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THE ENTHALPY OF FROMATION AND QUADRUOLE
MOMENTS OF ACETYLENE AND DOUBLY SUBSTITUTED
ACETYLENES AND ACETYLIDES, INTERMOLECULAR
INTERACTIONS, AND COLLISION-INDUCED MOLECULAR
FRAME DISTORTIONS

presented by

Dorothy J. Gearhart

has been accepted towards fulfillment
of the requirements for the

Doctoral degree in Chemistry

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ACETYLENE AND DOUBLY SUBSTITUTED ACETYLENES AND ACETYLIDES,
INTERMOLECULAR INTERACTIONS, AND COLLISION-INDUCED
MOLECULAR FRAME DISTORTIONS

By

Dorothy J. Gearhart

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ABSTRACT

THE ENTHALPY OF FORMATION AND QUADRUPOLE MOMENTS OF ACETYLENE AND DOUBLY SUBSTITUTED ACETYLENES AND ACETYLIDES, INTERMOLECULAR INTERACTIONS, AND COLLISION-INDUCED MOLECULAR FRAME DISTORTIONS

By

Dorothy J. Gearhart

This thesis is broken into five chapters. The first chapter is a short summary of the calculations for this report. The second chapter concerns the calculation of CCSD(T) heats of formation at the complete basis set limit for HCCH, FCCF, ClCCCl, linear Li_2C_2 , planar Li_2C_2 , linear Na_2C_2 , and planar Na_2C_2 . CCSD(T) optimized geometries and CCSD(T) vibrational frequencies are calculated to aid in the calculation of the heats of formation. Core-valence, spin-orbit coupling, and relativistic corrections are made to the calculated heats of formation. Calculated values are compared to experimental and theoretical values with success. The third chapter concerns the calculation of SCF, DFT(B3LYP), and CCSD(T) molecular quadrupole moments of HCCH, FCCF, ClCCCl, linear Li_2C_2 planar Li_2C_2 , linear Na_2C_2 , and planar Na_2C_2 . The linear molecules have one unique component of the quadrupole moment whereas the planar molecules have two. The quadrupole moments of HCCH, FCCF, and ClCCCl are compared to experimental and theoretical results of other researchers with success. Molecular quadrupoles are broken into partition of charges to compare algebraic charges of terminal atoms. The fourth chapter concerns the development of the third-order two-body interaction energies of molecules. The second-order two-body and the third-order two-body interaction energies are derived and developed using the Unsold Theorem. Numerical estimates are made for the two-body second- and third-order interaction energies for two- and three-

body configurations as a function of internuclear separation. The fifth chapter concerns the frame distortion of CH₄ in CH₄+X pairs where X is N₂, H₂, or He. The methane molecule is approached by each molecule or atom, and the frame distortion is calculated. Additional energy calculations are made to determine energy influences in the methane pairs.

To my mother, Marjory

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CHAPTER 1
INTRODUCTION

1.1 Introduction

The purpose of Chapter 2 of this thesis is to report the most accurate heats of formation data for dilithium and disodium acetylide. Accurate enthalpies of formation values are important for thermodynamic study of molecules. In general, chemical theory can calculate the heat of formation to within 2 kcal/mol of experimentally determined heats of formation. In order to calculate the heat of formation, accurate vibrational frequencies are needed. For the dilithium and disodium acetylides, this information is not available. Optimized geometries, vibrational frequencies and the heats of formation are calculated. The HCCH, FCCF, ClCCCl geometries, vibrational frequencies, and heats of formation are calculated as reference points to check accuracy. The optimized geometries and heats of formation for all molecules discussed are extrapolated to the complete basis set limit using four extrapolation equations. A comparison of the results for each extrapolation method was made. Core-valence, spin-orbit coupling, and relativistic corrections are added to attempt to determine the most accurate heats of formation.

In Chapter 3, the quadrupole moments of HCCH, FCCF, ClCCCl, Li_2C_2 , and Na_2C_2 are calculated. For these molecules, the quadrupole moment is the first non-vanishing multipole moment, and as the dipole moment provides information about the electron distribution in a dipolar molecule, the quadrupole moment provides information about the electron distribution for these doubly substituted acetylenes and acetylides. For HCCH, FCCF, ClCCCl, and the linear acetylides, there is only one unique component for the quadrupole moment, but for the planar acetylides, the quadrupole moment has two unique components. After calculating the quadrupole

moment for each molecule, the quadrupole moment is broken down into its various components. Discussions are made concerning inferences that can be made between the quadrupole moment components and the electron distribution in the molecule. The quadrupoles are then partitioned into algebraic charges and compared in an attempt to draw conclusions about the nature of the bonding in the disubstituted acetylides. The shortcomings of the theory are discussed.

Chapter 4 and Chapter 5 concern van der Waals forces and the influences of those interactions. Van der Waals forces explain the boiling points of noble gases and collision induced absorption of compressed gases. In Chapter 4, the two body second order and two body third order interaction energies are derived. The interaction energies are broken into categories and physical explanations for each type of interaction are given. Using the Unsold's Theorem, numerical estimates are made including estimates for newly developed terms in the third-order interaction energy. Using HCl as an example, the two body second- and third-order interaction energies are compared for two configurations. The three and two body third-order interaction energies are compared for three HCl configurations.

Finally, Chapter 5 deals with the effects of two body interactions. $\text{CH}_4 + \text{X}$ compressed gases, where $\text{X} = \text{N}_2$, H_2 , or He , are studied due to their intriguing behavior when examined using IR. Each pair exhibits unusual absorption in the far-infrared region of their spectrum. There is belief that some of this absorption is due to induced dipoles from distortion of the molecular frame of CH_4 . This distortion is due to the collision of CH_4 with N_2 , H_2 , or He . Two collision paths are defined and calculations to determine the distortion of the methane molecule caused by these

approaching molecules are made. Electrostatic interactions within the CH_4+X pairs are discussed. In addition, the dipole moment and potential difference due to distortion are calculated as are the interaction energies within the pairs.

Chapter 2

The Enthalpy of Formation of Doubly Halogenated Acetylenes and Alkali Acetylides

2.1 Introduction

Gas phase Li_2C_2 and Na_2C_2 are intriguing compounds for which there is no experimental thermochemical or geometric data available and little to no theoretical information available. During an investigation into the electronic properties of these doubly alkalized acetylides, the two geometry configurations of these acetylides were shown to be viable minima on the potential energy surface¹. Although a linear configuration is the form of acetylene and many substituted acetylenes, the lowest energy arrangement for Li_2C_2 and Na_2C_2 is a doubly bridged molecule. In this report, the geometries for Li_2C_2 and Na_2C_2 at both the linear and doubly bridged configurations are tabulated, and the respective enthalpy of formation for each species is calculated. Because there is a lack of experimental and theoretical data available for these two metal acetylides, we calibrated our calculations by determining the geometry and the enthalpy of formation for acetylene^{2,3} and the two doubly substituted halogenated acetylenes, ClCCCCl ³ and FCCF ^{3,4}, and then compared those results to those found by previous researchers.

There have been several experimental studies for HCCH , ClCCCCl , and FCCF . Acetylene, due to its commonality, is well documented theoretically and experimentally, and its properties have been used in comparative studies to determine the accuracy of theoretical methods. ClCCCCl and FCCF , on the other hand, are very reactive molecules making such extensive study harder. Although the equilibrium geometry and the enthalpy of formation for ClCCCCl are known, the experimental heat of formation for dichloroethyne has error bars which are approximately a fifth of the experimental value. Due to its wider range of experimental values, FCCF is even more intriguing. There are

two experimental heats of formation available, which describe the enthalpy of formation of difluoroacetylene as both an endothermic or exothermic process.

2.1.1 Method

For the general reaction, $Y_2X_{2(g)} \longrightarrow 2X_{(g)} + 2Y_{(g)}$, the first step taken in determining the enthalpy of formation for Y_2X_2 was to determine the energy change after the reaction moves from reactant to products. The total energy of the reactants and products are a sum of the electronic energies, as well as translational, vibrational, and rotational contributions. Since the products are atoms, only the reactant has rotational and vibrational contributions. Assuming that Y_2X_2 is linear, as in the case of HCCH, FCCF, ClCCCl, linear Li_2C_2 , and linear Na_2C_2 , the reactant only has two rotational degrees of freedom.

$$E_{\text{products}} = 2E_X + \underbrace{\frac{3RT}{2}}_{\text{translations}} + 2E_Y + \underbrace{\frac{3RT}{2}}_{\text{translations}}. \quad (1)$$

$$E_{\text{reactant}} = E_{YXXY} + \underbrace{\frac{3}{2}RT}_{\text{translations}} + \underbrace{RT}_{\text{rotations}} + N_A \underbrace{\sum_j^{3n-5} \left(\frac{h\nu_j}{2} + \frac{h\nu_j}{\exp\left(\frac{h\nu_j}{k_b T}\right) - 1} \right)}_{\text{vibrations}}. \quad (2)$$

In the case of doubly bridged Li_2C_2 and Na_2C_2 , the reactant has three rotational degrees of freedom.

$$E_{\text{reactant}} = E_{Y_2X_2} + \underbrace{\frac{3}{2}RT}_{\text{translations}} + \underbrace{\frac{3}{2}RT}_{\text{rotations}} + N_A \underbrace{\sum_j^{3n-6} \left(\frac{h\nu_j}{2} + \frac{h\nu_j}{\exp\left(\frac{h\nu_j}{k_b T}\right) - 1} \right)}_{\text{vibrations}}. \quad (3)$$

The difference in the initial and final states gives the energy change, and Equation (5) shows the generic relation between the energy change and the enthalpy of atomization.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}} \quad (4)$$

$$\Delta H_{\text{atm}} = \Delta E + \Delta nRT \quad (5)$$

Shown in Equation (6) is the relation between the energy change and the enthalpy of atomization for the reactions described in this manuscript.

$$\Delta H_{\text{atm}} = \Delta E + 3RT \quad (6)$$

In any reaction, the enthalpy of reaction is related to the heat of formation of the products and reactants through Equation (7).

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{f}}(\text{products}) - \sum \Delta H_{\text{f}}(\text{reactants}) \quad (7)$$

For the specific case of Y_2X_2 , the heat of reaction is described by Equation (8).

$$\Delta H_{\text{atm}} = 2\Delta H_{\text{f}}(\text{X}_{(\text{g})}) + 2\Delta H_{\text{f}}(\text{Y}_{(\text{g})}) - \Delta H_{\text{f}}(\text{Y}_2\text{X}_{2(\text{g})}) \quad (8)$$

Equation (8) can be rearranged to express the enthalpy of formation of Y_2X_2 as a sum of the heats of formation of the constituent atoms and the enthalpy of atomization.

$$\Delta H_{\text{f}}(\text{Y}_2\text{X}_{2(\text{g})}) = 2\Delta H_{\text{f}}(\text{X}_{(\text{g})}) + 2\Delta H_{\text{f}}(\text{Y}_{(\text{g})}) - \Delta H_{\text{atm}} \quad (9)$$

The enthalpies of formation for the atoms are nonzero because the atoms are not the standard state of the elements. A table of the standard enthalpy of formation for the atoms is in the appendix. Using experimental heats of formation for the atoms and the calculated heat of atomization, the enthalpy of formation for the reactant, Y_2X_2 , was determined.

2.1.2 Computational Details

Using the MOLPRO 2000⁵ and Gaussian 98⁶ software packages, we calculated geometry optimization, fundamental vibrational frequency, and single point energy. Dunning CC-PVXZ, AUG-CC-PVXZ, and D-AUG-CC-PVXZ basis sets^{7,8,9,10} were used, as well as augmented basis sets which were constructed on site by augmenting the Li and Na Dunning CC-PVXZ basis sets with even-tempered diffuse functions. X is the cardinal index of the basis set. Therefore, the CC-PVXZ basis set where X equals 2 refers to the CC-PVDZ basis set. Since the core-valence correlation was not captured using the suite of Dunning polarized valence basis sets, Dunning's CC-PCVXZ and AUG-CC-PVXZ basis sets were used to determine core-valence correlation corrections.

The standard enthalpy of formation and optimized geometries for each of the aforementioned molecules were calculated as a function of basis set at the CCSD(T) level and then extrapolated to the complete basis set limit. After extrapolation, the thermochemical values were corrected for spin-orbit coupling, core-valence correlation, and mass dependent relativistic effects. The atomic spin-orbit effects were computed using atomic energy levels tabulated by Charlotte Moore¹¹. Core-valence correlation was determined as a function of basis set from CCSD(T) single point energy calculations and extrapolated to the basis set limit. The mass dependent relativistic energy corrections were determined from a Hartree-Fock calculation using the Cowan-Griffin approach from expectation values of the mass-velocity and Darwin terms using a CC-PVDZ basis set.

2.1.3 Corrections

The non-relativistic Hamiltonian commonly used in quantum calculations only accounts for the kinetic energy of the electrons and the electrostatic potential energy due

to nuclear-nuclear, nuclear-electron, and electron-electron interactions. Since there is no consideration of spin or relativistic effects, any consideration of the mass-velocity correction, Darwin term, or spin-orbit coupling corrections is considered relativistic. The only non-relativistic correction made to the enthalpy of formation in this manuscript was the addition of core-valence correlation.

The dissociation energy (D_e) for these acetylene and doubly substituted acetylene molecules was calculated from CCSD(T) energy calculations in which the non-valence shell electrons were frozen. In addition to this inability of the core electrons to be excited to unoccupied molecular orbitals, the Dunning basis sets used were not designed to pick up core-valence correlation. To include core-valence correlation absent from the CCSD(T) single point energy calculations, a core-valence correction was determined using the Dunning CC-PCVXZ and AUG-CC-PCVXZ basis sets. These polarized core-valence basis sets are different from polarized valence basis sets because of additional gaussian functions, which have been added to the polarized valence basis sets. These added gaussian functions have exponents, which place them in the electron shell directly below the valence shell. Because these new basis functions are located in the “core” of the atom or molecule, additional information concerning the core-valence interactions can be extracted. The additional functions were added to the carbon, lithium, and fluorine 1s orbital and the sodium and chlorine 2s and 2p orbitals.

We calculated the D_e for each molecule twice using the polarized core-valence basis sets. The first calculation was done using a set of CCSD(T) single point energy calculations where the atomic and molecular electronic cores were frozen, and the second was made from a set of CCSD(T) calculations in which the core electrons were unfrozen.

The energy difference between the two dissociation energies is representative of the core-valence correlation, and this energy difference is considered the core-valence correction.

Often with lighter atoms and molecules during quantum calculations, the relativistic effects within the atom or molecule are ignored. In general, this approximation is valid because for light species the energy differences for relativistic effects between energy states or geometric orientations are negligible. Even though this approximation tends to diminish the importance of the relativistic effects, the contribution of relativistic effects to the total energy of an atom or molecule is significant. Therefore, we made two corrections. The first correction is for the change in the mass of the electrons and the resulting change in the velocity due to the mass change. The second correction is for the “Zitterbewegung” or “trembling” of the electrons, which is the relativistic smearing of an electron’s charge. In the Dirac theory, this correction is often referred to as the Darwin term. The Darwin term correction can be thought of as a correction for the “size” of the electrons.

As stated above, the mass-velocity and the Darwin term relativistic energy contributions were determined using a Hartree-Fock wavefunction consisting of CC-PVDZ basis functions. We added the mass-velocity and Darwin term operators to the non-relativistic Hamiltonian as a perturbation, and the first-order energy correction was computed. Having determined these corrections for the atoms and the molecule of interest, a correction to the D_e was calculated producing the mass-dependent relativistic energy correction.

The remaining relativistic energy correction is spin-orbit coupling. Resulting from the interaction between the magnetic moments created by an electron’s spin and

orbital angular momentum, this splitting in the energy levels is generally referred to as the fine structure, and it is the cause for the unique optical spectra of atoms. A carbon atom in its ground electronic state is 3P . Due to the spin-orbit interaction, this 3P state divides into sets of one 3P_0 state, three 3P_1 states, and five 3P_2 states. For halogens such as chlorine and fluorine, the ground state is a 2P state, which divides into four $^2P_{3/2}$ and two $^2P_{1/2}$ states. For hydrogen, lithium, sodium, acetylene, and the doubly substituted acetylene molecules, the ground state does not split. The multiple energy levels created by this splitting are not degenerate, and since the possibility that a ground state atom can be in one of these ground state energy levels, the distribution must be taken into account.

The single point energy calculations for the atoms and molecules used in this study are run at zero degrees Kelvin (0 K), and only the lowest lying state is taken into consideration. At this temperature, the probability of an atom being in any of the higher energy levels is equal to a Boltzmann distribution. Therefore, the average energy of the ground-state atoms is described by Equation (10).

$$\langle E \rangle = -\frac{\partial \ln q}{\partial \beta} \text{ where, } q = \sum_i g_i e^{-\epsilon_i \beta} . \quad (10)$$

After completing the derivative, the average energy takes the form of Equation (11).

$$\langle E \rangle = \frac{\sum_i g_i \epsilon_i}{\sum_i g_i e^{-\epsilon_i \beta}} . \quad (11)$$

Since the temperature is 0 K, the average energy is equal to the mean energy as seen in Equation (12).

$$\langle E \rangle = \frac{\sum_i g_i \epsilon_i}{\sum_i g_i} . \quad (12)$$

Because the D_e values are calculated for the lowest lying energy states of the molecule and its constituent atoms, the spin-orbit correction for HCCH, Li_2C_2 , and Na_2C_2 is the difference between the energy of the lowest lying state of carbon and the average energy of the carbon atom. Equation (13) shows this relation.

$$\Delta E_{s-o} = 2\langle E_{\text{carbon}} \rangle - 2E_{\text{carbon}} . \quad (13)$$

The spin-orbit correction for ClCCCl and FCCF is equal to the spin-orbit correction for acetylene and the doubly substituted acetylides plus the difference between the energy of the lowest lying state of the halogen and the average energy of the halogen atom.

Equation (14) expresses this relation.

$$\Delta E_{s-o} = 2\langle E_{\text{carbon}} \rangle - 2E_{\text{carbon}} + 2\langle E_{\text{halogen}} \rangle - 2E_{\text{halogen}} . \quad (14)$$

The tables of atomic energy levels that Charlotte Moore¹¹ published list the energy of these spin-orbit states. Using these values, the correction for average energy of the atoms (the spin-orbit correction) was subtracted from the dissociation energy.

2.1.4 Extrapolations to CBS limit

Extrapolated values are done using two extrapolation techniques: extrapolating only the property to the basis set limit, $P(\infty)$, and calculating the property from extrapolated energies of the molecule and its constituent atoms at the basis set limit, $P(E(\infty))$. For example, in order to determine the D_e of a molecule at the basis set limit, first the molecular and atomic energies are calculated as a function of basis set. From these single point calculations, the D_e is calculated as a function of basis set. To

extrapolate to the basis set limit, one could either extrapolate the property (D_e) to the basis set limit, or one could individually extrapolate the single point molecular and atomic energies to the basis set limit and calculate the D_e from those extrapolated energies.

This concept of extrapolating a property to the basis set limit is dependent on a property of the variational theorem. For the non-relativistic time-independent Hamiltonian operator, there is a lowest energy eigenvalue. In quantum mechanics, the wavefunction of an atom or molecule is approximated. As the wavefunction becomes more accurate for the system in question, the resulting eigenvalue approaches this lowest value. The point where an infinite basis set is used is referred to as the basis set limit, and it is the limit of accuracy for the particular method used. Since the energy converges in this manner, this same methodology is applied to the calculation of properties by extrapolating to the basis set limit.

Many researchers have investigated the relation between basis set size and the convergence of the energy of a system. The Feller equation, as Martin calls it, originates from an empirical development. There is no quantitative development made to reach that nonlinear equation except to note how well the equation models the behavior of the system. The Schwartz equations originate from a quantitative derivation of how the energy converges as higher order angular momentum functions are added to the basis set. The Martin¹³ paper compares the behavior of each extrapolation equation for small molecules.

For each of the extrapolation techniques, the CCSD(T) values were fit to four different nonlinear equations. Dunning and associates use an exponential equation originated by Feller¹² where X is again the cardinal index and α is a variable power.

$$P(X) = P(\infty) + Ae^{-\alpha X}. \quad (\text{Feller}) \quad (15)$$

In a recent paper, Martin¹³ offers three alternative polynomial equations for nonlinear fitting referred to as Schwartz-type formulas derived from the works of Schwartz¹⁴, Kutzelnigg^{15,16}, Morgan¹⁶, and Hill¹⁷.

$$P(X) = P(\infty) + \frac{A}{\left(X + \frac{1}{2}\right)^\alpha}. \quad (\text{Schwartz}\alpha) \quad (16)$$

$$P(X) = P(\infty) + \frac{A}{\left(X + \frac{1}{2}\right)^4} + \frac{B}{\left(X + \frac{1}{2}\right)^6}. \quad (\text{Schwartz6}) \quad (17)$$

$$P(X) = P(\infty) + \frac{A}{\left(X + \frac{1}{2}\right)^4}. \quad (\text{Schwartz4}) \quad (18)$$

Both $P(\infty)$ and $P(E(\infty))$ methods should not necessarily produce the same value. For the Schwartz4 and Schwartz6 methods, the $P(\infty)$ and $P(E(\infty))$ results are more likely to be equivalent because the extrapolation equations for the atoms and molecules are consistent. If the error in the complete basis set (CBS) limit is consistent for all the extrapolated properties and energies, then the results produced will be consistent. Feller and Schwartz α equations allow more freedom for the extrapolation equation because of the variable α exponent. This freedom provides an opportunity for the fit for the atoms to be tighter than the fit for the molecule, and this inconsistency will cause differences between the $P(\infty)$ and $P(E(\infty))$ results.

Removing the data points from calculations in which smaller basis sets were used is another option in extrapolating to CBS limit. Using the most accurate data points for extrapolation can aid in producing a more accurate extrapolated value. For this report, many smaller data sets were created from each complete data set collected. For example, the energy of the carbon atom was calculated using a spectrum of basis sets ranging from CC-PVDZ to CC-PV6Z. The original set contained all the data points calculated. Then, subsequent sets were created by systematically removing the data calculated at smaller basis sets such as the CC-PVDZ and CC-PVTZ basis sets. By removing carbon atom energies calculated at smaller basis sets, the only values remaining are the most accurate values. Extrapolations were done for each of these data sets and listed to show the change in the extrapolated values as the less accurate values were removed. The extrapolated core-valence correction was extrapolated using only the results from the larger basis sets.

2.2 HCCH

Table 1 lists calculated CCSD(T) optimized geometries for HCCH as a function of the Dunning unaugmented and augmented CC-PVXZ basis sets. Table 1 also tabulates HCCH extrapolated bond distances and an experimental geometry provided by Strey and Mills¹⁸. The notation for each extrapolation designates both the nonlinear fitting equation and the cardinal indices of the basis sets included in the extrapolation. Therefore, a Schwartz4(Q56) value is an extrapolated value using Equation (18) or the Schwartz4 equation from extrapolated properties calculated using basis sets where the cardinal index X is equal to the set {Q,5,6}.

Table 1. Optimized Geometries of HCCH as a Function of Basis Set					
Basis	RCC (ang)	RCH (ang)	Basis	RCC (ang)	RCH (ang)
CC-PVDZ	1.22877	1.07899	AUG-CC-PVDZ	1.22998	1.07866
CC-PVTZ	1.20973	1.06372	AUG-CC-PVTZ	1.21016	1.06387
CC-PVQZ	1.20634	1.06337	AUG-CC-PVQZ	1.20686	1.06355
CC-PV5Z	1.20557	1.06303	AUG-CC-PV5Z	1.20587	1.06314
CC-PV6Z	1.20534	1.06300	AUG-CC-PV6Z	1.20556	1.06312
Feller(DTQ56)	1.2054	1.0631	Feller(DTQ56)	1.2057	1.0633
Feller(TQ56)	1.2053	1.0628	Feller(TQ56)	1.2054	1.0628
Feller(Q56)	1.2052	1.0630	Feller(Q56)	1.2054	1.0631
Schwartz α (DTQ56)	1.2051	1.0631	Schwartz α (DTQ56)	1.2053	1.0632
Schwartz α (TQ56)	1.2052	1.0626	Schwartz α (TQ56)	1.2052	1.0623
Schwartz α (Q56)	1.2052	1.0630	Schwartz α (Q56)	1.2053	1.0631
Schwartz4(DTQ56)	1.2042	1.0617	Schwartz4(DTQ56)	1.2045	1.0618
Schwartz4(TQ56)	1.2048	1.0630	Schwartz4(TQ56)	1.2051	1.0631
Schwartz4(Q56)	1.2050	1.0629	Schwartz4(Q56)	1.2051	1.0629
Schwartz4(56)	1.2051	1.0630	Schwartz4(56)	1.2052	1.0631
Schwartz6(DTQ56)	1.2050	1.0634	Schwartz6(DTQ56)	1.2052	1.0635
Schwartz6(TQ56)	1.2052	1.0628	Schwartz6(TQ56)	1.2052	1.0629
Schwartz6(Q56)	1.2052	1.0631	Schwartz6(Q56)	1.2053	1.0632
Schwartz6(56)	1.2051	1.0630	Schwartz6(56)	1.2052	1.0631
			¹⁸ experimental	1.2033	1.0605

In Table 1, the augmented and unaugmented basis sets carbon-carbon bond length has converged to three decimal places by the 5-zeta basis set, and the carbon-hydrogen bond length has converged to three decimal places by the Q-zeta basis set. The extrapolated bond lengths confirm that at the 6-zeta basis set both the augmented and unaugmented basis sets are very close to the basis set limit. There is no general trend in the extrapolated values as optimized geometries calculated at smaller basis sets are removed. Compared to the experimental geometry, the basis sets are not converging towards the Strey and Mills experimental geometry. Although the geometry at the basis set limit is not the true HCCH geometry, the CCSD(T) method limit is within three thousandths of an angstrom, which is a small deviation and will have no effect on the calculated heat of formation.

Using the Strey and Mills experimental geometry listed in Table 1, we completed single point CCSD(T) calculations for the acetylene molecule. Taking advantage of experimental vibrational frequencies provided by Schimanouchi¹⁹ listed in Table 2, and using standard heats of formation for the constituent atoms provided by Chase² listed in the appendix, we calculated the enthalpy of formation of HCCH as a function basis set.

Table 2. Vibrational Frequencies of HCCH	
Symmetry	Frequency (cm ⁻¹)
Cis-bend (Π_u)	730
Trans-bend (Π_g)	612
CC stretch(Σ_g)	1974
s-CH stretch (Σ_g)	3374
a-CH stretch (Σ_u)	3289

Shown in Table 3 are dissociation energies of HCCH at 0 K and heats of formation for HCCH at 298K for the unaugmented and augmented CC-PVXZ Dunning basis sets.

Table 3. Calculated Dissociation Energies and Heats of Formation for HCCH as a Function of Basis Set		
Basis Set	D_e (kcal/mol)	ΔH_f (kcal/mol)
CC-PVDZ	370.20	89.23
CC-PVTZ	393.35	66.08
CC-PVQZ	399.59	59.84
CC-PV5Z	401.47	57.96
CC-PV6Z	402.19	57.24
AUG-CC-PVDZ	371.09	88.34
AUG-CC-PVTZ	394.56	64.87
AUG-CC-PVQZ	400.09	59.35
AUG-CC-PV5Z	401.73	57.70
AUG-CC-PV6Z	402.33	57.11

Augmentation of the CC-PVXZ basis set does not alter the magnitude of either the D_e or the heat of formation greatly, and the enthalpy of formation is near convergence for both basis sets. Note that as the D_e increases, the enthalpy of formation decreases.

This behavior is due to the mathematical nature of the relation between the two values. Equation (9) shows the inverse dependence of the enthalpy of formation on the enthalpy of atomization in which the enthalpy of atomization is merely the D_e with thermal corrections. Table 4 lists the dissociation energies and enthalpies of formation at the complete basis set limit for each nonlinear extrapolation equation for both $P(\infty)$ and $P(E(\infty))$ methods.

Table 4. Heats of Formation for HCCH Extrapolated to the Complete Basis Set Limit		
Basis sets CC-PVXZ	$\Delta H_f(\infty)$ (kcal/mol)	$\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ56)	57.18	57.18
Feller(Q56)	56.79	56.82
Schwartz α (DTQ56)	56.03	56.03
Schwartz α (Q56)	56.51	56.57
Schwartz4(DTQ56)	56.81	56.81
Schwartz4(56)	56.48	56.48
Schwartz6(DTQ56)	56.25	56.25
Schwartz6(56)	56.48	56.48
AUG-CC-PVXZ		
Feller(DTQ56)	57.16	57.18
Feller(Q56)	56.77	56.78
Schwartz α (DTQ56)	56.29	56.34
Schwartz α (Q56)	56.57	56.59
Schwartz4(DTQ56)	56.39	56.39
Schwartz4(56)	56.48	56.48
Schwartz6(DTQ56)	56.30	56.30
Schwartz6(56)	56.48	56.48

Table 4 has two columns of data. The rightmost column contains the enthalpy of formation calculated using extrapolated energies for the constituent atoms and the acetylene molecule. The left data column contains the heat of formation where values for the enthalpy of formation were extrapolated to the complete basis set limit. As required, the Schwartz4 and the Schwartz6 results are consistent for each method at both suites of

basis sets, and when only the two best points are used for extrapolation, the Schwartz4 and Schwartz6 results are equal to each other. Looking at the Feller and Schwartz α results, the differences between the two methods for each equation is minute. *For all the extrapolation methods and fitting equations, the extrapolated value was within 1 kcal/mol of the enthalpy of formation computed at the AUG-CC-PV6Z basis set.*

To correct for missing core-valence correlation, we used the Dunning unaugmented CC-PCVXZ basis sets, and the results are shown as a function of basis set and tabulated in Table 5.

Table 5. Core-Valence Correction for HCCH as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-1.13
CC-PCVTZ	-1.88
CC-PCVQZ	-2.28
CC-PCV5Z	-2.41

Using the data in Table 5, we extrapolated the core-valence correction to a complete basis set for both $P(\infty)$ and $P(E(\infty))$ extrapolation techniques. Table 6 lists the corrections.

Table 6. Core-Valence Correction for HCCH at the Complete Basis Set Limit		
Basis sets	$\Delta CV(\infty)$	$\Delta CV(E(\infty))$
CC-PCVXZ	(kcal/mol)	(kcal/mol)
Feller(TQ5)	-2.46	-2.47
Schwartz α (TQ5)	-2.50	-2.51
Schwartz4(Q5)	-2.51	-2.51
Schwartz6(Q5)	-2.51	-2.51

As mentioned before, not all data points were included in the extrapolations. Only corrections calculated with the larger basis sets were kept for extrapolation, and those extrapolated corrections were used as core-valence corrections. Table 6 illustrates the core-valence corrections at the basis set limit. From the table we can see, the core-

valence correction extrapolations are consistent between methods and differ only slightly between extrapolation equations.

In Table 7, we collected enthalpy of formation values corrected for relativistic effects (0.25 kcal/mol), spin-orbit coupling (0.17 kcal/mol), and the core-valence corrections from Table 6. As we can now see, the relativistic corrections to the energy were not negligible. We added the core-valence corrections to the enthalpy of formation values from Table 4. We calculated the Feller(TQ5) core-valence correction using the $P(\infty)$ method and combined it with the Feller(DTQ56) and Feller (Q56) heat of formation values calculated using the $P(\infty)$ method. This methodology was used for all extrapolation equations and methods. Table 7 includes also the difference between the calculated enthalpy of formation and the expected experimental value of 54.19 ± 0.19 kcal/mol provided by Chase².

Table 7. ΔH_f Values Corrected for Core-Valence Correlation Spin-Orbit Coupling and Relativistic Effects for HCCH at the Complete Basis Set Limit for each Method				
Basis sets	Corrected $\Delta H_f(\infty)$	Difference from experimental value	Corrected $\Delta H_f(E(\infty))$	Difference from experimental value
CC-PVXZ	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
Feller(DTQ56)	55.14	0.95	55.14	0.95
Feller(Q56)	54.74	0.55	54.77	0.58
Schwartz α (DTQ56)	53.95	-0.24	53.94	-0.25
Schwartz α (Q56)	54.43	0.24	54.48	0.29
Schwartz4(DTQ56)	54.72	0.53	54.72	0.53
Schwartz4(56)	54.39	0.20	54.39	0.20
Schwartz6(DTQ56)	54.16	-0.03	54.16	-0.03
Schwartz6(56)	54.39	0.20	54.39	0.20
AUG-CC-PVXZ				
Feller(DTQ56)	55.12	0.93	55.14	0.95
Feller(Q56)	54.73	0.54	54.74	0.55
Schwartz α (DTQ56)	54.21	0.02	54.25	0.06
Schwartz α (Q56)	54.49	0.30	54.50	0.31
Schwartz4(DTQ56)	54.30	0.11	54.30	0.11
Schwartz4(56)	54.39	0.20	54.39	0.20
Schwartz6(DTQ56)	54.22	0.03	54.22	0.03
Schwartz6(56)	54.39	0.20	54.39	0.20

The first thing to note is the loss of accuracy with the removal of points calculated at smaller basis sets. When only the best data points were used, the error increased by at least 0.1 kcal/mol; however, regardless of the basis sets used, the resulting enthalpy of formation is within 1 kcal/mol of the experimental value. In addition, the difference between the two extrapolation methods is very small, presumably due to the high convergence of the values before extrapolation. The more accurately the fitted equation matches the true convergence curve, the less discrepancy exists between the two extrapolation methods, $P(\infty)$ and $P(E(\infty))$. Of the four extrapolation equations, the best performing equations are the Schwartz-type equations. These three equations yield results, which fall within the experimental error bars. However, the Feller equation does

not provide such accuracy. These general trends are consistent with Martin's¹³ findings in his study of the D_e of HCCH. In Table 8, we collect the best-extrapolated heats of formation from the AUG-CC-PVXZ basis sets from this work, as well as experimental and select theoretical results from the literature.

Table 8. Comparison of Heats of Formation of HCCH		
	ΔH_f kcal/mol	Error kcal/mol
^a This work	54.73	0.54
^b This work	54.21	0.02
^c This work	54.30	0.11
^d This work	54.22	0.03
³ Parthiban(W1)	54.41	0.22
³ Parthiban(W2)	54.48	0.29
² experiment	54.19	± 0.19
^a Feller(Q56) extrapolation of augmented basis set values with $P(\infty)$ method		
^b Schwartz α (DTQ56) extrapolation of augmented basis set values with $P(\infty)$ method		
^c Schwartz4(DTQ56) extrapolation of augmented basis set values with $P(\infty)$ method		
^d Schwartz6(DTQ56) extrapolation of augmented basis set values with $P(\infty)$ method		

The acknowledged values for the enthalpies of formation are the experimental values provided by Chase². As mentioned earlier, most of the results from this work are within the error bars associated with Chase's work. The Parthiban³ values are calculated in a similar manner as this report using the Schwartz4, 6, and α equations, but the initial geometries and vibrational frequencies for HCCH were calculated using *ab initio* and DFT methods. In this study, the experimental geometries and fundamental vibrational frequencies from the literature were used.

2.3 FCCF

Experimental values for FCCF are difficult to determine as stated by Parthiban³ *et al.*,

“...there remains no direct determination of the heat of formation of any haloacetylene-these species are simply too unstable and/or reactive to allow for such measurements.”

Because FCCF is so reactive, there are no reliable experimental data to use for comparison. Therefore, we used the equilibrium geometry and vibrational frequencies from theoretical work done by Breidung²⁰ *et al.* Table 9 and Table 10 list these values. Calculated CCSD(T) optimized geometries as a function of the CC-PVXZ and AUG-CC-PVXZ basis sets are listed in Table 9 along with the extrapolated geometries and the reference geometry provided by Breidung.²⁰

Table 9. Optimized Geometries of FCCF as a Function of Basis Set					
Basis Sets	RCC (ang)	RCF (ang)	Basis	RCC (ang)	RCF (ang)
CC-PVDZ	1.20969	1.30039	AUG-CC-PVDZ	1.21157	1.30594
CC-PVTZ	1.19277	1.28859	AUG-CC-PVTZ	1.19280	1.28948
CC-PVQZ	1.18918	1.28586	AUG-CC-PVQZ	1.18951	1.28613
CC-PV5Z	1.18857	1.28512	AUG-CC-PV5Z	1.18868	1.28524
Feller(DTQ5)	1.1883	1.2850	Feller(DTQ5)	1.1886	1.2851
Feller(TQ5)	1.1884	1.2849	Feller(TQ5)	1.1884	1.2849
Schwartz α (DTQ5)	1.1878	1.2844	Schwartz α (DTQ5)	1.1881	1.2845
Schwartz α (TQ5)	1.1884	1.2847	Schwartz α (TQ5)	1.1882	1.2847
Schwartz4(DTQ5)	1.1872	1.2844	Schwartz4(DTQ5)	1.1872	1.2841
Schwartz4(TQ5)	1.1875	1.2844	Schwartz4(TQ5)	1.1878	1.2845
Schwartz4(Q5)	1.1881	1.2845	Schwartz4(Q5)	1.1880	1.2845
Schwartz6(DTQ5)	1.1877	1.2844	Schwartz6(DTQ5)	1.1880	1.2844
Schwartz6(TQ5)	1.1884	1.2846	Schwartz6(TQ5)	1.1882	1.2846
Schwartz6(Q5)	1.1881	1.2845	Schwartz6(Q5)	1.1880	1.2845
²⁰ reference				1.186	1.2835

The optimized geometries in Table 9 show that the augmentation of CC-PVXZ basis set does not affect the convergence of the basis set. Like the HCCH geometries, the carbon-carbon and carbon-fluorine bonds, if rounded, converges to three decimal places by the 5-zeta basis set. Note the extrapolated geometries differ by less than a thousandth of an Å from the 5-zeta result for both the unaugmented and augmented basis sets. Also,

note the CCSD(T) optimized geometries are converging to a value that differs only 0.002Å from the reference value.

We used the unaugmented, augmented, and doubly augmented Dunning basis sets to make single point CCSD(T) calculations at the reference geometry provided in Table 9. We used vibrational frequencies provided by Breidung²⁰ *et al* listed in Table 10 and the heats of formation for the fluorine and carbon atoms provided by Chase² to determine the enthalpy of formation for FCCF.

