11s11p8d]

Te2 $\equiv$ Te(T52.1.1) + s(0.05), p(0.04950, 0.02475, 0.012375),
d(0.411034, 0.164414, 0.065760, 0.0359, 0.01645) [11s11p9d]

a. Te1, H-(TZV) + s(0.05), p(0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
160 bfs [11s11p8d / 4s4p3d]

b. Te1, H-(TZV) + s(0.05), p(1.0, 0.125, 0.0625), d(0.125, 0.0625)
142 bfs [11s11p8d / 4s3p2d]

c. Te2, H-(TZV) + s(0.05), p(1.0, 0.125, 0.0625), d(0.125, 0.0625)
148 bfs [11s11p9d / 4s3p2d]

d. Te1, H-(TZV) + s(0.05), p(0.125, 0.0625), d(0.125, 0.0625) **136 bfs**
[11s11p8d / 4s2p2d]

e. Te1, H-(TZV) + s(0.05) **100 bfs** [11s11p8d / 4s]

This discrepancy is probably due to the differences between the hydrogen pfs in our calculation versus Sadlej's. Since the DP values are so similar, a precise analysis of the differences is left to future work.

In the second calculation II / 5.12 the innermost hydrogen d(0.25) pf set is removed and a p(1.0) pf set is added on the hydrogen. There is a very slight increase in the DM (1%) and there are similar small changes in the NLO properties. In III / 5.12, the bs used in II / 5.12 is supplemented by a diffuse d(0.01645) pf set on tellurium. The results are slightly different from II / 5.12, but are very close to those of I / 5.12. When the innermost p(1.0) pf set is removed from the hydrogen in IV / 5.12, there is as expected a relatively large drop in the DM (7.7%), a slight drop in $\bar{\alpha}$ (0.3%), and changes in β_{xxz} of +1%, β_{yyz} of -13.4%, β_{zzz} of -2.1%, b of -6.3%, $\Delta\beta$ of +13.4%, indicating that if one is willing to forgo an accurate DM one could omit the inner p pf set on hydrogen. This is an important finding since the inclusion of this particular pf set introduces very troublesome convergence problems. In V / 5.9 all the p and d pf sets on hydrogen are removed, and there is a further drop in the DM, but surprisingly the DPs and $\Delta\alpha$ remain a reasonable value. The β tensor values are however unacceptable, while $\bar{\gamma}$ is 18.7% too low compared to the reference (I / 5.12). This shows the absolute need for at least some p and d pfs on the hydrogen.

2. Table 5.13 Results

Due to convergence difficulties encountered in the calculations of Table 5.12, the bs of IV / 5.12 is used as reference state to evaluate how much further the bs can be reduced without significant loss of accuracy in NLO properties calculated. In the first two calculations of Table 5.13, successive tellurium p pfs are removed. In I / 5.13 there is virtually no change in the DM, the DP and second DH (γ values), and only slight changes in the β tensor values.

Table 5.13 H₂Te T52.1.1 Results - Study of hydrogen pfs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
μ (A.U.)	0.155	0.155	0.158	0.151	0.152	0.149
μ (Deb.)	0.395	0.395	0.400	0.384	0.385	0.378
α_{xx}	43.27	43.18	43.12	43.01	42.89	43.31
α_{yy}	43.83	43.65	43.32	43.00	42.33	43.48
α_{zz}	42.73	42.67	42.62	42.35	43.43	42.60
$\bar{\alpha}$	43.27	43.17	43.02	42.79	42.88	43.13
$\Delta\alpha$	0.95	0.85	0.63	0.66	0.95	0.81
β_{xxz}	-6.99	-8.21	-11.28	-8.42	-8.84	-2.04
β_{yyz}	19.46	21.06	23.55	19.07	23.87	20.52
β_{zzz}	48.08	46.14	39.92	44.64	43.01	52.72
$\bar{\beta}$	36.33	35.39	31.31	33.17	34.82	42.72
$\Delta\beta$	29.38	26.87	21.51	28.67	20.46	25.00
γ_{xxxx}	8592.19	7971.60	7532.30	7880.24	7267.01	8831.39
γ_{xxyy}	8291.28	7100.94	6203.99	6754.29	6340.79	8765.79
γ_{xxzz}	4058.57	3876.31	3552.12	3708.16	3571.75	3915.11
γ_{yyyy}	36844.65	31749.90	26279.22	27294.06	29249.56	35492.47
γ_{yyzz}	8798.93	7598.43	6565.17	7159.02	6715.59	8829.00
γ_{zzzz}	11930.45	11258.26	10035.77	10957.71	10341.93	12158.90
γ	19932.97	17626.22	15297.97	16274.99	16022.95	19900.51

Te1 $\equiv$ Te(T52.1.1) +s(0.05), p(0.04950, 0.02475, 0.012375),
d(0.411034, 0.164414, 0.065760, 0.0329) [11s11p8d]

Te3 $\equiv$ Te(T52.1.1) +s(0.05), p(0.04950, 0.02475),
d(0.411034, 0.164414, 0.065760, 0.0329) [11s10p8d]

Te4 $\equiv$ Te3-p(0.02475) [11s9p8d]

Te5 $\equiv$ Te4-d(0.0329) [11s9p7d]

a. Te3, H-(TZV) + s(0.05), p(0.125, 0.0625), d(0.125, 0.0625) **133 bfs**
[11s10p8d / 4s2p2d]

b. Te4, H-(TZV) + s(0.05), p(0.125, 0.0625), d(0.125, 0.0625) **130 bfs**
[11s9p8d / 4s2p2d]

c. Te5, H-(TZV) + s(0.05), p(0.125, 0.0625), d(0.125, 0.0625) **124 bfs**
[11s9p7d / 4s2p2d]

d. Te4, H-(TZV) + s(0.05), p(0.0625), d(0.125, 0.0625) **124 bfs**
[11s9p8d / 4s1p2d]

e. Te4, H-(TZV) + s(0.05), p(0.125, 0.0625), d(0.0625) **118 bfs**
[11s9p8d / 4s2p1d]

f. Te1, H-(TZV) + s(0.05), p(0.0625), d(0.0625) **118 bfs**
[11s11p8d / 4s1p1d]

When however the next outermost p(0.02475) pf set is removed (in II / 5.13), it can be seen that the DM and DP values are hardly affected, there are sizeable changes in the β tensor values (i.e., β_{xxz} increases by 17.5%, β_{yyz} increases by 8.2%, and β_{zzz} decreases by 3.9%, leading to a change in $\bar{\beta}$ of -2.6%, and $\Delta\beta$ of -8.5%). The average second DH, $\bar{\gamma}$, is also reduced by 11.6%. In III / 5.13 are tabulated the results obtained when the outermost tellurium d(0.12375) pf set is removed. Again there are significant changes in $\Delta\alpha$ (a drop of 33.7%), in the β tensor values (i.e., β_{xxz} increases by 61.4%, β_{yyz} increases by 21.02%, and β_{zzz} decreases by 17%, leading to a change in $\bar{\beta}$ of -13.8%, and $\Delta\beta$ of -26.8%), and $\bar{\gamma}$, is also reduced by 23.3% (compared to I / 5.13). The average DP, $\bar{\alpha}$, only drops by 0.6%. These results show it would unwise to reduce the tellurium pf set beyond the [11s10p8d] bs used in I / 5.13. In IV / 5.13, the hydrogen bs is further reduced by removing the p(0.125) pf set. The changes in the results are relatively small except for $\Delta\alpha$, which again drops by 22.35% (compared to II / 5.13). In V / 5.13, the innermost d(0.125) pf set on hydrogen is removed. The changes again are relatively small except for $\Delta\alpha$, which increases by 11.8% (compared to II / 5.13) (i.e., returning to the same $\Delta\alpha$ value of I / 5.13). Based upon these results a calculation using the full tellurium [11s11p8d] bs and a small 1p1d pf set on hydrogen (both of 0.0625 exponent) was performed (VI / 5.13). The results show unexpectedly large changes in the β tensor values, especially β_{xxz} , which is reduced to 30.4% of the value in IV / 5.12. This demonstrates again that the changes in NLO properties caused by pf changes are not additive. Overall it would appear that the bs used for IV / 5.12 is about the smallest bs that can be used to obtain accurate values of the DM, and NLO properties. The behavior of this bs with the addition of f type pfs on tellurium will be explored in the next section.

3. Table 5.14 Results - Effect of f type pfs on tellurium (H_2Te)

Experience would indicate that the addition of f type pfs might influence the NLO properties of H_2Te . When this work was started, there had been no previous attempt to include f type pfs on tellurium in NLO properties calculations, so a series of calculations were performed, each with a set of f pfs of different exponents on tellurium. The results of these calculations are summarized in Tables 5.14 and 5.15.

In I / 5.14 (Table 5.14), a very diffuse f(0.125) pf is used on tellurium. Very little change of the DM and NLO properties occurred compared to II / 5.12 (142 bfs), except for β_{xxz} which decreased by 19.6%. However, in the next calculation II / 5.14, which used a f(0.25) pf on tellurium, the DM, DP, and $\bar{\gamma}$ are unchanged when compared to I / 5.14 (i.e., there is a similar decrease in β_{xxz} of 17.8% compared to II / 5.12). Very similar changes were observed in III / 5.14, which used a f(0.5) pf, and in IV / 5.14 which used a f(1.0) pf. However, in V / 5.14, which used two f pfs, the f(7.5,3.75) pf set, all the properties (the DM and NLO properties) are not influenced by the presence of the f pfs. In VI / 5.14, two f pfs of different exponents were used, the f(1.0,0.5) pf set, and the results show that again the effect is not additive (i.e., not the same as III / 5.14 plus IV / 5.14). However, when a third f(2.0) pf is added (i.e., 3f pfs), in I / 5.15, no further changes in all the properties are observed. Finally, a MP2 calculation was performed on the bs of VI / 5.14 (reported in II / 5.15). The DM is reduced by 17%, and $\bar{\alpha}$ is increased only by 1%. Whereas the HF SCF value of the DM is close to that of Sadlej's HF (SCF) result [48] (VI / 5.14 compared to I / 5.11, Sadlej's reported results), our MP2 result is 23.3% larger than Sadlej's MBPT(2) value quoted of 0.1095 a.u. by Sadlej [48] (reported in II / 5.11). For $\bar{\alpha}$ the HF SCF value (II / 5.15) (Table 5.15) is close to Sadlej's value of 43.27 a.u., but our MP2 value is 6.2% smaller than Sadlej's MBPT(2) value of 43.25 a.u.

Table 5.14 H₂Te T52.1.1 Results - Study of tellurium f pfs

	I ^a	II ^b	III ^c	IV ^d	Ve	VI ^f
μ (A.U.)	0.168	0.168	0.165	0.162	0.167	0.163
μ (Deb.)	0.427	0.426	0.420	0.412	0.424	0.414
α_{xx}	43.38	43.31	43.26	43.26	43.33	43.25
α_{yy}	43.96	43.92	43.80	43.92	43.93	43.82
α_{zz}	42.80	42.76	42.73	42.76	42.81	42.72
$\bar{\alpha}$	43.38	43.33	43.26	43.31	43.36	43.26
$\Delta\alpha$	1.00	1.00	0.93	1.01	0.97	0.95
β_{xxz}	-5.74	-5.87	-5.69	-6.71	-7.16	-5.23
β_{yyz}	20.74	22.29	20.61	21.88	20.78	21.14
β_{zzz}	48.17	48.91	48.53	49.20	48.33	49.52
$\bar{\beta}$	37.90	39.20	38.07	38.62	37.17	39.26
$\Delta\beta$	25.67	24.28	26.15	26.45	27.90	25.66
γ_{xxxx}	8611.20	8639.97	8590.73	8710.54	8705.13	8568.14
γ_{xxyy}	8200.46	8272.66	8212.84	8380.32	8361.93	8208.46
γ_{xxzz}	3979.05	3983.27	3988.13	4075.45	4081.98	3973.11
γ_{yyyy}	36775.12	36406.75	36032.98	36390.57	36418.25	36021.32
γ_{yyzz}	8636.78	8610.78	8576.63	8798.11	8782.63	8561.80
γ_{zzzz}	11994.50	11997.36	11863.09	11952.72	11976.10	11812.32
$\bar{\gamma}$	19802.68	19755.50	19608.40	19912.32	19910.51	19577.71

Te1 $\equiv$ Te(T52.1.1) +s(0.05), p(0.04950, 0.02475, 0.012375),
d(0.411034, 0.164414, 0.065760, 0.0329) [11s11p8d]

- Te1+f(0.125), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **152 bfs**
[11s10p8d1f / 4s2p2d]
- Te1+f(0.25), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **152 bfs**
[11s10p8d1f / 4s2p2d]
- Te1+f(0.5), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **152 bfs**
[11s10p8d1f / 4s2p2d]
- Te1+f(1.0), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **152 bfs**
[11s10p8d1f / 4s2p2d]
- Te1+f(7.5,3.25), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **162 bfs**
[11s10p8d2f / 4s2p2d]
- Te1+f(1.0,0.5), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **162 bfs**
[11s10p8d2f / 4s2p2d]

Table 5.15 H₂Te T52.1.1 Results - f pfs and MP2

	I ^a	II ^b
μ (A.U.)	0.162	0.135
μ (Deb.)	0.411	0.342
α_{xx}	43.23	43.09
α_{yy}	43.83	43.91
α_{zz}	42.71	43.12
$\bar{\alpha}$	43.26	43.37
$\Delta\alpha$	0.95	0.80
β_{xxz}	-5.10	-8.42
β_{yyz}	21.57	-6.38
β_{zzz}	49.94	22.78
$\bar{\beta}$	39.85	4.79
$\Delta\beta$	25.24	44.98
γ_{xxxx}	8567.18	-----
γ_{xxyy}	8213.13	-----
γ_{xxzz}	3968.01	-----
γ_{yyyy}	36019.40	-----
γ_{yyzz}	8558.42	-----
γ_{zzzz}	11802.74	-----
$\bar{\gamma}$	19573.69	-----

Te1 $\equiv$ Te(T52.1.1) +s(0.05), p(0.04950, 0.02475, 0.012375),
d(0.411034, 0.164414, 0.065760, 0.0329) [11s11p8d]

- a. Te1+f(2.0,1.0,0.5), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **172 bfs**
[11s10p8d3f / 4s2p2d]
- b. Te1+f(1.0,0.5), H-(TZV) + s(0.05), p(1.0,0.125), d(0.125, 0.0625) **162 bfs**
[11s10p8d2f / 4s2p2d] **MP2**

For the β tensor, our results are the first values reported for H_2Te . As is the case in H_2S , the correlation effect introduced by the MP2 method, the results show large changes in the DM and β tensor values.

CHAPTER VI

CALCULATION RESULTS FOR METHANE, SILANE, AND GERMANE

It has been surprising that there have been few previous studies on NLO properties of methane, silane, and germane. We have performed a systematic study of the DM and NLO properties of these molecules as a function of added pfs.

The methane (CH_4) calculations are based upon a 6-31G bs. The silane (SiH_4) calculations are based upon the TZV bs. The germane (GeH_4) calculations are based upon the Binning / Curtiss bs [26].

Methane (CH_4)

In the reference calculation (154 bfs) I / 6.2 (Table 6.2) the carbon 6-31G bs is augmented by the s(0.05), p(0.03,0.005), and d(0.94, 0.15, 0.05) pf sets, and the hydrogen 6-31G bs is augmented by the s(0.06), p(0.25,0.125,0.0625), d(0.25,0.125,0.0625) pf sets. In I / 6.3 (Table 6.3) the same carbon bs is used, and the hydrogen 6-31G bs is augmented by the s(0.05), p(0.9, 0.1), d(0.1) pf sets. A comparison of I / 6.3 to I / 6.2 does not show much difference. Calculation I / 6.3 gives the following: $\bar{\alpha}$ of 16.21, β_{xyz} of -12.33, $\bar{\gamma}$ of 1908.02. Comparing I / 6.3 to Guan et al. [98] show that $\bar{\alpha}$ differs by +1.6%, and a comparison to Bose, Soschanski, and Cole's experimental result [100] (III / 6.1) (Table 6.1) shows that this HF (SCF) $\bar{\alpha}$ differs by -7.4%.

