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I am submitting herewith a dissertation written by Robert A. Paysen entitled "Ab Initio Calculations Using Bond Polarization Functions." 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.

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AB INITIO CALCULATIONS USING BOND POLARIZATION FUNCTIONS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Robert A. Paysen

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ABSTRACT

Ab initio calculations have been performed using basis sets both with and without polarization functions to test the utility of employing bond polarization functions to augment a double zeta basis set. Several one-electron properties were calculated and these results compared to known experimental values. Two series of polar molecules were used, a set of small carbonyl and thiocarbonyl structures and a series of nitro compounds. Better agreement was obtained for several of the properties calculated, using the basis set including bond polarization functions than with the other basis sets. It appears that a proper test of a proposed basis sets must involve testing the various regions of the electron density through the one-electron properties.

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CHAPTER I

AB INITIO METHOD

A. INTRODUCTION

There have been in the last half century many attempts[1-5] to provide some theoretical foundation for some of the empirical relationships relating molecular electronic structure to geometry,[7,8] to physical properties[3,9,10] and to reactivity.[2-6] Much success has been claimed for these efforts to model experimental behavior theoretically. However, with respect to theoretical studies on the properties of an isolated molecule, most of the success has been in the prediction of energy related properties, such as molecular geometries,[7,8] rotational barriers,[11] relative conformational stabilities,[12] orbital energies[13] and electronic transition energies.[14] In special cases it has also been found possible to compute heats of formation.[8]

These properties may be represented by quantum-mechanical operators containing interelectronic distances and are classified therefore as two-electron properties. By contrast, one-electron properties, or first order properties, have been relatively little studied, with the exception of the dipole moment.[15] One-electron properties are defined as the expectation values of quantum-mechanical operators which can be written as a linear combination of operators containing the coordinates of one or zero electrons. Typical one-electron properties are dipole moments, electric field gradients, molecular quadrupole moments and higher moments, and the potential and the electric fields.

The quantum-mechanical operators corresponding to these properties are given in Appendix 1. Experimental measurements of many of the one-electron properties are available[16-18] and these can be used to evaluate the success of a particular theoretical model in producing realistic wave functions (WFs). As can be seen from the definitions in Appendix 1, various molecular properties depend on different regions of space in a molecule. Thus a wave function may only be regarded as satisfactory if it is successful in reproducing several molecular properties ranging from the nuclear quadrupole coupling constants (eqQ) which are sensitive to the electron density close to the nucleus[19] through the higher moments which are sensitive to the electron density on the periphery of a molecule.[18] The evaluation of different methods for calculating one-electron properties of polyatomic molecules is the major topic of this work. This type of evaluation of a wave function would seem to be necessary before attempts are made to use the WFs, calculated by different methods, to produce electron densities which are then used to analyze substituent effects in molecules,[20,22] and chemical reactivities.[4,6,21]

The need for such an evaluation arises because for polyatomic molecules the Schroedinger equation cannot be solved accurately and compromises must be made. The need for compromise has given rise to numerous theoretical models ranging from empirical rules to the many semiempirical methods,[23,24] to variations of the Hartree-Fock ab initio method[24-26] and, more recently, to attempts to include electron correlation. Since the work presented here is based upon the Hartree-Fock (HF) ab initio method, this is the only one to be

described. Also, since the details of the HF ab initio method have been presented many times, only an outline will be given.

B. THE HARTREE FOCK AB INITIO METHOD

The term ab initio implies that, unlike the semiempirical methods, no integrals are neglected or approximated by a simpler expression or by using empirical parameters. In this work all electrons are treated explicitly and integrals are calculated to be accurate to 8 digits. Since the solution to the Schroedinger equation cannot be performed exactly the major approximations employed for polyatomic molecules are:

1. The Born-Oppenheimer Approximation

Because nuclear motion is so much slower than electron motion, the electrons are considered to move in a potential given by fixed nuclei.[24-26] The Hamiltonian used is then:

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

where the A, B indices run over nuclei, and i and j run over electrons. Z_A, Z_B are nuclear charges and atomic units are used (Appendix 1).

2. The Non-Relativistic Approximation

The Hamiltonian of equation (1) ignores relativistic effects and is the one generally used for lighter atoms since it is difficult to estimate the relativistic effects accurately in molecules. From a knowledge of the relativistic effect in an atom, it is known that the correction to the total energy is comparable to chemical bond energies

in all but the lightest of atoms.[26] For example[26] Li has a relativistic correction of -0.0005504 hartrees or 0.3460 kcals per mole, but F has a correction of -0.0820816 hartrees or 51.6 kcals per mole which is quite large considering that the bond dissociation energy of F_2 is 37.5±2.3 kcal per mole. It is known that the largest portion of the relativistic energy correction is due to the inner shells of electrons and that for the lighter elements at least the relativistic energy is little affected by ionization of valence electrons or by the chemical environment and is not considered explicitly in this work.

3. The Hartree Fock Approximation

Exchange is introduced by the requirement that an acceptable WF must be antisymmetric with respect to interchange of both the space and spin coordinates of any pair of fermions. A determinantal form of ψ given by Slater includes this effect.

$$\psi(1,2,3\ldots 2n) = \frac{1}{2n!}\begin{vmatrix} \phi_1(1)\alpha(1)\phi_2(1)\beta(1)\ldots\ldots\phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2)\phi_2(2)\beta(2)\ldots\ldots \\ \vdots \\ \phi_1(2n)\alpha(2n)\ldots\ldots\ldots\ldots\phi_n(2n)\beta(2n) \end{vmatrix} \quad (2)$$

where the ϕ_i function is spatial and the α and β are spin functions. The ϕ_i are chosen so as to minimize the total energy of the system.

$$E_t = \int\psi^*(1,2,3\ldots 2n)H\psi(1,2,3\ldots 2n)d\tau_1 d\tau_2\ldots d\tau_{2n}\left[\int\psi^*\psi d\tau\right]^{-1} \quad (3)$$

Fock introduced the idea of treating electron-electron interaction in an average way, so that electron motions are not correlated. This is the essence of the Hartree-Fock (HF) method. It is used in

conjunction with the variational principle to derive a set of one-electron equations, the HF equations for closed shell molecules.

$$F\left|\phi_j(1)\right\rangle = \left[H + \sum_{j=1}^{n}(2J_j - K_j)\right]\left|\phi_i(1)\right\rangle = \sum_{j=i}\lambda_{ij}\left|\phi_j(1)\right\rangle \qquad (4)$$

where

$$H\left|\phi_i(1)\right\rangle = \left[-\frac{1}{2}\bar{\nabla}^2(1) - \sum_{\mu} Z_{\mu}/r_{i\mu}\right]\left|\phi_i(1)\right\rangle \qquad (5)$$

and the two-electron operators become

$$J_j\left|\phi_i(1)\right\rangle = \left\langle\phi_j(2)\left|1/r_{12}\right|\phi_j(2)\right\rangle\left|\phi_i(1)\right\rangle \qquad (6)$$

and

$$K_j\left|\phi_i(1)\right\rangle = \left\langle\phi_j(2)\left|1/r_{12}\right|\phi_i(2)\right\rangle\left|\phi_j(1)\right\rangle \qquad (7)$$

In equation (4) F is the Fock operator and the λ_{ij} are the undetermined Lagrangian multipliers.

One can always diagonalize the right-hand side of Equation (4) to a form

$$F\left|\phi_i(1)\right\rangle = \lambda_{ii}\left|\phi_i(1)\right. \qquad (8)$$

by making use of the invariance of F and ψ.

The energy may now be written as

$$E_e = \sum_{i=1}^{n}\left[2\lambda_{ii} - \sum_{j=1}^{n}(2J_{ij} - K_{ij})\right] \qquad (9)$$

where J_{ij} and K_{ij} are the well known coulomb and exchange integrals over the as yet unspecified one-electron orbitals ϕ_i and ϕ_j. Since the integrals J_{ij} and K_{ij} are themselves dependent on the solutions

ϕ_i and ϕ_j of the Fock equations, it is necessary to give these solutions an explicit form. The method used almost universally for polyatomic molecules is the Roothaan LCAO approximate method described in the next paragraph.[4]

4. The Roothaan LCAO Approximation

In this approximation[24,27] each orbital ϕ_i is expanded as a linear combination of functions χ_μ similar in analytical form to those used in atomic calculations (LCAO approximation).

$$\phi_i = \sum_\mu c_{\mu i} \chi_\mu \tag{10}$$

In theory the χ_μ functions should be a complete set.[26] The total energy obtained using this complete set is the lowest possible using this particular method and is termed the HF Limit for the energy EHF. The difference between this value, EHF, and the exact (true) energy of a molecule, is known as the correlation energy. It is only recently that attempts to calculate the correlation energy by going beyond the Hartree-Fock approximation have been successful.[26]

The one-electron equations obtained by putting equation (10) into the Fock equations are known as the Roothaan equations and are of the form:

$$\Sigma(F_{\mu\nu}-\varepsilon_i S_{\mu\nu})c_{\mu i} = 0 \tag{11}$$

where

$$S_{\mu\nu} = \int \chi_\mu(1)\chi_\nu(1)\, d\tau_1 \tag{12}$$

and is called the overlap integral, ε_i is the energy of an electron associated with ϕ_i and $F_{\mu\nu}$ is a matrix element given by

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda}\sum_{\sigma} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\lambda\sigma)\right] \tag{13}$$

$$H_{\mu\nu} = \int\chi_{\mu}(1)\left[-\frac{1}{2}\nabla^2\right]\chi_{\nu}(1)d\tau_1 + \sum_{A}^{\text{nuclei}} \chi_{\mu}(1)\left[\frac{1}{r_{1A}}\right]\chi_{\mu}(1)d\tau_1 \tag{14}$$

where $H_{\mu\nu}$ describes the motion of one electron in the field of the bare nuclei and where $(\mu\nu|\lambda\sigma)$ is a two-electron integral.

$$(\mu\nu|\lambda\sigma) = \int\int\chi_{\mu}(1)\chi_{\nu}(1)\frac{1}{r_{12}}\chi_{\lambda}(2)\chi_{\sigma}(2)d\tau_1 d\tau_2 \tag{15}$$

The two-electron integral $(\mu\nu|\lambda\sigma)$ is called a coulomb integral and is abbreviated $J_{\mu\nu}$. The integral $(\mu\lambda|\nu\sigma)$ is called an exchange integral and is abbreviated $K_{\mu\nu}$.

The $P_{\lambda\sigma}$ is the one-electron density matrix and is given by equation (16).

$$P_{\lambda\sigma} = 2\sum_{i}^{\text{occupied orbitals}} c_{\lambda i}\, c_{\sigma i} \tag{16}$$

Since one is seeking the $c_{\mu i}$ which are already contained in the formulation, there is no closed form solution to the Roothaan equation. Instead one chooses a suitable starting set of $c_{\mu i}$ and iterates to a solution that is considered self consistent. Many programs are available that will solve these equations satisfactorily, e.g., IBMOL-6, POLYATOM II, MOLECULE, GAUSSIAN-70,-76,-80, and HONDO.[26]

C. CHOICE OF BASIS SET

A major practical limitation of the HF method is the necessity of truncating the basis set in order to reduce computational times and covergence difficulties. Only a complete set containing an infinite number of terms in equation (10) will give an energy corresponding to the HF limit.[26,29] However, it has been shown that certain incomplete basis sets give SCF energies near the HF limit.[29] There is no guarantee that an approximate WF which gives an energy close to the HF limit will also give good one-electron properties. It has been shown by Moller and Plesset[30] that one-electron properties calculated from an exact HF function are correct to first order. However, improvements in the energy for a basis set not close to the HF limit will not presage corresponding improvements in the one-electron properties.[31] It is possible that a given selection of a basis set could allow more flexibility in a region that heavily influences one expectation value, but has little effect on another property. The production of a basis set suitable for the practical calculation of properties good enough to compare to experiment might require both a great deal of intuition and scientific experience. The basis sets used in most molecular calculations can be categorized[31] as (a) minimal, (b) double zeta (DZ), (c) double zeta, plus polarization (d) extended. For all but the simplest molecules the use of category (d) type basis sets is very costly in computer time and money. It is generally thought that, depending on the property of interest, one might safely stop at double zeta, or even minimal basis set calculations without sacrificing much in accuracy. It is one of the main purposes of this work, to examine several

molecular properties and see at what level, in size of basis set, one needs to work to get satisfactory results.

A tremendous quantity of work has been performed on two-electron (i.e. energy dependent) properties[1,2,7,9,10,24-27] and from these results a number of standard basis sets have been suggested[27,29,30] as particularly useful for this type of property. There have, however, been fewer attempts to systematically examine these basis sets with respect to their effectiveness in calculating one-electron properties although frequently it has been assumed that they give accurate WF's for both one and two-electron properties. This is particularly so in the case of discussions on substituent effects[20-22] and on electrostatic potentials and their relationship to chemical reactivity.[3-6]

There are two types of basis functions generally in use,[8,26] Slater type orbitals (STO's)[26] and Gaussian type functions (GTF's).[8,26] There are two major requirements for a proper function (1) fast convergence for a truncated basis set and (2) ease of evaluation of integrals. Neither STO's nor GTF's satisfy these requirements simultaneously. Slater exponential functions do have fast convergence and have the proper cusp behavior at the nucleus but the two electron, three and four center integrals are cumbersome and time consuming to evaluate. The integrals over GTF's are more easily evaluated but convergence is slower than for the Slater types and Gaussians do not satisfy the cusp condition at the nucleus. Because comparable results may be obtained with GTF's in as little as 1/10th the time as with STO's, all generally available modern SCF ab initio computer programs are written in terms of Gaussian functions.

Each atomic orbital needs several Gaussians to describe it. For example, a STO-3G[8] minimal basis set is one in which each STO with a given exponent is fitted using a three Gaussian expansion.

$$\chi_{1s}(\zeta=1,r) = \sum_{k=1}^{3} d_{1s,k}\, g_{1s}(\alpha_{1k,r}) \tag{17}$$

$$\chi_{2s}(\zeta=1,r) = \sum_{k=1}^{3} d_{2s,k}\, g_{1s}(\alpha_{2k,r}) \tag{18}$$

$$\chi_{2p}(\zeta=1,r) = \sum_{k=1}^{3} d_{2p,k} g_{2p}(\alpha_{2k,r}) \tag{19}$$

where

$$g_{1s}(\alpha,r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2) \tag{20}$$

$$g_{2p_x} = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} \exp(-\alpha r^2) \tag{21}$$

with analogous expressions for the g_{2py} and g_{2pz} functions. The values of the Gaussian exponents, α, and the linear expansion coefficients, d, have been determined by a least-squares condition, assuming the Slater exponent, ζ, to be 1. Best fits to Slater functions of arbitrary ζ, chosen so as to be appropriate for the description of average molecular environments, may then be simply expressed as equation (22).

$$\chi(\zeta,r) = \zeta^{3/2} \chi(\zeta=1,r) \tag{22}$$

Numerical values for such average ζ exponents have been given by Hehre *et al.*[32]

In Gaussian basis sets of double zeta quality, the STO's are no longer mimicked although the term originated for STO's. Each of the components of the double zeta GTF set χ_μ is composed of a contracted or linear combination of primitive Gaussian functions, g_j.

$$\chi_\mu = \Sigma d_{\mu j} g_j \tag{23}$$

where the $d_{\mu j}$ coefficients are fixed by atomic calculations. A double zeta set[27,29] is further labelled by giving the number of primitive functions per contracted function. For example, a split valence 4-31G set[33] is one in which the core orbitals (i.e. for 1st row elements, 1s, and for 2nd row elements, 1s, 2s and 2p) are described by four Gaussians and each valence orbital is represented by two contracted functions, one consisting of three primitives and the other consisting of one primitive. The Gaussian expansions in the 4-31G set proposed by Ditchfield[33] *et al.* were chosen to minimize the ground state energy of each atom and then were rescaled in order that they might give a more realistic picture of the electron distribution of an "average" molecule.

The full DZSB set[27] has two contracted functions for both core and valence orbitals. Studies on the dependence of molecular properties, both two electron and one-electron, on the type and number of contractions have been made.[34] Recently, reviews[39,31] of Gaussian basis sets produced recommendations on selecting the proper contractions. Early calculations on water,[35] formaldehyde[36] and ammonia[37] showed that even the double zeta basis set had to be

extended by the addition of polarization functions in order to obtain reasonable one-electron properties.

Two types of polarization functions are in general use, nuclear centered (NCPF's) and bond centered (BPF's). The nuclear centered functions are usually higher ℓ-quantum number functions, with d and f type functions added to a good double zeta set composed s and p type functions, (p type functions are often added to hydrogen). Studies by Kari et al.[38] and Rosenberg and Shavitt[39] have indicated the necessity of looking at a number of one-electron properties in order to evaluate the usefulness of additional polarization functions.

The use of bond centered functions, although proposed very early,[40] as a complete substitute for nuclear centered functions has only recently received extensive use, not as a substitute for nuclear centered functions, but as functions added as an improvement to good but small basis sets, i.e., as bond polarization functions (BPF's). The use of bond functions as polarization functions (BPF's) originated because they possess computational advantages compared to the use of a set of conventional NCPF's. However Metzgar[41] in a study of one-electron properties of hydrocarbons and their fluorine and chlorine derivatives has shown that in many cases the use of BPF's produces molecular properties in better agreement with experiment than when conventional NCPF's are used. He also found that frequently the residual Hellmann-Feynman force is smaller when BPF's were used compared to when NCPF's are used. This implies that BPF's produce a more realistic picture of the electron distribution than when the more conventional

NCPF's are used. It is this need for more information on this latter prospect which has resulted in the work to be described in the following chapters.

Since Metzgar's work a considerable number of papers have appeared on the use of bond functions in molecular calculations[42-49] and a number of procedures for optimizing them have been suggested.[41,42,44] However, apart from the work of Vladirimoff et al. on the diatomics CO and N_2[42,43] all the previous work is on two-electron properties with little or no attention to one-electron properties.

CHAPTER II

CALCULATIONAL PROCEDURES

Before analyzing in detail the properties of the molecules chosen for study, it is necessary to establish how the calculations were carried out to produce the wave function. It is also necessary to provide some justification for the basis set proposed.

A. COMPUTATIONAL DETAILS

In order to perform an *ab initio* calculation one must choose the basis set, the molecular geometry and the computer program.

1. Basis Sets

The main basis set used was the 4-31G split valence basis proposed by Ditchfield *et al.*[32,33] As indicated in Chapter I, at the least a double zeta (DZ) quality set is needed for the valence electrons to serve as a foundation for the addition of polarization function. Although there are several DZ type basis sets available,[26,27,29,31,36] the 4-31G set has the very important computational advantage in that it uses a single exponent for both s and p function in a given shell. This results in considerable savings in computer time over a more general DZ set especially in larger molecules. The STO-3G basis set was also used for comparison purposes and as a test of it's usefulness in predicting properties. Even though the total energies obtained using this basis set are far from the HF limit, it is computationally very fast to use and has been widely employed on organic molecules.[7,8]

2. Molecular Geometries

The molecular geometries used were selected from available experimental values, generally from recent microwave work. Table I gives the sources[50-63] of the geometries for the molecules studied.

3. Computer Programs

The integral and SCF calculations were done with two computer programs. The program POLYATOM version II[64] was used in the early stages of the work. This program included a packaged routine (PA60) which was used to calculate all the one-electron properties reported here. Later, the much faster program Gaussian 70 was obtained[65] and modified to allow for the inclusion of bond functions and to produce output suitable for use in the one-electron properties program PA60. Several errors in this program and additional errors found in POLYATOM were corrected in the course of the work. Convergence difficulties which arose in the calculations on polar molecules using bond functions were solved in part by incorporating a density matrix averaging technique developed by de Montgolfier and Hoareau[66] into both GAUSSIAN 70 and POLYATOM II. A density matrix is generated from the equation

$$P^{n+1} = \varepsilon P^{n} + (1-\varepsilon) P^{n+1} \tag{24}$$

where the ε is determined by direct minimization of the energy functional to give

$$\varepsilon = -\frac{\frac{1}{2}\Sigma[P^{n}_{\mu\nu}-P^{n+1}_{\mu\nu})(H_{\mu\nu}+F_{\mu\nu}{}^{n+2})+P^{n+1}_{\mu\nu}(F^{n+1}_{\mu\nu}-F^{n+2}_{\mu\nu})]}{\Sigma_{\mu\nu}(P_{\mu\nu}{}^{n}-P^{n+1}_{\mu\nu})(F^{n+1}_{\mu\nu}-F^{n+2}_{\mu\nu})} \tag{25}$$

TABLE I

SOURCES OF MOLECULAR GEOMETRIES

Molecule	Source
CO	Ref 50
CS	Ref 51
H_2CO	Ref 52
H_2CS	Ref 53
trans HC:OOH	Ref 54
cis HC:OOH	Ref 55
trans HC:OSH	Ref 56,57
cis HC:OSH	Ref 56,57
CH_3NO_2	Ref 58
$HONO_2$	Ref 59
NO_2	Ref 60
NO_2^-	Ref 61
NO_3^-	Ref 62
FNO_2	Ref 63

where $P^{n}_{\mu\nu}$ and $P^{n+1}_{\mu\nu}$ are individual elements of the density matrix of the nth and (n+1)th iteration, $H_{\mu\nu}$ is an element of the core Hamiltonian and $F^{n+1}_{\mu\nu}$, $F^{n+2}_{\mu\nu}$ are elements of the Fock matrix for the (n+1)th and the (n+2)th iterations. Use of the above technique allowed faster convergence for several molecules, including the thioformic acid isomers, but no detailed study was done to determine whether the method has lasting value. A program for electron density plots, SNOOPY[67] was available and modified to accept data from the SCF program.

B. BOND POLARIZATION FUNCTION OPTIMIZATION

From the earlier work of Metzgar, it was known that large improvements in the electron density representation of the bonds could be realized by using bond polarization function. A set of optimized bond functions was first obtained for each individual diatomic species. These were then used for more complex structures without re-optimizing.

Metzgar has reported bond functions for the CH, CF, CCl and CC diatomic structures. In unpublished work in this laboratory values for the CN, CO and OH structures were obtained. However for the calculations to be described in later chapters bond functions were required for the CS, the SH, and the NO bonds. The parameters used for these bonds are given in Table II. The method of optimization is described below for the CS diatomic structure. A similar optimization was performed for the NO structure. However for the SH bond an optimization study was not performed because in an initial study in which the parameters for the OH structure were transferred to the SH

TABLE II

BOND POLARIZATION FUNCTION PARAMETERS

Diatomic Structure	Gaussian Exponent α_s	Gaussian Exponent α_p	R/RA-B[a]	Source
C-H	1.50		0.59	Metzgar[b]
O-H	0.85		0.50	c
S-H	0.85		0.50	c
N-O	1.05	0.75	0.50	Optimization
C-N	1.35	0.90	0.52	Interpolation
C-O	1.20	0.85	0.56	Interpolation
C-S	0.55	0.55	0.76	Optimization

[a]Fractional distance of bond function center along A-B bond from Atom A in column 1.

[b]Ph.D. Dissertation, Ref. 41.

[c]Unpublished work.

bonds in H_2S, the results (Table III) turned out to be very satisfactory, and as will be demonstrated in detail for CS (Table IV), it was found that once a set of bond functions has been added the extra improvement achieved by optimization is small. There is also no guarantee that just because a bond function is optimized on a diatomic structure that optimization is transferrable to the same bond in a polyatomic molecule.

