Computational methods

3.1 Property derivative calculations

As described in the previous Chapter, a great deal of useful information may be obtained from studies of property (hyper)surfaces and the property derivatives used to parametrize such surfaces. Although energy derivatives have been calculated for *ab initio* prediction of spectroscopic constants and vibrational fundamental frequencies [1-10], other molecular properties have not been widely studied. This is partly due to the lack of suitable methods and *ab initio* computational codes for obtaining property derivatives. Therefore, in this section the implementation of a suitable method for *ab initio* least-squares evaluation of property derivatives is described, along with other methods for routine *ab initio* calculation of property derivatives. Emphasis is placed on the advantages and disadvantages of particular methods as well as the information available from different procedures.

3.1.1 Least-squares derivatives method

Least-squares methods may be numerically unstable for calculating energy derivatives if care is not taken in selecting both the distribution of geometries and the parameters used in the fitting procedure [3]. However, least-squares methods have been successfully used by many workers for calculating both energy [5, 11, 12] and property derivatives [11, 13-23]. Through experimentation on energy and property surface fitting in the present work, it has been found that they are capable of providing both accurate and precise results of comparable quality to those obtained from numerical finite difference and central-difference procedures. Least-squares methods also offer the advantage of being applicable with equal ease to calculations using either Slater or Gaussian type functions, and to all levels of theory from SCF to highly correlated methods.

For each molecule, using a particular basis set and level of theory, a geometry optimization is first performed to locate the potential energy minimum followed by an analytic second derivative calculation to obtain the vibrational frequencies and normal modes for the molecule. The cartesian force constant matrix is mass-weighted and diagonalized to give the *l* transformation matrix (eigenvectors) and the harmonic vibrational frequencies, ω_i [4, 24] using equation (2.7). In the present procedure, all cartesian gradients are required to be less than 10⁻⁶ hartree/bohr to minimize the forces acting on the nuclei at the optimized geometry. A density matrix criterion of ε (SCF) < 10⁻⁸ is also used to provide highly converged energies and properties in order to reduce numerical noise in the fitting procedure. A suitable grid of displaced geometries about the potential energy minimum is then chosen for the molecule. The choice of these grids is dependent on the system under investigation and the property derivatives required. To simplify the description of the grids used for the studies described in following Chapters, a standard cubic grid is described as

- 1. Single mode displacements $-2\Delta q_i$, $-\Delta q_i$, $+\Delta q_i$ and $+2\Delta q_i$ along each of the *i* normal modes.
- 2. Double or pair-wise displacements, derived from using all combinations of single displacements for two modes, are also used leading to a "square grid" for any two normal modes *i* and *j* (($-\Delta q_i, -\Delta q_i$), ($-\Delta q_i, +\Delta q_i$), ($+\Delta q_i, -\Delta q_i$), and ($+\Delta q_i, +\Delta q_i$)).

This grid choice should be sufficient to determine all "diagonal" property derivatives of the form P_i , P_{ii} , P_{iii} and all "off-diagonal" property derivatives P_{ij} , P_{iij} and P_{iijj} . In favourable cases, it may be possible to determine quartic derivatives P_{iiii} but the numerical accuracy of the derivatives may be compromised and should be checked. Based on the molecular system under investigation, an appropriate step-size Δq in the range 0.02 to 0.20 is chosen. A standard quartic grid is defined as including the set of points obtained from the cubic grid scheme and two additional single mode displacements for each *i*th normal mode, represented as $(-3\Delta q_i, +3\Delta q_i)$. For this type of grid, triple-displacements from coupling of three normal modes are also included $(+\Delta q_i, +\Delta q_j, +\Delta q_k)$. Inclusion of all triple displacements leads to a large number of grid points, C_3^{3N-6} , for an *N*-atomic molecule, where C_r^n is the binomial coefficient. For example, a calculation on ethene would require 220 separate triple displacements, in addition to 72 single displacements and 264 double displacements. Therefore, only displacements related to symmetry-allowed cubic P_{ijk} property derivatives are included in the set of grid points. This helps to reduce the large number of possible

displacements to a manageable size, so that for a calculation on ethene, only 24 triple displacements are required from a possible 220. Obviously, for a large molecule without symmetry, the number of triple displacements required would be exceptionally large and it may be necessary to neglect these displacements from the set of grid points, such that only diagonal derivatives are determined.

Degenerate modes are treated by varying only one mode of the degenerate set providing that the degenerate modes are properly aligned with respect to symmetry planes of the molecule. Degenerate modes for symmetric and spherical tops are aligned with respect to symmetry planes of the molecules to match the usual conventions as outlined by Cyvin *et al.* [25]. For a degenerate mode of a symmetric top, the modes t_a and t_b are rotated to lie in the *xz* and *yz* planes respectively. Triply degenerate (t_x, t_y, t_z) modes are aligned so that the t_x and t_y modes are symmetric with respect to a σ_d plane and the t_z is antisymmetric. Linear molecules are treated as symmetric tops and are aligned along the *z* axis. With proper alignment, displacements along the t_a modes for symmetric tops, and the t_z modes for spherical tops should allow calculation of all of the required cubic force constants and property derivatives for the *A* term coefficients in equation (2.34). If quartic property derivatives are required, then extra displacements along the t_b modes for symmetric tops and (t_x, t_y) modes for spherical tops are necessary.

Geometries in terms of cartesian coordinates for input into a suitable *ab initio* program are then calculated via the inverse of the matrix equation, given by Schneider and Thiel [24], for transformation of cartesian coordinates to dimensionless normal coordinates. Point group symmetry can also help reduce the number of displaced cartesian geometries required. If two displaced cartesian geometries, $r_{\alpha i}$ and $r_{\beta i}$, are related by a symmetry operation *R*, such that

$$r_{\alpha i} = D_{\alpha \beta}(R) r_{\beta i} \tag{3.1}$$

is satisfied, where $D_{\alpha\beta}(R)$ is the symmetry representation matrix for the *R*th symmetry operation, then property calculations may be skipped at one of the geometries. Properties calculated at the $r_{\beta i}$ geometry are then used to generate symmetry related properties at the $r_{\alpha i}$ geometry by use of appropriate tensor transformation matrices. For the dipole moment, which is a first rank tensor (vector), the symmetry transformation is represented as

$$\mu_{\alpha} = T_{\alpha\beta}^{(1)}(R)\mu_{\beta} \tag{3.2}$$

where $T_{\alpha\beta}^{(1)}$ is the transformation matrix for the *R*th symmetry operation. Similar transformation matrices are constructed for second-rank tensor properties, such as the quadrupole moment and polarizability tensor. If the molecule possesses symmetry elements other than the identity element, then the procedure outlined above effectively searches for symmetry related geometries within the complete set of grid points and constructs a subset or petite grid of symmetry-unique geometries at which energy and property calculations are to be carried out. Once the computations for the petite grid have been completed, then properties for the complete set of grid points may be generated by the symmetry transformations outlined above. Additionally, if a particular displaced geometry transforms as the totally symmetric representation, molecular symmetry is utilised within the *ab initio* code for the property calculations, thus saving computational time and storage. Energies and properties were computed at each displaced geometry using CADPAC Versions 4 [26] and 5.2 [27] with dipole polarizabilities obtained analytically via the coupled-perturbed Hartree-Fock (CPHF) formalism [28, 29]. Dipole and quadrupole moments have been obtained as energy derivatives rather than expectation values.

Least-squares fitting of the resulting energies and properties to polynomials (equations (2.17) and (2.33)) in terms of the dimensionless normal coordinates, is then carried out. Required property derivatives were calculated from the properties at the displaced geometries, using a least-squares singular value decomposition (SVD) algorithm [30]. A computer program, ANHARPS [31] (described in Section 3.1.3) was written for this purpose and used for all least-squares fitting, geometry generation, normal coordinate and rotational-vibrational calculations. As with all least-squares fitting procedures, there is considerable flexibility in the choice of fitting parameters, although the number of parameters to be determined must always be less than the number of data points to be fitted. For the standard cubic grids, initially all terms up to quartic level are included in the energy fit and up to cubic terms for each of the property components. For standard quartic grids, all symmetry-allowed derivatives are included in the fit as well as diagonal quintic and sextic derivatives. The higher order quintic and sextic terms are necessary to obtain converged quartic property derivatives. Fitted parameters possessing large uncertainties are excluded and subsequent fits performed to obtain smaller parameter uncertainties. Although energy gradient terms should be numerically close to zero for a stationary point (the optimized

geometry), their inclusion in the least-squares fit is found to improve the accuracy of the cubic force constants due to strong correlation between these parameters. Off-diagonal second derivatives of the form P_{ii} are also included and significantly improve the overall description of the property surfaces. These derivatives are related to infrared and Raman overtone and combination bands [32] if P is the dipole moment or polarizability respectively, and their non-zero behaviour will depend on the symmetry species of both the property and the *i*th and *j*th normal modes. Off-diagonal second derivatives of the energy are initially included in the fitting procedure but can be deleted if the number of parameters to be fitted becomes too large with respect to the number of data points. Generally, the property surface fitting procedure is found to be more numerically robust than fitting the energy surface since all parameters up to cubic or quartic property derivatives can be routinely used without significantly altering the choice of parameters in the fit. Energy surface fitting usually required more trial and error with (n+1)th order diagonal derivatives required in the fit to improve the uncertainties of the *n*th order derivatives. Increasing the number of displaced geometries (at larger distances from the energy minimum) in the procedure is expected to alleviate this problem of parameter choice, as the quartic and higher order force constants would be accurately determined thus also leading to improved lower order force constants. However, a compromise must be reached between the number of displaced geometries and the accuracy of the derivatives obtained from the least-squares fitting procedure.

The accuracy and precision of the least-squares procedure adopted in this thesis has been established through careful comparison of the least-squares numerical and analytic property derivatives. Details and results of the calibration procedure have been published elsewhere [33] and a reprint of the paper is supplied in Appendix V.

3.1.2 Central differences derivatives method

The above least-squares method for calculation of property derivatives is not the most efficient method possible since the analytic derivative capabilities of CADPAC have not been fully exploited. Analytic second derivatives of the energy and first derivatives of the polarizability, dipole and quadrupole moments, with respect to cartesian coordinates, are available from CADPAC (and similar programs) at the SCF level. The CADPAC program also features analytic MP2 second derivatives of the energy [34] and dipole moment [35]. Therefore, taking central differences of the analytic second derivatives of the energy and the

property first derivatives would undoubtedly be a much more efficient procedure. However, the least-squares method does have the advantage that it is not limited to a particular theoretical electron correlation treatment or geometry-dependent property since all required derivatives could be obtained from any "black-box" *ab initio* program computing energies and properties for a given nuclear configuration.