Table 10. Vibrational Frequencies of FCCF	
Symmetry	Frequencies (cm ⁻¹)
Cis-bend (Π_u)	276
Trans-bend (Π_g)	284
s-CF stretch (Σ_g)	792
a-CF stretch (Σ_u)	1375
CC stretch (Σ_g)	2527

Table 11 lists the calculated standard enthalpy of formation values at 298 K and dissociation energies at 0 K as a function of basis set.

Table 11. Calculated Dissociation Energies and Heats of Formation for FCCF as a Function of Basis Set		
Basis sets	D _e (kcal/mol)	ΔH_f (kcal/mol)
CC-PVDZ	343.01	43.15
CC-PVTZ	370.27	15.89
CC-PVQZ	378.47	7.70
CC-PV5Z	381.10	5.06
AUG-CC-PVDZ	344.37	41.80
AUG-CC-PVTZ	372.44	13.73
AUG-CC-PVQZ	379.67	6.50
AUG-CC-PV5Z	381.65	4.51
D-AUG-CC-PVDZ	346.83	39.33
D-AUG-CC-PVTZ	373.75	12.42
D-AUG-CC-PVQZ	380.36	5.80
D-AUG-CC-PV5Z	381.87	4.29

Unlike HCCH, the dissociation energies of FCCF are not as closely converged at these basis set levels. The heats of formation show that the difference between the Q-zeta and 5-zeta results is a large percentage of the calculated value. The level of augmentation seems to aid in the rate of convergence, but the differences between unaugmented, augmented, and doubly augmented values are small but significant in comparison to the magnitude of the reported 5-zeta value. Therefore, the addition of higher angular momentum functions to the wave function influences the enthalpy of formation of FCCF greatly. Table 12 illustrates heats of formation values extrapolated to the basis set limit.

Table 12. Heats of Formation for FCCF Extrapolated to the Complete Basis Set Limit		
Basis sets CC-PVXZ	$\Delta H_f(\infty)$ (kcal/mol)	$\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ5)	4.00	4.08
Feller(TQ5)	3.81	3.87
Schwartz α (DTQ5)	1.55	1.76
Schwartz α (TQ5)	2.88	3.01
Schwartz4(DTQ5)	4.24	4.24
Schwartz4(Q5)	2.92	2.92
Schwartz6(DTQ5)	2.52	2.52
Schwartz6(Q5)	2.92	2.92
AUG-CC-PVXZ		
Feller(DTQ5)	3.88	4.08
Feller(TQ5)	3.76	3.93
Schwartz α (DTQ5)	2.23	2.71
Schwartz α (TQ5)	3.22	3.57
Schwartz4(DTQ5)	3.05	3.05
Schwartz4(Q5)	2.90	2.90
Schwartz6(DTQ5)	2.44	2.44
Schwartz6(Q5)	2.90	2.90
D-AUG-CC-PVXZ		
Feller(DTQ5)	3.75	4.03
Feller(TQ5)	3.84	3.10
Schwartz α (DTQ5)	2.42	3.08
Schwartz α (TQ5)	3.52	4.04
Schwartz4(DTQ5)	2.61	2.61
Schwartz4(Q5)	3.06	3.06
Schwartz6(DTQ5)	2.44	2.44
Schwartz6(Q5)	3.07	3.07

Varying from around 1 kcal/mol to over 3 kcal/mol between extrapolation equations and from 0.06 kcal/mol to 0.8 kcal/mol between methods, the results in Table 12 seem erratic. This behavior is true only because all the extrapolated results describe the heat of formation of FCCF as only a few kcal/mol above zero. Due to the relative magnitude of the calculated enthalpy of formation, the difference in extrapolated values is a large percentage of the heat of formation.

In all the single point calculations on FCCF and its component atoms, the 1s core on carbon and fluorine was frozen. Table 13 reports the calculated core-valence corrections tabulated as a function of basis set for the unaugmented and augmented polarized core-valence basis sets.

Table 13. Core-Valence Correction for FCCF as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-1.40
CC-PCVTZ	-2.29
CC-PCVQZ	-2.71
CC-PCV5Z	-2.85
AUG-CC-PCVDZ	-1.99
AUG-CC-PCVTZ	-2.48
AUG-CC-PCVQZ	-2.75
AUG-CC-PCV5Z	-2.86

As seen in Table 13, the level of augmentation has little effect on the core-valence correction. In Table 14, the values of the core-valence correction are extrapolated to the basis set limit using the same procedure as previously discussed.

Table 14. Core-Valence Correction for FCCF at the Complete Basis Set Limit		
Basis sets	$\Delta CV(\infty)$ (kcal/mol)	$\Delta CV(E(\infty))$ (kcal/mol)
CC-PCVXZ		
Feller(TQ5)	-2.90	-2.90
Schwartz α (TQ5)	-2.95	-2.94
Schwartz4(Q5)	-2.95	-2.95
Schwartz6(Q5)	-2.95	-2.95
AUG-CC-PCVXZ		
Feller(TQ5)	-2.93	-2.93
Schwartz α (TQ5)	-2.98	-2.99
Schwartz4(Q5)	-2.94	-2.94
Schwartz6(Q5)	-2.94	-2.94

Between the two extrapolation methods, the difference between the core-valence corrections is negligible; and amongst extrapolation equations, the difference in the correction is less than 0.1 kcal/mol. Table 15 lists heat of formation values corrected for

the core-valence correlation, spin-orbit coupling (0.94 kcal/mol), and the relativistic effects (0.70 kcal/mol) not originally included in the values in Table 11.

Table 15. ΔH_f Values Corrected for Core-Valence Correlation, Spin-Orbit Coupling, and Relativistic Effects for FCCF at the Complete Basis Set Limit for each Method		
Basis sets	Corrected $\Delta H_f(\infty)$ (kcal/mol)	Corrected $\Delta H_f(E(\infty))$ (kcal/mol)
CC-PVXZ		
Feller(DTQ5)	2.71	2.79
Feller(TQ5)	2.52	2.58
Schwartz α (DTQ5)	0.21	0.41
Schwartz α (TQ5)	1.54	1.67
Schwartz4(DTQ5)	2.94	2.94
Schwartz4(Q5)	1.62	1.62
Schwartz6(DTQ5)	1.21	1.21
Schwartz6(Q5)	1.62	1.62
AUG-CC-PVXZ		
Feller(DTQ5)	2.59	2.79
Feller(TQ5)	2.47	2.64
Schwartz α (DTQ5)	0.88	1.37
Schwartz α (TQ5)	1.88	2.23
Schwartz4(DTQ5)	1.75	1.75
Schwartz4(Q5)	1.60	1.60
Schwartz6(DTQ5)	1.14	1.14
Schwartz6(Q5)	1.60	1.60
D-AUG-CC-PVXZ		
Feller(DTQ5)	2.46	2.74
Feller(TQ5)	2.56	1.81
Schwartz α (DTQ5)	1.08	1.73
Schwartz α (TQ5)	2.18	2.69
Schwartz4(DTQ5)	1.31	1.31
Schwartz4(Q5)	1.76	1.76
Schwartz6(DTQ5)	1.14	1.14
Schwartz6(Q5)	1.76	1.76

Even though the results in Table 15 show that the heat of formation values between methods change by substantial percentages, the results describe the enthalpy of formation for FCCF as an endothermic process. We used the D-AUG-CCPVXZ basis set extrapolations performed using the $P(\infty)$ method to produce a list of calculated and

experimental heats of formation. The results are presented in Table 16. Theoretical contributions by Bauschlicher⁴ and Parthiban³ and experimental results provided by Chase² and Ehlert²¹ are also listed in Table 16.

Table 16. Comparison of Heats of Formation of FCCF	
	ΔH_f kcal/mol
^a This work	2.46
^b This work	1.08
^c This work	1.31
^d This work	1.14
³ Parthiban(W1)	0.48
³ Parthiban(W2)	1.38
⁴ Bauschlicher	1.433
² experiment	5.00 $\pm$ 5.00
²¹ experiment	-45 $\pm$ 6.00
^a Feller(DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method	
^b Schwartz α (DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method	
^c Schwartz4(DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method	
^d Schwartz6(DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method	

The computational work done by Bauschlicher⁴ and Parthiban³ is a mixture of CCSD(T), DFT, and other *ab initio* calculations. The discrepancies between theoretical values produced in this research and other computational methods are due mainly to a use of different starting geometries and vibrational frequencies and a different core-valence correction. Because we calculated the heat of formation values using many similar techniques, it is not surprising that the values are within a kcal/mol of each other. Since the experimental values are inconsistent and the error bars broad, all of the calculated heats of formation fall within experimental accuracy.

2.4 ClCCCl

Table 17 is a collection of CCSD(T) optimized geometries as a function of augmented and unaugmented basis sets, the experimental geometry of ClCCCl²², and geometries extrapolated to the complete basis set limit.

Table 17. Optimized Geometries of ClCCCl as a Function of Basis Set					
Basis	RCC (ang)	RCCl (ang)	Basis	RCC (ang)	RCCl (ang)
CC-PVDZ	1.22442	1.66458	AUG-CC-PVDZ	1.22560	1.66890
CC-PVTZ	1.20872	1.64891	AUG-CC-PVTZ	1.20889	1.64883
CC-PVQZ	1.20530	1.64339	AUG-CC-PVQZ	1.20551	1.64339
CC-PV5Z	1.20506	1.63965	AUG-CC-PV5Z	1.20533	1.63970
Feller(DTQ5)	1.2048	1.6379	Feller(DTQ5)	1.2050	1.6390
Feller(TQ5)	1.2050	1.6318	Feller(TQ5)	1.2053	1.6319
Schwartz α (DTQ5)	1.2043	1.6339	Schwartz α (DTQ5)	1.2046	1.6365
Schwartz α (TQ5)	1.2050	1.6162	Schwartz α (TQ5)	1.2053	1.6162
Schwartz4(DTQ5)	1.2037	1.6406	Schwartz4(DTQ5)	1.2037	1.6400
Schwartz4(TQ5)	1.2040	1.6386	Schwartz4(TQ5)	1.2043	1.6387
Schwartz4(Q5)	1.2049	1.6366	Schwartz4(Q5)	1.2052	1.6367
Schwartz6(DTQ5)	1.2042	1.6379	Schwartz6(DTQ5)	1.2045	1.6382
Schwartz6(TQ5)	1.2054	1.6353	Schwartz6(TQ5)	1.2057	1.6354
Schwartz6(Q5)	1.2049	1.6366	Schwartz6(Q5)	1.2052	1.6367
			²² experimental	1.205	1.635

The augmentation of the CC-PVXZ basis set lends little to the accuracy and speed of convergence of the optimized geometries listed in Table 17. The optimized geometries are slower to converge than HCCH and FCCF, but the carbon-carbon bond distance has converged to within three decimal places by the 5-zeta basis set, and the carbon-chlorine bond has converged to within two decimal places by the Q-zeta. Interestingly, it seems the optimized geometries are converging to within 0.001Å of the experimental geometry and the converged geometry is within 0.004Å of the 5-zeta optimized geometry.

Table 18. Vibrational Frequencies of ClCCCl	
Symmetry	Frequency (cm ⁻¹)
Cis-bend (Π_u)	172
Trans-bend (Π_g)	333
s-CCl stretch (Σ_g)	477
a-CCl stretch (Σ_u)	988
CC stretch (Σ_g)	2234

We used the experimental geometry provided in Table 17, the Schimanouchi¹⁹ vibrational frequencies provided in Table 18, and the standard heats of formation for the carbon and chlorine atoms provided by Chase² to compute the heat of formation at 298K and dissociation energy at 0 K for ClCCCl. We compiled these results as a function of the suite of Dunning unaugmented, augmented, and doubly augmented basis sets. Table 19 reports our results.

Table 19. Calculated Dissociation Energies and Heats of Formation for ClCCCl as a Function of Basis Set		
Basis sets	D _e (kcal/mol)	ΔH_f (kcal/mol)
CC-PVDZ	306.97	97.89
CC-PVTZ	332.28	72.58
CC-PVQZ	341.61	63.24
CC-PV5Z	345.74	59.12
AUG-CC-PVDZ	306.89	97.97
AUG-CC-PVTZ	334.55	70.31
AUG-CC-PVQZ	342.76	62.10
AUG-CC-PV5Z	346.32	58.54
D-AUG-CC-PVDZ	308.71	96.14
D-AUG-CC-PVTZ	335.61	69.25
D-AUG-CC-PVQZ	343.35	61.51
D-AUG-CC-PV5Z	346.62	58.24

If we compare the calculations in Table 19 to the corresponding tables for HCCH and FCCF, we notice a general trend. Regardless of basis set, the heats of formation calculations seem to be essentially independent of the level of augmentation. Similar to FCCF, for ClCCCl neither the dissociation energy at 0 K nor the heat of formation at 298

K converges, but the change in values between the Q- and 5-zeta basis sets is only 10 percent of the computed value for CCCCCI compared to 40 percent for FCCF. We made extrapolations of the heat of formation to the complete basis set limit. Table 20 reports our results.

Table 20. Heats of Formation for CCCCCI Extrapolated to the Complete Basis Set Limit		
Basis sets CC-PVXZ	$\Delta H_f(\infty)$ (kcal/mol)	$\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ5)	56.91	57.33
Feller(TQ5)	55.86	56.39
Schwartz α (DTQ5)	52.26	53.31
Schwartz α (TQ5)	53.08	54.29
Schwartz4(DTQ5)	59.60	59.60
Schwartz4(Q5)	55.77	55.77
Schwartz6(DTQ5)	55.99	55.99
Schwartz6(Q5)	55.78	55.78
AUG-CC-PVXZ		
Feller(DTQ5)	57.45	57.49
Feller(TQ5)	55.81	56.22
Schwartz α (DTQ5)	54.53	54.62
Schwartz α (TQ5)	53.51	54.43
Schwartz4(DTQ5)	58.19	58.19
Schwartz4(Q5)	55.65	55.65
Schwartz6(DTQ5)	56.03	56.03
Schwartz6(Q5)	55.65	55.65
D-AUG-CC-PVXZ		
Feller(DTQ5)	57.31	57.33
Feller(TQ5)	55.84	55.12
Schwartz α (DTQ5)	54.72	54.75
Schwartz α (TQ5)	53.86	54.45
Schwartz4(DTQ5)	57.75	57.75
Schwartz4(Q5)	55.58	55.58
Schwartz6(DTQ5)	55.91	55.91
Schwartz6(Q5)	55.59	55.59

Table 20 shows that the Feller, Schwartz4, and Schwartz6 extrapolation equations consistently extrapolate to a higher value than the Schwartz α equation. Using only the values from larger basis sets, the resultant enthalpy drops. There is little difference

within methods, but there are differences of up to several kcal/mol between extrapolation equations.

To be physically viable, the extrapolated values for the enthalpy of formation can not be higher than the best unextrapolated value. In Table 20, the Schwartz4(DTQ5) extrapolated value exceeds the unextrapolated CC-PV5Z heat of formation. This result is in italics and is the first example of how these extrapolation equations are fallible. Although that value is the only result higher than the unextrapolated value in Table 20, other values do lie very close to the unextrapolated values. These results in bold italics, and they occur when data points calculated at smaller basis sets are included in the extrapolation. This problem does seem to right itself once the smaller data points are removed from involvement in the extrapolations.

Table 21 contains the core-valence correction to the values in Table 14 due to the frozen 1s, 2s, and 2p core on chlorine and frozen 1s core on carbon in the atomic and molecular CCSD(T) energy calculations.

Table 21. Core-Valence Correction for ClCCCl as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-2.09
CC-PCVTZ	-2.61
CC-PCVQZ	-2.81

The core-valence correction is close to convergence. Table 22 contains the core-valence correction at the basis set limit.

Table 22. Core-Valence Correction for ClCCCl at the Complete Basis Set Limit		
Basis sets CC-PCVXZ	$\Delta CV(\infty)$ (kcal/mol)	$\Delta CV(E(\infty))$ (kcal/mol)
Feller(DTQ)	-2.93	-1.23
Schwartz α (DTQ)	-3.06	2.09
Schwartz4(TQ)	-2.92	-2.92
Schwartz6(TQ)	-2.92	-2.92

Notice in Table 22 that between methods for the Feller extrapolations, the energy difference is 1.7 kcal/mol, and the value for the core-valence correction changes sign between methods for the Schwartz α extrapolations. The cause for this sign change, an unusual result, depends, most likely, on how closely the data had converged before fitting of nonlinear equations to the data points. Notice that the $\Delta CV(\infty)$ value for the Feller and Schwartz α fitting equations is approximately equal to the results for Schwartz4 and Schwartz6. As mentioned earlier, since the Feller and Schwartz α fitting equations have variable exponents, there is a chance that the relative consistency in how tightly the atomic and molecular data was fit could cause inconsistency in the extrapolated result.

This discrepancy between the two methods for the Schwartz and Feller equations would have a tremendous impact on their respective corrected $\Delta H_f(E(\infty))$ values in Table 23. As stated earlier, instead of calculating the corrected ΔH_f values by combining the enthalpy of formation and core-valence corrections from like methods and extrapolation equations, we added a constant -2.92 kcal/mol core-valence correction to all the extrapolated ΔH_f values. Table 23 contains the enthalpy of formation values for ClCCCl after we added the core-valence correction, spin-orbit coupling correction (1.85 kcal/mol), and the correction due to relativistic effects (0.99 kcal/mol).

Table 23. ΔH_f Values Corrected for Core-Valance Correlation, Spin-Orbit Coupling, and Relativistic Effects for ClCCCl at the Complete Basis Set Limit for each Method		
Basis sets CC-PVXZ	Corrected $\Delta H_f(\infty)$ (kcal/mol)	Corrected $\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ5)	56.83	57.25
Feller(TQ5)	55.78	56.31
Schwartz α (DTQ5)	52.18	53.23
Schwartz α (TQ5)	53.00	54.21
Schwartz4(DTQ5)	59.52	59.52
Schwartz4(Q5)	55.70	55.70
Schwartz6(DTQ5)	55.91	55.91
Schwartz6(Q5)	55.70	55.70
AUG-CC-PVXZ		
Feller(DTQ5)	57.37	57.41
Feller(TQ5)	55.73	56.14
Schwartz α (DTQ5)	54.45	54.54
Schwartz α (TQ5)	53.43	54.35
Schwartz4(DTQ5)	58.11	58.11
Schwartz4(Q5)	55.57	55.57
Schwartz6(DTQ5)	55.95	55.95
Schwartz6(Q5)	55.57	55.57
D-AUG-CC-PVXZ		
Feller(DTQ5)	57.23	57.25
Feller(TQ5)	55.76	55.04
Schwartz α (DTQ5)	54.64	54.67
Schwartz α (TQ5)	53.78	54.37
Schwartz4(DTQ5)	57.67	57.67
Schwartz4(Q5)	55.50	55.50
Schwartz6(DTQ5)	55.83	55.83
Schwartz6(Q5)	55.51	55.51

Table 24 presents a few values from Table 23 along with results from the works of Parthiban³ and Chase² for comparison.

Table 24. Comparison of Heats of Formation of ClCCCl		
	ΔH_f kcal/mol	Error kcal/mol
^a This work	57.23	7.13
^b This work	54.64	4.54
^c This work	57.67	7.57
^d This work	55.83	5.73
³ Parthiban(W1)	56.46	6.36
³ Parthiban(W2)	56.21	6.11
² experiment	50.1	± 10
^a Feller(DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method		
^b Schwartz α (DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method		
^c Schwartz4(DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method		
^d Schwartz6(DTQ5) extrapolation of doubly augmented basis set values with $P(\infty)$ method		

All the heat of formation values in Table 24 are within the experimental error bars. The calculated values from this manuscript differ from Parthiban's work due to Parthiban's use of calculated DFT geometries and frequencies. Having completed the three molecules for which there is experimental data available, it is evident that the procedure used for evaluation is adequate for determining the enthalpy of formation for HCCH and the halogenated acetylenes. Almost all values fall very near the experimental result, and most fall within experimental error bars.

2.5 Linear Li₂C₂

We generated augmented lithium CC-PVXZ basis sets for CCSD(T) calculations single point, geometry optimization, and vibrational frequency calculations by adding even-tempered basis functions to the Dunning lithium CC-PVXZ basis sets. Table 25 lists the added gaussian function exponents for the constructed AUG-CC-PVDZ, AUG-CC-PVTZ, and AUG-CC-PVQZ basis sets.

Table 25. Added Diffuse Function Exponents to Create Li AUG-CC-PVXZ Basis Sets			
	AUG-CC-PVDZ	AUG-CC-PVTZ	AUG-CC-PVQZ
S	0.01122	0.01104	0.01067
P	0.01047	0.007649	0.007978
D	0.04765	0.03560	0.03207
F	---	0.08627	0.07383
G	---	---	0.1253

To calculate the heat of formation, we used the equilibrium geometry and fundamental vibrational frequencies. Table 26 lists CCSD(T) optimized geometries, extrapolated geometries, other theoretical geometries, and the geometry used for the heat of formation calculations.

Table 26. Optimized Geometries of Linear Li₂C₂ as a Function of Basis Set		
Basis	RCC (ang)	RCLi (ang)
CC-PVDZ	1.2765	1.9255
CC-PVTZ	1.2577	1.8939
CC-PVQZ	1.2540	1.8939
Feller(DTQ)	1.2531	1.8939
Schwartz α (DTQ)	1.2522	1.8939
Schwartz4(DTQ)	1.2515	1.8876
Schwartz4(TQ)	1.2519	1.8939
Schwartz6(DTQ)	1.2520	1.8963
Schwartz6(TQ)	1.2519	1.8939
²³ MP2	1.267	1.883
²⁴ RHF	1.2314	1.8845
USED	1.2531	1.8943

Table 26 demonstrates that the optimized geometries are close to convergence. The extrapolated values are within 0.002Å of the optimized geometry calculated at the highest basis set and are within a few thousandths of an angstrom of the value used in the heat of formation calculations. The results of other researchers are within 0.01Å for the carbon lithium bond and 0.03Å of the carbon-carbon bond. We calculated the vibrational frequencies using the CC-PVTZ and AUG-CC-PVTZ basis sets wherein the basis sets

had all the higher angular momentum functions intact. These values are shown in Table 27.

Table 27. Vibrational Frequencies for Linear Li₂C₂		
	Basis Sets	
Symmetry	CC-PVTZ	AUG-CC-PVTZ
(D) Cis-bend (Π_u)	86	86
(E) Trans-bend (Π_g)	147	157
(A) s-CLi stretch (Σ_g)	582	577
(C) a-CLi stretch (Σ_u)	737	733
(B) CC stretch (Σ_g)	1943	1937

Figure 1 provides a visual description of the vibrational modes. Each of these vibrations is the same type of vibration for linear four atom molecules. The A vibration is normally referred to as the symmetric carbon-lithium stretches, and the vibration C is the asymmetric carbon-lithium stretch. The B stretch is the carbon-carbon stretch, and the D and E vibrations are doubly degenerate cis and trans-bends, respectively. Because there are no imaginary frequencies, the linear configuration is a viable geometric minimum on the Li₂C₂ potential energy surface.

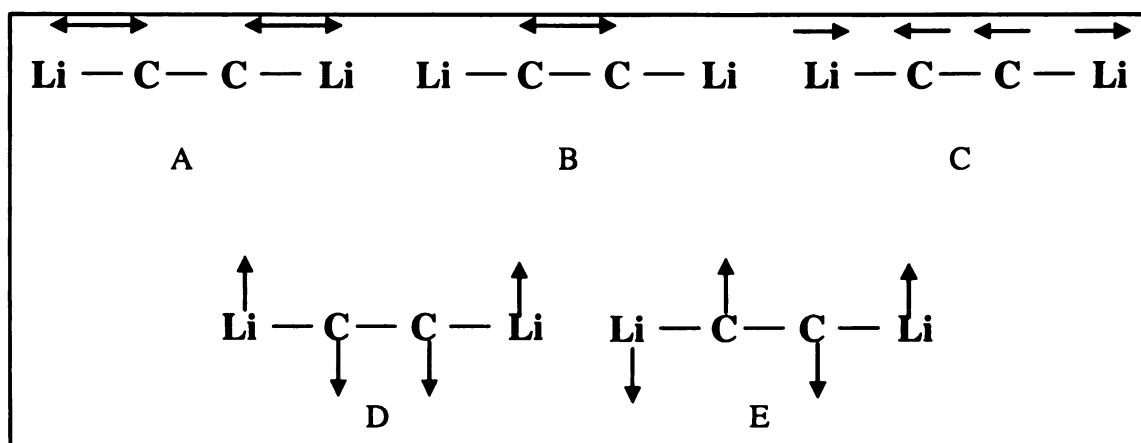


Figure 1: Vibrational Modes of Linear Li₂C₂

Using the CCSD(T) vibrational frequencies calculated at the AUG-CC-PVTZ basis set described in Table 27, the geometry $R_{CC} = 1.2531 \text{ \AA}$, $R_{CLi} = 1.8943 \text{ \AA}$ from

Table 26, and the heats of formation of atomic carbon and lithium provided by Chase² from the appendix, we calculated dissociation energy at 0 K and heat of formation at 298 K for linear Li₂C₂. Table 28 shows our results.

Table 28. Calculated Dissociation Energies and Heats of Formation for Linear Li₂C₂ as a Function of Basis Set		
Basis sets	D_e (kcal/mol)	ΔH_f (kcal/mol)
CC-PVDZ	291.44	130.69
CC-PVTZ	315.98	106.16
CC-PVQZ	323.21	98.92
^a CC-PV(QZ-5Z)	325.12	97.01
^b CC-PV(QZ-6Z)	326.04	96.10
AUG-CC-PVDZ	298.01	124.12
AUG-CC-PVTZ	318.99	103.14
AUG-CC-PVQZ	324.20	97.93
^c AUG-CC-PV(QZ-5Z)	325.80	96.33
^d AUG-CC-PV(QZ-6Z)	326.43	95.71
^a Li CC-PVQZ basis set with C CC-PV5Z basis set		
^b Li CC-PVQZ basis set with C CC-PV6Z basis set		
^c Li AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set		
^d Li AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set		

The enthalpy of formation is not converged by the Q-zeta basis set for the unaugmented and augmented basis sets. Table 28 shows also results from mixed basis set calculations. In these calculations, we allowed the carbon basis set to progress beyond the Q-zeta level, but the lithium basis set did not progress pass the Q-zeta level. These basis sets are unusual, so the extrapolations in Table 29 do not include those values. We did not attempt extrapolation of the augmented basis sets. Since the constructed basis sets were not optimized, the extrapolation behavior would be unlike that of the Dunning optimized basis sets. We used the data from the unaugmented basis sets, excluding the mixed basis set calculations, to extrapolate to the complete basis set limit. Table 29 reports the extrapolations.

Table 29. Heats of Formation for Linear Li₂C₂ Extrapolated to the Complete Basis Set Limit		
Basis sets CC-PVXZ	$\Delta H_f(\infty)$ (kcal/mol)	$\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ)	95.90	95.94
Schwartz α (DTQ)	92.78	92.87
Schwartz4(DTQ)	96.33	96.33
Schwartz4(TQ)	94.75	94.75
Schwartz6(DTQ)	94.16	94.16
Schwartz6(TQ)	94.77	94.77

The extrapolated enthalpies of formation in Table 29 range from around 93 to around 97 kcal/mol. Again, any extrapolated heat of formation that is higher than the best-unextrapolated value is not physically viable and highlighted in red. Keep in mind that we determined the highlighted values in Table 29 from extrapolations of the pure basis sets. The extrapolated value is higher than the value from unextrapolated mixed basis set values. Previously for HCCH, FCCF, and ClCCCl by the 5-zeta basis set, the enthalpy of formation was near convergence. It seems that the same may be true for Li. Without the 5-zeta basis set, the extrapolations are not as precise as previous examples.

To correct for the core-valence correlation of the 1s shell on carbon and lithium, we made core-valence corrections. Table 30 presents those results as a function of basis set.

Table 30. Core-Valence Correction for Linear Li₂C₂ as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-1.15
CC-PCVTZ	-2.09
CC-PCVQZ	-2.62
^a CC-PCV(QZ-5Z)	-2.74
^a Li with CC-PCVQZ basis set C with cc-pCV5Z basis set	

The core-valence correction did not converge, but the magnitude of the correction is approximately the same as for the halogenated molecules. Table 31 reports complete

basis set extrapolation values that we calculated using the results calculated using the three unmixed basis sets.

Table 31. Core-Valence Correction for Linear Li₂C₂ at the Complete Basis Set Limit		
Basis sets CC-PCVXZ	$\Delta CV(\infty)$ (kcal/mol)	$\Delta CV(E(\infty))$ (kcal/mol)
Schwartz α (DTQ)	-4.65	1.07
Schwartz4(TQ)	-2.93	-2.93
Schwartz6(TQ)	-2.93	-2.93

Similar to ClCCCl, the differences between the methods and extrapolation equations are large. These discrepancies may be due to differences among the nonlinear fit equations and the fitting methods created by inconsistencies in how accurate the fit for each equation and the method is to the data. In previous core-valence calculations, such as HCCH and FCCF, we used a 5-zeta basis set. Similar to the ClCCCl molecule, we set the ΔCV correction for all the extrapolated linear Li₂C₂ heat of formation values to -2.93 kcal/mol. Table 32 shows the values of the enthalpy of formation that we added after the missing core-valence correlation (-2.93 kcal/mol), spin-orbit coupling (0.17 kcal/mol) and relativistic effect (0.19 kcal/mol) corrections.

Table 32. ΔH_f Values Corrected for Core-Valence Correlation, Spin-Orbit Coupling, and Relativistic Effects for Linear Li₂C₂ at the Complete Basis Set Limit for each Method		
Basis sets CC-PVXZ	Corrected $\Delta H_f(\infty)$ (kcal/mol)	Corrected $\Delta H_f(E(\infty))$ (kcal/mol)
Schwartz α (DTQ)	90.21	90.28
Schwartz4(TQ)	92.18	92.18
Schwartz6(DTQ)	91.59	91.59
Schwartz6(TQ)	92.20	92.20

The enthalpy of formation of linear Li₂C₂ seems to be substantially larger than the enthalpy of formation of the previous acetylenes. The largest inconsistency between extrapolation equations is the range of 2 kcal/mol between the Schwartz α and Schwartz6

extrapolation equations. Table 33 presents selected values from Table 32, the value for the enthalpy of formation calculated from the unextrapolated enthalpy of formation in Table 28, and core-valence correction at the largest basis set.

Table 33. Comparison of Heats of Formation of Linear Li_2C_2	
Basis Set	$\Delta H_f(\infty)$ kcal/mol
^a This work	90.21
^b This work	92.18
^c This work	91.59
^d Unextrapolated value	93.30
^a Schwartz α (DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^b Schwartz4(TQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^c Schwartz6(DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^d ΔH_f from AUG-CC-PV(QZ-6Z) using ΔCV from CC-PCV(QZ-5Z) basis set	

Table 33 shows that the unextrapolated result from the AUG-CC-PV(QZ-6Z) heat of formation and the CC-PCV(QZ-6Z) core-valence correction is the largest heat of formation. The enthalpy values from Table 33 are generally around 92 kcal/mol, but the Schwartz α result is closer to 90 kcal/mol.

2.6 Planar Li_2C_2

The doubly bridged or planar Li_2C_2 complex is the lowest energy configuration for the Li_2C_2 species with a 7.3 kcal/mol (11.7 millihartree) energy difference between the linear and doubly bridged geometries. To find the equilibrium geometry, we calculated CCSD(T) optimized geometries for the planar Li_2C_2 species. These optimized geometries are extrapolated to the complete basis set and compared to previously determined theoretical geometries. Table 34 lists the geometry used in the heat of formation calculations.

Table 34. Optimized Geometries of Planar Li₂C₂ as a Function of Basis Set		
Basis	RCC (ang)	RCLi (ang)
CC-PVDZ	1.2932	2.0406
CC-PVTZ	1.2730	2.0072
CC-PVQZ	1.2686	2.0049
Feller(DTQ)	1.2673	2.0047
Schwartz α (DTQ)	1.2661	2.0045
Schwartz4(DTQ)	1.2660	1.9989
Schwartz4(TQ)	1.2660	2.0036
Schwartz6(DTQ)	1.2661	2.0053
Schwartz6(TQ)	1.2660	2.0053
²⁴ MBPT(2)	1.2808	1.9954
²³ MP2	1.282	2.017
USED	1.2673	2.0086

The optimized geometries in Table 34 are close to converging, and the extrapolated geometries are within 0.003Å of the best-unextrapolated geometry and within 0.001Å of the geometry used to calculate the heat of formation. The literature values from previous studies differ by 0.02Å for the carbon-carbon bond and 0.002Å for the carbon-lithium bond. Table 35 lists the vibrational frequencies of planar Li₂C₂ at the CC-PVTZ and AUG-CC-PVTZ basis sets. To conserve computation time, we removed the d and f gaussian functions from the lithium AUG-CC-PVTZ basis set, but we retained them for the carbon AUG-CC-PVTZ basis set.

Table 35. Vibrational Frequencies for Planar Li₂C₂		
Symmetry	Basis Sets	
	CC-PVTZ	AUG-CC-PVTZ
vibration A (B _{3u})	66	64
vibration B (B _{2u})	199	193
vibration C (B _{3g})	306	302
vibration D (A _g)	564	557
vibration E (B _{1u})	685	681
vibration F (A _g)	1799	1793

Again, there are no imaginary frequencies to indicate that the planar complex is not a minimum. Figure 2 is a visual representation of the vibrational frequencies of

planar Li_2C_2 . Vibration A is a side view of the doubly bridged molecule. The second carbon atom is located directly behind the labeled carbon. Note that the vibration C resembles the type of motion which might move the planar species towards the formation of the linear species.

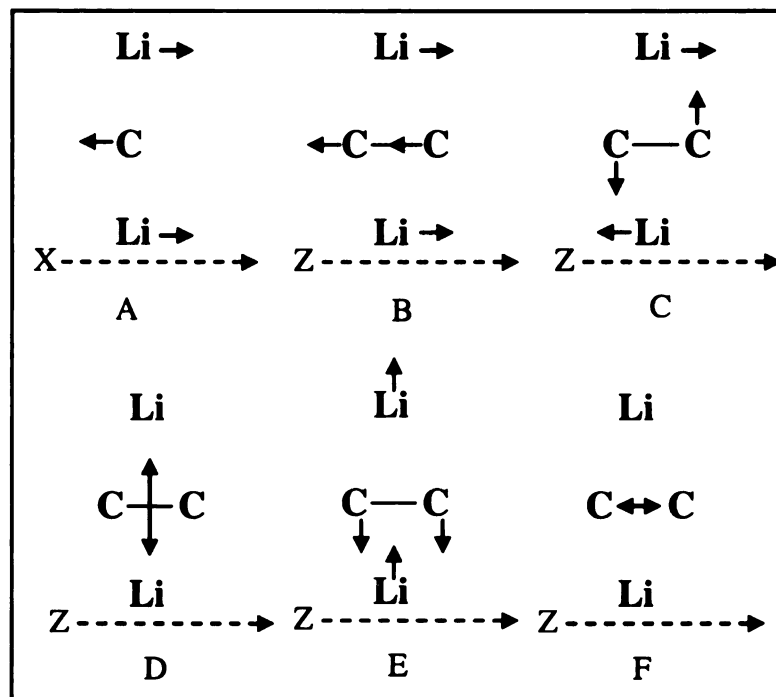


Figure 2: Vibrational Modes for Planar Li_2C_2

Using the geometry $R_{\text{CC}} = 1.2673 \text{ \AA}$, $R_{\text{LiC}} = 2.0086 \text{ \AA}$, $\angle \text{CCLi} = 71.6$ from Table 34 and vibrational frequencies calculated at the CCSD(T) level using the mixed AUG-CC-PVTZ basis set, we calculated dissociation energies at 0 K and heat of formation values at 298 K for the doubly bridged species. Table 36 shows our results.

Table 36. Calculated Dissociation Energies and Heats of Formation for Planar Li₂C₂ as a Function of Basis Set		
Basis Set	D _e kcal/mol	ΔH _f kcal/mol
CC-PVDZ	300.86	119.87
CC-PVTZ	324.15	96.57
CC-PVQZ	330.84	89.89
^a CC-PV(5Z-QZ)	332.62	88.11
^b CC-PV(6Z-QZ)	333.47	87.26
AUG-CC-PVDZ	304.54	116.19
AUG-CC-PVTZ	326.28	94.45
AUG-CC-PVQZ	331.52	89.21
^c AUG-CC-PV(5Z-QZ)	333.12	87.61
^d AUG-CC-PV(6Z-QZ)	333.77	86.96
^a Li CC-PVQZ basis set with C CC-PV5Z basis set ^b Li CC-PVQZ basis set with C CC-PV6Z basis set ^c Li AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set ^d Li AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set		

The unaugmented and augmented basis sets are not converged by the Q-zeta basis set. We extrapolated the data from the unaugmented basis sets, excluding the mixed basis set calculations, to the complete basis set limit. Table 37 shows the results of this investigation.

Table 37. Heats of Formation for Planar Li₂C₂ Extrapolated to the Complete Basis Set Limit		
Basis sets	ΔH _f (∞) (kcal/mol)	ΔH _f (E(∞)) (kcal/mol)
CC-PVXZ		
Feller(DTQ)	87.19	87.23
Schwartzα(DTQ)	84.43	84.50
Schwartz4(DTQ)	87.36	87.36
Schwartz4(TQ)	86.03	86.03
Schwartz6(DTQ)	85.52	85.52
Schwartz6(TQ)	86.05	86.05

Again, the Schwartz4(DTQ) and Feller extrapolation results in an unphysical value higher than the unextrapolated values.

To correct for the frozen 1s core on lithium and carbon, we calculated core-valence corrections using the Dunning CC-PCVXZ basis sets. Table 38 reports the results of these calculations.