Table 6.1 CH₄ quoted values

	I ^a	II ^b	III ^c
$\bar{\alpha}$	15.95	17.90	17.5
β_{xyz}	-11.64	-----	-----

- Guan et al. NHF calculation [98]
- Sim et al. DZP+++ calculation [73]
- Bose, Sochanski, and Cole's experimental result [100]

Table 6.2 CH₄ 6-31G Results - large bs calculation

	I ^a
$\bar{\alpha}$	16.19
β_{xyz}	-11.58
γ_{xxxx}	1825.40
γ_{xxyy}	674.94
γ	1905.17

C1 $\equiv$ C(6-31G) + s(0.05), p(0.03, 0.0105), d(0.94, 0.15, 0.05)

- C1, H-(6-31G) + s(0.06), p(0.25,0.125,0.0625), d(0.25,0.125,0.0625)
154 Basis Functions [4s4p3d / 3s3p3d]

Table 6.3 CH₄ 6-31G Results - Study of hydrogen pfs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
$\bar{\alpha}$	16.21	16.05	15.97	16.21	16.22	16.79
β_{xyz}	-12.33	-12.79	-10.50	-12.33	-12.01	-8.78
γ_{xxxx}	1817.83	1815.41	1752.51	1817.24	1830.05	-----
γ_{xxyy}	681.10	681.37	627.09	681.33	673.61	-----
γ	1908.02	1906.88	1804.02	1907.83	1906.36	-----

C1 $\equiv$ C(6-31G) + s(0.05), p(0.03, 0.0105), d(0.94, 0.15, 0.05)

C2 $\equiv$ C(6-31G) + s(0.05), p(0.03), d(0.94, 0.15, 0.05)

a. C1, H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1)

94 Basis Functions [4s4p3d / 3s2p1d]

b. C1, H-(6-31G) + s(0.06), p(0.1), d(0.1)

82 Basis Functions [4s4p3d / 3s1p1d]

c. C1, H-(6-31G) + s(0.06), p(0.1)

58 Basis Functions [4s4p3d / 3s1p]

d. C2, H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1)

91 Basis Functions [4s3p3d / 3s2p1d]

e. C2+f(0.125), H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1)

101 Basis Functions [4s3p3d1f / 3s1p1d]

f. C2+f(0.125), H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1)

101 Basis Functions MP2 [4s3p3d1f / 3s1p1d]

In II / 6.3 the p(0.9) pf sets are removed from the hydrogen, and comparing to I / 6.3 does not show much difference ($\bar{\alpha}$ differs by -1%, β_{xyz} differs by +3.7%, $\bar{\gamma}$ differs by -0.06%). In III / 6.3 the d(0.1) pf set is removed from the hydrogen, and comparing to II / 6.3 shows a larger change: $\bar{\alpha}$ differs by -0.5%, β_{xyz} differs by -17.9%, $\bar{\gamma}$ differs by -5.4%. Thus as in the results of previous chapters, the hydrogen d(0.1) pf set again is shown to be important. In IV / 6.3 a p(0.0105) pf set is removed from the carbon bs of calculation I / 6.3, and the results are virtually the same. In V / 6.3, a f(0.125) pf set was added to the carbon bs of IV / 6.3, and when compared to calculation IV / 6.3, produces very small changes (β_{xyz} differs by -2.6%, $\bar{\alpha}$ and $\bar{\gamma}$ are virtually unchanged). In VI / 6.3, a MP2 calculation using the bs of V / 6.3 was performed, and comparing to V / 6.2 produces the results: $\bar{\alpha}$ differs by +3.5%, β_{xyz} differs by -26.9%. When VI / 6.3 is compared to Sim et al. calculation [73] (II / 6.1), $\bar{\alpha}$ differs by -6.2%, and when compared to the experimental result [100] (III / 6.1), $\bar{\alpha}$ differs by -4%. Thus, in summary the only significant changes in Table 6.3 is the removal of the hydrogen d(0.1) pf, and the inclusion of correlation from V / 6.3 to VI / 6.3. The 1p1d pf set combination of II / 6.3 serves as a good minimum bs for CH₄.

Silane (SiH₄)

1. Table 6.4 - TZV Results (SiH₄)

The reference calculation for silane of 188 basis functions consists of a TZV silicon bs supplemented by the: s(0.05), p(0.0262, 0.0105), and d(0.0745, 0.0298, 0.0192) pf sets and a TZV hydrogen bs supplemented by s(0.06), p(0.5, 0.25, 0.125, 0.0625), and d(0.25, 0.125, 0.0625) pf sets, and is reported in I / 6.4 (Table 6.4). Calculation I / 6.4 produces the following results: $\bar{\alpha} = 29.45$, $\beta_{xyz} = -10.91$, $\gamma_{xxxx} = 5006.97$, $\gamma_{xxyy} = 1774.55$, and $\bar{\gamma} = 5133.23$.

Table 6.4 SiH₄ TZV Results - Study of hydrogen pfs

	Ia	II ^b	III ^c	IV ^d	Ve	VI ^f
$\bar{\alpha}$	29.54	29.56	29.56	29.55	29.34	29.31
β_{xyz}	-10.91	-11.21	-10.53	-12.00	-10.71	-12.65
γ_{xxxx}	5006.97	5137.19	4980.39	4797.90	4960.46	4800.04
γ_{xxyy}	1774.55	1726.47	1749.32	1746.00	1720.69	1742.02
γ	5133.23	5154.08	5087.42	4973.94	5040.73	4970.45

Si1 $\equiv$ Si(TZV) + s(0.05), p(0.0262, 0.0105), d((0.505,0.186),0.0745, 0.0298, 0.01192)

- a. Si1, H-(TZV) + s(0.06), p(0.5, 0.25, 0.125, 0.0625), d(0.25,0.125, 0.0625)
188 Basis Functions [7s7p4d / 4s4p3d]
- b. Si1, H-(TZV) + s(0.06), p(0.9, 0.1), d(0.0625)
116 Basis Functions [7s7p4d / 4s2p1d]
- c. Si1, H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1)
116 Basis Functions [7s7p4d / 4s2p1d]
- d. Si1, H-(TZV) + s(0.06), p(0.9, 0.1)
92 Basis Functions [7s7p4d / 4s2p]
- e. Si1, H-(TZV) + s(0.06), p(0.1), d(0.1)
104 Basis Functions [7s7p4d / 4s1p1d]
- f. Si1, H-(TZV) + s(0.06), p(0.1)
80 Basis Functions [7s7p4d / 4s1p]

The calculated polarizability compares quite well with values calculated by Spackman [46] of $\bar{\alpha}(\text{HF}) = 29.75$, $\bar{\alpha}(\text{MP2}) = 31.13$, and an experimental value (Landolt-Bornstein's Zahlenwerte und Functionen) [50] of $\bar{\alpha}(\text{exp.}) = 31.96$. Sadlej [45] also calculated DP values for SiH_4 of $\bar{\alpha}(\text{HF}) = 30.11$, $\bar{\alpha}(\text{MBPT}(2)) = 31.12$. The DP value of I / 6.4 differs from the HF value of Sadlej by -2.2%, and by -5.4% from Sadlej's MBPT(2) value.

In II / 6.4, the same bs on the silicon is used, however a much smaller of pf sets is used on the hydrogen, that is- the s(0.06), p(0.9, 0.1), d(0.0625) pf sets (116 contracted bfs), which produces the results: $\bar{\alpha}$ differs by +0.4%, β_{xyz} differs by +2.7%, $\bar{\gamma}$ differs by +0.4% (comparing II / 6.4 to I / 6.4). Thus calculation II / 6.4 gives similar results except for a small change in the β_{xyz} value than that of calculation I / 6.4, with a much smaller basis. In III / 6.4 a d(0.1) pf set is used on the hydrogen instead of the d(0.0625) pf set, which gives similar results to II / 6.4, that is: β_{xyz} differs by -3.5%, $\bar{\gamma}$ differs by -0.9% (comparing III / 6.4 to I / 6.4). Calculation IV / 6.4 was performed with the d(0.1) pf set removed on hydrogen, which produces the results: β_{xyz} differs by +10%, $\bar{\gamma}$ differs by -3.1% (comparing IV / 6.4 to I / 6.4). In V / 6.4, the s(0.06), p(0.1), d(0.1) pf sets are used on the hydrogen, which produces results: $\bar{\alpha}$ differs by -0.37%, β_{xyz} differs by -1.83%, $\bar{\gamma}$ differs by -1.80% (comparing V / 6.4 to I / 6.4). In VI / 6.4, the s(0.06), p(0.1) pf sets are used on hydrogen which produces the results: $\bar{\alpha}$ differs by -0.5%, β_{xyz} differs by +16%, $\bar{\gamma}$ differs by -3.2% (comparing VI / 6.4 to I / 6.4). Thus in summary of the TZV results for SiH_4 , the addition of the d(0.1) pf set is important for good β tensor results. Calculation II / 6.4 which had 2p1d pf sets on the hydrogen (116 bf), and calculation V / 6.4 which had 1p1d pf sets (104 bf) produced relatively good results compared to I / 6.4 (188 bf).

2. Table 6.5 TZV Results (SiH₄)

Calculation I / 6.5 (Table 6.5) also had the same silicon bs as I / 6.4, but the p(0.25, 0.125, 0.0625) and d(0.25, 0.125, 0.0625) pf sets are used on the hydrogen which produces the results: $\bar{\alpha}$ differs by -0.4%, β_{xyz} differs by -1.8%, $\bar{\gamma}$ differs by -1.8% (comparing I / 6.5 to I / 6.4). Calculation II / 6.5 uses a silicon TZV bs augmented by a p(0.05) and d(0.94, 0.15, 0.05) pf sets and a hydrogen TZV bs augmented by the s(0.06), p(0.1), and d(0.1) pf sets which produces the results: $\bar{\alpha}$ differs by -0.4%, β_{xyz} differs by -1.8%, $\bar{\gamma}$ differs by -1.8% (comparing II / 6.5 to I / 6.5). In III / 6.5 a silicon f(0.125) pf set is added to the bs of III / 6.4 (116 bfs), which only produces minor changes in β_{xyz} (-4.7%) and $\bar{\gamma}$ (+0.3%) (comparing III / 6.5 to II / 6.5). In IV / 6.5, this same bs is used for a MP2 calculation, and produces the results: $\bar{\alpha}$ differs by +3.7%, β_{xyz} differs by -13.6%. The $\bar{\alpha}$ value (IV / 6.5) when compared to Spackman's MP2 [46] result differs by -1.6%, and when compared to the experimental result differs by -4.2%.

3. Table 6.6 Results - Study of the silicon bs

Several calculations in Table 6.6 were performed on SiH₄ to determine if the bs of silicon can be reduced without affecting the accuracy of DP and DH results. In I / 6.6, the bs is very similar to III / 6.4, except the d(0.01192) pf set on silicon is removed, and comparing I / 6.6 to III / 6.4 produces the results: $\bar{\alpha}$ differs by -0.07%, β_{xyz} differs by +3%, $\bar{\gamma}$ differs by -0.2%. In II / 6.6, the d(0.1) pf set on hydrogen is replaced by a d(0.0625) pf set, and comparing II / 6.6 to I / 6.6 produces the results: β_{xyz} differs by +5%, $\bar{\gamma}$ differs by +1.4%. In III / 6.6, the p(0.0262, 0.0105) pf sets on silicon are replaced by the p(0.025) pf set, and comparing III / 6.6 to II / 6.6 produces the results: β_{xyz} differs by +5.4%, $\bar{\gamma}$ differs by -0.8%. In IV / 6.6, the TZV bs of silicon and hydrogen were replaced by the 6-31G basis sets, and comparing IV / 6.6 to I / 6.6 produces the results: β_{xyz} differs by +12%, $\bar{\gamma}$ differs by +1.5%.

Table 6.5 SiH₄ TZV Results - further study of bs

	I ^a	II ^b	III ^c	IV ^d
$\bar{\alpha}$	29.58	29.30	29.53	30.63
β_{xyz}	-11.63	-10.20	-10.04	-8.67
γ_{xxxx}	5004.94	4626.02	5066.47	-----
γ_{xxyy}	1801.24	1574.97	1720.03	-----
γ	5164.43	4665.57	5103.92	-----

Si1 $\equiv$ Si(TZV) + s(0.05), p(0.0262, 0.0105), d((0.505,0.186),0.0745, 0.0298, 0.01192)

a. Si1, H-(TZV) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
176 Basis Functions [7s7p4d / 4s3p3d]

b. Si(TZV)+p(0.05)+d(0.94,0.15,0.05), H-(TZV) + s(0.06), p(0.1), d(0.1)
82 Basis Functions [6s6p3d / 4s1p1d]

c. Si1+f(0.125), H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1) **126 Basis Functions**
[7s7p4d1f / 4s2p1d]

d. Si1+f(0.125), H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1) **126 Basis Functions**
MP2 [7s7p4d1f / 4s2p1d]

Table 6.6 SiH₄ Results - more study of bs

	Ia	IIb	IIIc	IVd	Ve
$\bar{\alpha}$	29.54	29.54	29.57	29.58	29.43
β_{xyz}	-10.85	-11.40	-12.02	-12.15	-10.77
γ_{xxxx}	4964.51	5144.91	4924.58	4928.39	4678.45
γ_{xxyy}	1750.76	1721.24	1797.11	1832.18	1760.86
γ	5079.64	5152.43	5111.26	5155.65	4920.11

Si2 $\equiv$ Si(TZV) + s(0.05), p(0.0262, 0.0105), d((0.505,0.186),0.0745, 0.0298)

Si3 $\equiv$ Si(6-31G) + s(0.05), p(0.0262, 0.0105), d((0.505,0.186),0.0745, 0.0298)

Si4 $\equiv$ Si(6-31G) + s(0.05), p(0.025), d((0.505,0.186),0.0745, 0.0298)

a. Si2, H-(TZV) + s(0.06), p(1, 0.1), d(0.1)
110 Basis Functions [7s7p3d / 4s2p1d]

b. Si2, H-(TZV) + s(0.06), p(1, 0.1), d(0.0625)
110 Basis Functions [7s7p3d / 4s2p1d]

c. Si3, H-(6-31G) + s(0.06), p(1, 0.1), d(0.1)
98 Basis Functions [5s5p3d / 3s2p1d]

d. Si4, H-(6-31G) + s(0.06), p(1, 0.1), d(0.1)
95 Basis Functions [5s4p3d / 3s2p1d]

e. Si(6-31G) + s(0.05), p(0.025), d(0.94, 0.15, 0.05),
H-(6-31G) + s(0.06), p(1, 0.1), d(0.1)
95 Basis Functions [5s4p3d / 3s2p1d]

In V / 6.6, the d(0.94, 0.15, 0.05) pf set is used on silicon rather than the d((0.505, 0.186), 0.0745, 0.0298) pf sets, and comparing V / 6.6 to IV / 6.6 produces the results: $\bar{\alpha}$ differs by -0.5%, β_{xyz} differs by -11.4%, $\bar{\gamma}$ differs by -4.6%.

Calculation I / 6.6 shows that removing the d(0.01192) pf set on silicon affected β_{xyz} only slightly. Calculation II / 6.6 showed that the d(0.0625) pf set on hydrogen is slightly better than the d(0.1) pf set. Calculation III / 6.6 showed that replacement of the p(0.0262, 0.0105) pf sets on silicon by the p(0.025) pf set has only a slight effect on the β_{xyz} value. Calculation IV / 6.6 showed that using the 6-31G basis sets in place of the TZV basis sets has a significant effect on the β_{xyz} value. Calculation V / 6.5 shows that the d(0.94, 0.15, 0.05) pf set on silicon is not as good as the d((0.505, 0.186), 0.0745, 0.0298) pf set.