The PHI34 routine, written for calculation of numerical third and fourth derivatives of the energy and dipole moment [4, 10, 36] within CADPAC and kindly provided by Dr Dylan Jayatilaka of the University of Western Australia, was modified to incorporate the calculation of quadrupole moment and polarizability derivatives. Utilising CADPAC and taking central differences of analytic second derivatives, cubic and quartic force constants, dipole moment derivatives, quadrupole moment derivatives and polarizability derivatives, up to third-order, may be obtained at the SCF level of theory. For the MP2 level of theory, both cubic and quartic force constants may be calculated but only the dipole moment derivatives to third-order may be obtained. The central differences formulae for calculating the third and fourth-order derivatives of the energy, with respect to dimensionless normal coordinates, are

$$\phi_{ijk} = \frac{\phi_{ij}\Big|_{q_k = +\Delta} - \phi_{ij}\Big|_{q_k = -\Delta}}{2\Delta}$$
(3.3)

$$\phi_{ijkk} = \frac{\phi_{ij}\Big|_{q_k = +\Delta} + \phi_{ij}\Big|_{q_k = -\Delta} - 2\phi_{ij}\Big|_{q_k = 0}}{\Delta^2}$$
(3.4)

where ϕ_{ij} are the second derivatives of the energy with respect to dimensionless normal coordinates in cm⁻¹ and Δ is an appropriately chosen step-size. For a general property, the second and third-derivatives with respect to dimensionless normal coordinates are given by

$$P_{ij} = \frac{P_i|_{q_j = +\Delta} - P_i|_{q_j = -\Delta}}{2\Delta}$$
(3.5)

$$P_{ijj} = \frac{P_i|_{q_j = +\Delta} + P_i|_{q_j = -\Delta} - 2P_i|_{q_j = 0}}{\Delta^2}$$
(3.6)

This procedure requires a maximum of 2(3N-6) analytic second derivative calculations for N atoms and if higher order derivatives are required, then many more calculations are likely to be necessary. The central-differences method is quite efficient and is especially useful for large molecules where the grid-based least-squares method is likely to prove costly. It should be noted that the property derivatives obtained from the central differences method do not include cubic P_{iik} property derivatives or the quartic P_{iiii} and P_{iiii} property derivatives. Therefore, these derivatives are not included in equation (2.34) for the property rotationalvibrational average. The effect on the vibrational average should be minimal since the leading A term coefficients involve the linear P_i and diagonal quadratic P_{ii} property derivatives and cubic P_{iii} and P_{iij} derivatives are still present in the expression. However, the neglect of particular derivatives must be carefully considered if vibrational corrections from the least-squares method are to be compared with those from the central-differences Pure vibrational polarizabilities from Bishop and Kirtman's perturbation procedure. formulae [37, 38] depend only on linear P_i and quadratic P_{ii} , P_{ij} dipole moment derivatives and are therefore unaffected by the omission of cubic P_{iik} property derivatives or the quartic P_{iiii} and P_{iijj} property derivatives.

3.1.3 Anharmonic property surfaces package (ANHARPS)

A suitable computational package is indispensable for investigations of vibrational and rotational corrections to molecular properties. It would prove to be extremely tedious (or impossible) to "hand-calculate" spectroscopic constants, vibrational and rotational contributions, thermal corrections and the effects of isotopic substitution on molecular properties from property derivatives. Therefore, almost all vibrational and rotational calculations reported in the present thesis have been carried out with the ANHARPS program [31]. This package was originally written to obtain molecular property derivatives from least-squares fitting. However, the program has been significantly extended to include calculation of:

- least-squares property derivatives;
- anharmonic constants and fundamental frequencies;
- properties in arbitrary vibrational-rotational states;
- pure vibrational polarizabilities;
- vibrationally averaged rotational constants and geometries;
- thermal corrections to molecular properties;

- the effects of isotopic substitution on molecular properties;
- property derivatives in internal coordinates via non-linear transformations;
- anharmonic infrared and Raman transition intensities

Most of the theory for calculation of the quantities above has been described in the previous Chapter. Similar computer programs exist for computation of fundamental frequencies and spectroscopic constants from energy derivatives, such as the SPECTRO package [39]. However, ANHARPS also treats other properties such as electric multipole moments and polarizabilities. The program has been designed to allow simple addition of other molecular properties, such as hyperpolarizabilities and electric field gradients, and an attempt has been made to keep the program completely independent of the *ab initio* code (CADPAC) so that other *ab initio* computational programs may be easily interfaced to ANHARPS. The calculation of least-squares derivatives (described in Section 3.1.1) involves normal mode calculations, automatic generation of displaced geometries as well as handling and leastsquares fitting of the *ab initio* properties data for the displaced geometries. Property derivatives from a central-differences calculation can also be utilised for the vibrational and rotational calculations with symmetry widely utilised in the program to minimise computational cost for any *ab initio* computations. Written in Fortran90, ANHARPS makes extensive use of modular programming methods and information hiding. Input to the program is straightforward and a keyword driven method has been utilised to control program execution.

3.2 Ab initio theoretical methods

A wide variety of *ab initio* theoretical methods have been utilised in the present thesis. Standard methods most often used are the SCF, MP2, BD and BD(T) levels of theory that represent a convenient order of increasing theoretical completeness in the treatment of electron-correlation. Generally, SCF methods are commonly used for property derivative studies because they offer the simplest approach to analytic derivative theory [8, 40-42], and the straightforward evaluation of many electrical properties from a variety of different computational codes. Analytic evaluation of the dipole moment, quadrupole moment and polarizability at the MP2 level is possible with CADPAC [27] so the MP2 method has been utilised for the present least-squares property derivatives procedure. Dipole moment

derivatives at the MP2 level are also able to be calculated from CADPAC. This simple electron correlation treatment also yields good results for molecular properties, especially if the basis set is large. Apart from the good quality results able to be obtained from this method, MP2 theory also scales properly with molecular size (size-extensive) as opposed to other theoretical methods such as CISD [43].

The Brueckner doubles (BD) variant [44] of coupled-cluster (CC) theory utilises Brueckner orbitals that have been shown to have maximal overlap with a full-CI wavefunction. The Brueckner orbitals are constructed via a rotation of the Hartree-Fock (HF) orbitals,

$$|BD\rangle = e^{\kappa T}|HF\rangle$$

where *T* is a cluster operator that includes double and higher excitations and κ describes the orbital rotations. The singles amplitudes are effectively absorbed into the HF orbitals via the orbital rotation procedure. Therefore the BD equations are simpler than the analogous CC equations leading to less complicated expressions for the analytic derivatives of the BD wavefunction. The perturbative triples correction is included to make BD theory correct to fourth-order in a Møller-Plesset perturbation theory analysis and is the same as used for CCSD(T) theory. Very few electrical property studies have been carried out using BD or BD(T) methods so relatively little is known about their behaviour with various basis sets and properties [45] as compared with other electron-correlation methods. It has been shown [45, 46] that BD(T) theory yields results that are almost identical to CCSD(T) and that BD is more complete than either CCSD or QCISD at fifth order in a Møller-Plesset perturbation theory analysis [44]. Additionally, the Brueckner method utilises relaxed orbitals by virtue of the fact that the singles amplitudes are absorbed into the wavefunction. Methods based upon the CC method do not utilise relaxed orbitals and there is some question as to which method gives the most reliable and accurate results for molecular properties [45, 47].

3.3 Finite-field methods for electrical property calculations

Electrical property calculations can be carried out using either analytic or numerical methods. For wavefunctions that have explicit formulae for the analytic derivatives, the calculation of electrical properties such as the dipole moment, quadrupole moment and polarizability are routine [27]. However, for wavefunctions such as those based on coupledcluster theory [43] and Møller-Plesset perturbation theory [48, 49], the formulae required for the calculation of the first and second derivatives are complicated and, as yet, not available in many computational chemistry codes. The finite-field approach, originally proposed by Cohen and Roothaan [50], is a numerical method where the field or field-gradient is introduced into the one-electron part of the molecular Hamiltonian as a perturbation. The field or field-gradient may also be produced by arrays of point-charges at suitable distances from the molecule or atom. Only the one-electron integrals are affected by the field or fieldgradient perturbation and so the method is straightforwardly incorporated into ab initio The energy is calculated in the presence of known field or field-gradient programs. strengths for the species of interest and then the equation for the charge distribution in the presence of a field or field-gradient (equation (2.74)) is numerically differentiated to a suitable order to yield the electrical properties defined as derivatives of the energy with respect to the perturbation. The method is flexible since different combinations of fields and field-gradients allow calculation of almost any electrical property component. As with any numerical procedure, the possibility of numerical inaccuracy through poor choice of field or field-gradient strength is present and this is especially true for higher order properties such as the second hyperpolarizability, γ , where several different field strengths may be required to obtain sufficient accuracy. The molecular electron density and energies must also be well-converged for the numerical differentiation procedure. Computational requirements for the finite-field calculations may also be substantial since the symmetry of the molecule is lowered when placed in an external field or field-gradient. However, the finite-field method does have the advantage that the computed electrical properties obey the Hellmann-Feynman theorem [51] since they are defined in terms of energy derivatives and not as expectation values of the wavefunction [52].

Finite-field methods have been utilised in the present thesis for calculation of dipole and quadrupole moments, polarizabilities and polarizability anisotropies for wavefunctions involving sophisticated electron correlation treatments. Examples of such theoretical methods include BD and BD(T), QCISD(T) and MP4, procedures for which analytic derivative methods are unavailable and/or computationally expensive. For large basis set MP2 calculations, finite-field methods were also utilised. Finite-field strengths in the range 0.0005 to 0.002 au have been used in conjunction with first- and second-derivative central difference formulae for computation of dipole moments and polarizabilities. Quadrupole moments have been calculated using field-gradient strengths of 0.0005 au. Expected numerical errors are supplied in the respective methods sections of the following Chapters and have been estimated from comparison of analytic and numerical SCF and MP2 electrical property calculations.

3.4 Strategy for obtaining high-quality electrical properties

The strategy for obtaining high-quality predictions of *ab initio* electrical properties for the vibrational ground state involves two distinct steps:

- (1) Geometry optimization and calculation of energy and property derivatives at the SCF or MP2 level of theory with a moderately sized basis set to reduce computational cost. The derivatives are then used for calculation of zero-point vibrational corrections and other spectroscopic quantities corresponding to the optimized theoretical geometries, $r_e(1)$.
- (2) Vibrationless electrical properties are then calculated with a more complete basis set at a high-level theoretical or experimental geometry, $r_e(2)$. In this thesis, the level of theory used for this step is usually BD or BD(T), but other high-level correlated methods such as QCISD(T), CCSD(T) or MP4 could be used with similar outcomes. The ZPVC from step (1) is then added to the vibrationless electrical property P_e to give a ground state vibrationally averaged property

$$\langle P \rangle_0 \approx P_e(r_e(2)) + \text{ZPVC}(r_e(1))$$

The above approach circumvents the calculation of energy and property derivatives at a non-stationary point on the potential energy surface (PES), thus avoiding projection of the gradient contribution from the second and higher-order energy derivatives at a nonstationary point [53]. The success of the approximation relies on the similarity of the PES about the true $r_e(2)$ and the theoretical PES about the optimized $r_e(1)$ geometry (a situation that should be well satisfied for regions close to the potential energy minima). Obviously, a full BD(T) calculation with a large basis set would render the above approximation unnecessary as both vibrationless properties and the ZPVC could be computed to the same accuracy. However, such large BD(T) or similar calculations are presently not feasible, even for small polyatomic molecules, and hence the above approximation is utilised in the present thesis.