Table 38. Core-Valence Correction for Planar Li₂C₂ as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-1.31
CC-PCVTZ	-2.19
CC-PCVQZ	-2.68
^a CC-PCV(QZ-5Z)	-2.79
^a Li with CC-PCVQZ basis set C with CC-PCV5Z basis set	

Similar to the linear species, the core-valence correction for planar Li₂C₂ has not converged. Yet, the core-valence correction for the planar molecule differs by less than 0.1 kcal/mol from the linear core-valence correction. Table 39 reports the core-valence correction extrapolated to an infinite basis set.

Table 39. Core-Valence Correction for Planar Li₂C₂ at the Complete Basis Set Limit		
Basis sets	$\Delta CV(\infty)$ (kcal/mol)	$\Delta CV(E(\infty))$ (kcal/mol)
CC-PCVXZ		
Feller(DTQ)	-3.30	-2.95
Schwartz α (DTQ)	-4.43	1.14
Schwartz4(TQ)	-2.96	-2.96
Schwartz6(TQ)	-2.96	-2.96

Similar to the linear species, the extrapolated values for the variable exponent equations are erratic, so the core-valence correction used for the planar molecule is -2.96 kcal/mol. Table 40 reports the enthalpy of formation for the planar species after we added the core-valence corrections (-2.96 kcal/mol), spin-orbit coupling (0.17 kcal/mol), and relativistic corrections (0.15 kcal/mol).

Table 40. ΔH_f Values Corrected for Core-Valance Correlation, Spin-Orbit Coupling, and Relativistic Effects for Planar Li_2C_2 at the Complete Basis Set Limit for each Method		
Basis sets CC-PVXZ	Corrected $\Delta H_f(\infty)$ (kcal/mol)	Corrected $\Delta H_f(E(\infty))$ (kcal/mol)
Schwartz α (DTQ)	81.79	81.87
Schwartz4(TQ)	83.39	83.39
Schwartz6(DTQ)	82.89	82.89
Schwartz6(TQ)	83.41	83.41

The heat of formation results reported in Table 40 span a range of 2 kcal/mol.

Table 41 reports the better values from Table 40 and the combination of the heat of formation calculated with the AUG-CC-PV(QZ-6Z) basis set and the core-valence correction calculated using the CC-PCV(QZ-5Z) basis set.

Table 41. Comparison of Heats of Formation of Planar Li_2C_2	
Basis Set	ΔH_f kcal/mol
^a This work	81.79
^b This work	82.89
^c This work	83.41
^d Unextrapolated value	84.49
^a Schwartz α (DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^b Schwartz4(TQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^c Schwartz6(DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^d ΔH_f from AUG-CC-PV(QZ-6Z) using ΔCV from CC-PCV(QZ-5Z) basis set	

Table 41 shows that the extrapolated heats of formation are a kcal/mol smaller than the unextrapolated heat of formation using larger basis sets. Table 42 shows a comparison of the enthalpy of formation for Li_2C_2 at its two ground-state geometries.

Table 42. Energy Difference between Linear and Planar Li₂C₂			
Basis Set	Planar Li ₂ C ₂ ΔH_f	Linear Li ₂ C ₂ ΔH_f	Difference kcal/mol
^a This work	81.79	90.21	8.42
^b This work	83.39	92.18	8.79
^c This work	83.41	92.20	8.79
^d Unextrapolated value	84.49	93.30	8.81
^a Schwartz α (DTQ) extrapolation of unaugmented basis set values with P(∞) method			
^b Schwartz4(TQ) extrapolation of unaugmented basis set values with P(∞) method			
^c Schwartz6(TQ) extrapolation of unaugmented basis set values with P(∞) method			
^d ΔH_f from AUG-CC-PV(QZ-6Z) using ΔCV from CC-PCV(QZ-5Z) basis set			

We compared the enthalpy of formation for both the linear and planar species and found the energy difference between the two configurations to be 8 kcal/mol. We found the energy difference between the two configurations using D_e values with no thermal corrections to be 7.3 kcal/mol.

2.7 Linear Na₂C₂

Using the same process followed for calculating the properties of the Li₂C₂ molecules, we calculated the molecular geometries, vibrational frequencies, and enthalpy of formation of both Na₂C₂ species. We generated augmented CC-PVXZ basis sets by adding even-tempered basis functions to the sodium Dunning CC-PVXZ basis sets.

Table 43 lists the gaussian function exponents added for augmentation of the CC-PVDZ, CC-PVTZ, and CC-PVQZ basis sets.

Table 43. Added Diffuse Function Exponents to Create Na AUG-CC-PVXZ Basis Sets			
	AUG-CC-PVDZ	AUG-CC-PVTZ	AUG-CC-PVQZ
S	0.00995	0.00942	0.00790
P	0.00648	0.00602	0.00323
D	0.0228	0.0296	0.02740
F	---	0.05588	0.0560
G	---	---	0.0861

We calculated CCSD(T) single point energy, geometry optimization, and vibrational frequency using these generated basis sets. Table 44 reports the calculations.

Table 44. Optimized Geometries of Linear Na₂C₂ as a Function of Basis Set		
Basis	RCC (ang)	RCNa (ang)
CC-PVDZ	1.2777	2.2427
CC-PVTZ	1.2592	2.2373
CC-PVQZ	1.2560	2.2378
Feller(DTQ)	1.2553	2.2376
Schwartz α (DTQ)	1.2546	2.2376
Schwartz4(DTQ)	1.2533	2.2366
Schwartz4(TQ)	1.2541	2.2382
Schwartz6(DTQ)	1.2544	2.2387
Schwartz6(TQ)	1.2541	2.2382
USED	1.2549	2.2341

Table 44 shows that both the carbon-carbon and carbon-sodium bond length are converged to within 0.004Å by the Q-zeta basis set. The extrapolated values differ less than 0.003Å from the unextrapolated geometries, but the carbon-sodium bond length differs by 0.004Å from the geometry used to calculate the enthalpy of formation. We calculated CCSD(T) vibrational frequencies at the CC-PVTZ and AUG-CC-PVTZ basis sets where the sodium basis set is void of any higher order angular momentum functions above a p orbital. Table 45 lists these frequencies.

Table 45. Vibrational Frequencies of Linear Na₂C₂		
	Basis Sets	
Symmetry	CC-PVTZ	AUG-CC-PVTZ
(D) Cis-bend (Π_u)	45cm ⁻¹	51 cm ⁻¹
(E) Trans-bend (Π_g)	85i cm ⁻¹	69 cm ⁻¹
(A) s-CNa stretch (Σ_g)	278 cm ⁻¹	275 cm ⁻¹
(C) a-CNa stretch (Σ_u)	475 cm ⁻¹	473 cm ⁻¹
(B) CC stretch (Σ_g)	1922 cm ⁻¹	1907 cm ⁻¹

Figure 3 illustrates the motion of atoms during each of the vibrations. Table 45 shows that the trans-bend or vibration E is imaginary at the CC-PVTZ basis set, but it is real

when the basis set is augmented. Therefore, there is a question as to whether the linear Na_2C_2 is a viable minimum. The vibration E diagram, Figure 3 shows that the trans-bend vibration is similar to the motion the linear molecule might take to form the planar configuration. Maybe the potential energy surface calculated using the CC-PVTZ basis set does not accurately describe the shallow well that is the linear Na_2C_2 minimum.

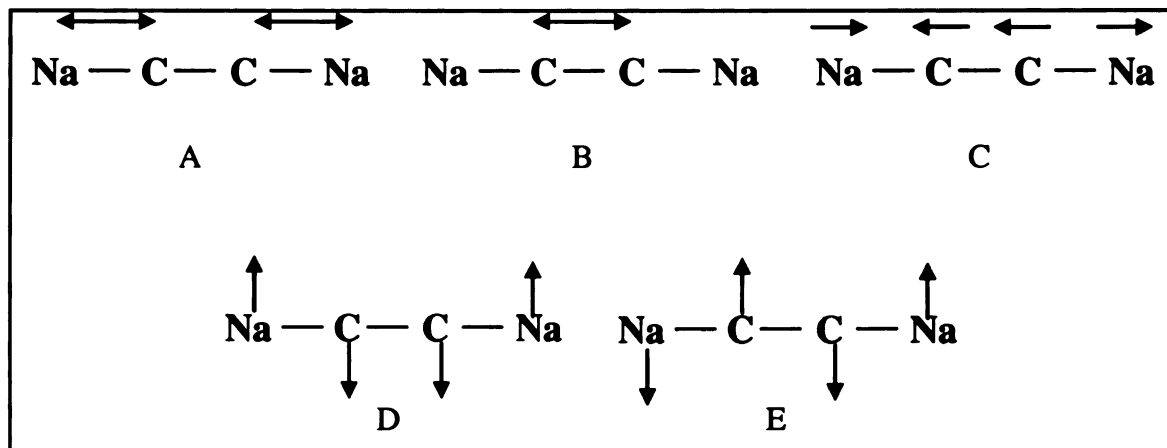


Figure 3: Vibrational Modes of Linear Na_2C_2

Using the optimized geometry obtained in previous work¹, $R_{\text{CC}} = 1.255 \text{ \AA}$, $R_{\text{CNa}} = 2.234 \text{ \AA}$, and CCSD(T) vibrational frequencies from Table 45, we calculated the enthalpy of formation. Table 46 presents the heats of formation at 273 K and dissociation energies at 0 K for linear Na_2C_2 as a function of basis set.

Table 46. Calculated Dissociation Energies and Heats of Formation for Linear Na₂C₂ as a Function of Basis Set		
Basis sets	D _e (kcal/mol)	ΔH _f (kcal/mol)
CC-PVDZ	258.94	137.70
CC-PVTZ	280.18	116.46
CC-PVQZ	287.59	109.05
^a CC-PV(QZ-5Z)	289.62	107.02
^b CC-PV(QZ-6Z)	290.57	106.07
AUG-CC-PVDZ	265.19	131.45
AUG-CC-PVTZ	283.78	112.86
AUG-CC-PVQZ	288.92	107.73
^c AUG-CC-PV(QZ-5Z)	290.53	106.11
^d AUG-CC-PV(QZ-6Z)	291.23	105.41
^a Na CC-PVQZ basis set with C CC-PV5Z basis set ^b Na CC-PVQZ basis set with C CC-PV6Z basis set ^c Na AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set ^d Na AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set		

The enthalpy of formation is not converged by the Q-zeta basis set for either the unaugmented or augmented basis sets. The extrapolations shown in Table 47 do not include the larger basis sets above the unaugmented Q-zeta basis set.

Table 47. Heats of Formation for Linear Na₂C₂ Extrapolated to the Complete Basis Set Limit		
Basis sets	ΔH _f (∞) (kcal/mol)	ΔH _f (E(∞)) (kcal/mol)
CC-PVXZ		
Feller(DTQ)	105.09	105.65
Schwartzα(DTQ)	100.79	102.13
Schwartz4(DTQ)	107.17	107.17
Schwartz4(TQ)	104.78	104.78
Schwartz6(DTQ)	103.88	103.88
Schwartz6(TQ)	104.80	104.80

The extrapolated enthalpies of formation in Table 47 range from about 100 to about 107 kcal/mol. Most of the extrapolated enthalpies of formation are very close to the 105.41 kcal/mol value that we found using the AUG-CC-PV(QZ-6Z) basis set.

To correct for the core-valence correlation of the 2s and 2p shells on sodium and the frozen 1s orbital on carbon, we made core-valence corrections. Table 48 presents those results as a function of basis set.

Table 48. Core-Valence Correction for Linear Na₂C₂ as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-1.14
CC-PCVTZ	-0.74
CC-PCVQZ	-0.74
^a CC-PCV(QZ-5Z)	-0.97
^a Na with CC-PCVQZ basis set C with CC-PCV5Z basis set	

The core-valence correction converges, and the magnitude of the correction is much smaller than that of the halogenated molecules and the two lithium complexes. The mixed basis set calculation provides a correction that is larger than the unmixed basis set. This result is unusual, but the mixing of basis sets does not insure a proper convergence to the basis set limit. Table 49 reports the complete basis set extrapolation values using the results that we calculated using the three unmixed basis sets.

Table 49. Core-Valence Correction for Linear Na₂C₂ at the Complete Basis Set Limit		
Basis sets	$\Delta CV(\infty)$ (kcal/mol)	$\Delta CV(E(\infty))$ (kcal/mol)
CC-PCVXZ		
Feller(DTQ)	-0.74	----
Schwartz α (DTQ)	-0.74	----
Schwartz4(TQ)	-0.73	-0.73
Schwartz6(TQ)	-0.73	-0.73

The core-valence correction for the Feller(DTQ) and Schwartz α equations using the $P(E(\infty))$ method are not reported because the resulting values are not realistic.

Similar to the lithium species, the differences between the methods for Schwartz α and Feller extrapolation equations are large. As done previously in the ClCCCl and the lithium species, the ΔCV correction for all the extrapolated ΔH_f we set values to -0.73

kcal/mol. Table 50 shows the values of the enthalpy of formation after we added the missing core-valence correlation (-0.73 kcal/mol), spin-orbit coupling (0.17 kcal/mol), and relativistic effect (0.21 kcal/mol) corrections.

Table 50. ΔH_f Values Corrected for Core-Valence Correlation, Spin-Orbit Coupling, and Relativistic Effects for Linear Na_2C_2 at the Complete Basis Set Limit for each Method		
Basis sets CC-PVXZ	Corrected $\Delta H_f(\infty)$ (kcal/mol)	Corrected $\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ)	104.74	----
Schwartz α (DTQ)	100.44	101.78
Schwartz4(TQ)	104.43	104.43
Schwartz6(DTQ)	103.53	103.53
Schwartz6(TQ)	104.45	104.45

The enthalpy of formation of linear Na_2C_2 seems to be about 10 kcal/mol larger than the enthalpy of formation of linear Li_2C_2 . The largest inconsistency between extrapolation techniques is a 7 kcal/mol difference between Schwartz α and Schwartz4 extrapolation results. Table 51 presents selected values from Table 50 and the value for the enthalpy of formation calculated from the enthalpy of formation and core-valence correction at the largest basis set.

Table 51. Comparison of Heats of Formation of Linear Na_2C_2	
Basis Set	$\Delta H_f(\infty)$ kcal/mol
^a This work	104.74
^b This work	100.44
^c This work	104.43
^d This work	104.45
^e Unextrapolated value	104.82
^a Feller(DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^b Schwartz α (DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^c Schwartz4(TQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^d Schwartz6(TQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^e ΔH_f from AUG-CC-PV(QZ-6Z) using ΔCV from CC-PCV(QZ-5Z) basis set	

Table 51 shows the unextrapolated result from the AUG-CC-PV(QZ-6Z) heat of formation and the CC-PCV(QZ-5Z) core-valence correction to be closer to the fixed exponent extrapolations.

2.8 Planar Na₂C₂

The doubly bridged or planar Na₂C₂ complex is the lowest energy configuration for the Na₂C₂ species with a 11.2 kcal/mol (17.8 millihartree) energy difference between the linear and doubly bridged geometries. Table 52 lists CCSD(T) optimized geometries as a function of basis set. Table 52 lists also the optimized geometries, extrapolated geometries to the basis set limit, and the geometry that we used to calculate the enthalpy of formation for planar Na₂C₂.

Table 52. Optimized Geometries of Planar Na₂C₂ as a Function of Basis Set		
Basis	RCC (ang)	RCNa (ang)
CC-PVDZ	1.2958	2.3612
CC-PVTZ	1.2761	2.3543
CC-PVQZ	1.2716	2.3497
Feller(DTQ)	1.2703	2.3394
Schwartz α (DTQ)	1.2689	2.2883
Schwartz4(DTQ)	1.2691	2.3498
Schwartz4(TQ)	1.2690	2.3470
Schwartz6(DTQ)	1.2690	2.3459
Schwartz6(TQ)	1.2690	2.3470
USED	1.2704	2.3427

Both the carbon-carbon bond length and the carbon-sodium bond length have converged to two decimal places by the Q-zeta basis set. The extrapolated geometries vary only 0.001Å from the carbon-carbon bond length we used to calculate the heat of formation, but the sodium-carbon bond length differs by as much as 0.008Å from the bond length that we used to calculate the heat of formation. Even a geometry difference of this size will not affect the enthalpy of formation to any substantial amount. Table 53 lists the CCSD(T) vibrational frequencies for the planar sodium species. Similar to our

investigation of linear Na_2C_2 , we removed the d and f gaussian functions from the sodium CC-PVTZ and AUG-CC-PVTZ basis set for the frequency calculations.

Table 53. Vibrational Frequencies of Planar Na_2C_2		
	Basis sets	
Symmetry	CC-PVTZ	AUG-CC-PVTZ
vibration A (B_{3u})	42 cm^{-1}	48 cm^{-1}
vibration B (B_{2u})	122 cm^{-1}	119 cm^{-1}
vibration C (B_{3g})	297 cm^{-1}	296 cm^{-1}
vibration D (A_g)	276 cm^{-1}	275 cm^{-1}
vibration E (B_{1u})	462 cm^{-1}	460 cm^{-1}
vibration F (A_g)	1790 cm^{-1}	1782 cm^{-1}

The vibrational frequencies listed in Table 53 are not imaginary. This data leads to the conclusion that both the linear and planar configurations are minima on the potential energy surface. Figure 4 is a visual representation for the planar Na_2C_2 vibrational frequencies.

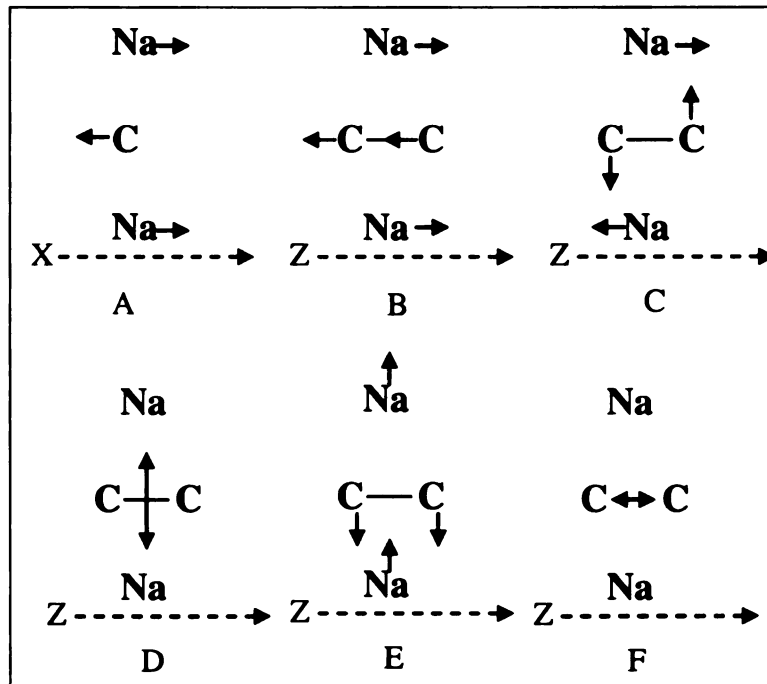


Figure 4: Vibrational Frequencies of Planar Na_2C_2

Using the geometry, $R_{\text{CC}}=1.2704 \text{ \AA}$, $R_{\text{NaC}}=2.3427 \text{ \AA}$, $\angle\text{CCNa}=74.31$ from Table 52 and vibrational frequencies calculated at the CCSD(T) level using the AUG-CC-

PVTZ basis set from Table 53, we calculated dissociation energies at 0 K and heat of formation values at 298 K for the doubly bridged species. Table 54 reports the results.

Table 54. Calculated Dissociation Energies and Heats of Formation for Planar Na₂C₂ as a Function of Basis Set		
Basis Set	D _e kcal/mol	ΔH _f kcal/mol
CC-PVDZ	271.95	123.412
CC-PVTZ	292.44	102.921
CC-PVQZ	299.14	96.226
^a CC-PV(5Z-QZ)	301.03	94.33
^b CC-PV(6Z-QZ)	301.97	93.39
AUG-CC-PVDZ	275.87	119.50
AUG-CC-PVTZ	295.01	100.35
AUG-CC-PVQZ	300.09	95.28
^c AUG-CC-PV(5Z-QZ)	301.71	93.65
^d AUG-CC-PV(6Z-QZ)	302.40	92.96
^a Na CC-PVQZ basis set with C CC-PV5Z basis set		
^b Na CC-PVQZ basis set with C CC-PV6Z basis set		
^c Na AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set		
^d Na AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set		

Table 55 presents extrapolations to the complete basis set limit for the enthalpy of formation using the unaugmented unmixed basis set results.

Table 55. Heats of Formation for Planar Na₂C₂ Extrapolated to the Complete Basis Set Limit		
Basis sets	ΔH _f (∞) (kcal/mol)	ΔH _f (E(∞)) (kcal/mol)
CC-PVXZ		
Feller(DTQ)	92.98	93.39
Schwartzα(DTQ)	89.54	90.49
Schwartz4(DTQ)	94.27	94.27
Schwartz4(TQ)	92.36	92.36
Schwartz6(DTQ)	91.65	91.65
Schwartz6(TQ)	92.38	92.38

The difference between the heat of formation between the linear and planar Na₂C₂ species is approximately 11 kcal/mol.

To correct for the frozen 2s and 2p core on sodium and 1s core on carbon, we calculated core-valence corrections using the Dunning CC-PCVXZ basis sets. Table 56 reports the results of these calculations.

Table 56. Core-Valence Correction for Planar Na₂C₂ as a Function of Basis Set	
Basis Sets	Core-Valence Correction (kcal/mol)
CC-PCVDZ	-1.09
CC-PCVTZ	-0.57
CC-PCVQZ	-0.71
^a CC-PCV(QZ-5Z)	-0.97
^a Na with CC-PCVQZ basis set C with CC-PCV5Z basis set	

Like the linear species, the core-valence correction for planar Na₂C₂ has not converged, but more importantly, the core-valence correction for the planar molecule differs from the linear molecule at the T-zeta basis set. Otherwise, the core-valence correction for both the linear and planar species is approximately the same. Table 57 reports the core-valence correction extrapolated to an infinite basis set.

Table 57. Core-Valence Correction for Planar Na₂C₂ at the Complete Basis Set Limit		
Basis sets	$\Delta CV(\infty)$ (kcal/mol)	$\Delta CV(E(\infty))$ (kcal/mol)
CC-PCVXZ		
Feller(DTQ)	-0.64	----
Schwartz α (DTQ)	-0.64	----
Schwartz4(TQ)	-0.80	-0.80
Schwartz6(TQ)	-0.80	-0.80

Similar to the linear species, the extrapolated values for the variable exponent equations are erratic or non-physical. For the planar molecule, we used the core-valence correction of -0.73 kcal/mol. Table 58 reports the enthalpy of formation for the planar species after we added the core-valence correction (-0.73 kcal/mol), spin-orbit coupling (0.17 kcal/mol), and relativistic corrections (0.21 kcal/mol).

Table 58. ΔH_f Values Corrected for Core-Valance Correlation, Spin-Orbit Coupling, and Relativistic Effects for Planar Na_2C_2 at the Complete Basis Set Limit for each Method		
Basis sets CC-PVXZ	Corrected $\Delta H_f(\infty)$ (kcal/mol)	Corrected $\Delta H_f(E(\infty))$ (kcal/mol)
Feller(DTQ)	92.63	93.04
Schwartz α (DTQ)	89.19	90.14
Schwartz4(TQ)	92.01	92.01
Schwartz6(DTQ)	91.30	91.30
Schwartz6(TQ)	92.03	92.03

The heat of formation results reported in Table 58 span a range of 5 kcal/mol.

Table 59 reports the better values from Table 58 and the combination of the heat of formation calculated with the AUG-CC-PV(QZ-6Z) basis set and the core-valence correction calculated using the CC-PCV(QZ-6Z) basis set.

Table 59. Comparison of Heats of Formation of Planar Na_2C_2	
Basis Set	ΔH_f kcal/mol
^a This work	92.63
^b This work	89.19
^c This work	92.01
^d This work	92.03
^e Unextrapolated value	92.37
^a Feller(DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^b Schwartz α (DTQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^c Schwartz4(TQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^d Schwartz6(TQ) extrapolation of unaugmented basis set values with $P(\infty)$ method	
^e ΔH_f from AUG-CC-PV(QZ-6Z) using ΔCV from CC-PCV(QZ-5Z) basis set	

Table 60 lists the difference in the enthalpy of formation between the linear and planar Na_2C_2 species.

Table 60. Energy Difference Between Linear and Planar Na_2C_2			
Basis Set	Planar Li_2C_2 ΔH_f	Linear Li_2C_2 ΔH_f	Difference kcal/mol
^a Feller(DTQ)	92.63	104.74	12.11
^a Schwartz α (DTQ)	89.19	100.44	11.25
^a Schwartz4(TQ)	92.01	104.43	12.42
^a Schwartz6(TQ)	92.03	104.45	12.42
^b Unextrapolated value	92.37	104.82	12.45
^a Extrapolations of CC-PVXZ basis set values using $P(\infty)$ method			
^b ΔH_f from AUG-CC-PV(QZ-6Z) using ΔCV from CC-PCV(QZ-5Z) basis set			

Similar to the lithium molecules, the energy difference between the heats of formation for the linear and planar sodium species is a kcal/mol larger than the differences between the D_e values where there is no correction for thermal effects.

2.9 Discussion

The heats of atomization at zero Kelvin (0 K) for ClCCCl, FCCF, and HCCH are very similar values. The dissociation energy difference between HCCH and ClCCCl is approximately 60 kcal/mol, whereas the difference between the enthalpies of formation is closer to 4 kcal/mol. The difference between the FCCF and ClCCCl dissociation energies is approximately 35 kcal/mol, but the difference between the enthalpies of formation are around 40 kcal/mol. This behavior is primarily due to differences in the enthalpy of formation of the constituent atoms and the size of the zero point energy.

Table 61. Dissociation Energies and Heats of Atomization for All Molecules							
	HCCH	FCCF	CICCCI	Linear Li ₂ C ₂	Planar Li ₂ C ₂	Linear Na ₂ C ₂	Planar Na ₂ C ₂
D _e (kcal/mol)	408 ^a	388 ^b	355 ^c	335 ^d	342 ^d	300 ^c	310 ^c
D _o (kcal/mol)	392 ^a	379 ^b	348 ^c	331 ^d	337 ^d	296 ^c	305 ^c
ΔH _{atm} (kcal/mol)	393 ^a	380 ^b	348 ^c	330 ^d	338 ^d	296 ^c	306 ^c
^a Schwartzα(Q56) extrapolation of augmented basis set values with P(∞) method ^b Schwartzα(TQ5) extrapolation of doubly augmented basis set values with P(∞) method ^c Schwartzα(TQ5) extrapolation of doubly augmented basis set values with P(∞) method ^d Schwartzα(DTQ) extrapolation of unaugmented basis set values with P(∞) method ^e Schwartzα(DTQ) extrapolation of unaugmented basis set values with P(∞) method							

All the substituted acetylenes and acetylene itself have dissociation energies of the same magnitude and very different heats of formation. This behavior is primarily due to the contributions from the vibrational frequencies of the molecule discussed and the heats of formation of its constituent atoms. The core-valence corrections for all the molecules, except the sodium molecule, are comparable.

2.10 References

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Chapter 3

Quadrupole Moments of HCCH, FCCF, ClCCCl, Li_2C_2 , and Na_2C_2

3.1 Introduction

An important facet of intermolecular interactions and key in understanding intermolecular interactions is the permanent electronic moment of a molecule. For the HCCH, FCCF, ClCCCl, Li₂C₂, and Na₂C₂ molecules, the first permanent non-vanishing electric moment is the quadrupole moment, and since quadrupole moments have been shown to play an important role in chemistry^{1,2,3,4,5,6,7}, the quadrupole moments of these molecules influences the interactions of these molecules with others. Although quadrupole moments of molecules are difficult to determine experimentally, they are very simple to calculate. Unfortunately, the composition of and chemical implications of quadrupole moments and the basis set and electron correlation dependence of quadrupole moment calculations are still under investigation.

From the work of Lawson and Harrison⁸, it was shown for the P₂(¹Σ_g⁺) molecule, the quadrupole moment was heavily influenced by the level of correlation in the calculation. Using a T-AUG-CC-PV5Z basis set, the quadrupole moment at the MRCI level was 0.4759 *ea*₀², whereas the RHF result reported a value of 1.055 *ea*₀². It was later shown that this large difference was due to the insufficient description of π bonding in the P₂ molecule within the SCF calculation. The Lawson prediction of the quadrupole moment of the Cl₂ (¹Σ_g⁺) molecule showed the differences between the SCF (2.2846 *ea*₀²) and MRCI (2.2998 *ea*₀²) calculated values were minute which is due to the lack of π bonding in Cl₂.

From the same work, the size of the basis set used in calculations greatly influenced the magnitude and sometimes the sign of the calculated quadrupole moments.

For all the addressed molecules, the convergence of the quadrupole moments with unaugmented basis sets was considerably slower than that of the augmented basis sets. For $P_2(^1\Sigma_g^+)$ the difference between the MRCI quadrupole moment calculated at the CC-PVDZ and CC-PV5Z basis set was 0.6822 ea_0^2 , whereas the difference between the AUG-CC-PVDZ and AUG-CC-PV5Z quadrupole moments was only 0.1888 atomic units. The difference between the AUG-CC-PV5Z and CC-PV5Z quadrupole moments was 0.0978 atomic units. From this data, it was determined that the addition of diffuse s, p, and d functions upon augmentation not only allowed the quadrupole to converge faster, but the augmentation of the basis sets was necessary for a proper description of the quadrupole moment of diatomics.

In this manuscript we studied seven molecules. Two of those molecules have two different geometry types, a linear and a doubly bridged geometry. For the linear molecules—acetylene, the doubly halogenated acetylenes, and the linear doubly alkalized acetylides—there is only one unique quadrupole making the description of the quadrupole simple, but during our investigation of the quadrupole moments of the doubly alkalized acetylides, the existence of a second geometric minimum on the potential energy surface was reaffirmed. The second geometry, a doubly bridged geometry, has two unique quadrupole moments, making the interpretation slightly more complicated.

Therefore, we hope that further investigation of the quadrupole moments of these alkalized acetylides, as well as the doubly halogenated acetylenes, will provide additional enlightenment about the relationship between the magnitude and the sign of the quadrupole moment, as well as the molecule's electronic structure. The intention of this discussion is to investigate the basis set dependence of the quadrupole moments for the

aforementioned molecules and the influence of different correlation methods on the calculated results.

Although there has been at least one theoretical study on the FCCF and ClCCCl quadrupole moments, experimental quadrupole moments of the doubly halogenated acetylenes have yet to be determined due to the high reactivity of these molecules. The metal acetylides have neither experimental nor calculated quadrupole moment results with which to compare our results. Therefore, similar to Chapter 2, because of the limited information for the Li_2C_2 , Na_2C_2 , FCCF, and ClCCCl quadrupole moments, we calculated the quadrupole moment of a heavily studied molecule, HCCH, as a gauge for the accuracy of the calculated quadrupole moments in this manuscript.

3.1.1 Computational Details

Using Molpro2000, we determined all CCSD(T), DFT(B3LYP) and SCF single point and geometry optimization calculations. We used the Dunning CC-PVXZ, AUG-CC-PVXZ, and D-AUG-CC-PVXZ basis sets, as well as AUG-CC-PVXZ basis sets constructed on site from Dunning CC-PVXZ basis sets in our calculations. We used a field gradient of 0.0001 atomic unit to make field gradient calculations. We determined quadrupole densities using locally written codes.

We used the Z-axis as the internuclear axis for the linear molecules. For the linear molecules, the quadrupole moment defined is the traceless quadrupole moment so that $\Theta_{xx} = \Theta_{yy} = \frac{1}{2}\Theta_{zz}$, and by convention the Θ_{zz} component is taken as the quadrupole moment.

For the nonlinear molecules, the metal atoms lie on the Z-axis while the carbon atoms lie on the Y-axis. The quadrupole moment of the planar molecules is traceless so

that $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$, but since $\Theta_{yy} \neq \Theta_{xx}$, both of the two quadrupole moment components, Θ_{zz} and Θ_{yy} , are needed for a full description of the molecular quadrupole moment.

3.1.2 Multipole Expansion

The definition of the quadrupole moment stems from an expansion of the electrostatic potential. Figure 1 illustrates a charged particle Q located at a distance $\vec{\epsilon}$ from the origin with a potential at a point P equal to the magnitude of Q divided by the distance between Q and the point P. Equation (1) gives the mathematical representation of the relationship.

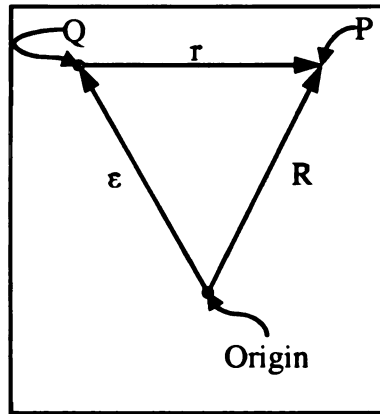


Figure 1: Diagram of Point Charge not located at Origin

$$\Phi(\vec{R}) = \frac{Q}{|\vec{r}|} = \frac{Q}{|\vec{R} - \vec{\epsilon}|} \quad (1)$$

Expanding the potential around $\vec{\epsilon} = 0$ results in the expression in equation (2),

$$\Phi(\vec{R}) = \frac{Q}{R} - Q\epsilon_{\alpha} \left(\nabla_{\alpha} \frac{1}{R} \right) + \frac{1}{3} Q \left(\frac{1}{2} (3\epsilon_{\alpha}\epsilon_{\beta} - \delta_{\alpha\beta}\epsilon^2) \right) \left(\nabla_{\alpha} \nabla_{\beta} \frac{1}{R} \right) + \dots \quad (2)$$

where $\nabla_{\alpha} = \frac{1}{\partial R_{\alpha}}$ and the Greek indices are summed over the three Cartesian vectors.

Equations 3 and 4 define the $\alpha\beta$ component of the quadrupole moment, $\Theta_{\alpha\beta}$, and the α component of the dipole moment, μ_{α} .

$$\Theta_{\alpha\beta} = Q \left(\frac{1}{2} (3\varepsilon_{\alpha}\varepsilon_{\beta} - \delta_{\alpha\beta}\varepsilon^2) \right). \quad (3)$$

$$\mu_{\alpha} = Q\varepsilon_{\alpha} \quad (4)$$

Even though these purely mathematical definitions of the electronic moments do not provide much chemical insight into the concept of multipoles, a discussion of the most commonly recognized electronic moment, the dipole moment, customarily involves an argument about differences in electronegativity between the two atoms of a diatomic molecule. Therefore, the dipole is perceived as the difference between the charge distribution of a molecule and the charge distribution of the atoms. This interpretation is very different from the process used to calculate the molecular dipole moment, which involves the summing of the electronic and nuclear contributions to the overall dipole moment as shown in equation (5) where $n(\vec{r})$ is the electron density and Z_k is the atomic number of the Kth nucleus.

$$\mu_{\alpha} = - \int n(\vec{r}) r_{\alpha} dV + \sum_{K=1}^{NUC} Z_k R_{K\alpha}. \quad (5)$$

If the atoms of the molecule are separated by a large distance, so that the atoms are not interacting, the dipole moment is zero. Rearrangement of the expression for the dipole results in equation (6) .

$$\int n_{\text{atoms}}(\vec{r}) r_{\alpha} dV = \sum_{K=1}^{NUC} Z_k R_{K\alpha}. \quad (6)$$

Since this expression holds at all distances, equation (5) can be rearranged into equation (7).

$$\mu_{\alpha} = - \int n(\vec{r}) r_{\alpha} dV + \int n_{\text{atoms}}(\vec{r}) r_{\alpha} dV, \text{ or } \mu_{\alpha}^{\text{cr}} = - \int \delta n(\vec{r}) r_{\alpha} dV . \quad (7)$$

Now the dipole is represented as an integral involving the charge redistribution occurring at molecular formation.

$$\mu_{\alpha} = \mu_{\alpha}^{\text{cr}} \quad (8)$$

Using this same rationale, an expression for the quadrupole moment as a function of the charge redistribution upon molecular formation results in equation (9),

$$\Theta_{\alpha\beta} = \Theta_{\alpha\beta}^{\text{atoms}} + \Theta_{\alpha\beta}^{\text{cr}} . \quad (9)$$

where the components of the quadrupole moment of a molecule are represented by equation (10).

$$\begin{aligned} \Theta_{\alpha\beta}^{\text{atoms}} &= \sum_{K=1}^{\text{atoms}} \Theta_{\alpha\beta}^{(K)} \\ \Theta_{\alpha\beta}^{\text{cr}} &= -\frac{1}{2} \int \delta n(\vec{r}) (3r_{\alpha} r_{\beta} - \delta_{\alpha\beta} r^2) dV. \end{aligned} \quad (10)$$

In the molecular dipole moment the dipole due to the atoms is zero, atoms can have quadrupole moments, so it is important to consider this influence.