The set of bond functions for the CS diatomic structure given in Table II (p 18) was found by minimization of the total energy, using both the s and p exponents of the single primitive gaussians and the position of the s and p functions in the bond as variables. Table V illustrates the procedure. The exponent of a single s type function, placed at the midpoint of the bond was first varied until an energy minimum was reached. The s exponent that gave the lowest energy was then used with additional p functions to optimize the exponent of the latter functions. The entire set of functions was then moved along the bond to find a third minimum energy and finally all variables were adjusted over a range of 10% to re-check this minimum. The lowest energy was found with an s exponent of 0.55 and a p exponent of 0.58 with both placed at a position corresponding to 0.76 of the total bond length taking the position of the carbon nucleus as the origin. Since one of the main advantages of the 4-31G basis set is the use of identical s and p exponents, both the s and p exponents in the bond function set were given the value of 0.55 and used in later calculations. The addition of the single s bond function lowered the total energy by about 0.025 a.u. Adding the three p function set dropped the energy

TABLE III

ONE AND TWO ELECTRON PROPERTIES[a] FOR H_2S

Property	Expt'l	4-31G	4-31G + BPF's	DZ + NCPF's[b]	DZ + NCPF's[c]
Energy (a.u.)	---	-398.202	-398.241	-398.686	-398.682
Diss. Energy (eV)	6.96[b]	4.15	5.20	5.58	
Gross Atomic Pop.					
on S	---	16.983	16.057	16.098	16.16
on H	---	0.908	0.971	0.951	0.92
Moments of Charge					
μ(debyes)	1.02[d]	1.78	1.52	1.33	1.28
Θ_{xx} ($\times 10^{-26}$ esu cm^2)		0.632	0.646	0.990	0.94
Θ_{yy}		2.324	2.447	2.892	2.94
Θ_{zz}		-2.956	-3.093	-3.883	-3.88
Diamagnetic Susceptibility ($\times 10^{-6}$ erg/g^{2}mole)					
χ^d_{xx}	---	-32.929	-32.567	-33.377	-33.39
χ^d_{yy}	---	-32.726	-32.429	-33.298	-33.31
χ^d_{zz}	---	-37.387	-36.936	-37.078	-37.12
χ^d_{av}	---	-34.347	-33.977	-34.584	-34.61
Hellmann-Feynman Force (a.u.)					
F(H)	0.0	0.088	0.020	0.009	0.00
F(S)	0.0	-2.061	-1.181	-0.675	0.43
F total	0.0	-1.884	-0.787	-0.656	0.43
Quadrupole Coupling Constants (kHz)					
e^2Qa_{aa}/h(D)[e]	154.7±1.6[f]	215	146	179	
e^2Qq_{bb}/h(D)	(149)[g]	121	86	105	
$e\,Qq_{cc}/h$(D)		94	59	75	
η	0.12±0.13[h]	0.13	0.01	0.17	
e^2Qq_{xx}/h(S)	-8,000	-8,840	-7,600	-5,600	-6,100
e^2Qq_{yy}/h(S)	-32,000	-29,980	-32,280	-31,600	-35,000
e^2Qq_{zz}/h(S)	40,000	38,720	39,880	37,200	41,100

[a] Appendix 1.

[b] Rothenburg, Ref. 68, (12s9p2d/4s1p) contracted to [6s4p2d/2s1p].

[c] Roos, Ref. 69, (12s9p2d/4s1p) contracted to [6s4p2d/2s1p].

[d] Hillgar, Ref. 70.

[e] In principal axis system for deuteron.

[f] Thaddeus, Ref. 71.

[g] deLucia, Ref. 72.

[h] Burrus, Ref. 73.

TABLE IV

EFFECT OF OPTIMIZATION ON CS PROPERTIES

Property	4-31G	Basis Set I[b]	II[b]	III[b]
		α_s = 0.70	0.70	0.55
		α_s^p = 0.58	0.58	0.58
		R_{BF}/R_{CS} = 0.50	0.76	0.76
Dipole μ[a]	0.386	0.481	0.510	0.512
Quadrupole $\Theta_\perp$[a]	1.862	1.116	1.039	1.025
Electric Field[a]				
on C	-0.179	-0.066	-0.085	-0.084
on S	0.105	-0.005	-0.063	0.029
Electric Field[a] Gradient				
on C	-0.551	-0.559	-0.543	-0.537
on S	1.101	1.118	1.086	1.074
	-0.194	-0.176	-0.209	-0.166
Mulliken Populations				
on C σ	5.072	4.913	4.841	4.842
Π	0.538	0.468	0.491	0.493
on S σ	8.928	8.728	8.711	8.650
Π	3.462	3.387	3.283	3.279
on BPF σ	---	0.358	0.448	0.508
Π	---	0.145	0.226	0.228

[a]Properties expressed in atomic units.

[b]4-31G plus bond functions between the C and S atoms.

TABLE V

RESULTS OF PARAMETER OPTIMIZATION FOR CS

Fixed Parameter (S)	Variable Parameter	Energy (a.u.)
R/Rcs = 0.500	α_s = 1.30	-434.79517
	1.00	-434.79972
	0.70	-434.80371
	0.50	-434.80192
α_s = 0.70	α_p = 0.65	-434.83581
	0.58	-434.83718[a]
	0.35	-434.83082
α_s = 0.70	R/Rcs = 0.45	-434.83413
α_p = 0.58	0.60	-434.84425
	0.71	-434.84908
	0.76	-434.84972[b]
	0.81	-434.84918
α_p = 0.58	α_s = 0.80	-434.84770
R/Rcs = 0.76	0.60	-434.85240
	0.55	-434.85343[c]
α_s = 0.55	α_p = 0.45	-434.84950
R/Rcs = 0.76	0.60	-434.85249
α_s = 0.55	R/Rcs = 0.70	-434.85284
α_p = 0.58	0.80	-434.85266

[a]Denoted basis set I in Table IV (p 21).

[b]Denoted basis set II in Table IV.

[c]Denoted basis set III in Table IV.

another 0.035 a.u. Optimizing the position, improved the energy by another 0.02 a.u. In this case it appeared that position optimization was about as important as exponent optimization insofar as total energy, unlike the results of Vladimiroff for CO.[42a]

Because the energy was not the only criterion which might be used in determining the best wave function, one-electron properties of the wave function were also computed at the various stages of optimization of the bond functions. Table V (p 22) contains a summary of some of these results.

For the dipole and quadrupole moments, the use of the bond functions, even those only partially optimized (from calculation I) gave a substantial change from the 4-31G set. However, subsequent optimization gave a much smaller change. For example, the dipole moment increased by 25% using basis set I instead of the 4-31G. The dipole moment then was changed by about 6% by continued optimization (set I was the least optimized, set III the most optimized). For the electric field the changes were not as uniform. Inclusion of the bond functions did reduce the electric fields on both nuclei dramatically (40-90%), but unevenly. If the best electric fields for the individual carbon and sulfur atoms, and thereby the lowest Hellmann-Feynman force on the molecule, are used as the criteria, basis set III gave the best results with the total net force reduced by 93% from the 4-31G set and 92% from set I. An examination of the orbital contributions to the electronic component to the electric field revealed that the major change upon adding the BPF's occurred in the valence MO's, (80%) with the pi system, more important than the sigma system for bases I and

III. Basis set II had a larger change in the core orbitals and a much larger total change in electric field. The net total force calculated using basis II was much higher than for even the 4-31G set alone, which indicates that this basis set had a serious deficiency in describing one region of the electron density. Both the dipole and quadrupole moments calculated using basis set II were quite similar to those of basis set III. However for the electric field gradient on sulfur, the results of basis set II are not in line with those from sets I and III. Finally, the Mulliken populations are little changed by continued optimization. These results show very clearly that the common practice of relying on just one one-electron property like the dipole moment to judge a basis set could lead to an erroneous result and the use of a seriously unbalanced basis set.

The results also show that the initial addition of BPF's can have a considerable effect on the value of the one-electron properties but further optimization of the bond function positions and exponents have a much smaller effect on most of the one-electron properties. They also demonstrate that the Hellmann-Feynman force is an extremely sensitive property which might be utilized rather than, or in addition to, the total energy as a means of optimizing polarization functions.

C. ADEQUACY OF THE BASIS SET

A final question which needs to be examined in some detail is the exact role played by polarization functions added to a relatively small basis set such as the 4-31G set. Do they act as true polarization functions or do they merely correct the deficiencies of the

4-31G set relative to a more complete set of s and p functions by increasing the flexibility of the set. Unfortunately there have been few reports of molecular properties calculated first with a high quality s and p basis set and then with a set of nuclear centered polarization functions. The only polar organic molecule for which there has been extensive work on the effect of basis sets on one-electron properties is formaldehyde.[36] However the availability of these results is ideal for this work as will be seen in the next chapter on the use of the 4-31G+BPF's set to obtain the molecular properties of formic and thioformic acids. To check whether the 4-31G + BPF's basis set is suitable, calculations were performed on CO and H_2CO using the 4-31G; the 4-31G + NCPF's and the 4-31G + BPF's basis sets. The results are shown in Tables VI and VII. The 4-31G set was originally chosen as a medium sized set which takes into consideration with respect to the small number of gaussians used, those changes in the valence shell which are responsible for molecule formation. Thus one would expect the 4-31G set to give at least as good, or better values of binding energies (i.e., atomization energies) compared to similar basis sets which differ largely in the number of gaussians allocated to take care of the core orbital energies, e.g., the full double zeta set of Snyder and Basch.[27]

The results of the binding (atomization) energies for CO, and H_2CO, are given in Tables VI and VII for a number of different basis sets namely the 4-31G set, a set in which d and p orbitals were added as NCPF's and finally a 4-31G set to which BPF's were added. In addition the full double zeta set and double zeta plus polarization

TABLE VI

CALCULATED PROPERTIES OF CO[a]

	DZSB[b]	EDZMN[c]	STO-3G	4-31G	4-31G + NCPF's	4-31G + BPF's
Total Energy a.u.	-112.6763	-112.7622	-111.2246	-112.5532	-112.6074	-112.6095
Binding Energy eV	-5.77	-7.19		-5.74	-7.21	-7.26
μ debyes	0.394	0.245	-0.168	0.564	0.240	0.312
$\Theta_{\parallel}$ $x10^{-26}$esu cm^2	-3.058	-2.089	-3.028	-2.861	-1.971	-2.557
$\Theta_{\perp}$ $x10^{-26}$esu cm^2	1.529	1.036	1.514	1.430	0.986	1.278
$\langle a^2 \rangle$, $\langle b^2 \rangle$ $x10^{-16}cm^2$	2.094	2.108	1.811	2.058	2.057	2.022
$\langle c^2 \rangle$ $x10^{-16}cm^2$	7.095	6.907	6.805	7.018	6.832	6.918
F_z(C) a.u.	-1.123	-0.153	-1.533	-1.047	-0.449	-0.634
F_z(O) a.u.	2.326	0.361	2.996	2.163	1.146	0.430
F_z (total) a.u.	1.203	0.208	1.463	1.116	0.697	-0.203
$q_{\parallel}$(C) a.u.	0.861	1.135	0.442	0.922	0.972	1.000
$q_{\perp}$(C) a.u.	-0.430	-0.565	-0.221	-0.461	-0.486	-0.500
$q_{\parallel}$(O) a.u.	0.303	0.697	-0.068	0.481	0.447	0.636
$q_{\perp}$(O) a.u.	-0.151	-0.348	0.034	-0.240	-0.224	-0.318

[a]Appendix 1. [b]Snyder, Ref. 27. [c]Neumann, Ref. 36.

TABLE VII

SELECTED CALCULATED MOLECULAR PROPERTIES OF H_2CO[a]

		DZSB	EDZNM	4-31G	4-31G+NCBF's	4-31G+BPF's	STO-3G
Total Energy	a.u.	-113.8208	-113.8917	-113.69131	-113.74228	-113.73867	-112.35369
Binding Energy	eV	-9.74	-11.83	-9.53	-10.92	-10.82	-16.22
μ		3.110	2.821	2.950	2.601	2.626	1.525
$\Theta_{aa(zz)}$	$\times 10^{-26}$ esu cm^2	-0.406	0.0056	-0.449	0.063	-0.182	-0.685
$\Theta_{bb(xx)}$	$\times 10^{-26}$ esu cm^2	0.421	0.250	0.370	0.165	0.125	0.299
$\Theta_{cc(yy)}$	$\times 10^{-26}$ esu cm^2	-0.014	0.0	0.079	-0.228	0.057	0.386
$\langle a^2 \rangle$	$\times 10^{-16}$ cm^2	10.474	10.340	10.433	10.298	10.339	10.258
$\langle b^2 \rangle$	$\times 10^{-16}$ cm^2	4.176	4.164	4.183	4.148	4.160	3.985
$\langle c^2 \rangle$	$\times 10^{-16}$ cm^2	2.456	2.433	2.422	2.401	2.368	2.171
$F_z(C)$	a.u.	-0.348	0.012	-0.330	-0.044	-0.160	-0.318
$F^z(O)$	a.u.	2.101	0.416	1.973	1.121	0.393	2.810
$F^z(H)$	a.u.	-0.030	0.005	-0.026	-0.025	0.003	-0.022
$F^z(H)$	a.u.	±0.056		±0.058	±0.033	±0.013	±0.039
F_z^y(total)	a.u.	1.693	0.438	1.591	1.027	0.239	2.448
$q_{aa}(C)$	a.u.	0.153	0.347	0.213	0.260	0.270	0.051
$q_{bb}(C)$	a.u.	0.339	0.301	0.302	0.295	0.297	0.110
$q_{cc}(C)$	a.u.	-0.492	-0.648	-0.515	-0.555	-0.568	-0.162
$q_{aa}(O)$	a.u.	-0.697	-0.404	-0.519	-0.529	-0.436	-0.913
$q_{bb}(O)$	a.u.	2.612	2.270	2.433	2.253	2.266	2.444
$q_{cc}(O)$	a.u.	-1.916	-1.866	-1.914	-1.724	-1.830	-1.531
$q_{\alpha\alpha}(D)$	a.u.	-0.286	-0.262	-0.279	-0.272	-0.209	-0.278
$q_{\beta\beta}(D)$	a.u.	0.1441	0.133	0.139	0.135	0.102	0.139
$q_{\gamma\gamma}(D)$	a.u.	0.1420	0.130	0.140	0.137	0.103	0.139

[a]Appendix 1. [b]Snyder, Ref. 27. [c]Neumann, Ref. 36.

function calculations from the literature are reported. The double zeta set of Snyder and Basch[27] would be denoted a (10s5p/4s) basis set contracted to [4s2p/2s] and the double zeta plus NCPF's set of Newmann and Moskowitz[36] which is (10s5p2d/4s1p) set contracted to [5s3p2d/2s1p] basis set.

It can be seen that, as expected, the total electronic energies are very similar. Moreover, the improvement in the binding energy on adding both types of polarization function is considerable, showing their importance in describing changes in electronic charge distribution on molecule formation. When the results of the effect of polarization functions on full double zeta basis sets are compared with the effect of adding polarization functions to the 4-31G set it is seen that the effect is similar in magnitude. This demonstrates the very important point that the addition of BPF's to the 4-31G set does much more than simply "make up" for the deficiency of the set in describing the s and p orbital spatial distribution relative to the full double zeta set. Also the final result, at least for the binding energy, is the same when polarization functions are added to the 4-31G set as when they are added to a full double zeta set.

A similar comparison between the results of different basis sets of a number of different one-electron molecular properties is a much more severe test of the accuracy of a basis set than the simple comparison of energies because each molecular property is sensitive to the electron density in different regions of space surrounding a molecule. Thus there are properties which depend on expectation values (e.g., molecular quadrupole moments, second moments and diamagnetic

susceptibilities) which, as defined in Appendix 1, are sensitive to the peripheral parts of the molecular wave functions, i.e. on $\langle r^2 \rangle$, and there are properties which reflect the interaction of the electronic density with the atomic nuclei (electric field gradients, nuclear magnetic resonance chemical shifts and Mossbauer chemical shifts) that are more sensitive to the inner parts of the electronic density (i.e. on $\langle r^n \rangle$ where $n<0$). A sampling of some of the properties for CO and H_2CO using different basis sets are given in Tables VI (p 26) and VII (p 27). Again the similarity of the results of adding polarization functions to the 4-31G set, compared to the results of adding polarization functions to a full double zeta set, is clearly seen.

These results and the earlier results of Metzgar[41] are a strong justification of the use of the 4-31G set augmented by BPF's on larger molecules as described in later chapters. In the following chapter, for example, the results of calculations on CS, H_2CS, HCOOH and HCOSH are described and a detailed comparison is made of these theoretical results, and those of CO and H_2CO, with experimental values.

CHAPTER III

CARBONYL AND THIOCARBONYL COMPOUNDS

A. INTRODUCTION

In the previous chapter it was shown that the 4-31G basis set behaves for carbon monoxide and formaldehyde like a full double zeta basis set when it is augmented by polarization functions, and that use of BPF's as polarization functions results in improvements of the wavefunction in a manner quite similar to other work using NCPF's.

In this chapter the results of an exhaustive study of the molecular properties of CS, H_2CS, the thio analogues of CO and H_2CO, and the cis and trans isomers of formic and thioformic acid are presented. These molecules were chosen because recent careful experimental studies of their molecular properties have been reported. Also they constitute some of the simplest cases of organic molecules containing the carboxyl group. The effectiveness of the CS bond functions can also be tested by placing them in a variety of environments as is present in the CS, H_2CS and HCOSH structures for which the CS bond has triple, double and single bond character. Moreover in the case of formic acid, there is great intrinsic interest since it is the smallest carboxylic acid.[74-79] This aspect has given rise to many calculations on this molecule in an attempt to provide charge densities for use as a starting point in molecular interaction studies. Ab initio calculations on formic acid have been done using very small basis sets,[75-79] e.g. Pople's STO-3G set, also semiempirical[78-82] calculations have been performed, however there has been no previous

attempt to assess how good these calculations really are by comparing comparing molecular properties, calculated using these wave functions, with either experiment or those of more accurate calculations.

As discussed in Chapter II the total electronic energies calculated by the 4-31G basis set are higher than those using full double zeta sets, but binding energies are quite similar. Table VIII shows both the total electronic energies (column 2) and the binding energies (column 3) both calculated and experimental for the molecules of interest. When double zeta and double zeta plus polarization function calculations are available they are also shown for comparison. Both the NCPF's and BPF's improve the binding energies considerably.

B. ONE ELECTRON PROPERTIES

The results of Table VIII demonstrate that the addition of BPF's to a 4-31G set has an effect on the binding energies very similar to the addition of standard NCPF's to full double zeta sets. This is in accordance with the findings of some similar studies on adding BPF's to double zeta sets which have appeared in the literature since this work was completed.[46,47] However, the other studies concentrated entirely on total energies and discussed neither binding energies nor one-electron molecular properties. This is in contrast to this and other studies at the University of Tennessee. In these studies the major emphasis has been to assess the effectiveness of practical medium sized basis sets in calculating reasonable values of one-electron molecular properties and in producing molecular electron distributions which mirror fairly realistically the changes which take place on chemical

TABLE VIII

CALCULATED BINDING ENERGIES[a]

	Basis Set	Total Energy (a.u.)	Binding Energy (eV)
CO	4-31G	-112.55324	-5.74
	4-31G+NCPF's	-112.60739	-7.21
	4-31G+BPF's	-112.60953	-7.26
	DZSB[b]	-112.6763	-5.77
	EDZNM[c]	-112.7622	-7.19[d]
	expt'l		-11.24[d]
H_2CO	4-31G	-113.69131	-9.53
	4-31G+NCPF's	-113.74228	-10.92
	4-31G+BPF's	-113.73867	-10.82
	DZSB[b]	-113.8208	-9.74
	EDZNM[c]	-113.8917	-11.83[e,f]
	expt'l		-16.22[e,f]
CS	4-31G	-434.77603	-2.38
	4-31G+NCPF's	-434.84496	-4.25
	4-31G+BPF's	-434.85328	-4.48
	DZB[g]	-435.30781	
	DZDSDC[h]	-435.31537	
	expt'l		-7.61[i]
H_2CS	4-31G	-435.99125	-8.28
	4-31G+NCPF's	-436.04549	-9.75
	4-31G+BPF's	-436.05737	-10.07
	DZ[j]	-436.4561	-9.03[k]
	expt'l		-13.66[k]

TABLE VIII (CONTINUED)

	Basis Set	Total Energy (a.u.)	Binding Energy (eV)
t-HCOOH	4-31G	-188.47289	-11.6
	4-31G+BPF's	-188.56178	-14.0
	DZSB[b]	-188.6888	-11.5[l]
	expt'l		-18.8[l]
c-HCOOH	4-31G	-188.46284	-11.33
	4-31G+BPF's	-188.54792	-13.69
t-HCOSH	4-31G	-510.75074	-9.80
	4-3G+BPF's	-510.86257	-12.85
	expt'l		-16.9[m]
c-HCOSH	4-31G	-510.74618	-9.68
	4-31G+BPF's	-510.86135	-12.81

[a]Appendix 1.

[b]Snyder, Ref. 27.

[c]Neumann, Ref. 36.

[d]Gaydon, Ref. 83.

[e]Lewis, Ref. 84.

[f]Shimanouchi, Ref. 85.

[g]DZ+BPF's Bruna, Ref. 86.

[h]DZ+d's, Bruna, Ref. 86.

[i]Douglas, Ref. 87.

[j]Bruna, Ref. 88.

[k]Jones, Ref. 89.

[l]Estimate from ΔH_f of HCOOH, H_2O, and CO and De of H_2O and CO.

[m]Estimate from ΔH_f of HCOOH.

bond formation. The use of the 4-31G set for this purpose is questionable. However, the comparison of the effects of adding polarization functions to this set on calculated molecular properties of CO and H_2O (Tables VI-VII, p 26-27) with the effects of adding polarization functions to larger basis sets shows that the use of the 4-31G is indeed a suitable starting point for improving wave functions by the addition of polarization functions. Thus the way is opened for the use of the 4-31G augmented by BPF's for larger molecules. This approach should prove to be a more feasible alternative to using full double zeta basis sets augmented by standard nuclear centered polarization functions.

In order to assess how good this proposed medium size basis set is in calculating molecular properties, calculations have been performed on the two isomers of formic acid and on the two isomers of the thioformic acid and also on the sulfur analogues of CO and H_2CO. These results are best reported by discussing each individual property for all eight molecules. This should permit one to determine more easily whether any property is given badly by the proposed basis sets.