3.5 Pseudo-BD(T) method for dynamic polarizabilities

As mentioned in the previous Chapter, electrical properties such as the polarizability and hyperpolarizabilities are frequency-dependent and many experiments yield polarizabilities that depend on the frequency of the incident light. Theoretical approaches to calculation of dynamic polarizabilities have been based upon SCF methods [54] and the second-order polarization propagator approach (SOPPA) [55], although recent developments have allowed calculation of dynamic (hyper)polarizabilities that include the effects of electron-correlation at both the MCSCF [56-58], MP2 [59-61] and coupled-cluster linear response (CCLR) theory [62, 63].

To circumvent the lack of availability of a suitable *ab initio* code for calculation of dynamic MP2 or BD(T) polarizabilities, the pseudo-BD(T) method was developed to incorporate some degree of electron-correlation effects into predictions of available SCF frequency-dependent polarizabilities. Dynamic polarizabilities are obtained at the SCF level of theory using time-dependent Hartree-Fock theory (TDHF) and are scaled by the $\langle BD(T) \rangle_0 / SCF$ ratio. This yields approximate vibrationally averaged BD(T) theoretical values for the polarizability tensor. The procedure assumes that the relative dispersion of the TDHF and BD(T) curves is identical or that the relative contribution of electron correlation is independent of the optical frequency, $\omega_{\sigma\tau}$ of the dynamic polarizability. Therefore, for a polarizability frequency dependence or dispersion function $f(\omega_{\sigma})$, the following equations are obtained:

$$\alpha_{\alpha\beta}(\omega_{\sigma})(\text{TDHF}) \approx \alpha_{\alpha\beta}(0)(\text{TDHF})\left\{1 + f(\omega_{\sigma})\right\}$$
$$\alpha_{\alpha\beta}(\omega_{\sigma})(\text{BD}(\text{T})) \approx \alpha_{\alpha\beta}(0)(\text{BD}(\text{T}))\left\{1 + f(\omega_{\sigma})\right\}$$

Combining these equations, with inclusion of a zero-point vibrational correction, leads to

$$\left\langle \alpha_{\alpha\beta}(\omega_{\sigma})(\text{pseudo}-\text{BD}(\text{T})) \right\rangle_{0} \approx \left[\frac{\left\langle \alpha_{\alpha\beta}(0)(\text{BD}(\text{T})) \right\rangle_{0}}{\alpha_{\alpha\beta}(0)(\text{TDHF})} \right] \alpha_{\alpha\beta}(\omega_{\sigma})(\text{TDHF})$$
(3.7)

The above approximation also avoids assuming that the correlation contribution is independent of ω_{σ} . Scaling of the tensor components in this manner is expected to lead to a dispersion curve ($\alpha(\omega_{\sigma})$ vs ω_{σ}^2 plot) that rises a little faster than that found for the conventional TDHF dispersion.

3.6 Basis sets for molecular property calculations

Calculations of vibrational averages of electrical properties and pure vibrational polarizabilities require basis sets that can not only reproduce the electrical properties and their derivatives with accuracy, but also provide a good description of the energy hypersurface (the derivatives of the energy). Reliable estimates of the geometries and vibrational frequencies of the molecule are necessary since it has been concluded from a number of studies of anharmonic force constants that the largest source of error in these constants arises from errors in the geometry and harmonic frequencies and not from errors in the cubic, quartic and higher-order force constants [1, 53]. Therefore, if a basis set for calculating reliable geometries and vibrational frequencies can be successfully developed, then there is a greater likelihood of calculating a good quality anharmonic energy surface and corresponding anharmonic corrections. It is indeed fortunate that basis sets for computing geometries and harmonic frequencies have already been constructed and much work has been performed on determining the optimum basis set requirements for various systems [2, 4, 5, 64-68]. Basis set requirements for electrical property calculations are discussed in the following section, along with a novel approach for development of basis sets using atomic natural orbitals (ANOs).

Basis sets for accurate prediction of electrical properties have been successfully constructed using either well-founded rules-of-thumb [69] or a systematic method [70-75]. Optimizing basis sets for reproducing specific properties may be a troublesome and time-consuming task with an inordinate amount of trial and error involved in the process; this is especially true if the basis set is to be restricted to a manageable size. Dynamical electron correlation effects are rarely incorporated into the one-particle basis set as most basis set optimization for electrical properties takes place at the SCF level. This is despite the fact that the majority of electrical property calculations are subsequently performed at correlated levels of theory. Therefore, the present work is motivated by a need to obtain electrical property basis sets, via a simple method, that (1) reproduce both the accuracy of larger basis

sets, (2) incorporate dynamical electron correlation effects and (3) are also economical to use in combination with sophisticated electron correlation treatments.

Basis sets for molecular properties require polarization and diffuse functions to describe the electron distribution at a range of distances from the nuclei. If a basis set contains sufficient functions to effectively saturate the orbital space for a given symmetry type or angular momentum, then accurate molecular properties should be obtained. Eventempered basis set expansions should well satisfy this criterion provided that the parameters used to define the even-tempered series are carefully chosen. Basis sets constructed in this way have proven to be particularly useful in obtaining the convergence behaviour for many molecular properties [70, 76] and although there is no mathematical theorem to suggest that an even-tempered expansion will offer the fastest convergence to the Hartree-Fock limit or basis set limit for a given property, Woon and Dunning [70] have found it to be more reliable and stable than other construction methods. The primary difficulty that arises from the even-tempered method is the rapid increase in basis set size thus leading to sets that either suffer from linear-dependence problems or are too large for high level electroncorrelation calculations on molecules. Correlation consistent basis sets developed by Woon and Dunning are based on augmented cc-pVXZ sets where X = D, T, Q, 5 for double, triple, quadruple and quintuple-zeta sets. The augmented-cc-pVTZ basis set is a suitable candidate for calculation of electrical properties since it has been systematically constructed with augmenting functions optimized for anion energies. However, the size of the basis set, represented as [5s4p3d2f/4s3p2d], places it out of reach for many molecular studies. The approach taken in the present work involves construction of a slightly smaller [6s4p3d1f/4s3p1d] basis set for electrical property calculations that yields an accuracy greater than or equal to, the accuracy of the aug-cc-pVTZ basis set for electrical properties.

3.7 Atomic natural orbital basis sets for electrical properties

Atomic natural orbital (ANO) contraction methods were originally proposed by Almlöf and Taylor [77-79] to deliver efficient contracted basis sets possessing small contraction errors for molecular properties with respect to large uncontracted primitive sets. In their landmark papers, large uncontracted (13*s*8*p*) substrates were augmented with both polarization and diffuse functions then generally contracted using CISD atomic natural orbitals to yield smaller basis sets that reproduced both the SCF and correlation energy with high accuracy. While their method was extremely successful for the energy and slightly less successful for multipole moments, the method appeared not to perform as well for response properties such as the polarizability [79]; extra diffuse functions were required to augment the ANO basis sets to obtain sufficient accuracy. Widmark *et al.* [72] have also utilised density matrix averaged ANOs in contracting basis sets for electrical properties with some success for computation of ionisation potentials. However, the accuracy of polarizabilities using the large [6s5p4d3f] sets was less satisfactory.

The basis set construction method proposed in the present work is based on MP2 atomic natural orbitals (MP2-ANOs) for obtaining highly accurate basis sets that reproduce the electrical properties of the uncontracted set. It is believed that if the characteristics of even-tempered expansions can be reproduced within smaller basis sets by contracting the even-tempered functions with ANOs, then highly accurate and cost effective sets should result. Both Almlöf and Taylor [77, 79] and Widmark et al. [72] contracted the entire set (substrate and polarization functions) using ANOs to obtain improved energies and minimize contraction errors in the substrate. However, in the present study, the substrate is left completely contracted in the construction of the basis sets so that only the polarization functions are contracted using MP2-ANOs. Although MP2-ANOs have been utilised in the present work, similar results are expected using ANOs from CISD or other correlated wavefunctions. One particular criticism of ANO sets is the heavy contraction of large numbers of primitive gaussians into a single basis function thereby increasing the time required to compute the two-electron integrals. This problem may be partially remedied by using general contractions. However, the majority of computational codes utilise segmented contractions and consequently these basis sets are probably unsuitable for SCF calculations where the integral calculation would be the limiting step. For correlated methods that approximately scale as n^5 , iterative n^6 or n^7 (for *n* basis functions) the computation of integrals is no longer the limiting step of the calculation and in many instances need only be performed once. However, as the smaller ANO contracted sets should obtain most of the accuracy of the uncontracted sets, the cost is effectively the same. The method of basis set construction is now outlined in detail.

3.8 Construction of ANO basis sets for first and second-row atoms

Restricted open-shell second-order Møller-Plesset perturbation theory (ROMP2) has been outlined by Amos *et al.* [80] and Knowles *et al.* [81]. Good quality contracted triplezeta valence (TZV) substrates of Schäfer *et al.* [82, 83] were used and may be represented by [3s], [5s3p] and [5s4p] for H/first-row/second-row atoms respectively. The substrates were left fully contracted in the construction procedure. Polarization function exponents were taken from Dunning and Woon [70, 84, 85] where the *d*- and *f*-type cc-pVTZ and *s*-, *p*-, *d*and *f*-type aug-cc-pVTZ exponents were utilised.

For heavy atoms, the *s*, *p* and *f* orbital spaces were extended by 2 functions each and the *d* orbital space by 4 functions, which should be sufficient for the present purposes. For hydrogen, the *s*, *p* and *d* orbital spaces were increased by 2, 4 and 2 functions respectively. As an example of the construction procedure for oxygen, the substrate and augmenting function exponents are supplied in Table 3.1. The most diffuse *s*- and *p*-type function exponents were determined by even-tempering the aug-cc-pVTZ *s*- and *p*-type functions with respect to the most diffuse functions of the substrate. The most diffuse *d*-type function was generated by even-tempering the aug-cc-pVTZ and cc-pVTZ basis sets. A similar construction procedure was followed for hydrogen with the exponents of the augmenting functions shown below.