3.1.3 Method

There are two independent theoretical methods to determine the quadrupole moment. The first method is to determine the expectation value of the quadrupole moment or the average value of the property by evaluating equation (11) where the quadrupole moment operator is defined by equation (12).

$$\langle \Psi | \hat{\Theta}_{\alpha\beta} | \Psi \rangle = \Theta_{\alpha\beta} . \quad (11)$$

$$\hat{\Theta}_{\alpha\beta} = \frac{1}{2} \sum_{i=1}^N 3\hat{r}_{\alpha i} \hat{r}_{\beta i} - \hat{r}_i^2 + \frac{1}{2} \sum_{K=1}^{N_K} 3\hat{r}_{\alpha K} \hat{r}_{\beta K} - \hat{r}_K^2. \quad (12)$$

Although the expectation value of the quadrupole moment is the most accurate method, at the time of these calculations, there was no software to allow this type of calculation to be done at the CCSD(T) level. Instead we calculated the CCSD(T) quadrupole moments using a finite field calculation. If the energy of a system is expanded as a function of the field gradient, the expression for the energy takes the form of equation (13).

$$\begin{aligned} E(F') = E_0 &+ \frac{\partial E}{\partial F'_{\alpha\beta}} F'_{\alpha\beta} + \frac{1}{2} \frac{\partial^2 E}{\partial F'_{\alpha\beta} \partial F'_{\gamma\delta}} F'_{\alpha\beta} F'_{\gamma\delta} \\ &+ \frac{1}{3!} \frac{\partial^3 E}{\partial F'_{\alpha\beta} \partial F'_{\gamma\delta} \partial F'_{\epsilon\phi}} F'_{\alpha\beta} F'_{\gamma\delta} F'_{\epsilon\phi} + \dots \end{aligned} \quad (13)$$

The derivatives of the energy with respect to the field gradient are assigned physical interpretations. Equation (14) reflects the quadrupole moment as the leading term in the expansion of the energy as a function of the field gradient. Equation (14) includes a few of the trailing terms. We interpret these trailing terms as the change in the quadrupole as a function of the field gradient.

$$\begin{aligned} \frac{\partial E}{\partial F'_{\alpha\beta}} &= -\frac{1}{3} \Theta_{\alpha\beta} \\ \frac{\partial^2 E}{\partial F'_{\alpha\beta} \partial F'_{\gamma\delta}} &= -\frac{1}{3} \frac{\partial \Theta_{\alpha\beta}}{\partial F'_{\gamma\delta}} = -\frac{1}{3} C_{\alpha\beta;\gamma\delta} \\ \frac{\partial^3 E}{\partial F'_{\alpha\beta} \partial F'_{\gamma\delta} \partial F'_{\epsilon\phi}} &= -\frac{1}{3} \frac{\partial \Theta_{\alpha\beta}}{\partial F'_{\gamma\delta} \partial F'_{\epsilon\phi}} = -\frac{1}{3} G_{\alpha\beta;\gamma\delta;\epsilon\phi} \end{aligned} \quad (14)$$

If we substitute the results of equation (14) into equation (13) (which is the energy of a molecule as a function of the field gradient), the quadrupole moment and other terms take the form of equation (15).

$$E(F') = E_0 - \frac{1}{3} \Theta_{\alpha\beta} F'_{\alpha\beta} - \frac{1}{6} C_{\alpha\beta;\gamma\delta} F'_{\alpha\beta} F'_{\gamma\delta} - \frac{1}{18} G_{\alpha\beta;\gamma\delta;\epsilon\varphi} F'_{\alpha\beta} F'_{\gamma\delta} F'_{\epsilon\varphi} - \dots \quad (15)$$

If we calculate the energy of a molecule with a positive and negative field gradient, the difference between the two energies takes the form of equation (16).

$$\begin{aligned} E(-F') &= E_0 + \frac{1}{3} \Theta_{\alpha\beta} F'_{\alpha\beta} - \frac{1}{6} C_{\alpha\beta;\gamma\delta} F'_{\alpha\beta} F'_{\gamma\delta} + \frac{1}{18} G_{\alpha\beta;\gamma\delta;\epsilon\varphi} F'_{\alpha\beta} F'_{\gamma\delta} F'_{\epsilon\varphi} \\ -E(F') &= E_0 + \frac{1}{3} \Theta_{\alpha\beta} F'_{\alpha\beta} + \frac{1}{6} C_{\alpha\beta;\gamma\delta} F'_{\alpha\beta} F'_{\gamma\delta} + \frac{1}{18} G_{\alpha\beta;\gamma\delta;\epsilon\varphi} F'_{\alpha\beta} F'_{\gamma\delta} F'_{\epsilon\varphi} \\ \hline E(F') - E(-F') &= \frac{2}{3} \Theta_{\alpha\beta} F'_{\alpha\beta} + \frac{1}{9} G_{\alpha\beta;\gamma\delta;\epsilon\varphi} F'_{\alpha\beta} F'_{\gamma\delta} F'_{\epsilon\varphi}. \end{aligned} \quad (16)$$

Examination of equation (16): By choosing a field gradient small enough to cause the contributions of the trailing terms to be minute, the quadrupole moment is isolated. A comparison of the results of both the expectation value of the quadrupole moment and the finite field quadrupole moment shows that not only is there an ability to select a gradient small enough to minimize the contribution of the higher order terms, but there is also a quick check of both methods.

3.2 HCCH

We calculated the CCSD(T), DFT(B3LYP), and SCF quadrupole moments for the nonvibrating HCCH molecule at the Strey and Mills⁹ experimental geometry, $R_{CC} = 1.2033 \text{ \AA}$ and $R_{CH} = 1.0605 \text{ \AA}$. Table 1 lists each result as a function of basis set.

Table 1. Quadrupole Moment, Θ (ea_0^2), of HCCH					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	5.2112	5.2112	4.5078	4.6171	4.6172
CC-PVTZ	5.4186	5.4187	4.8010	4.9014	4.9014
CC-PVQZ	5.4345	5.4345	4.8428	4.8981	4.8981
CC-PV5Z	5.4444	5.4444	4.8608	4.9090	4.9092
CC-PV6Z	5.4442	5.4442	4.8652	4.9079	4.9115
AUG-CC-PVDZ	5.4689	5.4689	4.7721	4.8739	4.8739
AUG-CC-PVTZ	5.4577	5.4577	4.8451	4.9173	4.9171
AUG-CC-PVQZ	5.4456	5.4455	4.8570	4.8722	4.8723
AUG-CC-PV5Z	5.4445	5.4445	4.8634	4.9078	4.9068
AUG-CC-PV6Z	5.4435	5.4435	4.8661	4.8903	4.8901
D-AUG-CC-PVDZ	5.4557	5.4557	4.7584	4.8650	4.8643
D-AUG-CC-PVTZ	5.4456	5.4456	4.8333	4.8934	4.8940
D-AUG-CC-PVQZ	5.4441	5.4441	4.8359	4.8907	4.8896

Table 1 compares the two computational methods that we used to calculate the SCF and DFT quadrupole moments. The results of the two methods should be equal, but the difference between the results for the SCF quadrupole moments at each basis set is slight and only affects the quadrupole moment at the fourth decimal place. We found that the difference between some SCF quadrupole moments was zero. The DFT results differ between the two methods at the third decimal place.

The SCF quadrupole moment converges to two decimal places by the 5Z basis set and is unaffected by augmentation by the QZ basis set. By the 5Z basis set the CCSD(T) quadrupole moment has converged to two decimal places. The two correlated methods converge and agree to one decimal place, while the DFT(B3LYP) method converges to a larger value than that of the CCSD(T) method. The difference between the correlated and uncorrelated quadrupole moment is less than $1 \text{ } ea_0^2$. Table 2 is a tabulation of experimental and calculated values for the quadrupole of HCCH.

Table 2. HCCH Quadrupole Moments		
$\Theta(ea_0^2)$	Method	Reference
5.366	SCF	10
5.443	SCF	11
5.460	SCF	12
5.426	SCF	13
5.05, 5.24	SCF	14
5.444	SCF	This work
4.703	BLYP	11
4.890	DFT(B3LYP)	This work
4.925	CC	13
4.88	MP4	15
4.787, 4.795, 4.806	MP4, QCISD, BD(T)	11
4.717	MRCI	16
4.866	CCSD(T)	This work
4.71 $\pm$ 0.14	Field gradient-induced birefringence	17
5.65 $\pm$ 0.07	Cotton-Mouton effect	18
4.03 $\pm$ 0.30	Collision-induced far-infrared absorption	19

The range in experimental values for the quadrupole moment of HCCH is as wide as the range in theoretical values. Although the SCF calculated results of other researchers are comparable to the SCF quadrupole moment calculated in this work, the correlated quadrupole moments vary within methods and even between methods. The correlated quadrupole moments differ from the experimental values, but these values are not corrected for molecular vibrations. By correcting the CCSD(T) quadrupole moment for vibrational contributions²⁰, the CCSD(T) quadrupole moment falls within experimental error of the field gradient-induced birefringence quadrupole¹⁷.

3.3 FCCF

We examine FCCF as one of two doubly halogenated acetylenes in this chapter. The doubly halogenated acetylenes are very reactive, making the calculation of the quadrupole moment possibly the only route available for determining the quadrupole. We used the equilibrium geometry provided by Briedung et al²¹, $R_{CC} = 1.186 \text{ \AA}$ and

$R_{CF}=1.2835 \text{ \AA}$, to calculate the SCF, CCSD(T), and DFT(B3LYP) quadrupole moments as a function of basis set. Table 3 reports the results.

Table 3. Quadrupole Moment, Θ (ea_0^2), of FCCF					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	-0.9726	-0.9726	-0.4090	-0.0534	-0.0534
CC-PVTZ	-0.8457	-0.8457	-0.4569	-0.2783	-0.2783
CC-PVQZ	-0.8986	-0.8986	-0.5825	-0.4419	-0.4419
CC-PV5Z	-0.9225	-0.9225	-0.6343	-0.5104	-0.5108
AUG-CC-PVDZ	-1.0335	-1.0335	-0.7860	-0.6003	-0.6004
AUG-CC-PVTZ	-0.9430	-0.9429	-0.6485	-0.5404	-0.5391
AUG-CC-PVQZ	-0.9130	-0.9130	-0.6357	-0.5163	-0.5180
AUG-CC-PV5Z	-0.9168	-0.9168	-0.6400	-0.5218	-0.5245
D-AUG-CC-PVDZ	-0.8547	-0.8547	-0.6367	-0.5128	-0.5126
D-AUG-CC-PVTZ	-0.9067	-0.9067	-0.6156	-0.5060	-0.5069
D-AUG-CC-PVQZ	-0.9119	-0.9119	-0.6331	-0.5141	-0.5152
D-AUG-CC-PV5Z	-0.9157	-0.9157	-0.6389	-0.5182	-0.5193

Interestingly, the substitution of fluoride for hydrogen in acetylene causes a change in the sign of the quadrupole moment and lowers the magnitude greatly. We discuss this result later. The change in sign is attributed to the size of the fluorine atom quadrupole moment and the electronegativity of the fluoride atom.

The quadrupole expectation value for the SCF reproduces an equivalent to the quadrupole that the field gradient method produces, as expected. Again, there is some discrepancy in the DFT values, but in general they are consistent to the second decimal place. Table 3 shows that the convergence is slow for all three methods. All the calculated quadrupoles are dependent on the level of augmentation of the basis set, especially the DFT(B3LYP) quadrupoles. The SCF quadrupoles have only converged to one decimal place by the augmented 5Z basis set, whereas the correlated methods have converged to two decimal places by the augmented QZ basis set. The two correlated

quadrupoles are within 0.1 atomic unit of each other, and the uncorrelated quadrupole is within 0.4 atomic units of the two correlated methods. Table 4 lists the results of this work with other calculated results for the quadrupole of FCCF.

Table 4. FCCF Quadrupole Moments		
$\Theta(ea_0^2)$	Method	Reference
-0.9085	SCF	22
-0.9157	SCF	This work
-0.6524	MP2	22
-0.5193	DFT(B3LYP)	This work
-0.6389	CCSD(T)	This work

The results of this work and the results of Maroulis are equivalent to one decimal place for the SCF quadrupole and are within 0.1 atomic unit of each other for the correlated calculations. The FCCF calculated quadrupole moments were not corrected for vibration.

3.4 ClCCCl

We calculated SCF, CCSD(T), and DFT(B3LYP) quadrupoles for the second doubly halogenated acetylene, ClCCCl, at the experimental geometry, $R_{CC}=1.205 \text{ \AA}$ and $R_{ClC}=1.635 \text{ \AA}$, as a function of the Dunning basis sets. Table 5 lists these results.

Table 5. Quadrupole Moment, Θ (ea_0^2), of ClCCCCl					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	3.9317	3.9316	3.7337	4.1042	4.1037
CC-PVTZ	3.9343	3.9342	3.8524	3.9956	3.9960
CC-PVQZ	3.9253	3.9252	3.7892	3.9157	3.9167
CC-PV5Z	3.9353	3.9352	3.8054	3.8977	3.8949
AUG-CC-PVDZ	4.0586	4.0586	3.7755	3.8246	3.8236
AUG-CC-PVTZ	3.8568	3.8568	3.7970	3.7688	3.7674
AUG-CC-PVQZ	3.8783	3.8782	3.7595	3.7787	3.7787
AUG-CC-PV5Z	3.8988	3.8987	3.7672	3.7909	3.7905
D-AUG-CC-PVDZ	3.9381	3.9379	3.6686	3.7565	3.7563
D-AUG-CC-PVTZ	3.8219	3.8217	3.7492	3.7387	3.7384
D-AUG-CC-PVQZ	3.8685	3.8684	3.7478	3.7712	3.7674
D-AUG-CC-PV5Z	3.9006	3.9005	3.7683	3.7918	3.7952

Remarkably, the quadrupole moment of the chlorinated acetylene has the same sign and close to the same magnitude as that of HCCH. This similarity comes as a surprise when compared to the quadrupole of FCCF. Therefore, the negative quadrupole of FCCF is not solely due to electronegativity. The differences in quadrupoles calculated by expectation value and field gradient are slight. We detected most differences in the fourth decimal place within the SCF calculations. Again, the DFT results are not equivalent, but still comparable.

The results for all calculations are slow to converge beyond the second decimal place, but they are comparably close in magnitude. All the quadrupoles have converged to one decimal place by the QZ basis set. The SCF is converging to a higher value than the correlated methods, and the difference between the correlated methods is less than 0.04 atomic units. The relative difference between the DFT and CCSD(T) results may be an indication of the level of covalent bonding in the ClCCCCl molecule. Table 6 lists other calculated results for the quadrupole moment of ClCCCCl.

Table 6. ClCCCl Quadrupole Moments		
$\Theta(ea_0^2)$	Method	Reference
3.9140	SCF	22
3.9006	SCF	This work
3.6612	MP2	22
3.7952	DFT(B3LYP)	This work
3.7683	CCSD(T)	This work

The SCF results of this work are equivalent to one decimal place with the SCF result provided by Maroulis, and the correlated results are within $0.2\text{ }ea_0^2$ of the result provided by Maroulis. Again, the quadrupole moment of ClCCCl was not corrected for vibration.

3.5 Li₂C₂

Since there is no experimental geometric information provided for dilithium acetylide in the literature, we calculated an equilibrium geometry. In Chapter 2, we explain the process used to calculate the equilibrium geometries and reaffirm that the metal acetylides have two equilibrium geometries. First, the linear molecule geometry of $R_{CC} = 1.2531\text{ \AA}$, $R_{CLi} = 1.8943\text{ \AA}$, and the doubly bridged molecule geometry of $R_{CC} = 1.2673\text{ \AA}$, $R_{CLi} = 2.0086\text{ \AA}$, and $\angle CCLi = 71.6^\circ$, seem to locate the lithium atoms very far from the carbon atoms, so that the atoms seem to be hanging off a C₂ species.

3.5.1 Molecular Quadrupole Moment

Each geometry has its own quadrupole moment. The linear molecule, like the other linear species discussed in this paper, has one unique component to the quadrupole moment, which lies along the internuclear line, while the doubly bridged or planar molecule has two unique quadrupole moment components, one parallel to the carbon atoms and one parallel to the Li atoms.

3.5.2 Linear

We used the geometry, $R_{CC} = 1.531 \text{ \AA}$, $R_{CLi} = 1.8943 \text{ \AA}$, to calculate the quadrupole moment of linear dilithium acetylide. Table 7 lists the results.

Table 7. Quadrupole Moment, Θ (ea_0^2), of Linear Li_2C_2					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	35.9211	35.9209	34.7707	34.2305	34.2295
CC-PVTZ	36.1191	36.1189	35.1960	34.5417	34.5412
CC-PVQZ	36.3687	36.3685	35.4927	34.7938	34.7934
^a CC-(5Z-QZ)	36.4222	36.4221	35.5717	34.8403	34.8388
^b CC-(6Z-QZ)	36.4878	36.4877	35.6443	34.8973	34.8978
AUG-CC-PVDZ	36.6568	36.6566	35.7495	35.0863	35.0855
AUG-CC-PVTZ	36.5193	36.5191	35.6585	34.9204	34.9184
AUG-CC-PVQZ	36.5094	36.5093	35.6662	34.9233	34.9228
^c AUG-CC-(5Z-QZ)	36.5083	36.5082	35.6749	34.9248	34.9241
^d AUG-CC-(6Z-QZ)	36.5078	36.5077	35.6787	--	--
^a Li CC-PVQZ basis set with C CC-PV5Z basis set					
^b Li CC-PVQZ basis set with C CC-PV6Z basis set					
^c Li AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set					
^d Li AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set					

One of the most interesting aspects of the Li_2C_2 quadrupole moment is the magnitude. The magnitude of linear Li_2C_2 is nearly 10 times the magnitude of the ClCCCl quadrupole moment. The quadrupole is so large that the differences in the quadrupole moment between the unaugmented and augmented basis sets is minute. The differences are only 2% of the total value at the DZ basis set and 0.05% at the largest basis set. Again, the difference between the expectation value and field gradient methods is minute for the SCF quadrupoles; however, the DFT results show the field gradient has some strong influence beyond the first decimal place. Also note that the CCSD(T) results are sandwiched between the DFT and SCF results as the SCF results are converging to

the higher value. The difference between the DFT and SCF results is less than 2 atomic units which is around 6% of the total quadrupole moment.

3.5.3 Planar

Since there are two unique quadrupole moment components for the planar quadrupole, a unique property of doubly bridged molecules with D_{2h} symmetry, we calculate the ZZ and YY components. By calculating two components, the third is known since the quadrupole moment is traceless. For these calculations, keep in mind that the carbon atoms lie on the Y axis and that the Li atoms lie on the Z axis. We used the geometry provided in Chapter 2, $R_{CC} = 1.2673\text{\AA}$, $R_{CLi} = 2.0086\text{\AA}$, and $\angle CCLi = 71.6^\circ$, to calculate the SCF, CCSD(T), and DFT Θ_{zz} for planar dilithium acetylide. Table 8 reports the results as a function of basis set.

Table 8. Quadrupole Moment, Θ_{zz} (ea_0^2), of Planar Li_2C_2					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	26.4236	26.4235	25.8323	25.3724	25.3720
CC-PVTZ	26.2621	26.2619	25.8399	25.2043	25.2023
CC-PVQZ	26.2875	26.2874	25.9046	25.2641	25.2632
^a CC-(5Z-QZ)	26.3001	26.2999	25.9366	25.2872	25.2871
^b CC-(6Z-QZ)	26.3076	26.3074	25.9538	25.3017	25.2999
AUG-CC-PVDZ	26.4269	26.4267	26.0478	25.4179	25.4198
AUG-CC-PVTZ	26.3124	26.3123	25.9502	25.2977	25.2967
AUG-CC-PVQZ	26.3115	26.3114	25.9538	25.3068	25.3067
^c AUG-CC-(5Z-QZ)	26.3094	26.3092	25.9564	25.3070	25.3054
^d AUG-CC-(6Z-QZ)	26.3089	26.3088	25.9578	25.3064	25.3051
^a Li CC-PVQZ basis set with C CC-PV5Z basis set					
^b Li CC-PVQZ basis set with C CC-PV6Z basis set					
^c Li AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set					
^d Li AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set					

Note the magnitude and sign of the quadrupole component. Like the linear species it is large, but it is not as positive. We compared the unaugmented and

augmented quadrupoles and found no need for augmentation in order to calculate the quadrupole component to three significant figures. The unaugmented and augmented suites of basis sets are equivalent to the units place when rounded. The differences between the two calculation methods are consistent with previous results in this study. Also note, the SCF and CCSD(T) quadrupole moments are close in magnitude while the DFT result is a slight outlier.

We used the same geometry to calculate the SCF, CCSD(T), and DFT results for the YY component of the planar molecule's quadrupole moment. Table 9 lists the results.

Table 9. Quadrupole Moment, Θ_{yy} (ea_0^2), of Planar Li_2C_2					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{yy} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{yy} \rangle$	Field Gradient
CC-PVDZ	-16.0693	-16.0693	-15.8702	-15.4046	-15.4047
CC-PVTZ	-16.1829	-16.1829	-16.1661	-15.6996	-15.6995
CC-PVQZ	-16.2317	-16.2317	-16.2694	-15.8119	-15.8110
^a CC-(5Z-QZ)	-16.2663	-16.2663	-16.3300	-15.8685	-15.8674
^b CC-(6Z-QZ)	-16.2831	-16.2831	-16.3687	-15.9055	-15.9046
AUG-CC-PVDZ	-16.1994	-16.1995	-16.3309	-15.8374	-15.8384
AUG-CC-PVTZ	-16.2843	-16.2843	-16.3798	-15.9184	-15.9165
AUG-CC-PVQZ	-16.2761	-16.2761	-16.3706	-15.9114	-15.9088
^c AUG-CC-(5Z-QZ)	-16.2739	-16.2739	-16.3697	-15.9099	-15.9107
^d AUG-CC-(6Z-QZ)	-16.2736	-16.2737	-16.3699	-15.9095	-15.9112
^a Li CC-PVQZ basis set with C CC-PV5Z basis set					
^b Li CC-PVQZ basis set with C CC-PV6Z basis set					
^c Li AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set					
^d Li AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set					

Again, due to the magnitude of the quadrupole, we determined little need for the augmentation of the basis set. The two methods are consistent with the remainder of the study. The SCF behaves well, while the DFT results differ in the second decimal place. The YY component quadrupoles are nearly equivalent. The CCSD(T) and SCF YY component are closer to each other than they are to the DFT result.

3.6 Na₂C₂

Similar to Li₂C₂, there are two viable minima on the potential surface. The linear geometry is $R_{CC} = 1.2549\text{\AA}$, $R_{CNa} = 2.2341\text{\AA}$, and the planar geometry is $R_{CC} = 1.2704\text{\AA}$, $R_{CNa} = 2.3427\text{\AA}$, $\angle CCNa = 74.3^\circ$. Again, the large separations between the Na atoms and carbon atoms seem to describe two sodium ions attached to a C₂ molecule.

3.6.1 Linear

Table 10 lists SCF, DFT, CCSD(T) quadrupole calculations at the aforementioned linear geometry as a function of the Dunning basis sets.

Table 10. Quadrupole Moment, Θ (ea_0^2), of Linear Na₂C₂					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	47.5156	47.5143	44.4711	42.4321	42.4258
CC-PVTZ	48.4753	48.4741	46.0046	43.2959	43.2893
CC-PVQZ	48.6964	48.6953	46.4453	43.5136	43.5060
^a CC-(5Z-QZ)	48.6933	48.6922	46.5153	43.5297	43.5241
^b CC-(6Z-QZ)	48.7012	48.7001	46.5590	43.5392	43.5260
AUG-CC-PVDZ	49.0474	49.0462	46.4530	43.8956	43.8890
AUG-CC-PVTZ	48.8505	48.8494	46.5903	43.6743	43.6638
AUG-CC-PVQZ	48.7065	48.7054	46.5634	43.5591	43.5563
^c AUG-CC-(5Z-QZ)	48.6725	48.6714	46.5663	--	--
^d AUG-CC-(6Z-QZ)	48.6368	48.6357	46.5490	--	--
^a Na CC-PVQZ basis set with C CC-PV5Z basis set					
^b Na CC-PVQZ basis set with C CC-PV6Z basis set					
^c Na AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set					
^d Na AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set					

Again, due to the magnitude of the quadrupole moment, the level of augmentation has a small influence. The magnitude of the calculated quadrupole is larger than the magnitude in the Li case. The SCF and CCSD(T) results are not nearly as equivalent as they were in the Li case. The SCF converges to a higher value than the CCSD(T) results, and the DFT quadrupole converges to the lowest value which is the same as in the Li case. The two

computation methods behave differently than previously in this study with the SCF values deviating as much as the DFT values.

3.6.2 Planar

We used the calculated planar geometry for Na_2C_2 , $R_{\text{CC}} = 1.2704\text{\AA}$, $R_{\text{CNa}} = 2.3427\text{\AA}$, $\angle \text{CCNa} = 74.3^\circ$, to calculate SCF, CCSD(T), and DFT quadrupoles at various basis sets for the ZZ component of the quadrupole moment. Table 11 lists the results.

Table 11. Quadrupole Moment, Θ_{zz} (ea_0^2), of Planar Na_2C_2					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{zz} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{zz} \rangle$	Field Gradient
CC-PVDZ	36.3662	36.3655	35.3337	33.4682	33.4645
CC-PVTZ	36.4226	36.4218	35.7632	33.5028	33.4990
CC-PVQZ	36.4039	36.4032	35.8558	33.5168	33.5159
^a CC-(5Z-QZ)	36.3964	36.3957	35.8854	33.5276	33.5265
^b CC-(6Z-QZ)	36.3738	36.3732	35.8846	33.5310	33.5298
AUG-CC-PVDZ	36.7047	36.7040	36.0321	33.8974	33.8914
AUG-CC-PVTZ	36.4725	36.4719	35.9317	33.6177	33.6135
AUG-CC-PVQZ	36.3394	36.3745	35.8768	33.4561	33.4506
^c AUG-CC-(5Z-QZ)	36.3619	36.3612	35.8777	33.5289	33.5323
^d AUG-CC-(6Z-QZ)	36.3448	36.3441	35.8669	33.5225	33.5247
^a Na CC-PVQZ basis set with C CC-PV5Z basis set					
^b Na CC-PVQZ basis set with C CC-PV6Z basis set					
^c Na AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set					
^d Na AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set					

The magnitude of the ZZ component is, again, smaller than that of the linear species, and again the level of augmentation seems unimportant with such a large property. The two computational methods are behaving well while DFT still differs in the second decimal place. The SCF and CCSD(T) results for the ZZ component are close. DFT reports results with the lowest magnitude.

We used the same geometry to calculate the YY component at the SCF, CCSD(T), and DFT levels. Table 12 shows the results.

Table 12. Quadrupole Moment, Θ_{yy} (ea_0^2), of Planar Na_2C_2					
Basis Set	SCF		CCSD(T)	DFT(B3LYP)	
	$\langle \Theta_{yy} \rangle$	Field Gradient	Field Gradient	$\langle \Theta_{yy} \rangle$	Field Gradient
CC-PVDZ	-21.3517	-21.3515	-20.8689	-19.6638	-19.6634
CC-PVTZ	-21.5251	-21.5249	-21.4147	-20.0101	-20.0093
CC-PVQZ	-21.5899	-21.5898	-21.6085	-20.1510	-20.1498
^a CC-(5Z-QZ)	-21.6039	-21.6039	-21.6500	-20.1775	-20.1760
^b CC-(6Z-QZ)	-21.5957	-21.5957	-21.6660	-20.1939	-20.1977
AUG-CC-PVDZ	-21.6850	-21.6851	-21.7050	-20.3114	-20.3091
AUG-CC-PVTZ	-21.6563	-21.6564	-21.7172	-20.2745	-20.2722
AUG-CC-PVQZ	-21.5714	-21.5898	-21.6713	-20.1717	-20.2101
^c AUG-CC-(5Z-QZ)	-21.5844	-21.5844	-21.6729	-20.2068	-20.2082
^d AUG-CC-(6Z-QZ)	-21.5757	-21.5758	-21.6668	-20.2048	-20.2050
^a Na CC-PVQZ basis set with C CC-PV5Z basis set					
^b Na CC-PVQZ basis set with C CC-PV6Z basis set					
^c Na AUG-CC-PVQZ basis set with C AUG-CC-PV5Z basis set					
^d Na AUG-CC-PVQZ basis set with C AUG-CC-PV6Z basis set					

Again, due to the magnitude of the quadrupole moment, there is little need for the augmentation of the basis set. The behavior of the two methods is consistent with the remainder of the study. The SCF behaves well, while the DFT results differ in the second decimal place. Note the quadrupoles are nearly equivalent with the magnitude of the CCSD(T) and SCF YY component closer to each other than to the DFT result. Overall, the YY component to the planar Na molecule quadrupole moment is larger in magnitude than the YY components of the planar Li molecule.

3.7 Partition Quadrupole Moment into Point Charges

We used the algebraic definition of the quadrupole moment to partition the quadrupole moments of the aforementioned molecules into a collection of charges. When conceptualizing the dipole moment, the general argument made is that the dipole consists of two charges that are opposite in sign, but equal in magnitude, and separated by a distance R. The LiF dipole, for example, is discussed as having a positive charge located at Li and a negative charge of equal magnitude located at F. The value of the

dipole is expressed as the magnitude of the charge times the internuclear separation.

Based on the principle that a dipole moment of a molecule is a collection of two charges separated by a distance such that the total system has no charge, the quadrupole moment of a molecule is broken up in much the same manner as four charges arranged such that the system has no dipole. We partitioned the quadrupole moment of each molecule into a collection of four charges, and we used equation (3) to calculate the magnitude of those charges. Equation (3) shows that the quadrupole moment equals the contribution of each charge in the system in the manner described in equation (17).

$$\Theta_{\alpha\beta}^{cr} = \sum_{i=1}^4 q_i \left(\frac{1}{2} \left(3r_{\alpha i} r_{\beta i} - \delta_{\alpha\beta} (x_i^2 + y_i^2 + z_i^2) \right) \right). \quad (17)$$

So, for linear molecules like HCCH, equation (18) describes the Θ_{zz}^{cr} component of the quadrupole moment,

$$\Theta_{zz}^{cr} = 2q_H(R_{CC} + R_{CH})R_{CH}. \quad (18)$$

where, R_{CC} is the carbon-carbon bond length and R_{CH} is the carbon-hydrogen bond length. For the nonlinear molecules like Li_2C_2 , equation (19) describes the Θ_{zz}

component of the quadrupole moment, and equation (20) describes the Θ_{yy} component,

$$\Theta_{zz}^{cr} = q_{Li} \left(2R_{LiC}^2 - \frac{1}{4}R_{CC}^2 \right) \quad (19)$$

where, R_{CC} is the carbon-carbon bond length and R_{LiC} is the carbon-lithium bond length.

$$\Theta_{yy}^{cr} = q_{Li} \left(R_{LiC}^2 + \frac{1}{4}R_{CC}^2 \right) \quad (20)$$

3.8 Discussion

Recall that the molecular quadrupole moment consists of contributions from the atomic quadrupoles and the contribution from charge redistribution upon molecular

formation. To determine the atomic contributions, we calculated the atomic quadrupoles of $C(^3P_0)$, $F(^2P_0)$, and $Cl(^2P_0)$, and we used these calculated atomic quadrupoles to determine the molecular quadrupole due to charge redistribution. Table 13 lists the results from determining the partitioning of each of the charge redistribution quadrupole moments of the titled linear molecules into a collection of point charges.

Table 13. Linear Molecules (XCCX) Partitioned into Point Charges				
	$\Theta_{zz}(ea_0^2)$	$\Theta_{(zz)atoms}^a(ea_0^2)$	$\Theta_{cr}(ea_0^2)$	$q_x(\Theta_{zz})$
HCCH	4.8558	2.8406	2.0152	+0.104
FCCF	-0.6389	4.1976	-3.5587	-0.214
ClCCCl	3.7685	5.8730	-2.1045	-0.063
Linear Li_2C_2	35.6787	2.8406	32.8381	+0.771
Linear Na_2C_2	46.5490	2.8406	43.7084	+0.785
^a Atomic quadrupoles $C(1.4203 ea_0^2)$, $F(0.6785 ea_0^2)$, $Cl(1.5162 ea_0^2)$				

Beginning with HCCH, Table 13 lists the ZZ component to the molecular quadrupole moment that we calculated at the CCSD(T) level with an AUG-PV6Z basis set. By subtracting out the contribution due to the atomic quadrupoles, the remaining portion of the quadrupole moment is due to the redistribution of charge on the formation of the molecule. Partitioning that quantity into algebraic charges shows the terminal hydrogen atoms to be slightly positive. Positive hydrogen atoms are consistent with the basic understanding of molecular bond formation. Electron density moves from occupying, in this case, four individual atoms to surrounding one molecule in which some of the electron density occupies the newly created bonds. It is evident that upon molecular formation the electron density around the hydrogen atoms shifts toward the carbon atoms. Figure 2 is a graphical representation of this redistribution of charge.

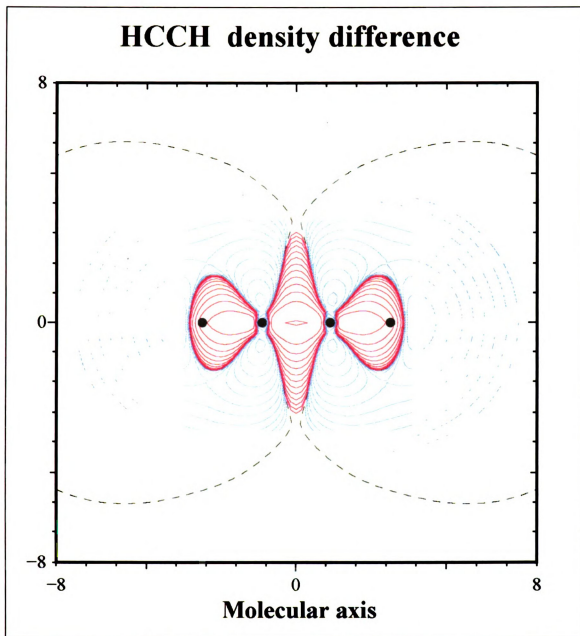


Figure 2: HCCH Density Difference Plot.
Images in this dissertation are presented in color.

Figure 2 shows a plot with blue and red regions. The blue regions are descriptive of areas that are electron deficient in comparison with the atomic electron distribution, and the red regions are descriptive of electron rich areas. The electronegativity argument holds in this example. Carbon is more electronegative which pulls electron density away from the hydrogen atoms. This distribution of charge removes some of the shielding

from the hydrogen nucleus which results in a positive charge on hydrogen and an overall positive quadrupole moment.

It is important to note the magnitude of the atomic quadrupoles of FCCF. After removal of the atomic quadrupoles, the quadrupole moment due to redistribution is more negative. When partitioned into charges, the fluorine atom has a negative charge twice that of hydrogen. The density difference between the atomic and molecular densities is plotted in Figure 3.

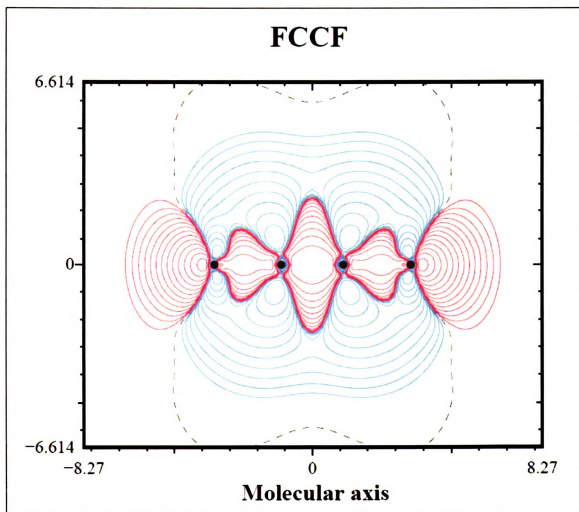


Figure 3: FCCF Density Difference Plot
Images in this dissertation are presented in color.

Figure 3 makes the electronegativity of fluorine obvious. In HCCH the electron density is pulled from the hydrogen atom leaving the nucleus slightly unshielded; however, in FCCF the electron density moves toward the fluorine atoms creating two islands of negative charge at the terminus of the molecule. Islands of negative charge at the terminus of the molecule are not present in the plot of HCCH. The charge distribution shows clearly the negative quadrupole moment of the molecule and the negative charge of the fluorine atoms.

ClCCCl is the second case of a doubly halogenated acetylene. Table 13 shows the magnitude of the atomic quadrupoles to be larger than in the case of FCCF. This discrepancy is not unusual if one considers that the atomic radii of chlorine are larger than the radii of fluorine and that the quadrupole moment has a square dependence on distance. The atomic quadrupoles are large enough that when removed from the molecular quadrupole the quadrupole moment due to charge redistribution is negative. Therefore, when the redistribution quadrupole is partitioned into point charges, the charge on the chlorine atom is negative, which gives credence to the following electronegativity arguments: Fluorine is the most electronegative element on the periodic table followed by chlorine, and hydrogen has a small electronegativity in comparison to chlorine and fluorine. The charge redistribution of the ClCCCl molecule on molecular formation is plotted in Figure 4.

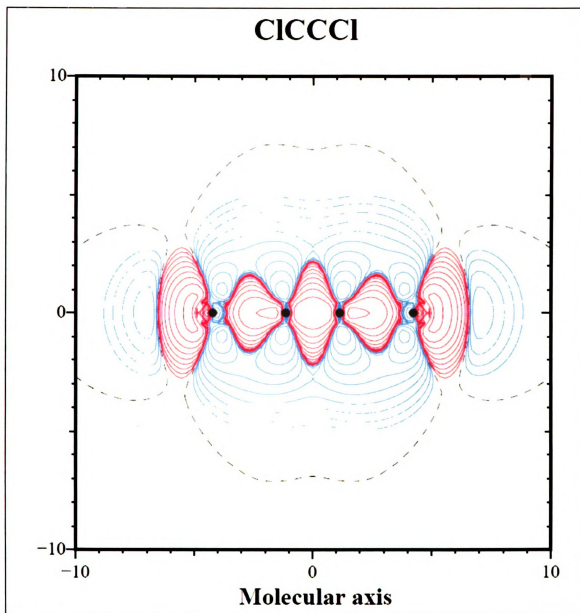


Figure 4: CICCCI Density Difference Plot
Images in this dissertation are presented in color.

Chlorine is very electronegative, and it is pulling electron density toward it. The molecular quadrupole of CICCCI is positive, but this is true only because the quadrupole moments of the constituent atoms are positive, and they compensate for the negative quadrupole created during charge redistribution.

The last of the linear molecules that we discuss are the metal acetylides. Note the enormous magnitude of the partitioned charges on the metal atoms. This type of magnitude lends itself to the interpretation that the metal complexes are ionic in nature. Also note that the partitioned charge on Na is larger than that on Li. This phenomenon is explained by electronegativity arguments which state that sodium is easier to ionize into positively charged particles than lithium. Figure 5 is a plot of the density difference for the linear Li_2C_2 molecule.