4. Table 6.7 - 6-31G Results

In I / 6.7 (Table 6.7), a 6-31G bs was used on silicon plus the p(0.05), d(0.94, 0.15, 0.05) pf sets, and on the hydrogen a 6-31G bs plus the s(0.06), p(0.1), and d(0.1) pf sets are used which produces the results: $\bar{\alpha}$ differs by -0.5%, β_{xyz} differs by -6.7%, $\bar{\gamma}$ differs by -9.2% (comparing I / 6.7 to I / 6.4). Calculation II / 6.7 was performed with the d(0.1) pf set on the hydrogen removed, which produces the results: $\bar{\alpha}$ differs by -0.14%, β_{xyz} differs by -30.4%, $\bar{\gamma}$ differs by -0.8% (comparing II / 6.7 to I / 6.7). The p(0.1) pf set on the hydrogen is removed in calculation III / 6.7, which produces the results: β_{xyz} differs by +347.20%, $\bar{\gamma}$ differs by -1.53% (comparing III / 6.7 to I / 6.7). Calculation IV / 6.7 was performed with the s(0.06) pf set on the hydrogen removed which produces the results of a β_{xyz} that differs by +220% (comparing IV / 6.7 to I / 6.7). Calculation I / 6.7 illustrates that even with smaller starting basis sets the use of a few pf sets on silicon (i.e., 1p3d), and a minimal group of pf sets on hydrogen (i.e., 1s1p1d) produced a relatively good β or first DH values and γ or second DH values.

Table 6.7 SiH₄ 6-31G Results

	I ^a	II ^b	III ^c	IV ^d
$\bar{\alpha}$	29.30	29.26	27.80	27.66
β_{xyz}	-10.19	-7.09	-45.57	-32.62
γ_{xxxx}	4624.75	4554.50	4340.14	3952.62
γ_{xxyy}	1574.14	1578.85	1656.81	1450.19
γ	4663.68	4627.32	4592.26	4111.80

- Si(6-31G) + p(0.05), d(0.94, 0.15, 0.05), H-(6-31G) + s(0.06), p(0.1), d(0.1) **82 Basis Functions** [4s4p3d / 3s1p1d]
- Si(6-31G) + p(0.05), d(0.94, 0.15, 0.05), H-(6-31G) + s(0.06), p(0.1) **58 Basis Functions** [4s4p3d / 3s1p]
- Si(6-31G) + p(0.05), d(0.94, 0.15, 0.05), H-(6-31G) + s(0.06) **46 Basis Functions** [4s4p3d / 3s]
- Si(6-31G) + p(0.05), d(0.94, 0.15, 0.05), H-(6-31G) **42 Basis Functions** [4s4p3d / 2s]

Calculations II / 6.7 and III / 6.7 show the importance of the d(0.1) and p(0.1) pf sets on the hydrogen. The results of calculation IV / 6.7 show that the addition of the s(0.06) pf set on hydrogen improves the $\bar{\gamma}$ results (i.e., a -10.5% difference, comparing IV / 6.7 with III / 6.7).

Germane (GeH_4)

1. Table 6.8 - Binning / Curtiss Results

The reference calculation I / 6.8 (Table 6.8) of GeH_4 used a Binning / Curtiss bs [26] plus the p(0.03336, 0.013344), and d(0.1328, 0.05312, 0.021248, 0.008499) pf sets, and the hydrogen uses a TZV bs plus the s(0.06), p(0.25, 0.125, 0.0625), and d(0.25, 0.125, 0.0625) pf sets, which produces the results: $\bar{\alpha} = 32.81$, $\beta_{xyz} = -12.65$, $\gamma_{xxxx} = 6068.37$, $\gamma_{xxyy} = 2187.56$, and $\bar{\gamma} = 6266.09$. Sadlej [47] reports an $\bar{\alpha}(\text{HF})$ of 32.99 which is a difference of +0.6% from the result of I / 6.8, and also a $\bar{\alpha}(\text{MBPT}(2))$ of 33.99 which is a difference of +3.6% from the result of I / 6.8. Calculation I / 6.8 has 192 contracted basis functions (bfs). In II / 6.8, a p(0.9, 0.1), and d(0.1) pf set is used on the hydrogen, which produces the results: β_{xyz} differs by -5.3%, $\bar{\gamma}$ differs by -3.2% (comparing II / 6.8 to I / 6.8). In III / 6.8 a d(0.0625) is used instead of the d(0.1) pf set on hydrogen which produces the results: β_{xyz} differs by +3.4%, $\bar{\gamma}$ differs by +0.3% (comparing III / 6.8 to I / 6.8), and thus the d(0.0625) pf set produced better DP and DH results than the d(0.1) pf set on hydrogen. Calculation IV / 6.8 was performed with the d pf set removed from the hydrogen bs, which produces the results of : $\bar{\alpha}$ differs by -0.43%, β_{xyz} differs by +3.7%, $\bar{\gamma}$ differs by -5.4% (comparing IV / 6.8 to I / 6.8).

Table 6.8 GeH₄ Binning / Curtiss Results - Study of hydrogen pfs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
$\bar{\alpha}$	32.81	32.71	32.68	32.67	32.46	32.38
β_{xyz}	-12.65	-11.98	-13.08	-13.12	-12.58	-12.87
γ_{xxx}	6068.37	5901.76	6063.13	5760.62	5850.53	5746.85
γ_{xyy}	2187.56	2106.10	2205.83	2059.89	2079.86	2029.31
γ	6266.09	6068.50	6284.87	5928.25	6006.27	5883.29

Ge1 $\equiv$ Ge(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248, 0.008499)
[6s6p6d]

- a. Ge1, H-(TZV) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
192 Basis Functions [6s6p6d / 3s4p3d]
- b. Ge1, H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1) **120 Basis Functions**
[6s6p6d / 3s2p1d]
- c. Ge1, H-(TZV) + s(0.06), p(0.9, 0.1), d(0.0625) **120 Basis Functions**
[6s6p6d / 3s2p1d]
- d. Ge1, H-(TZV) + s(0.06), p(0.9, 0.1) **96 Basis Functions**
[6s6p6d / 3s2p]
- e. Ge1, H-(TZV) + s(0.06), p(0.1), d(0.1) **108 Basis Functions**
[6s6p6d / 3s1p1d]
- f. Ge1, H-(TZV) + s(0.06), p(0.1) **84 Basis Functions**
[6s6p6d / 3s1p]

In V / 6.8, the p(0.1) and d(0.1) pf sets are used on the hydrogen, which produces the results: $\bar{\alpha}$ differs by -1.1%, β_{xyz} differs by -0.6%, $\bar{\gamma}$ differs by -4.2% (comparing V / 6.8 to I / 6.8). Calculation VI / 6.8 was performed with the d(0.1) pf set on the hydrogen removed, which produces the results: $\bar{\alpha}$ differs by -1.3%, β_{xyz} differs by +1.7%, $\bar{\gamma}$ differs by -6.1% (comparing VI / 6.8 to I / 6.8).

In summary, of the smaller calculations II / 6.8 through VI / 6.8, the 2p1d calculation III produces the best results, although the 1p1d calculation V / 6.8 is next best. The results of Table 6.8 also show that for GeH₄, the DP and DH properties are relative insensitive to hydrogen bs changes compared to calculations on other molecules in this dissertation (i.e., Chapters III and V).

2. Table 6.9 - f pf set and MP2

In I / 6.9 (Table 6.9) a silicon f(0.125) pf set is added to the bs of II / 6.8. When compared to II / 6.8, produces the results: $\bar{\alpha}$ differs by +0.15%, β_{xyz} differs by +10.4%, $\bar{\gamma}$ differs by +3.7% (comparing I / 6.9 to II / 6.8). In II / 6.9, the MP2 calculation of the bs of I / 6.9 is performed, and produces the results: $\bar{\alpha}$ differs by +3.4%, β_{xyz} differs by -7.9%, (comparing II / 6.9 to I / 6.9). The a value differs by -0.35% from that of Sadlej's MBPT(2) result [47]. Again correlation through MP2 produces a noticeable change, but comparatively is not as large as those calculated in Chapter III and V.

3. Table 6.10 Results

Two more Curtiss Binning type GeH₄ calculations were performed for comparison purposes with other calculations on Ge₂H₄ and Ge₂H₂. Calculation I / 6.10 (Table 6.10) consists of a germanium Curtiss Binning bs augmented by p(0.03336, 0.013344) and d(0.33320, 0.1328, 0.05312, 0.021248) pf sets, and a hydrogen TZV bs augmented by s(0.06), p(0.1), d(0.1) pf sets.

Table 6.9 GeH₄ Binning / Curtiss Results - MP2

	Ia	IIb
$\bar{\alpha}$	32.76	33.87
β_{xyz}	-13.23	-12.19
γ_{xxxx}	6056.69	-----
γ_{xxyy}	2218.38	-----
γ	6295.86	-----

Ge1 $\equiv$ Ge(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248, 0.008499)
[6s6p6d]

a. Ge1+f(0.125), H-(TZV) + s(0.06), p(0.9, 0.1), d(0.0625)
130 Basis Functions [6s6p6d1f / 3s2p1d]

a. Ge1+f(0.125), H-(TZV) + s(0.06), p(0.9, 0.1), d(0.0625)
130 Basis Functions MP2 [6s6p6d1f / 3s2p1d]

Table 6.10 GeH_4 Binning / Curtiss Results - Study of germanium p pfs

	Ia	IIb
$\bar{\alpha}$	32.46	32.44
β_{xyz}	-12.52	-12.05
γ_{xxx}	5850.48	5754.71
γ_{xyy}	2070.73	2013.82
γ	5995.28	5869.49

$\text{Ge2} \equiv \text{Ge}(\text{BC}) + \text{p}(0.03336, 0.013344), \text{d}(0.1328, 0.05312, 0.021248)$
 [6s6p5d]

a. $\text{Ge2}, \text{H}-(\text{TZV}) + \text{s}(0.06), \text{p}(0.1), \text{d}(0.1)$
102 Basis Functions [6s6p5d / 3s1p1d]

b. $\text{Ge2-p}(0.013344), \text{H}-(\text{TZV}) + \text{s}(0.06), \text{p}(0.1), \text{d}(0.1)$
99 Basis Functions [6s5p5d / 3s1p1d]

Calculation I / 6.10 produces the results: $\bar{\alpha}$ is unchanged, β_{xyz} differs by -0.5%, $\bar{\gamma}$ differs by -0.2% (comparing I / 6.10 to V / 6.8). In II / 6.10, the p(0.013344) pf set on germanium is removed which produces the results: $\bar{\alpha}$ differs by -0.06%, β_{xyz} differs by -3.8%, $\bar{\gamma}$ differs by -2.1% (comparing II / 6.10 to I / 6.10).

4. Table 6.11 - 3-21G Results

Calculation I / 6.11 (Table 6.11) was performed with a 3-21G bs on germanium augmented by a p(0.05), and the d(1, 0.4, 0.16, 0.064, 0.0256) pf sets, and a 3-21G bs on hydrogen augmented by the s(0.06), p(0.9, 0.1), and d(0.1) pf sets, which produces the results: $\bar{\alpha}$ differs by +0.7%, β_{xyz} differs by -5.8%, and a $\bar{\gamma}$ differs by -4.8% (comparing I / 6.11 to I / 6.8). In II / 6.11 the p(0.9) pf set on hydrogen is removed, which produces a β that compares better with I / 6.8, that is: β_{xyz} differs by -1.19% (comparing II / 6.11 to I / 6.8). The d(0.1) pf set is further removed in calculation III / 6.11, which produced the results: β_{xyz} differs by +6.64%, $\bar{\gamma}$ differs by -0.51% (comparing III / 6.11 to I / 6.8). Calculation IV / 6.11 was performed with only a s(0.06) pf set on the hydrogen, which produced the results: β_{xyz} differs by +362.92%, $\bar{\gamma}$ differs by -9.07% (comparing IV / 6.11 to I / 6.8). In V / 6.11, no pf sets were used on the hydrogen, which produced the results: β_{xyz} differs by +183.2%, $\bar{\gamma}$ differs by -24.2% (comparing V / 6.11 to I / 6.8).

Thus in summary of the results of Table 6.11, the calculations I / 6.11 through III / 6.11 showed that even with a small number of well chosen pf sets on germanium and hydrogen, that relatively good DP and DH results can be obtained. Here, just as in previous calculations (Chapters III and V), the β value is very sensitive to bs choice, and a good set of pf sets must be used to obtain reasonable values of β .

Table 6.11 GeH₄ 3-21G Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	V ^e
$\bar{\alpha}$	33.03	32.79	32.81	31.23	30.94
β_{xyz}	-11.92	-12.50	-13.49	-58.56	-35.83
γ_{xxxx}	5761.17	5753.38	6046.16	5180.41	4552.20
γ_{xxyy}	2092.21	2075.18	2171.98	2158.16	1682.42
γ	5967.22	5942.37	6233.99	5698.04	4750.22

- Ge(3-21G) + p(0.05), d(1, 0.4, 0.16, 0.064, 0.0256), H-(3-21G) + s(0.06), p(0.9, 0.1), d(0.1) **116 Basis Functions** [5s5p6d / 3s2p1d]
- Ge(3-21G) + p(0.05), d(1, 0.4, 0.16, 0.064, 0.0256), H-(3-21G) + s(0.06), p(0.1), d(0.1) **104 Basis Functions** [5s5p6d / 3s1p1d]
- Ge(3-21G) + p(0.05), d(1, 0.4, 0.16, 0.064, 0.0256), H-(3-21G) + s(0.06), p(0.1) **80 Basis Functions** [5s5p6d / 3s1p]
- Ge(3-21G) + p(0.05), d(1, 0.4, 0.16, 0.064, 0.0256), H-(3-21G) + s(0.06) **68 Basis Functions** [5s5p6d / 3s]
- Ge(3-21G) + p(0.05), d(1, 0.4, 0.16, 0.064, 0.0256), H-(3-21G) **64 Basis Functions** [5s5p6d / 2s]

Note that if the larger [6s6p6d] Curtiss / Binning bs is used, this sensitivity is diminished somewhat. The calculations IV / 6.11 and V / 6.11 show that by the addition of the s(0.06) pf set on hydrogen better γ results are obtained, but more pf sets must be added even to get qualitative values of β .

5. Table 6.12 Results

Another 3-21G type GeH_4 calculation was performed for comparison purposes with other calculations of Ge_2H_4 and Ge_2H_2 . Calculation I / 6.12 (Table 6.12) consists of a germanium 3-21G bs augmented by p(0.05) and d(1.3, 0.65, 0.15), and a hydrogen 3-21G bs augmented by the s(0.06), p(0.1), d(0.1) pf sets. Calculation I / 6.12 produces the results: β_{xyz} differs by -2.2%, $\bar{\gamma}$ differs by -6% (comparing I / 6.12 to II / 6.11). Thus the two smaller exponent d pf sets on germanium did not make much difference to the DH and second DH results.

Table 6.12 GeH₄ 3-21G Results : another calculation

	Ia
$\bar{\alpha}$	32.81
β_{xyz}	-12.23
γ_{xxxx}	5326.12
γ_{xxyy}	1992.43
γ	5585.60

- a. Ge(3-21G) + p(0.05), d(1.3, 0.64, 0.15), H-(3-21G) + s(0.06), p(0.1), d(0.1) **92 Basis Functions** [5s5p4d / 3s1p1d]

CHAPTER VII

CALCULATION RESULTS FOR C_2H_4 , Si_2H_4 , AND Ge_2H_4

There have been some previous results for ethylene NLO properties, and some of them are summarized in Tables 7.1 and 7.2. There are by far less results for silene, and even less on germene. These series of calculations were performed to study the trend going from CH_4 to C_2H_4 to C_2H_2 , and the trend going from C_2H_4 to Si_2H_4 to Ge_2H_4 . For this reason the same model geometry and shape was used for all these molecules, even though it is known that the ground state of silene and germene do not possess a double bond structure like ethylene.

The calculations of ethylene (C_2H_4) are based upon the 6-31G bs extended by various pf sets. The calculations of silene (Si_2H_4) are based upon the 6-31G bs extended by various pf sets. The calculations of germene (Ge_2H_4) are based upon the 3-21G bs extended by various pf sets.

Ethylene (C_2H_4)

There were several recent calculations performed on ethylene [36, 46, 49, 52, 55, 65] as well as experimental data quoted [46, 50], and these results are summarized in Tables 7.1 and 7.2. The correlated results of Jordan [52], Spackman [46] and Salahub [55] compare favorably with the experimental results [46, 50]. Prasad et al. also quotes a γ_{xxxx} of 1626 and a γ_{zzzz} of 3094 [49]. In order to be able to make exact comparisons with the Si and Ge molecules, the calculations in the next two sections were performed.