1. Dipole Moment

The dipole moment is by far the most commonly reported experimentally measured and theoretically calculated one-electron property. Fortunately, the property is fairly sensitive to basis set so that a good prediction of a dipole moment value is probably a necessary achievement for a satisfactory basis set but it is NOT, although it is often taken to be, a sufficient criterion. For example, it is often

reported that the subminimal STO-3G basis set gives good dipole moments and therefore reasonable charge distributions.[90,91] Consequently a number of workers have used STO-3G basis sets to obtain wave functions to be used in discussions of electronic distributions and substituent effects, while others have used them as a starting point in intermolecular interaction calculations.[75,76] Table IX shows the calculated and experimental dipole moment values for the CO, H_2CO, CS and H_2CS molecules. For the STO-3G set the results are rather uneven. For CO the STO-3G calculation has the correct sign and is very close to the experimental value. Even the large DZ + NCPF's calculation with CEPA included does not match it. This good agreement is however fortuitous since similar agreement is not obtained for the other molecules. For these, the STO-3G basis set seriously underestimates (by as much as 100%) the experimental dipole moments. The 4-31G set usually gives a value too large and this is true for H_2CO and H_2CS, for which the values are both about 28% too high. The CS moment is still a little low but is improved over the STO-3G; for CO the 4-31G set is quite high. The additional of polarization functions to the 4-31G set, improves the calculated moments in every case with the BPF's results closely matching the NCPF's results. For the small molecules such as those presented here the overall best results for calculated dipole moments are obtained by including correlation efforts as in the CEPA method developed by Meyer.[96] It appears that to get much better agreement than that seen in Table IX it is necessary to go beyond the SCF Hartree-Fock method and include extensive configuration interaction.[15]

TABLE IX

DIPOLE MOMENTS FOR CO, H_2CO, CS AND H_2CS (debyes)[a]

Basis Set	CO	H_2CO	CS	H_2CS
STO-3G	-0.168	1.525	0.935	0.895
4-31G	0.564	2.950	0.980	2.132
4-31G+NCPF'	0.240	2.601	1.428	1.929
4-31G+BPF's	0.312	2.626	1.361	1.926
DZSB[b]	0.394	3.110		
EDZNM[c]	0.245	2.821		
SCF[d]	0.144	2.747		1.999
CEPA[e]	-0.275	2.219		1.493
expt'l	-0.112 ± 0.005[f]	2.3321 ± 0.0005[g]	1.99 ± 0.04[h]	1.6491 ± 0.0004[i]
	(C^-O^+)[j]	(C^+O^-)[j]	(C^-S^+)[j]	

[a]Appendix 1.

[b]Double zeta, Snyder, Ref. 27.

[c]Double zeta plus NCPF's, Neuman, Ref. 36.

[d]Large basis set. Jaquet, Ref. 92.

[e]Using CEPA technique on large basis set, ibid.

[f]Burrus, Ref. 93.

[g]Fabricant, Ref. 94.

[h]McGurk, Ref. 95.

[i]Johnson, Ref. 53.

[j]Experimentally determined polarity of structure.

In evaluating the results of calculations for molecules such as formic and thioformic acids in which the direction of the dipole moment does not coincide with one of the principal axes of inertia it is important to consider both the magnitude of the dipole moment and its direction. Both quantities are reported in Table X. The first entry in the Table shows that the STO-3G set can be unreliable for both the magnitude of the dipole moment and its direction. The 4-31G set, which is usually thought to give poorer values of the magnitude of dipole moments than the STO-3G set, does slightly better for the molecules under discussion. However, for the direction of the moment it does much better. This is an important finding since getting the direction of dipole moment correct is a very strong criterion in assessing the value of a charge distribution for use in creating intermolecular potentials. These results demonstrate that potentials generated using STO-3G basis sets should not be accepted without more scrutiny than is often the case, i.e., both the magnitude and the direction of the dipole moment should be examined, whereas many workers use the magnitude as the sole criterion.[90] The results listed in Table X for the 4-31G+BPF's show that the calculated directions are in good agreement for all of the four molecules but, with respect to the magnitude, only the results for the trans isomers are really very satisfactory.

2. Hellmann-Feynman Force

The force on each individual nucleus, which (Appendix 1) is the product of electric field and the nuclear charge should be zero for a molecule in its equilibrium geometry. For a calculation performed at the Hartree-Fock limit and at the theoretical molecular geometry, the

TABLE X

DIPOLE MOMENTS FOR HCOOH AND HCOSH (debyes)[a]

Basis Set	t-HCOOH		c-HCOOH		t-HCOSH		c-HCOSH	
	μ	θ[b]	μ	θ	μ	θ	μ	θ
STO-3G	0.789	14.4	3.048	68.8	1.034	37.7	2.288	70.2
4-31G	1.379	35.5	4.839	67.3	1.809	45.0	3.930	75.8
4-31G+BPF's	1.471	31.4	4.508	70.2	1.885	42.3	3.562	72.0
DZSB[c]	1.50	36.7						
GL+CI[d]	1.42	17.1						
expt'l	1.415	34.4[e]	3.79	74.6[e]	1.536	43.8[f]	2.868	70.5[f]

[a]Appendix.

[b]θ is the angle between the positive end of the dipole and the C-O bond rotating toward the C-H bond.

[c]Double zeta, Snyder Ref. 27.

[d]Peyerimhoff, Ref. 97.

[e]Hocking, Ref. 98.

[f]Hocking, Ref. 99.

sum of the force on all the nuclei and the forces at each individual nuclei should be zero. This requirement enables one to assess the accuracy of an approximate wave function on purely theoretical grounds without recourse to comparison with experiment. Moreover, it has been shown that in the case of water,[39] in contrast to the behavior of some molecules, the reduction of the Hellmann-Feynman force (HFF) with improvement of basis set is fairly regular. It is known that the HFF is very sensitive to the basis set. However, even in very good calculations the individual residual forces are still substantial, and few workers have reported values for either the total force or the forces at individual nuclei. The exploratory work of Metzgar,[41] and some of the work in the literature,[34,38] strongly suggests that the values of the HFF's do offer a valid way of comparing basis sets on an absolute scale. Moreover, an examination of the relative values of the force at different nuclei, seems to be a likely way of improving basis sets in the future. A high value of the force at one particular type of nucleus in a group of compounds may indicate that the basis set used for that particular element is either of poor quality or is not balanced with respect to those used for the other elements in the molecule. By improving the quality of the orbitals for that nucleus, one could improve the overall quality of the calculation. One of the main reasons for performing the calculations described in this work was to obtain information about how the HFF's changed with basis set charge.

In Table XI, the HFF's of the individual nuclei for H_2CO and CO for various basis sets are compared. These results show a dramatic

TABLE XI

FORCES ON THE NUCLEI FOR CO AND H_2CO (a.u.)[a]

Molecule	Basis Set	H	C	O	Total
CO	STO-3G		-1.533	2.996	1.463
	4-31G		-1.047	2.163	1.116
	4-31G+NCPF's		-0.449	1.146	0.697
	4-31G+BPF's		-0.634	0.430	-0.203
	DZSB[b]		-1.123	2.326	1.203
	EDZNM[c]		-0.153	0.361	0.208
H_2CO	STO-3G	-0.021	-0.318	2.810	2.449
	4-31G	-0.026	-0.330	1.973	1.591
	4-31G+NCPF's	-0.025	-0.044	1.121	1.027
	4-31G+BPF's	0.003	-0.160	0.393	0.239
	DZSB[b]	-0.030	-0.348	2.101	1.693
	EDZNM[c]	0.005	0.012	0.416	0.438

[a]Appendix 1.

[b]Double zeta, Snyder, Ref. 27.

[c]Double zeta plus NCPF's, Neumann, Ref. 36.

lowering in going from a STO-3G set to a 4-31G set, and a further substantial lowering on adding the polarization functions. The total forces for CO and H_2CO with BPF's are surprisingly similar to those obtained by Neumann and Moskowitz[36] using a much larger (EDZ) basis set and were lower than the total forces obtained using NCPF's. The forces at individual atoms are not as low as those found in the EDZ calculation. Since the results of the EDZ calculation for the two atoms in CO are very similar and because the calculations were performed at the experimental geometry, rather than at the theoretically optimized geometry, one can only conclude that basis sets for the carbon and the oxygen are equally good or equally poor depending on one's point of view. On the other hand, the uneven results for the NCPF's carbon and oxygen in the calculations using NCPF's indicate that perhaps these could be improved by optimizing the d orbital exponents of the oxygen. Improvement of NCPF's is not, however, a subject of concern in the present work.

Similar results on CS and H_2CS are given in Table XII. Only one calculation of either forces or electric field has been reported for H_2CS and none for CS.[100] The result for the total force on the CS molecule when BPF's are used is extremely low. Unfortunately, a similar result was not found for H_2CS. For this molecule the resulting total force was larger than when NCPF's were used. Both the residual force on the sulfur and the total residual force on the molecule are similar in magnitude to those reported elsewhere for molecules containing third row atoms where the calculations are of double zeta, or better, quality.[101] The FSGO (floating spherical gaussian

TABLE XII

FORCES ON THE NUCLEI FOR CS AND H_2CS (a.u.)[a]

Molecule	Basis Set	H	C	S	Total
CS	STO-3G		-1.337	2.641	1.3041
	4-31G		-1.075	1.681	0.606
	4-31G+NCPF's		-0.458	0.205	-0.253
	4-31G+BPF's		-0.495	0.439	-0.056
H_2CS	STO-3G	-0.024	-0.083	2.643	2.513
	4-31G	-0.0318	-0.283	1.670	1.323
	4-31G+NCPF's	-0.003	-0.089	0.654	0.559
	4-31G+BPF's	-0.004	0.017	0.867	0.877
	FSGO[b]	0.012	0.198	2.736	c

[a]Appendix 1.

[b]Nitzsche, Ref. 100.

[c]Not given, data for nuclei in absolute values.

orbital) calculation gave forces similar in size to the STO-3G calculation although some polarization function character exists implicit in this method of using non-nuclear centers. Recently reported results for SOF_2 and COF_2[102] would have offered a good comparison but the abnormally large values for the forces tabulated there are probably in error.

The results of the forces for the two formic and two thioformic acids are given in Tables XIII-XIV for the STO-3G, 4-31G and 4-31G + BPF's basis sets. In the case of the trans formic acid, comparison can be made with the double zeta calculations of Snyder and Basch.[27] The results of the total forces for all four calculations are very similar with the 4-31G + BPF's calculation being the worst. A similar result can be seen in the calculations on the trans thioformic acid for which the STO-3G calculation gives the lowest total force. Examination of the forces on the individual atoms reveals that in both cases the addition of the extra functions results in a lowering of the residual forces on each atom with the 4-31G set values very similar values to the DZSB double zeta set. However the addition of BPF's gives an unbalanced reduction of the HFF's for the two oxygen atoms and results in a larger total force on the molecule. A similar lack of cancelling out of the same two components, but this time one is on the oxygen and one is on the sulfur, occurs in the trans thioformic acid calculation. In the case of the cis isomers, the 4-31G + BPF's calculations have both total and individual residual forces much less than those found for the other basis sets. These results demonstrate that one must be very careful when making conclusions about basis sets on the basis of

TABLE XIII

FORCES ON THE NUCLEI FOR HCOOH (a.u.)[a]

Molecule	Basis Set	H_α[b]	C	O_α	O_β	H_β	Total
t-HCOOH	STO-3G	0.002[c]	-0.012	2.492	-2.474	-0.025	-0.018
		-0.068	-0.278	1.585	-1.539	0.080	-0.221
	4-31G	0.001	0.014	1.757	-1.686	-0.024	0.062
		-0.068	-0.370	1.053	-0.927	0.103	-0.208
	4-31G	0.002	0.104	0.454	-0.389	-0.015	0.156
	+ BPF's	-0.013	-0.239	0.275	-0.531	0.030	-0.478
	DZSB[b]	0.004	-0.017	1.882	-1.769	-0.025	0.080
		-0.070	-0.369	1.126	-0.881	0.095	-0.099
c-HCOOH	STO-3G	0.088	0.034	-2.587	0.324	-0.010	-2.150
		0.038	0.217	-1.491	-2.943	0.066	-4.112
	4-31G	0.105	0.002	-1.772	0.303	-0.003	-1.365
		0.052	0.277	-1.038	-1.938	0.070	-2.576
	4-31G	0.046	-0.075	-0.460	-0.218	-0.005	-0.712
	+ BPF's	0.012	0.173	-0.288	-0.776	0.014	-0.864

[a]Appendix 1.

[b]The subscripts refer to the structure $H_\alpha CO_\alpha O_\beta H_\beta$.

[c]The top value is the X component and the bottom is the Z component.

[d]Snyder, Ref. 27.

TABLE XIV

FORCES ON THE NUCLEI FOR HCOSH (a.u.)[a]

Molecule	Basis Set	H_α[b]	C	O	S	H_β	Total
t-HCOSH	STO-3G	-0.092[c]	-0.218	2.229	-2.325	-0.052	-0.458
		0.015	0.043	-1.693	2.145	-0.030	0.480
	4-31G	0.123	-0.278	1.553	-1.351	-0.060	-0.013
		0.013	-0.062	-1.210	1.347	-0.034	0.054
	4-31G	0.021	-0.102	0.380	-0.963	-0.012	-0.675
	+ BPF's	-0.003	-0.006	-0.348	0.994	-0.034	0.603
c-HCOSH	STO-3G	0.101	0.217	-2.383	-2.458	0.050	-4.473
		0.022	0.055	-1.543	2.146	-0.034	0.646
	4-31G	0.136	0.277	-1.672	-1.520	0.059	-2.720
		0.021	-0.059	-1.099	1.354	-0.039	0.179
	4-31G	0.029	0.130	-0.430	-1.091	0.012	-1.349
	+ BPF's	0.003	0.010	-0.283	0.814	-0.015	0.530

[a] Appendix 1.

[b] The subscripts refer to the structure $H_\alpha COSH_\beta$.

[c] The top value is the X component and the bottom value is the Z component.

HFF's. The total force taken by itself is not sufficient. A well balanced basis set should produce low residual forces on each atom. For calculations on polyatomic molecules, the use of limited basis sets is a necessity. If the residual forces of individual components are reduced in an unbalanced way as a basis set is improved, this can produce large increases in the total force.

3. Second Moments and Diamagnetic Susceptibilities

In the last decade the second moments of charge of a fairly large number of molecules have been determined through the use of microwave spectroscopy and good agreement with these results has often been used as evidence that certain basis sets are of high quality. However, Bloor and Maksic[103] have shown that the individual second moments ($\langle a^2 \rangle$, $\langle b^2 \rangle$, $\langle c^2 \rangle$) and the diamagnetic susceptibilities (χ_{aa}^d, χ_{bb}^d, χ_{cc}^d) that are derived from them (See Appendix 1) are in general very insensitive to changes in the basis set for a given geometry. They demonstrated this insensitivity by developing a semiempirical model in which the second moments are written as a sum of atomic terms, obtained from atomic data, placed at the experimental nuclear coordinates. This model gave good agreement with experiment for a wide range of data. Further support for the claim that the individual second moments are insensitive to changes in the basis set can be seen in Goddard and Czismadia's work on the effect of basis set changes on electron properties of ammonia,[34] and in Rosenberg and Shavitt's work on the water molecule.[39] In both cases improving the

basis set changed the second moments and the diamagnetic susceptibilities very little. However, in more recent work, Maksic et al.[104,105] have shown that, in order to obtain agreement with experiment for very polar molecules, the atomic model must be modified by the inclusion of intramolecular charge transfer effects.

There can often be an uncertainty in the establishment of reliable experimental values of some second moments and a well proven theoretical method would frequently be of value in making the choice among different possible interpretations. A case in point is the formaldehyde molecule.[106,107] In obtaining values of the individual second moment tensors along with inertial principal axes, it is necessary to carry out an analysis of the rotational (microwave) Zeeman effect to obtain the molecular g tensors and the anisotropies of the diagonal elements of the magnetic susceptibility tensor.

$$\Delta\chi_{aa} = 2\chi_{aa} - \chi_{bb} - \chi_{cc} \text{ etc.} \tag{26}$$

In order to get the individual elements of the diamagnetic susceptibility tensor, it is necessary to know the molecular geometry and the bulk magnetic susceptibilities. Once these are known, the second moments of the electronic charge distribution can easily be calculated using

$$\langle a^2 \rangle = \sum Z_n (a_n^2) + \frac{h}{4\pi M_p}\left(\frac{g_{aa}}{}\right) + \frac{4mc^2}{3e^2}\{2\chi_{aa} - \chi_{bb} - \chi_{cc}\} \tag{27}$$

with cyclic permutations of a, b and c. The bulk magnetic susceptibilities have usually been measured in the liquid phase and may be unsuitable for use for the vapor state. Also many of the bulk susceptibilities in the literature are unreliable. For example for formaldehyde Flygare et al.[106] used a value of $-15.0 \pm 1.0 \times 10^{-6}$ erg^{-2} mole

as the bulk susceptibility. As discussed in the next section, this gave values for the quadrupole moments very different from the theoretical values and this led Hamer et al.[108] to suggest a value of -7.5×10^{-6} erg^{-2} mol^{-1} for the bulk susceptibility. This agrees with a value of -7.0×10^{-6} erg^{-2} mole^{-1} reported in a 1972 paper by Rock and Flygare[107] and with the value -8.0×10^{-6} erg^{-2} mole^{-1} estimated from a table of atom susceptibilities compiled recently by Sutter and Flygare.[18] The latter used a least squares fitting of a set of experimental values of the second moments derived using an empirical set of rules suggested earlier by Blickensderfer et al.[109] for calculating the out-of-plane moments. All the later methods for obtaining the value for the bulk susceptibility of formaldehyde now agree that it is in the region of -7.0 to -8.0×10^{-6} erg^{-2} mole^{-1}. The values of the out-of-plane second moment $\langle c^2 \rangle$ calculated using any of the four basis sets under investigation could have been used with the experimental information to extract the second moments and other information without any ambiguity. This is in contrast to the results of semiempirical calculations which sometimes underestimate the value of $\langle c^2 \rangle$. All the second moments and the diamagnetic susceptibilities shown in Tables XV-XVIII are within the experimental error for all four basis sets used. This shows the great insensitivity of these properties to the electronic distribution calculated using a balanced basis set.

Rock and Flygare[107] have compared the second moments of formaldehyde and thioformaldehyde and explained the large increase in the in-plane moment $\langle a^2 \rangle$ on replacing oxygen by sulfur as being due to "the

TABLE XV

SECOND MOMENTS OF CHARGE FOR CO, H_2CO, CS AND H_2CS ($x10^{-16}cm^2$)[a]

Basis Set		CO	H_2CO	CS	H_2CS
STO-3G	$\langle a^2 \rangle$	6.805	10.260	14.241	20.482
	$\langle b^2 \rangle$	1.811	4.000	3.145	5.348
	$\langle c^2 \rangle$	1.811	2.170	3.145	3.421
4-31G	$\langle a^2 \rangle$	7.018	10.433	14.771	20.633
	$\langle b^2 \rangle$	2.058	4.183	3.734	5.859
	$\langle c^2 \rangle$	2.058	2.422	3.734	4.064
4-31G+NCPF's	$\langle a^2 \rangle$	6.832	10.298	14.435	20.427
	$\langle b^2 \rangle$	2.057	4.148	3.706	5.834
	$\langle c^2 \rangle$	2.057	2.401	3.706	4.008
4-31G+BPF's	$\langle a^2 \rangle$	6.918	10.339	14.527	20.466
	$\langle b^2 \rangle$	2.022	4.160	3.679	5.841
	$\langle c^2 \rangle$	2.022	2.368	3.679	3.989
DZSB[b]	$\langle a^2 \rangle$	7.095	10.474		
	$\langle b^2 \rangle$	2.094	4.174		
	$\langle c^2 \rangle$	2.094	2.456		
EDZNM[c]	$\langle a^2 \rangle$	6.907	10.340		
	$\langle b^2 \rangle$	2.108	4.164		
	$\langle c^2 \rangle$	2.108	2.433		
Expt'l	$\langle a^2 \rangle$	4.8 ± 0.2[d,f]	10.4[e]	10.3 ± 0.7[d,f]	21.1 ± 0.6[e]
	$\langle b^2 \rangle$		4.2		6.6 ± 0.5
	$\langle c^2 \rangle$		2.4		4.6 ± 0.4

[a] Appendix 1.

[b] Double zeta, Snyder Ref. 27.

[c] Double zeta plus NCPF's, Neumann, Ref. 36.

[d] $\langle a^2 \rangle - \langle b^2 \rangle$.

[e] Rock, Ref. 107.

[f] McGurk, Ref. 95.

[g] FSGO calculation of Nitzsche, Ref. 101, on H_2CS gave 20.4, 5.4 and 3.7 respectively.

TABLE XVI

SECOND MOMENTS OF CHARGE FOR HCOOH AND HCOSH ($x10^{-16}cm^2$)[a]

Basis Set		t-HCOOH	c-HCOOH	t-HCOSH	c-HCOSH
STO-3G	$\langle a^2 \rangle$	25.451	26.413	47.227	47.811
	$\langle b^2 \rangle$	7.650	7.219	10.378	10.166
	$\langle c^2 \rangle$	3.077	3.077	4.534	4.534
4-31G	$\langle a^2 \rangle$	26.315	26.858	48.373	48.717
	$\langle b^2 \rangle$	7.684	7.487	10.632	10.571
	$\langle c^2 \rangle$	3.500	3.500	5.318	5.311
4-31G+BPF's	$\langle a^2 \rangle$	26.026	26.664	48.016	48.437
	$\langle b^2 \rangle$	7.647	7.416	10.552	10.459
	$\langle c^2 \rangle$	3.410	3.418	5.199	5.193
DZSB	$\langle a^2 \rangle$	26.370[b]			
	$\langle b^2 \rangle$	7.740			
	$\langle c^2 \rangle$	3.467			
expt'l	$\langle a^2 \rangle$[e]	26.6±0.3[c]		47.7[d]	48.0[d]
	$\langle b^2 \rangle$	7.7±0.3		10.5±2.1	10.4±2.3
	$\langle c^2 \rangle$	3.5±0.2		5.3	5.5

[a] Appendix 1.

[b] Double zeta, Snyder, Ref. 27.

[c] Kukolich, Ref. 110.

[d] Pandey, Ref. 111.

[e] Principal axes for structures below.

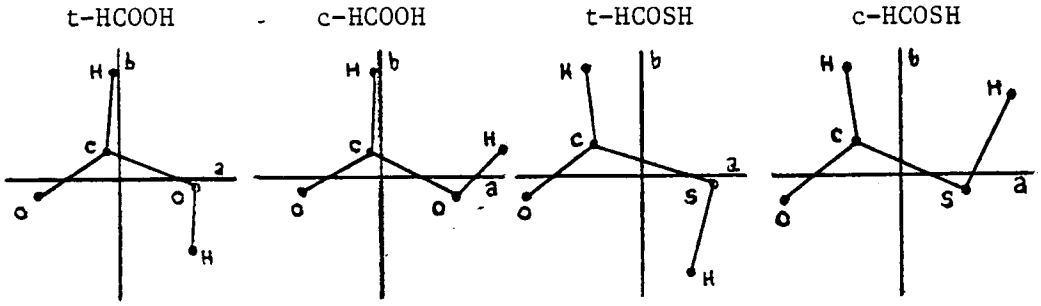

TABLE XVII

DIAMAGNETIC SUSCEPTIBILITIES FOR CO, H_2CO, CS AND H_2CS ($\times 10^{-6}$ erg/g^2 mole)[a]

BASIS SET		CO	H_2CO	CS	H_2CS
	χ^d_{aa}		-26.178		-37.203
STO-3G	$\chi^d_{\perp}$ χ^d_{bb}	-36.555	-52.739	-73.769	-101.409
	$\chi^d_{\parallel}$ χ^d_{cc}	-15.366	-60.503	-26.686	-109.583
4-31G	χ^d_{aa}		-28.020		-42.103
	$\chi^d_{\perp}$ χ^d_{bb}	-38.506	-54.539	-78.510	-104.787
	$\chi^d_{\parallel}$ χ^d_{cc}	-17.465	-62.011	-31.687	-112.407
4-31G+	χ^d_{aa}		-27.736		-41.762
NCPF's	$\chi^d_{\perp}$ χ^d_{bb}	-37.711	-53.796	-76.965	-103.677
	$\chi^d_{\parallel}$ χ^d_{cc}	-17.456	-61.262	-31.448	-111.425
4-31G+	χ^d_{aa}		-27.695		-41.706
BPF's	$\chi^d_{\perp}$ χ^d_{bb}	-37.930	-53.913	-77.171	-103.763
	$\chi^d_{\parallel}$ χ^d_{cc}	-17.158	-61.517	-31.150	-111.619
DZSB[b]	χ^d_{aa}		-28.140		
	$\chi^d_{\perp}$ χ^d_{bb}	-38.689	-54.859	---	---
	$\chi^d_{\parallel}$ χ^d_{cc}	-17.770	-62.157		
expt'l	χ^d_{aa}	-20.4±0.5[c]	-28.1[d]	-43.0±0.8[e]	-47.5±2.5[f]
	χ^d_{bb}		-54.3		-109.1±3.0
	χ^d_{cc}		-61.8		-117.6±3.4

[a] Appendix 1.