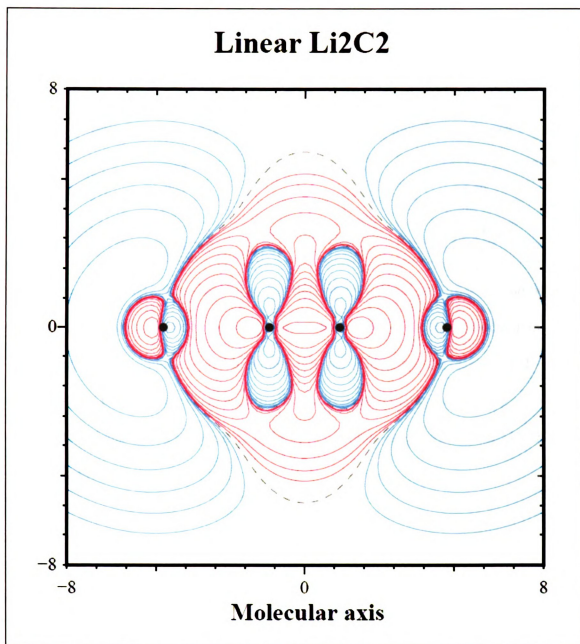


Figure 5: Linear LiCCLi Density Difference Plot
Images in this dissertation are presented in color.

The most noticeable feature of Figure 5 is the highly positive Li atoms. Most of the electron density has moved to the carbon atoms leaving the Li nucleus unshielded. Most of the electron density is surrounding the carbon atoms making the center of the molecule very negatively charged. The density difference for the Na complex behaves

the same way; however, the positive regions will be more electron deficient and farther reaching.

Table 14 contains the partitioned charges of the titled planar molecules.

Table 14. Planar Molecules (X₂C₂) Partitioned into Point Chages				
	Θ_{zz}	$\Theta_{(zz)atoms}^a$	$\Theta_{(zz)cr}$	$q_x(\Theta_{zz})$
Li ₂ C ₂	25.958	2.841	23.117	0.844
Na ₂ C ₂	35.867	2.841	33.026	0.870
	Θ_{yy}	$\Theta_{(yy)atoms}^b$	$\Theta_{(zz)cr}$	$q_x(\Theta_{yy})$
Li ₂ C ₂	-16.370	-1.420	-14.950	0.944
Na ₂ C ₂	-21.667	-1.420	-20.247	0.958

Again, the partitioned charges are large, but the partitioned charges are not equal between the two components. This discrepancy, which has been shown by other research in the laboratory, is due to induced dipoles in the molecule. Therefore, the model which illustrates that the molecules can be partitioned into point charges does not adequately describe the planar molecules. Figure 6 shows the density difference for the Li₂C₂ planar complex.

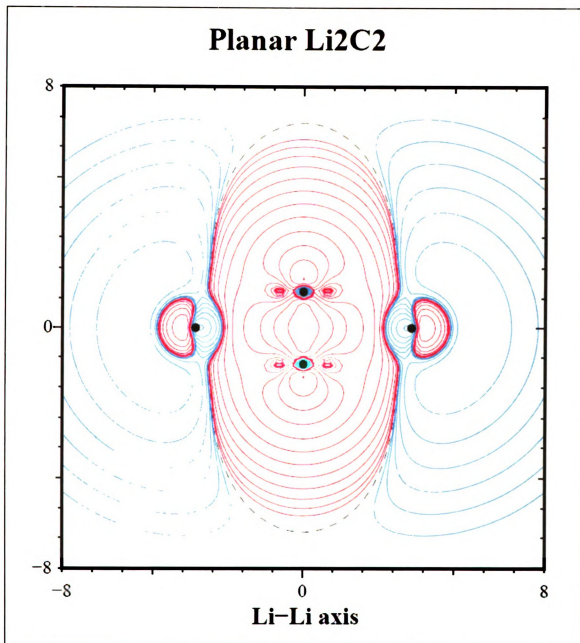


Figure 6: Planar Li₂C₂ Density Difference Plot
Images in this dissertation are presented in color.

Figure 6 shows the planar molecule as what seems to be a collection of four charged species with positively charged Li atoms and negatively charged carbon atoms.

3.9 References

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Chapter 4

Higher-order van der Waals Interactions and Nonlinear Response Tensors

4.1 Introduction

Van der Waals forces are the intermolecular forces that arise from electrostatic interactions, induction, and fluctuations in the charge distribution within each molecule¹. Van der Waals interactions also affect the dipoles and polarizabilities of the interacting molecules². In this chapter we derive the van der Waals interaction energy between two molecules to third order. Our analytical results at second order are identical to known results. Our results at third order are consistent with those of Piecuch, but we provide new equations for the third-order two-body van der Waals interaction energy: We express the fluctuation effects in terms of hyperpolarizabilities at imaginary frequencies. We also make numerical estimates for the second- and third-order interaction energies due to charge-density fluctuations and compare those results with various other second- and third-order interaction energies.

4.1.1 Interaction Energy

Consider two molecules A and B which are well-separated, so that the electronic overlap between the two molecules is essentially negligible. The energy of these two weakly interacting systems is equal to the sum of the energy of molecule A (E_A), the energy of molecule B (E_B), and the energy due to the interaction of A with B (E_{A+B}), as shown in equation (1).

$$E_{AB} = E_A + E_B + E_{A+B}. \quad (1)$$

We obtain the operator for the interaction between A and B by considering the interaction between two classical charge distributions. If the two molecules are represented as collections of positive and negative point charges, the classical electrostatic interaction

energy is $E_{A+B} = \sum_i q_i^A \Phi_i^B$ where q_i^A is the charge of the i th particle in system A and

Φ_i^B is the potential at the i th particle due to molecule B. If the potential due to B is expanded around an origin in A, the electrostatic interaction energy takes the form of equation (2), where Q^A , μ^A , and Θ^A are the overall charge, dipole, and quadrupole moment of system A, and F_α^B and $F_{\alpha\beta}^B$ are the field and field gradient generated by system B. Each Greek subscript refers to the x, y, or z component of the electric moment or field quantity.

$$E_{A+B} = Q^A \Phi^B - \mu_\alpha^A F_\alpha^B - \frac{1}{3} \Theta_{\alpha\beta}^A F_{\alpha\beta}^B - \dots \quad (2)$$

In equation (2), we follow the Einstein Convention of Summations over Greek indices, such that equation (2) equals equation (3).

$$\begin{aligned} E_{A+B} = & Q^A \Phi^B - \mu_x^A F_x^B - \mu_y^A F_y^B - \mu_z^A F_z^B \\ & - \frac{1}{3} \Theta_{xx}^A F_{xx}^B - \frac{1}{3} \Theta_{xy}^A F_{xy}^B - \frac{1}{3} \Theta_{xz}^A F_{xz}^B - \frac{1}{3} \Theta_{yx}^A F_{yx}^B - \frac{1}{3} \Theta_{yy}^A F_{yy}^B \\ & - \frac{1}{3} \Theta_{yz}^A F_{yz}^B - \frac{1}{3} \Theta_{zx}^A F_{zx}^B - \frac{1}{3} \Theta_{zy}^A F_{zy}^B - \frac{1}{3} \Theta_{zz}^A F_{zz}^B - \dots \end{aligned} \quad (3)$$

The dipole and field are tensors of rank one (or vectors) described by equations (4) and (5).

$$\mu = \mu_x \mathbf{x} + \mu_y \mathbf{y} + \mu_z \mathbf{z} . \quad (4)$$

$$\mathbf{F} = F_x \mathbf{x} + F_y \mathbf{y} + F_z \mathbf{z} . \quad (5)$$

The quadrupole and field gradient are tensors of rank two and can be represented in matrix format as seen in equations (6) and (7).

$$\Theta = \begin{pmatrix} \Theta_{xx} & \Theta_{xy} & \Theta_{xz} \\ \Theta_{yx} & \Theta_{yy} & \Theta_{yz} \\ \Theta_{zx} & \Theta_{zy} & \Theta_{zz} \end{pmatrix}. \quad (6)$$

$$\mathbf{F} = \begin{pmatrix} F'_{xx} & F'_{xy} & F'_{xz} \\ F'_{yx} & F'_{yy} & F'_{yz} \\ F'_{zx} & F'_{zy} & F'_{zz} \end{pmatrix}. \quad (7)$$

$\mathbf{R}$ is a vector, between the origin in A and the origin in B, which points from B to A. From the multipole expansion, equations (8), (9), and (10) give the potential, field, and field gradient due to B, respectively.

$$\Phi^B(\mathbf{R}) = \frac{Q^B}{R} - T_\alpha \mu_\alpha^B + \frac{1}{3} T_{\alpha\beta} \Theta_{\alpha\beta}^B + \dots \quad (8)$$

$$F_\alpha^B = -\frac{\partial}{\partial R_\alpha} \Phi^B(\mathbf{R}) = -T_\alpha Q^B + T_{\alpha\beta} \mu_\beta^B - \frac{1}{3} T_{\alpha\beta\gamma} \Theta_{\beta\gamma}^B + \dots \quad (9)$$

$$F_{\alpha\beta}^B = -\frac{\partial^2}{\partial R_\alpha \partial R_\beta} \Phi^B(\mathbf{R}) = -T_{\alpha\beta} Q^B + T_{\alpha\beta\gamma} \mu_\gamma^B - \frac{1}{3} T_{\alpha\beta\gamma\delta} \Theta_{\gamma\delta}^B + \dots \quad (10)$$

Equations (11) and (12) are explicit definitions of the first and second rank T tensors.

$$T_\alpha = \frac{\partial}{\partial R_\alpha} \frac{1}{R} = \frac{-R_\alpha}{R^3}. \quad (11)$$

$$T_{\alpha\beta} = \frac{\partial^2}{\partial R_\alpha \partial R_\beta} \frac{1}{R} = \frac{3R_\alpha R_\beta - \delta_{\alpha\beta} R^2}{R^5} \text{ where } \delta_{\alpha\beta} = \begin{pmatrix} 1 \text{ if } \alpha = \beta \\ 0 \text{ if } \alpha \neq \beta \end{pmatrix}. \quad (12)$$

Assuming that systems A and B have no net charge, the leading terms of the interaction energy depend on the dipole and quadrupole moments of both systems as shown in equation (13).

$$\begin{aligned}
E_{A+B} = & -\mu_{\alpha}^A T_{\alpha\beta} \mu_{\beta}^B + \frac{1}{3} \mu_{\alpha}^A T_{\alpha\beta\gamma} \Theta_{\beta\gamma}^B \\
& - \frac{1}{3} \Theta_{\alpha\beta}^A T_{\alpha\beta\gamma} \mu_{\gamma}^B + \frac{1}{9} \Theta_{\alpha\beta}^A T_{\alpha\beta\gamma\delta} \Theta_{\gamma\delta}^B + \dots
\end{aligned}
\tag{13}$$

Using the dipole propagators or T tensors, we can determine the distance dependence of the interaction energy on a particular interaction. For example, $-\mu_{\alpha}^A T_{\alpha\beta} \mu_{\beta}^B$ is the energy of interaction between the dipoles on systems A and B. As the distance, R, between A and B is increased, the interaction energy decreases as $\frac{1}{R^3}$. For the second and third terms, the dipole-quadrupole and quadrupole-dipole interactions, the energy decreases as $\frac{1}{R^4}$. Therefore, the long-range interaction energy between the two systems depends more on the leading dipole-dipole term than on the dipole-quadrupole or quadrupole-quadrupole terms.

Next, we construct a Hamiltonian operator for the two interacting systems, $\hat{H}_{AB}$, for use in the time-independent Schrödinger equation, $\hat{H}_{AB}\Psi = E\Psi$. In equation (14), the unperturbed Hamiltonians for each of the two molecules, $\hat{H}_A$ and $\hat{H}_B$, are summed into the unperturbed Hamiltonian $\hat{H}_0$, and the portion of the Hamiltonian from which the interaction energy originates ($\hat{V}_{AB}$) is treated as a perturbation. The form of the operator $\hat{V}_{AB}$ is determined from the classical electrostatic interaction energy, given in equation (13).

$$\hat{H}_{AB} = \underbrace{\hat{H}_A + \hat{H}_B}_{\hat{H}_0} + \underbrace{\left(-\mu_\alpha^A T_{\alpha\beta} \mu_\beta^B + \frac{1}{3} \mu_\alpha^A T_{\alpha\beta\gamma} \Theta_{\beta\gamma}^B - \frac{1}{3} \Theta_{\alpha\beta}^A T_{\alpha\beta\gamma} \mu_\gamma^B + \frac{1}{9} \Theta_{\alpha\beta}^A T_{\alpha\beta\gamma\delta} \Theta_{\gamma\delta}^B + \dots \right)}_{\hat{V}_{AB}}. \quad (14)$$

In this work, we focus on the dipole-dipole interactions, which give the leading contribution to the interaction energy at each order. Corrections to the first- and second-order interaction energies due to higher multipolar effects have been given by Buckingham³, Stogryn^{4,5}, Piecuch^{6,7,8,9} etc. Thus we take

$$\hat{H}_{AB}|\Psi\rangle = \left(\hat{H}_0 - \underbrace{\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B}_{\hat{V}_1} \right) |\Psi\rangle = (\hat{H}_0 + \hat{V}_1) |\Psi\rangle = E_{AB}|\Psi\rangle. \quad (15)$$

4.1.2 Perturbation Theory

Rayleigh-Schrödinger perturbation theory is based on the premise that, for a particular system for which the eigenfunctions and eigenvalues of the time-independent Schrödinger equation are unknown, there exists a second system, similar to the first, for which the eigenfunctions and eigenvalues are known. Using the eigenvalues and eigenfunctions of the second system we may approximate the eigenfunctions and eigenvalues of the first system. For example, we need to solve equation (15), but the eigenfunctions and eigenvalues are unknown; however, we do know the eigenvalues and eigenfunctions of equation (16),

$$\hat{H}_0|\Psi_0\rangle = E_0|\Psi_0\rangle. \quad (16)$$

where $\Psi_0 = |0\rangle = \Psi_0^A \Psi_0^B = |0_A 0_B\rangle$, which is the product of the unperturbed ground state wavefunctions of system A and system B, and where $E_0 = E_0^A + E_0^B$ is the sum of the unperturbed ground state energies of systems A and B. Electron exchange between A and B is neglected in the zeroth-order wavefunction.

Introducing an ordering parameter λ , which we will eventually set equal to one, we can expand the exact eigenfunctions and eigenvalues from equation (15) as series in λ , yielding equations (17) and (18).

$$E_{AB} = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \dots \quad (17)$$

$$\Psi = |\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle + \lambda^2 |\Psi_0^{(2)}\rangle + \lambda^3 |\Psi_0^{(3)}\rangle + \dots \quad (18)$$

Substituting back into equation (15), we derive equation (19).

$$\begin{aligned} & (\hat{H}_0 + \lambda \hat{V}_1) \left(|\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle + \lambda^2 |\Psi_0^{(2)}\rangle + \dots \right) = \\ & \left(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots \right) \left(|\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle + \lambda^2 |\Psi_0^{(2)}\rangle + \dots \right) \end{aligned} \quad (19)$$

If we expand the expressions and equate terms with equal powers of λ^n , we obtain equations (20), (21), and (22):

$$\hat{H}_0 |0\rangle = E_0^{(0)} |0\rangle, \text{ for } n = 0. \quad (20)$$

$$\hat{H}_0 |\Psi_0^{(1)}\rangle + \hat{V}_1 |0\rangle = E_0^{(1)} |0\rangle + E_0^{(0)} |\Psi_0^{(1)}\rangle, \text{ for } n = 1. \quad (21)$$

$$\hat{H}_0 |\Psi_0^{(2)}\rangle + \hat{V}_1 |\Psi_0^{(1)}\rangle = E_0^{(2)} |0\rangle + E_0^{(1)} |\Psi_0^{(1)}\rangle + E_0^{(0)} |\Psi_0^{(2)}\rangle, \text{ for } n = 2. \quad (22)$$

Using the condition that the m th correction to the unperturbed wavefunction is a sum of

the excited states of the unperturbed system, $\Psi_0^{(m)} = \sum_{k \neq 0} c_k^{(m)} \Psi_k^{(0)}$ where k is the k th

excited state (so $k \neq 0$), and using the result that the excited states are orthogonal to the unperturbed ground-state wavefunction, $\langle 0 | \Psi_m^{(0)} \rangle = \langle 0 | m \rangle = 0$, for $m > 0$, we can take the scalar product of equations (20), (21), and (22) with $\Psi_0^{(0)} \equiv |0\rangle$. From these scalar product equations, we obtain equations (23), (24), (25) and (26).

$$E_0^{(0)} = E_0. \quad (23)$$

$$E_0^{(1)} = \langle 0 | \hat{V}_1 | 0 \rangle. \quad (24)$$

$$E_0^{(2)} = \sum_{k \neq 0} \frac{\langle 0 | \hat{V}_1 | k \rangle \langle k | \hat{V}_1 | 0 \rangle}{E_0^{(0)} - E_k^{(0)}}. \quad (25)$$

$$E_0^{(3)} = \sum_{k, m \neq 0} \frac{\langle 0 | \hat{V}_1 | k \rangle \langle k | \bar{V} | m \rangle \langle m | \hat{V}_1 | 0 \rangle}{(E_0^{(0)} - E_k^{(0)})(E_0^{(0)} - E_m^{(0)})}, \text{ where } \bar{V} = \hat{V}_1 - E_0^{(1)}. \quad (26)$$

Equation (23) is an equality involving the unperturbed energy (in this case, the energies of the noninteracting systems A and B). Equation (24) gives the first-order energy correction, which yields the permanent dipole-dipole interaction, while equation (25) and equation (26) give the second- and third-order energy corrections, respectively.

4.2 Second-Order Energy Correction

By defining an operator $\hat{G}$ known as the reduced resolvent,

$$\hat{G} = (1 - P_0)(\hat{H}_0 - E_0)^{-1}(1 - P_0) = \sum_{k \neq 0} \frac{|k\rangle\langle k|}{(E_k - E_0)}. \quad (27)$$

where $P_0 = |0\rangle\langle 0|$, the second-order energy correction takes form in equation (28).

$$E_0^{(2)} = -\langle 0 | \hat{V}_1 \hat{G} \hat{V}_1 | 0 \rangle. \quad (28)$$

For a pair of molecules A and B, the G operator is equal to a sum of three operators.

$$\hat{G} = (\hat{G}^A + \hat{G}^B + \hat{G}^{A \oplus B}) \text{ such that}$$

$$\hat{G}^A = \sum_{j \neq 0} \frac{|j_A 0_B\rangle \langle j_A 0_B|}{E_j^A - E_0^A}. \quad (29)$$

$$\hat{G}^B = \sum_{m \neq 0} \frac{|0_A m_B\rangle \langle 0_A m_B|}{E_m^B - E_0^B}. \quad (30)$$

$$\hat{G}^{A \oplus B} = \sum_{j, m \neq 0} \frac{|j_A m_B\rangle \langle j_A m_B|}{(E_j^A - E_0^A) + (E_m^B - E_0^B)}. \quad (31)$$

$\hat{G}^A$ is the reduced resolvent for excitations of system A only, $\hat{G}^B$ is the reduced resolvent for excitations of system B only, and $\hat{G}^{A \oplus B}$ is the reduced resolvent for excitations in both system A and B. Substituting $\hat{V}_1 = -\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B$ into equation (28) results in equation (32):

$$E_0^{(2)} = \langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) \left(G^A + G^B + G^{A \oplus B} \right) \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle. \quad (32)$$

Expanding equation (32) results in equation (33).

$$\begin{aligned} E_0^{(2)} = & \langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) G^A \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle \\ & + \langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) G^B \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle \\ & + \langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) G^{A \oplus B} \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle. \end{aligned} \quad (33)$$

For simplicity, equation (33) is broken into portions of the second-order energy which depend on excitations only in A ($E_A^{(2)}$), excitations only in B ($E_B^{(2)}$), and excitations in both A and B ($E_{A \oplus B}^{(2)}$). The second-order energy correction now has the form in equation (34), where $E_A^{(2)}$ is given in equation (35), $E_B^{(2)}$ is given in equation (36) and $E_{A \oplus B}^{(2)}$ is given in equation (37).

$$E_0^{(2)} = E_A^{(2)} + E_B^{(2)} + E_{A \oplus B}^{(2)}. \quad (34)$$

$$E_A^{(2)} = -\langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) \hat{G}^A \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle. \quad (35)$$

$$E_B^{(2)} = -\langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) \hat{G}^B \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle. \quad (36)$$

$$E_{A \oplus B}^{(2)} = -\langle 0_A 0_B | \left(-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B \right) \hat{G}^{A \oplus B} \left(-\hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B \right) | 0_A 0_B \rangle. \quad (37)$$

Equation (38) for $E_A^{(2)}$ which simplifies to equation (39), where μ^{B0} is the static ground-state dipole moment of system B and E_m^A is the energy of the mth-excited state of molecule A.

$$E_A^{(2)} = - \sum_{m \neq 0} \frac{\langle 0_A 0_B | \hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B | m_A 0_B \rangle \langle m_A 0_B | \hat{\mu}_\gamma^A T_{\gamma\delta} \hat{\mu}_\delta^B | 0_A 0_B \rangle}{E_m^A - E_0^A}. \quad (38)$$

$$E_A^{(2)} = -T_{\alpha\beta} T_{\gamma\delta} \mu_\beta^{B0} \mu_\delta^{B0} \sum_{m \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle}{E_m^A - E_0^A}. \quad (39)$$

If we expand equation (39) into a sum of two terms, it becomes equation (40).

$$\begin{aligned} E_A^{(2)} = & -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \mu_\beta^{B0} \mu_\delta^{B0} \sum_{m \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle}{E_m^A - E_0^A} \\ & -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \mu_\beta^{B0} \mu_\delta^{B0} \sum_{m \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle}{E_m^A - E_0^A}. \end{aligned} \quad (40)$$

Since the Greek indices are dummy variables, by interchanging the labels β and δ and simultaneously interchanging α and γ , we convert equation (40) into equation (41).

$$\begin{aligned} E_A^{(2)} = & -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \mu_\beta^{B0} \mu_\delta^{B0} \sum_{m \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle}{E_m^A - E_0^A} \\ & -\frac{1}{2} T_{\gamma\delta} T_{\alpha\beta} \mu_\delta^{B0} \mu_\beta^{B0} \sum_{m \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle}{E_m^A - E_0^A}. \end{aligned} \quad (41)$$

Now the sum over states in equation (41) has the form of the static polarizability.

If we use the definition of the static polarizability of system A given in equation (42), equation (41) becomes equation (43).

$$\alpha_{\alpha\gamma}^A = \sum_{m \neq 0} \left[\frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle}{E_m^A - E_0^A} + \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle}{E_m^A - E_0^A} \right]. \quad (42)$$

$$E_A^{(2)} = -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \mu_\beta^{B0} \mu_\delta^{B0} \alpha_{\alpha\gamma}^A. \quad (43)$$

Following the same procedure, we can expand and rearrange $E_B^{(2)}$ to obtain equation (44).

$$E_B^{(2)} = -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \mu_\alpha^{A0} \mu_\gamma^{A0} \alpha_{\beta\delta}^B. \quad (44)$$

The final term in the second-order interaction energy is given in equation (45).

$$E_{A \oplus B}^{(2)} = -T_{\alpha\beta} T_{\gamma\delta} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_m^A - E_0^A) + (E_k^B - E_0^B)}. \quad (45)$$

Using the integral relation¹⁰, $\frac{\pi}{a+b} = \int_{-\infty}^{\infty} du \frac{a}{a^2 + u^2} * \frac{b}{b^2 + u^2}$ and

$\frac{a}{a^2 + u^2} = \frac{1/2}{a + iu} + \frac{1/2}{a - iu}$, we can rearrange the denominator of equation (45) to obtain

equation (46), where $E_{m0}^A = E_m^A - E_0^A$ and $E_{k0}^B = E_k^B - E_0^B$.

$$\frac{1}{E_{k0}^B + E_{m0}^A} = \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{1}{E_{k0}^B + i\omega\hbar} + \frac{1}{E_{k0}^B - i\omega\hbar} \right) \left(\frac{1}{E_{m0}^A + i\omega\hbar} + \frac{1}{E_{m0}^A - i\omega\hbar} \right). \quad (46)$$

Substituting the right side of equation (46) back into equation (45) and expanding, we obtain equation (47).

$$\begin{aligned}
E_{A \oplus B}^{(2)} &= -T_{\alpha\beta} T_{\gamma\delta} \\
&\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{k,m \neq 0} \langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle 0_A | \hat{\mu}_{\beta}^B | k_B \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle \\
&\times \left(\frac{1}{(E_{m0}^A + i\omega\hbar)} + \frac{1}{(E_{m0}^A - i\omega\hbar)} \right) \times \left(\frac{1}{(E_{k0}^B + i\omega\hbar)} + \frac{1}{(E_{k0}^B - i\omega\hbar)} \right).
\end{aligned} \tag{47}$$

Equation (47) can be rearranged into equation (48).

$$\begin{aligned}
E_{A \oplus B}^{(2)} &= -T_{\alpha\beta} T_{\gamma\delta} \frac{\hbar}{4\pi} \\
&\times \int_{-\infty}^{\infty} d\omega \left(\sum_{m \neq 0} \left(\frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle}{(E_{m0}^A + i\omega\hbar)} + \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle}{(E_{m0}^A - i\omega\hbar)} \right) \right. \\
&\quad \left. \times \sum_{k \neq 0} \left(\frac{\langle 0_B | \hat{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_{k0}^B + i\omega\hbar)} + \frac{\langle 0_B | \hat{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_{k0}^B - i\omega\hbar)} \right) \right).
\end{aligned} \tag{48}$$

From Orr and Ward¹¹, the frequency-dependent polarizability of A is given by equation (49).

$$\alpha_{\alpha\gamma}^A(\omega) = \sum_{m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle}{E_{m0}^A - \hbar\omega} + \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle}{E_{m0}^A + \hbar\omega} \tag{49}$$

The dipole operators are Hermitian. If $|0_A\rangle$, $|0_B\rangle$, $|m_A\rangle$, and $|k_A\rangle$ are real eigenstates,

then $\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle = \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle$ and $\langle 0_B | \hat{\mu}_{\beta}^B | k_B \rangle = \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle$. Using these

equalities and the definition of the frequency-dependent polarizability from equation (49), equation (48) becomes equation (50).

$$E_{A \oplus B}^{(2)} = -T_{\alpha\beta} T_{\gamma\delta} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \alpha_{\alpha\gamma}^A(i\omega) \alpha_{\beta\delta}^B(i\omega) d\omega. \tag{50}$$

Summing equations (39), (40), and (46) gives the second-order energy correction as a function of the static polarizabilities of A and B and the imaginary-frequency dependent polarizability of A and B, as seen in equation (51).

$$E_0^{(2)} = -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \left(\mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \alpha_{\beta\delta}^B + \mu_{\beta}^{B0} \mu_{\delta}^{B0} \alpha_{\alpha\gamma}^A + \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \alpha_{\alpha\gamma}^A(i\omega) \alpha_{\beta\delta}^B(i\omega) d\omega \right). \quad (51)$$

This result has been obtained previously by Buckingham³, Dalgarno¹², Longuet-Higgins^{13,14,15}, Stogryn^{4,5}, Piecuch^{6,7,8,9}, etc.

4.3 Third-Order Correction to the Energy

From equation (26), after substituting in the reduced resolvent, we see that the third-order correction to the energy takes the form of equation (52).

$$E_0^{(3)} = \sum_{k,m \neq 0} \langle 0 | \hat{V}_1 (G^A + G^B + G^{A \oplus B}) \bar{V} (G^A + G^B + G^{A \oplus B}) \hat{V}_1 | 0 \rangle. \quad (52)$$

The $\bar{V}$ operator is defined by $\bar{V} = \hat{V}_1 - E_0^{(1)}$. If we substitute the perturbation into the $\bar{V}$ operator we have equation (53).

$$\hat{V}_1 - E_0^{(1)} = -\hat{\mu}_{\alpha}^A T_{\alpha\beta} \hat{\mu}_{\beta}^B + \langle 0_A 0_B | \hat{\mu}_{\alpha}^A T_{\alpha\beta} \hat{\mu}_{\beta}^B | 0_A 0_B \rangle. \quad (53)$$

We can rearrange equation (53) into equation (54), where $\bar{\mu}_{\alpha}^A = \hat{\mu}_{\alpha}^A - \mu_{\alpha}^{A0}$.

$$\hat{V}_1 - E_0^{(1)} = -\bar{\mu}_{\alpha}^A T_{\alpha\beta} \bar{\mu}_{\beta}^B - \mu_{\alpha}^{A0} T_{\alpha\beta} \bar{\mu}_{\beta}^B - \bar{\mu}_{\alpha}^A T_{\alpha\beta} \mu_{\beta}^{B0}. \quad (54)$$

If equation (54) is substituted into equation (52) and the result is expanded, a 27-term expression is generated. Fortunately, not all 27 terms are non-zero. For example, the left hand side of equation (55) equals zero, as shown below.

$$\langle 0 | \hat{V}_1 G^A \bar{\mu}_{\alpha}^A T_{\alpha\beta} \bar{\mu}_{\beta}^B G^A \hat{V}_1 | 0 \rangle = 0. \quad (55)$$

Expanding equation (55), we obtain equation (56).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = \\ \langle 0_A 0_B | \hat{V}_1 \sum_{m \neq 0} \frac{|m_A 0_B\rangle \langle m_A 0_B|}{(E_{m0}^A - E_0^{(0)})} \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B \sum_{n \neq 0} \frac{|n_A 0_B\rangle \langle n_A 0_B|}{(E_{n0}^A - E_0^{(0)})} \hat{V}_1 | 0_A 0_B \rangle. \end{aligned} \quad (56)$$

Equation (56) then simplifies to equation (57).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} \sum_{m,n \neq 0} \frac{\langle 0_A 0_B | \hat{V}_1 | m_A 0_B \rangle \langle m_A | \bar{\mu}_\alpha^A | n_A \rangle \langle 0_B | \bar{\mu}_\beta^B | 0_B \rangle \langle n_A 0_B | \hat{V}_1 | 0_A 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A)}. \end{aligned} \quad (57)$$

Now, because the $\langle 0_B | \bar{\mu}_\beta^B | 0_B \rangle = 0$ as shown in equation (58), the term given on the left in equation (55) does not contribute to the third-order interaction energy in equation (52).

$$\langle 0_B | \bar{\mu}_\beta^B | 0_B \rangle = \langle 0_B | \hat{\mu}_\beta^B | 0_B \rangle - \langle 0_B | \mu_\beta^{B0} | 0_B \rangle = \mu_\beta^{B0} - \mu_\beta^{B0} = 0. \quad (58)$$

Similarly the term on the left in equation (59) also equals zero, as shown next.

$$\langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A \oplus B} \hat{V}_1 | 0 \rangle = 0. \quad (59)$$

Expanding equation (59) and simplifying we obtain equation (60).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A \oplus B} \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} \sum_{k,m,n \neq 0} \frac{\langle 0_A 0_B | \hat{V}_1 | m_A 0_B \rangle \langle m_A | \bar{\mu}_\alpha^A | n_A \rangle \langle 0_B | \mu_\beta^{B0} | k_B \rangle \langle n_A k_B | \hat{V}_1 | 0_A 0_B \rangle}{(E_m^A - E_0^A)[(E_k^B - E_0^B) + (E_n^A - E_0^A)]}. \end{aligned} \quad (60)$$

The matrix element $\langle 0_A | \mu_\beta^{B0} | k_B \rangle$ equals zero, as shown in equation (61); therefore, the term on the left in equation (59) does not contribute to the third-order energy.

$$\langle 0_A | \mu_\beta^{B0} | k_B \rangle = \mu_\beta^{B0} \langle 0_A | k_B \rangle = 0. \quad (61)$$

Of the 27 terms, 12 equal zero and those terms are listed in equations (62) through (73).

$$\langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = 0 \quad \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = 0 \quad (62-63)$$

$$\langle 0 | \hat{V}_1 G^A \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = 0 \quad \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^A \hat{V}_1 | 0 \rangle = 0 \quad (64-65)$$

$$\langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = 0 \quad \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^B \hat{V}_1 | 0 \rangle = 0 \quad (66-67)$$

$$\langle 0 | \hat{V}_1 G^A \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = 0 \quad \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^B \hat{V}_1 | 0 \rangle = 0 \quad (68-69)$$

$$\langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}_1 | 0 \rangle = 0 \quad \langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1 | 0 \rangle = 0 \quad (70-71)$$

$$\langle 0 | \hat{V}_1 G^{A\oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^A \hat{V}_1 | 0 \rangle = 0 \quad \langle 0 | \hat{V}_1 G^{A\oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = 0 \quad (72-73)$$

The remaining 15 nonzero terms break into one of four categories based on their dependence on the static dipole moment of system A and system B. Terms of order p in μ^{A0} and order q in μ^{B0} are classified as p-q terms in the discussion below.

4.3.1 Third-Order Terms in the Static Dipole of A or B

Listed in equations (74) and (75) are the 3-0 and 0-3 terms respectively. If we expand equation (74), we obtain equation (76).

$$T_{3-0} = \langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle. \quad (74)$$

$$T_{0-3} = \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^A \hat{V}_1 | 0 \rangle. \quad (75)$$

$$\begin{aligned} \langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = \\ \sum_{k,j \neq 0} \frac{\langle 0_A 0_B | \mu_\gamma^A T_{\gamma\delta} \mu_\delta^B | 0_A k_B \rangle \langle 0_A k_B | \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B | 0_A j_B \rangle \langle 0_A j_B | \mu_\epsilon^A T_{\epsilon\phi} \mu_\phi^B | 0_A 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)}. \end{aligned} \quad (76)$$

Equation (76) simplifies to equation (77).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\phi} \mu_\alpha^{A0} \mu_\gamma^{A0} \mu_\epsilon^{A0} \frac{\langle 0_B | \mu_\delta^B | k_B \rangle \langle k_B | \bar{\mu}_\beta^B | j_B \rangle \langle j_B | \mu_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)}. \end{aligned} \quad (77)$$

We can now see that the term represented by equation (74) depends on the permanent dipole of system A to order 3 and depends on the permanent dipole of system B to order 0.

We know that the static hyperpolarizability of system B has the form given in equation (78)¹¹.

$$\begin{aligned}
 \beta_{\beta\delta\phi}^B = & \frac{\langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \bar{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
 & + \frac{\langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \bar{\mu}_\phi^B | j_B \rangle \langle j_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
 & + \frac{\langle 0_B | \hat{\mu}_\delta^B | k_B \rangle \langle k_B | \bar{\mu}_\beta^B | j_B \rangle \langle j_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
 & + \frac{\langle 0_B | \hat{\mu}_\delta^B | k_B \rangle \langle k_B | \bar{\mu}_\phi^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
 & + \frac{\langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \bar{\mu}_\beta^B | j_B \rangle \langle j_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
 & + \frac{\langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \bar{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)}.
 \end{aligned} \tag{78}$$

Reassigning the Greek indices in a similar manner to the reassignment done with the second-order energy correction, equation (77) can be rearranged into equation (79).

$$\begin{aligned}
& \langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = \\
& \frac{1}{6} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\alpha^{A0} \mu_\gamma^{A0} \mu_\varepsilon^{A0} \sum_{k,j \neq 0} \left[\begin{aligned}
& \frac{\langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \bar{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
& + \frac{\langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \bar{\mu}_\varphi^B | j_B \rangle \langle j_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
& + \frac{\langle 0_B | \hat{\mu}_\delta^B | k_B \rangle \langle k_B | \bar{\mu}_\beta^B | j_B \rangle \langle j_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
& + \frac{\langle 0_B | \hat{\mu}_\delta^B | k_B \rangle \langle k_B | \bar{\mu}_\varphi^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
& + \frac{\langle 0_B | \hat{\mu}_\varphi^B | k_B \rangle \langle k_B | \bar{\mu}_\beta^B | j_B \rangle \langle j_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)} \\
& + \frac{\langle 0_B | \hat{\mu}_\varphi^B | k_B \rangle \langle k_B | \bar{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_j^B - E_0^B)}
\end{aligned} \right]. \quad (79)
\end{aligned}$$

Now the matrix element on the left in equation (74) has the form given in equation (80).

$$\langle 0 | \hat{V}_1 G^B \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = \frac{1}{6} \mu_\alpha^{A0} \mu_\gamma^{A0} \mu_\varepsilon^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \beta_{\beta\delta\varphi}^B. \quad (80)$$

The second term in this classification is given in equation (75). By following the same procedure, we can show that the matrix elements on the left in equation (75) depend on the permanent dipole of system B to order 3 and depend on the permanent dipole of system A to order 0. If we expand equation (75), we get equation (81).

$$\begin{aligned}
T_{0-3} &= \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^A \hat{V}_1 | 0 \rangle \\
&= T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\beta^{B0} \mu_\delta^{B0} \mu_\varphi^{B0} \sum_{m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \bar{\mu}_\alpha^A | n_A \rangle \langle n_A | \hat{\mu}_\varepsilon^A | 0_A \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A)}. \quad (81)
\end{aligned}$$

Then as in equation (77), we can rearrange indices and represent equation (75) as equation (82).

$$\langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^A \hat{V}_1 | 0 \rangle = \frac{1}{6} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\beta^{B0} \mu_\delta^{B0} \mu_\phi^{B0} \beta_{\alpha\gamma\varepsilon}^A, \quad (82)$$

The net contribution to the energy from this term is $-\frac{1}{6} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\beta^{B0} \mu_\delta^{B0} \mu_\phi^{B0} \beta_{\alpha\gamma\varepsilon}^A$.

From equations (80) and (82), the 3-0 and 0-3 terms refer to a classical interaction between the two systems, where system A generates a static field, which polarizes system B through the β -hyperpolarizability of B, and vice versa. Figure 1 shows the 3-0 terms in a graphical manner.