> H atom : 2s (0.039469, 0.011081) 4p (1.407, 0.388, 0.102, 0.026814) 2d (1.057, 0.247)

The most diffuse *s*- and *p*-type functions for hydrogen were derived from even-tempered expansions with the *s*-type exponents scaled by $(1.25)^2$ to match the scaled TZV substrate *s*-type exponents [82, 83]. All other exponent values for hydrogen were taken from cc-pVTZ or aug-cc-pVTZ basis sets. The resulting size of the uncontracted basis is [7s5p4d2f/5s4p2d] for first-row atoms/hydrogen and [7s6p4d2f] for second-row atoms.

For each atom, closed-shell and open-shell MP2 gradient calculations were then performed for the ground electronic states of the atoms to obtain the MP2 relaxed density matrix which was subsequently diagonalized to obtain the natural orbitals and occupation numbers.

Table 3.1.

Oxygen atom *s*-, *p*-, *d*- and *f*-type function exponents (in au) for the MP2–ANO basis set. Shaded functions belong to the TZV (11s6p)/[5s3p] substrate from Schäfer *et al.* [82, 83].





The MP2–ANOs were averaged and contracted to yield a basis for first-row and second-row atoms of [6s4p3d1f] and [6s5p3d1f] respectively with contraction coefficients and exponents supplied in Appendix IV. Appropriate contraction coefficients can be obtained from the following averaging formulae for *p*-, *d*- and *f*-type functions [72],

$$C(p) = \frac{1}{3} (C(p_x) + C(p_y) + C(p_z))$$
(3.8)

$$C(d) = \frac{1}{5} \Big(2C(d_{xx}) + 2C(d_{yy}) + 2C(d_{zz}) + C(d_{xy}) + C(d_{xz}) + C(d_{yz}) \Big)$$
(3.9)

$$C(f) = \frac{6}{7} \Big(C(f_{xxx}) + C(f_{yyy}) + C(f_{zzz}) \Big) + \frac{1}{7} C(f_{xyz}) \\ + \frac{2}{7} \Big(C(f_{xxy}) + C(f_{xxz}) + C(f_{xyy}) + C(f_{xzz}) + C(f_{yyz}) + C(f_{yzz}) \Big)$$
(3.10)

However, the averaging for d- and f-type functions was actually carried out using the simple average of the six d-type and ten f-type component coefficients. The difference in the resulting contraction coefficients for the two methods is small. The coefficients for the s-, p-, d- and f-type primitives were also normalized for use in molecular calculations.

Obviously, the MP2–ANO contraction scheme cannot be applied to the hydrogen atom and other one-electron species. Therefore a suitable hydrogen atom basis set was derived from MP2 calculations on the H₂ molecule, at the r_e bond-length of 0.74144 Å [86], with the MP2–ANO contraction method used to give a basis set represented as [4s3p1d]. Although a larger uncontracted set could have been used in the present procedure by adding extra s and p functions, linear dependence problems generally resulted.

The basis set specification for both the substrate and the resulting contracted polarized basis set may then be summarised as follows:

Atom	Contraction Scheme	Uncontracted	Contracted
Н	41111/1111/11	8s4p2d	4 <i>s</i> 3 <i>p</i> 1 <i>d</i>
B-Ne	6211111/41111/1111/11	13 <i>s</i> 8 <i>p</i> 4 <i>d</i> 2 <i>f</i>	6s4p3d1f
Al–Ar	7321111/61111/1111/11	16s10p4d2f	6s5p3d1f

Cartesian 6-membered *d*-type and 10-membered *f*-type basis functions were utilised within the *ab initio* program CADPAC [27] for all calculations. It should be noted that the present method is entirely general and is only limited by the number of primitives that may be contracted into a given shell. Therefore, in principal, any combinations of exponents and primitive gaussians may be used, but in practice integral times will be substantially increased if the number of contracted primitives is excessively large. With the exception of hydrogen, the basis sets are also derived entirely from atomic calculations and do not include any explicit optimization for the molecular environment. However, field-dependent and/or anion-optimized functions have been used in constructing the even-tempered expansion so it is likely that these functions will compensate for rearrangement of the electron-density within a molecular environment.

3.9 Validation of ANO basis sets for first and second-row atoms

To demonstrate the accuracy of the present basis sets, a number of example calculations using both uncontracted and MP2–ANO contracted sets, are reported in this section. It should be noted that all of the ANO sets have been explicitly designed for electrical properties and may be slightly deficient in reproducing geometries, energies and frequencies since high exponent polarization functions have not been added to improve the energies calculated from these sets. Contraction errors for the various properties and the accuracy of the sets with respect to size of the basis are the primary concern.

The polarization and diffuse functions obtained from the contraction procedure may be transferred to different substrates such as double-zeta (DZ). Additionally, some of the functions may be removed from a particular atom for correlated calculations where the size of the basis set must be restricted to save computational resources.

Neon and argon

Mean polarizabilities of neon and argon atoms are presented in Table 3.2 for various basis sets and have been calculated via finite-field methods with field-strengths of 0.001 au. The uncontracted (7s5p4d2f) set for neon yields SCF results that are quite close to the Hartree-Fock limit for the polarizability and are comparable in quality to results from the d-aug-cc-pVTZ [6s5p4d3f] and t-aug-cc-pVTZ [7s6p5d4f] basis sets for this property. The BD(T) theoretical estimate for the polarizability of neon agrees well with experimental estimates. Contraction of the basis functions leads to an SCF polarizability of 2.361 au which is more accurate than the aug-cc-pVTZ [5s4p3d2f] result of 2.194 au and closer to the

d-aug-cc-pVTZ value. This is particularly encouraging as one of the criteria for using MP2– ANO contractions was to obtain the accuracy of the aug-cc-pVTZ set and in favourable circumstances, acquire the accuracy of the d-aug-cc-pVTZ set for the polarizability. An alternative method of constructing basis sets for electrical properties through optimizing diffuse functions in the presence of a field is a less efficient and more tedious process than the present single MP2 gradient calculation for an atom. A strong disadvantage of any exponent optimization method is that removal of the optimized diffuse functions often leads to poor predictions of the properties if other diffuse functions are not present in the basis set. This is not the case for the MP2–ANO contracted set, as demonstrated by the results in Table 3.2 for neon, where the removal of the 3rd *d*-type polarization function and *f*-type function, to give the [6s4p2d] set, does not markedly affect the value of the mean polarizability.

The MP2–ANO [6s5p3d1f] contracted basis set for argon appears to be less successful in reproducing the accuracy of the uncontracted set since, at the MP2 level, the differences between polarizabilities are larger than found for neon. Nevertheless, the MP2– ANO set still acquires the accuracy of the aug-cc-pVTZ basis, yielding an MP2 mean polarizability of 10.937 au which is in reasonable agreement with the d-aug-cc-pVTZ result of 11.169 au. Core correlation may be responsible for some of the discrepancy between the present uncontracted (7s6p4d2f) set MP2 values and the results of Woon and Dunning for the largest augmented basis sets, since the frozen core approximation was used by Woon and Dunning for their finite-field polarizability calculations. However, it should be noted that atoms perhaps represent a worst-case scenario for polarizability calculations as there is no possibility of interatomic polarization, such as that found for molecules [87].

							The Party of California and th
	Basis Set	NBF	SCF	MP2	BD	BD(T)	Experiment
Ne							
	(7s5p4d2f)	56	2.376	2.699	2.619	2.673	$2.67(2)^b, 2.669^c$
	[6s4p3d1f]	36	2.361	2.667	2.593	2.641	
	[6s4p2d]	30	2.325	2.632	2.573	2.618	
	cc-pVTZ	35	1.026	1.028			
	aug-cc-pVTZ	55	2.194	2.437			
	d-aug-cc-pVTZ	75	2.375	2.711			
	t-aug-cc-pVTZ	95	2.375	2.712			
Ar							
	(7 <i>s</i> 6 <i>p</i> 4 <i>d</i> 2 <i>f</i>)	69	10.697	11.132	11.063	11.153	11.092(9) ^b ,11.08 ^c
	[6s5p3d1f]	49	10.626	10.937	10.882	10.950	
	[6s5p2d]	33	10.204	10.468	10.481	10.554	
	aug-cc-pVTZ	59	10.438	10.814			
	d-aug-cc-pVTZ	79	10.701	11.169			
	t-aug-cc-pVTZ	99	10.702	11.170			

Table 3.2.

Mean polarizabilities of neon and argon obtained with various basis sets and levels of theory.^a

basis sets have ANO-contracted polarization functions. The cc-pVTZ and augmented-cc-pVTZ results were taken from Woon and Dunning [70].
NBF is the number of basis functions for the basis set. The values for the Woon and Dunning sets were calculated assuming six-member *d*-type and ten-member *f*-type functions, although Woon and Dunning carried out the calculations using spherical harmonic five-member *d*- and seven-member *f*-type basis functions.

^{*a*} All polarizabilities are in atomic units. The (7s5p4d2f) and (7s6p4d2f) basis sets have uncontracted polarization functions, the [6s4p3d1f], [6s4p2d] and [6s5p3d1f], [6s5p2d]

- ^b Static mean polarizability from a quadratic extrapolation of refractivity data [88].
- ^c Static dipole oscillator strength distributions (DOSD) estimate [89, 90].

Ammonia

Although the MP2-ANO basis sets were developed from atomic calculations, they perform equally well for molecular property calculations. For both uncontracted and contracted basis set calculations reported in Table 3.3, the hydrogen atom utilised the TZPOL1 basis set (reported in [91] as TZP1), with an additional *d*-type function (exponent of 1.057 a_0^{-2}). This basis set was used on hydrogen to only focus on the contraction error for the nitrogen atom rather than utilising contracted sets for both nitrogen and hydrogen. The experimental r_e geometry of Benedict and Plyler [92]($r_{\text{NH}} = 1.0124$ Å, $\theta_{\text{HNH}} = 106.67$ °) was used for these calculations. Energies and electrical properties of NH₃ are presented in Table 3.3 for the uncontracted and MP2-ANO contracted basis sets. The contraction error for the SCF energy is only 5.8 µHartrees and this is increased to 6.1 mHartrees at the MP2 level. For dipole and quadrupole moments, differences between the uncontracted and contracted basis set values for both the SCF and MP2 levels of theory are relatively insignificant; < 0.0014 au and < 0.0025 au for the dipole and quadrupole moments respectively. Mean polarizability differences are also quite small (0.003 au) for SCF and only a little larger at the MP2 level (0.005 au). Generally for NH₃, the contraction errors for the properties from this basis set on nitrogen are exceptionally small.

Results in Table 3.4 demonstrate the contraction error for the properties when MP2– ANO basis sets are used on both nitrogen and hydrogen atoms. Although the contraction error for the SCF dipole moment is exceedingly small (< 0.0001 au), contraction errors for other properties are larger for this basis set. A different basis set optimization procedure should probably be used for hydrogen as the polarization functions from the H₂ molecule MP2–ANOs may not be well-suited towards general molecular calculations. However, the contracted basis set yields relatively good quality results which compare quite well with the uncontracted (7*s*5*p*4*d*2*f*/4*s*3*p*1*d*) basis set values reported in Table 3.4.