Table 7.1 C_2H_4 quoted values

	Ia	IIb		IIIc
source:	exp.	Jordan		Dykstra
type:		HF	CISD	
α_{xx}	22.93	21.7	21.8	22.78
α_{yy}	26.02	23.8	24.9	24.69
α_{zz}	36.45	35.6	34.0	36.77
$\bar{\alpha}$	28.43	27.0	26.9	28.08
$\Delta\alpha$	12.25	13.0	10.9	13.14

Table 7.2 C_2H_4 more quoted values

	IVd	Ve		VI ^f	VIIg
source:	Prasad	Spackman		Salahub	Bartlett
type:		HF	MP2		SDQ-MBPT
α_{xx}	23.69	21.28	21.43	21.72	23.06
α_{yy}	23.69	24.07	24.82	26.68	24.62
α_{zz}	36.53	36.37	33.93	35.19	36.37
$\bar{\alpha}$	27.24	27.24	26.73	27.86	28.02
$\Delta\alpha$	13.91	13.91	11.90	11.80	12.60
γ_{xxxx}	-----	-----	-----	-----	3300
γ_{xxyy}	-----	-----	-----	-----	1600
γ_{xxzz}	-----	-----	-----	-----	3100
γ_{yyyy}	-----	-----	-----	-----	2800
γ_{yyzz}	-----	-----	-----	-----	2500
γ_{zzzz}	-----	-----	-----	-----	11900
$\bar{\gamma}$	-----	-----	-----	-----	6500

- a. experimental results [50]
 b. Jordan's results [52]
 c. Dykstra's results [36]
 d. Prasad et al. results [49]
 e. Spackman's results [46]
 f. Salahub's results [55]
 g. Sekino and Bartlett's [65]

1. Table 7.3 Results

Calculation I / 7.3 (Table 7.3) is the largest calculation on ethylene in this dissertation. In calculation I / 7.3, the s(0.05), p(0.03, 0.005), and d(0.94, 0.15, 0.05) pf sets are used on the carbon, and the s(0.06), p(0.25, 0.125, 0.0625) and d(0.25, 0.125, 0.0625) pf sets are used on the hydrogen. This calculation (I / 7.3), which has 188 contracted bfs will be used as the reference calculation for ethylene. The $\bar{\alpha}$ of 28.07 in calculation I / 7.3 differs -1.3% from the experimental value of I / 7.1 [50]. The $\bar{\alpha}$ result of I / 7.3 is very close to Sekino and Bartlett's result of 28.02 [65] (+0.02% difference), and the $\bar{\gamma}$ differs by -3.1% compared to that of [65] (VII / 7.2). In calculation II / 7.3, the s(0.06), p(0.9, 0.1) and d(0.1) pf sets are used on the hydrogen, which produces the results: $\bar{\alpha}$ differs by -0.03%, $\bar{\gamma}$ differs by +1.3% (comparing calculation II / 7.3 with I / 7.3). Calculation III / 7.3 was performed by removing the d(0.1) pf set, and the results are virtually unchanged. Calculation IV / 7.3 was performed using the s(0.06), p(0.1) and d(0.1) pf sets on the hydrogen, which produces the result: $\bar{\gamma}$ differs by +2% (comparing IV / 7.3 with I / 7.3). The s(0.06) and p(0.1) pf sets are used on the hydrogen in calculation V / 7.3, which produces the result: $\bar{\gamma}$ differs by -1.3% (comparing V / 7.3 with I / 7.3). The results of Table 7.3 show that with a relatively good set of pfs on the carbon, the DP and the second DH values are relatively insensitive to the number of p and d pf sets on the hydrogen. A finding vastly different from the findings of previous chapters (i.e., Chapters III and IV).

Table 7.3 C₂H₄ 6-31G Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	V ^e
α_{xx}	35.96	36.00	36.00	35.74	35.70
α_{yy}	25.10	25.19	25.27	25.13	25.09
α_{zz}	23.14	23.05	22.95	22.89	22.83
$\bar{\alpha}$	28.07	28.08	28.07	27.92	27.87
$\Delta\alpha$	11.96	12.02	12.06	11.89	11.90
γ_{xxxx}	3381.65	3417.78	3546.22	3426.49	3503.48
γ_{xxyy}	1598.74	1692.19	1738.86	1697.34	1700.15
γ_{xxzz}	2942.99	2954.37	3019.86	2962.53	2976.91
γ_{yyyy}	3133.01	3041.18	2375.20	3080.95	2352.69
γ_{yyzz}	2443.54	2500.56	2630.52	2569.87	2576.41
γ_{zzzz}	11018.00	11171.41	10825.13	11168.10	10734.52
γ	6300.64	6384.92	6305.01	6427.01	6219.53

C1 $\equiv$ C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05) [4s4p3d]

a. C1, H-(6-31G) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
188 Basis Functions [4s4p3d / 3s3p3d]

b. C1, H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) **128 Basis Functions**
[4s4p3d / 3s2p1d]

c. C1, H-(6-31G) + s(0.06), p(0.9, 0.1) **104 Basis Functions**
[4s4p3d / 3s2p]

d. C1, H-(6-31G) + s(0.06), p(0.1), d(0.1) **116 Basis Functions**
[4s4p3d / 3s1p1d]

e. C1, H-(6-31G) + s(0.06), p(0.1) **92 Basis Functions** [4s4p3d / 3s1p]

2. Table 7.4 Results

The calculations I / 7.4 through IV / 7.4 (Table 7.4) were performed with only one d(0.0234) pf set on the carbon versus the 3d pf sets of Table 7.3. In calculation I / 7.4, the p(0.25, 0.125, 0.0625), and d(0.125, 0.0625) pf sets are used on the hydrogen, which produces the results: $\Delta\alpha$ differs by +4.4%, and $\bar{\gamma}$ differs -2.7% (comparing I / 7.4 with I / 7.3). The hydrogens of II / 7.4 has the p(0.25, 0.125, 0.0625) pf sets and no d pf sets, which produces the results: $\Delta\alpha$ differs by +13.9%, $\bar{\gamma}$ differs by -3.3% (comparing II / 7.4 with I / 7.3). Calculation III / 7.4 was performed using the p(0.9, 0.1) and d(0.1) pf sets on the hydrogen, which produces the results: $\Delta\alpha$ differs by +9%, $\bar{\gamma}$ differs by +13.1% (comparing III / 7.4 with I / 7.3). In calculation IV / 7.4, the hydrogen d(0.1) pf set was removed, which produces the results: $\bar{\alpha}$ differs by -2%, $\Delta\alpha$ differs by +19.4%, $\bar{\gamma}$ differs by +12.4% (comparing III / 7.4 with I / 7.3).

In V / 7.4, a carbon f(0.125) pf is added to the bs of II / 7.3, and the results are virtually unchanged. In VI / 7.4, a MP2 calculation of the bs in V / 7.4 is performed. This produces the results: $\bar{\alpha}$ differs by -2.2%, and $\Delta\alpha$ differs by -20.3% (comparing VI / 7.4 with V / 7.4). The $\bar{\alpha}$ result of VI / 7.4 when compared with Spackman's MP2 result [46] differs by +2.8%, compared with Salahub's result [55] differs by -1.4%, compared with Sekino and Bartlett's SDQ-MBPT(4) result [65] differs by -1.9%, and compared with the experimental result [50] differs by -3.3%. These differences are probably well with the range of error in the experimental result.

Table 7.4 C₂H₄ 6-31G Results - further study of bs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
α_{xx}	36.22	36.79	36.34	36.87	35.97	33.62
α_{yy}	24.86	24.45	24.99	24.38	25.17	25.83
α_{zz}	22.84	22.18	22.11	21.31	23.12	23.00
$\bar{\alpha}$	27.97	27.80	27.81	27.52	28.09	27.48
$\Delta\alpha$	12.49	13.62	13.03	14.28	11.96	9.53
γ_{xxxx}	3256.08	1807.15	3538.51	2068.31	3305.06	-----
γ_{xxyy}	1613.20	2094.95	1674.75	1981.57	1617.81	-----
γ_{xxzz}	2911.88	2982.57	3301.10	3418.84	2856.78	-----
γ_{yyyy}	2914.69	2592.70	3199.48	2580.52	3014.40	-----
γ_{yyzz}	2144.81	2691.37	2960.83	2925.78	2516.95	-----
γ_{zzzz}	11154.52	10532.72	13025.60	14118.57	11699.21	-----
γ	6133.01	6094.07	7127.39	7083.95	6400.35	-----

C1 $\equiv$ C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05) [4s4p3d]

C2 $\equiv$ C(6-31G) + s(0.05), p(0.03, 0.005), d(0.0234) [4s4p1d]

a. C2, H-(6-31G) + s(0.06), p(0.25, 0.125, 0.0625), d(0.125, 0.0625)
140 Basis Functions [4s4p1d / 3s3p2d]

b. C2, H-(6-31G) + s(0.06), p(0.25, 0.125, 0.0625) 92 Basis Functions
[4s4p1d / 3s3p]

c. C2, H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) 104 Basis Functions
[4s4p1d / 3s2p1d]

d. C2, H-(6-31G) + s(0.06), p(0.9, 0.1) 80 Basis Functions
[4s4p1d / 3s2p]

e. C1+f(0.125), H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) 148 Basis Functions
[4s4p3d1f / 3s2p1d]

f. C1+f(0.125), H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) 148 Basis Functions
MP2 [4s4p3d1f / 3s2p1d]

These four calculations in Table 7.4 (I / 7.4 through IV / 7.4) show that the DP anisotropy factor, $\Delta\alpha$, is very sensitive to the bs pf representation on the hydrogen. These calculations uses only one d(0.0234) pf set on the carbon bs, and as the result there is great sensitivity to changes in the hydrogen pf set of the NLO properties. The results of Table 7.3 which uses a 3d carbon pf set are less sensitive to changes in the hydrogen pf set. Thus, the 3d pf set on the carbon is very important for obtaining good results. These results also show that calculations I / 7.4 and II / 7.4 are better than III / 7.4 and IV / 7.4.

Si₂H₄

1. Table 7.5 Results

The calculations I / 7.5 through V / 7.5 (Table 7.5) of Si₂H₄ were performed with the s(0.05), p(0.03, 0.005), and d(0.94, 0.15, 0.05) pf sets on the silicon, and a s(0.06) pf plus various p and d pf sets on the hydrogen. Calculation I / 7.5, with 196 contracted bfs serves as the reference calculation for Si₂H₄, which has the p(0.25, 0.125, 0.0625) and d(0.25, 0.125, 0.0625) pf sets on hydrogen. Calculation I / 7.5 produces the results: $\bar{\alpha} = 75.31$, $\Delta\alpha = 38.15$, $\bar{\gamma} = 50474.16$. In calculation II / 7.5, the p(0.9, 0.1) and d(0.1) pf sets are used on hydrogen, which produces the result: $\bar{\gamma}$ differs by -3.9% (comparing II / 7.5 with I / 7.5). Calculation III / 7.5 was performed with the d(0.1) pf set removed, which produces the results: $\Delta\alpha$ differs by -4.2%, $\bar{\gamma}$ differs by -9% (comparing III / 7.5 with I / 7.5). The hydrogen p(0.1) and d(0.1) pf sets are used in calculation IV / 7.5, which produces the result: $\bar{\gamma}$ differs by -5.7% (comparing IV / 7.5 with I / 7.5). Calculation V / 7.5 was performed with a p(0.1) pf set on the hydrogen, which produces the result: $\bar{\gamma}$ differs by -11.2% (comparing V / 7.5 with I / 7.5). In calculation VI / 7.4, the p(0.9, 0.1) pf sets are used on the hydrogen, which produces the results: $\Delta\alpha$ differs by -2.6%, $\bar{\gamma}$ differs by -9.6% (comparing VI / 7.4 with I / 7.4). The results of Table 7.5 show that the d pf set on hydrogen is important, and especially in calculation VI / 7.5 which has the one d(0.0234) pf set on the silicon.

Table 7.5 Si₂H₄ 6-31G Results - more study of hydrogen pfs

	Ia	IIb	IIIc	IVd	Ve	VI ^f
α_{xx}	100.04	100.13	100.31	99.66	99.74	103.23
α_{yy}	57.82	57.76	58.09	57.70	58.02	57.31
α_{zz}	68.06	67.95	67.05	67.42	66.59	66.27
$\bar{\alpha}$	75.31	75.28	75.15	74.93	74.78	75.60
$\Delta\alpha$	38.15	38.31	38.53	38.04	38.16	42.16
γ_{xxxx}	24155.91	24362.47	26228.45	23789.17	25622.63	23876.00
γ_{xxyy}	9566.08	9665.26	9704.69	9474.47	9493.21	10717.99
γ_{xxzz}	29120.97	29056.50	29711.34	28220.96	28744.39	28363.37
γ_{yyyy}	17271.94	12854.84	11998.80	12696.86	11847.75	15227.99
γ_{yyzz}	21154.13	20245.73	18830.42	19940.51	18467.17	19268.34
γ_{zzzz}	91260.58	87499.99	74960.26	86220.46	73235.32	72396.95
γ	50474.16	48530.46	45936.09	47595.68	44823.05	45640.05

Si1 $\equiv$ Si(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05) [5s5p3d]

a. S1, H-(6-31G) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
196 Basis Functions [5s5p3d / 3s3p3d]

b. S1, H-(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) 136 Basis Functions
[5s5p3d / 3s2p1d]

c. S1, H-(6-31G) + s(0.06), p(0.9, 0.1) 112 Basis Functions
[5s5p3d / 3s2p]

d. S1, H-(6-31G) + s(0.06), p(0.1), d(0.1) 124 Basis Functions
[5s5p3d / 3s1p1d]

e. S1, H-(6-31G) + s(0.06), p(0.1) 100 Basis Functions
[5s5p3d / 3s1p]

f. Si-(6-31G) + s(0.05), p(0.03, 0.005,), d(0.0234)
H-(6-31G) + s(0.06), p(0.9, 0.1) 112 Basis Functions [5s5p1d / 3s2p]

When silicon has a larger d pf set (i.e., 3d), then there is some compensation for the lack of a d pf set on hydrogen. Therefore, removal of the d pf set on hydrogen in a calculation with 1d silicon pf set is more pronounced than in a calculation with a 3d silicon pf set. The results of Table 7.5 show that the hydrogen 1p1d pf set is again a good comprise for a minimum bs without compromise in accuracy of NLO properties.

2. Table 7.6 Results

Another 6-31G calculation on Si_2H_4 was performed with the p(0.05) and d(0.94, 0.15, 0.05) pf sets on silicon and the hydrogen bs augmented by the s(0.06), p(0.1), and d(0.1) pf sets (I / 7.6). Calculation I / 7.6 (Table 7.6) produces the following results: $\bar{\alpha}$ differs by -3.74%, $\Delta\alpha$ differs by +6.94%, $\bar{\gamma}$ differs by -62.80% (comparing I / 7.6 to IV / 7.5). This is somewhat a surprising result, since by changing the silicon p(0.03) pf to p(0.05) and removal of the p(0.005) pf, it was not expected to see any significant change in $\bar{\gamma}$ (i.e., Chapters III and V results).

In II / 7.6, the bs of II / 7.6 is augmented by a f(0.125) pf set on silicon. This produces a change in $\bar{\gamma}$ by +2.7%, which is not very significant. In III / 7.6, a MP2 calculation of the bs in II / 7.6 was performed, which produces the following results: $\bar{\alpha}$ differs by -1.5%, $\Delta\alpha$ differs by -5.1% (comparing III / 7.6 to II / 7.6).

Ge_2H_4

Calculation I / 7.7 (Table 7.7) is the reference calculation for Ge_2H_4 , which used the Binning / Curtiss [26] bs for germanium augmented by the p(0.03336, 0.013344) and d(0.1328, 0.05312, 0.021248) pf sets, and the hydrogen 6-31G bs is augmented by the s(0.06), p(0.1) and d(0.1) pf sets, which consists of 156 contracted bfs. This calculation I / 7.7 took 3 weeks of continuous computation time on the IBM Risc 6000 / 320h computer. Some of the representative results of calculation I / 7.7 (Table 7.7) are: $\bar{\alpha} = 85.55$, $\Delta\alpha = 53.72$, $\bar{\gamma} = 61590.19$. The other three calculations, II / 7.7 through IV / 7.7 used the 3-21G bs of germanium.