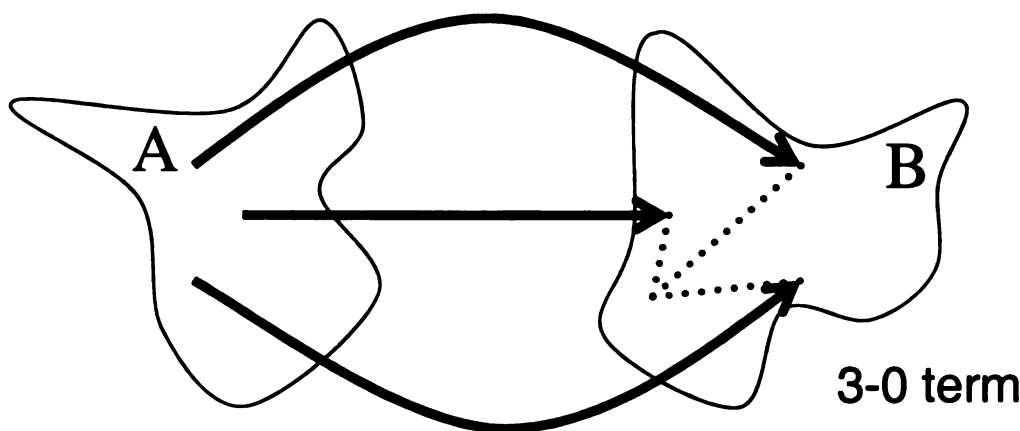


Figure 1: Representation of the 3-0 term.
Images in this dissertation are presented in color.

In the figure, the three solid black lines represent the field generated by A. The dotted green lines represent the polarization of system B through its β -hyperpolarizability.

There has been previous study of this contribution to the third-order energy by Stogryn^{4,5} and Piecuch^{6,7,8,9}.

4.3.2 First-Order Terms in the Dipoles of Both A and B

The next category of nonzero terms in the third-order energy correction are the 1-1 terms, two terms that are first-order in the ground-state dipoles of both A and B. Listed in equations (83) to (88) are those terms.

$$T_{1-1,a} = \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle. \quad (83)$$

$$T_{1-1,b} = \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle. \quad (84)$$

$$T_{1-1,c} = \langle 0 | \hat{V}_1 G^A \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1 | 0 \rangle. \quad (85)$$

$$T_{1-1,d} = \langle 0 | \hat{V}_1 G^{A\oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle. \quad (86)$$

$$T_{1-1,e} = \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}_1 | 0 \rangle. \quad (87)$$

$$T_{1-1,f} = \langle 0 | \hat{V}_1 G^{A\oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^B \hat{V}_1 | 0 \rangle. \quad (88)$$

We begin with equation (83). If we expand the term on the left and simplify, we obtain equation (89).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^B \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\varepsilon^{A0} \mu_\delta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_m^A - E_0^A)(E_k^B - E_0^B)}. \end{aligned} \quad (89)$$

If we expand equation (84) and simplify, we obtain equation (90).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\gamma^{A0} \mu_\phi^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\varepsilon^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_m^A - E_0^A)(E_k^B - E_0^B)}. \end{aligned} \quad (90)$$

In equation (90), if we interchange γ and ε and simultaneously interchange δ and ϕ , then equation (90) becomes equation (91).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} T_{\varepsilon\phi} T_{\gamma\delta} \mu_\varepsilon^{A0} \mu_\delta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_m^A - E_0^A)(E_k^B - E_0^B)}. \end{aligned} \quad (91)$$

Then the $T_{1-1,a}$ and $T_{1-1,b}$ terms both depend on the ϵ component of the ground-state dipole of system A and the δ component of the ground-state dipole of system B. Taking equation (85), after expanding and simplifying, we obtain equation (92).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^A \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1 | 0 \rangle = \\ T_{\alpha\beta} T_{\epsilon\varphi} T_{\gamma\delta} \hat{\mu}_\alpha^{A0} \mu_\delta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\epsilon^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_m^A - E_0^A)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (92)$$

In equation (92), interchanging ϵ and α while simultaneously interchanging β and φ yields equation (93).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^A \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1 | 0 \rangle = \\ T_{\epsilon\varphi} T_{\alpha\beta} T_{\gamma\delta} \hat{\mu}_\epsilon^{A0} \mu_\delta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\varphi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_m^A - E_0^A)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (93)$$

Similarly, if we expand and simplify equation (87), we obtain equation (94).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}_1 | 0 \rangle = \\ T_{\epsilon\varphi} T_{\alpha\beta} T_{\gamma\delta} \hat{\mu}_\gamma^{A0} \mu_\beta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \mu_\epsilon^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (94)$$

In equation (94), we interchange ϵ and γ while simultaneously interchanging β and δ ; we also assume that the dipole matrix elements are real. This yields equation (95).

$$\begin{aligned} \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}_1 | 0 \rangle = \\ T_{\gamma\delta} T_{\alpha\beta} T_{\epsilon\varphi} \hat{\mu}_\epsilon^{A0} \mu_\delta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\varphi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (95)$$

If we add equations (93) and (95), collect like terms, and simplify, we obtain equation (96).

$$\begin{aligned} &\langle 0|\hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}_1|0\rangle + \langle 0|\hat{V}_1 G^A \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1|0\rangle = \\ &T_{\gamma\delta} T_{\alpha\beta} T_{\varepsilon\varphi} \hat{\mu}_\varepsilon^{A0} \mu_\delta^{B0} \sum_{m,k \neq 0} \frac{\langle 0_A|\hat{\mu}_\gamma^A|m_A\rangle \langle m_A|\mu_\alpha^A|0_A\rangle \langle 0_B|\hat{\mu}_\varphi^B|k_B\rangle \langle k_B|\hat{\mu}_\beta^B|0_B\rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)}. \end{aligned} \quad (96)$$

Expanding and simplifying equation (86) results in equation (97).

$$\begin{aligned} &\langle 0|\hat{V}_1 G^{A\oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1|0\rangle = \\ &T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\varphi^{B0} \mu_\alpha^{A0} \sum_{k,m \neq 0} \frac{\langle 0_A|\hat{\mu}_\gamma^A|m_A\rangle \langle m_A|\mu_\varepsilon^A|0_A\rangle \langle 0_B|\hat{\mu}_\delta^B|k_B\rangle \langle k_B|\hat{\mu}_\beta^B|0_B\rangle}{(E_m^A - E_0^A)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (97)$$

To rearrange equation (97) so that it depends on the ε -component of the permanent dipole of system A and the δ -component of the permanent dipole of system B, we interchange φ with δ and α with ε ; we also assume that the dipole matrix elements are real. This gives equation (98).

$$\begin{aligned} &\langle 0|\hat{V}_1 G^{A\oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1|0\rangle = \\ &T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\delta^{B0} \mu_\varepsilon^{A0} \sum_{k,m \neq 0} \frac{\langle 0_A|\hat{\mu}_\alpha^A|m_A\rangle \langle m_A|\mu_\gamma^A|0_A\rangle \langle 0_B|\hat{\mu}_\beta^B|k_B\rangle \langle k_B|\hat{\mu}_\varphi^B|0_B\rangle}{(E_m^A - E_0^A)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (98)$$

Expanding equation (88) and simplifying, we obtain equation (99).

$$\begin{aligned} &\langle 0|\hat{V}_1 G^{A\oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^B \hat{V}_1|0\rangle = \\ &T_{\gamma\delta} T_{\alpha\beta} T_{\varepsilon\varphi} \mu_\beta^{B0} \mu_\varepsilon^{A0} \sum_{k,m \neq 0} \frac{\langle 0_A|\hat{\mu}_\gamma^A|m_A\rangle \langle m_A|\mu_\alpha^A|0_A\rangle \langle 0_B|\hat{\mu}_\beta^B|k_B\rangle \langle k_B|\hat{\mu}_\varphi^B|0_B\rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (99)$$

Rearranging Greek indices so that equation (99) depends on the ε -component of the permanent dipole of system A and the δ -component of the permanent dipole of system B and assuming that the dipole matrix elements are real, we obtain equation (100).

$$\begin{aligned} &\langle 0|\hat{V}_1 G^{A\oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^B \hat{V}_1|0\rangle = \\ &T_{\gamma\delta} T_{\alpha\beta} T_{\varepsilon\varphi} \mu_\delta^{B0} \mu_\varepsilon^{A0} \sum_{k,m \neq 0} \frac{\langle 0_A|\hat{\mu}_\alpha^A|m_A\rangle \langle m_A|\mu_\gamma^A|0_A\rangle \langle 0_B|\hat{\mu}_\beta^B|k_B\rangle \langle k_B|\hat{\mu}_\varphi^B|0_B\rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^B)}. \end{aligned} \quad (100)$$

We combine equation (100) with equation (98), collect like terms, and obtain equation (101).

$$\begin{aligned} & \langle 0 | \hat{V}_1 G^{A \oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^B \hat{V}_1 | 0 \rangle + \langle 0 | \hat{V}_1 G^{A \oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle = \\ & T_{\gamma\delta} T_{\alpha\beta} T_{\varepsilon\phi} \mu_\delta^{B0} \mu_\varepsilon^{A0} \sum_{k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \mu_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)}. \end{aligned} \quad (101)$$

If we add equations (101), (96), (89), (91) we obtain equation (102).

$$\begin{aligned} & T_{1-1,a} + T_{1-1,b} + T_{1-1,c} + T_{1-1,d} + T_{1-1,e} + T_{1-1,f} \\ & = T_{\gamma\delta} T_{\alpha\beta} T_{\varepsilon\phi} \mu_\delta^{B0} \mu_\varepsilon^{A0} \\ & \times \sum_{k,m \neq 0} \left[\begin{aligned} & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \\ & + \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \mu_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \\ & + \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \\ & + \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \mu_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \end{aligned} \right]. \end{aligned} \quad (102)$$

The product of two polarizabilities, one on A and one on B, is shown in equation (103).

$$\alpha_{\gamma\alpha}^A \alpha_{\beta\phi}^B = \sum_{k,m \neq 0} \left[\begin{aligned} & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \\ & + \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \mu_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \\ & + \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \mu_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\phi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \\ & + \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \mu_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A)} \end{aligned} \right]. \quad (103)$$

Thus the sum of all of the 1-1 terms is given by equation (104).

$$\begin{aligned}
& T_{1-1,a} + T_{1-1,b} + T_{1-1,c} + T_{1-1,d} + T_{1-1,e} + T_{1-1,f} \\
& = T_{\gamma\delta} T_{\alpha\beta} T_{\varepsilon\varphi} \mu_{\delta}^{B0} \mu_{\varepsilon}^{A0} \alpha_{\gamma\alpha}^A \alpha_{\beta\varphi}^B.
\end{aligned} \tag{104}$$

We can further simplify equation (104). As shown in equation (105), the dipole on A produces a field that acts on B.

$$\underbrace{\mu_{\varepsilon}^{A0} T_{\varepsilon\varphi}}_{F_{\varphi}^A} \alpha_{\beta\varphi}^B T_{\alpha\beta} \alpha_{\gamma\alpha}^A T_{\gamma\delta} \mu_{\delta}^{B0} = F_{\varphi}^A \alpha_{\beta\varphi}^B T_{\alpha\beta} \alpha_{\gamma\alpha}^A T_{\gamma\delta} \mu_{\delta}^{B0}. \tag{105}$$

That field then induces a dipole in B as seen from equation (106).

$$\underbrace{F_{\varphi}^A \alpha_{\beta\varphi}^B}_{\mu_{\beta}^B} T_{\alpha\beta} \alpha_{\gamma\alpha}^A T_{\gamma\delta} \mu_{\delta}^{B0} = \mu_{\beta}^B T_{\alpha\beta} \alpha_{\gamma\alpha}^A T_{\gamma\delta} \mu_{\delta}^{B0}. \tag{106}$$

The induced dipole in B then generates a field that acts on A.

$$\underbrace{\mu_{\beta}^B T_{\alpha\beta} \alpha_{\gamma\alpha}^A T_{\gamma\delta} \mu_{\delta}^{B0}}_{F_{\alpha}^B} = F_{\alpha}^B \alpha_{\gamma\alpha}^A T_{\gamma\delta} \mu_{\delta}^{B0}. \tag{107}$$

The field from the induced dipole in B induces a dipole in A.

$$\underbrace{F_{\alpha}^B \alpha_{\gamma\alpha}^A}_{\mu_{\gamma}^A} T_{\gamma\delta} \mu_{\delta}^{B0} = \mu_{\gamma}^A T_{\gamma\delta} \mu_{\delta}^{B0}. \tag{108}$$

The dipole induced in A then interacts with the permanent dipole of B.

$$\underbrace{\mu_{\gamma}^A T_{\gamma\delta} \mu_{\delta}^{B0}}_{F_{\delta}^A} = F_{\delta}^A \mu_{\delta}^{B0} \tag{109}$$

This explanation of the 1-1 terms is represented in Figure 2.

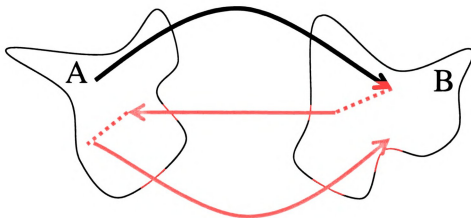


Figure 2: Representation of the 1-1 terms.
Images in this dissertation are presented in color.

The solid black line from A to B represents the field produced by the permanent dipole of A. That field induces a dipole in B, via the α -polarizability of B, as shown in dotted red lines. This induced dipole of B generates a field represented by the solid red line from B to A. This generated field influences A through the polarizability of A, as shown by dotted red lines. In turn, the induced dipole of A generates a reaction field which then acts back on B as shown by a solid red line from A to B. The same induction mechanism operates beginning with the field from the permanent dipole of B. The net contribution to the energy is $-T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\phi} \mu_{\epsilon}^{A0} \alpha_{\beta\phi}^B \alpha_{\gamma\alpha}^A \mu_{\delta}^{B0}$. This contribution to the third-order energy has been analyzed by Stogryn^{4,5} and Piecuch^{6,7,8,9}.

4.3.3 First-Order Terms in the Static Dipole of System A or B, But Not Both

The next category of nonzero terms includes the 1-0 and 0-1 terms. Listed in equations (110)-(112) are the 1-0 terms, which depend on the dipole of A to order 1 and the dipole of B to order 0.

$$T_{1-0,a} = \langle 0 | \hat{V}_1 G^B \bar{\mu}_{\alpha}^A T_{\alpha\beta} \bar{\mu}_{\beta}^B G^{A\oplus B} \hat{V}_1 | 0 \rangle. \quad (110)$$

$$T_{1-0,b} = \langle 0 | \hat{V}_1 G^{A\oplus B} \bar{\mu}_{\alpha}^A T_{\alpha\beta} \bar{\mu}_{\beta}^B G^B \hat{V}_1 | 0 \rangle. \quad (111)$$

$$T_{1-0,c} = \langle 0 | \hat{V}_1 G^{A \oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \bar{\mu}_\beta^B G^{A \oplus B} \hat{V}_1 | 0 \rangle. \quad (112)$$

If we expand and simplify equation (110), we obtain equation (113).

$$T_{1-0,a} = \langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^{A \oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\gamma^{A0} \\ \times \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\varepsilon^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\phi^B | 0_B \rangle}{(E_j^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^A)}. \quad (113)$$

We interchange ε and γ while simultaneously interchanging ϕ and δ . Then equation (113) becomes equation (114), which depends on the ε -component of the permanent dipole of system A (as above).

$$\langle 0 | \hat{V}_1 G^B \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^{A \oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\varepsilon^{A0} \\ \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\phi^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_j^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^A)}. \quad (114)$$

We know from equation (46) that we can rewrite equation (114) as equation (115), given that F is defined by equation (116).

$$\sum_{m,j,k \neq 0} \frac{F}{(E_j^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^A)} = \\ \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left[\begin{aligned} & \sum_{m,j,k \neq 0} \times \left(\frac{1}{(E_m^A - E_0^A + i\hbar\omega)} + \frac{1}{(E_m^A - E_0^A - i\hbar\omega)} \right) \\ & \times \left(\frac{1}{(E_k^B - E_0^B + i\hbar\omega)} + \frac{1}{(E_k^B - E_0^B - i\hbar\omega)} \right) \end{aligned} \right]. \quad (115)$$

$$F = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\varepsilon^{A0} \langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \\ \times \langle 0_B | \hat{\mu}_\phi^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle. \quad (116)$$

Expanding the integrand in equation (116) and then taking the first term $T_{1,115}$ of the result we obtain equation (117).

$$T_{1,115} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{m,j,k \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\varphi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_k^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B)}. \quad (117)$$

Since we have assumed that the eigenstates are real, we can rearrange the numerator to convert equation (117) into equation (118) below. First we interchange the summation indices j and k . Then we replace $\langle 0_B | \hat{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \bar{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle$ by

$\langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\varphi}^B | 0_B \rangle$, and we replace $\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle$ by

$\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle$. This gives equation (118).

$$T_{1,115} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \sum_{m,j,k \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\varphi}^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_k^B - E_0^B)}. \quad (118)$$

We can transform each term in the integrand of equation (115), so that the integrand in equation (115) is a sum of the four terms $T_{1,115}$, $T_{2,115}$, $T_{3,115}$, and $T_{4,115}$, given in equations (118)-(121).

$$T_{2,115} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{m,j,k \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\varphi}^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_k^B - E_0^B)}. \quad (119)$$

$$T_{3,115} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{m,j,k \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\varphi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_k^B - E_0^B - i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B)}. \quad (120)$$

$$T_{4,115} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \times \sum_{m,j,k \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\phi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_k^B - E_0^B - i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B)}. \quad (121)$$

The next term comes from equation (111). Expanding and simplifying, we obtain equation (122)

$$\langle 0 | \hat{V}_1 G^{A \oplus B} \bar{\mu}_{\alpha}^A T_{\alpha\beta} \bar{\mu}_{\beta}^B G^B \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \times \sum_{m,j,k \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | k_B \rangle \langle k_B | \bar{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\phi}^B | 0_B \rangle}{(E_j^B - E_0^B)(E_m^A - E_0^A + E_k^B - E_0^B)}. \quad (122)$$

Using equation (122) and following the same procedure as was used for equation (115), we can re-express the denominator in equation (122) as an integral over frequencies, where the integrand is a sum of four terms with different denominators. With appropriate relabeling of the matrix elements in the numerator, we obtain the following four equations for the terms generated from equation (122).

$$T_{1,122} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\phi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\delta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_k^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^A)} \quad (123)$$

$$T_{2,122} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\phi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\delta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_k^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^A)} \quad (124)$$

$$T_{3,122} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\phi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\delta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^A - i\hbar\omega)} \quad (125)$$

$$T_{4,122} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\delta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\phi}^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^A - i\hbar\omega)}. \quad (126)$$

The final 1-0 term comes from equation (112). Expanding and simplifying equation (112), we obtain equation (127).

$$\langle 0 | \hat{V}_1 G^{A\oplus B} \mu_{\alpha}^{A0} T_{\alpha\beta} \bar{\mu}_{\beta}^B G^{A\oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\alpha}^{A0} \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \hat{\mu}_{\phi}^B | 0_B \rangle}{(E_m^A - E_0^A + E_k^B - E_0^B)(E_m^A - E_0^A + E_j^B - E_0^A)}. \quad (127)$$

We know from the work of Craig and Thirunamachandran¹⁶ that we can represent the denominator of equation (127) by use of equation (128).

$$\frac{1}{(E_m^A - E_0^A + E_k^B - E_0^B)(E_m^A - E_0^A + E_j^B - E_0^A)} = \int_{-\infty}^{\infty} d\omega \left[\left(\frac{1}{(E_m^A - E_0^A + i\hbar\omega)} + \frac{1}{(E_m^A - E_0^A - i\hbar\omega)} \right) \times \left(\frac{1}{(E_k^B - E_0^B + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \frac{1}{(E_k^B - E_0^B - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} \right) \right]. \quad (128)$$

By reassigning Greek indices so that the result will depend on the ε -component of the permanent dipole moment of A, we obtain equation (129)

$$\langle 0 | \hat{V}_1 G^{A\oplus B} \mu_{\alpha}^{A0} T_{\alpha\beta} \bar{\mu}_{\beta}^B G^{A\oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\phi}^B | k_B \rangle \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A + E_k^B - E_0^B)(E_m^A - E_0^A + E_j^B - E_0^B)}. \quad (129)$$

Substituting equation (128) into (129) gives an integral with four frequency-dependent terms in the integrand. Rearranging the matrix elements in the numerator, we obtain the following equations for these four terms in the integrand.

$$T_{1,129} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B + i\hbar\omega)}. \quad (130)$$

$$T_{2,129} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B + i\hbar\omega)}. \quad (131)$$

$$T_{3,129} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B - i\hbar\omega)}. \quad (132)$$

$$T_{4,129} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0} \times \sum_{j,k,m \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B - i\hbar\omega)}. \quad (133)$$

If we use equations (118)-(121), (123)-(126), and (130)-(133), then for the sum of the 1-0 terms we obtain equation (134). By factoring equation (134), we obtain equation (135). Then from equations (136) and (137), we can see that equation (135) can be re-written as equation (138), which gives the contribution from the 1-0 term in terms of the imaginary frequency-dependent polarizability of A and β -hyperpolarizability of B.

$$T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\varepsilon^{A0}$$

$$\frac{\hbar}{4\pi} \times \sum_{j,k,m \neq 0} \int_{-\infty}^{\infty} d\omega \left(\begin{aligned} & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_k^B - E_0^B)} + \\ & \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_k^B - E_0^B)} + \\ & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\varphi^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_k^B - E_0^B - i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B)} + \\ & \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\varphi^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_k^B - E_0^B - i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B)} + \\ & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\varphi^B | j_B \rangle \langle j_B | \bar{\mu}_\delta^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^A)} + \\ & \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\varphi^B | j_B \rangle \langle j_B | \bar{\mu}_\delta^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_k^B - E_0^B + i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^A)} + \\ & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | j_B \rangle \langle j_B | \bar{\mu}_\delta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^A - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | j_B \rangle \langle j_B | \bar{\mu}_\delta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle}{(E_k^B - E_0^B)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^A - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\varphi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\varphi^B | k_B \rangle \langle k_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | j_B \rangle \langle j_B | \bar{\mu}_\varphi^B | k_B \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | j_B \rangle \langle j_B | \bar{\mu}_\varphi^B | k_B \rangle \langle k_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B - i\hbar\omega)} \end{aligned} \right)$$

(134)

$$T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varepsilon}^{A0}$$

$$\times \frac{\hbar}{4\pi} \sum_{j,k,m \neq 0} \int_{-\infty}^{\infty} \left(\left(\frac{\langle 0_A | \mu_{\alpha}^A | m_A \rangle \langle m_A | \mu_{\gamma}^A | 0_A \rangle}{(E_m^A - E_0^A - i\hbar\omega)} + \frac{\langle 0_A | \mu_{\gamma}^A | m_A \rangle \langle m_A | \mu_{\alpha}^A | 0_A \rangle}{(E_m^A - E_0^A + i\hbar\omega)} \right) \right. \\ \times \left(\frac{\langle 0_B | \mu_{\beta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \mu_{\delta}^B | 0_B \rangle}{(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B - i\hbar\omega)} \right. \\ + \frac{\langle 0_B | \mu_{\beta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\delta}^B | k_B \rangle \langle k_B | \mu_{\varphi}^B | 0_B \rangle}{(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B)} \\ + \frac{\langle 0_B | \mu_{\varphi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\delta}^B | k_B \rangle \langle k_B | \mu_{\beta}^B | 0_B \rangle}{(E_j^B - E_0^B)(E_k^B - E_0^B + i\hbar\omega)} \\ + \frac{\langle 0_B | \mu_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\varphi}^B | k_B \rangle \langle k_B | \mu_{\beta}^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B + i\hbar\omega)} \\ + \frac{\langle 0_B | \mu_{\varphi}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \mu_{\delta}^B | 0_B \rangle}{(E_j^B - E_0^B)(E_k^B - E_0^B - i\hbar\omega)} \\ \left. \left. + \frac{\langle 0_B | \mu_{\delta}^B | j_B \rangle \langle j_B | \bar{\mu}_{\beta}^B | k_B \rangle \langle k_B | \mu_{\varphi}^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B)} \right) \right) d\omega \quad . (135)$$

The dipole polarizability for A at the imaginary frequency $i\omega$ is given by equation (136),

$$\alpha_{\alpha\gamma}^A(i\omega) = \sum_{m \neq 0} \frac{\langle 0_A | \mu_{\alpha}^A | m_A \rangle \langle m_A | \mu_{\gamma}^A | 0_A \rangle}{(E_m^A - E_0^A - i\hbar\omega)} + \frac{\langle 0_A | \mu_{\gamma}^A | m_A \rangle \langle m_A | \mu_{\alpha}^A | 0_A \rangle}{(E_m^A - E_0^A + i\hbar\omega)}. \quad (136)$$

and the β -hyperpolarizability with $\omega_1 = i\omega$, $\omega_2 = 0$, and $\omega_{\sigma} = i\omega$ is given by equation

(137), according to Orr and Ward¹¹.

$$\beta_{\beta\delta\phi}^B(-i\omega; i\omega, 0) = \sum_{j,k \neq 0} \left(\begin{aligned} & \frac{\langle 0_B | \mu_\beta^B | j_B \rangle \langle j_B | \bar{\mu}_\phi^B | k_B \rangle \langle k_B | \mu_\delta^B | 0_B \rangle}{(E_j^B - E_0^B - i\hbar\omega)(E_k^B - E_0^B - i\hbar\omega)} \\ & + \frac{\langle 0_B | \mu_\beta^B | j_B \rangle \langle j_B | \bar{\mu}_\delta^B | k_B \rangle \langle k_B | \mu_\phi^B | 0_B \rangle}{(E_j^B - E_0^B - i\hbar\omega)(E_k^B - iE_0^B)} \\ & + \frac{\langle 0_B | \mu_\phi^B | j_B \rangle \langle j_B | \bar{\mu}_\delta^B | k_B \rangle \langle k_B | \mu_\beta^B | 0_B \rangle}{(E_j^B - E_0^B)(E_k^B - E_0^B + i\hbar\omega)} \\ & + \frac{\langle 0_B | \mu_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\phi^B | k_B \rangle \langle k_B | \mu_\beta^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B + i\hbar\omega)} \\ & + \frac{\langle 0_B | \mu_\phi^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \mu_\delta^B | 0_B \rangle}{(E_j^B - E_0^B)(E_k^B - E_0^B - i\hbar\omega)} \\ & + \frac{\langle 0_B | \mu_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \mu_\phi^B | 0_B \rangle}{(E_j^B - E_0^B + i\hbar\omega)(E_k^B - E_0^B)} \end{aligned} \right). \quad (137)$$

The net contribution to the energy from the 1-0 terms is

$$E_{1-0}^{(3)} = -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_\varepsilon^{A0} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \alpha_{\alpha\gamma}^A(i\omega) \beta_{\beta\delta\phi}^B(-i\omega; i\omega, 0) d\omega, \quad (138)$$

to third order in the interaction.

This same type of manipulation can be done in the case of the 0-1 terms to generate a term that depends on the imaginary-frequency polarizability of B and the β -hyperpolarizability of A. Listed as equations (139) – (141) are the 0-1 terms.

$$T_{0-1,a} = \langle 0 | \hat{V}_1 G^A \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1 | 0 \rangle. \quad (139)$$

$$T_{0-1,b} = \langle 0 | \hat{V}_1 G^{A\oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^A \hat{V}_1 | 0 \rangle. \quad (140)$$

$$T_{0-1,c} = \langle 0 | \hat{V}_1 G^{A\oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}_1 | 0 \rangle. \quad (141)$$

If we expand equation (139), we obtain equation (142).

$$T_{0-1,a} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\delta}^{B0} \\ \times \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\varphi}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A + E_j^B - E_0^B)} \quad (142)$$

By reassigning Greek indices so that the expression depends on the φ -component of the permanent dipole of system B in equation (142), we obtain equation (143).

$$T_{0-1,a} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B \\ \times \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A + E_j^B - E_0^B)} \quad (143)$$

Using the same relation as in equation (115), the denominator can be rewritten as in equation (144).

$$\frac{1}{(E_m^A - E_0^A)(E_n^A - E_0^A + E_j^B - E_0^B)} = \\ \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{1}{(E_m^A - E_0^A)} \times \left[\frac{1}{(E_n^A - E_0^A + i\hbar\omega)} + \frac{1}{(E_n^A - E_0^A - i\hbar\omega)} \right] \right. \\ \left. \times \left[\frac{1}{(E_j^B - E_0^B + i\hbar\omega)} + \frac{1}{(E_j^B - E_0^B - i\hbar\omega)} \right] \right) \quad (144)$$

Beginning with equations (143) and (144), we can rearrange the numerator to generate equations (145)-(148), with the assumption that the dipole matrix elements are real.

$$T_{0-1,a1} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B \\ \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} \quad (145)$$

$$T_{0-1,a2} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)}. \quad (146)$$

$$T_{0-1,a3} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)}. \quad (147)$$

$$T_{0-1,a4} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)}. \quad (148)$$

$T_{0-1,b}$ in equation (140) becomes the sum of terms in equations (149)-(152), after expanding, simplifying, and substituting for the denominator and rearranging the numerator.

$$T_{0-1,b1} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)}. \quad (149)$$

$$T_{0-1,b2} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)}. \quad (150)$$

$$T_{0-1,b3} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)}. \quad (151)$$

$$T_{0-1,b4} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_{\varphi}^B$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)}. \quad (152)$$

After expansion, the last 0-1 term, $T_{0-1,c}$ from equation (141), is given by equation (153).

$$T_{0-1,c} = \langle 0 | \hat{V}_1 G^{A \oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A \oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\varphi^{B0} \\ \times \sum_{m,n,j \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \bar{\mu}_\varepsilon^A | n_A \rangle \langle n_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_m^A - E_0^A + E_j^B - E_0^B)(E_n^A - E_0^A + E_j^B - E_0^B)}. \quad (153)$$

We can use equation (154) to replace the energy denominator in equation (153).

$$\frac{1}{(E_m^A - E_0^A + E_j^B - E_0^B)(E_n^A - E_0^A + E_j^B - E_0^B)} = \\ \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\left(\frac{1}{(E_m^A - E_0^A + i\hbar\omega)(E_n^A - E_0^A + i\hbar\omega)} \right) + \frac{1}{(E_m^A - E_0^A - i\hbar\omega)(E_n^A - E_0^A - i\hbar\omega)} \right) \\ \times \left(\frac{1}{(E_j^B - E_0^B + i\hbar\omega)} + \frac{1}{(E_j^B - E_0^B - i\hbar\omega)} \right). \quad (154)$$

Then we can rearrange each of the terms and obtain $T_{0-1,c}$ as a sum of four terms ($T_{0-1,c1}$ to $T_{0-1,c4}$) given in the following four equations:

$$T_{0-1,c1} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\varphi^{B0} \\ \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \bar{\mu}_\varepsilon^A | n_A \rangle \langle n_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_n^A - E_0^A + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)}. \quad (155)$$

$$T_{0-1,c2} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\varphi^{B0} \\ \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \bar{\mu}_\varepsilon^A | n_A \rangle \langle n_A | \hat{\mu}_\alpha^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_n^A - E_0^A + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)}. \quad (156)$$

$$T_{0-1,c3} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \mu_\varphi^{B0} \\ \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \bar{\mu}_\varepsilon^A | n_A \rangle \langle n_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \hat{\mu}_\beta^B | 0_B \rangle}{(E_n^A - E_0^A - i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)}. \quad (157)$$

$$T_{0-1,c4} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\phi}^{B0} \\ \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\varepsilon}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_n^A - E_0^A - i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)}. \quad (158)$$

Summing the terms in equations (145)-(148), (149)-(152), and (155)-(158), we obtain the net T_{0-1} term given in equation (159).

$$T_{0-1} = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\phi}^{B0}$$

$$\times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \sum_{j,m,n \neq 0} \left(\begin{aligned} & \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\alpha}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\varepsilon}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_m^A - E_0^A)(E_n^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\gamma}^A | n_A \rangle \langle n_A | \hat{\mu}_{\varepsilon}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_n^A - E_0^A)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\varepsilon}^A | n_A \rangle \langle n_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\gamma}^A | m_A \rangle \langle m_A | \bar{\mu}_{\varepsilon}^A | n_A \rangle \langle n_A | \hat{\mu}_{\alpha}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_n^A - E_0^A + i\hbar\omega)(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\varepsilon}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\delta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\beta}^B | 0_B \rangle}{(E_n^A - E_0^A - i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} + \\ & \frac{\langle 0_A | \hat{\mu}_{\alpha}^A | m_A \rangle \langle m_A | \bar{\mu}_{\varepsilon}^A | n_A \rangle \langle n_A | \hat{\mu}_{\gamma}^A | 0_A \rangle \langle 0_B | \hat{\mu}_{\beta}^B | j_B \rangle \langle j_B | \hat{\mu}_{\delta}^B | 0_B \rangle}{(E_n^A - E_0^A - i\hbar\omega)(E_m^A - E_0^A - i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} \end{aligned} \right). \quad (159)$$

Factoring and substituting the definition of the imaginary-frequency dependent polarizability of B and β -hyperpolarizability of A, we obtain equation (160) for the 0-1 term in the third-order energy.

$$E_{0-1}^{(3)} = -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\phi}^{B0} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \beta_{\alpha\gamma\varepsilon}^A(-i\omega; i\omega, 0) \alpha_{\beta\delta}^B(i\omega) d\omega. \quad (160)$$

Figure 3 represents the 1-0 term. System A sets up a fluctuating field represented by the two red dashed lines and a static field due to its permanent dipole moment. B responds nonlinearly to the fields from A through its frequency-dependent β -hyperpolarizability, as represented by the green dotted lines.

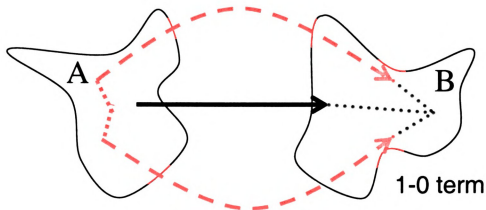


Figure 3: Representation of the 1-0 term in the Third-Order Energy.
Images in this dissertation are presented in color.

4.3.4 Zero-Order Term in the Static Dipole Moments of Systems A and B.

The final third-order term is the nonzero 0-0 term, listed in equation (161).

$$T_{0-0} = \langle 0 | \hat{V}_1 G^{A\oplus B} \bar{\mu}_a^A T_{\alpha\beta} \bar{\mu}_\beta^B G^{A\oplus B} \hat{V}_1 | 0 \rangle. \quad (161)$$

Expanding equation (161), we get equation (162).

$$\begin{aligned}
T_{0-0} &= \langle 0 | \hat{V}_1 G^{A \oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^{A \oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \\
&\times \sum_{j,k,m,n \neq 0} \left(\frac{1}{(E_m^A - E_0^A + E_j^B - E_0^B)} \right) \left(\frac{1}{(E_n^A - E_0^A + E_k^B - E_0^B)} \right) \\
&\times \langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \bar{\mu}_\alpha^A | n_A \rangle \langle n_A | \hat{\mu}_\varepsilon^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle.
\end{aligned} \tag{162}$$

If we use the analog of equation (46), then the energy denominator can be represented as the form given in equation (163).

$$\begin{aligned}
&\left(\frac{1}{(E_m^A - E_0^A + E_j^B - E_0^B)} \right) \left(\frac{1}{(E_n^A - E_0^A + E_k^B - E_0^B)} \right) = \\
&\left(\frac{\hbar}{4\pi} \right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left[\left(\frac{1}{(E_m^A - E_0^A + i\hbar\omega)} + \frac{1}{(E_m^A - E_0^A - i\hbar\omega)} \right) \times \right. \\
&\left. \left(\frac{1}{(E_n^A - E_0^A + i\hbar\omega')} + \frac{1}{(E_n^A - E_0^A - i\hbar\omega')} \right) \times \right. \\
&\left. \left(\frac{1}{(E_j^B - E_0^B + i\hbar\omega)} + \frac{1}{(E_j^B - E_0^B - i\hbar\omega)} \right) \times \right. \\
&\left. \left(\frac{1}{(E_k^B - E_0^B + i\hbar\omega')} + \frac{1}{(E_k^B - E_0^B - i\hbar\omega')} \right) \right].
\end{aligned} \tag{163}$$

Using equation (164), we can rearrange equation (163) into equation (165).

$$\int_{-\infty}^{\infty} [f(x) + f(-x)] dx = 2 \int_{-\infty}^{\infty} f(x) dx. \tag{164}$$

$$\begin{aligned}
& \left(\frac{1}{(E_m^A - E_0^A + E_j^B - E_0^B)} \right) \left(\frac{1}{(E_n^A - E_0^A + E_k^B - E_0^B)} \right) = \left(\frac{\hbar}{2\pi} \right)^2 \\
& \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left[\left(\frac{1}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} \right) \right. \\
& \quad \left. + \frac{1}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} \right) \\
& \quad \times \left(\frac{1}{(E_n^A - E_0^A + i\hbar\omega')(E_k^B - E_0^B + i\hbar\omega')} \right) \\
& \quad \left. + \frac{1}{(E_n^A - E_0^A + i\hbar\omega')(E_k^B - E_0^B - i\hbar\omega')} \right) \Bigg] . \tag{165}
\end{aligned}$$

By use of equation (165), we obtain equation (166).

$$\begin{aligned}
T_{0-0} &= T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \left(\frac{\hbar}{2\pi} \right)^2 \\
& \times \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \sum_{j,k,m,n \neq 0} \left[\left(\frac{1}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B + i\hbar\omega)} \right) \right. \\
& \quad \left. + \frac{1}{(E_m^A - E_0^A + i\hbar\omega)(E_j^B - E_0^B - i\hbar\omega)} \right) \\
& \quad \times \left(\frac{1}{(E_n^A - E_0^A + i\hbar\omega')(E_k^B - E_0^B + i\hbar\omega')} \right) \\
& \quad \left. + \frac{1}{(E_n^A - E_0^A + i\hbar\omega')(E_k^B - E_0^B - i\hbar\omega')} \right) \\
& \quad \times \langle 0_A | \hat{\mu}_\gamma^A | m_A \rangle \langle m_A | \bar{\mu}_\alpha^A | n_A \rangle \langle n_A | \hat{\mu}_\varepsilon^A | 0_A \rangle \\
& \quad \times \langle 0_B | \hat{\mu}_\delta^B | j_B \rangle \langle j_B | \bar{\mu}_\beta^B | k_B \rangle \langle k_B | \hat{\mu}_\varphi^B | 0_B \rangle \Bigg] . \tag{166}
\end{aligned}$$

Equation (166) can be rewritten as equation (167), where the b tensor elements are given by equation (168).

$$\begin{aligned}
T_{0-0} &= \langle 0 | \hat{V}_1 G^{A \oplus B} \bar{\mu}_\alpha^A T_{\alpha\beta} \bar{\mu}_\beta^B G^{A \oplus B} \hat{V}_1 | 0 \rangle = T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\varphi} \\
& \times \left(\frac{\hbar}{2\pi} \right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left(\begin{aligned} & \left[b_{\gamma\alpha\varepsilon}^A(i\omega; -i\omega - i\omega', i\omega') + b_{\gamma\alpha\varepsilon}^A(i\omega; -i\omega + i\omega', -i\omega') \right] \\ & \times \left[b_{\delta\beta\varphi}^B(i\omega; -i\omega - i\omega', i\omega') + b_{\delta\beta\varphi}^B(-i\omega; i\omega - i\omega', i\omega') \right] \end{aligned} \right) . \tag{167}
\end{aligned}$$

$$b_{\alpha\gamma\beta}^A(-(\omega_1 + \omega_2); \omega_2, \omega_1) = \sum_{m,n \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | n_A \rangle \langle n_A | \hat{\mu}_\beta^A | 0_A \rangle}{(E_m^A - E_0^A - \hbar(\omega_1 + \omega_2))(E_n^A - E_0^A - \hbar\omega_1)}. \quad (168)$$

The result in equation (167) is new. It gives the third-order pure dispersion energy as a double integral over imaginary frequencies, since $E_{0-0}^{(3)} = -T_{0-0}$. Figure 4 shows a graphical representation of the 0-0 term. Both A and B are mutually polarized by each other through specific terms in the frequency-dependent hyperpolarizability.