Table 3.3.

	SC	CF	MP2		
Property	Uncontr.	Contr.	Uncontr.	Contr.	
E	-56.222803	-56.222745	-56.484156	-56.478072	
μ_z	-0.6374	-0.6372	-0.6027	-0.6013	
Θ_{zz}	-2.1515	-2.1490	-2.2405	-2.2395	
$lpha \Delta lpha$	12.948 0.530	12.945 0.520	14.262 1.844	14.257 1.840	

SCF and MP2 energies and electrical properties of ammonia using the uncontracted and contracted MP2–ANO basis sets on the nitrogen atom. ^a

^{*a*} All properties are in atomic units. The uncontracted basis set has uncontracted polarization functions on nitrogen and is represented as (7s5p4d2f) (123 basis functions). The contracted basis set has polarization functions on nitrogen constructed from MP2–ANOs and is represented as [6s4p3d1f] (103 basis functions). The basis set for hydrogen is the TZPOL1 basis set supplied in [91] with an additional *d*-type function (exponent of 1.057).

Table 3.4.

SCF and MP2 calculations on ammonia using the uncontracted and contracted MP2–ANO basis sets for both nitrogen and hydrogen atoms. ^a

	SC	CF	MP2		
Property	Uncontr.	Contr.	Uncontr.	Contr.	
E	-56.222863	-56.222053	-56.485223	-56.472205	
μ_z	-0.6375	-0.6376	-0.6022	-0.6033	
Θ_{zz}	-2.1459	-2.1554	-2.2359	-2.2527	
α	12.954	12.935	14.293	14.302	
$\Delta \alpha$	0.516	0.543	1.847	1.909	

^{*a*} All properties are in atomic units. The uncontracted basis set has uncontracted polarization functions on nitrogen and hydrogen and is represented as (7s5p4d2f/5s4p2d) (153 basis functions). The contracted basis set has polarization functions on both nitrogen and hydrogen constructed from MP2–ANOs and is represented as [6s4p3d1f/4s3p1d] (103 basis functions). The basis set for hydrogen was constructed using MP2–ANOs for the H₂ molecule.

Carbon Dioxide

Highly accurate electrical property calculations using electron-correlation treatments such as MP4, BD(T) and CCSD(T) require considerable computational time and disk storage. Approximate costs for BD(T) and CCSD(T) theory are iterative n^6 + a single n^7 step for *n* basis functions, while MP4 requires a single n^7 step. The MP2–ANO basis sets offer one way to circumvent the computational cost problems since they reduce the number of basis functions to an acceptable size while still retaining nearly all of the accuracy of the uncontracted set. Calculations of the mean polarizability and polarizability anisotropy for CO₂ using a variety of basis sets, at the experimental r_e geometry of Graner *et al.* [93, 94](r_{co} = 1.15995884 Å), are presented in Table 3.5. For these calculations, the finite-field method was utilised with field-strengths of 0.002 au. The calculations with *f*-type functions on all atoms with the [6*s*4*p*3*d*1*f*] basis set exceeded available computational resources for BD(T) calculations. Therefore *f*-type functions on oxygen where removed and the *d*-type functions. The contracted set used in Table 3.5 is built from MP2–ANO contracted *d*-type functions.

CO ₂	Basis Set	SCF	MP2	BD	BD(T)
α	Uncontracted	15.849	17.835	17.299	17.521
	Contracted	15.836	17.802	17.277	17.497
	Difference	0.013	0.033	0.022	0.024
Δα	Uncontracted	11.711	14.545	13.880	13.943
	Contracted	11.812	14.659	13.997	14.061
	Difference	-0.101	0.114	0.117	-0.118

Table 3.5. Carbon dioxide α and $\Delta \alpha$ using uncontracted and the contracted MP2–ANO basis sets.^{*a*}

^{*a*} All properties are in atomic units. The uncontracted basis set with uncontracted *d*-type functions is represented as [6s4p4d1f/6s4p4d](136 basis functions) (carbon/oxygen). The contracted basis set has *d*-type polarization functions contracted using MP2–ANOs and is represented as [6s4p3d1f/6s4p3d] (118 basis functions). Apparently, the contraction of the *d*-type functions only leads to small differences in the mean polarizability with a maximum contraction error of 0.033 au (< 0.19% of α from the uncontracted basis set) found for MP2 theory. Differences between the polarizability anisotropy for the two basis sets are also quite small with respect to the uncontracted property. However, the uncontracted basis set calculation required 1.8 times the disk storage and 1.7 times the cpu time of the contracted basis set calculation. Obviously, the required computational cost must be weighed against the accuracy obtained from the calculation. Nevertheless, the MP2–ANO contraction scheme does offer another way of retaining accuracy in a truncated basis set while avoiding the time-consuming optimization of exponents for a given molecule or basis set.

It has been shown that basis sets possessing MP2–ANO contracted polarization and diffuse functions are capable of reproducing electrical properties with an accuracy close to that of their uncontracted counterparts. Polarization and diffuse functions obtained from the present contraction scheme should be transferable to other substrates such as double-zeta (DZ) with minimal loss of accuracy. Full contraction of the substrates and polarization functions would prove to be computationally very costly and likely to lead to inefficient basis sets; this procedure has been avoided in the present work. The transferability approach has been used for construction of the DZP–ANOx type basis sets (x = 1, 2, 3), for later studies on the fluoromethanes (Chapter 6), ethene (Chapter 7) and ethane (Chapter 8), where the MP2–ANO polarization and diffuse functions have been combined with the DZ substrate of Thakkar *et al.* [95].

Although electrical properties such as the polarizability have been targeted in the study, the MP2–ANO contraction is open-ended and may be used with any combination of gaussian primitives or choice of molecular properties. It is not recommended that these sets be used for SCF calculations since the time to compute two-electron integrals is expected to dominate such computations. However, the MP2–ANO sets are suitable for accurate electrical property investigations involving high-level electron correlation methods, where the cost of the calculations is dominated by the approximate iterative n^6 + single step n^7 cost for *n* basis functions and not by the evaluation of two-electron integrals.

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Second-row hydrides : SiH_4 , PH_3 , H_2S and HCl

4.1 Introduction

Of all molecules studied to date, the first-row hydrides CH_4 , NH_3 , H_2O and HF appear to be among the most popular due to their relatively small size and simple structures. Zero-point vibrational corrections (ZPVCs) to the electrical properties of the first-row hydrides have already been published [1] as part of a validation of the least-squares derivative method and that work demonstrated the feasibility of routinely incorporating ZPVCs into *ab initio* electrical property calculations. However, very few theoretical electrical property studies have been performed on the analogous second-row series: SiH₄, PH₃, H₂S and HCl. Highly accurate *ab initio* electrical property calculations are able to be carried out on the second-row hydride molecules since large basis sets can be utilised in conjunction with accurate electron correlation methods. In this respect, a study of the second-row hydrides provides the possibility of calibrating theoretical methods and a serious attempt is made to provide high quality theoretical predictions in the present Chapter.

Experimental dipole moments of these molecules have been determined with high precision from microwave Stark and molecular beam electric resonance (MBER) spectroscopy [2-5]. Unfortunately, there have been no experimental estimates of quadrupole moments published for PH₃ or H₂S. Reliable experimental mean polarizabilities from refractivity data exist for the molecules SiH₄ [6, 7], H₂S [8-10] and HCl [11, 12], but the mean polarizability of PH₃ has only been investigated via a single dielectric constant study [13]. The polarizability anisotropies for HCl and H₂S have been studied experimentally via Rayleigh light scattering and rotational Raman spectroscopy [14-16]. The polarizability anisotropy of H₂S is exceptionally small and should provide an illuminating test of the accuracy of the present *ab initio* procedures.

Considering incompleteness of some of the experimental data and as an extension of the work on the first-row hydrides [1], a study of the second-row hydrides SiH₄, PH₃, H₂S and HCl was undertaken with an emphasis on providing reliable predictions of dipole and quadrupole moments, polarizabilities and polarizability anisotropies for these molecules. The Brueckner orbital variant of CCSD(T) theory [17], namely Brueckner doubles (BD) with perturbatively linked triples, BD(T), has been combined with large triple-zeta polarized basis sets in order to establish the basis set and correlation limit for the vibrationless properties. Vibrational effects have been included through calculation of the ZPVCs for the ground vibrational state, with pure vibrational polarizabilities also presented. The effect of deuterium substitution on the properties is investigated and the frequency dependence of the dipole polarizability is also explored. Theoretical values are critically compared with available experimental results in an effort to highlight any discrepancies between theory and experiment. Where there is little or no data for the studied properties, it is hoped that the present predictions will perhaps act as an incentive for further experimental study on these molecules. The research presented in this Chapter has already been published [18] and a reprint of that work is included in Appendix V. The majority of that material is included in the present thesis as it makes an important contribution to the overall discussion. Where precise details have been omitted, they may be found in the published paper.

4.2 Computational methods

4.2.1 Vibrational averaging and property derivative calculations

The required property derivatives up to fourth-order for the energy, dipole and quadrupole moments, polarizabilities and polarizability anisotropies were computed via the least-squares technique described in Chapter 3. Degenerate modes for PH_3 and SiH_4 were aligned with respect to symmetry planes of the molecules to match the usual conventions as outlined by Cyvin *et al.* [19]. In all cases, the principal axis of rotation was chosen to be the *z* axis with the heavy atom lying along the positive *z* direction. For H_2S , the molecule was chosen to lie in the *xz* plane. Quadrupole moments were calculated with respect to the molecular centre of mass. All least-squares fitting, generation of grid points, calculation of derivatives, vibrational corrections and pure vibrational polarizabilities was carried out using ANHARPS [20]. Unless otherwise specified, all calculations reported in this Chapter refer to the ${}^{28}SiH_4$, ${}^{31}PH_3$, $H_2{}^{32}S$ and $H^{35}Cl$ isotopomers corresponding to the most abundant isotopes of the heavy atoms, with isotopic masses supplied in Appendix II. Isotope effects

arising from deuterium substitution for SiD_4 , PD_3 , D_2S and DCl were obtained using the theory and methods outlined in Chapters 2 and 3.

4.2.2 Basis sets and ab initio methods

Two types of basis sets were used in the present study, both of which are based on the triple-zeta valence substrates of Schäfer *et al.* [21, 22]. For the vibrational averaging and property derivative calculations, the TZPOL1 molecular basis set was used and may be represented as [7s6p2d1f/4s3p] for heavy atoms / hydrogen. Exponents and contraction coefficients for the TZPOL1 basis set are reported in the published work [18]. To obtain higher accuracy in frequencies and geometries, *d*-type functions on H are probably warranted but were omitted from this work for reasons of high computational cost.