Table 7.6 Si₂H₄ 6-31G Results- f pfs and MP2

	I ^a	II ^b	III ^c
α_{xx}	99.33	100.30	98.20
α_{yy}	57.46	58.00	59.03
α_{zz}	66.96	67.90	65.50
$\bar{\alpha}$	74.58	75.40	74.24
$\Delta\alpha$	38.02	38.32	36.37
γ_{xxxx}	19074.78	24390.90	-----
γ_{xxyy}	8329.37	9894.83	-----
γ_{xxzz}	23954.67	29046.67	-----
γ_{yyyy}	11136.53	14058.44	-----
γ_{yyzz}	17754.31	21385.17	-----
γ_{zzzz}	66725.59	90071.46	-----
$\bar{\gamma}$	39402.72	49834.83	-----

Si1 $\equiv$ Si(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05) [5s5p3d]

Si2 $\equiv$ Si(6-31G) + s(0.05), p(0.03), d(0.94, 0.15, 0.05) [5s4p3d]

a. S2, H-(6-31G) + s(0.06), p(0.1), d(0.1) **118 Basis Functions**
[5s4p3d / 3s1p1d]

b. S1+f(0.125), H-(6-31G) + s(0.06), p(0.9,0.1), d(0.1) **156 Basis Functions**
[5s5p3d1f / 3s2p1d]

c. S1+f(0.125), H-(6-31G) + s(0.06), p(0.9,0.1), d(0.1) **156 Basis Functions**
MP2 [5s5p3d1f / 3s2p1d]

Table 7.7 Ge_2H_4 Binning / Curtiss and 3-21G Results

	Ia	IIb	IIIc	IVd	Ve	VI ^f
α_{xx}	120.85	120.59	118.42	114.34	120.88	116.17
α_{yy}	73.10	60.88	58.75	63.93	72.91	70.62
α_{zz}	62.69	65.70	64.83	72.33	60.93	61.88
$\bar{\alpha}$	85.55	82.35	80.67	83.53	84.91	82.89
$\Delta\alpha$	53.72	57.45	56.87	46.78	54.95	50.49
γ_{xxxx}	124702.53	25551.72	7814.70	25473.89	83984.72	-----
γ_{xxyy}	22533.90	8471.57	4705.10	9691.25	14140.48	-----
γ_{xxzz}	27164.62	9526.18	4735.82	30770.74	17814.31	-----
γ_{yyyy}	26422.89	5388.92	11638.80	8102.45	17379.52	-----
γ_{yyzz}	12306.52	10242.35	8253.15	14285.74	10247.26	-----
γ_{zzzz}	32815.48	14610.56	7422.04	61408.54	13623.82	-----
$\bar{\gamma}$	61590.19	22906.40	12452.73	40896.07	39878.43	-----

- a. Ge-(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248)
H-(6-31G) + s(0.06), p(0.1), d(0.1) **156 Basis Functions** [6s6p5d / 3s1p1d]
- b. Ge-(3-21G) + d(1.3, 0.65, 0.15), H-(3-21G) + s(0.06),
p(0.9, 0.1), d(0.1) **142 Basis Functions** [5s4p4d / 3s2p1d]
- c. Ge-(3-21G) + d(1.3, 0.65, 0.15), H-(3-21G) + s(0.06),
p(0.9, 0.1) **118 Basis Functions** [5s4p4d / 3s2p]
- d. Ge-(3-21G) + d(1.3, 0.65, 0.15, 0.05), H-(3-21G) **108 Basis Functions**
[5s4p4d / 3s]
- e. Ge-(3-21G) + p(0.05), d(1.3, 0.65, 0.15), H-(3-21G) + s(0.06),
p(0.1), d(0.1) **136Basis Functions** [5s4p4d / 3s1p1d]
- f. Ge-(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248)
H-(6-31G) + s(0.06), p(0.1), d(0.1) **156 Basis Functions MP2**
[6s6p5d / 3s1p1d]

Calculation II / 7.7 has the d(1.3, 0.65, 0.15) pf sets on the germanium, and the s(0.06), p(0.9, 0.1) and d(0.1) pf sets on the hydrogen, which produces the results: $\bar{\alpha}$ differs by -3.7%, $\Delta\alpha$ differs by +7%, and $\bar{\gamma}$ differs by -62.8% (comparing II / 7.7 to I / 7.7). Calculation II / 7.7 took 300 minutes of CPU on the 3090 / 400. In calculation III / 7.7, the d(0.10) pf set on the hydrogen is removed, which produces the results: $\bar{\alpha}$ differs by -5.7%, $\Delta\alpha$ differs by +5.9%, $\bar{\gamma}$ differs by -79.8% (comparing III / 7.7 to I / 7.7). Calculation IV / 7.7 was performed with an additional d(0.05) pf set on the germanium, and no pf sets on the hydrogen, which produces the results: $\bar{\alpha}$ differs by -0.75%, $\Delta\alpha$ differs by +2.3%, $\bar{\gamma}$ differs by -33.6% (comparing IV / 7.7 to I / 7.7). In V / 7.7, a more compact bs using the germanium 3-21G bs augmented by the p(0.05), d(1.3, 0.65, 0.15) pf sets, and the hydrogen 3-21G bs augmented by the s(0.06), p(0.1), d(0.1) pf sets was performed, and comparing V / 7.7 to I / 7.7 produces the results: $\bar{\alpha}$ differs by -0.75%, $\Delta\alpha$ differs by +2.3%, $\bar{\gamma}$ differs by -35.3%. Thus with exception of the γ value, calculation V / 7.7 produces fairly good results compared to I / 7.7 with only several days of CPU time. In VI / 7.7, a MP2 calculation using the bs of I / 7.7 was performed, and a comparison with I / 7.7 shows the following: $\bar{\alpha}$ differs by -3.1%, $\Delta\alpha$ differs by -6%.

The results of these five calculations in Table 7.7 suggest that I / 7.7 produces by far the best results, but at the great expense of three weeks of CPU time.

CHAPTER VIII

CALCULATION RESULTS FOR C_2H_2 , Si_2H_2 , Ge_2H_2

The calculations for ethyne (C_2H_2) are based upon the TZV and 6-31G bss.

The silyne (Si_2H_2) calculations are based upon the TZV bs. The calculations of germyne (Ge_2H_2) are based upon the Binning / Curtiss [26] bs for germanium, and the TZV bs on the hydrogen.

Ethyne (C_2H_2)

There has been several recent theoretical calculations on ethyne (C_2H_2) [36, 46, 49, 51, 55] as well as quoted experimental results on the DP [46, 53, 54]. These results are summarized in Tables 8.1 and 8.2. The values for $\bar{\alpha}$ and $\Delta\alpha$, which matches experimental values the best are the results of Prasad [49]. However, there have not been any previous results on the second DH, which we have calculated.

1. Table 8.3 Results

Calculation I / 8.3 (Table 8.3) was performed with the TZV bs for carbon augmented by the s(0.05), p(0.036424, 0.014570) and d(0.94, 0.15, 0.05) pf sets, and on the hydrogen a TZV bs augmented by the s(0.06), p(0.25, 0.125, 0.0625), and d(0.25, 0.125, 0.0625) pf sets, which has 140 contracted bfs. Calculation I / 8.3 is the reference calculation for ethyne, and produces the following: $\alpha_{xx} = 19.34$, $\alpha_{zz} = 31.32$, $\bar{\alpha} = 23.34$, $\Delta\alpha = 11.98$, and $\bar{\gamma} = 4980.04$. Comparing I / 8.3 to experimental results: $\bar{\alpha}$ differs by +2.9%, and $\Delta\alpha$ differs by +1.3%. Calculation II / 8.3 was performed with pf sets indicated in footnote b of Table 8.3. This produces the result: $\bar{\gamma}$ differs by -3.04% (comparing II / 8.2 with I / 8.2).

Table 8.1 C_2H_2 quoted values

	I ^a	II ^b	III ^c	IV ^d
source:	exp.	Maroulis	Dykstra	Prasad
type:				
α_{xx}	18.74	19.35	19.04	18.22
α_{zz}	30.57	31.42	31.36	30.08
$\bar{\alpha}$	22.68	23.38	23.15	22.17
$\Delta\alpha$	11.83	12.06	12.32	11.86

Table 8.2 C_2H_2 more quoted values

	V ^e	VI ^f	
source:	Salahub	Spackman	
type:		HF	MP2
α_{xx}	18.77	17.18	16.89
α_{zz}	31.85	32.08	30.73
$\bar{\alpha}$	23.13	22.15	21.51
$\Delta\alpha$	13.08	14.90	13.83

- a. Bogaard et al. experimental results [53]
- b. Maroulis' results [51]
- c. Dykstra's results [36]
- d. Prasad et al. results [49]
- e. Salahub's results [55]
- f. Spackman's results [46]

Table 8.3 C₂H₂ TZV and 6-31G Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	V ^e	VI ^f
α_{xx}	19.34	19.35	19.42	19.39	19.37	19.39
α_{yy}	19.34	19.35	19.42	19.39	19.37	19.39
α_{zz}	31.32	31.32	31.42	31.24	31.20	31.23
$\bar{\alpha}$	23.34	23.34	23.42	23.34	23.31	23.34
$\Delta\alpha$	11.98	11.97	12.00	11.85	11.83	11.84
γ_{xxxx}	5595.15	5394.94	5810.37	5951.09	5948.73	5843.62
γ_{xxyy}	1864.87	1798.31	1936.91	1983.82	1982.91	1948.00
γ_{xxzz}	1724.51	1650.60	1717.02	1693.12	1696.92	1693.12
γ_{yyyy}	5595.17	5394.94	5810.37	5951.09	5948.73	5843.62
γ_{yyzz}	1724.52	1650.60	1716.93	1692.95	1696.75	1692.95
γ_{zzzz}	3082.09	3153.29	3212.94	3148.27	3058.42	3019.26
γ	4980.04	4828.44	5115.08	5158.05	5141.81	5074.92

- a. C(TZV) + s(0.05), p(0.036424, 0.014570), d(0.94, 0.15, 0.05)
H(TZV) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
140 Basis Functions [6s5p3d / 4s3p3d]
- b. C(TZV) + d(0.8, 0.4, 0.2, 0.1, 0.05, 0.025)
H(TZV) + s(0.06), p(0.25, 0.125, 0.0625) **124 Basis Functions**
[5s3p6d / 4s3p]
- c. C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05)
H(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) **98 Basis Functions**
[4s4p3d / 3s2p1d]
- d. C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05)
H(6-31G) + s(0.06), p(0.1), d(0.1) **92 Basis Functions**
[4s4p3d / 3s1p1d]
- e. C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05)
H(6-31G) + s(0.06), p(0.1) **80 Basis Functions**
[4s4p3d / 3s1p]
- f. C(6-31G) + s(0.05), p(0.036424, 0.014570), d(0.94, 0.15, 0.05)
H(6-31G) + s(0.06), p(0.1) **80 Basis Functions**
[4s4p3d / 3s1p]

Calculation III / 8.3 uses a carbon 6-31G bs augmented by the s(0.05), p(0.03, 0.005), and d(0.94, 0.15, 0.05) pf sets, and a hydrogen 6-31G bs augmented by the s(0.06), p(0.9, 0.1), d(0.1) pf sets which has 98 bfs. When compared with I / 8.3, the produces the following: $\bar{\alpha}$ differs by +0.34%, $\bar{\gamma}$ differs by +2.71%. In IV / 8.3, the p(0.9) pf set on hydrogen is removed, and comparing IV / 8.3 to III / 8.3 produces the following: $\bar{\alpha}$ differs by -0.34%, $\bar{\gamma}$ differs by +0.84%. In calculation V / 8.3, the d(0.1) pf set on hydrogen is removed, and comparing V / 8.3 to IV / 8.3 produces the results: $\bar{\alpha}$ differs by -0.13%, $\bar{\gamma}$ differs by -0.31%. Thus the calculations III / 8.3, IV / 8.3, and V / 8.3 are very similar to I / 8.3. In calculation VI / 8.3, the carbon p(0.03, 0.005) pf set was replace by the p(0.036424, 0.014570) pf set, and when compared to V / 8.3 produces the following: $\bar{\gamma}$ differs by -1.30%. Thus the change in the outer p pf set on carbon did not cause any signifigant changes.

2. Table 8.4 Results

In I / 8.4 (Table 8.4), a carbon f(0.125)pf set is added to the bs of III / 8.3, which produces a very small change in $\bar{\gamma}$ of +5.8% (compared to III / 8.3). In II / 8.4, a MP2 calculation of the bs used in I / 8.4 was performed, which produces the following: $\bar{\alpha}$ differs by -1.8%, and $\Delta\alpha$ differs by -6.2% (comparing II / 8.4 with I / 8.4). When $\bar{\alpha}$ is compared with Spackman's MP2 result [46], it differs by +3.8%, and compared with the experimental result [53], it differs by +1.4%. When $\Delta\alpha$ is compared with Spackman's MP2 result [46], it differs by -18.9%, and compared with the experimental result [53], it differs by -5.2%. The comparison with Spackman's results indicates once again that there is a dificiency in Spackman's bs. The differences are probably well within experimental error.

Table 8.4 C₂H₂ TZV and 6-31G Results - f pfs and MP2

	I ^a	II ^b
α_{xx}	19.45	19.26
α_{yy}	19.45	19.26
α_{zz}	31.40	30.47
$\bar{\alpha}$	23.43	23.00
$\Delta\alpha$	11.95	11.21
γ_{xxxx}	6441.72	-----
γ_{xxyy}	2147.37	-----
γ_{xxzz}	1705.80	-----
γ_{yyyy}	6441.72	-----
γ_{yyzz}	1705.71	-----
γ_{zzzz}	3053.23	-----
$\bar{\gamma}$	5410.88	-----

- a. C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05), f(0.125)
 H(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) **118 Basis Functions**
 [4s4p3d1f / 3s2p1d]
- b. C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05), f(0.125)
 H(6-31G) + s(0.06), p(0.9, 0.1), d(0.1) **118 Basis Functions MP2**
 [4s4p3d1f / 3s2p1d]

Si₂H₂

1. Table 8.5 Results

Calculation I / 8.5 (Table 8.5) uses a TZV bs for silicon augmented by the s(0.05), p(0.0262, 0.0105), and d(0.0745, 0.0298, 0.01192) pf sets, and the TZV bs for hydrogen augmented by the s(0.06), p(0.25, 0.125, 0.0625) and d(0.25, 0.125, 0.0625) pf sets, which has of 166 contracted bfs. Calculation I / 8.5 is used as the reference calculation for Si₂H₂, and the following results are obtained: $\bar{\alpha} = 87.31$, $\Delta\alpha = 42.87$, and $\bar{\gamma} = 77445.03$. In calculation II / 8.5, the s(0.06), p(0.9, 0.1) and d(0.1) pf sets are used on hydrogen which produces the result: $\bar{\gamma}$ differs by +0.46% (comparing II / 8.5 with I / 8.5). Calculation III / 8.5 was performed with the d(0.1) pf set removed on hydrogen. There are virtually no changes. Calculation IV / 8.5 uses only the p(0.1) and d(0.1) pf sets on hydrogen to produce again very small changes ($\Delta\alpha$ differs only by -1.5%, compared with I / 8.5). In calculation V / 8.5, only a p(0.1) pf set is used on hydrogen, produces again no significant changes.. The results of Table 8.5 show again, that the NLO properties are relatively insensitive to the pfs on hydrogen for this hydrocarbon analog.

2. Table 8.6 Results

In I / 8.6 (Table 8.6), a silicon f(0.125) pf set is added to the bs of II / 8.5, to produce only insignificant changes (i.e., less than 1%). In II / 8.6, a MP2 calculation of the bs used in I / 8.6 was performed, which produces the following: $\bar{\alpha}$ differs by -5.2%, and $\Delta\alpha$ differs by +7.7% (comparing II / 8.6 with I / 8.6).