This interaction energy is a nonlinear analog of the second-order van der Waals dispersion energy. A fluctuation in the charge density of molecule A polarizes B nonlinearly, via β , inducing a fluctuating charge in B. The field from the fluctuating charge in B acts on A, shifting the energy of A in a way that depends on the β -hyperpolarizability of A, because it depends on the correlation of the original fluctuation in the charge density of A and the nonlinear response to the field from B. There is a corresponding contribution to the energy with the roles of A and B reversed. Equation (167) provides an efficient means of computing the third-order dispersion energy for various A-B pairs.

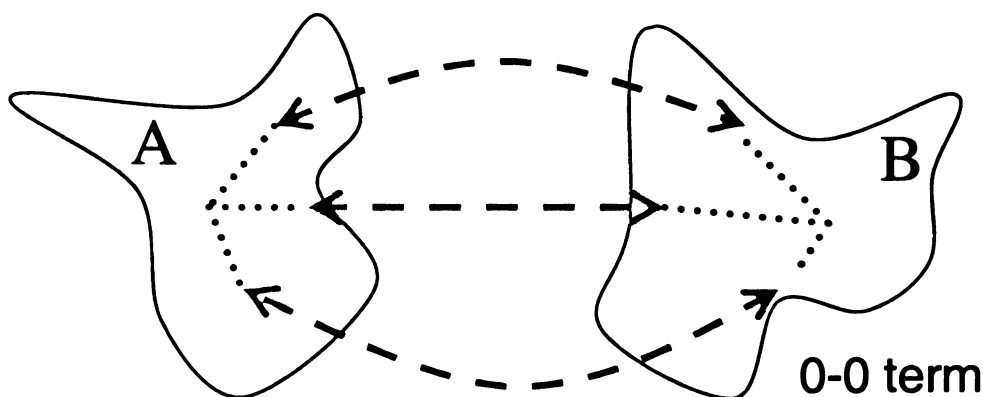


Figure 4: Representation of the Third-Order Pure Dispersion Energy.
Images in this dissertation are presented in color.

The effects of higher-multipole interactions can be derived by replacing the dipole operators with polarization density operators, replacing the dipole propagators $T_{\alpha\beta}$ with point-to-point dipole propagators $T_{\alpha\beta}(r, r')$, and then Taylor-expanding about the vectors R_A and R_B as origins of the spatial variables.

4.4 Numerical Estimates

Although the derivation of the third-order interaction energy provides insight into the types of interactions that occur at third order, estimates of the magnitude of these interactions will aid in their interpretation. To determine rough, approximate values of the third-order terms, we have assumed that all excitation energies are approximately equal to the ionization potential. This approximation allows us to simplify the perturbation expressions and find numerical values for the frequency-dependent polarizability and hyperpolarizability. The definition of the static polarizability is shown in equation (169).

$$\alpha_{\alpha\beta} = \sum_{k \neq 0} \frac{\langle 0 | \mu_\alpha | k \rangle \langle k | \mu_\beta | 0 \rangle}{(E_k - E_0)} + \frac{\langle 0 | \mu_\beta | k \rangle \langle k | \mu_\alpha | 0 \rangle}{(E_k - E_0)}. \quad (169)$$

Since the eigenstates are real, $\langle 0 | \mu_\alpha | k \rangle \langle k | \mu_\beta | 0 \rangle = \langle 0 | \mu_\beta | k \rangle \langle k | \mu_\alpha | 0 \rangle$. We are assuming

all excitation energies are approximately equal to the ionization potential,

$(E_k - E_0) \approx \text{Ionization Potential (IP)}$. Then, we solve for the sum of the matrix elements as shown in equation (170).

$$\sum_{k \neq 0} \langle 0 | \mu_\alpha | k \rangle \langle k | \mu_\beta | 0 \rangle = \frac{\alpha_{\alpha\beta}}{2} \text{IP}. \quad (170)$$

Equation (171) gives the frequency-dependent polarizability. Now that we have solved for the sum of the matrix elements in the static polarizability, we can use those results to approximate the numerical value of the imaginary-frequency dependent polarizability.

$$\alpha_{\alpha\beta}(i\omega) = \left(\frac{1}{IP + i\omega} + \frac{1}{IP - i\omega} \right) \sum_{k \neq 0} \langle 0 | \mu_\alpha | k \rangle \langle k | \mu_\beta | 0 \rangle. \quad (171)$$

Substituting in the expression for the sum of the matrix elements, we have equation (172).

$$\alpha_{\alpha\beta}(i\omega) = \frac{\alpha_{\alpha\beta}}{2} IP \left(\frac{1}{IP + i\omega} + \frac{1}{IP - i\omega} \right) = \frac{\alpha_{\alpha\beta} IP^2}{IP^2 + \omega^2}. \quad (172)$$

The same method can be used to find a numerical value for the frequency-dependent hyperpolarizability. Starting with the static hyperpolarizability in equation (173), we can again solve for the sum of the matrix elements.

$$\beta_{\alpha\beta\gamma} = \sum_{j,k \neq 0} \left[\frac{\langle 0 | \mu_\alpha | j \rangle \langle j | \bar{\mu}_\beta | k \rangle \langle k | \hat{\mu}_\gamma | 0 \rangle}{(E_j - E_0)(E_k - E_0)} + \frac{\langle 0 | \mu_\gamma | j \rangle \langle j | \bar{\mu}_\beta | k \rangle \langle k | \hat{\mu}_\alpha | 0 \rangle}{(E_j - E_0)(E_k - E_0)} \right. \\ \left. + \frac{\langle 0 | \mu_\beta | j \rangle \langle j | \bar{\mu}_\alpha | k \rangle \langle k | \hat{\mu}_\gamma | 0 \rangle}{(E_j - E_0)(E_k - E_0)} + \frac{\langle 0 | \mu_\gamma | j \rangle \langle j | \bar{\mu}_\alpha | k \rangle \langle k | \hat{\mu}_\beta | 0 \rangle}{(E_j - E_0)(E_k - E_0)} \right. \\ \left. + \frac{\langle 0 | \mu_\alpha | j \rangle \langle j | \bar{\mu}_\gamma | k \rangle \langle k | \hat{\mu}_\beta | 0 \rangle}{(E_j - E_0)(E_k - E_0)} + \frac{\langle 0 | \mu_\beta | j \rangle \langle j | \bar{\mu}_\gamma | k \rangle \langle k | \hat{\mu}_\alpha | 0 \rangle}{(E_j - E_0)(E_k - E_0)} \right]. \quad (173)$$

Because the eigenstates are assumed to be real, we can equate pairs of matrix elements.

$$\beta_{\alpha\beta\gamma} = \frac{2}{IP^2} \sum_{k,j \neq 0} \left[\begin{aligned} &\langle 0 | \mu_\alpha | j \rangle \langle j | \bar{\mu}_\beta | k \rangle \langle k | \hat{\mu}_\gamma | 0 \rangle \\ &+ \langle 0 | \mu_\gamma | j \rangle \langle j | \bar{\mu}_\alpha | k \rangle \langle k | \hat{\mu}_\beta | 0 \rangle \\ &+ \langle 0 | \mu_\beta | j \rangle \langle j | \bar{\mu}_\gamma | k \rangle \langle k | \hat{\mu}_\alpha | 0 \rangle \end{aligned} \right]. \quad (174)$$

Then if $\bar{C}_{\alpha\beta\gamma}$ denotes the operator that takes the average of cyclic permutations of α , β , and γ in the expression that follows, we obtain equation (175).

$$\bar{C}_{\alpha\beta\gamma} \sum_{j,k \neq 0} \langle 0 | \mu_\alpha | j \rangle \langle j | \bar{\mu}_\beta | k \rangle \langle k | \hat{\mu}_\gamma | 0 \rangle = \frac{\beta_{\alpha\beta\gamma}}{6} IP^2. \quad (175)$$

Equation (176) gives the frequency-dependent hyperpolarizability¹¹.

$$\beta_{\alpha\beta\gamma}(-(\omega_1 + \omega_2), \omega_1, \omega_2) = \sum_{j,k \neq 0} \left(\begin{aligned} & \frac{\langle 0|\mu_\alpha|j\rangle\langle j|\bar{\mu}_\beta|k\rangle\langle k|\hat{\mu}_\gamma|0\rangle}{(E_j - E_0 - \hbar(\omega_1 + \omega_2))(E_k - E_0 - \hbar\omega_2)} \\ & + \frac{\langle 0|\mu_\gamma|j\rangle\langle j|\bar{\mu}_\beta|k\rangle\langle k|\hat{\mu}_\alpha|0\rangle}{(E_j - E_0 + \hbar\omega_2)(E_k - E_0 + \hbar(\omega_1 + \omega_2))} \\ & + \frac{\langle 0|\mu_\beta|j\rangle\langle j|\bar{\mu}_\alpha|k\rangle\langle k|\hat{\mu}_\gamma|0\rangle}{(E_j - E_0 + \hbar\omega_1)(E_k - E_0 - \hbar\omega_2)} \\ & + \frac{\langle 0|\mu_\gamma|j\rangle\langle j|\bar{\mu}_\alpha|k\rangle\langle k|\hat{\mu}_\beta|0\rangle}{(E_j - E_0 + \hbar\omega_2)(E_k - E_0 - \hbar\omega_1)} \\ & + \frac{\langle 0|\mu_\alpha|j\rangle\langle j|\bar{\mu}_\gamma|k\rangle\langle k|\hat{\mu}_\beta|0\rangle}{(E_j - E_0 - \hbar(\omega_1 + \omega_2))(E_k - E_0 - \hbar\omega_1)} \\ & + \frac{\langle 0|\mu_\beta|j\rangle\langle j|\bar{\mu}_\gamma|k\rangle\langle k|\hat{\mu}_\alpha|0\rangle}{(E_j - E_0 + \hbar\omega_1)(E_k - E_0 + \hbar(\omega_1 + \omega_2))} \end{aligned} \right). \quad (176)$$

We use equation (175) and also approximate each sum of the form

$\sum_{j,k \neq 0} \langle 0|\mu_\alpha|j\rangle\langle j|\bar{\mu}_\beta|k\rangle\langle k|\hat{\mu}_\gamma|0\rangle$ by the average over the cyclic permutations of Greek

subscripts. Approximating the excitation energies by the ionization potential (as above)

gives equation (177), in units with $\hbar = 1$.

$$\beta_{\alpha\beta\gamma}(-(\omega_1 + \omega_2), \omega_1, \omega_2) = \frac{\beta_{\alpha\beta\gamma}}{3} \text{IP}^2 \left(\frac{3\text{IP}^4 - \text{IP}^2(\omega_1^2 + \omega_2^2 + \omega_1\omega_2)}{(\text{IP}^2 - (\omega_1 + \omega_2)^2)(\text{IP}^2 - \omega_1^2)(\text{IP}^2 - \omega_2^2)} \right). \quad (177)$$

Equation (178) gives the approximation for the specific β -hyperpolarizability needed in this study.

$$\beta_{\alpha\beta\gamma}(-i\omega; i\omega, 0) = \frac{\beta_{\alpha\beta\gamma}}{3} \left(\frac{3\text{IP}^4 + \text{IP}^2\omega^2}{(\text{IP}^2 + \omega^2)^2} \right). \quad (178)$$

As for the b tensors, a generic approximation is shown in equation (179).

$$b(-i\omega; (i\omega' - i\omega), -i\omega') = \frac{\beta_{\alpha\beta\gamma}\text{IP}^2}{6(\text{IP} + i\omega)(\text{IP} + i\omega')}. \quad (179)$$

The specific frequency-dependent b tensors needed in this work are approximated in equations (180)-(183).

$$b(i\omega; (i\omega' - i\omega), -i\omega') = \frac{\beta_{\alpha\beta\gamma} IP^2}{6(IP + i\omega)(IP + i\omega')}. \quad (180)$$

$$b(i\omega; (-i\omega' - i\omega), i\omega') = \frac{\beta_{\alpha\beta\gamma} IP^2}{6(IP + i\omega)(IP - i\omega')}. \quad (181)$$

$$b(-i\omega; (i\omega' + i\omega), -i\omega') = \frac{\beta_{\alpha\beta\gamma} IP^2}{6(IP - i\omega)(IP + i\omega')}. \quad (182)$$

$$b(-i\omega; (-i\omega' + i\omega), i\omega') = \frac{\beta_{\alpha\beta\gamma} IP^2}{6(IP - i\omega)(IP - i\omega')}. \quad (183)$$

Equation (51) gives the known result for the second-order energy correction.

Equation (184) approximates the second-order energy correction in terms of quantities that are more readily available.

$$E_0^{(2)} = -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \left(\begin{array}{l} \mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \alpha_{\beta\delta}^B \\ + \mu_{\beta}^{B0} \mu_{\delta}^{B0} \alpha_{\alpha\gamma}^A \\ + \frac{\hbar}{2\pi} \alpha_{\alpha\gamma}^A \alpha_{\beta\delta}^B IP_A^2 IP_B^2 \int_{-\infty}^{\infty} \frac{1}{(IP_A^2 + \omega^2)(IP_B^2 + \omega^2)} d\omega \end{array} \right). \quad (184)$$

Now we will approximate the third-order energy in terms of readily available quantities. The classical contribution to the third-order energy is the sum of the 3-0, 0-3, and 1-1 terms, given in equation (185).

$$\begin{aligned} E_{\text{class}}^{(3)} = & -\frac{1}{6} T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\phi} \mu_{\beta}^{B0} \mu_{\delta}^{B0} \mu_{\phi}^{B0} \beta_{\alpha\gamma\epsilon}^A \\ & -\frac{1}{6} \mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \mu_{\epsilon}^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\phi} \beta_{\beta\delta\phi}^B \\ & -\mu_{\delta}^{B0} \mu_{\epsilon}^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\phi} \alpha_{\gamma\alpha}^A \alpha_{\beta\phi}^B. \end{aligned} \quad (185)$$

The non-classical contribution to the third-order energy is the sum of the 1-0, 0-1, and 0-0, terms, given in equation (186).

$$\begin{aligned}
E_{\text{nonclassical}}^{(3)} = & -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \alpha_{\alpha\gamma}^A(i\omega) \beta_{\beta\delta\phi}^B(-i\omega, i\omega, 0) \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\phi}^{B0} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \beta_{\alpha\gamma\varepsilon}^A(-i\omega, i\omega, 0) \alpha_{\beta\delta}^B(i\omega) \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \\
& \times \left(\frac{\hbar}{2\pi} \right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left(\begin{aligned} & \left[b_{\gamma\alpha\varepsilon}^A(i\omega; -i\omega - i\omega', i\omega') + b_{\gamma\alpha\varepsilon}^A(i\omega; -i\omega + i\omega', -i\omega') \right] \\ & \times \left[b_{\delta\beta\phi}^B(i\omega; -i\omega - i\omega', i\omega') + b_{\delta\beta\phi}^B(-i\omega; i\omega - i\omega', i\omega') \right] \end{aligned} \right)
\end{aligned} \tag{186}$$

This includes both induction-dispersion effects (the first two terms) in equation (186) and pure dispersion effects (the last term). Substituting the approximations converts equation (186) into equation (187).

$$\begin{aligned}
E_{\text{nonclassical}}^{(3)} = & -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \frac{\alpha_{\alpha\gamma}^A \beta_{\beta\delta\phi}^B}{3} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{3IP_B^4 + IP_B^2 \omega^2}{(IP_B^2 + \omega^2)^2} \right) \frac{IP_A^2}{IP_A^2 + \omega^2} \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\phi}^{B0} \frac{\alpha_{\beta\delta}^B \beta_{\alpha\gamma\varepsilon}^A}{3} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{3IP_A^4 + IP_A^2 \omega^2}{(IP_A^2 + \omega^2)^2} \right) \frac{IP_B^2}{IP_B^2 + \omega^2} \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \left(\frac{\beta_{\alpha\gamma\varepsilon}^A IP_A^2}{6} \right) \left(\frac{\beta_{\delta\beta\phi}^B IP_B^2}{6} \right) \\
& \times \left(\frac{\hbar}{2\pi} \right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left(\begin{aligned} & \left[\frac{1}{(IP_A + i\omega)(IP_A - i\omega')} + \frac{1}{(IP_A + i\omega)(IP_A + i\omega')} \right] \\ & \times \left[\frac{1}{(IP_B + i\omega)(IP_B - i\omega')} + \frac{1}{(IP_B - i\omega)(IP_B - i\omega')} \right] \end{aligned} \right)
\end{aligned} \tag{187}$$

Therefore, the total third-order energy is approximated by equation (188).

$$\begin{aligned}
E^{(3)} = & -\frac{1}{6} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\beta}^{B0} \mu_{\delta}^{B0} \mu_{\phi}^{B0} \beta_{\alpha\gamma\varepsilon}^A \\
& -\frac{1}{6} \mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \mu_{\varepsilon}^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \beta_{\beta\delta\phi}^B \\
& -\mu_{\delta}^{B0} \mu_{\varepsilon}^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \alpha_{\gamma\alpha}^A \alpha_{\beta\phi}^B \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\varepsilon}^{A0} \frac{\alpha_{\alpha\gamma}^A \beta_{\beta\delta\phi}^B}{3} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{3IP_B^4 + IP_B^2 \omega^2}{(IP_B^2 + \omega^2)^2} \right) \frac{IP_A^2}{IP_A^2 + \omega^2} \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \mu_{\phi}^{B0} \frac{\alpha_{\beta\delta}^B \beta_{\alpha\gamma\varepsilon}^A}{3} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{3IP_A^4 + IP_A^2 \omega^2}{(IP_A^2 + \omega^2)^2} \right) \frac{IP_B^2}{IP_B^2 + \omega^2} \\
& -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \left(\frac{\beta_{\alpha\gamma\varepsilon}^A IP_A^2}{6} \right) \left(\frac{\beta_{\delta\beta\phi}^B IP_B^2}{6} \right) \\
& \times \left(\frac{\hbar}{2\pi} \right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left(\left[\frac{1}{(IP_A + i\omega)(IP_A - i\omega')} + \frac{1}{(IP_A + i\omega)(IP_A + i\omega')} \right] \right. \\
& \left. \times \left[\frac{1}{(IP_B + i\omega)(IP_B - i\omega')} + \frac{1}{(IP_B - i\omega)(IP_B - i\omega')} \right] \right). \quad (188)
\end{aligned}$$

Equation (188) gives a general approximation for the third-order interaction energy.

4.4.1 HCl Dimer

Using the HCl dimer as an example, we compare the two-body third-order interaction energy to the two-body second-order interaction energy for two specific geometrical configurations. The first is a configuration in which the centers of mass of both HCl molecules lie on the Z-axis and the internuclear axes of both molecules run parallel to the Z-axis. This configuration is shown in Figure (5).

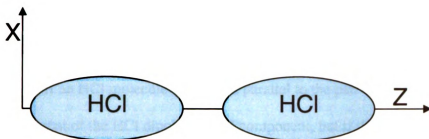


Figure 5: First Configuration of the HCl Dimer
Images in this dissertation are presented in color.

The second configuration has the centers of mass of the two molecules remaining on the Z-axis, with both of the HCl molecules rotated 90 degrees, so that the dipole moments of the molecules are parallel to each other and perpendicular to the Z-axis, as shown in Figure (6).

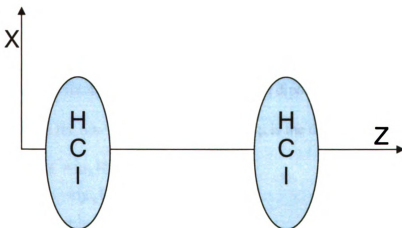


Figure 6: Second Configuration of the HCl Dimer
Images in this dissertation are presented in color.

There are two sets of coordinate systems involved in these configurations. The first is the laboratory coordinate system. In Figures 5 and 6, the Z-axis vector of the lab frame points from the center of mass of the first HCl molecule to the center of mass of the second HCl molecule. The dipole propagator $T_{\alpha\beta}$ and higher-order T tensors are written in the laboratory coordinate system. In addition to the laboratory coordinate

system, there is a molecular coordinate system for each of the two HCl molecules. The Z-axis of the molecular coordinate system lies along the bond.

If an HCl molecule is oriented parallel to the pair-fixed Z-axis, the only nonzero component of the HCl dipole is the Z component, but if the molecule is rotated in the plane defined by the pair-fixed X- and Z-axes, the dipole has both Z and X components. It is not until the molecule has rotated 90 degrees that the dipole of HCl has only an X component. A rotation matrix is needed to calculate all of the components of the dipole if the molecule is not oriented parallel to an axis in the pair-fixed frame. This rotation matrix, R , is shown in equation (189) where Θ is the angle of rotation.

$$R = \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} = \begin{pmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{pmatrix}. \quad (189)$$

Using this rotation matrix, one can find the dipole from equation (190), where μ' is the dipole in the new coordinate system and μ is the dipole in the old coordinate system.

$$\begin{aligned} \mu' = & (\mu_x R_{xx} + \mu_y R_{yx} + \mu_z R_{zx})x' \\ & + (\mu_x R_{xy} + \mu_y R_{yy} + \mu_z R_{zy})y' \\ & + (\mu_x R_{xz} + \mu_y R_{yz} + \mu_z R_{zz})z'. \end{aligned} \quad (190)$$

(The primes are the new coordinate system.)

such that

$$\mu' = -\sin(\theta)\mu_z x' + 0y' + \cos(\theta)\mu_z z'.$$

Note: In this situation the old coordinate system is the molecular frame's coordinate system, the new system is the lab frame, and Θ is negative.

Again, if the HCl molecule lies parallel to the Z-axis, then the nonzero components of the polarizability are α_{xx} , α_{yy} , and α_{zz} . Due to the symmetry of the HCl molecule, $\alpha_{xx} = \alpha_{yy}$.

In addition, the nonzero components of the hyperpolarizability are β_{zzz} , β_{xxz} , β_{xzx} , β_{zxx} , β_{yyz} , β_{yzy} , and β_{zyy} . Also due to the symmetry of the HCl molecule, $\beta_{xxz} = \beta_{xzx} = \beta_{zxx} = \beta_{yyz} = \beta_{yzy} = \beta_{zyy}$. As the molecule rotates, the components of the polarizability and hyperpolarizability change as well. The components of the polarizability in the new coordinate system are given by equation (191), where the Greek indices refer to Cartesian coordinates.

$$\alpha'_{\alpha'\beta'} = \alpha_{\alpha\beta} R_{\alpha\alpha'} R_{\beta\beta'} . \quad (191)$$

The hyperpolarizability transforms under rotation as described by equation (192).

$$\beta'_{\alpha'\beta'\gamma'} = \beta_{\alpha\beta\gamma} R_{\alpha\alpha'} R_{\beta\beta'} R_{\gamma\gamma'} . \quad (192)$$

Referring back to the laboratory coordinate system, if the arrangement of the centers of mass changes, the dipole propagators change as well. For example, in Figure (7), one of the HCl molecules has been moved off the laboratory Z-axis. The dipole propagators in this case are shown in equations (193)-(198), where φ is the angle that the vector between HCl molecules makes with the Z-axis and R is the distance between the centers of mass of the two molecules.

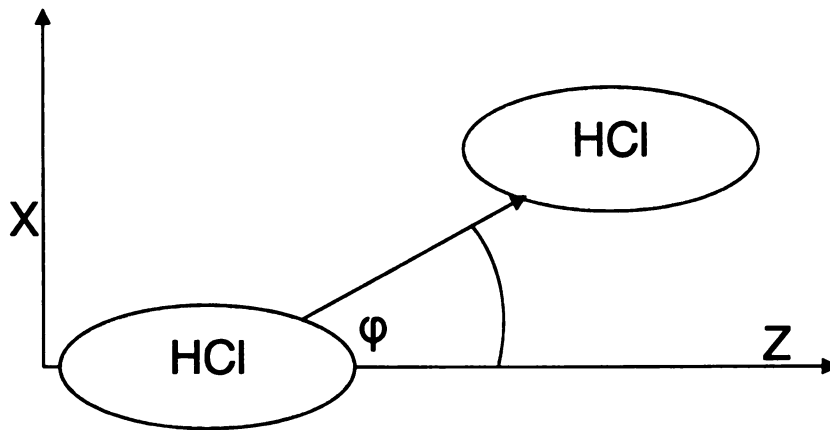


Figure 7: Third Configuration of the HCl Dimer.
Images in this dissertation are presented in color.

$$T_{xx}(R, \varphi) = \frac{3\sin^2(\varphi) - 1}{R^3}. \quad (193)$$

$$T_{xy} = T_{yx} = 0. \quad (194)$$

$$T_{xz}(R, \varphi) = T_{zx}(R, \varphi) = \frac{3\cos(\varphi)\sin(\varphi)}{R^3}. \quad (195)$$

$$T_{yy}(R) = -\frac{1}{R^3}. \quad (196)$$

$$T_{yz} = T_{zy} = 0. \quad (197)$$

$$T_{zz}(R, \varphi) = \frac{3\cos^2(\varphi) - 1}{R^3}. \quad (198)$$

4.4.1.1 Second-Order Two-Body Terms

Recall from the previous section that the second-order interaction energy for two bodies is approximated by equation (199).

$$E_0^{(2)} = -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \left(\begin{array}{l} \mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \alpha_{\beta\delta}^B \\ + \mu_{\beta}^{B0} \mu_{\delta}^{B0} \alpha_{\alpha\gamma}^A \\ + \frac{\hbar}{2\pi} \alpha_{\alpha\gamma}^A \alpha_{\beta\delta}^B IP_A^2 IP_B^2 \int_{-\infty}^{\infty} \frac{1}{(IP_A^2 + \omega^2)(IP_B^2 + \omega^2)} d\omega \end{array} \right). \quad (199)$$

The second-order two-body interaction energy is a sum of a classical induction effect given by equation (200) and a dispersion effect approximated by equation (201). The notation $E^{(m,n)}$ is used for the mth-order interaction energy for n bodies.

$$E_{\text{classical}}^{(2,2)} = -\frac{1}{2} T_{\alpha\beta} T_{\gamma\delta} \left(\mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \alpha_{\beta\delta}^B + \mu_{\beta}^{B0} \mu_{\delta}^{B0} \alpha_{\alpha\gamma}^A \right) \quad (200)$$

$$E_{\text{dispersion}}^{(2,2)} = -T_{\alpha\beta} T_{\gamma\delta} \frac{\hbar}{4\pi} \alpha_{\alpha\gamma}^A \alpha_{\beta\delta}^B IP_A^2 IP_B^2 \int_{-\infty}^{\infty} \frac{1}{(IP_A^2 + \omega^2)(IP_B^2 + \omega^2)} d\omega. \quad (201)$$

We have used Mathematica 4.0 to evaluate the expressions in equations (200) and (201). The second-order two-body interaction energy for the collinear configuration is given in equation (202), and the result for the stacked configuration is given in equation (203).

$$\Delta E_{\text{collinear}}^{(2,2)} = \frac{-90.70}{R^6}. \quad (202)$$

$$\Delta E_{\text{stacked}}^{(2,2)} = \frac{-91.58}{R^6}. \quad (203)$$

4.4.1.2 Third-Order Two-Body Terms

The third-order interaction energy for two bodies is approximated by equation (188). The third-order two-body energy is a sum of classical induction, induction-dispersion, and pure dispersion interactions. Equation (204) shows the classical induction interactions, equation (205) describes the induction-dispersion energy, and equation (206) describes the pure dispersion interactions.

$$E_{\text{ind}}^{(3,2)} = -\mu_{\delta}^{B0} \mu_{\epsilon}^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\varphi} \alpha_{\gamma\alpha}^A \alpha_{\beta\varphi}^B - \frac{1}{6} \left(T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\varphi} \mu_{\beta}^{B0} \mu_{\delta}^{B0} \mu_{\varphi}^{B0} \beta_{\alpha\gamma\epsilon}^A + \mu_{\alpha}^{A0} \mu_{\gamma}^{A0} \mu_{\epsilon}^{A0} T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\varphi} \beta_{\beta\delta\varphi}^B \right). \quad (204)$$

$$E_{\text{ind-disp}}^{(3,2)} = -T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\varphi} \mu_{\epsilon}^{A0} \frac{\alpha_{\alpha\gamma}^A \beta_{\beta\delta\varphi}^B}{3} \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{3IP_B^4 + IP_B^2 \omega^2}{(IP_B^2 + \omega^2)^2} \right) \frac{IP_A^2}{IP_A^2 + \omega^2} - T_{\alpha\beta} T_{\gamma\delta} T_{\epsilon\varphi} \mu_{\varphi}^{B0} \frac{\alpha_{\beta\delta}^B \beta_{\alpha\gamma\epsilon}^A}{3} \times \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \left(\frac{3IP_A^4 + IP_A^2 \omega^2}{(IP_A^2 + \omega^2)^2} \right) \frac{IP_B^2}{IP_B^2 + \omega^2}. \quad (205)$$

$$\begin{aligned}
E_{\text{disp}}^{(3,2)} = & -T_{\alpha\beta} T_{\gamma\delta} T_{\varepsilon\phi} \left(\frac{\beta_{\alpha\gamma\varepsilon}^A \text{IP}_A^2}{6} \right) \left(\frac{\beta_{\delta\beta\phi}^B \text{IP}_B^2}{6} \right) \\
& \times \left(\frac{\hbar}{2\pi} \right)^2 \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \left[\frac{1}{(\text{IP}_A + i\omega)(\text{IP}_A - i\omega')} + \frac{1}{(\text{IP}_A + i\omega)(\text{IP}_A + i\omega')} \right] \\
& \times \left[\frac{1}{(\text{IP}_B + i\omega)(\text{IP}_B - i\omega')} + \frac{1}{(\text{IP}_B - i\omega)(\text{IP}_B - i\omega')} \right] \quad (206)
\end{aligned}$$

Again, using Mathematica 4.0 to evaluate the expressions, we have obtained the third-order two-body interaction energy for the collinear configuration as shown in equation (207) and the energy for the stacked configuration as shown in equation (208). The experimental values for the dipole, α -polarizability, β -hyperpolarizability, and ionization potential are listed in Table 1.

Table 1. Values for Use in Approximations			
Property	Value in atomic units	Value in electron volts	References
μ_z	0.4643		Maroulis ¹⁷
α_{zz}	17.96		Maroulis ¹⁷
$\alpha_{xx} = \alpha_{yy}$	16.17		Maroulis ¹⁷
β_{zzz}	-10.6		Maroulis ¹⁷
$\beta_{zxx} = \beta_{zyy} = \beta_{xzx} =$ $\beta_{yzy} = \beta_{xxz} = \beta_{yyz}$	2.2		Maroulis ¹⁷
IP	0.46852	12.749	CRC ¹⁸

$$\Delta E_{\text{collinear}}^{(3,2)} = -\frac{492.35}{R^9}. \quad (207)$$

$$\Delta E_{\text{stacked}}^{(3,2)} = \frac{68.90}{R^9}. \quad (208)$$

There is a much larger difference at the third order for the HCl dimers. Within the approximation used here, there is a stronger interaction for the collinear dimer than for the stacked dimer.

4.4.2 HCl Trimer

Using the HCl trimer as an example, we have estimated the third-order three-body interaction energy and the third-order two-body interaction energy, and we have compared their values for three geometrical configurations. The first configuration is shown in Figure 8, where the centers of mass of three HCl molecules lie on the laboratory Z-axis and the internuclear axis for each molecule runs parallel to the Z-axis.

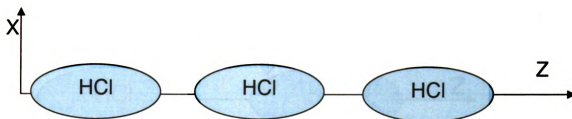


Figure 8: First Trimer Configuration.
Images in this dissertation are presented in color.

The second configuration has the three centers of mass on the Z-axis, but each of the HCl molecules is rotated 90 degrees, so that the internuclear axis runs parallel to the laboratory X-axis as shown in Figure 9.

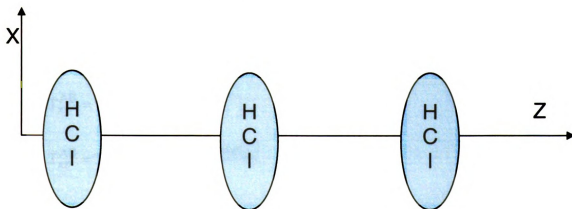
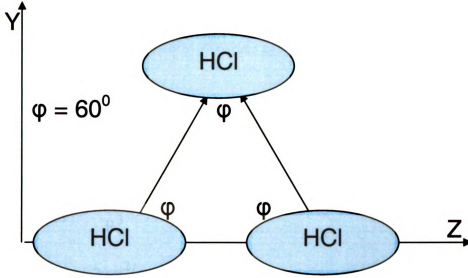


Figure 9: Second Trimer Configuration.
Images in this dissertation are presented in color.

The final arrangement has the HCl molecules arranged such that the centers of mass generate an equilateral triangle with the internuclear axis for each molecule still parallel

to the laboratory Z-axis. This configuration, known as the triangle formation, is shown in

Figure 10.



**Figure 10: Third Trimer Configuration (the triangle formation).
Images in this dissertation are presented in color.**

For three-body interactions, we need three dipole propagators. The first dipole propagator connects systems A with B. These tensors are described by equations (209)-(213).

$$T_{xx}^{AB} = \frac{3\sin^2(\varphi_{ab}) - 1}{R_{ab}^3}. \quad (209)$$

$$T_{xy}^{AB} = T_{yx}^{AB} = 0. \quad (210)$$

$$T_{xz}^{AB} = T_{zx}^{AB} = \frac{3\cos(\varphi_{ab})\sin(\varphi_{ab})}{R_{ab}^3}. \quad (211)$$

$$T_{yy}^{AB} = -\frac{1}{R_{ab}^3}. \quad (212)$$

$$T_{zz}^{AB} = \frac{3\cos^2(\varphi_{ab}) - 1}{R_{ab}^3}. \quad (213)$$

A second dipole propagator connects system A with system C. These propagators are described in equations (214)-(218).

$$T_{xx}^{CA} = \frac{3\sin^2(\varphi_{ca})-1}{R_{ca}^3}. \quad (214)$$

$$T_{xy}^{CA} = T_{yx}^{CA} = 0. \quad (215)$$

$$T_{xz}^{CA} = T_{zx}^{CA} = \frac{3\cos(\varphi_{ca})\sin(\varphi_{ca})}{R_{ca}^3}. \quad (216)$$

$$T_{yy}^{CA} = -\frac{1}{R_{ca}^3}. \quad (217)$$

$$T_{zz}^{CA} = \frac{3\cos^2(\varphi_{ca})-1}{R_{ca}^3}. \quad (218)$$

The third and final dipole propagator is needed to connect system B with system C.