[b] Double Zeta Snyder, Ref. 27.

[c] $\chi^d_{\perp}$-$\chi^d_{\parallel}$s Gustafson, Ref. 112.

[d] Flygare, Ref. 106.

[e] $\chi^d_{\perp}$-$\chi^d_{\parallel}$, McGurk, Ref. 95.

[f] Rock, Ref. 107.

TABLE XVIII

DIAMAGNETIC SUSCEPTIBILITIES FOR HCOOH AND HCOSH ($\times 10^{-6}$ erg/g^{2}mole)[a]

Basis Set		t-HCOOH	c-HCOOH	t-HCOSH	c-HCOSH
STO-3G	χ^d_{aa}	-45.507	-43.680	-63.260	-62.367
	χ^d_{bb}	-121.026	-125.108	-219.592	-222.072
	χ^d_{cc}	-140.427	-142.680	-244.386	-245.964
4-31G	χ^d_{aa}	-47.444	-46.614	-67.671	-67.380
	χ^d_{bb}	-126.486	-128.792	-227.785	-229.213
	χ^d_{cc}	-144.237	-145.706	-250.329	-251.526
4-31G+ BPF's	χ^d_{aa}	-46.911	-45.962	-66.823	-66.401
	χ^d_{bb}	-124.882	-127.620	-225.765	-227.242
	χ^d_{cc}	-142.859	-144.583	-248.473	-249.863
DZSB	χ^d_{aa}	-47.544[b]			
	χ^d_{bb}	-126.581			
	χ^d_{cc}	-144.708			
expt'l	χ^d_{aa}	-47.6±0.8[c]		-67.0±5.7[d]	-67.2±6.0[d]
	χ^d_{bb}	-123.3±0.8	---	-224.6±5.7	-226.9±6.0
	χ^d_{cc}	-141.4±0.8		-247.0±6.0	-247.6±6.8

[a]Appendix 1.

[b]Double Zeta, Snyder, Ref. 27.

[c]Kukolich, Ref. 110.

[d]Pandey, Ref. 111.

large increase in the electron density along the a axis on replacing oxygen by sulfur." However, the calculations show that the difference is largely a result of the larger C=S bond distance and the increase in nuclear charge on the atom from 8 to 16 which causes the nuclear moment along the a axis to increase from $7.9 \times 10^{-16} cm^2$ in formaldehyde to $17.0 \times 10^{-16} cm^2$ in thioformaldehyde, i.e., the actual electronic redistribution on molecule formation plays little or no part in determining these properties.

4. Molecular Quadrupole Moments

Unlike the electronic second moments, and the diamagnetic susceptibilities discussed in the previous section, the molecular quadrupole moments do show a large sensitivity to basis set variation. This is because the nuclear term is subtracted out and the remaining electronic term, which is the difference between two terms of comparable magnitude, becomes sensitive to the electronic charge distribution in different directions in the molecule, and is particularly sensitive to the outermost parts of the wave function. Thus the quadrupole moments represent a very sensitive measure of the success of a basis set in depicting the subtle redistribution of charge on molecule formation.

Molecular quadrupole moments feature very strongly in theoretical expressions describing the long range potential needed to understand scattering phenomena such as electron scattering and gas phase broadening due to molecular collisions. Unfortunately, they are very difficult quantities to measure so that the computation of even approximate values of quadrupole moments is a very desirble goal for a theoretical method.

Recently, McCullough[113] has attempted to assess basis set and electron correlation errors in some very large basis sets in a number of diatomic molecules (HF, N_2, CO, NO^+ and F_2). He concludes that, even for basis sets substantially larger than those which were feasible for polyatomics, the calculations are rather unreliable. Moreover he could uncover no discernable pattern in the basis set errors and found that the total energy is a useless criterion for assessing quadrupole moment accuracy.

Contrary to these findings, Metzgar, in his work on hydrocarbons, their monosubstituted halogen (F and Cl) derivatives and on a number of interhalogen derivatives[41] found that the 431-G + BPF's results for molecular quadrupole moments followed experimental trends and the results are certainly accurate enough to be used in intermolecular interaction calculations. They also are probably more reliable than those "experimental" values extracted from experimental data by fitting a theoretical multipole expansion to observed scattering cross sections.

The results summarized in Tables XIX and XX are a natural extension of Metzgar's work to another group of compounds which are more anisotropic than those previously investigated. Also there are available a number of fairly carefully determined experimental values of the quadrupole moments of the molecules under study.

Unfortunately for CO and CS the experimental errors in the quadrupole moments are so large that all the basis sets give values within the experimental error range. However, McCullough[114,115] has developed a numerical method which he claims gives accurate Hartree Fock quadrupole moments for diatomic molecules. For CO he quotes a

TABLE XIX

QUADRUPOLE MOMENTS FOR CO, H_2CO, CS AND H_2CS ($x10^{-26}$esu cm^2)[a]

Basis Set		CO	H_2CO	CS	H_2CS
STO-3G	$\Theta_{\parallel}(\Theta_{aa})$	-3.028	-0.682	-3.957	0.228
	$\Theta_{\perp}(\Theta_{bb})$	1.689	0.296	1.978	-0.811
	(Θ_{cc})		0.287		0.584
4-31G	$\Theta_{\parallel}(\Theta_{aa})$	-2.861	-0.449	-3.663	2.264
	$\Theta_{\perp}(\Theta_{bb})$	1.430	0.370	1.831	-1.359
	(Θ_{cc})		0.079		-0.905
4-31G	$\Theta_{\parallel}(\Theta_{aa})$	-1.971	0.632	-2.185	3.062
+NCPF's	$\Theta_{\perp}(\Theta_{bb})$	0.986	0.165	1.092	-1.868
	(Θ_{cc})		-0.228		-1.195
4-31G	$\Theta_{\parallel}(\Theta_{aa})$	-2.557	-0.182	-2.755	2.840
+BPF's	$\Theta_{\perp}(\Theta_{bb})$	1.278	0.125	1.378	-1.850
	(Θ_{cc})		0.057		-0.992
DZSB[b]	$\Theta_{\parallel}(\Theta_{aa})$	-3.057	-0.406		
	$\Theta_{\perp}(\Theta_{bb})$	1.529	0.566		
	(Θ_{cc})		-0.159		
EDZMN[c]	$\Theta_{\parallel}(\Theta_{aa})$	-2.090	0.006		
	$\Theta_{\perp}(\Theta_{bb})$	1.045	0.250		
	(Θ_{cc})		-0.256		
expt'l	$\Theta_{\parallel}(\Theta_{aa})$	-2.0±1.0[d]	-0.1±0.3[e]	0.1±3.0[d]	3.0±0.7[e]
	$\Theta_{\perp}(\Theta_{bb})$	1.0±0.5	0.2±0.2	-0.05±1.5	-2.4±0.5
	(Θ_{cc})		-0.1±0.5		-0.6±1.1

[a]Appendix 1.

[b]Snyder, Ref. 27.

[c]Neumann, Ref. 36.

[d]Gustafson, Ref. 112.

[e]Rock, Ref. 107.

[f]FSGO calculation, Nitzsche, Ref. 100, for H_2CS gave 1.58, -0.58 and -1.04.

TABLE XX

QUADRUPOLE MOMENTS FOR HCOOH AND HCOSH ($x10^{-26}$esu cm^2)[a]

Basis Set		t-HCOOH	c-HCOOH	t-HCOSH	C-HCOSH
STO-3G	Θ^{b}	-5.574	-0.694	-4.967	-3.170
	Θ_{aa}	4.280	0.345	3.703	2.288
	Θ_{bb}	1.294	0.349	1.264	0.882
	Θ_{cc}				
4-31G	Θ	-8.628	-1.170	-7.976	-4.686
	Θ_{aa}	7.208	1.141	7.118	4.387
	Θ_{bb}	1.420	0.029	0.858	0.299
	Θ_{cc}				
4-31 +BPF's	Θ_{aa}	-7.543	-0.609	-6.742	-3.896
	Θ_{bb}	6.474	0.819	6.362	3.968
	Θ_{cc}	1.069	-0.210	0.380	-0.072
DZSB[c]	Θ	-8.925			
	Θ_{aa}	7.485			
	Θ_{bb}	1.440			
	Θ_{cc}				
expt'l	Θ_{aa}	-5.3±0.4[d]		-5.0±0.6[e]	-1.3±0.8[e]
	Θ_{bb}	5.2±0.4		5.8±0.5	4.1±0.8
	Θ_{cc}	0.1±0.4		-0.8±0.9	-2.8±1.2

[a]Appendix 1.

[b]See Table XVI for principal axes.

[c]Snyder, Ref. 27

[d]Kukolich, Ref. 110.

[e]Pandey, Ref. 111.

value of -2.058 esu cm^2.[113] The large EDZNM basis set calculation gives a value in very good agreement with this result. The results with no PF's are too negative by as much as thirty percent. The 4-31G + NCPF's also gives a good result but the addition of BPF's to the 4-31G calculation gives a very disappointing value. It accounts for only thirty percent of the change produced by the NCPF's. By contrast for formaldehyde the improvement introduced by the use of BPF's gives a value similar to that found in the corresponding EDZNM calculation. Again all three results are well within the error bounds quoted for the experimental data. For CS there have been no previous calculations and although the experimental error bounds are very great the STO-3G and 4-31G calculations are more negative than the lower experimental error bound (Table XIX, p 55). The 4-31G + BPF's again account for less than (60%) of the charge produced by using the NCPF's. For thioformaldehyde the experimental errors are much smaller so that again one can claim that the calculation without polarization functions give results which are not satisfactory, but upon adding either NCPF's or BPF's results are obtained which are within the experimental error bounds. These results demonstrate the very important point that a basis set found to be unsatisfactory for a diatomic molecule may be satisfactory for a polyatomic molecule and that the medium size basis sets we are proposing apparently give results similar to those obtained experimentally. Although the author agrees with McCullough[113] that this is probably due to a cancelling out of basis set and correlation error, this feature is a necessary evil of <u>all calculations on polyatomic molecules</u> for properties which are known to be dependent on correlation effects.

For the trans isomers of formic and thioformic acid, an unusual situation arises. The STO-3G calculations are in better agreement with experiment than are the other calculations! The 4-31G results (and the full DZ results) are too large and are not reduced enough to be satisfactory by the BPF's. The experimental results for the trans-thioformic acid are virtually identical to the results for the trans-formic acid whereas the theoretical calculations predict the (a) component to be less negative and the out of plane moment (c) of the compound be reduced accordingly. In the case of the cis-thioformic acid, there is a very serious disagreement between the experimental results and all the calculations. This could be resolved by interchanging the values quoted for the Q_{aa} and Q_{cc} (out-of-plane) components but the experimental assignments seem sound. It is possible that the error lies in the nuclear term for which the experimental geometry was used. It would have been better if a geometry search had been done but this would have been prohibitively expensive in computer time.

5. Electric Field Gradients

Calculated electric field gradients (EFG's) are a very valuable probe in investigating the electron density at a nucleus and how it changes when the molecular environment is changed. However, the detailed interpretation of experimental EFG's, which are derived from nuclear quadrupole coupling constants (NQCC's) is hindered by the need for values of certain parameters, such as the directions of the principal axes of the electric field gradient tensor, and the asymmetry parameter (defined in Appendix 1). Also, since most measurements of NQCC's are made in condensed phases, a knowledge of the factors

responsible for any differences between the gas phase and the liquid or solid phase would help the experimentalist a great deal in his task of deriving structural and bonding information from his experimental observations. These problems have recently been discussed by Gready[116] with respect to the interpretation of deuteron and oxygen coupling constants in the solid state. Most of the previous theoretical work has been on deuteron, nitrogen and chlorine EFG's and has been reviewed elsewhere.[117-119] Metzgar performed a number of calculations on D EFG's in hydrocarbons and halogen hydrocarbons and found, in accord with more recent work, that double zeta calculations alone gave values considerably higher than experimental values and even when NCPF's were added the results were improved but were still too high. However, when BPF's were added to a 4-31G set the results for EFG's of a number of hydrocarbons and their monohalogen derivatives were found by Metzgar to agree very well with experiments.[41] This work has been extended to include a number of other substituted hydrocarbons and again the results were in better agreement with experiment than the recent results of Snyder who added conventional NCPF's to his double zeta set specifically with the aim of getting good deuterium coupling constants, an endeavor in which he was only partially successful.[120]

The calculation of the nuclear quadrupole coupling constant of a deuteron attached to an oxygen and a sulfur atom offers a more severe challenge to the use of BPF's than do Metzgar's previous calculations on the coupling constants of D atoms attached to carbon. Moreover, in the case of <u>trans</u> formic acid,[121] good vapor phase experimental results are available and also very recently Gready has examined the

use of conventional polarization functions on several different basis sets in attempting to calculate all the EFG's and NQCC's in the two formic acid isomers for all the atoms so providing a wealth of data, using conventional calculations, against which to compare the effect of BPF's.[116]

6. Deuteron Coupling Constants

A detailed study of the general problem of the calculation of deuteron coupling constants (e^2q_aQ/h) from theoretically calculated EFG's (eq_a) will be presented in Chapter V. Here only the results on the two formic acids and the two thioformic acids will be presented (Tables XXI-XXII). Until recently the assignments of the two observed transitions in trans formic acid were in doubt. However, Kukolich[121,122] has now reversed his previous assignments so that his work, which assigns in the lowest frequency at 166 kHz and the second frequency at 272 kHz to the deuteron attached to the carbon and to the deuteron attached to the oxygen respectively, are in qualitative agreement with the order found in most theoretical calculations. There is little doubt that a knowledge and appreciation of calculations of the type presented here would have prevented the original misassignment.

Table XXI contains a comparison with experiment of the results of five different calculations of the deuteron EFG tensors along the appropriate principal axes, the asymmetry values, and θ, the angle of deviation from the bond axis of the principal EFG tensor component. It can be seen immediately that only the 4-31G + BPF's basis set agrees at all well with experiment. Even for the GDZ + PF basis, which is the

TABLE XXI

H ELECTRIC FIELD GRADIENTS, DEUTERON QUADRUPOLE COUPLING CONSTANTS FOR HCOOH ACID

	Basis Set	q_{zz}(a.u.)	q_{xx}(a.u.)	e^2qQ/h(KHz)[a]	η[a]	Θ[b](deg)
t-$H_\alpha COOH_\beta$						
for H_α	STO-3G	0.320	-0.159	215	0.004	0.32
	4-31G	0.304	-0.149	204	0.018	0.52
	4-31G+BPF's	0.235	-0.117	158	0.002	0.69
	GDZ[c]	0.310	-0.154	209	0.006	0.59
	GDZ+PF[d]	0.297	-0.147	199	0.008	0.57
	GDZD[e]	0.313	-0.155	210[f]	0.007	0.35
	expt'l			166[f]		
for H_β	STO-3G	0.451	-0.202	303	0.040	2.99
	4-31G	0.483	-0.215	325	0.109	3.48
	4-31G+BPF's	0.414	-0.190	278	0.080	2.61
	GDZ[c]	0.492	-0.219	330	0.111	3.70
	GDZ+PF[d]	0.469	-0.204	315	0.130	3.84
	GDZD[e]	0.477	-0.211	320[f]	0.114	3.40
	expt'l			272[f]		
c-$H_\alpha COOH_\beta$						
for H_α	STO-3G	0.302	-0.144	203	0.047	0.08
	4-31G	0.291	-0.135	195	0.069	0.05
	4-31G+BPF's	0.222	-0.105	149	0.058	0.14
for H_β	STO-3G	0.510	-0.228	342	0.103	0.48
	4-31G	0.537	-0.239	361	0.108	0.78
	4-31G+BPF's	0.469	-0.212	315	0.098	0.24

[a] Appendix 1.

[b] Angle of principal EFG tensor (q_{zz}) with respect to CH or OH bond.

[c] Gready, Ref. 116, using [4s2p/2s] contraction.

[d] Gready, Ref. 116, using [4s2p/2s1p] contraction.

[e] Gready, Ref. 116, using [5s3p/3s] contraction.

[f] Ruben, Ref. 121.

TABLE XXII

H ELECTRIC FIELD GRADIENTS, DEUTERON QUADRUPOLE COUPLING CONSTANTS FOR HCOSH

	Basis Set	q_{zz}(a.u.)	q_{xx}(a.u.)	e^2qQ/h(KHz)[a]	η[a]	Θ[b]
t-$H_\alpha COSH_\beta$						
for H_α	STO-3G	0.304	-0.149	204	0.022	0.06
	4-31G	0.300	-0.145	202	0.034	0.16
	4-31G+BPF's	0.229	-0.112	154	0.022	0.08
for H_β	STO-3G	0.258	-0.115	173	0.106	7.45
	4-31G	0.284	-0.124	191	0.277	7.35
	4-31G+BPF's	0.182	-0.076	122	0.168	6.14
c-$H_\alpha COSH_\beta$						
for H_α	STO-3G	0.304	-0.147	204	0.031	0.32
	4-31G	0.299	-0.143	201	0.043	0.55
	4-31G+BPF's	0.230	-0.112	155	0.024	0.40
for H_β	STO-3G	0.279	-0.123	187	0.119	10.83
	4-31G	0.302	-0.130	203	0.142	10.50
	4-31G+BPF's	0.197	-0.079	132	0.196	9.10

[a]Appendix 1.

[b]Angle of principal EFG tensor (q_{zz}) with respect to CH or SH bond.

most accurate calculation of Gready (i.e. her calculation no. 3), is in error by 26% compared to only 5% error for the BPF's result. In fact, Gready's best calculation is little better than the 4-31G calculation even though a full double zeta set with NCPF's on the deuterons was utilized. This result clearly demonstrates the importance of the electron distribution in the bond rather than on the atoms. This feature is one of the main characteristics of deuteron coupling constants. The relatively poor results obtained by Gready[116] and by Snyder[120] on other molecules shows that a single set of NCPF's is not adequate to describe the electron distribution in the X-H bond, whereas this seems to be achieved in a much more satisfactory manner by the addition of s type bond functions to the X-H bond for all X-H bonds.

The coupling constants of deuterons attached to third row elements are much smaller (about half) than those attached to the corresponding second row elements. Thus a deuteron attached to sulfur in HDS has a coupling constant of 155 kHz[71] compared to a value of 308 kHz observed in D_2O.[123] In qualitative agreement with this the BPF's calculations on the thioformic acids predict the sulfur deuterons to have coupling constants over 150 kHz lower than the corresponding oxygen deuterons. Moreover, the predicted magnitude of 122 kHz for the trans-isomer is in accord with the observed values of 154.7 and 149.0 kHz[72] observed for HSD and D_2S respectively. The slightly higher value of 132 kHz found for the cis isomer is accounted for by the shorter S-D distance found experimentally and used in the calculation. The large drop of about 70 kHz in the coupling constant on adding BPF's to the 4-31G basis set for these polyatomic molecules is similar to

that found for H_2S for which the BPF's calculation was in very good agreement with experiment (expt'l., 154.7 kHz, theor., 146 kHz). A previous calculation on H_2S using NC d orbitals as polarization functions gave a coupling constant too high by 24 Hz.[68]

7. Oxygen Coupling Constants

There are no experimental gas phase results for ^{17}O coupling constants in either formic acid or thioformic acid. The results for the former molecule are compared with the result of Gready's largest basis set calculation in Table XXIII the results for the latter molecule in Table XXIV. The η values for the hydroxyl oxygen (O_β) are in good agreement with Greadys while the η value for the BPF's calculation on the carbonyl oxygen is considerably larger, in agreement with Greadys suggestion that a more flexible basis set than those which she used would allow the electrons around the oxygen to adopt a more asymmetric (and more correct) configuration. The actual values of the EFG tensors are considerably smaller than Gready's values, which is expected, since she had concluded that the double zeta results considerably over-estimate the EFG tensors. Many corrections have to be made before the monomer gas phase values calculated in this work may be compared to the observed solid state values, which are much lower. This makes a comparison of the calculated values with experiment not very meaningful as a way of assessing the accuracy of wave functions. However, accurate values of the ^{17}O EFG tensors for gaseous formaldehyde, for CO, and for water vapor are known. The results for formaldehyde using the 4-31G + BPF's shown in Table XXV are very similar to those obtained by using the much larger EDZNM set.[36] Both

TABLE XXIII

^{17}O ELECTRIC FIELD GRADIENTS, NUCLEAR QUADRUPOLE COUPLING CONSTANTS IN HCOOH

	Basis Set	q_{zz}(a.u.)	q_{xx}(a.u.)	e^2qQ/h(MHz)[a]	η[a]	θ[b]
t-$HCO_\alpha O_\beta H$[c]						
for O_α	STO-3G[f]	-2.138	1.168	13.3	0.093	89.81
	4-31G[f]	-1.876	1.088	11.7	0.161	89.86
	4-31G+BPF's	1.678	0.614	10.4	0.268	89.43
	SBDZ[d]	-2.088	0.810	13.0	0.048	89.14
	GDZ[e]	-1.947	0.994	12.1	0.167	89.13
for O_β	STO-3G	2.128	-0.089	-13.3	0.916	38.58
	4-31G	1.648	-0.241	-10.3	0.708	34.21
	4-31G+BPF's	1.719	-0.343	-10.7	0.601	40.17
	SBDZ[d]	1.760	-0.276	-11.0	-0.686	33.58
	GDZ[e]	1.805	-0.269	-11.2	0.702	34.13
c-$HCO_\alpha O_\beta H$[c]						
for O_α	STO-3G[f]	2.156	+1.104	13.4	0.024	89.17
	4-31G	-1.992	+0.726	12.4	0.272	89.01
	4-31G+BPF[f]'s	-1.756	+1.192	10.9	0.358	89.14
for O_β	STO-3G	2.726	-0.172	13.9	0.846	37.24
	4-31G	1.717	-0.268	10.7	0.687	33.71
	4-31G+BPF's	1.782	-0.334	11a1	0.624	39.36

[a]Appendix 1.

[b]Angle of principal EFG tensor (q_{zz}) with respect to CO_α or CO_β bond.

[c]O_α is carbonyl oxygen, O_β is hydroxyl oxygen.

[d]Snyder, Ref. 27.