Table 8.5 Si₂H₂ TZV Results- Study of hydrogen pfs

	Ia	IIb	IIIc	IVd	Ve
α_{xx}	73.02	73.12	72.94	73.03	72.83
α_{yy}	73.02	73.12	72.94	73.03	72.83
α_{zz}	115.89	115.68	115.87	115.24	115.47
$\bar{\alpha}$	87.31	87.31	87.25	87.10	87.04
$\Delta\alpha$	42.87	42.56	42.93	42.21	42.64
γ_{xxxx}	83771.83	84629.98	85028.14	84357.32	84689.61
γ_{xxyy}	27925.15	28212.52	28343.27	28121.58	28230.41
γ_{xxzz}	29353.09	29934.83	29360.41	29868.30	29175.64
γ_{yyyy}	83779.09	84645.11	85031.46	84372.16	84692.85
γ_{yyzz}	29355.37	29939.67	29361.44	29873.06	29176.64
γ_{zzzz}	46457.00	43581.13	43666.61	43433.59	43521.34
$\bar{\gamma}$	77445.03	77806.05	77571.28	77577.81	77213.84

Si1 $\equiv$ Si(TZV)+ s(0.05), p(0.0262, 0.0105), d((0.505,0.1863), 0.0745, 0.0298, 0.01192) [7s7p4d]

- Si1, H-(TZV) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
166 Basis Functions [7s7p4d / 4s3p3d]
- Si1, H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1) 136 Basis Functions
[7s7p4d / 4s2p1d]
- Si1, H-(TZV) + s(0.06), p(0.9, 0.1) 124 Basis Functions [7s7p4d / 4s2p]
- Si1, H-(TZV) + s(0.06), p(0.1), d(0.1) 130 Basis Functions
[7s7p4d / 4s1p1d]
- Si1, H-(TZV) + s(0.06), p(0.1) 118 Basis Functions [7s7p4d / 4s1p]

Table 8.6 Si₂H₂ TZV Results - f pfs and MP2

	Ia	IIb
α_{xx}	73.02	67.42
α_{yy}	73.02	67.42
α_{zz}	115.77	113.48
$\bar{\alpha}$	87.27	82.77
$\Delta\alpha$	42.75	46.06
γ_{xxxx}	86308.87	-----
γ_{xxyy}	28769.63	-----
γ_{xxzz}	29833.78	-----
γ_{yyyy}	86308.92	-----
γ_{yyzz}	29833.80	-----
γ_{zzzz}	43148.31	-----
$\bar{\gamma}$	78528.10	-----

Si1 $\equiv$ Si(TZV)+ s(0.05), p(0.0262, 0.0105), d((0.505,0.1863), 0.0745, 0.0298, 0.01192) [7s7p4d]

- a. Si1+f(0.125), H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1) **156 Basis Functions**
[7s7p4d1f / 4s2p1d]
- b. Si1+f(0.125), H-(TZV) + s(0.06), p(0.9, 0.1), d(0.1) **156 Basis Functions**
MP2 [7s7p4d1f / 4s2p1d]

3. Table 8.7 Results

Calculation I / 8.7 (Table 8.7) has an extra hydrogen p(0.5) pf set compared to I / 8.5, which again produces insignificant changes. Calculation II / 8.7 was performed with the TZV bs on silicon augmented by the p(0.0262, 0.0105) and d(0.0298) pf sets, and the TZV bs on hydrogen augmented by the p(0.9, 0.1) and d(0.1) pf sets, which produces the considerable changes: $\bar{\alpha}$ differs by -9.5%, $\Delta\alpha$ differs by +26.4%, $\bar{\gamma}$ differs by +17% (comparing II / 8.7 with I / 8.5). Calculation III / 8.7 was performed with the 6-31G bs on silicon augmented by the p(0.05) and d(0.94, 0.15, 0.05) pf sets, and the 6-31G bs on hydrogen augmented by the s(0.06), p(0.1), and d(0.1) pf sets. When III / 8.7 is compared to calculation IV / 8.5, which used the TZV basis sets for silicon and hydrogen and had the different d((0.505, 0.1863), 0.0745, 0.0298, 0.01192) pf sets on silicon, only $\bar{\gamma}$ is different: $\bar{\alpha}$ differs by -1.2%, $\bar{\gamma}$ differs by -35.9%.

The results of Tables 8.5 and 8.7 show that in the case of Si_2H_2 , the calculated properties are relatively insensitive to changes in the pf set on the hydrogen, if there is an adequate group of pf sets on the silicon. Calculation II / 8.7 shows that even with a fair representation of pf sets on hydrogen, the 2p1d, an inadequacy of d type pf sets on the silicon produces relative poor results for $\bar{\alpha}$, $\Delta\alpha$ and $\bar{\gamma}$.

Table 8.7 Si₂H₂ Results - further study of bs

	I ^a	II ^b	III ^c
α_{xx}	73.18	60.93	71.99
α_{yy}	73.18	60.93	71.99
α_{zz}	115.99	115.11	114.17
$\bar{\alpha}$	87.45	78.99	86.05
$\Delta\alpha$	42.81	54.18	42.18
γ_{xxxx}	84335.23	99015.73	50045.21
γ_{xxyy}	28112.30	33005.51	16681.74
γ_{xxzz}	29954.87	36135.16	21270.17
γ_{yyyy}	84338.59	99017.68	50045.21
γ_{yyzz}	29955.95	36135.65	21270.17
γ_{zzzz}	42851.68	44540.62	30094.97
γ	77514.35	90625.33	49725.90

- a. Si-(TZV) + s(0.05), p(0.0262, 0.0105), d((0.505, 0.1863), 0.0745, 0.0298, 0.01192) H-(TZV) + s(0.06), p(0.5, 0.25, 0.125, 0.0625), d(0.5, 0.025, 0.125)
172 Basis Functions [7s7p4d / 4s4p3d]
- b. Si-(TZV) + s(0.05), p(0.0262, 0.0105), d(0.0298)
H-(TZV) + p(0.9, 0.1), d(0.1) **98 Basis Functions** [7s7p1d / 4s2p1d]
- c. Si-(6-31G) + p(0.05), d(0.94, 0.15, 0.05),
H-(6-31G) + s(0.06), p(0.1), d(0.1) **92 Basis Functions** [4s4p3d / 3s1p1d]

Ge₂H₂

1. Table 8.8 Results

The calculations of Ge₂H₂ uses a Binning / Curtiss [26] bs for germanium augmented by the p(0.03336, 0.013344) and d(0.1328, 0.05312, 0.028248, 0.008499) pf sets and the TZV bs for hydrogen augmented by various combinations of p and d pf sets. In calculation I / 8.8 (Table 8.8), the p(0.25, 0.125, 0.0625) and d(0.25, 0.125, 0.0625) pf sets are used on the hydrogen, which produces the results: $\bar{\alpha} = 85.53$, $\Delta\alpha = 41.40$, $\bar{\gamma} = 72766.67$. Calculation I / 8.8 has 180 contracted bfs. Calculation II / 8.8 was performed with the p(0.9, 0.1) and d(0.1) pf sets on the hydrogen, and produces the result: $\bar{\gamma}$ differs by +2.79% (comparing II / 8.8 to I / 8.8).

Calculation III / 8.8 was performed with the d(0.1) pf set removed on the hydrogen, which produces the result: $\bar{\gamma}$ differs by +3.82% (comparing III / 8.8 to I / 8.8). In calculation IV / 8.8, the p(0.1) and d(0.1) pf sets are used on the hydrogen, which produces the result: $\bar{\gamma}$ differs by +2.97% (comparing IV / 8.8 to I / 8.8). Calculation V / 8.8 was performed with the p(0.1) pf set on the hydrogen, which produces the result: $\bar{\gamma}$ differs by +4.23% (comparing V / 8.5 to I / 8.5). Calculation VI / 8.8 was performed with an extra d(0.05) pf set added to the bs of II / 8.8, which produces the result: $\bar{\gamma}$ differs by +1.12% (comparing VI / 8.8 to I / 8.8).

These results of the calculations of Ge₂H₂ in Table 8.8 shows that as for Si₂H₂, if there is an adequate group of pf sets on germanium, the variations of pf sets on hydrogen does not change the calculated NLO properties significantly.

Table 8.8 Ge₂H₂ Binning / Curtiss Results - Study of hydrogen pfs

	I ^a	II ^b	III ^c	IV ^d	V ^e	VI ^f
α_{xx}	71.73	71.81	71.69	71.78	71.65	71.80
α_{yy}	71.73	71.81	71.69	71.78	71.65	71.80
α_{zz}	113.13	113.01	113.05	112.66	112.69	113.08
$\bar{\alpha}$	85.53	85.54	85.47	85.41	85.33	85.56
$\Delta\alpha$	41.40	41.20	41.36	40.88	41.04	41.28
γ_{xxxx}	79482.52	81388.12	83048.91	81437.85	83498.32	80356.03
γ_{xxyy}	26493.68	27126.91	27680.42	27145.07	27831.55	26786.81
γ_{xxzz}	27454.04	28567.41	28159.22	28744.80	28255.19	27190.24
γ_{yyyy}	79479.60	81375.82	83036.11	81432.58	83490.99	80364.82
γ_{yyzz}	27453.16	28563.69	28155.50	28743.20	28253.08	27192.90
γ_{zzzz}	42069.48	42704.42	43658.87	42496.84	43558.35	44846.09
$\bar{\gamma}$	72766.67	74796.88	75546.84	74926.68	75845.46	73581.37

Ge1 $\equiv$ Ge(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248, 0.008499)
[6s6p6d]

- Ge1, H-(TZV) + p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
180 Basis Functions [6s6p6d / 3s3p3d]
- Ge1, H-(TZV) + p(0.9, 0.1), d(0.1) **150 Basis Functions**
[6s6p6d / 3s2p1d]
- Ge1, H-(TZV) + p(0.9, 0.1), **138 Basis Functions** [6s6p6d / 3s2p]
- Ge1, H-(TZV) + p(0.1), d(0.1) **144 Basis Functions** [6s6p6d / 3s1p1d]
- Ge1, H-(TZV) + p(0.1) **132 Basis Functions** [6s6p6d / 3s1p]
- Ge1, H-(TZV) + p(0.9, 0.1), d(0.1, 0.05) **162 Basis Functions**
[6s6p6d / 3s2p2d]

2. Table 8.9 Results

Another calculation (I / 8.9) (Table 8.9) was performed with a germanium d(0.008499) pf set removed from the bs of IV / 8.8. Calculation I / 8.9 produces the following results: $\bar{\alpha}$ differs by +1.15%, $\Delta\alpha$ differs by +0.07%, $\bar{\gamma}$ differs by +3.82% (comparing I / 8.9 to IV / 8.8). In II / 8.9, a MP2 calculation of the bs of IV / 8.8 was performed. This produces the results: $\bar{\alpha}$ differs by -4.3%, $\Delta\alpha$ differs by +9.8% (comparing II / 8.9 to IV / 8.8).

3. Table 8.10 Results

Another calculation of Ge_2H_2 (I / 8.10) (Table 8.10) was performed using the 3-21G bs for germanium augmented by the p(0.05) and d(1.3, 0.65, 0.15) pf sets and the hydrogen 3-21G bs augmented by the s(0.06), p(0.1), and d(0.1) pf sets. Calculation I / 8.10 produces the results: $\bar{\alpha}$ differs by -8.37%, $\Delta\alpha$ differs by +33.90%, $\bar{\gamma}$ differs by -64.10% (comparing I / 8.10 to IV / 8.8). Thus the 3-21G bs results are much poorer than the Curtiss / Binning bs results (i.e., $\Delta\alpha$ and $\bar{\gamma}$ suffers in accuracy).

Chapter Summary

In summary, it was found that if there is adequate pf set representation on the heavy atom, the NLO properties are relatively insensitive to changes in the attached hydrogen's pf sets. Also it was found that MP2 calculations are important for accurate values of $\Delta\alpha$, but the changes of $\bar{\alpha}$ from HF (SCF) to MP2 may be smaller than the range of experimental error of the experimental result. If convergence difficulties are not encountered, the calculations only take several hours of CPU time, whereas the MP2 calculations performed by a Sun Sparc 2 took about one week of CPU time using the G92 code.

Table 8.9 Ge₂H₂ Binning / Curtiss Results - MP2

	Ia	IIb
α_{xx}	71.74	66.79
α_{yy}	71.75	66.79
α_{zz}	112065	111.69
$\bar{\alpha}$	85.38	81.76
$\Delta\alpha$	40.91	44.90
γ_{xxxx}	79315.41	-----
γ_{xxyy}	26439.63	-----
γ_{xxzz}	28883.04	-----
γ_{yyyy}	79326.85	-----
γ_{yyzz}	28886.62	-----
γ_{zzzz}	44249.85	-----
$\bar{\gamma}$	74262.14	-----

Ge1 $\equiv$ Ge(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248, 0.008499)
[6s6p6d]

Ge2 $\equiv$ Ge(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248)
[6s6p5d]

a. Ge2, H-(TZV) + s(0.06), p(0.1), d(0.1) **132 Basis Functions**
[6s6p5d / 3s1p1d]

b. Ge1, H-(TZV) + p(0.1), d(0.1) **144 Basis Functions MP2** [6s6p6d / 2s1p1d]

Table 8.10 Ge_2H_2 3-21G Results

	Ia
α_{xx}	60.01
α_{yy}	60.01
α_{zz}	114.75
$\bar{\alpha}$	78.26
$\Delta\alpha$	54.74
γ_{xxxx}	17797.94
γ_{xxyy}	5932.65
γ_{xxzz}	16679.98
γ_{yyyy}	17797.97
γ_{yyzz}	16680.04
γ_{zzzz}	20300.99
$\bar{\gamma}$	26896.45

$\text{Ge3} \equiv \text{Ge}(3-21\text{G}) + \text{p}(0.05), \text{d}(1.3, 0.65, 0.15)$

a. $\text{Ge3}, \text{H}-(3-21\text{G}) + \text{s}(0.06), \text{p}(0.1), \text{d}(0.1)$ 112 Basis Functions
[5s5p4d / 3s1p1d]

CHAPTER IX

SUMMARY AND CONCLUSIONS

The calculations described in this dissertation were performed with the idea of obtaining at least some of the answers to the following questions:

1. How do NLO properties change as we ascend a given group of the periodic table?
2. How important is electron correlation, and how may it be included in a calculation?
3. How important are the p and d pf sets on an attached hydrogen?
4. How important are the roles of diffuse p, d, and f pfs on atoms other than hydrogen?
5. How large a bs is necessary to give accurate values (to within 10%) of NLO properties, and can these bss obtained for one molecule be transferred to other molecules (i.e., bs pfs developed on one molecule used in a calculation of another molecule)?
6. Are there any general rules which can be deduced from the experience gained in performing these calculations which will help in planning future calculations?
7. How do the accurate ab initio results compare to the results of semi-empirical methods now widely in use?
8. Are there modifications to the standard finite field SCF method which might be used to extend the size of the molecules which can be studied by ab initio methods?

Answers to most of these questions are given throughout the dissertation. However it is constructive to summarize the major findings here.

Summary of Reference Calculations - Trends (Question 1)

Tables 9.1 through 9.5 summarize the $\bar{\alpha}$, $\bar{\beta}$, and $\bar{\gamma}$ values of the reference calculations for each molecule. These tables can be useful to show trend which we will now discuss. The DP and second DH (γ) increase markedly as we go up a particular group (i.e., larger atomic number).