For high-accuracy electrical property calculations at the experimental r_e geometries, the MP2–ANO basis set, described in Chapter 3, was utilised. To improve the energies calculated with the MP2–ANO set and partially address core correlation effects, uncontracted high exponent *d*-type functions were added to the heavy atoms. The inclusion of diffuse *d*-type functions on hydrogen was also found to have a dramatic effect on correlated polarizabilities. The MP2–ANO basis set for second-row atoms may be represented by [6s6p4d1f/4s3p1d] for heavy atoms/hydrogen and is designated as TZP– ANO1 in the present work. Exponents and contraction coefficients for the TZP–ANO1 basis are supplied in Appendix IV. Although larger basis sets could be utilised, especially for calculations on H₂S and HCl, high level BD and BD(T) calculations with the same high quality basis set are to be performed without exceeding current computational resources; the MP2–ANO type of basis set well satisfied this requirement.

Calculations of the electrical properties using the TZP–ANO1 set were performed at the experimental r_e geometries for SiH₄ ($r_{SiH} = 1.4707$ Å [23]), PH₃ ($r_{PH} = 1.41175$ Å, $\theta_{HPH} =$ 93.4210 ° [24]), H₂S ($r_{SH} = 1.3356$ Å, $\theta_{HSH} = 92.12$ ° [25]) and HCl ($r_{HCl} = 1.2746$ Å [26]). All dipole moments and dipole polarizabilities were obtained via finite-field techniques using central differences of field-dependent energies in CADPAC 5.2 [27]. Electric field strengths of 0.001 au were found to be suitable for these calculations, with quadrupole moments calculated from central differences of energies in the presence of finite-field-gradients of strength 0.0005 au. Numerical errors in the properties are estimated to be less than 10⁻⁵ au for the dipole moment and less than 10⁻³ au for the polarizability tensor components, with an error of less than 0.0002 au expected for the quadrupole moments. Atomic units are used throughout and conversion factors to SI units are provided in Appendix I. Although the present results are not explicitly compared with other theoretical estimates, it is noted that several studies have been performed on HCl, the most extensive on the dipole and quadrupole moments [28, 29], dipole polarizability and hyperpolarizabilities [28, 30]. Many other dipole moment and polarizability calculations on HCl are summarised by Maroulis [28]. Other electrical properties studies on the second-row hydrides include those of Dougherty and Spackman [31, 32] and Sadlej [33].

4.3 Results and discussion

4.3.1 Zero-point vibrational corrections

Zero-point vibrational corrections to the various properties are presented in Table 4.1. Dipole moment corrections for PH_3 decrease the magnitude of the dipole moment with the largest contribution to the ZPVC arising from the degenerate v_3 "asymmetric stretching" mode. For HCl, bond stretching causes an expected increase in the dipole moment with SCF and MP2 ZPVCs in good agreement. It is interesting to find that both SCF and MP2 vibrational corrections have the same sign for PH_3 and HCl, whereas for H_2S the SCF corrections are of opposite sign to their MP2 counterparts. This is not too surprising given that the vibrational correction for this molecule is of very small magnitude.

It is difficult to discern any firm trends from the ZPVCs for dipole and quadrupole moments. However, for the mean polarizabilities there is a regular decrease across the row where the MP2 percentage corrections to the vibrationless property are 4.0, 2.8, 1.6 and 0.9% respectively for SiH₄, PH₃, H₂S and HCl. This can be explained by the decrease in the number of vibrational modes able to influence α since, to a rough approximation, the MP2 vibrational contribution per mode for SiH₄, PH₃, H₂S and HCl is 0.135, 0.139, 0.133 and 0.150 au respectively. This simple analysis obviously neglects the fact that different types of modes, both bending and stretching, are contributing various amounts to the ZPVC, but it does show that the contribution to the mean polarizability per mode is approximately constant. Agreement between SCF and MP2 ZPVCs for this property is also exceptionally Corrections to the polarizability anisotropy are particularly important, with good. percentage corrections to the vibrationless property of as much as 49% for H₂S at the MP2 level of theory. Such large percentage corrections are primarily due to the small magnitude of the uncorrected $\Delta \alpha$, but they do highlight the fact that the ZPVC should not be neglected for this property in any *ab initio* study aiming for definitive results.

SiH ₄	Property α	<i>P_e</i>	ZPVC	P_e	ZPVC
SiH ₄	α	20 (07		C.	
		29.697	1.1690	30.670	1.2135
PH_{2}	μ_{-}	-0.2972	0.01365	-0.2400	0.00948
5	Θ.	-1.960	0.0327	-1.669	0.0309
	α	29.608	0.8257	30.200	0.8326
	$\Delta \alpha$	1.252	-0.2717	1.772	-0.2049
H_2S	μ_z	-0.4289	0.00046	-0.3920	-0.00135
	$\Theta_{_{XX}}$	2.250	0.0063	2.087	0.0076
	Θ_{yy}	-2.924	-0.0301	-2.883	-0.0359
	Θ_{zz}	0.674	0.0238	0.796	0.0283
	α_{xx}	23.841	0.6096	24.326	0.5789
	α_{yy}	24.008	0.0936	25.044	0.1360
	α_{zz}	23.385	0.4787	24.268	0.4778
	α	23.744	0.3940	24.546	0.3975
	$\Delta \alpha$	0.559	-0.0474 ^b	0.748	-0.3681 ^b
HCI	μ_z	-0.4651	-0.00712	-0.4370	-0.00706
	Θ_{zz}	2.820	0.0534	2.766	0.0550
	α	16.689	0.1466	17.325	0.1500
	$\Delta lpha$	1.689	0.3013	1.624	0.2747

Table 4.1.
SCF and MP2 TZPOL1 vibrationless properties and zero-point vibrational corrections
(ZPVCs) (in au) to the electrical properties of the second row hydrides. ^{a}

^{*a*} In each case the principal rotation axis was chosen to be the *z* axis with the heavier atom lying along the +*z* axis; hydrogen sulfide lies in the *xz* plane. Quadrupole moment corrections were derived from quadrupole moments relative to the molecular centre of mass. Equilibrium vibrationless properties P_e were calculated at the respective SCF and MP2 optimized geometries (supplied in Appendix III) using the TZPOL1 basis set.

^b Calculated using the method described in Chapter 2, Section 2.4.

4.3.2 Pure vibrational polarizabilities and polarizability anisotropies

Pure vibrational polarizabilities for the ground vibrational state and infinite wavelength have been computed using the Bishop and Kirtman perturbation theory formalism [34, 35], implemented as described in Chapter 3, and are compared with experimental results in Table 4.2. In all cases, the SCF values of α^{v} are systematically larger than their MP2 counterparts. This is likely to be due to an improved description of the dipole moment surface at the MP2 level of theory, yielding a decrease in the magnitude of the dipole moment first derivatives which form the leading doubly harmonic term of the perturbation theory expressions [35] (i.e. $[\mu^2]^{0,0}$ in Bishop's notation [35]). For SiH₄, there appear to be unusually large discrepancies between theory and experiment with both SCF and MP2 results overestimating experiment by 15.3 and 6.7% respectively. An extensive study of infrared intensities, which are closely related to the pure vibrational polarizabilities [36, 37], showed that IR intensities generally decrease with improvements in the treatment of electron correlation [38]. An improved electron correlation method is therefore expected to yield more accurate results since the dominant doubly harmonic term involves the dipole moment first derivatives and the harmonic vibrational frequencies. Nevertheless, the MP2 method used in this work is sufficiently accurate to provide reliable estimates of the pure vibrational polarizability. It should be noted that the experimental determination of the integrated infrared intensities, and hence vibrational polarizabilities, is difficult and susceptible to many problems, especially where fundamental bands overlap. A case in point occurs for PH₃. Comparing theoretical results with experiment, it was found that although the pure vibrational mean polarizability from Bishop and Cheung [36] agrees well with the present theoretical estimates, this was not so for $\Delta \alpha$, where their experimentally derived value overestimated the MP2 results by a factor of 2.6. When an improved set of experimental infrared intensities for v_1 and v_3 [39] are used in Bishop and Cheung's formula, the agreement with theory is excellent, the present theoretical results lying within 1.6 and 0.4% of experiment for α^{v} and $\Delta \alpha^{v}$ respectively. Further information regarding the accuracy of the experimental infrared intensities is supplied in the publication [18]. It is interesting to see that the pure vibrational polarizabilities for H₂S are exceptionally small compared to the other molecules, reflecting the fact that the dipole moment for this molecule shows very little variation with nuclear motion.

		Level		
	-	SCF	MP2	Experiment
SiH ₄	$lpha^{v}$	5.6472	5.2291	4.90(7), ^b 4.84(7) ^c
PH_3	α^{v}	0.7654	0.5882	0.579(6), ^d 0.58(6) ^e
	$\Delta \alpha^{v}$	0.1384	0.1693	0.170(2), ^d 0.44(9) ^e
H ₂ S	α_{xx}^{v}	0.0021	0.0024	
	α_{zz}^{v}	0.0240	0.0128	
	$lpha^{v}$	0.0087	0.0051	0.0038(2) <i>f</i>
	$\Delta lpha^{v}$	0.0231	0.0118	0.0111(6) <i>f</i>
HCl	α^{v}	0.0516	0.0491	$0.041(1), g \ 0.036(2)$
	$\Delta \alpha^{v}$	0.1548	0.1474	0.124(2), 8 0.108(5)

SCF and MP2 TZPOL1 pure vibrational polarizabilities and polarizability anisotropies (in au) for the second row hydrides.^a

^{*a*} In each case z is the principal rotation axis with the heavier atom lying along the +z axis. The hydrogen sulfide molecule lies in the xz plane and the yy component of the vibrational polarizability is therefore zero.

^b Derived from experimental infrared intensities [40] with a precision estimate of 1.5%. A value of 3.8(3) au has been derived from another set of IR intensities [36, 41] but appears to be too low due to the small intensity measurement for the v_4 fundamental band.

^c Calculated from an experimental IR intensity measurement for the v_4 fundamental [40] and a recent intensity measurement for the v_3 fundamental [42].

^d Calculated from experimental IR intensities [39]. Precision estimates representing 1% of the measured result have been applied.

e Derived from experimental IR intensities within the harmonic oscillator approximation
 [36] using the supplied precision estimates.

f Calculated from experimental IR intensities for the v_1 , v_3 and $2v_2$ bands [43] and the v_2 band [44, 45].

⁸ Calculated from experimental IR intensities [45, 46]. A precision estimate of 2% has been assumed.

Table 4.2.

4.3.3 Dipole and quadrupole moments

In this and subsequent Chapters, an effort is made to critically compare the present best estimates of vibrationally averaged molecular properties with available experimental data. Comparing the present theoretical vibrationally averaged dipole and quadrupole moments with experiment (Table 4.3), it may be readily observed that the improved treatment of electron correlation results in a decrease in the magnitude of μ_z for all molecules considered. Quadrupole *zz* components for PH₃, HCl and the *xx* and *yy* components for H₂S also vary in this manner. Surprisingly, all of the current BD(T) predictions appear to be underestimates, with BD values closest to experiment.