[e]Gready, Ref. 116.

[f]q_{xx} is the smaller in plane tensor, but not the smallest tensor in this case.

TABLE XXIV

^{17}O ELECTRIC FIELD GRADIENTS, NUCLEAR QUADRUPOLE COUPLING CONSTANTS IN HCOSH

	Basis Set	q_{zz}(a.u.)	q_{xx}(a.u.)	e^2qQ/h(MHz)[a]	η[a]	Θ[b]
t-HCOSH						
for O	STO-3G	-2.263	1.102	14.1	0.026	88.85
	4-31G	-2.142	0.766	13.3	0.285	87.91
	4-31G+BPF's	-1.952	0.636	12.2	0.349	88.22
c-HCOSH						
for O	STO-3G	-2.265	1.045	14.1	0.078	89.52
	4-31G	-2.175	0.704	13.5	0.353	88.39
	4-31G+BPF's	-1.958	0.570	12.2	0.418	88.64

[a]Appendix 1.

[b]Angle of principal EFG tensor makes with CO bond.

TABLE XXV

^{17}O ELECTRIC FIELD GRADIENTS AND NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR H_2CO, CO AND H_2O

	Basis Set	q_{zz}(a.u.)	q_{xx}(a.u.)	e^2qQ/h(MHz)[a]	η[a]
H_2CO	STO-3G	-2.444	0.913	15.223	0.253
	4-31G	-2.433	0.519	15.15	0.573
	4-31G+NCP's	-2.272	0.537	14.15	0.527
	4-31G+BPF's	-2.266	0.436	14.11	0.614
	DZSB[b]	-2.612	0.697	16.26	0.466
	EDZNM[c]	-2.270	0.404	14.14	0.644
	expt'l			12.37±0.01[d]	0.694
CO	STO-3G	0.067	0.034	0.417	
	4-31G	0.481	-0.240	2.995	
	4-31G+NCPF's	0.477	-0.224	2.783	
	DZSB[b]	0.303	-0.151	1.887	
	EDZNM[c]	0.697	-0.348	4.340	
	expt'l			4.48[e]	
H_2O	4-31G	-2.030	1.784	12.64	0.758
	4-31G+BPF's	-2.188	2.004	13.62	0.831
	DZSB[b]	-2.048	1.809	12.76	0.766
	RSHF[f]	-1.891	1.692	11.77	0.790
	RSHF+CI[g]	-1.778	1.580	11.07	0.777
	expt'l			10.17±0.07[h]	0.75±0.01

[a] Appendix 1.

[b] Snyder, Ref. 27.

[c] Neumann, Ref. 36.

[d] Flygare, Ref. 124.

[e] Flygare, Ref. 125.

[f] Using 37 CGTO basis set, Rosenberg, Ref. 39.

[g] Using 37 CGTO basis set including CI, Rosenberg, Ref. 9.

[h] Verhoeven, Ref. 126.

are in reasonable agreement with experiment and the effect of the BPF's is small. The results for a calculation on carbon monoxide do not agree well with experiment except for the EDZNM. The 4-31G + BPF's results are better than the results using 4-31G + NCPF's basis set but not as good as results of the the EDZNM set.

In the case of water the 4-31G + BPF's results are higher than the near Hartree-Fock results of Rosenberg and Shavitt and of the experiment. However, Rosenberg and Shavitt showed that correlation effects could account for a further change of at least 10% so the 431-G + BPF's results are about as good as one might expect to get for this property without a) enlarging the basis set considerably and b) introducing correlation effects by performing considerable configuration interaction.[39]

8. Potentials

The potential calculated at a nucleus is proportional to the expectation value $\langle \frac{1}{r} \rangle$ where r is the distance of an electron from the nucleus. There is considerable interest in this property because it can be linked to a) the total energy of a molecule[127,128] b) the experimentally determined electron density (from very accurate electron diffraction measurements)[128] c) the diamagnetic part of the nuclear magnetic resonance chemical shift[131] and d) to the ESCA chemical shifts or to changes in their core electron binding energy.[131,132]

The data given in Tables XXVI and XXVII for all structures show that the potential is usually a very insensitive property to changes in basis set. This insensitivity is implicit in the success of Flygare and Goodisman[133] and of later workers[134,135] in correlating the

TABLE XXVI

POTENTIALS AT THE NUCLEI FOR CO, H_2CO, CS, AND H_2CS (esu/cm)[a]

Basis Set		CO	H_2CO	CS	H_2CS
STO-3G	Φ(C)	-132.189	-131.233	-133.025	-132.095
	Φ(O,S)	-198.587	-199.613	-530.482	-531.004
	Φ(H)	---	-10.205	---	-10.326
4-31G	Φ(C)	-132.533	132.525	-132.712	-132.872
	Φ(O,S)	-201.514	-202.277	-536.660	-537.107
	Φ(H)	---	-9.595	---	-9.598
4-31G+NCPF's	Φ(C)	-132.712	-132.440	-132.806	-132.745
	Φ(O,S)	-201.546	-202.324	-536.630	-537.066
	Φ(H)	---	-9.775	---	-9.750
4-31G+BPF's	Φ(C)	-132.478	-132.401	-132.796	-132.818
	Φ(O,S)	-201.506	-202.335	-536.022	-536.485
	Φ(H)	---	-9.758	---	-9.727

[a]Appendix 1.

TABLE XXVII

POTENTIALS AT THE NUCLEI FOR HCOOH AND HCOSH (esu/cm)[a]

Basis Set		t-HCOOH	c-HCOOH	t-HCOOH	c-HCOSH
STO-3G	$\Phi(H_a)$[b]	-9.966	-8.991	-10.056	-10.038
	$\Phi(C)$	-130.701	130.684	-131.284	-131.253
	$\Phi(O_\alpha)$	-199.972	-199.889	-199.842	-199.792
	$\Phi(O_\beta,S)$	-199.430	-199.480	-530.297	-530.314
	(H_β)	-9.067	-9.996	-10.135	-10.055
4-31G	$\Phi(H_\alpha)$	-9.360	-8.262	-8.664	-8.685
	$\Phi(C^\alpha)$	-131.913	-131.911	-132.175	-132.166
	$\Phi(O_\alpha)$	-202.298	-202.356	-202.219	-202.224
	$\Phi(O_\beta^\alpha,S)$	-201.820	-201.872	-536.672	-536.678
	$\Phi(H_\beta)$	-8.264	-9.253	-9.371	-9.306
4-31G+BPF's	$\Phi(H_\alpha)$	-9.589	-8.412	-8.988	-9.014
	$\Phi(C^\alpha)$	-131.684	-131.729	-131.998	-131.988
	$\Phi(O_\alpha)$	-202.410	-202.420	-202.281	-202.281
	$\Phi(O_\beta^\alpha,S)$	-201.785	-201.819	-536.091	-536.102
	$\Phi(H_\beta)$	-8.440	-9.500	-9.592	-9.609

[a] Appendix 1.

[b] Subscripts refer to structures $H_\alpha CO_\alpha O_\beta H_\beta$ and $H_\alpha COSH_\beta$.

electrostatic potential with molecular properties. In some more recent work[136] on attempts to relate electrostatic potentials to molecular binding energies this insensitivity has been largely forgotten. Since the present work is largely focussed on molecular properties which are sensitive to basis set, the electrostatic potential will not be discussed further.

C. MULLIKEN POPULATIONS

The standard Mulliken population analysis were done using the ab initio wave functions generated in this work. The results obtained with the STO-3G, 4-31G, and 4-31G with BPF's, and where calculated, 4-31G + NCPF's are shown in Tables XXVIII-XXXI. The populations that would normally be assigned to the bond function centers have been divided equally between the two nuclei of the bond. Although this division may seem a rather arbitrary method of partitioning, so also is the partitioning of the bond density in the standard Mulliken analysis itself[137]. By treating the electron population in this way, a comparison can be made of the different methods. It should be pointed out, however, that the BPF's might not shift electron density in the same way as the NCPF's for a given molecule even though the population analysis could still be very similar. In general, the STO-3G basis set results in a smaller polarization of the bonds than the 4-31G basis. This parallels the dipole moment results discussed earlier. The polarization functions, whether NCPF's or BPF's, largely "correct" this tendency to over polarize the bonds when the 4-31G basis is used. All basis sets leave the carbon positive in CO and H_2CO and negative in CS and H_2CS. However, the basis sets are not consistent in the way

TABLE XXVIII

MULLIKEN POPULATIONS[a] OF CO AND H_2CO

	Basis Set			
	STO-3G	4-31G	4-31G+NCPF's	4-31G+BPF's
CO C π	0.573	0.476	0.500	0.507
σ	4.653	4.675	4.786	4.654
Total	5.799	5.626	5.786	5.668
O π	1.427	1.524	1.500	1.494
σ	5.347	5.325	5.214	5.345
Total	8.201	8.374	8.214	8.332
H_2CO H π			0.002	
σ	0.945	0.847	0.910	0.879
Total	0.945	0.847	0.912	0.879
C π	0.914	0.730	0.688	0.738
σ	5.003	5.112	5.075	5.130
Total	5.917	5.843	5.763	5.867
O π	1.086	1.270	1.307	1.262
σ	7.106	7.193	7.106	7.113
Total	8.192	8.462	8.413	8.375

[a]Appendix 1.

TABLE XXIX

MULLIKEN POPULATIONS[a] OF CS AND H_2CS

	Basis Set			
CS	STO-3G	4-31G	4-31G+NCPF's	4-31G+BPF's
C Π	0.544	0.538	0.548	0.614
σ	5.028	5.072	5.000	5.089
Total	6.116	6.147	6.096	6.318
S Π*	1.990	1.971	1.971	1.971
Π**	1.465	1.491	1.481	1.414
σ*	5.980	5.982	5.980	5.945
σ**	2.992	2.946	3.020	2.967
Total	15.884	15.853	15.904	15.682
H_2CS H Π			0.003	
σ	0.938	0.782	0.852	0.824
Total	0.938	0.782	0.855	0.824
C Π	0.930	0.839	0.821	0.906
σ	5.294	5.690	5.402	5.619
Total	6.225	6.528	6.254	6.525
S Π*	1.984	1.968	1.968	1.968
Π**	1.086	1.194	1.206	1.126
σ*	7.976	7.957	7.950	7.920
σ**	4.853	4.791	4.904	4.812
Total	15.899	15.909	16.035	15.826

[a]Appendix 1.

*Core electron population.

**Valence electron population.

TABLE XXX

MULLIKEN POPULATIONS[a] FOR HCOOH

		Basis Set		
		STO-3G	4-31G	4-31G+BPF
t-$H_\alpha C{:}O_\alpha O_\beta H_\beta$	H_α	0.930	0.784	0.825
	C π	0.908	0.706	0.723
	σ	4.823	4.691	4.738
	Total	5.732	5.397	5.461
	$O_\alpha \pi$	1.228	1.429	1.432
	$O_\alpha \sigma$	7.034	7.126	7.099
	Total	8.263	8.555	8.531
	$O_\beta \pi$	1.863	1.865	1.871
	$O_\beta \sigma$	6.435	6.831	6.662
	Total	8.298	8.696	8.508
	H_β	0.778	0.568	0.675
c-$H_\alpha C{:}O_\alpha O_\beta H_\beta$	H_α	0.953	0.823	0.860
	C π	0.926	0.742	0.757
	α	4.800	4.657	4.713
	Total	5.726	5.399	5.469
	$O_\alpha \pi$	1.203	1.384	1.368
	$O_\alpha \sigma$	7.037	7.131	7.020
	Total	8.240	8.515	8.388
	$O_\beta \pi$	1.872	1.874	1.885
	$O_\beta \sigma$	6.434	6.812	6.710
	Total	8.306	8.686	8.595
	H_β	0.776	0.577	0.688

[a]Appendix 1.

TABLE XXXI

MULLIKEN POPULATIONS[a] FOR HCOSH

		Basis Set		
		STO-3G	4-31G	4-31G+BPF's
t-$H_\alpha COSH_\beta$	H_α	1.015	0.855	0.839
	C Π	0.913	0.763	0.784
	σ	5.046	5.141	5.131
	Total	5.960	5.904	5.916
	O Π	1.174	1.359	1.367
	σ	7.048	7.144	7.115
	Total	8.222	8.503	8.481
	SΠ*	1.998	1.976	1.976
	Π**	1.914	1.902	1.873
	σ*	7.958	7.950	7.920
	σ**	3.992	4.127	4.066
	Total	15.863	15.955	15.834
	H_β	0.940	0.782	0.930
c-$H_\alpha COSH_\beta$	H_α	0.941	0.793	0.976
	C Π	0.924	0.787	0.791
	σ	5.031	5.132	5.126
	Total	5.955	5.920	5.917
	O Π	1.159	1.330	1.351
	σ	7.056	7.138	7.120
	Total	8.215	8.468	8.471
	S Π*	1.998	1.976	1.976
	Π**	1.919	1.907	1.880
	σ*	7.958	7.950	7.920
	σ**	3.986	4.082	4.009
	Total	15.861	15.915	15.795
	H_β	1.028	0.904	0.841

[a]Appendix 1.

*Core electron population.

**Valence electron population.

the sigma, and pi electrons are shifted. For example, in CO the STO-3G sigma populations are quite similar to both the 4-31G and the 4-31G + BPF's, differing by 0.02e or less, while the pi population is shifted onto the C in STO-3G more heavily than the others, by 0.07e to 0.10e per pi orbital. For CS, both the sigma and the pi population are similar for both the STO-3G and 4-31G basis set, and it is the 4-31G + BPF's calculation that shifts more electrons onto the carbon. For the H_2CO system, the STO-3G calculation shows a small positive charge on the H's and the C, but on going to the 4-31G calculation each H atom aquires a positive charge of 0.15e even though the total change on the C is less than 0.07e. So the increased polarization has been extended into the C=O bond thru both the sigma and pi orbitals. The polarization functions (both NCPF's and BPF's) redistribute this charge back towards the hydrogens, the NCPF's leave the carbon still more positive than the 4-31G calculation and the BPF's leave it less positive. Generally, the relative polarity of the carbonyl structure is maintained within a basis set, with the 4-31G + NCPF's the least consistent. With the latter basis set the carbonyl group C=O in H_2CO is more polar by 0.2e than for CO. In the case of H_2CS, the CH bond decreases in polarity in the order

4-31G>4-31G+BPF's>4-31G+NCPF's>STO-3G.

For the two isomers of formic acid the polarization of the bonds is very pronounced for the 4-31G compared to the STO-3G results but the bond polarization is reduced with the addition of bond functions. The polarization functions affect the 4-31G calculation mainly in the sigma orbitals, leaving the pi system still more polarized than for the

STO-3G results. A comparison of the trans and cis isomers of formic acid for the same basis set shows a consistent set of charges with only small changes in net charge, mainly on the hydrogens. For the thioformic acid isomers the calculations do not show quite the same uniformity as in the formic acid pair. The STO-3G and 4-31G calculations show a small shift of electronic charge away from the H on C in the trans form (~ 0.07e) to the thiol hydrogen in the cis isomer. The 4-31G + BPF's calculation has the carbon H gaining electrons from both the thiol H and from the sulfur itself. The use of the Mulliken analysis to assign partial charge on atoms and groups of atoms does not appear to be possible, given the lack of consistency among the basic sets.

CHAPTER IV

NITRO COMPOUNDS

A. INTRODUCTION

An analysis of the literature reveals that most basis sets of at least minimum basis set size give reasonable results in calculating molecular properties of hydrocarbons, but that problems develop as soon as heteroatoms are introduced.[138,139] Some of these problems were discussed in Chapter III for molecules whose polarity is not too large. Nitro compounds, because of their extreme polar character compared to other covalent molecules, might be expected to reveal more clearly than the molecules of Chapter III, any deficiencies in the proposed medium sized basis set (4-31G+BPF's) in calculating molecular properties. Such calculations form the subject of this chapter. The molecules discussed are the NO_2 radical, the series XNO_2 (where X = H, CH_3, F and OH) and the NO_2^- and NO_3^- anions.

The only one of these molecules for which there has been any attempt to perform a systematic study of molecular properties is the NO_2 radical. Of the many previous papers on this molecule two are relevant to the present study. A paper by Rothenburg and Schaefer[140] contains values of many molecular properties calculated with a full double zeta basis set (Dunning [4s/2p]) and the DZ basis set adding a set of d type NCPF's. Later, Jackels and Davidson[141] reported molecular properties obtained with a similar [4s/2p] double zeta set, but they also augmented it by an unusual type of polarization function consisting of two sets of four s type gaussians arranged in a

clover-leaf pattern at the mid points of the N-O bonds and in planes perpendicular to these bonds, i.e. a set of gaussian lobe BPF's. They also reported the effect of configuration interaction (2962 configurations) (CI) on the molecular properties thus providing a very valuable set of reference calculations against which calculations performed without CI can be evaluated. Since these results provide a unique reference set with which to evaluate smaller basis sets, the first part of this chapter is devoted to comparing the results of different basis sets for the $\cdot NO_2$ radical. Then, based on this brief study a more extensive study of the results for the other XNO_2 molecules is reported for individual properties, and finally selected properties of NO_2^- and NO_3^- are presented.

B. NITROGEN DIOXIDE

1. Multipole Moments

The dipole moment has been frequently used in the past as the sole one-electron molecular property against which to evaluate the performance of a basis set. The results of Table XXXII are a prime example of the folly of relying only on this one property as a criterion for producing a satisfactory wave function. The STO-3G calculation is the only calculation, out of the six Hartree-Fock level calculations displayed, which gives a dipole moment in reasonable agreement with experiment. However the result of the seventh calculation which includes CI demonstrates that the good agreement obtained with the STO-3G basis set is due to a remarkable cancellation of the basis set deficiencies by the unusually large effect of CI on the

TABLE XXXII

MULTIPLE MOMENTS OF $\cdot NO_2$

			STO-3G	4-31G	DZ+BPF's[b]	RSDZ[c]	RSDZ[c] + NCBF's	JDSCF[d]	JDCI[d]	expt'l
μ	debyes		0.241	0.698	0.801	0.76	0.79	0.79	0.45	0.316 ± 0.01[e]
Θ_{aa}[a]	$\times 10^{-26}$	esu cm^2	0.994	1.941	1.620	2.04	1.48			$\{0.294$[f]
Θ_{bb}	$\times 10^{-26}$	esu cm^2	-3.323	-5.018	-4.142	-5.14	-3.65			
Θ_{cc}	$\times 10^{-26}$	esu cm^2	2.329	3.077	2.522	3.10	2.17			
$\langle a^2 \rangle$	$\times 10^{-16}$	cm^2	3.936	4.307	4.204	4.31	4.23	4.22	4.27	
$\langle b^2 \rangle$	$\times 10^{-16}$	cm^2	22.802	23.480	23.270	23.57	23.21	23.05	23.23	
$\langle c^2 \rangle$	$\times 10^{-16}$	cm^2	2.696	3.100	3.025	3.10	3.08	3.04	3.04	

[a] Axis a along C_{2v} axis, b in plane, c $\perp$ to NO_2 plane.

[b] Dunnings [4s2p/2p] basis set plus BPF's.

[c] Rothenburg, Ref. 140.

[d] Jackels, Ref. 141.

[e] Hodgson, Ref. 142.

[f] Esterwitz, Ref. 143.

dipole moment. This large effect is at least partly due to the open shell character of the $\cdot NO_2$ molecule which means that Brillouin's theory is no longer valid and there are a number of low lying singly and doubly excited configurations which undergo considerable mixing with the original ground state of $^2A_1$ symmetry. Thus when the basis set is improved at the Hartree Fock level the dipole moment changes dramatically to a value of 0.8 debyes, which is more than twice the size of the experimentally observed value. CI then reduces this value by 45 percent so restoring agreement with experiment. Experimental results for the second moments and molecular quadrupole coupling constants of NO_2 are not available. However, a comparison of columns seven and eight for the second moments show that the effect of CI on this property is negligible. Comparison of column two (STO-3G) with the other results for the second moments demonstrates once again the inadequacy of this basis set for even the second moments, even though this property is one of the most insensitive properties with respect to basis set change. The similarity of the results of column three (4-31G) and column five (RSDZ, Dunning basis set) show once again the equivalence of the double zeta split valence set and a full double zeta set.

2. Electric Field and Electric Field Gradient

The two remaining properties, namely the Hellmann-Feynman Force (HFF) and the electric field gradients (EFG's) which are sensitive to basis set changes are tabulated in Table XXXIII. The importance of the size of the residual HFF at each atom as a criterion for the evaluation of basis sets are discussed in the previous chapter. As expected from

TABLE XXXIII

MOLECULAR PROPERTIES OF $\cdot NO_2$ AT THE NUCLEI

Property	STO-3G	4-31G	DZ+BPF's	RSDZ[b]	RSDZ+NCPF's[b]	JDSCF[c]	JDCI[c]	expt'l
Hellmann Feynman Force (au)[a]								
F_x(N)	-1.432	-1.041	-0.344	-1.02	-0.31	-0.336	-0.469	
F_x(O)	1.086	0.869	0.446	0.85	0.38	0.464	0.432	
F_y(O)	2.897	2.179	0.987	2.22	0.92	1.120	1.120	
Total x	0.740	0.697	0.548	0.68	0.45	0.592	0.395	
Electric Field Gradient (au)[a]								[d]
q_{xx}(N)	0.699	0.801	0.928	0.850	0.790	0.819	0.750	0.930
q_{yy}(N)	-0.525	0.112	-0.142	-0.059	0.054	0.053	-0.210	-0.245
q_{zz}(N)	-0.174	-0.914	-0.787	-0.791	-0.844	-0.872	-0.540	-0.688[e]
q_{xx}(O)	0.801	0.969	1.024	1.092	0.977	1.087	0.993	0.672
q_{yy}(O)	-1.277	-1.074	-1.045	-1.268	-1.078	-1.013	-0.949	-0.702
q_{zz}(O)	-0.476	0.106	0.020	0.176	0.102	-0.074	-0.044	0.030
q_{xy}(O)	-1.507	-1.529	-1.472	-1.744	-0.575	-1.633	-1.388	

[a]Appendix 1.

[b]Rothenburg, Ref. 140.

[c]Jackels, Ref. 141.

[d]Lees, Ref. 144 converted from NQCC values using 1 a.u. = 3.66 MHz.

[e]Foster, Ref. 145, converted from NQCC values using 1 a.u. = 6.01 MHz.

the previous work the STO-3G basis gives the highest and the CI calculation gave the lowest total residual force. However the total residual force for even the best calculation is still considerable (0.395 a.u.) supporting the idea that a value of about ±0.5 a.u. is about the best one has any right to expect for a basis set which is of a size that is practical for use with molecules of more than three multielectron atoms. The addition of BPF's to the double zeta set results in considerable reduction of the force, although for the oxygen atom the residual force in the y direction is still higher than one would desire. This finding is in agreement with the conclusions reached in the previous chapter that there is room for improvement in the oxygen basis set. However a comparison of columns four and six show that the reduction in residual force using the BPF's with the double zeta basis set is about the same as that achieved by using NCPF's and is better than the results of Jackels and Davidson (column seven) utilizing gaussian lobe BPF's. It should also be noted that even the inclusion of extensive CI (column eight) left a $F_y(O)$ value of 1.12 a.u. compared to the DZ+BPF value of 0.987 a.u.