Table 9.1 XH_3 reference values

	I ^a	II ^b	III ^c
	NH_3	PH_3	AsH_3
μ	0.6263	0.2608	0.1674
$\bar{\alpha}$	12.96	29.83	34.66
β	15.21	24.14	29.47
γ	2457.21	7628.49	9611.60

a. calculation IV / 3.3

N-(TZV) + s(0.06),p(0.0536, 0.02144, 0.01072), d(2.74, 0.94, 0.32, 0.11, 0.042, 0.016) H-(TZV) + s(0.06),p(1.0, 0.5, 0.25, 0.125), d(0.5, 0.25, 0.125)
162 bfs [6s6p6d / 4s4p3d]

b. calculation I / 3.13

P-(T15.16.1) + s(0.0626), p(0.04188, 0.02094, 0.01047), d(2.34, 0.94, 0.38, 0.15, 0.075, 0.0375), H-(6-31G) + p(0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625) **164 bfs** [8s8p6d / 2s4p3d]

c. calculation I / 3.19

As-(BC) + s(0.0569), p(0.0534,0.0267,0.01335), d(0.49135, 0.19654, 0.07862, 0.03145, 0.01258), H-(T1.42.1) + p(1, 0.5, 0.25, 0.125, 0.0625), d(0.5, 0.25, 0.125, 0.0625) **184 bfs** [7s7p6d / 1s5p4d]

(all units are in a.u. s)

Table 9.2 H₂X reference values

	I ^a	II ^b	III ^c
	H ₂ S	H ₂ Se	H ₂ Te
μ	0.4240	0.3254	0.1680
$\bar{\alpha}$	23.77	30.35	43.37
β	1.33	8.8	38.42
$\bar{\gamma}$	6195.78	10049.98	19885.59

a. calculation I / 5.4

S1 $\equiv$ S(TZV) + p(0.045, 0.0225), d(2.34, 0.94, 0.38, 0.19, 0.095, 0.047, 0.0235)
 S1, H(TZV) + s(0.06), p(1.0, 0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
143 bfs [6s7p7d / 4s5p3d]

b. calculation I / 5.9

Se1 $\equiv$ Se(BC) +s(0.05), p(0.0492, 0.0196, 0.00784), d(0.5725, 0.28625, 0.14313, 0.07156, 0.03578, 0.01789) [7s7p7d]
 Se1, H-(TZV) + s(0.05), p(1.0, 0.5, 0.25, 0.125, 0.0625, 0.03125),
 d(0.5, 0.25, 0.125, 0.0625, 0.03125) **174 bfs** [7s7p7d / 4s6p5d]

c. calculation I / 5.12

Te1 $\equiv$ Te(T52.1.1) +s(0.05), p(0.04950, 0.02475, 0.012375),
 d(0.411034, 0.164414, 0.065760, 0.0329) [11s11p8d]
 Te1, H-(TZV) + s(0.05), p(0.5, 0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)
160 bfs [11s11p8d / 4s4p3d]

(all units are in a.u. s)

Table 9.3 XH_4 reference values

	I ^a	II ^b	III ^c
	CH_4	SiH_4	GeH_4
$\bar{\alpha}$	16.21	29.54	32.81
β	-12.33	-10.91	-12.65
γ	1908.02	5133.23	6266.09

a. calculation I / 6.1

$\text{C1} \equiv \text{C}(6\text{-}31\text{G}) + \text{s}(0.05), \text{p}(0.03, 0.0105), \text{d}(0.94, 0.15, 0.05)$

$\text{C1}, \text{H}-(6\text{-}31\text{G}) + \text{s}(0.06), \text{p}(0.9, 0.1), \text{d}(0.1)$

94 Basis Functions [$4\text{s}4\text{p}3\text{d} / 3\text{s}2\text{p}1\text{d}$]

b. calculation I / 6.2

$\text{Si1} \equiv \text{Si}(\text{TZV}) + \text{s}(0.05), \text{p}(0.0262, 0.0105), \text{d}((0.505, 0.186), 0.0745, 0.0298, 0.01192)$

$\text{Si1}, \text{H}-(\text{TZV}) + \text{s}(0.06), \text{p}(0.25, 0.125, 0.0625), \text{d}(0.25, 0.125, 0.0625)$

176 Basis Functions [$7\text{s}7\text{p}4\text{d} / 4\text{s}3\text{p}3\text{d}$]

c. calculation I / 6.6

$\text{Ge1} \equiv \text{Ge}(\text{BC}) + \text{p}(0.03336, 0.013344), \text{d}(0.1328, 0.05312, 0.021248, 0.008499)$

$\text{Ge1}, \text{H}-(\text{TZV}) + \text{s}(0.06), \text{p}(0.25, 0.125, 0.0625), \text{d}(0.25, 0.125, 0.0625)$

192 Basis Functions [$6\text{s}6\text{p}6\text{d} / 3\text{s}4\text{p}3\text{d}$]

(all units are in a.u. s)

Table 9.4 X_2H_4 reference values

	I ^a	II ^b	III ^c
	C ₂ H ₄	Si ₂ H ₄	Ge ₂ H ₄
$\bar{\alpha}$	28.07	75.31	85.55
γ	6300.64	50474.16	61590.19

a. calculation I / 7.2

C1 $\equiv$ C(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05) [4s4p3d]

C1, H-(6-31G) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)

188 Basis Functions [4s4p3d / 3s3p3d]

b. calculation I / 7.4

Si1 $\equiv$ Si(6-31G) + s(0.05), p(0.03, 0.005), d(0.94, 0.15, 0.05) [5s5p3d]

Si1, H-(6-31G) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)

196 Basis Functions [5s5p3d / 3s3p3d]

c. calculation I / 7.6

Ge-(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248)

H-(6-31G) + s(0.06), p(0.1), d(0.1) **156 Basis Functions** [6s6p5d / 3s1p1d]

(all units are in a.u. s)

Table 2.5 X_2H_2 reference values

	I ^a	II ^b	III ^c
	C ₂ H ₂	Si ₂ H ₂	Ge ₂ H ₂
$\bar{\alpha}$	23.34	87.31	87.45
γ	4980.04	77445.03	77514.35

a. calculation I / 8.2

C(TZV) + s(0.05), p(0.036424, 0.014570), d(0.94, 0.15, 0.05)

H(TZV) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)

140 Basis Functions [6s5p3d / 4s3p3d]

b. calculation I / 8.5

Si1 $\equiv$ Si(TZV)+ s(0.05), p(0.0262, 0.0105), d((0.505,0.1863), 0.0745, 0.0298, 0.01192)

Si1, H-(TZV) + s(0.06), p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)

166 Basis Functions [7s7p4d / 4s3p3d]

c. calculation I / 8.9

Ge1 $\equiv$ Ge(BC) + p(0.03336, 0.013344), d(0.1328, 0.05312, 0.021248, 0.008499)

Ge1, H-(TZV) + p(0.25, 0.125, 0.0625), d(0.25, 0.125, 0.0625)

180 Basis Functions [6s6p6d / 3s3p3d]

(all units are in a.u. s)

The results for the β values show no distinct trend. The results in Chapter VII (X_2H_4 molecules) show that the γ values of a silicon double bond are almost an order of magnitude greater than that of a carbon double bond, but that the germanium double bond has values very close to that of the silicon double bond. This would indicate that stable molecules containing silicon double bonds could well have very attractive NLO properties from a practical material design point of view. Note that a similar statement could be made for triple bonds of molecules in Chapter VIII. Whereas the increase found in going from carbon to silicon was gratifying, the absence of a further increase in going from silicon to germanium was both unexpected and disappointing.

Electron Correlation (Question 2)

The results of the electron correlation calculations demonstrate that electron correlation is of minor importance in calculation of the DM and DP (only 2-5% changes are found), but is absolutely essential to calculate meaningful values of the β tensor. Its inclusion produces changes in the individual b tensor values by an order of magnitude (and in turn affecting $\bar{\beta}$ and $\Delta\beta$). Fortunately most of the electron correlation can be accounted for by performing calculations at the MP2 level.

Importance of p,d, pf sets on attached hydrogen (Question 3)

Prior to the work at the University of Tennessee, very little attention had been paid to the importance of multiple p and d pfs on the attached hydrogen. The calculations described in the dissertation show very clearly the need for multiple p and d pf sets on the hydrogen if accurate NLO properties are desired. The calculations also establish that frequently the effect of removal or addition of these pfs on NLO properties is not additive. This is especially so for the individual values of the β tensor. Reliable values of all these values at both the HF (SCF) and MP2 levels are extraordinarily difficult to obtain as each individual value have different sensitivities to different pfs (i.e., exponent, and angular momentum / type - kind).

General Rules (Question 6)

In the initial stages of this work (results not reported here), the approach was to start with a good valence bs, and to gradually add diffuse pfs. This approach turned out to be not fruitful because of the following: a) the great sensitivity of the β and γ values to different types of pfs, b) linear dependencies between the effects of different type pfs (exponent and kind), c) the fact that the effect of adding different pfs was non additive (cancelling out effects et cetera). It was only until the opposite approach described in this dissertation of starting with the largest set of pfs possible (depends on computational resources available) and gradually reducing the bs, until it was possible to make sense out of the calculations performed.

Relationship to semi-empirical methods (Question 7)

With what little comparison with semi-empirical methods, it has been possible to make indications that present semi-empirical methods just do not include enough parameters to mimic the complex behavior found in the ab initio calculations. This is especially true in conjugated molecules in which the out of plane matrix elements are usually given very badly.

Extensions to the Finite Field SCF method (Question 8)

Recently, options for including electron correlation by the local density functional (LDF) method have been introduced into molecular structure codes. Some work on small molecules which contain carbon, nitrogen, and oxygen have recently been reported. The results would be very valuable if the results contained within this dissertation could be used to obtain bss to use in conjunction with LDF functionals. Work is already in progress in this laboratory on a number of molecules containing nitrogen, phosphorus, oxygen, and sulfur using the smaller bss developed here.

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BIBLIOGRAPHY

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APPENDICES

APPENDIX A

JCL for Hondo-8 Installation

```

//PCYHND8 JOB, 'PETER C.YIH', GROUP=J1092, USER=P78658,
// NOTIFY=P78658, MSGLEVEL=(1,1), TIME=(29,59), MSGCLASS=H,
// REGION=8M, PASSWORD=?
/*JOBPARM LINES=3000
/*ROUTE CMSRJO USERID=PC78658
/*ROUTE PRINT RMT1, ROOM=GRAD
//PROCLIB DD DSN=SYS1.FORTVS25.PROCLIB, DISP=SHR
//COMPILE PROC
//FORT EXEC PGM=FORTVS2, REGION=4100K,
// PARM=('NOSOURCE', 'OPT(3)', 'DC(SCM)', 'FLAG(E)',
// 'NOVECTOR')
/*STEPLIB DD DSN=SYS1.VSF2COMP, DISP=SHR
//SYSIN DD DSN=J1092.HONDO.FORTRAN(&FORTSRC), DISP=SHR
//SYSPRINT DD DUMMY
//SYSTEM DD DUMMY
//SYSLIN DD DSN=&&LOADSET(&FORTSRC), DISP=(OLD, PASS)
// PEND
//*****
/*
/* Now compile the HONDO Fortran files
/*
//*****
//ALLOC EXEC PGM=IEFBR14
//TEXTLIB DD DSN=&&LOADSET, DISP=(NEW, PASS),
// UNIT=SYSDA, SPACE=(CYL, (5,2,2)),
// DCB=BLKSIZE=3200
//CTL EXEC COMPILE, FORTSRC=CTL, COND=(4,LT)
//DRV EXEC COMPILE, FORTSRC=DRV, COND=(4,LT)
//DR2 EXEC COMPILE, FORTSRC=DR2, COND=(4,LT)
//MOL EXEC COMPILE, FORTSRC=MOL, COND=(4,LT)
//BAS EXEC COMPILE, FORTSRC=BAS, COND=(4,LT)
//SYM EXEC COMPILE, FORTSRC=SYM, COND=(4,LT)
//FLD EXEC COMPILE, FORTSRC=FLD, COND=(4,LT)
//ECP EXEC COMPILE, FORTSRC=ECP, COND=(4,LT)
//GSS EXEC COMPILE, FORTSRC=GSS, COND=(4,LT)
//INT EXEC COMPILE, FORTSRC=INT, COND=(4,LT)
//WFN EXEC COMPILE, FORTSRC=WFN, COND=(4,LT)

```

```

//SCF      EXEC COMPILE,FORTSRC=SCF,COND=(4,LT)
//DIR      EXEC COMPILE,FORTSRC=DIR,COND=(4,LT)
//MP2      EXEC COMPILE,FORTSRC=MP2,COND=(4,LT)
//MP4      EXEC COMPILE,FORTSRC=MP4,COND=(4,LT)
//NIN      EXEC COMPILE,FORTSRC=NIN,COND=(4,LT)
//CI1      EXEC COMPILE,FORTSRC=CI1,COND=(4,LT)
//CI2      EXEC COMPILE,FORTSRC=CI2,COND=(4,LT)
//PRP      EXEC COMPILE,FORTSRC=PRP,COND=(4,LT)
//NLO      EXEC COMPILE,FORTSRC=NLO,COND=(4,LT)
//DER      EXEC COMPILE,FORTSRC=DER,COND=(4,LT)
//HSS      EXEC COMPILE,FORTSRC=HSS,COND=(4,LT)
//VEC      EXEC COMPILE,FORTSRC=VEC,COND=(4,LT)
//SEC      EXEC COMPILE,FORTSRC=SEC,COND=(4,LT)
//*****
//*
//*   Now Link edit the HONDO Fortran files
//*
//*****
//LINK      EXEC PGM=IEWL,REGION=2048K,COND=(4,LT),
//           PARM='LET,NOLIST,SIZE=(512K,128K)'
//SYSPRINT DD SYSOUT=*
//SYSUT1    DD UNIT=SYSDA,SPACE=(CYL,(5,1)),DISP=(NEW,DELETE)
//SYSLIB    DD DSN=SYS1.FORTVS25.VSF2LINK,DISP=SHR
//          DD DSN=UTCC.ESSL.VECTORLB,DISP=SHR
//          DD DSN=SYS1.FORTVS25.VSF2FORT,DISP=SHR
//SYSLMOD   DD DSN=J1092.HONDO8V.LOAD(HONDO),
//           DISP=(NEW,CATLG),UNIT=ONLINE,
//           SPACE=(TRK,(25,15,5)),DCB=BLKSIZE=3200
//HONDO     DD DSN=&&LOADSET,DISP=(OLD,PASS)
//OBJCLK    DD DSN=J1092.HONDO.CLKOBJ,DISP=(SHR,KEEP)
//OBJDAT    DD DSN=J1092.HONDO.DATOBJ,DISP=(SHR,KEEP)
//SYSLIN DD *
INCLUDE HONDO(VEC,SEC)
INCLUDE HONDO(CTL,DRV,DR2,MOL,BAS,SYM,FLD,ECP,GSS,INT)
INCLUDE HONDO(WFN,SCF,DIR,MP2,MP4,NIN,CI1,CI2)
INCLUDE HONDO(PRP,NLO)
INCLUDE HONDO(DER,HSS)
INCLUDE OBJCLK
INCLUDE OBJDAT
MODE AMODE(31),RMODE(24)
/*

```

APPENDIX B

Basis SetsTable B.1 Czismadia Table 7.73.2 - Nitrogen Basis Set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
7.4761715d+04	5.0000000d-05	1.2666657d+02	1.1520000d-03
1.1123654d+04	3.9400000d-04	2.9837389d+01	9.0160000d-03
2.5126857d+03	2.0880000d-03	9.3940380d+00	4.0814000d-02
7.0377729d+02	8.9060000d-03	3.4051040d+00	1.3010100d-01
2.2547879d+02	3.2081000d-02		
7.9615810d+01	9.7424000d-02	1.3500000d+00	2.7767900d-01
		5.5769600d-01	3.8073600d-01
3.0237283d+01	2.3172800d-01		
1.2263622d+01	3.7754000d-01	2.3244900d-01	1.0000000d+00
5.2650860d+00	1.0000000d+00	9.42640000d-02	1.0000000d+00
2.334710d+00	1.0000000d+00		
9.0185600d-01	1.0000000d+00		
3.5833600d-01	1.0000000d+00		
1.4109300d-01	1.0000000d+00		

[7s4p]

Table B.2 TZV- Nitrogen Basis Set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
13520.0	7.6000d-04	35.91	0.016916
1999.0	6.0760d-03	8.48	0.102200
440.0	3.2847d-02	2.706	0.338134
120.9	0.132396	0.9921	0.669281
38.47	0.393261		
13.46	0.546339	0.3727	1.0000000d+00
13.46	0.252036	0.1346	1.0000000d+00
4.993	0.779385		
1.569	1.0000000d+00		
0.580	1.0000000d+00		
0.1923	1.0000000d+00		

[5s3p]