Table 4.3.

Vibrationally averaged TZP–ANO1 dipole and quadrupole moments (in au) for the second-row hydrides.^{*a*}

		SCF	MP2	BD	BD(T)	Experiment
PH ₃	$\mu_z \ \Theta_{zz}$	-0.2545 -1.7182	-0.2225 -1.6040	-0.2211 -1.5643	-0.2190 -1.5566	-0.2258(1) ^b
H_2S	μ_z	-0.4218	-0.3876	-0.3818	-0.3771	-0.383(2) ^c
	$egin{array}{llllllllllllllllllllllllllllllllllll$	2.1360 -2.9220 0.7861	2.0747 -2.8739 0.7996	2.0266 2.8061 0.7798	2.0222 -2.8017 0.7800	
HCI	$\mu_z \ \Theta_z$	-0.4721 2.8875	-0.4407 2.8162	-0.4336 2.7590	-0.4288 2.7491	-0.4361(1) ^d 2.78(9) ^e

^{*a*} TZPOL1 vibrational corrections have been applied to properties computed at the respective experimental r_e geometries using the TZP–ANO1 basis set (See text). SCF/TZPOL1 ZPVCs have been applied to SCF/TZP–ANO1 property calculations; MP2/TZPOL1 ZPVCs have been applied to TZP–ANO1 properties for other correlated levels of theory. In each case z is the principal rotation axis with the heavier atom lying along the +z axis; hydrogen sulfide molecule lies in the xz plane. Quadrupole moments refer to the molecular centre of mass.

^b Molecular beam electric resonance (MBER) measurement for the ground vibrational state [2].

^c Stark effect measurement for the ground vibrational state [3].

^{*d*} MBER measurement for the ground vibrational state [4].

^e MBER measurement for the ground vibrational state [5].

Several possible sources of the discrepancies between BD(T) theory and experiment were considered for the dipole moments of H₂S and HCl. Basis set incompleteness was explored with MP2 calculations at the respective experimental r_{e} geometries, using a large uncontracted form of the TZP-ANO1 basis [7s6p5d2f/5s4p2d], yielding vibrationless estimates of -0.3824 and -0.4307 au respectively. Utilising the MP2 ZPVCs gave predictions of -0.3838 and -0.4378 au which compare favourably with experimental results in Table 4.3. Applying correlation contributions, from the difference between BD(T) and MP2 TZP-ANO1 predictions, produced vibrationally averaged dipole moments of -0.3732 and -0.4259 au, both of which are even smaller in magnitude than the BD(T)/TZP-ANO1 values, and further underestimate experiment. A change of substrate for the TZP-ANO1 set from the TZV [5s4p/3s] substrate for heavy atoms/hydrogen to a much larger [9s6p/6s] set [47] had little effect for HCl, yielding an MP2 vibrationally averaged dipole moment of -0.4414 au which only differs from the TZP-ANO1 value in Table 4.3 by just 0.00074 au. Although not reported in detail in this work, the effects of rotational motion on the dipole moment have also been calculated using the methods of Chapter 2 and 3 and found to be relatively unimportant. Rotational corrections to the dipole moments were found to be typically $< 10^{-5}$ au and certainly smaller than the experimental uncertainties associated with the dipole moment measurements. Thermal effects were also examined and found to be negligible for the temperatures at which the dipole moment experiments were performed. Scaling of the experimental dipole moments for differences in the OCS reference dipole moments is also not required in the present work.

A number of possible reasons for the discrepancies between the presumably most accurate vibrationally averaged BD(T) estimates and experiment for the dipole moments have therefore been investigated. Considering this and the results presented in Table 4.3, it is possible that the BD method of electron correlation is sufficient to obtain accurate first-order electronic properties and the perturbative correction for connected triple excitations (T), used to make the BD method complete to fourth-order in a Møller-Plesset perturbation theory analysis [17], is actually overcorrecting the BD values in much the same manner as is found for the T(4) term of MP4 theory [48]. In this instance, full BDT calculations would be helpful in establishing the source of the discrepancy. Orbital relaxation effects [49, 50] are not really of issue since the present work utilises Brueckner orbitals for which the relaxation effect is explicitly included, as opposed to CCSD methods where calculations using unrelaxed or relaxed SCF orbitals are possible [49]. The question of whether the energy derivative or expectation value method for calculation of first-order properties is more

reliable also arises in this context since it is generally accepted that the energy derivative method is the more reliable approach, especially for small basis set calculations. However, as the basis set becomes progressively larger and approaches a complete set of functions, it becomes more likely that the Hellmann-Feynman theorem [51] will be satisfied. Further detailed work in this area is needed to reliably establish which of the two methods is the most appropriate for coupled-cluster and Brueckner methods. At this point, the discrepancies between the present vibrationally averaged BD(T) values and experiment for the dipole moments cannot be definitively explained.

4.3.4 Polarizabilities and polarizability anisotropies

Vibrationally averaged polarizabilities and polarizability anisotropies are compared with experimental results in Table 4.4. The superb agreement between present BD(T)estimates and experiment for α highlights the necessity of including zero-point vibrational corrections in the *ab initio* calculations: in all cases, the uncorrected properties are smaller than experiment by up to 5%. For SiH_4 , the mean polarizability increases systematically moving from SCF to BD(T) with the best estimate of 31.783 au within just 0.04% of a recent dipole oscillator strength distributions (DOSD) estimate [6]. Although there is only a single dielectric constant measurement for PH_3 , the difference between the BD(T) result and experiment is remarkably small and almost within experimental error. It is anticipated that the present BD(T) theoretical prediction for the mean polarizability of PH_3 is likely to be accurate to within 0.5% of any future experimental results since other calculated mean polarizabilities in the table lie within this tolerance. For H₂S and HCl, the older refractivity measurements of Cuthbertson and Cuthbertson [8, 11], published in 1909 for H₂S and 1913 for HCl, appear to be remarkably reliable, and in almost exact agreement with the present BD(T) estimates. The DOSD semi-empirical values for the mean polarizability [10, 12] also lie within 0.5% of the present results but slightly underestimate the numbers from Cuthbertson and Cuthbertson [8]. Unlike the situation for dipole moments, the perturbative triples correction in BD(T) theory is found to increase α from BD calculations by 0.33, 0.34, 0.74 and 0.95% for SiH₄, PH₃, H₂S and HCl respectively, and thereby improve the agreement between theory and experiment. For this second-order property, the triples correction appears to be necessary to obtain quantitative agreement with experiment.

			Level of T			
		SCF	MP2	BD	BD(T)	Experiment
SiH ₄	α	30.403	31.629	31.680	31.783	31.77, ^b 31.94(3) ^c
PH_3	α	30.392	31.120	30.681	30.787	30.9(1) d
	$\Delta lpha$	0.858	1.537	1.222	1.409	
H_2S	α_{xx}	24.507	24.980	24.676	24.785	
	$\alpha_{_{yy}}$	24.150	25.284	24.732	24.968	
	α_{zz}	24.080	24.855	24.465	24.662	
	α	24.246	25.040	24.624	24.805	24.77(2), ^e 24.71 ^f
	$\Delta \alpha$	0.396	0.382	0.244	0.267	0.669(73), <i>g</i> 0.678(74) <i>h</i>
HCl	α	16.895	17.478	17.269	17.433	17.43(2), ^{<i>i</i>} 17.39 ^{<i>j</i>}
	$\Delta \alpha$	2.063	1.896	1.966	1.944	1.96(67), ^k 1.94(6) ^l

Table 4.4. Vibrationally averaged TZP–ANO1 polarizabilities (in au) for the second-row hydrides.^{*a*}

^{*a*} See footnote (a) of Table 4.3.

^b Static estimate from dipole oscillator strength distributions (DOSD) [6].

^c Static estimate from quadratic extrapolation of refractivity data (five wavelengths between 436 and 644 nm) [7].

^d Re-analysis of dielectric constant data [13] (See Dougherty and Spackman [31]).

- ^e Static estimate from a quadratic extrapolation of refractivity data (four points between 486 and 656 nm) [8]. A static estimate of 24.83(3) au was obtained from a quadratic extrapolation of refractivity data using four points between 490 and 657 nm [9] with a quadratic extrapolation of all six data points between 404 and 657 nm yielding a static value of 24.71(4) au.
- f Static DOSD estimate [10].
- ^{*g*} Dynamic estimate (632.8 nm) using tensor components from a combination of Kerr effect, Rayleigh light scattering and refractive index data [14].
- ^h Dynamic estimate (488 nm) from Rayleigh light scattering and rotational Raman spectroscopy [15].
- ^{*i*} Static estimate from quadratic extrapolation of refractivity data (eight wavelengths between 480 and 670 nm) [11].
- *j* Static DOSD estimate [12].
- ^k Static molecular beam electric resonance (MBER) measurement [4].
- ¹ Dynamic estimate (632.8 nm) from Rayleigh light scattering [16] using the reported depolarization ratio and an interpolated dynamic value (632.8 nm) of the mean polarizability from refractivity data [11].

The simpler and less costly MP2 method also performs quite well for α yielding results in close accord with BD(T) numbers. It is interesting to find that the effect of electron correlation on α is similar for PH₃, H₂S and HCl. For these three molecules, it is apparent that the mean polarizability follows an "oscillatory" progression with SCF polarizabilities underestimating all correlated numbers but with BD(T) results lying almost midway between MP2 and BD. Silane represents an exception to this behaviour.

The frequency dependence of α and $\Delta \alpha$ has also been explored through calculation of the polarizability at several laser wavelengths using the pseudo-BD(T) method described in Chapter 3. Plots of $\alpha(\omega_{\sigma})$ against ω_{σ}^2 are displayed in Figure 4.1 and compared with available experimental dispersion curves. It is strikingly apparent from the dispersion plots that the theoretical mean polarizabilities are in close agreement with polarizabilities from refractivity data for H₂S and HCl. However, for SiH₄ the agreement between the theoretical and experimental dispersion is not as good and this is partly due to the differences between the theoretical and experimental static polarizabilities as well as the small number of optical frequencies at which the experimental refractivities were measured [7]. Although the method of scaling the dynamic polarizabilities is purely empirical and does not rigorously include electron correlation into the dynamic polarizability, it does slightly improve upon the TDHF frequency dependence characteristics for α .