The EFG's are found to be more influenced by including CI. The magnitude of the change, however, is very strongly dependent on the particular tensor component under consideration. It's effect on the EFG at the oxygen is considerably greater than its effect on the nitrogen tensors. The effect of CI on the smaller components is considerable and for $q_{yy}(N)$ it changes the sign. However, even the CI results differ considerably from experiment.

3. Mulliken Population

The Mulliken population analyses are reported in Table XXXIV. They show the transfer of about half an electron from the nitrogen to the two oxygens. The STO-3G calculation predicts the smallest amount of charge transfer which is consistent with the small dipole moment predicted from this calculation. However for the other calculations there is no relationship between the amount of electron transfer and the size of the dipole moment indicating that terms other than the simple charge term are important in determining the dipole moment. For example the atomic charges in the DZ+NCPF's calculation are very similar to atomic charges found in the CI calculation but the dipole moment expectation value for the latter calculation (0.45D) is only about one half of the value from the former calculation (0.79D).

In view of the attempts later in the chapter to relate substituent effects in terms of the Mulliken populations it is comforting to point out that the gross electronic populations on the N and O atoms are similar for all three calculations using PF's, i.e., the Mulliken population does not in this case depend very much on the type of PF used.

C. XNO_2 SERIES

1. Multipole Moments

As in the previous chapter the first one-electron properties to be discussed are the multipole moments, i.e., the expectation values $\langle r^n \rangle$ n=1,2. The dipole moments, n=1 are reported in Table XXXV. Experimental values are known for several of the nitro compounds but

TABLE XXXIV

MULLIKEN POPULATION ANALYSIS FOR $\cdot NO_2$[a]

	Basis Set						
	STO-3G	4-31G	DZ+BPF's[b]	RSDZ[c]	RSDZ+NCPF's[c]	JDSCF[d]	JDCI[d]
on N σ	5.757	5.443	5.658			5.36	5.27
Π	1.025	0.934	0.963			0.91	1.01
Total	6.782	6.377	6.621	6.548	6.537	6.275	6.384
on O1,O2 σ	6.621	6.778	6.671			6.74	6.72
Π	1.488	1.533	1.518			1.53	1.48
Total	8.109	8.311	8.189	8.226	8.232	8.278	8.195

[a]Appendix 1.

[b]Dunnings [4s2p/2s] basis augmented with BPF's, the populations on the bond functions divided equally and given to the nuclei of the bond.

[c]Rothenburg, Ref. 140.

[d]Jackels, Ref. 141, the populations in the bond functions are not assigned to the nuclei.

TABLE XXXV

DIPOLE MOMENTS OF XNO_2 COMPOUNDS (debye)[a]

Basis Set	HNO_2	CH_3NO_2	$HONO_2$	FNO_2
STO-3G	2.488	3.087	0.850	0.575
4-31G	3.545	4.540	2.832	-0.155
4-31G+BPF's	3.178	3.941	2.732	
HPSTO-3G[b]		3.58		
expt'l		3.46[c] ±0.02	2.16[d]	0.466[e] ±0.005

[a]Appendix 1.

[b]Hehre, Ref. 90.

[c]Tannenbaum, Ref. 146.

[d]Millen, Ref. 147.

[e]Legon, Ref. 63.

previous calculations exist only for nitromethane and nitrogen dioxide. A previous STO-3G calculation on nitromethane by Hehre and Pople[90] used a standardized molecular geometry which differed from the experimental structure used in the present calculation by small amounts (1 percent in CN and NO bond lengths and 4 percent in the NO_2 angle), this reported dipole moment differed by 10 percent from the present STO-3G calculation. The excellent agreement of their result with experiment should then be considered somewhat fortuitous. Even so, the present STO-3G underestimates the dipole moment by 11 percent contrasted with the 14 percent and 31 percent overestimation by the 4-31G+BPF's and 4-31G basis sets, respectively.

For nitric acid no other ab initio calculations of molecular properties are known. Here the STO-3G basis has seriously underestimated (by 60 percent) the dipole moment while the 4-31G and 4-31G+BPF's again overestimate it; (by 30 percent and 26 percent respectively). For nitryl fluoride there is an intriguing contrast. The dipole moments of the STO-3G and 4-31G results differ in direction with the STO-3G result giving the "normal" ($X^+NO_2^-$) polarity and the 4-31G the opposite. Unfortunately, no converged 4-31G+BPF's calculation is available at present. Since the addition of the BPF's normally reduce the bond polarities, the calculated dipole moment could be quite small. The direction of the experimental moment is not known, but Legon and Millen[63] interpret similarities in the NO_2 structure for nitric acid, nitryl chloride and nitryl fluoride as an indication of a "greater contribution of an ionic structure $O_2N^+F^-$ to the ground state of nitryl fluoride."[63] Naive electronegativity arguments do

lead to the idea of a dipole whose negative end is toward the fluorine, supporting the direction predicted by the 4-31G basis. Also, others have noted that the STO-3G basis set does a poor job at producing dipole moments of fluoro-substituted molecules.[90]

Experimental second moments of electronic charge, shown in Table XXXVI, have been determined only for nitromethane.[108] Although the 4-31G+BPF's results agree the best with experiment, all three calculations give values within experimental uncertainties. The molecular quadrupole moments are known to be far more sensitive to basis set than the second moment. Table XXXVII gives the calculated and known experimental values for the XNO_2 series. Here again the agreement of the 4-31G+BPF's values with experiment is excellent for nitromethane, with the 4-31G values, as usual, too high and the STO-3G values too low.

2. Forces and Electric Field Gradients

Tables XXXVIII through XL show the HFF for the XNO_2 series. The trend of a reduction of residual forces with increasing basis set size established for the carbonyl and thiocarbonyl compounds is clearly repeated here. However, the previously noted unfavorable result of an unbalanced reduction of forces on the heavy atoms does not appear. Indeed, the net forces for nitromethane are among the lowest published for a molecule of such size and polarity.[27] The major reductions in forces on increasing the basis set occurs on the oxygens. For nitromethane the 4-31G basis gave larger forces on the carbon and nitrogen than the STO-3G, and even the 4-31G+BPF's gave a higher carbon residual force. However, it is encouraging to find that the net total force on the structure is dramatically reduced on adding the polarization

TABLE XXXVI

SECOND MOMENTS FOR XNO_2 COMPOUNDS ($x10^{-16}cm^2$)[a]

Basis Set		HNO_2	CH_3NO_2	$HONO_2$	FNO_2
STO-3G	$\langle a^2 \rangle$[b]	6.055	31.665	25.920	25.290
	$\langle b^2 \rangle$	22.726	25.603	24.448	23.573
	$\langle c^2 \rangle$	2.862	5.680	3.802	3.506
	$\langle ab \rangle$			0.507	
4-31G	$\langle a^2 \rangle$	6.284	31.942	26.509	26.089
	$\langle a^2 \rangle$	23.468	26.375	25.105	24.205
	$\langle c^2 \rangle$	3.292	6.138	4.405	4.038
	$\langle ab \rangle$			0.253	
4-31G+BPF's	$\langle a^2 \rangle$	6.068	31.827	26.272	
	$\langle b^2 \rangle$	23.345	26.056	24.830	
	$\langle c^2 \rangle$	3.158	6.028	4.243	
	$\langle ab \rangle$			0.304	
expt'l	$\langle a^2 \rangle$		31.95[c]		
	$\langle b^2 \rangle$		26.09±0.8		
	$\langle c^2 \rangle$		6.03		

[a] Appendix 1.

[b] $\langle a^2 \rangle$ along C_{2v} axis, $\langle b^2 \rangle$ in NO_2 plane, $\langle c^2 \rangle \perp$ to NO_2 plane.

[c] Hamer, Ref. 108.

TABLE XXXVII

QUADRUPOLE MOMENTS OF XNO_2 COMPOUNDS ($x10^{-26}$esu cm^2)[a]

Basis Set		HNO_2	CH_3NO_2	$HONO_2$	FNO_2
STO-3G	Θ_{aa}[b]	3.578	1.783	0.202	0.039
	Θ_{bb}	-5.194	-4.506	-2.474	-3.336
	Θ_{cc}	1.615	2.723	2.272	3.297
4-31G	Θ_{aa}	-5.297	3.406	0.402	-1.003
	Θ_{bb}	-7.181	-6.452	-2.770	-3.174
	Θ_{cc}	1.884	3.046	2.368	4.177
4-31G+BPF's	Θ_{aa}	4.684	2.904	0.489	
	Θ_{bb}	-6.314	-5.480	-2.892	
	Θ_{cc}	1.629	2.576	1.913	
expt'l	Θ_{aa}		2.67±0.6[c]		
	Θ_{bb}		-5.37±0.6		
	Θ_{cc}		2.70±0.9		

[a] Appendix 1.

[b] Axes as in Table XXXVI (p 89).

[b] Hamer, Ref. 108.

TABLE XXXVIII

FORCES ON THE NUCLEI FOR CH_3NO_2[a]

Property	Basis Set STO-3G	4-31G	4-31G+BPF's
F_y(H1)[b]	0.050	0.062	0.015
F_z(H1)	0.018	0.018	0.006
F_y(H2,H3)	-0.026	-0.032	-0.010
F_z(H2,H3)	0.021	0.022	0.009
F_y(C)	0.018	0.019	0.020
F_z(C)	0.207	0.266	0.248
F_y(N)	-0.002	-0.001	-0.000
F_z(N)	0.280	0.490	0.183
F_y(O1)	-2.666	-1.925	-0.489
F_z(O1)	-1.408	-1.047	-0.249
F_y(O2)	2.660	1.921	0.487
F_z(O2)	-1.398	-1.042	-0.242
Total y	0.006	0.011	0.013
Total z	-2.260	-1.272	-0.035

[a]Appendix 1.

[b]H1 is in the plane and cis to O1, trans to O2.

TABLE XXXIX

FORCES ON THE NUCLEI FOR $HONO_2$

Property	Basis Set STO-3G	4-31G	4-31G+BPF's
F_y(H1)	-0.092	-0.112	-0.109
F_z(H1)	0.048	0.052	0.029
F_y(O1)	2.379	1.510	1.379
F_z(O1)	1.732	1.356	0.133
F_y(N)	-0.022	0.004	0.032
F_z(N)	0.116	0.125	0.026
F_y(O2)	-2.804	-2.018	-0.478
F_z(O2)	-1.449	-1.108	-0.339
F_y(O3)	2.953	2.124	0.540
F_z(O3)	-1.303	-0.944	-0.246
Total F_y	2.414	1.508	1.364
Total F_z	-0.856	-0.519	-0.423

[a]Appendix 1.

TABLE XL

FORCES ON THE NUCLEI FOR HNO_2 AND FNO_2[a]

Property		Basis Set STO-3G	4-31G	4-31G+BPF's
H-NO_2	F_z(H)	0.106	0.099	0.024
	F_z(N)[b]	0.117	0.397	0.108
	F_y(O)	2.669	1.948	0.484
	F_z(O)	-1.407	-1.055	-0.312
Total	F_z	-2.591	-1.614	-0.492
FNO_2	F_z(F)	2.273	1.646	
	F_z(N)	0.320	0.263	
	F_y(O)	3.129	2.268	
	F_z(O)	-1.231	-0.888	
Total	F_z	0.131	0.133	

[a]Appendix 1.

[b]The two equivalent oxygens have equal F_y values but of opposite sign.

functions; even though the NO diatomic fragment used to obtain the bond function parameters must be considered quite changed in the XNO_2 structure.

Both the deuteron and nitrogen-14 quadrupole coupling constants have been measured experimentally for nitromethane,[148,149,151-154] and at least the nitrogen values are known for the other $X-NO_2$ species.[63,147] The ^2H and ^{14}N electric field gradients calculated for the $X-NO_2$ series are shown in Tables XLI-XLIII along with the available experimental values. The STO-3G and 4-31G basis sets overestimate the deuteron quadrupole coupling constants (DQCC) by about 23 percent, the same amount noted by Snyder[120] using full DZ basis sets on several simple molecules. The 4-31G+BPF's gives a value about 1 percent low, which is better than Snyder's result using a DZ plus d and p NCPF's basis. Moreover, the BPF's are more efficient than the NCPF's in producing comparable improvements to the DZ basis set. Only about one half as many additional BPF's functions are used for structures like nitromethane or nitric acid compared to the required NCPF's. The DQCC for nitric acid has not yet been determined experimentally. However, other deuterons bonded to oxygen have been found to give rise to measured DQCC values in a range from 272 kHz for CHOOD[121] to 308 kHz for HDO.[123] Here the 4-31G+BPF's basis set has not reduced the 4-31G value by about 50 kHz as it has for other compounds. However, the 4-31G+BPF's calculation does show significant changes in both the asymmetry factor η and the angle the principle tensor makes with the bond compared to the smaller basis sets.

TABLE XLI

H ELECTRIC FIELD GRADIENTS, DEUTERON QUADRUPOLE COUPLING CONSTANTS FOR X-NO_2 COMPOUNDS

	Basis Set	q_{zz}(au)	q_{xx}(au)	e^2Q/h(kHz)[a]	η[a]	θ[b](deg)
CH_3NO_2[c]	STO-3G	0.314	-0.150	212	0.042	0.75
	4-31G	0.318	-0.145	215	0.09	1.08
	4-31G+BPF's	0.253	-0.114	171	0.10	1.35
	expt'l			173[d]		
$HONO_2$	STO-3G	0.480	-0.202	324	0.157	2.45
	4-31G	0.497	-0.207	335	0.166	3.01
	4-31G+BPF's	0.496	-0.220	335	0.112	0.94

[a]Appendix 1.

[b]Angle of principal EFG tensor (q_{zz}) with respect to CH or OH bond.

[c]H in plane used. Other H's closely agree.

[d]Rinne, Ref. 148.

TABLE XLII

^{14}N NUCLEAR QUADRUPOLE COUPLING CONSTANTS FOR NITROMETHANE (kHz)[a]

e^2qQ/h(kHz)[b]	Method	Source
1350	NMR on liquid	Moniz, Ref. 151
1450	NQR on liquid crystal	Geracé, Ref. 152
1050	NMR on liquid	Lenles, Ref. 153
1180	MW on vapor	Cox, Ref. 149
1695	NQR on liquid	Subbaro, Ref. 154

[a]Appendix 1.

[b]Principal tensor only.

TABLE XLIII

^{14}N ELECTRIC FIELD GRADIENTS FOR X-NO_2 COMPOUNDS[a]

	Basis Set	q_{aa}(a.u.)	q_{bb}(a.u.)	q_{cc}(a.u.)	θ(deg)
H-NO_2	STO-3G	0.420	-0.237	-0.183	
	4-31G	-0.544	0.137	0.406	
	4-31G+BPF's	-0.618	0.167	0.451	
CH_3NO_2	STO-3G	0.089	0.242	-0.331	
	4-31G	-0.472	-0.159	0.631	
	4-31G+BPF's	-0.550	-0.184	0.733	
	expt'l[c]	-0.644	-0.154	0.480	
$HONO_2$	STO-3G	0.195	0.165	-0.3609	16.53
	4-31G	0.119	-0.463	0.349	1.79
	4-31G+BPF's	0.088	-0.553	0.465	0
	expt'l[e]	0.584	-0.524	-0.060	
F-NO_2	STO-3G	0.106	0.259	-0.365	
	4-31G	0.452	-0.580	0.120	
	expt'l[f]	0.382	0.818	-1.200	

[a]Appendix 1.

[b]q_{aa} along NO_2 bisector, q_{bb} parallel to O-O, q_{cc} out of plane see Table XLIX.

[c]Angle principal axis makes with N-OH bond in nitric acid.

[d]Cox, Ref. 149, conversion factor 1 a.u. = 3.66 MHz.

[e]Millen, Ref. 147, conversion factor 1 a.u. = 3.66 MHz.

[f]Legon, Ref. 63, conversion factor 1 a.u. = 3.66 MHz.

The ^{14}N-NQCC for nitromethane has been determined several times with no consistent result (see Table XLII, p 96). One of the major difficulties present in the experiments is the assignment of the major axis. Without the use of single crystal studies, which can definitely fix the orientation of the largest electric field gradient value, arguments based on the electron population of the various bonds using the Townes-Dailey approximation[91] are used to assign the directions of the tensors. In this approximation the occupation numbers of the nitrogen p-orbitals are related to the q value through the equation

$$q_{zz} = \bar{\Sigma} N_i[n_{zi} - 1/2 (n_{xi} + n_{yi})]q_p \qquad (28)$$

where N_i is the number of nitrogen electrons in the bond described by the ith hybrid orbital, nx, ny nz are the weights of the px, py and pz orbitals in the hybrid and qp is the electric field gradient of a single p electron. Subbarao and Bray[155] recently restudied several $-NO_2$ compounds including nitromethane in order to fix the EFG direction using this approximation and concluded that the assignment of the major EFG tensor should be different from that previously given by Cox.[149]

It would be helpful if an ab initio theoretical determination of the EFG's with an adequate basis set could be used in place of the simpler rationale. Even if the EFG tensors are not calculated well in absolute terms a useful trend might be available. Table XLIII (p 97) shows the X-NO_2 series results. First, the STO-3G basis set does not produce EFG's at all consistent with either the 4-31G, the 4-31G+BPF's or where available, the experimental values. This basis

set was very insensitive to the large changes occurring in the electronic environment of the N atoms as the X group changed. For nitromethane, at least, the relative values of the EFG tensors are partially reproduced using the two larger basis sets, except for the magnitude of the out of plane tensor. However a comparison of the experimental values for $HONO_2$ and FNO_2 with those calculated using 4-31G or 4-31G+BPF's basis sets is quite disappointing with no pattern emerging. Cox[58,149] has argued that there is a pattern to the EFG's for $X-NO_2$ compounds if one considers the molecule to be composed of valence structures including the nitrite ion, $X^+NO_2^-$, with the nitrite like electron distribution making the major contribution to the molecular EFG value. Although the structures of nitric acid and nitryl fluoride are similar to nitromethane, the ^{14}N EFG's for these compounds differ greatly from nitromethane and from each other.

The one pattern that does appear in comparing the absolute values of the experimental q_{aa} and q_{bb} is the decrease in q_{aa} and the increase in q_{bb} that accompanies the increase in the polarity of the X substituent as the group attached to the NO_2 changes from CH_3 to OH to F. Even the $\cdot NO_2$ structure fits this trend, if one considers the single electron on the NO_2 group as being less electronegative than CH_3. The out of plane values q_{cc} do not fit any discernable pattern. None of the basis sets reproduce the apparent trend in q_{aa} and q_{bb}. Two other points should be made: (1) Tetravalent nitrogen poses a serious test of the method. Calculations on heterocyclics by Kochanski and Lehn[156] and more recently by Sheps[157] indicate that calculations on divalent nitrogen agree much closer to experiment than

do those on trivalent nitrogen. The basis sets used in this study are of similar quality to those used in ref. 156 but they fail (especially in the pi type tensor) to compare well with experiment. This indicates a lack of sufficient flexibility to accommodate this type of system (tetravalent nitrogen). Perhaps the 4-31G basis set is too inflexible even for correction by the BPF's for this property or perhaps the NO fragment used for the BPF's optimization is not applicable to this system. (2) The inclusion of CI, which proved useful for $\cdot NO_2$ is not a universal panacea as shown by Rosenberg and Shavitt for water.[39] More work needs to be done with this problem using a DZ basis set such as the 4-31G/4-31G+BPF's as a starting point.

3. Mulliken Population Analyses

One of the more difficult problems in the discussion of the polarity of molecules is in the definition of atomic charge. If an atomic charge could be assigned to the atoms in a molecule in an unequivocal manner, then a quantitative method of measuring the changes in charge that occur as the molecule changes would help in the description of intramolecular polarization and substituent group effects on molecular properties. Unfortunately, methods of counting atomic charge are not exact and never will be since neither the atomic charge nor the gross atomic population are direct observables in the sense of the other molecular properties.[158] The numerous attempts to give a usable definition of atomic charge vary from employment of the widely used Mulliken population analysis[137] (MPA) and its many variants to the division of the molecular electron density into regions and finding the local charge using numerical integration. Methods of performing the

numerical integration have been described in a recent paper by Grier and Streitweiser.[159] Both the polarity of the nitro group in the XNO_2 structure and the question of methyl group polarization in CH_3-X structures will be discussed here.

A group X is considered to be electropositive, or electron repelling, if in the compound X-B the electron content of the B group is greater than in the compound H-B. Ingold,[160] in discussing the inductive effect of the methyl group, argued that the methyl group is weakly electronegative in saturated alkanes, but with most electronegative B groups the methyl group is electropositive. The main point is that the methyl group is generally thought to be more electropositive or electron repelling than hydrogen.

Since the nitro ($-NO_2$) group is considered to be strongly electronegative with respect to polarizable groups such as alkyl groups, the proper basis set should accurately reflect this character. The three basis sets considered here have been shown earlier to exhibit large differences in the calculation of charge densities. The amount of polarization calculated for a bond or a molecule usually decreases in the order

4-31-G > 4-31G+BPFs > STO-3G

Tables XLIV-XLVI show the gross atomic populations from a MPA for the XNO_2 series. Both the H and CH_3 donate electrons to the NO_2 as expected from simple electronegativity considerations. What is surprising is that no basis set shows any significant π donation by the methyl group. (0.009e for the STO-3G set, 0.02e for 4-31G, 0.00e

TABLE XLIV

MULLIKEN POPULATIONS FOR CH_3NO_2[a]

	Basis Set		
	STO-3G	4-31G	4-31G+BPF's
H1	0.890	0.767	0.795
H2 A'[b]	0.428	0.486	0.368
H3 A"	0.463	0.276	0.426
Total	0.891	0.762	0.794
C A'	5.035	5.083	5.109
A"	1.065	1.163	1.133
Total	6.100	6.247	6.242
N A'	5.605	5.591	5.625
A"	1.224	1.094	1.087
Total	6.829	6.686	6.713
O1 A'	6.805	6.921	6.839
A"	1.397	1.469	1.463
Total	8.202	8.390	8.302
O2 A'	6.809	6.928	6.846
A"	1.388	1.457	1.450
Total	8.197	8.386	8.295

[a]Appendix 1.

[b]A' in plane, A" out of plane.

TABLE XLV

MULLIKEN POPULATIONS FOR $HONO_2$[a]

		Basis Set STO-3G	4-31G	4-31G+BPF's
H		0.752	0.540	0.606
01	σ	6.250	6.509	6.493
	Π	1.936	1.922	1.907
Total		8.186	8.431	8.400
N	σ	5.484	5.259	5.270
	Π	1.214	1.104	1.113
Total		6.698	6.363	6.383
02	σ	6.747	6.837	6.809
	Π	1.455	1.530	1.525
Total		8.202	8.367	8.334
03	σ	6.767	6.855	6.823
	Π	1.394	1.444	1.454
Total		8.161	8.299	8.277

[a]Appendix 1.