Table B.3 Czismadia Table 15.16.1 - Phosphorus Basis Set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
7.7718000d+04	3.2000000d-04	3.8532200d+02	3.7000000d-03
1.1609300d+04	2.5500000d-03	9.0626900d+01	2.8580000d-02
2.6442900d+03	1.3140000d-02	2.8778800d+01	1.2149000d-01
7.5332800d+02	5.1950000d-02	1.0664300d+01	3.0214000d-01
2.4852500d+02	1.5809000d-01	1.7376900d+00	2.9089000d-01
9.1069800d+01	1.0000000d+00	4.2436100d+00	1.0000000d+00
3.6191600d+01	4.0463000d-01	5.9584300d-01	1.0000000d+00
1.5206300d+01	1.7114000d-01		
		2.2855000d-01	1.0000000d+00
4.7137800d+00	1.0000000d+00		
		8.3760000d-02	1.0000000d+00
1.7831600d+00	1.0000000d+00		
3.4324900d-01	1.0000000d+00		
1.2520400d-01	1.0000000d+00		

[7s5p]

Table B.4 Binning and Curtiss- Arsenic Basis Set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
526200.0	2.20000d-04	3909.0	1.33000d-03
78310.0	1.72000d-03	924.0	1.14000d-02
17800.0	8.89000d-03	291.8	5.98100d-02
5070.0	3.53500d-02	107.5	2.05110d-01
1677.0	1.12260d-01	43.62	3.74320d-01
617.0	2.86250d-01	18.73	4.21410d-01
245.0	4.34060d-01		
101.5	3.08800d-01	7.841	2.19010d-01
		3.391	4.29550d-01
31.39	4.72990d-01	1.405	2.64000d-01
13.43	1.12375d+00		
		0.3441	1.0000000d+00
4.0	1.0000000d+00		
		0.1068	1.0000000d+00
1.683	1.0000000d+00	D	
		<u>Exponent</u>	<u>Coefficient</u>
0.3003	1.0000000d+00	81.59	2.55800d-02
		23.26	1.44920d-01
0.1137	1.0000000d+00	8.148	3.60440d-01
		2.954	4.6255d-01
		0.9827	2.6813d-01

[6s4p1d]

Table B.5 Binning and Curtiss- Germanium Basis Set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
489000.0	2.22000d-04	3596.0	1.44200d-03
73100.0	1.72800d-03	843.7	1.24420d-02
16640.0	8.95000d-03	266.2	6.46940d-02
4742.0	3.59050d-02	98.28	2.18660d-01
1569.0	1.12840d-01	39.93	3.93350d-01
577.0	2.87480d-01	17.14	4.34530d-01
229.0	4.34490d-01		
94.81	3.06830d-01	7.157	2.49980d-01
		3.068	4.69380d-01
29.22	4.77590d-01	1.246	2.88960d-01
12.45	1.11445d+00		
		0.2795	1.0000000d+00
3.642	1.0000000d+00		
		0.08340	1.0000000d+00
1.502	1.0000000d+00	D	
		<u>Exponent</u>	<u>Coefficient</u>
0.2462	1.0000000d+00	70.18	2.87700d-02
		20.07	1.55250d-01
0.09209	1.0000000d+00	7.059	3.68140d-01
		2.553	4.65780d-01
		0.8301	2.8648d-01

[6s4p1d]

Table B.6 Binning and Curtiss- Selenium Basis Set

S		P	
<u>Exponent</u>	<u>Coefficient</u>	<u>Exponent</u>	<u>Coefficient</u>
560600.0	2.20000d-04	4114.0	1.17000d-03
84010.0	1.70000d-03	980.4	9.85000d-03
19030.0	8.83000d-03	310.7	5.17700d-02
5419.0	3.50800d-02	114.2	1.78690d-01
1792.0	1.12660d-01	46.26	3.25040d-01
659.5	2.84710d-01	19.87	3.60890d-01
262.0	4.33480d-01		
108.6	3.11400d-01	8.309	2.14880d-01
		3.589	3.96290d-01
33.66	4.68230d-01	1.522	2.25080d-01
14.45	1.09261d+00		
		0.4032	1.0000000d+00
4.378	1.0000000d+00		
		0.1231	1.0000000d+00
1.876	1.0000000d+00	<u>D</u>	
		<u>Exponent</u>	<u>Coefficient</u>
0.3592	1.0000000d+00	94.03	2.06300d-02
		26.79	1.22270d-01
0.1367	1.0000000d+00	9.336	3.19720d-01
		3.383	4.17380d-01
		1.145	2.31840d-01

[6s4p1d]

Table B.7 Czismadia Table 52.1.1 - TelluriumBasis Set

S		P	
Exponent	Coefficient	Exponent	Coefficient
4.2369420d+05	8.9000000d-04	2.7983410d+03	1.2520000d-02
6.3645130d+04	6.9100000d-03	6.7315080d+02	8.8290000d-02
1.4291900d+04	3.6090000d-02	2.2258270d+02	3.0272000d-01
3.9643390d+03	1.3804000d-01	8.6575310d+01	4.872000d-01
1.2831170d+03	3.4900000d-01		
		3.6795840d+01	1.0000000d+00
4.7157040d+02	4.4260000d-01		
1.9019000d+02	1.6901000d-01	1.5944100d+01	1.0000000d+00
7.5836860d+01	1.0000000d+00	7.3155240d+00	1.0000000d+00
3.4008210d+01	1.0000000d+00	2.901480d+00	1.0000000d+00
1.2264790d+01	1.0000000d+00	1.2078910d+00	1.0000000d+00
6.1861660d+00	1.0000000d+00	3.0356200d-01	1.0000000d+00
2.3474690d+00	1.0000000d+00	9.9011900d-02	1.0000000d+00
		D	
1.0818700d+00	1.0000000d+00	Exponent	Coefficient
		2.4866920d+02	3.1750000d-02
2.6750810d-01	1.0000000d+00	7.2779990d+01	1.9134000d-01
		2.6056670d+01	4.7375000d-01
1.0377340d-01	1.0000000d+00		
		9.9712650d+00	1.0000000d+00
		3.1614990d+00	1.0000000d+00
		1.0275850d+00	1.0000000d+00

[10s8p4d]

Table B.8 3-21G - Germanium Basis Set

S		P
<u>Exponent</u>	<u>Coefficient</u>	<u>Coefficient</u>
5.0518331d+03	6.3000000d-02	
7.6560521d+02	3.7380000d-01	
1.6792334d+02	6.8395000d-01	
2.2443600d+02	-1.1151500d-01	1.4463950d-01
4.8955430d+01	9.1200000d-02	5.7537960d-01
1.5183700d+01	9.6344900d-01	4.4599490d-01
1.5912570d+01	-2.8956500d-01	2.2973020d-02
5.4414370d+00	2.9388300d-01	4.7324460d-01
1.7426030d+00	8.8919900d-01	6.0327790d-01
1.4665380d+00	-3.9673400d-01	2.7892940d-02
2.6309300d-01	1.1906700d+00	9.8749010d-01
8.4821000d-02	1.0000000d+00	1.0000000d+00

D

<u>Exponent</u>	<u>Coefficient</u>
2.4198050d+01	1.5871000d-01
6.1983700d+00	5.1173000d-01
1.5834100d+00	5.8485000d-01

[5s4p1d]

Table B.9 T1.42.1 - Hydrogen Basis Set

<u>S</u>	
<u>Exponent</u>	<u>Coefficient</u>
82.9486	0.001997
12.4547	0.015279
2.833203	0.075306
0.799997	0.256339
0.258580	0.497646
0.089964	0.296737

[1s]

Table B.10 TZV - Hydrogen Basis Set

<u>S</u>	
<u>Exponent</u>	<u>Coefficient</u>
33.64	0.025374
5.058	0.189684
1.147	0.852933
0.3211	1.000000
0.1013	1.000000

[3s]

Table B.11 Hondo 6-31G - Hydrogen Basis Set

<u>S</u>	
<u>Exponent</u>	<u>Coefficient</u>
18.731137	0.033495
2.825394	0.234727
0.640122	0.813757
0.161278	1.000000

[2s]

Table B.12 3-21G - Hydrogen Basis Set

<u>S</u>	
<u>Exponent</u>	<u>Coefficient</u>
5.447178	0.156285
0.824547	0.904691
0.183192	1.000000

[2s]

APPENDIX C

Molecular Geometries

All units are in atomic units.

NH ₃	x	y	z
N	0.0	0.0	0.1278608
H	-0.8858372	1.5343150	-0.5921777
H	-0.8858372	-1.5343150	-0.5921777
H	1.7716744	0.0	-0.5921777

PH ₃	x	y	z
P	0.0	0.0	-0.1295500
H	-1.1265150	1.9511812	1.3280100
H	-1.1265150	-1.9511812	1.3280100
H	2.2530300	0.0	1.3280100

AsH ₃	x	y	z
As	0.0	0.0	-0.1322487
H	-1.1868681	2.0557159	1.4547454
H	-1.1868681	-2.0557159	1.4547454
H	2.3737363	0.0	1.4547454

Formamide	x	y	z
N	0.0	0.0	0.0
C	0.0	0.0	2.5490141
O	1.8473436	0.0	3.8401167
H	-1.9024914	0.0	3.3431848
H	-1.6404091	0.0	-0.9215950
H	-1.5948024	0.0	-0.9885045

Pyridine	x	y	z
N	0.0	0.0	0.0
C	-2.1547075	0.0	-1.3229944
C	2.1547075	0.0	-1.3229944
C	-2.2581289	0.0	-3.9552411
C	2.2581289	0.0	-3.9552411
C	0.0	0.0	-5.3044554
H	0.0	0.0	-7.3472496
H	-3.9284085	0.0	-0.2906758
H	3.9284085	0.0	-0.2906758
H	-4.0659843	0.0	-4.9104331
H	4.0659843	0.0	-4.9104331

Benzene	x	y	z
C	1.3076906	2.2649866	0.0
C	-1.3076906	2.2649866	0.0
C	-2.6153813	0.0	0.0
C	-1.3076906	-2.2649866	0.0
C	1.3076906	-2.2649866	0.0
C	2.6153813	0.0	0.0
H	2.3205839	4.0193693	0.0
H	-2.3205839	4.0193693	0.0
H	-4.6411679	0.0	0.0
H	-2.3205839	-4.0193693	0.0
H	2.3205839	-4.0193693	0.0
H	4.6411679	0.0	0.0

Pyrrole	x	y	z
N	0.0	0.0	0.0
C	-2.1181283	0.0	-1.4886455
C	2.1181283	0.0	-1.4886455
C	-1.3388711	0.0	-3.9807412
C	1.3388711	0.0	-3.9807412
H	0.0	0.0	1.8821674
H	-3.9856472	0.0	-0.6843648
H	3.9856472	0.0	-0.6843648
H	-2.5207383	0.0	-5.6376578
H	2.5207383	0.0	-5.6376578

H ₂ S	x	y	z
S	0.0	0.0	0.1032170
H	0.0	1.8085800	-1.6372230
H	0.0	-1.8085800	-1.6372230

H ₂ Se	x	y	z
S	0.0	0.0	0.0
H	-1.9596462	0.0	1.9407490
H	1.9596462	0.0	1.9407490

H ₂ Te	x	y	z
Te	0.0	0.0	0.0
H	-2.2204285	0.0	2.2109798
H	2.2204285	0.0	2.2109798

SiH ₄	x	y	z
Si	0.0	0.0	0.0
H	1.6081834	-1.6081834	-1.6081834
H	-1.6081834	1.6081834	-1.6081834
H	-1.6081834	-1.6081834	1.6081834
H	1.6081834	1.6081834	1.6081834

GeH ₄	x	y	z
Si	0.0	0.0	0.0
H	1.6639040	-1.6639040	-1.6639040
H	-1.6639040	1.6639040	-1.6639040
H	-1.6639040	-1.6639040	1.6639040
H	1.6639040	1.6639040	1.6639040

C ₂ H ₄	x	y	z
C	-1.2651718	0.0	0.0
C	1.2651718	0.0	0.0
H	-2.2213733	-1.8137593	0.0
H	2.2213733	-1.8137593	0.0
H	-2.2213733	1.8137593	0.0
H	2.2213733	1.8137593	0.0

Si ₂ H ₄	x	y	z
Si	-2.0002753	0.0	0.0
Si	2.0002753	0.0	0.0
H	-3.4597412	-2.3439292	0.0
H	3.4597412	-2.3439292	0.0
H	-3.4597412	2.3439292	0.0
H	3.4597412	2.3439292	0.0

Ge ₂ H ₄	x	y	z
Ge	-2.1873582	0.0	0.0
Ge	2.1873582	0.0	0.0
H	-1.3562916	-2.3873754	1.0036029
H	1.3562916	2.3873754	-1.0036029
H	-1.3562916	-2.3873754	-1.0036029
H	1.3562916	2.3873754	1.0036029

C2H2	x	y	z
C	0.0	0.0	-1.1366704
C	0.0	0.0	1.1366704
H	0.0	0.0	-3.1416700
H	0.0	0.0	3.1416700

Si2H2	x	y	z
Si	0.0	0.0	-1.9747640
Si	0.0	0.0	1.9747640
H	0.0	0.0	-4.7942357
H	0.0	0.0	4.7942357

Ge2H2	x	y	z
Ge	0.0	0.0	-1.9160776
Ge	0.0	0.0	1.9160776
H	0.0	0.0	-4.7512548
H	0.0	0.0	4.7512548

APPENDIX D

Program for $\bar{\alpha}$ and $\Delta\alpha$ calculations

```

#include <stdio.h>
#include <math.h>
#define pi 3.1415927;
    float axx, ayy, azz, bxxz, byyz, bzzz, amean, bmean, da, db;
main()

{
    float tsq, da1, da2, da3;
    tsq=sqrt(2.0);

again:
    printf(" >> Program for calculation of amean, da<<\n\n");
    printf("Please input: axx  ");
    scanf("%f",&axx);
    printf("\n Please input: ayy  ");
    scanf("%f",&ayy);
    printf("\n Please input: azz  ");
    scanf("%f",&azz);
    printf("axx = %f ayy = %f azz = %f \n\n", axx, ayy, azz);

/*-----Calculation of amean, da -----*/

    amean=(axx+ayy+azz)/3.0;

    da1=(axx-ayy);
    da2=(axx-azz);
    da3=(azz-ayy);
    da=sqrt(da1*da1+da2*da2+da3*da3)/tsq;

/*-----Print out the results -----*/

    printf("The answer is  amean= %f  da= %f  \n", amean, da);
    printf("\n\n ----- \n\n");

    goto again;

}

```

Program for $\bar{\beta}$ and $\Delta\beta$ calculations

```
#include <stdio.h>
#include <math.h>
#define pi 3.1415927;
    float axx, ayy, azz, bxxz, byyz, bzzz, amean, bmean, da, db;
main()

{
    float tsq, da1, da2, da3;
    tsq=sqrt(2.0);

again:
    printf(" >> Program for calculation of bmean, db
<<\n\n");

    printf("Please input: bxxz  ");
    scanf("%f",&bxxz);
    printf("\n Please input: byyz  ");
    scanf("%f",&byyz);
    printf("\n Please input: bzzz  ");
    scanf("%f",&bzzz);
    printf("bxxz = %f byyz = %f bzzz = %f
\n\n",bxxz,byyz,bzzz);

/*-----Calculation of bmean, db -----*/

    bmean=0.6*(bxxz+byyz+bzzz);
    db=bzzz-1.5*(bxxz+byyz);

/*-----Print out the results -----*/

    printf("The answer is  bmean= %f  db= %f  \n",bmean,db);
    printf("\n\n ----- \n\n");

    goto again;

}
```

VITA

Peter Chien-Nan Yih was born in Hong Kong, Hong Kong B.C.C. on June 26, 1959. He attended elementary school through high school in Kingsport, Tennessee. He graduated from Dobyns-Bennett High School in Kingsport, Tennessee in June 1977. The following August he entered Cornell University in Ithaca, New York, and in January 1981 he received a Bachelor of Arts degree in Chemistry. In January 1981 he began study toward a Doctor of Philosophy degree in Chemistry at The University of Tennessee, Knoxville.

In August 1986 he began study toward a Master's degree in Electrical and Computer Engineering at The University of Tennessee, Knoxville, and in May 1991 this degree was awarded.

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