For $\Delta \alpha$ (Table 4.4) present values for HCl agree well with results from both MBER [4] and Rayleigh light scattering measurements [16]. Although at first glance the H₂S results appear to be inferior to experimental results, static values of $\Delta \alpha$ at infinite wavelength (zero optical frequency, $\omega_{\sigma} = 0$) have been calculated whereas the experimental values pertain to dynamic quantities measured at an optical wavelength ($\omega_{\sigma} > 0$). To enable a better comparison between experiment and theory for H₂S, various experimental estimates of $\Delta \alpha$ have been plotted with the theoretical pseudo BD(T) $\Delta \alpha$ as a function of the square of the optical frequency, ω_{σ}^2 , all of which are displayed in Figure 4.2. The 632.8 nm estimate of 0.669(73) au from Bogaard *et al.* [14] appears to be larger than the present numbers by 15.2% with the other estimate at 488.0 nm from Monan *et al.* [15] smaller than the theoretical values by 21.2%. It is emphasised that the experimental determination of $\Delta \alpha$ is exceedingly difficult for H₂S due to the very small depolarization ratio, ρ_0 . Furthermore, the vibrational Raman effect also influences the measured value of ρ_0 since the combined intensity from the v_1 and v_3 vibrational stretching fundamental bands is comparable to the intensity of the central



Figure 4.1. Frequency dependence of the mean polarizability for the second-row hydrides. The solid lines are calculated using the pseudo-BD(T) method and the chain-dotted lines are from experimental refractivities (SiH₄[7], H₂S [8], and HCl [11]).

unshifted Rayleigh line at the same frequency as the incident light, from which the polarized and depolarized intensities are measured [52]. The reported measurement from Monan *et al.* [15] explicitly excludes the vibrational Raman contribution whereas the measurements from Bogaard, Buckingham, Pierens and White (BBPW) [53] include this contribution. The effect on $\Delta \alpha$ from the vibrational Raman contribution is clearly demonstrated in Figure 4.2. where the BBPW estimates all lie significantly above the theoretical dispersion curve for $\Delta \alpha$. Rough estimates of the vibrational Raman contribution may be obtained by calculating the differences between the Monan *et al.* and Bogaard *et al.* [14] measurements and the appropriate BBPW results. The resulting estimated vibrational Raman contributions at 632.8 nm and 488.0 nm are calculated to be 1.40 and 1.84 au respectively. Interpolation of these quantities leads to a value at 514.5 nm of 1.72 au and when used to correct the measured value of $\Delta \alpha$ from BBPW, yields an estimate of 0.764(10) au which is surprisingly close to the present pseudo BD(T) value of 0.755 au for the same wavelength. Figure 4.2 displays these corrected BBPW values along with the other results.

Experimental values of $\Delta \alpha$ from Rayleigh light scattering rely on both the observed depolarization ratio, ρ_0 , and a dynamic value of the mean polarizability. Therefore, any errors in the experimental mean polarizability are carried through into the final value of $\Delta \alpha$. A more direct and less error prone method of comparison between experiment and theory would be to calculate theoretical vibrationally averaged depolarization ratios, ρ_0 , at various laser wavelengths and compare these with experimentally observed values. This procedure has been followed for H₂S and HCl with plots of theoretical and experimental depolarization ratios displayed in Figure 4.3. As previously discussed, the vibrational Raman effect is responsible for the large differences between the BBPW values and the theoretical curve for H₂S. The value of Monan *et al.* [15] is therefore much closer to the theoretical ρ_0 curve since the vibrational Raman contribution was excluded in their measurements. For HCl, there is only a single measurement of the depolarization ratio [16] but the agreement between theory and experiment is excellent. It is interesting that the magnitude of the frequency dependence for the depolarization ratios of these two molecules are quite similar but of opposite sign. It is apparent that further experimental work is required to firmly establish the role of the vibrational Raman contribution to the depolarization ratio and $\Delta \alpha$ for H₂S, preferably a number of Rayleigh light scattering measurements at different wavelengths with both inclusion and exclusion of the vibrational Raman contribution.



Figure 4.2. Comparison between present theoretical estimates of the frequency dependence of the polarizability anisotropy for H_2S and values derived from various experiments (Monan *et al.* [15], Bogaard, Buckingham, Pierens and White (BBPW) [53], Bogaard *et al.* [14]).



Figure 4.3. Comparison between present theoretical estimates of the frequency dependence of the Rayleigh depolarization ratio for H_2S and HCl and experimental measurements from Monan *et al.* [15], Bogaard, Buckingham, Pierens and White (BBPW) [53] for H_2S and Bridge and Buckingham [16] for HCl.

4.3.5 The effects of deuteration

The H/D property isotope effects for the ground vibrational state, calculated from the zero-point vibrationally averaged properties of the parent molecules and the perdeuterated species SiD₄, PD₃, D₂S and DCl, are presented in Table 4.6 and compared with available experimental data. The calculated isotopic difference for the ground vibrational state dipole moment of HCl is in excellent agreement with the experimental value of -0.0020(7) au from Kaiser [4]. Theoretical SCF and MP2 H/D isotopic differences for the first excited vibrational state are also tabulated and are both close to experiment considering the size of the estimated experimental uncertainty and the difficulty in obtaining the experimental measurement. For the mean polarizability of HCl it is apparent that both SCF and MP2 values concur with the experimental estimates despite the large uncertainties associated with the measurements. In the case of H_2S , excellent agreement is observed between the SCF and MP2 estimates of α and both numbers are extremely close to the measured isotopic difference reported by Frivold et al. [9] from refractivity measurements. Measurements of the polarizability anisotropy for H_2S and D_2S at 488.0 nm have been performed by Monan et al. [15] and a value of -0.07(9) au for the isotopic H/D difference has been obtained. No experimental uncertainty was supplied in that work however it has been assumed for the present purposes that the absolute error in a single measurement is the same as the absolute error in the isotopic difference. A measurement of the isotopic difference for $\Delta \alpha$ of H₂S is a formidable challenge and although the experimental uncertainty is larger than the estimate, the correct sign of the difference is supported by theoretical calculations. Using accurate BD(T)/TZP-ANO1 vibrationless estimates for the polarizability tensor components of H_2S , in conjunction with SCF and MP2 polarizability tensor ZPVCs, yields theoretical estimates of -0.1002 and -0.0968 au respectively for the isotopic difference of $\Delta \alpha$; values which are consistent with the experimental measurement. An experimental estimate of the isotopic difference for $\Delta \alpha$ of HCl has also been derived using the measured $\Delta \alpha$ for HCl [4] and DCl [54] but is considerably larger than either of the calculated values, and is accompanied by a massive precision estimate. Unfortunately, lack of other measurements of $\Delta \alpha$ for both HCl and DCl precludes any experimental isotopic differences of higher precision and accuracy.

SCF and MP2 TZPOL1 zero-point isotopic property differences, $\langle P(H) \rangle_0 - \langle P(D) \rangle_0$, (in au) for the electrical properties of the second row hydrides and perdeuterides.^{*a*}

		< <i>P</i> (H)> ₀	$- < P(D) >_0$	
	Property	SCF	MP2	Experiment
SiH ₄ / SiD ₄	α	0.3281	0.3416	
PH ₃ / PD ₃	$\begin{array}{c} \mu_z\\ \Theta_{zz}\\ \alpha\\ \Delta\alpha \end{array}$	0.00401 0.0723 0.2338 -0.0767	0.00250 0.0586 0.2358 -0.0630	
H_2S/D_2S	μ_z Θ_{xx} Θ_{zz}	0.00015 0.0383 0.0877	-0.00038 0.0352 -0.0837	
	$\begin{array}{l} \alpha_{xx} \\ \alpha_{yy} \\ \alpha_{zz} \\ \alpha \\ \Delta \alpha \end{array}$	0.1743 0.0265 0.1340 0.1116 -0.1002	0.1646 0.0383 0.1326 0.1118 -0.0968	0.1128(19) ^b –0.07(9) ^c
HCI/DCI	$\mu_{z} (v = 0)$ $\mu_{z} (v = 1)$ Θ_{zz} α $\Delta \alpha$	-0.00201 -0.00598 0.0792 0.0416 0.0856	-0.00199 -0.00589 0.0761 0.0424 0.0778	-0.0020(7) <i>d</i> -0.0053(6) <i>d</i> 0.043(10), <i>e</i> 0.051(8) <i>f</i> 0.41(70) <i>s</i>

^{*a*} See footnote (a) to Table 4.1. Quadrupole moment corrections were derived from quadrupole moments relative to the molecular centre of mass for each isotopomer.

^b Quadratic extrapolation of refractivity data (5 wavelengths between 420 and 700 nm) [9].

^{*c*} Derived from dynamic polarizability anisotropies at 488.0 nm [15].

^d MBER vibrational ground state (v = 0, J = 1) and first excited vibrational state (v = 1, J = 1) measurements [4].

e Quadratic extrapolation of refractivity data (17 wavelengths between 230 and 567 nm) [55].

f Linear extrapolation of refractivity data (5 wavelengths between 436 and 656 nm) [56].

8 Calculated from experimental MBER $\Delta \alpha$ values for HCl [4] and DCl [54].

It is noteworthy that for the properties considered here, with the exception of quadrupole moments, the zero-point vibrational corrections for the fully deuterated species can be calculated, to an excellent approximation, from the relation

$$\frac{\text{ZPVC}(\text{D})}{\text{ZPVC}(\text{H})} \approx 0.71$$

This relation holds particularly well for mean polarizabilities and is related to the product rule for harmonic vibrational frequencies, as outlined in Wilson, Decius and Cross [57]. Isotopic differences between quadrupole moments involve a contribution from a shift in the molecular centre of mass upon isotopic substitution and therefore this approximate relation does not apply to the calculated quadrupole moment differences in Table 4.6. The above expression for the ZPVCs also has the mixed blessing of making the complex non-linear property derivatives transformations (described in Chapter 3) almost redundant for most studies on fully-deuterated species interested in approximate results. Some progress has been made towards the establishment of simple sum rules for the properties of partially deuterated species (e.g. HDS) as well as the calculation of isotope shifts from the property derivatives of a single parent molecule [58] and although further study is required in the area of isotope effects on electrical properties, the simplicity of the present outcome is somewhat gratifying.

4.4 Conclusion

The present study has shown that when accurate electronic properties are corrected using zero-point vibrational corrections (ZPVCs) almost quantitative agreement with experiment is obtained for many of the properties studied. Perhaps the most convincing demonstration of the success of the vibrational averaging procedure is for the mean polarizabilities, where all of the present BD(T) estimates lie within 0.5% of the experimental values, and often agreement to better than 0.1% is obtained with the most accurate experiments. Agreement between theory and experiment is not as good for dipole and quadrupole moments, and further theoretical work is required to determine the source of the remaining discrepancies. For the polarizability anisotropy, the lack of accurate experimental data precludes a detailed comparison between theory and experiment for the present time. Further MBER and Rayleigh light scattering measurements are required to establish more precise and accurate experimental values of $\Delta \alpha$ and the frequency dependence of this property. The quadrupole moment perhaps requires the most experimental study as there are no estimates for PH_3 , H_2S or any of the isotopomers for these molecules. The present high-quality theoretical estimates will hopefully provide incentive for further experimental work on these molecules.

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