TABLE XLVI

MULLIKEN POPULATIONS FOR HNO_2 AND FNO_2[a]

	Basis Set		
	STO-3G	4-31G	4-31G+BPF's
H-NO_2 H	0.757	0.575	0.644
N σ	5.632	5.571	5.606
Π	1.258	1.121	1.134
Total	6.890	6.692	6.740
O1,O2 σ	6.805	6.927	6.892
Π	1.371	1.439	1.433
Total	8.176	8.366	8.308
F-NO_2 F σ	7.068	7.277	
Π	1.968	1.959	
Total	9.036	9.236	
N σ	5.465	5.103	
Π	1.207	1.109	
Total	6.663	6.212	
O1,O2 σ	6.738	6.810	
Π	1.412	1.466	
Total	8.150	8.276	

[a]Appendix 1.

for 4-31G-BPF's). The σ donation as expected follows the order of polarization given above, i.e.,

STO-3G (0.219e) < 4-31G+BPF's (0.310e) < 4-31G (0.44e)

For nitromethane the STO-3G and 4-31G+BPF results have the CH_3 electronegative with respect to H, and only the 4-31G basis set predicts the methyl to be less electronegative than the H. For its part, the NO_2 is much less electronegative in nitric acid. In nitryl fluoride the NO_2 group becomes electropositive with respect to F as shown in Tables XLV (p 103) and XLVI (p 104).

There are only small differences in charge donation by CH_3 vs H to NO_2 and these differences are basis set dependent so they cannot be used to come to conclusions about the nature of the methyl group as electropositive or electronegative. A study of a larger series of H-B and CH_3-B compounds seems to be in order to see if any general behavior is discernible. Table XLVII shows the amount of charge donated by CH_3 and H to a B group. Except for the one 4-31G calculation on nitromethane, the methyl group appears more electronegative than the H for both very polar groups (CH_3F) and those of low polarity ($CH_3CH{=}CH_2$). This finding does not agree with the generally accepted view. This disagreement could result from the artificial nature of the division of charge which is an essential feature of the MPA.

In their study of substituted carbonyl groups, Grier and Streitwieser noted that the STO-3G basis set could not adequately describe the π and lone pair bonding about the oxygen, but they found that the 4-31G basis set appeared reasonably adequate to establish

TABLE XLVII

DONATION OF CHARGE TO GROUP (B) BY METHYL GROUP AND H (MILLIELECTRONS)[a]

B-Group	Donated By	(Charge donated) STO-3G	4-31G	4-31G+BPF's
$-NO_2$	H	243	425	356
	CH_3	228	462	310
-F	H	211	478	439
	CH_3	150	460	346
-OH	H	203	392	303
	CH_3	115	338	269
$-C\equiv N$	H	150	331	309
	CH_3	121	218	210
$-C\equiv CH$	H	-	299	280
	CH_3	-	180	58
-Cl	H	-	229	131
	CH_3	-	116	39
$-CH=CH_2$	H	-	164	123
	CH_3	-	-9	7

[a]Positive value indicate donation to B group by H or CH_3.

trends of electron density change about the carbonyl oxygen. Calculations on a YCHO structure were used to compare the electron densities at the carbonyl oxygen by subtracting HCHO densities from densities calculated for the YCHO species. Only the oxygen population difference was calculated by integration. The authors found a close correspondence between the integrated electron population difference and the corresponding difference in the Mulliken population on that oxygen. The oxygen populations indicated the CH_3 group was more positive than H by a small amount with an electron transfer to the O atom of 10 to 40 millielectrons. The C of the carbonyl itself might have been more positive, so balancing the charge on the O but this was not discussed. However this aspect would have to be investigated before concluding that the CHO group behaves any differently than the other B groups shown in Table XLVII for the STO-3G, the 4-31G or 4-31G+BPF's basis sets. In fact this behavior of the β atom becoming more negative has been noted by others, for example Flizar in discussing C-13 NMR on substituted alkanes and alkenes, found the α carbon to have a decrease in electron density and the β carbon an increase.[161]

Perhaps one of the clearest examples of the type of analysis that is needed to decide whether the electron density can be described with any consistency is that of Wiberg.[49] The basis sets used were the 4-31G, 6-31G, 4-31G+BPF's and 6-31G+NCPF's; but a more important aspect of the work is that three methods were used to look at the electron distribution: (1) the MPA (2) numerical integration of electron density over regions of the molecule, and (3) electron density maps. Like Marchington et al.,[162] Wiberg chose a carbon radius of 0.77 Å to

define the region inside which the charge density would be integrated and found the integrated charge to be less than that given by the MPA using this basis set. However a radius of 0.85 Å gave atomic charges quite similar to those of the MPA. Using methane as his reference molecule, Wiberg found the changes in population on the methyl hydrogens, when one of the H's was substituted by the groups $-CH_3$, $-NH_2$, OH, SH, F, -Cl, CN, or C≡CH, were similar whether method (1) or the integration technique (2) was used to calculate the populations. Certainly the agreement was close enough to see the same trends with both methods, but with the methyl carbon itself no easy comparison could be made. It would appear that this combined approach could be very valuable for a fuller description of the electron distribution.

By using the third method, (electron density maps) for the pairs HC≡CH: $CH_3C{\equiv}N$, and HC≡N: $CH_3C{\equiv}N$ Wiberg showed that the methyl group donated electron density into the -C≡CH and -C≡N groups with respect to hydrogen, for both the σ and π system.

On these same compounds, Wiberg also performed a MPA using a 4-31G+BPF's basis set and showed a transfer of 300 me into the -C≡CH, and 443 me into the -C≡N, and; surprisingly for MeF only 202 me were transferred to -F by the methyl group using that same basis set. These results using the MPA method are very different from those reported in Table XLVII (p 106) for a supposedly similar 4-31G+BPF'sbasis set, which showed transfers of 58 me, 210 me, and 346 me respectively. Moreover for CH_3F, using the 4-31G basis set with no BPF's but a different geometry than this author, Wiberg showed a transfer of 457

me to F in excellent agreement with the result (460 me) using the same basis set in the present study. This good agreement serves to emphasize the great sensitivity of the calculated electron transfer in the CH_3B electronic structure with basis set and this in turn could easily lead to differences in interpretation concerning whether a methyl group is electron repelling or attracting for a given -B group.

Three additional items should be noted, (a) Wiberg used an idealized geometry with the CH_3 group frozen in the methane geometry, (b) the bond functions appeared not to have been optimized and were different than those used in the present work, and (c) there is no clear line dividing the methyl group and the rest of the molecule so that an integration technique will always arbitrarily divide space up for electron densities just as the MPA method divides electron populations up in an arbitrary manner.

D. NO_2^-, NO_3^- IONS

Only one property of these two anions has been measured experimentally, namely the ^{14}N-NQCC values in the crystals.[163,164] Calculations on anions using small basis sets are not as successful as for neutral species. The 4-31G basis set inverts the ordering of the highest occupied MO (HOMO) and the lowest unoccupied (LUMO) of NO_2^-, which changes the π electron occupation number from 4 to 6. This has serious consequences for the one-electron properties shown in Table XLVII and XLIX to the extent that the 4-31G results are meaningless.

TABLE XLVIII

FORCES AT THE NUCLEI[a] FOR NO_2^- AND NO_3^-[a]

	Property	STO-3G	4-31G	Basis Set 4-31-1G[b]	DZ[c]	DZ+BPF's[d]
NO_2^-	F_z(N)	2.001	0.724	1.586	1.564	0.679
	F_z(O)	-1.364	-1.114	-0.972	-1.064	-0.518
	F_y(O)	±2.245	±1.584	±1.670	±1.778	-0.771
	F_z Total	-0.726	-1.503	-0.358	-0.564	-0.357
NO_3^-	F_z(N)	0.00	0.00			
	F_z(O1)	2.978	2.176			
	F_z(O2,O3)	-1.489	-1.088			
	F_y(O2,O3)	±2.579	±1.885			
	$F_z$tot	0.0	0.0			
	$F_y$tot	0.0	0.0			

[a] Appendix 1.

[b] 4-31G basis set augmented with diffuse functions α_N=0.10 α_O=0.06

[c] Dunning, DZ [4s2p] Ref. 29.

[d] Dunning, DZ [4s2p] augmented with BPF's.

TABLE XLIX

^{14}N ELECTRIC FIELD GRADIENTS FOR NO_2^- AND NO_3^-[a] IONS[a]

	Basis Set	q_{aa}(au)[b]	q_{bb}(au)	q_{cc}(au)
NO_2^-	STO-3G	-1.102	0.674	0.427
	4-31G	2.196	0.848	-3.044
	4-31-1G [c]	-1.567	0.233	1.334
	DZ[d]	-1.694	0.364	1.330
	DZ+BPF's[e]	-1.647	0.245	1.402
	expt'l[f]	-1.583	0.471	1.112
NO_3^-	STO-3G	-0.106	-0.106	0.213
	4-31G	-0.335	-0.335	0.670
	expt'l[g]			0.207

[a] Appendix 1.

[b] q_{aa} along NO_2 bisector, q_{bb} parallel to O-O, q_{cc} out of plane.

[c] 4-31G basis augmented with addition s, p function α_N=0.10, α_O=0.60

[d] Dunning DZ [4s2p], Ref. 29.

[e] Dunning DZ [4s2p] plus BPF's.

[f] Oja, Ref. 163.

[g] Gourdji, Ref. 164.

The HFF calculated at the nuclei for a species in a lattice of counter ions should have the lattice simulated in the calculation of the wavefunction. The relative size of the forces calculated for an isolated species should however still give an indication of the suitability of a given basis set. Table XLVIII (p 110) shows how well several basis sets perform on anions. The erroneous WF for the 4-31G calculations gives a low force on nitrogen (where the inverted MO's were concentrated) but the highest total force of the several basis sets. With the addition of diffuse s and p functions to each of the atoms, the molecular orbital order was corrected and both the individual forces and the total forces improved. Since the 4-31G basis set could not be considered an adequate double zeta set to augment with BPF's in this instance, two other calculations were done. One using a Dunning DZ set, and another one in which BPF's were added. While the HFF's calculated using the Dunning DZ set are quite comparable to those calculated using the 4-31G + diffuse sp basis set, the DZ + BPF's basis set showed a marked improvement and is clearly the best set, reducing both individual forces on the nuclei and the total force. The nitrate ion did not pose the problem of an inverted order of MO's and the 4-31G basis set produced the general lowering of forces seen earlier in the XNO_2 calculations.

The electric field gradients, of NO_2^- calculated using the basis sets (with the exception of the 4-31G) agree rather well with experiment in absolute value. The larger basis sets (4-31G + diffuse sp, DZ, DZ + BPF's) also reproduce the trend of $|q_{cc}|>|q_{cd}|>|q_{bb}|$ shown in the experimental results. Since the experiments were not done

on single crystals, the directions of the electric field gradients were not uniquely determined but set to agree with calculations. Calculations using the semiempirical INDO (Intermediate Neglect of Differential Overlap) method were unsuccessful for both the NO_2^- and NO_3^- crystals until additional dipole and quadrupole terms representing interactions with the lattice were added.[165]

The MPA shown in Table L indicate that, for the anions, the STO-3G and DZ (4-31G for NO_3^-) give similar polarizations as shown earlier in the XNO_2 compounds, with the 4-31G or DZ basis set showing more polarization than the STO-3G basis set.

TABLE L

MULLIKEN POPULATIONS OF NO_2^- AND NO_3^- IONS[a]

		Basis Set				
		STO-3G	4-31G	4-31-1G[b]	DZ[c]	DZ+BPF's[d]
NO_2^-	N σ	6.0850	4.9512	5.6628	6.0052	6.1463
	π	1.0054	2.0136	0.8012	0.8387	0.7918
	Total	7.0904	6.9648	6.4640	6.8439	6.9381
	O1,O2 σ	6.9575	6.5244	7.1686	6.9974	6.9405
	π	1.4973	1.9932	1.5994	1.5807	1.5905
	Total	8.4548	8.5176	8.7680	8.5781	8.5310
NO_3^-	N σ	5.5457	5.2900			
	π	1.2023	1.0780	-	-	-
	Total	6.7480	6.3680			
	O σ	6.8182	6.9034			
	π	1.5992	1.6406	-	-	-
	Total	8.4174	8.5440			

[a]Appendix 1.

[b]4.31G basis set augmented with diffuse functions α_N=0.10, α_O=0.06.

[c]Dunning DZ [4s2p], Ref. 29.

[d]Dunning DZ [4s2p] augmented with BPF's.

CHAPTER V

DEUTERON QUADRUPOLE COUPLING CONSTANTS

A. INTRODUCTION

For many years the deuteron quadrupole coupling constant (DQCC) has been considered a sensitive measure of the electron distribution near the deuteron and the atom to which it is bonded. There have been many attempts to calculate the DQCC values of simple molecules[10,36,166-168] and there have been a few qualitative arguments presented about the major factors which control the value of the coupling constant. In many cases, general conclusions about the relationships between the values of the coupling constants and changes in molecular structure have been drawn in the absence of either high quality experimental results or theoretical calculations.

For example many authors have related the coupling constant to the force constant,[169-171] others have related it to the electronegativity of the adjacent atom while,[172] in the case of deuterocarbons, it has been claimed numerous times that there is a clear dependence of the deuteron coupling constant in the C-D fragment on the hybridization of the carbon atom.[150,173,174] In particular it has been suggested that the order is

$$DQCC(sp) > DQCC(sp^2) > DQCC(sp^3).$$

The DQCC is given by equation (29) where q_D is the electric field gradient at the deuteron and Q_D is the nuclear quadrupole moment.

$$DQCC = e^2 q_D Q_D / h \tag{29}$$

Q_D has been determined through comparison of accurate calculations on HD with experiment.[175] The electric field gradient (EFG) is given by equation (30) where the first term is summed over all nuclei and the second over all electrons

$$q_D = \sum Z_k(3\cos^2\theta_k - 1)/R_k^3 - \sum \langle\psi_o^{el}|(3\cos^2\theta_k - 1)/r_k^3|\psi_o^{el}\rangle \quad (30)$$

It has been also claimed that even approximate wave functions can be used to compute DQCC's for small molecules with reasonable accuracy.[167,168] The validity of some of these claims will be examined in this chapter.

B. EXPERIMENTAL MEASUREMENTS

Values of the DQCC can in principle be obtained from studies on the resonance spectra, from nuclear magnetic resonance (NMR) data or from molecular beam measurements.[19] Unfortunately the experimental error in many of the reported measurements is frequently high and different experimental methods have yielded different values for the DQCC's for the same compound.

This latter difficulty can sometimes be attributed to the different physical forms of the compounds studied: single crystal (SC), polycrystalline (PC), liquid crystal, (LC), liquid and gaseous phases, but this problem has made the drawing of broad conclusions about molecular structure effects from DQCC a perilous task. Moreover, although this fact has gone unnoticed by many writers, the total observed range for DQCC's on carbon is relatively small, i.e., only

(60kHz), and at times the experimental uncertainties have often been such that interpretations remain ambigous.

For example, the calculations of Olympia et al.,[174] using several different wave functions predict a change of the DQCC in going from sp^3 hybridization to sp hybridization on carbon of 55-75 kHz whereas the best measurements now available (on CH_3D and $CH{\equiv}CD$) show a difference of only 6 ± 8 kHz for these molecules. In order to make the claim that their calculations were in agreement with experiment Olympia et al. used for a typical sp^3 value the 1961 result of Ramsey (molecular beam method)[176] for monodeuterated methane (100 ± 59 kHz); for a typical sp^2 value the value for benzene-d_6 (193 ± kHz)[177]; and as the sp standard, a molecular beam measurement of deuteroacetylene (200 ± 10 kHz)[148] and a NMR value for monodeutero phenylacetylene of 215 ± 5 kHz. These results taken optimistically do support a considerable increase in the DQCC as the hybridization changes. A similar compilation in 1972 by Millett and Dailey[179] yielded similar results except that for a typical sp^3 molecule they used their own (liquid crystal measurement) value for deuteroethane (CH_3CD_3) of 167 ± 12 kHz. However in 1970 a very careful study of the electron resonance spectra of CH_3D was reported by Klemperer's group at Harvard which gave a DQCC value of 191.48 ± 0.77 kHz.[180] Although both the method used and the small error range claimed by the workers make this determination, by far, the most accurate DQCC value in the literature, it was ignored without comment in Millett and Dailey's 1972 paper in favor of their own liquid crystal measurements even though these measurements are notoriously both difficult to

perform and difficult to interpret unequivocally.[179,181] Moreover this mistake has been perpetuated in later work. In 1976 a liquid crystal study on monodeuteroethene[182] was used to yield a DQCC value of 175 ± 1.3 kHz, a value considerably lower than the value found for a number of benzene derivatives but which should be regarded as a more typical example for the NQCC of a deuteron attached to a sp^2 hybridized carbon atom. Thus the latest experimental results do not support the idea that there is a simple relationship between hybridization and DQCC and indeed the results strongly support the idea that the deuteron in acetylene has the highest NQCC with the methane deuteron NQCC slightly smaller, and the ethylene result considerably smaller. This idea is also supported by the better quality calculations but not in the more approximate calculations which support the earlier and often quoted simple dependency of the DQCC values on hybridization.

C. RECENT CALCULATIONS

There have been three recent reports of DQCC values on a relatively large number of small molecules. Ditchfield[10] has tabulated, without discussion, results using a 4-31G basis set and standardized geometry (all C-H bonds, of a given type therefore are the same). Snyder[120] has produced results using the Snyder-Basch double zeta set and, in some cases, has repeated the calculations with the addition of a set of NCPF's to the DZ basis set with experimental geometries used throughout. The third set of calculations by Barfield *et al.*[168] was performed using a semiempirical method very similar to

the much earlier work of Bloor and Maksic[103] which utilized experimental geometry to calculate molecular orbitals by their CNDO/2D procedure. These MO's were then used as if they were true Hartree Fock MO's to calculate q_d^{el} without further approximation using equations (29) and (30). The work of Barfield et al. differed from this earlier work only in that they used the INDO method (i.e., one-center exchange integrals are included), rather than the CNDO/2 method to obtain the initial orthogonal MO,s. The Barfield et al. results were very similar to the earlier results but unlike the earlier workers they claimed the newer results compared favorably both with experiment and with the results of nonempirical calculations performed using "extended basis sets with optimized orbital exponents."

A comparison of the results of the different methods for a number of hydrides is given in Table LI. It can be seen immediately that both the DZ and 4-31G basis sets give results consistently high by 15-25 percent. The addition of NCPF's improves the results considerably but the values are still too high by 5-15 percent. On the other hand, the effect of adding a set of BPF's to the 4-31G basis set is to give results in considerably better agreement with experiment. The semiempirical values (Barfield et al.) can be seen to be much too high and to contradict the authors own claims of good agreement indicated in the previous paragraph. The results shown in Table LI were encouraging enough to proceed with a more extensive study of DQCC values for deuterons, attached to carbon using the 4-31G+BPF's basis set. Table LII allows a comparison of calculated values for the DQCC using experimental geometries with experimental values.

TABLE LI

DEUTERON QUADRUPOLE COUPLING CONSTANTS OF SIMPLE HYDRIDES (kHz)[a]

$e^2q_DQ_D/h$

	r_{x-D} (Å)	4-31G	4-31G+BPF's	DZ	DZ+PF's	Other	Semi-Empirical[b]	expt'l,
HF	0.917	412[c]	337	428[d]	374[e]	383[f],		354[g], 340±40[h]
HCl	1.27	262	204			224[i]		190[j]
H_2O	0.957	370	327	380	341[k]	—	334.7	307.95±0.15[l]
H_2S	1.328	215	146	—	—	213[m]		155[n]
HCN	1.066	242	199	249[a]	214[p]	233[i]	269.6	199±3[q]
NH_3	1.014	297	252	310	310[r]	290[i]	297.2	290.6±0.7[s]
CH_4	1.085	232	190	227[t]	209[t.]	225[i]	214.6	191.48±0.77[u]

[a]Appendix 1.

[b]Barfield, Ref. 168.

[c]Using 0.92Å bond length.

[d]Snyder, Ref. 120.

[e]Bender, Ref 183.

[f]6-31G**, 6-31G + d and p NCPF's, Pettit, Ref. 184.

[g]Muenter, Ref. 185.

[h]Nelson, Ref. 186.

[i]4-31G+NCPF's, this work.

[j]Genin, Ref. 187.

[k]Rosenburg, Ref. 39.

[l]Bluyssen, Ref. 123.

[m]Rothenberg, Ref. 68.

[n]Thaddeus, Ref. 71.

[o]Using 1.0631Å bond length, Snyder, Ref. 120.

[p]O'Konski, Ref. 188.

[q]Millet, Ref. 179.

[r]Laws, Ref. 189.

[s]Kukolich, Ref. 190.

[t]Using 1.0938Å bond length, Snyder, Ref. 120.

[u]Wofsy, Ref. 180.

TABLE LII

DEUTERON QUADRUPOLE COUPLING CONSTANTS FOR DEUTERO-CARBON COMPOUNDS USING EXPERIMENTAL GEOMETRIES (kHz)[a]

$e^2q_DQ_D/h$

	4-31G	4-31G+BPF's	DZ	DZ+BPF's	expt'l
CH_3D	232	189	227[b]	209[b]	191.48±0.77[c]
CD_3F	214	168	215[b]	203[b]	133±7[d],161[e]
CD_3Cl	211	168	---	---	166±4.5[f]
CD_3NO_2	216	172	---	---	173[g]
CD_3OH	216	187	218[b]	---	144[g]
CD_3CN	206	162	209[b]	187[h]	167.5±4[i]
CD_3CCH	206	171	---	---	176±15[j]
CD_3CH_3	---	---	215[b]	---	167±12[k]
$CHDCH_2$	229[l]	185[l]	232[b]	211[l]	175±1.3[m]
$D_2C{=}O$	188	144	193[b]	179[n]	163±1;170±2[p]
$DC{=}OOH$	205	159	209[b]	---	166±2[q]
DCCD	258[l]	215[l]	260[b]	245[l]	198±7[k]
CH_3CCD	265	232	---	---	229[q],199.4±2.0[k]

[a]Appendix 1.
[b]Snyder, Ref. 120.
[c]Wofsy, Ref. 180.
[d]Bhattacharyya, Ref. 191.
[e]Snyder, Ref. 192.
[f]Kukolich, Ref. 193.
[g]Rinne, Ref. 150.
[h]Pettit, Ref. 184.
[i]Kukolich, Ref. 194.
[j]Shoemaker, Ref. 195.
[k]Millet, Ref. 179.
[l]Metzgar, Ref. 41.
[m]Kowalewski, Ref. 182.
[n]4-31G+NCPF's.
[o]Tucker, Ref. 196, 197.
[p]Thaddeus, Ref. 71.
[q]Ruben, Ref. 121.

The agreement of the calculated values using the 4-31G+BPF basis set is quite good, often within the experimental error. Two of the exceptions, those of CH_3F and CH_3OH have experimental DQCC values considerably lower than other methyl deuterons. The CH_3F determination was done by NMR on a liquid crystal and Snyder[192] has proposed a reasonable explanation for this discrepancy in the fluorine compound in that a different labeling of the axes for the EFG's would result in a change in the sign of η and a significant increase in the value of e^2qDQD/h along the bond axis. The deuteron NMR spectra of compounds obtained in nematic liquid crystal (LC) solutions consist of a doublet split by the quadrupolar interaction. The splitting were shown by Phillipps[198] to be

$$\Delta\nu_D = \frac{3}{2}\,(e^2Q_Dq_{zz}/h)S_{zz} \tag{31}$$

where q_{zz} is the electric yield gradient component along the major symmetry axis of the molecule and S_{zz} is the ordering parameter of the solute molecule in the LC phase. S_{zz} is then determined from the ^1H NMR spectrum of the nondeuterated compound. This comparison depends on the accuracy of the assumed molecular geometry. A transformation brings the EFG component into the principal axis system of the studied deuteron according to equation (32)

$$q_{33} = \frac{1}{2}\,q_{zz}\,(3\cos^2\theta - 1 - \eta\sin^2\theta) \tag{32}$$

where Θ in the angle between the C-D bond axis and the molecular symmetry axis; q_{zz} and η are values for the EFG in the principal axis

system for the studied deuteron. The asymmetry can not be determined by this method since one must either know the values for both θ and η or make a reliable estimate.

A similar miss labeling of axes might also account for the discrepancy for the CH_3OH results by Rinne.[150] Indeed Wooten et al.[199] obtained a value (LC measurements) for CDH_2OH of 158.9±2.9 kHz which is more in line with other CH_3X compounds although still low compared to the 4-31G+BPF's calculation. The third large difference between experiment and calculation occurs with $D_2C=O$ where the 4-31G+BPF's calculation underestimates the experimental value by 20-30kHz.

The standardized geometry 4-31G calculations by Ditchfield[10] provide a means of checking the importance of using the correct C-H bond distance. These calculations used a r(C-H) value of 1.09Å for all protons attached to an sp^3 carbon. For all protons attached to an sp^2 carbon an r(C-H) of 1.08Å was used while for the proton attached to an sp hybridized carbon a r(C-H) of 1.06Å was used. Some of these results are given in Table LIII. The theoretical DQCC's compared to methane for the methyl group of ethane, methyl acetylene, methyl cyanide, methyl fluoride, and fluoroform (CDF_3) span a range of only 8.0 kHz while the experimental values span a range of more than 30.0 kHz.

It is only when it is realized that the bond distances in all those C-D bonds with a DQCC much lower than methane tend to have long ($r_{C-D} > 1.10$Å), that this discrepancy between theory and experiment can be resolved. For example the Landolt Bornstein structure data

TABLE LIII

DEUTERON QUADRUPOLE COUPLING CONSTANTS USING STANDARD AND EXPERIMENTAL GEOMETRIES WITH THE 4-31G BASIS SET

	Standard[a]		Experimental[b]	
	r_{x-D}(Å)	$e^2q_DQ_D/h$(kHz)	r_{x-D}(Å)	$e^2q_DQ_b/h$(kHz)
CH_3D	1.09	226	1.085	232
CD_3F	1.09	212	1.095	214
CD_3CH_3	1.09	225	- - -	---
CD_3CHCH_2	1.09	224	- - -	220
CD_3CN	1.09	220	1.1036	206
CDF_3	1.09	197	- - -	---
D_2CO	1.08(1.101)	228(183)	1.116	188
C_2D_4	1.08	236	1.085	229[c]
DCOOH	1.08	225	1.097	205
DCCD	1.06	258	1.0608	258
CH_3CCD	1.06	259	1.058	265[c]
FCCD	1.06	257	1.053	226[c]
DCN	1.06	247	1.066	242

[a]Ditchfield, Ref. 10, corrected for change in Q_D from values in reference.

[b]This work.

[c]Metzgar, Ref. 41.

tables[200] shows for methyl groups attached to a carbon triple bond or a C≡N group the C-H bonds tend to be slightly longer than the C-H bonds in molecules of the type CH_3X where X is a substituent with lone pairs such as F, Cl, OH, and NH_2. Unfortunately, this observed lengthening of the bond is only 0.01-0.02Å and for any individual molecule this is within the probable experimental error of many of the reported measurements so one is not able to state that the proposed generalization has been proved conclusively. However the trend is clearly there for methyl acetylene, dimethyl acetylene and acetonitrile. The r(C-H) values are; 1.112Å (cpd. 367) for methylacetylene); 1.116Å for (cpd. 499) for dimethyl acetylene) and for methyl cyanide (cpd 218) there are two values of 1.1045Å and 1.107Å.[200] The corresponding DQCC values for methyl acetylene and methyl cyanide are similar, i.e. 176 ± 15 kHz and 167 ± 4 kHz respectively, suggesting that the direct electronic effect of the very polar CN group is small compared to the indirect effect of lengthening the C-H bond by .02Å. The standardized geometry 4-31G calculations are in agreement with this finding. The difference between the DQCC for methane and methyl cyanide is only 6 kHz leaving about 15 to 20 kHz to be accounted for by increasing the C-H bond distance. Indeed when the 4-31G calculations were performed using a C-H bond distance of 1.10Å the DQCC was lowered about 14 kHz to 206 kHz, which is still high, of course, but the difference between CH_4 and CH_3CN is now reasonably given. The experimental value with its quoted error of ± 15 kHz for $CD_3C{\equiv}CH$ highlights the need for better experimental measurements on DQCCs. Taking the upper bound of 191 kHz one would conclude that there is

virtually no change from the methane DQCC value as is found using the standardized geometry whereas taking the lower bound of 161 kHz one arrives at a value agreeing very well with the hypothesis that allowing the C-H bond to vary from compound to compound is necessary in order to calculate meaningful DQCC values. This would mean that future calculations will have to be done with geometry optimization. Unfortunately, theoretical geometry optimization is necessary because the experimental error in most mesurements of C-H bond distances is too high at present to make the distinction between the bond length effect and the polarization effect on the value of a DQCC. Thus a basis set such as the 4-31G, which has been shown to be reliable in the geometry optimization of a wide variety of molecules, can be made flexible enough by including BPF's to give realistic DQCC values.

CHAPTER VI

CONCLUSIONS

There are several general conclusions that can be drawn from the work described in the earlier chapters regarding the selection of a basis set capable of describing adequately the electronic environment of a molecule.

1. Although the STO-3G basis set has been, and still is, being widely used to calculate charge densities, it is severely limited in its ability to correctly describe the subtleties encountered in connection with the changes in charge density which take place on molecule formation. Reports which claim apparent good agreement on small and weakly polar molecules with respect to the geometry and dipole moments can not be extended to more complex systems especially those which have considerable polarity. The results described in the earlier chapters on a wide range of molecular systems show that the STO-3G basis set is clearly much inferior to the 4-31G basis set.[201] The major defect of the 4-31G basis set is to over polarize the molecule and in the earlier chapters it was demonstrated that this defect could be remedied to a large extent by the addition of bond polarization functions (BPF's). In support of this contention Wiberg has recently found that for CH_3F and CH_3Cl the addition of a second set of BPF's in the C-X bond results in a continued improvement in the dipole moment.[20]

2. Whereas simple basis sets, i.e., STO-3G, and 4-31G are reasonably good for properties that depend on r^n ($n \geq 1$) such as the expectation values $< r >$ and $<r^2>$ they are not sufficient for the $\left\langle \frac{1}{r^3} \right\rangle$ properties such as the electric field (Hellmann-Feynman force) and the electric field gradient (EFG). This is expecially true for the more polar molecules. The results of the earlier chapters show the basis set must be of at least double zeta quality and also have some polarization functions added before low HFFs are obtained and, in the case of electric field gradients, values within a few percent (5-10%) of experimental values can be obtained with such a basis set.
3. In several previous studies of basis set effectiveness one of the criteria used was to compare $<a^2>$, $<b^2>$, and $<c^2>$ (defined by equation 38) values. The present study has shown these to be a poor criteria. On the other hand the molecular quadrupole moment (θ_{aa}) which is calculated as the differences between the nuclear and electronic terms of $<r^2>$ is a very sensitive criterion (defined by equation 39) and can be used as a severe test of basis set quality. Thus, the 4-31G+BPF's basis set was found to produce more reasonable quadrupole moments than the 4-31G basis set, which tends to overestimate, and the STO-3G basis set, which underestimates the θ_{aa} values.
4. The molecular quadrupole moments and the $\left\langle \frac{1}{r^3} \right\rangle$ properties sample different portions of the charge density and ideally

both should be employed as well as the frequently utilized dipole moment in any test of the effectiveness of a basis set in producing a reasonable electron distribution. EFG's are also sensitive to the anisotropic behavior of the charge density and this introduces a new difficulty in getting an accurate wave function. The $-N\begin{smallmatrix}O\\O\end{smallmatrix}$ structure, for example, with its tetravalent nitrogen has not been adequately described by any of the basis sets used in this work, if the nitrogen EFG is used as the sole criterion. Previous difficulties with tetravalent nitrogen have been noted in calculations on compounds containing the aza N substituent, such as pyridine, by Kochanski et al.[156] Apparently in this type of molecule the bonding characters of the three p electrons are so delicately balanced that small inaccuracies destroy any agreement between theory and the observed EFGS. The basis sets used in Kochanski's et al.[156] work and in this work are clearly not quite flexible enough to properly describe this balance although some general trends in the relative values are qualitatively correctly reproduced.

5. The Hellmann-Feynman forces (HFF) which also depend on $\langle \frac{1}{r^3} \rangle$ have been found to be a good test of (a) the original atomic set and (b) the balance between different atoms in a molecule. In general both the individual forces on the nuclei and the total forces decline as the basis set is increased in size. Thus the 4-31G+BPF's calculations give relatively low forces for several large molecules while the smaller sets

give much larger values. The oxygen atom is not well described by the small 4-31G basis set and is not greatly improved in several cases such as formic acid when BPF's are added.

6. The attempt made here to clearly settle the controversy which surrounds the electron donating abilities of the methyl group (compared to hydrogen) in polar molecules, has not been successful. One reason is that only the Mulliken Population Analysis (MPA) was used as an index to describe the electron charges on the atoms in the molecules. This of course leaves one at the mercy of its arbitrariness, but even when more sophisticated methods such as those described in some very recent papers are used, they have also not given unequivocal results.[159,162] In fact the value of using the MPA has been demonstrated by the work of Wiberg in which changes in electron population for fixed molecular portions such as the hydrogen atoms on a methyl group derived using the MPA were compared with the changes found by numerically integrating the charge in selected regions.[49] However, unless the methyl group region over which the integration method will be used is distinctly defined, reliable comparisons between these alternative methods can not be done.
7. The DQCC's for deuterons attached to carbons have been calculated in Chapter V in a wide variety of bonding situations and for the first time very good agreement with experiment was found in most cases. Previously given relationships

between DQCC values and carbon hybridization were shown not to stand up to detailed analysis using recent experimental values for DQCC values. The use of BPF's as polarization functions was shown to be more successful in producing agreement with experiment than when the traditional NCPF's are used as polarization functions to be added to DZ basis sets.

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APPENDICES

APPENDIX 1

A. The one electron properties examined in this work are defined by the equations given below.

1. Potential (ea_o^{-1}) at the nucleus A.

$$\Phi(A) = \sum_k{}' Z_k \left(\frac{1}{|r_k - A_k|}\right) - 2\sum_i \langle \phi_i \left| \frac{1}{(r-A)} \right| \phi_i \rangle \tag{32}$$

2. Electric Field (ea_o^{-3}) at the nucleus A.

$$E_\gamma(A) = -\sum_k Z_k \left(\frac{r_{k\gamma} - A_\gamma}{|r_k - A|^3}\right) + 2\sum_i \langle \phi_i \left| \frac{(r_\gamma - A_\gamma)}{(r-A)^3} \right| \phi_i \rangle \tag{33}$$

3. Hellmann Feynman Force at the nucleus A.

$$F_\gamma(A) = Z_A E_\gamma(A) \tag{34}$$

4. Electric Field Gradient (ea_o^{-3}) at the nucleus A.

(30)
$$q_{\beta\gamma}(A) = -\sum_k{}' Z_k \left[\frac{3(r_{k\beta} - A_\beta)(r_{k\gamma} - A_\gamma) - \delta_{\beta\gamma}|r_k - A|^2}{|r-A|^5}\right] + 2\sum_i{}' \langle \phi_i \left| \left[\frac{3(r_\beta - A_\beta)(r_\gamma - A_\gamma) - \delta_{\beta\gamma}(r-A)^2}{(r-A)^5}\right] \right| \phi_i \rangle \tag{35}$$

The tensors are ranked $|q_{zz}| > |q_{yy}| > |q_{xx}|$ and η the assymetry parameter is defined as $\eta = q_{yy} - q_{xx}/q_{zz}$.

5. Nuclear Quadrupole Coupling Constants at the nucleus A.

$$e^2 q_{\beta\gamma} Q_A / h \tag{36}$$

6. Dipole Moment (ea_o).

$$\mu_\beta(A) = \sum_k Z_k (r_{k\beta} - A_\beta) - 2\sum_i \langle \phi_i \left| (r_\beta - A_\beta) \right| \phi_i \rangle \tag{37}$$

7. Second Moments (a_o^2)

$$Q_{\beta\gamma}(C) = \sum_k Z_k (r_{k\beta} - C_\beta)(r_{kr} - C_\gamma) - 2\sum_i \langle \phi_i \left| (r_\beta - C_\beta)(r_\gamma - C_\gamma) \right| \phi_i \rangle \tag{38}$$

8. Molecular Quadrupole Moment (ea_o^2).

$$\theta_{\beta\gamma}(C) = \frac{1}{2}\left[3Q_{\beta\gamma}(C) - \delta_{\beta\gamma}\sum_{\beta} Q_{\beta\beta}(C)\right] \tag{39}$$

9. Diamagnetic Susceptibilities (ea_o^2).

$$\langle r^2\rangle_C = \sum_i \langle \phi_i \left| \left| r-C \right|^2 \right| \phi_i \rangle \tag{40}$$

and

$$\chi^d_{\beta\gamma}(C) = -\left(\frac{e^2N}{4mc^2}\right) x 2 \sum_i \langle \phi_i \left| \left(\delta_{\beta\gamma} r_c^2 - r_{C\beta} r_{C\gamma}\right) \right| \phi_i \rangle \tag{41}$$

In the above equations the greek symbols α, β, and γ denote x, y and z directions, letter A stands for an individual nuclear center and letter C stands for the center of mass. Indices k and i run over all nuclei and all occupied MO's, respectively. A prime on a summation indicates that the term $r_k = A$ has been omitted, and the $\frac{1}{r}$ singularity has been removed from the electric field gradient. The symbol Q_N, in Equation 36 stands for the nuclear quadrupole of atom N. The Second Moment values reported are taken from the second term of Equation 38, the electronic term. The Molecular Quadrupole Moment values are the sum of both nuclear and electronic terms (Equation 39).

Conversion factors are used when comparing the results of calculations with experimental values. Table LIV shows those factors employed in this work.

B. Two other properties, the binding energy and the Mulliken Population Analysis also need to be defined.

1. The Mullikan Population Analysis represents a partitioning of the total electron population among the nuclei of the molecule. The total gross population for an atom K, N_K is given by

TABLE LIV

CONVERSION FACTORS FOR MOLECULAR PROPERTIES

Property	1 Atomic Unit =
Energy	27.2097 eV/molecule 627.5 kcal/mole
Potential	0.09076 esu/cm
Deuteron NQCC	675.3 kHz
Nitrogen-14 NQCC	3.66 MHz
Oxygen-17 NQCC	6.01 MHz
Drpole Moment	2.5418 Debyes
Second Moment	$0.28003 \times 10^{-16} cm^2$
Molecular Quadrupole Moment	1.3450×10^{-26} esu cm^2
Diamagnetic Susceptibility	$1.188 \times 10^{-6} erg/g^2$ mole

[a]Using Q(D) = $2.875 \times^{-27} cm^2$, Reid, Ref. 175.

[b]Using Q(^{14}N) = $1.56 \times 10^{-26} cm^2$, Whitten, Ref. 202.

[c]Using Q(^{17}O) = $-2.56 \times 10^{-26} cm^2$, O'Konski, Ref. 203, Schaefer, Ref. 204.

$$N_K = \Sigma_i N_{Ki} \tag{42}$$

where the N_{Ki} are the gross population for a basis function on atom k and are given by

$$N_{Ki} = \sum_i n_i\, c_{\mu i}\left(c_{\mu i} + \Sigma_{\mu \neq \mu'} c_{\mu' i} S_{\mu\mu'}\right) + \sum_i n_i c_{\mu i}\left(\sum_\nu c_{\nu i} S_{\mu\nu}\right) \tag{43}$$

where i runs over all occupied molecular orbitals

μ, μ' basis function on atom K.

ν basis function on other centers

n_i the occupation number for the ith molecular orbital

$c_{\mu i}$, $c_{\mu' i}$, $c_{\nu i}$ coefficients of basis function of the ith molecular orbital.

and $S_{\mu\mu'}$ and $S_{\mu\nu}$ are the overlap integrals between the basis functions.

where K is a non nuclear center, a bond function center, the populations are equally divided and added to the two nuclei of the bond.

2. The binding energies are defined as.

$$B.E. = E_{molecule} - \sum_k^{ALLNUC} E_{atom} \tag{44}$$

where the E_{atom} is given as the total energy of the isolated atom in a Hartree-Fock calculation.

APPENDIX 2

Several one-electron properties were calculated in one molecular coordinate axis system but were compared to experimentsl values in another coordinate axis system, the principle inertial axis system (PAS). The calculated properties were transformed by rotation into the PAS using rotation matices.

Example: Transform the nuclear terms of the second moments of charge for H_2S from an initial coordinate axis system that is rotated 40 degrees from the molecular principal axis system to the PAS.

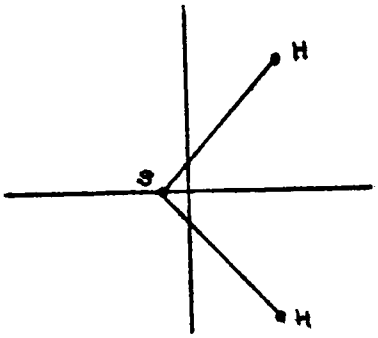

Figure 1a

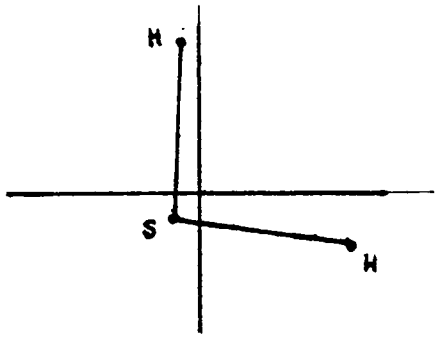

Figure 1b

The nuclear terms of the second moment are given by

$$N_{zz} = \sum_{i}^{NUC} A_i \Delta z_i^2 \quad \text{and} \quad N_{xz} = \sum_{i}^{NUC} A_i \, \Delta x_i \, \Delta z_i \tag{45}$$

where A_i is the charge on the ith nucleus and Δz_i is the difference in the z coordinates of the ith nucleus and the center of mass and the summation is over all nuclei. N_{xx}, N_{yy}, N_{xy}, and N_{yz} are found in like manner.

These nuclear terms can be written as a second-rank tensor.

$$\begin{pmatrix} N_{xx} & N_{xy} & N_{xz} \\ N_{yx} & N_{yy} & B_{yz} \\ N_{zx} & B_{xy} & N_{zz} \end{pmatrix} = \sum_{i=1}^{NUC} A_i \begin{pmatrix} \Delta x_i \\ \Delta y_i \\ \Delta z_i \end{pmatrix} (\Delta x_i \; \Delta y_i \; \Delta z_i) \tag{46}$$

To transform the $N_{\alpha\beta}$ in one coordinate system into the $N'_{\alpha\beta}$ of another follows from the procedure used to transform the coordinates of a particular atom from one system to another. To rotate, use the rotation matrix and either a row or column vector giving the coordinates of the nucleus. For example to rotate about the z axis,

$$\begin{pmatrix} \cos\theta & \sin\theta & 0.0 \\ -\sin\theta & \cos\theta & 0.0 \\ 0.0 & 0.0 & 1.0 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} x_i' \\ y_i' \\ z_i' \end{pmatrix} \tag{47}$$

or

$$(x_i\ y_i\ z_i) \begin{pmatrix} \cos\theta & -\sin\theta & 0.0 \\ \sin\theta & \cos\theta & 0.0 \\ 0.0 & 0.0 & 0.0 \end{pmatrix} = (x_i''\ y_i''\ z_i'') \tag{48}$$

If $B_i{}^c = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$ and $B_i{}^r = (x_i\ y_i\ z_i)$ for the ith nucleus and

$M^c = \begin{pmatrix} x_{cm} \\ y_{cm} \\ z_{cm} \end{pmatrix}$ and $M^r = (x_{cm}\ y_{cm}\ z_{cm})$ for the center of mass,

then the difference in the coordinates of the nuclei and the center of mass would be given as

$$C_i{}^c = B_i{}^c - M^c \quad \text{and} \quad C_i{}^r = B_i{}^r - M^r. \tag{49}$$

If R is the rotation matrix then

$$R \cdot C_i{}^c = C_i'^c \quad \text{and} \quad C_i{}^r \cdot T_R = C_i'^r$$

in the new coordinate system. From definitions stated earlier the $C_i^{\,c}$ and $C_i^{\,r}$ stand for $\begin{pmatrix}\Delta x_i\\ \Delta y_i\\ \Delta z_i\end{pmatrix}$ and $(\Delta x_i\ \Delta y_i\ \Delta z_i)$ respectively so that

$$R\begin{pmatrix}\Delta x_i\\ \Delta y_i\\ \Delta z_i\end{pmatrix} = (\Delta y_i)' \quad \text{and} \quad (\Delta x_i\ \Delta y_i\ \Delta z_i)^{T_R} = (\Delta x_i\ \Delta y_i\ \Delta z_i)'$$

thus

$$\begin{pmatrix}N_{xx} & N_{xy} & N_{xz}\\ N_{yx} & N_{yy} & N_{yz}\\ N_{zx} & N_{zy} & N_{zz}\end{pmatrix}' = \sum_i^{NUC} A_i\ C_i^{c'}\ C_i^{R'} \tag{50}$$

It should be possible to carry out this transformation using R and ^{T_R} on the matrix of $N_{\alpha\beta}$ values.

$$R\begin{pmatrix}N_{xx} & N_{xy} & N_{xz}\\ N_{yx} & N_{yy} & N_{yz}\\ N_{zx} & N_{zy} & N_{zz}\end{pmatrix}^{T_R} = \sum A_i\ R\ C_i^{\,c}\ C_i^{\,r}\ ^{T_R} \tag{51}$$

The second moments of H_2S were calculated at the center of mass using the coordinates corresponding to both Figures 1 and 2. The values for the coordinates corresponding to Figure 2 were also transformed by the similarity transform

$$
\underset{R}{\begin{pmatrix} \cos 40^\circ & -\sin 40^\circ & 0.0 \\ \sin 40^\circ & \cos 40^\circ & 0.0 \\ 0.0 & 0.0 & 0.0 \end{pmatrix}}
\underset{N_{\alpha\beta}}{\begin{pmatrix} 5.9475 & 0.4970 & 0.0 \\ 0.4970 & 6.1227 & 0.0 \\ 0.0 & 0.0 & 0.0 \end{pmatrix}}
\underset{T_R}{\begin{pmatrix} \cos 40^\circ & \sin 40^\circ & 0.0 \\ -\sin 40^\circ & \cos 40^\circ & 0.0 \\ 0.0 & 0.0 & 0.0 \end{pmatrix}}
$$

$$
= \underset{N'_{\alpha\beta}}{\begin{pmatrix} 5.5305 & 0.0 & 0.0 \\ 0.0 & 6.5398 & 0.0 \\ 0.0 & 0.0 & 0.0 \end{pmatrix}} \qquad (52)
$$

to the values already calculated for coordinates of Figure 1. Both the second moments and the diamagnetic susceptibilities of several irregular molecules were treated in this way.

VITA

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