These propagators are described by equations (219)-(223).

$$T_{xx}^{BC} = \frac{3\sin^2(\varphi_{bc})-1}{R_{bc}^3}. \quad (219)$$

$$T_{xy}^{BC} = T_{yx}^{BC} = 0. \quad (220)$$

$$T_{xz}^{BC} = T_{zx}^{BC} = \frac{3\cos(\varphi_{bc})\sin(\varphi_{bc})}{R_{bc}^3}. \quad (221)$$

$$T_{yy}^{BC} = -\frac{1}{R_{bc}^3}. \quad (222)$$

$$T_{zz}^{BC} = \frac{3\cos^2(\varphi_{bc})-1}{R_{bc}^3}. \quad (223)$$

4.4.2.1 Third-Order Three-Body Terms

The third-order three-body terms were derived in terms of nonlocal susceptibilities by Li and Hunt¹⁹. Li and Hunt separated the third-order three-body energy into three categories: energy due to induction, energy due to a mix of induction and dispersion forces, and energy due solely to dispersion interactions.

$$E^{(3,3)} = E_{\text{ind}}^{(3,3)} + E_{\text{i+d}}^{(3,3)} + E_{\text{disp}}^{(3,3)}. \quad (224)$$

The induction energy consists of classical forces, which fall into one of three sub-categories.

$$E_{\text{ind}}^{(3,3)} = E_{\text{srf}}^{(3,3)} + E_{\text{hyp}}^{(3,3)} + E_{\text{tbf}}^{(3,3)}. \quad (225)$$

The first component is the static reaction field energy, which is a sum of three components represented in equations (226) and (227).

$$E_{\text{srf}}^{(3,3)} = E_{\text{srf,A}}^{(3,3)} + E_{\text{srf,B}}^{(3,3)} + E_{\text{srf,C}}^{(3,3)}. \quad (226)$$

$$E_{\text{srf,A}}^{(3,3)} = - \int dr \dots dr^v P_0^A(r) \cdot T(r, r^{\wedge}) \cdot \alpha^B(r', r^{\wedge}) \cdot T(r'', r^{\wedge}) \cdot \alpha^C(r'', r^{iv}) \cdot T(r^{iv}, r^v) \cdot P_0^A(r^v). \quad (227)$$

The second is the third-body field terms described by equations (228) and (229).

$$E_{\text{tbf}}^{(3,3)} = E_{\text{tbf,ABC}}^{(3,3)} + E_{\text{tbf,ACB}}^{(3,3)} + E_{\text{tbf,BAC}}^{(3,3)} + E_{\text{tbf,BCA}}^{(3,3)} + E_{\text{tbf,CAB}}^{(3,3)} + E_{\text{tbf,CBA}}^{(3,3)}. \quad (228)$$

$$E_{\text{tbf,ABC}}^{(3,3)} = - \int dr \dots dr^v P_0^B(r) \cdot T(r, r^{\wedge}) \cdot \alpha^C(r', r^{\wedge}) \cdot T(r'', r^{\wedge}) \cdot \alpha^B(r'', r^{iv}) \cdot T(r^{iv}, r^v) \cdot P_0^A(r^v). \quad (229)$$

The third contribution to the classical induction energy comes from the three-body hyperpolarization effects, described by equations (230) and (231).

$$E_{\text{hyp}}^{(3,3)} = E_{\text{hyp,A}}^{(3,3)} + E_{\text{hyp,B}}^{(3,3)} + E_{\text{hyp,C}}^{(3,3)}. \quad (230)$$

$$\begin{aligned}
E_{\text{hyp,A}}^{(3,3)} = & -\frac{1}{2} \int d\mathbf{r} \cdots d\mathbf{r}^{\nu} \beta^{\text{A}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') [T(\mathbf{r}, \mathbf{r}'') \cdot \mathbf{P}_0^{\text{B}}(\mathbf{r}'')] \\
& \times [T(\mathbf{r}', \mathbf{r}^{\text{iv}}) \cdot \mathbf{P}_0^{\text{B}}(\mathbf{r}^{\text{iv}})] [T(\mathbf{r}'', \mathbf{r}^{\nu}) \mathbf{P}_0^{\text{C}}(\mathbf{r}^{\nu})] \\
& + -\frac{1}{2} \int d\mathbf{r} \cdots d\mathbf{r}^{\nu} \beta^{\text{A}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') [T(\mathbf{r}, \mathbf{r}'') \cdot \mathbf{P}_0^{\text{C}}(\mathbf{r}'')] \\
& \times [T(\mathbf{r}', \mathbf{r}^{\text{iv}}) \cdot \mathbf{P}_0^{\text{C}}(\mathbf{r}^{\text{iv}})] [T(\mathbf{r}'', \mathbf{r}^{\nu}) \mathbf{P}_0^{\text{B}}(\mathbf{r}^{\nu})] .
\end{aligned} \tag{231}$$

The induction-dispersion interaction energy is described by equations (232) and (233).

$$E_{\text{i+d}}^{(3,3)} = E_{(\text{A} \cdots \text{B}) \rightarrow \text{C}} + E_{(\text{C} \cdots \text{A}) \rightarrow \text{B}} + E_{(\text{B} \cdots \text{C}) \rightarrow \text{A}} . \tag{232}$$

$$\begin{aligned}
E_{(\text{A} \cdots \text{B} \rightarrow \text{C})}^{(3,3)} = & -\frac{\hbar}{2\pi} \int_0^{\infty} d\omega \int d\mathbf{r} \cdots d\mathbf{r}^{\nu} \left(\begin{aligned} & \beta_{\beta\gamma\alpha}^{\text{A}}(\mathbf{r}', \mathbf{r}'', \mathbf{r} : i\omega\omega, 0T_{\gamma\delta}(\mathbf{r}'', \mathbf{r}'')) \\ & \times \alpha_{\delta\epsilon}^{\text{B}}(\mathbf{r}'', \mathbf{r}^{\text{iv}}, i\omega\omega T_{\epsilon\beta}(\mathbf{r}^{\text{iv}}, \mathbf{r}')) \\ & \times T_{\alpha\varphi}(\mathbf{r}, \mathbf{r}^{\nu}) \mathbf{P}_{0\varphi}^{\text{C}}(\mathbf{r}^{\nu}) \end{aligned} \right) \\
& -\frac{\hbar}{2\pi} \int_0^{\infty} d\omega \int d\mathbf{r} \cdots d\mathbf{r}^{\nu} \left(\begin{aligned} & \beta_{\beta\gamma\alpha}^{\text{B}}(\mathbf{r}', \mathbf{r}'', \mathbf{r} : i\omega\omega, 0T_{\gamma\delta}(\mathbf{r}'', \mathbf{r}'')) \\ & \times \alpha_{\delta\epsilon}^{\text{A}}(\mathbf{r}'', \mathbf{r}^{\text{iv}}, i\omega\omega T_{\epsilon\beta}(\mathbf{r}^{\text{iv}}, \mathbf{r}')) \\ & \times T_{\alpha\varphi}(\mathbf{r}, \mathbf{r}^{\nu}) \mathbf{P}_{0\varphi}^{\text{C}}(\mathbf{r}^{\nu}) \end{aligned} \right) .
\end{aligned} \tag{233}$$

The dispersion energy is described by equation (234).

$$E_{\text{disp}}^{(3,3)} = -\frac{\hbar}{\pi} \int_0^{\infty} d\omega \int d\mathbf{r} \cdots d\mathbf{r}^{\nu} \text{Tr} \left[\begin{aligned} & T(\mathbf{r}^{\nu}, \mathbf{r}^{\text{iv}}) \cdot \alpha^{\text{C}}(\mathbf{r}^{\text{iv}}, \mathbf{r}'', i\omega\omega T(\mathbf{r}'', \mathbf{r}')) \\ & \times \alpha^{\text{B}}(\mathbf{r}'', \mathbf{r}'; i\omega) \cdot T(\mathbf{r}', \mathbf{r}) \cdot \alpha^{\text{A}}(\mathbf{r}, \mathbf{r}^{\nu}; i\omega) \end{aligned} \right] \tag{234}$$

Combining equations (224)-(234), we calculated the third-order three-body interaction energy at each of the three geometrical configurations. From the integrals over imaginary frequencies, we used the approximations to the frequency-dependent values of α and β described above. The results are listed in equations (235)-(237).

$$\Delta E_{\text{collinear}}^{(3,3)} = -\frac{1369.34}{R^9} . \tag{235}$$

$$\Delta E_{\text{stacked}}^{(3,3)} = \frac{223.68}{R^9} . \tag{236}$$

$$\Delta E_{\text{triangle}}^{(3,3)} = -\frac{36.96}{R^9}. \quad (237)$$

4.4.2.2 Third-Order Two-Body Terms

Finally, we compared the third-order three-body energies from equations (235)-(237) with the third-order two-body energies to generate the full third-order two-body results, we added three third-order two-body equations. as shown in equation (238).

$$E^{(3,2)} = E_{AB}^{(3,2)} + E_{BC}^{(3,2)} + E_{AC}^{(3,2)}. \quad (238)$$

Listed in equations (239)-(241) are the results for the calculation of the third-order two-body terms.

$$\Delta E_{\text{collinear}}^{(3,2)} = -\frac{985.65}{R^9}. \quad (239)$$

$$\Delta E_{\text{stacked}}^{(3,2)} = \frac{137.93}{R^9}. \quad (240)$$

$$\Delta E_{\text{triangle}}^{(3,2)} = -\frac{636.31}{R^9}. \quad (241)$$

4.5 References

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Chapter 5

Molecular Frame Distortions in CH₄+X Pairs, with X=He, N₂, or H₂

5.1 Introduction

Compressed gas mixtures containing $\text{CH}_4\text{-H}_2$, $\text{CH}_4\text{-N}_2$, and $\text{CH}_4\text{-He}$, although pertinent to astrophysics mainly due to the gaseous composition of the atmosphere of Titan^{1,2,3,4}, Saturn^{4,5}, and Neptune⁴, are of interest in chemical theory because of their collision-induced absorption in the infrared and far-infrared region. Induced dipoles produced during collisions within the compressed gas cause nearly all compressed gases to absorb infrared radiation. This behavior is true even if the individual constituents of the gas are infrared inactive^{6,7,8}. The same is also true of $\text{CH}_4\text{-N}_2$, $\text{CH}_4\text{-H}_2$, and $\text{CH}_4\text{-He}$ gas mixtures. Although the symmetric vibrational modes of CH_4 and the bond stretch of the homonuclear diatomics are infrared inactive, part of the collision-induced absorption in the infrared region is due to interacting $\text{CH}_4\text{-N}_2$, $\text{CH}_4\text{-H}_2$, and $\text{CH}_4\text{-He}$ pairs^{9,10,11}. Absorption in the far-infrared is due to translational and rotational modulation of the collision-induced dipoles. These collision-induced dipoles originate from four sources: multipolar induction, dispersion forces, intermolecular exchange forces, and frame distortion^{8,11,12}.

Although theorists have been able to predict the collision-induced infrared (IR) spectra and IR absorption intensities of other simple gas mixtures, they have been unable to predict absorption intensities correctly in the range⁸ $150\text{ cm}^{-1} - 450\text{ cm}^{-1}$ of the IR spectra of $\text{CH}_4\text{-N}_2$, $\text{CH}_4\text{-H}_2$, and $\text{CH}_4\text{-He}$ mixtures^{8,11,13}. The discrepancy between experiment and theory is due to an incomplete treatment of the forces between molecules in these gas mixtures. Previous theoretical examinations of other gas mixtures have taken into consideration the more commonly studied causes of collision-induced absorption: multipolar induction, dispersion forces, and intermolecular exchange forces, but the

influence of frame distortion has been investigated in only one case thus far: Weiss¹² studied frame distortion effects in He collisions with CO₂. He concluded that in CO₂-He gas mixtures frame distortions due to collisions between the He atom and CO₂ molecule generated induced dipoles of comparable size to exchange force-induced dipoles.

Collision-induced frame distortion in CH₄ mixtures has the potential to produce dipoles similar to those found in CO₂-He gas mixtures¹². In the CH₄ molecule, the bending constants are smaller than those in CO₂. Frame distortion in CH₄ will generate a dipole, due in large part to the bond dipoles in CH₄. In the equilibrium geometry, the bond dipoles cancel due to symmetry, but the movement of any hydrogen from its equilibrium position will generate a dipole¹¹. Not only will the frame distortion generate a dipole in the CH₄ molecule, but the CH₄ dipole generated by distortion may in turn influence the collision partner, adding to the electron cloud distortion in the collision partner. It is expected that in CH₄-He gas mixtures the frame-distortion dipole will be on the order of 0.003-0.03 Debye⁸. In this chapter, we study frame distortion in CH₄-N₂, CH₄-H₂, and CH₄-He pairs due to interactions within the mixed pairs.

5.1.1 Approaches

To examine the frame distortion of CH₄, we need to see the effects of approaching molecules on the methane molecular frame. Figure 1 shows that methane has two vertical planes of symmetry, A and B, such that plane A bisects the H1, H2, and C atoms, and plane B bisects H3, H4, and C atoms. Using this diagram, one can describe the collision paths used in this study.

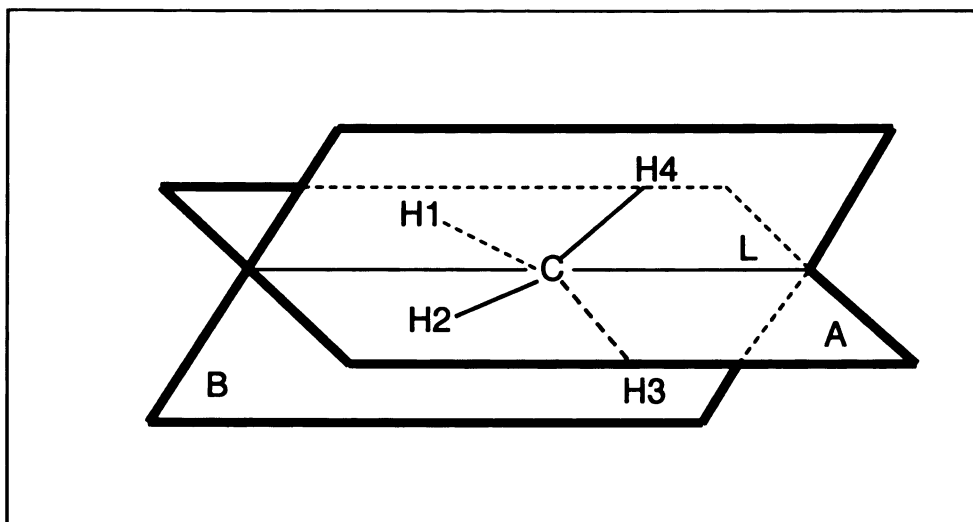


Figure 1: Reflection Planes in CH₄

In our work on collisions of helium and methane, we have positioned the helium atom on the C_2 axis, which bisects both HCH bond angles in methane. This axis is the line labeled L, where the two planes intersect, in Figure 1. In the work on collisions of a diatomic molecule with methane, we considered two approaches termed linear and perpendicular. In the linear approach, the nuclei (they are both terminal) of the homonuclear diatomic lie in both planes A and B along line L. This configuration is shown in Figure 2 and Figure 3.

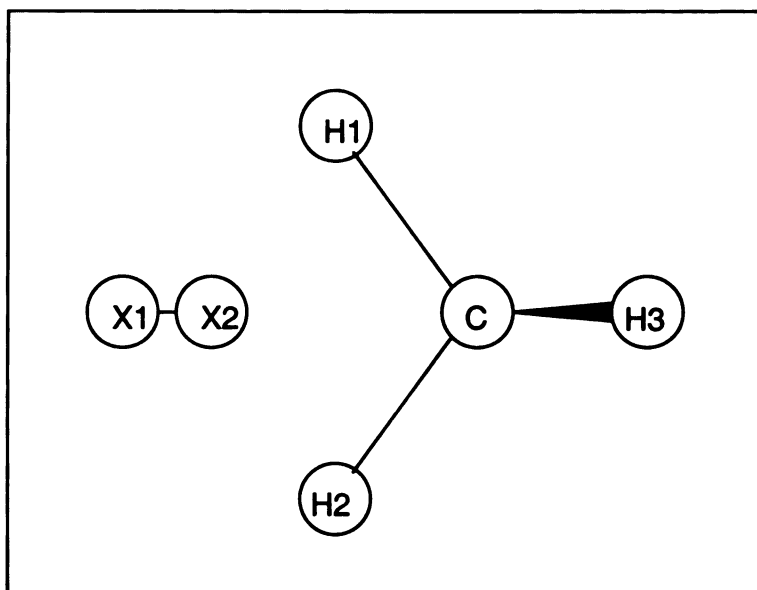


Figure 2: Diagram of Linear Approach, Viewed Looking Down on Plane A

Rotating the geometry in Figure 2 90 degrees about the axis bisecting the HCH bond angles, we reach the view in Figure 3.

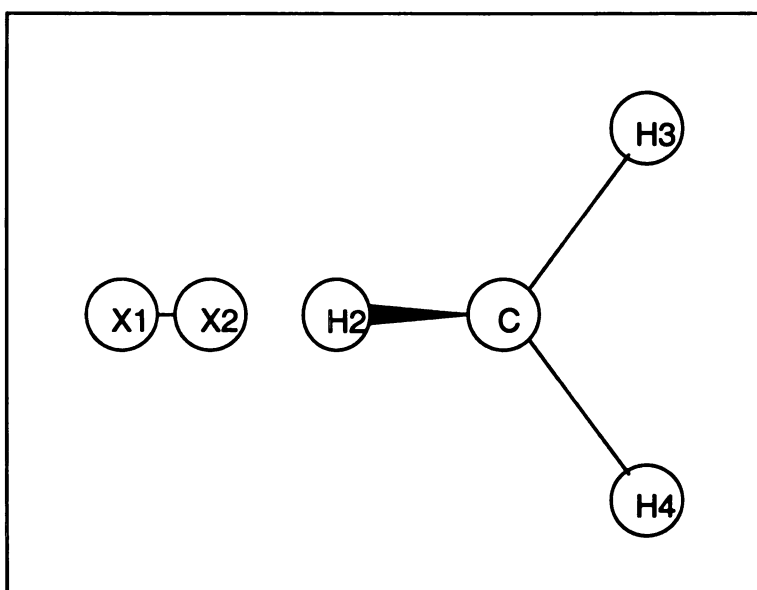


Figure 3: Diagram of Linear Approach, Viewed Looking Down on Plane B

In the perpendicular approach, plane B contains the nuclei of the diatomic, and plane A bisects the homonuclear diatomic bond. This configuration is shown in Figure 4 and Figure 5.

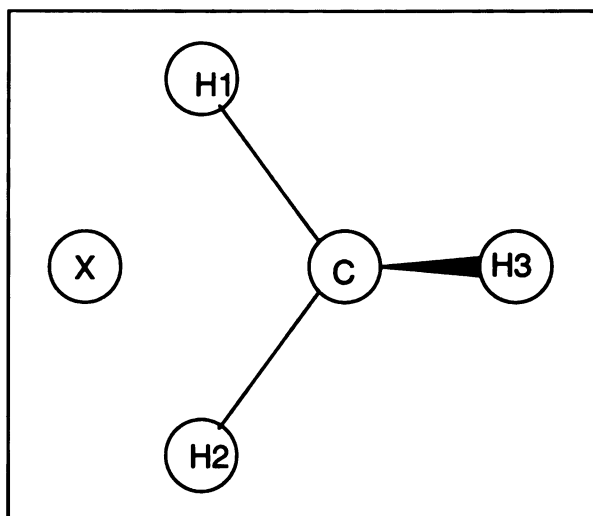


Figure 4: Diagram of Perpendicular Approach, Viewed Looking Down on Plane A

Rotating the geometry in Figure 4 90 degrees about the axis bisecting the HCH bond angles, we get Figure 5.

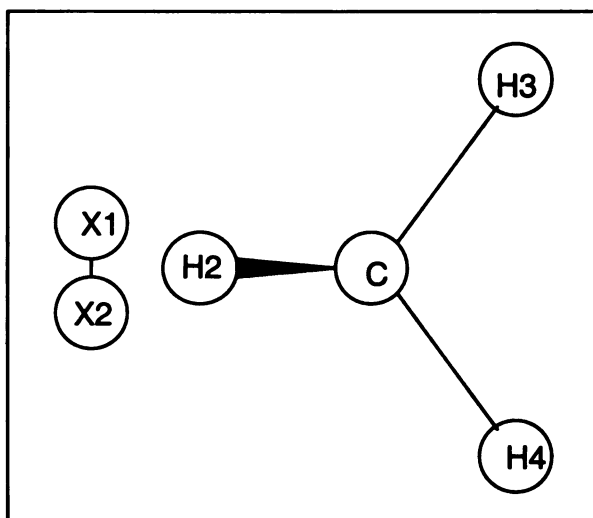


Figure 5: Diagram of Perpendicular Approach, Viewed Looking Down on Plane B

Using both paths of approach, the center of mass of the diatomic molecule, or the helium atom, was moved closer to the carbon atom along the line L.

5.1.2 Methods

At specific separations, single-point calculations were made at a range of H1-C-H2 bond angles. By fitting the energy values versus the H1-C-H2 bond angle to a third-order polynomial, the bond angle at the minimum of the potential well was determined; this is the optimized bond angle at that particular separation of helium, or the diatomic, from methane. Using this optimized bond angle, we calculated the dipole due to the collision-induced frame distortion, as well as the energy change on the potential surface due to the frame distortion. The dipole was calculated using equation (1), where $\hat{r}_1, \hat{r}_2, \hat{r}_3$, and $\hat{r}_4$ are unit vectors along the bonds in the CH₄ molecule, and the potential change was calculated from a potential energy surface generated by Marquardt¹⁴.

$$\hat{\mu}_{\text{ind}} = \mu_{\text{bond}}(\hat{r}_1 + \hat{r}_2 + \hat{r}_3 + \hat{r}_4). \quad (1)$$

The bond dipole was determined as described in a paper by Hollenstein¹⁵ et al.

5.1.3 Computational Details

Single point CCSD(T) calculations were performed with the Gaussian98¹⁶ software package using the Dunning aug-cc-pvtz basis sets for carbon^{17,18}, hydrogen¹⁷, nitrogen^{17,18}, and helium¹⁹. Mathematica 4.0²⁰ was used to fit the raw data to the third-order polynomial and to determine the optimized bond angle, as well as to determine the potential and interaction energies.

5.2 CH₄-N₂

For this study, the experimental geometries for methane and nitrogen were used, as provided by the 86th edition of the *CRC Handbook of Chemistry and Physics*²¹. The methane bond lengths are $R_{\text{CH}} = 1.087 \text{ \AA}$, and all the HCH bond angles are equal to 109.4712° except for the H1-C-H2 bond angle, which is varied as described below. For

nitrogen, the bond length is $R_{\text{NN}} = 1.9077 \text{ \AA}$. Using these parameters, we collected two sets of single-point energy calculations: single-point energy values from the linear approach and single point energy values from the perpendicular approach. The linear approach is discussed first.

5.2.1 Linear Approach

The separation between the N_2 center of mass and the methane center of mass was set to distances of $5.0 \text{ \AA}$, $4.0 \text{ \AA}$, $3.5 \text{ \AA}$, $3.25 \text{ \AA}$, and $3.0 \text{ \AA}$. At each distance, the H1-C-H2 bond angle was varied from 104° to 114° in increments of 1° , also including the angle 109.4712° . The minimum of the curve in each slice is the optimized H1-C-H2 bond angle for the respective nitrogen-methane separation. Using the aforementioned data points, the minimum of the potential curve was determined. Plots of the total energy of the system as a function of the H1-C-H2 bond angle can be seen in Figures 6-10.

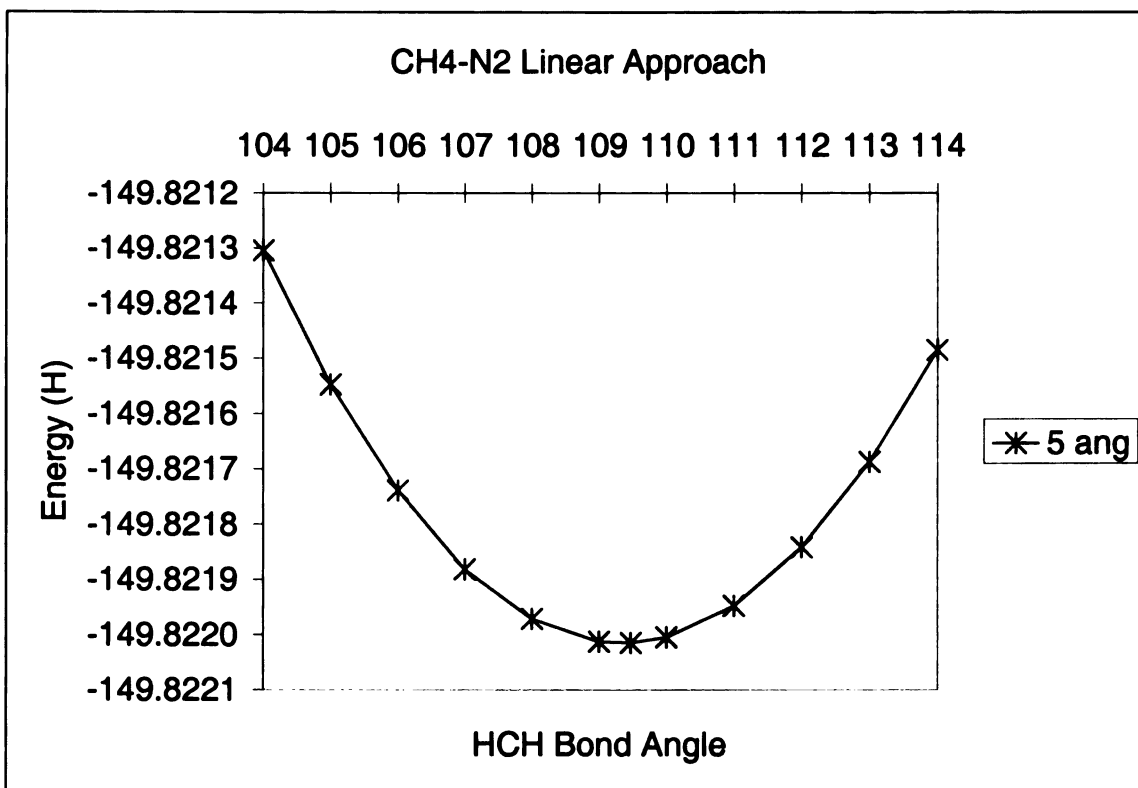


Figure 6: Energy as a Function of Bond Angle at 5.0 Å Separation for Methane-Nitrogen: Linear Approach

A first glance at Figures 6-8 may give the impression that the H1-C-H2 bond angle is unaffected by the approach of the nitrogen molecule, but a closer examination reveals the bond angle has changed from its equilibrium value. At a 5 Å separation, the optimized bond angle is 109.34° compared to the equilibrium bond angle of 109.4712°.

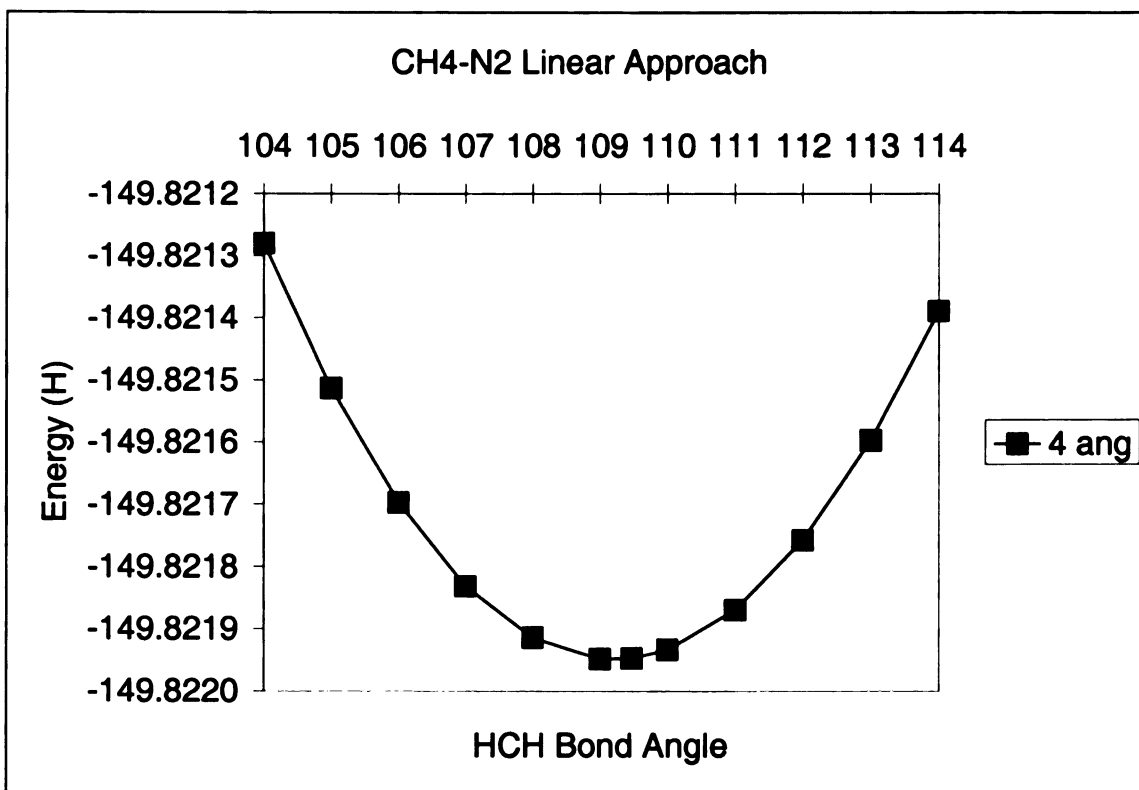


Figure 7: Energy as a Function of Bond Angle at 4.0 Å Separation for Methane-Nitrogen: Linear Approach

At a 4 Å separation, the optimized bond angle is 109.19°. This data suggests that the bond angle is becoming more acute as the nitrogen approaches.

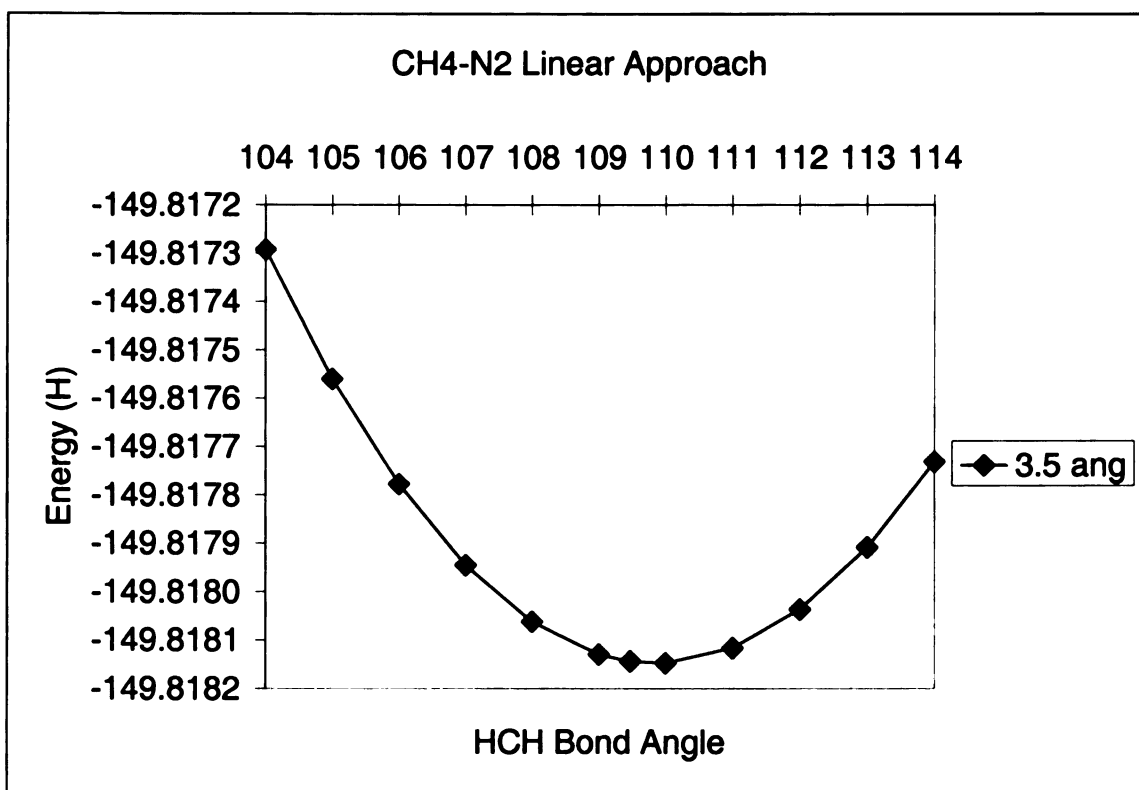


Figure 8: Energy as a Function of Bond Angle at 3.5 Å Separation for Methane-Nitrogen: Linear Approach

When the separation is decreased to 3.5 Å, the bond angle opens to an angle of 109.87°.

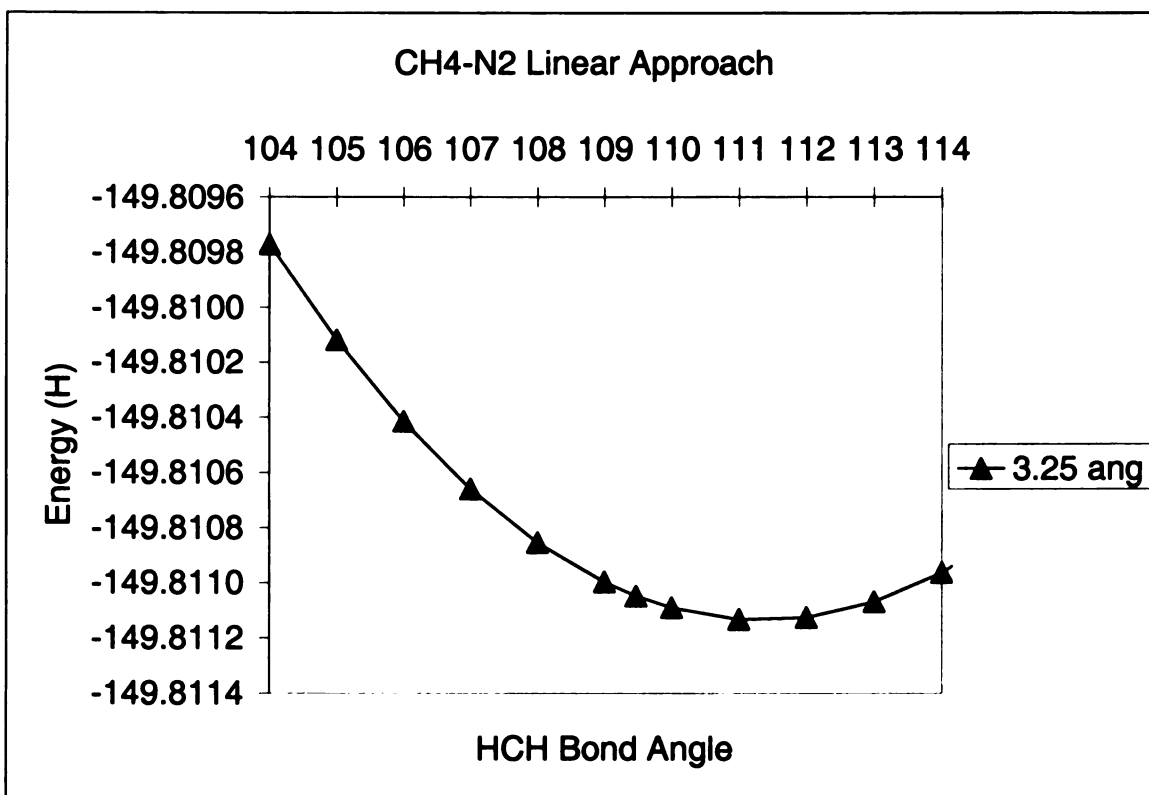


Figure 9: Energy as a Function of Bond Angle at 3.25 Å Separation for Methane-Nitrogen: Linear Approach

At 3.25 Å the bond angle opens to 111.34° , and at 3 Å the bond angle opens to 114.83° , as shown in Figure 10. (In this case, we expanded the set of the H1-C-H2.bond angles to include angles that range from 104 to 119 degrees in one degree increments.) The range shown in Figure 10 is 109° to 119° .

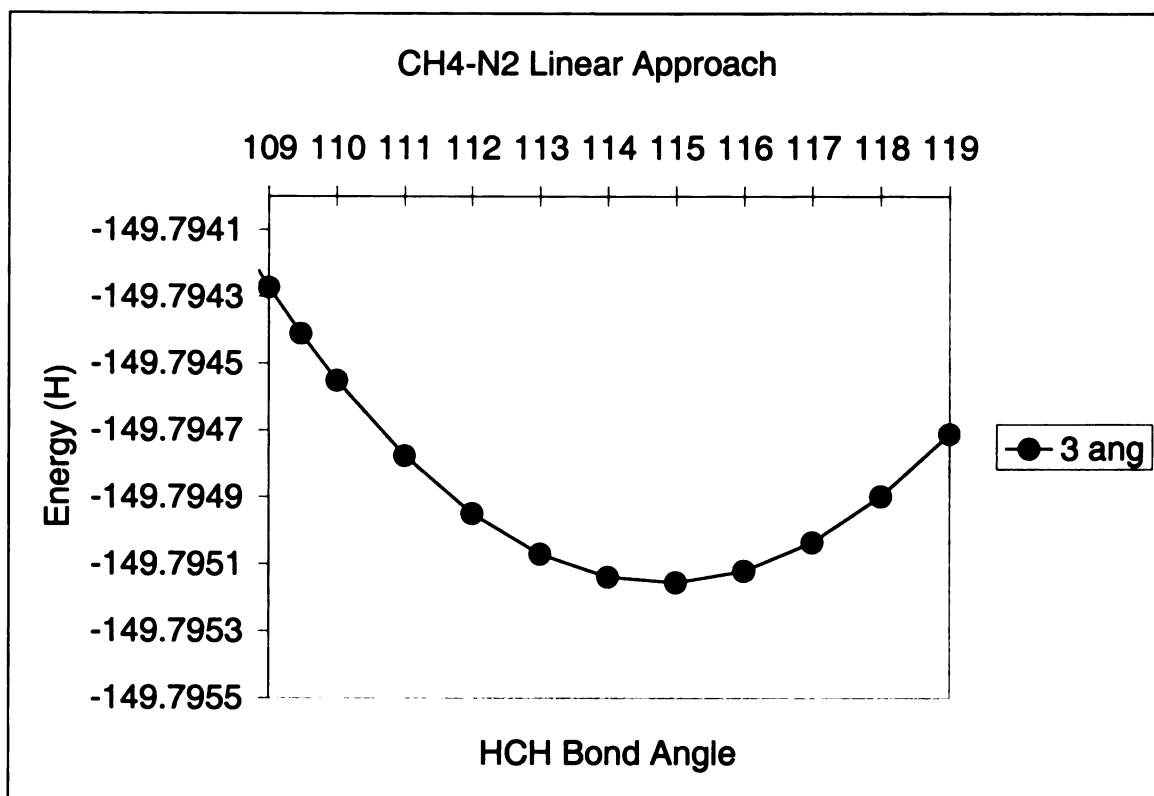


Figure 10: Energy as a Function of Bond Angle at 3.0 Å Separation for Methane-Nitrogen: Linear Approach

It is evident that as the nitrogen molecule approaches methane, in the configurations shown in Figures 2 and 3, the H1-C-H2 angle decreases at first, and then increases as N₂ approaches more closely. Table 1 lists the optimized bond angle at each N₂-CH₄ separation.

Table 1. CH₄-N₂ Linear Approach	
Distance (Å)	Distorted bond angle
5.00	109.34
4.00	109.19
3.50	109.87
3.25	111.34
3.00	114.83

We have calculated the potential energy difference between the equilibrium CH₄ structure and the distorted CH₄ structure twice, once with a potential surface generated by Marquardt and Quack¹⁴ and again using Gaussian98. Also calculated twice was the

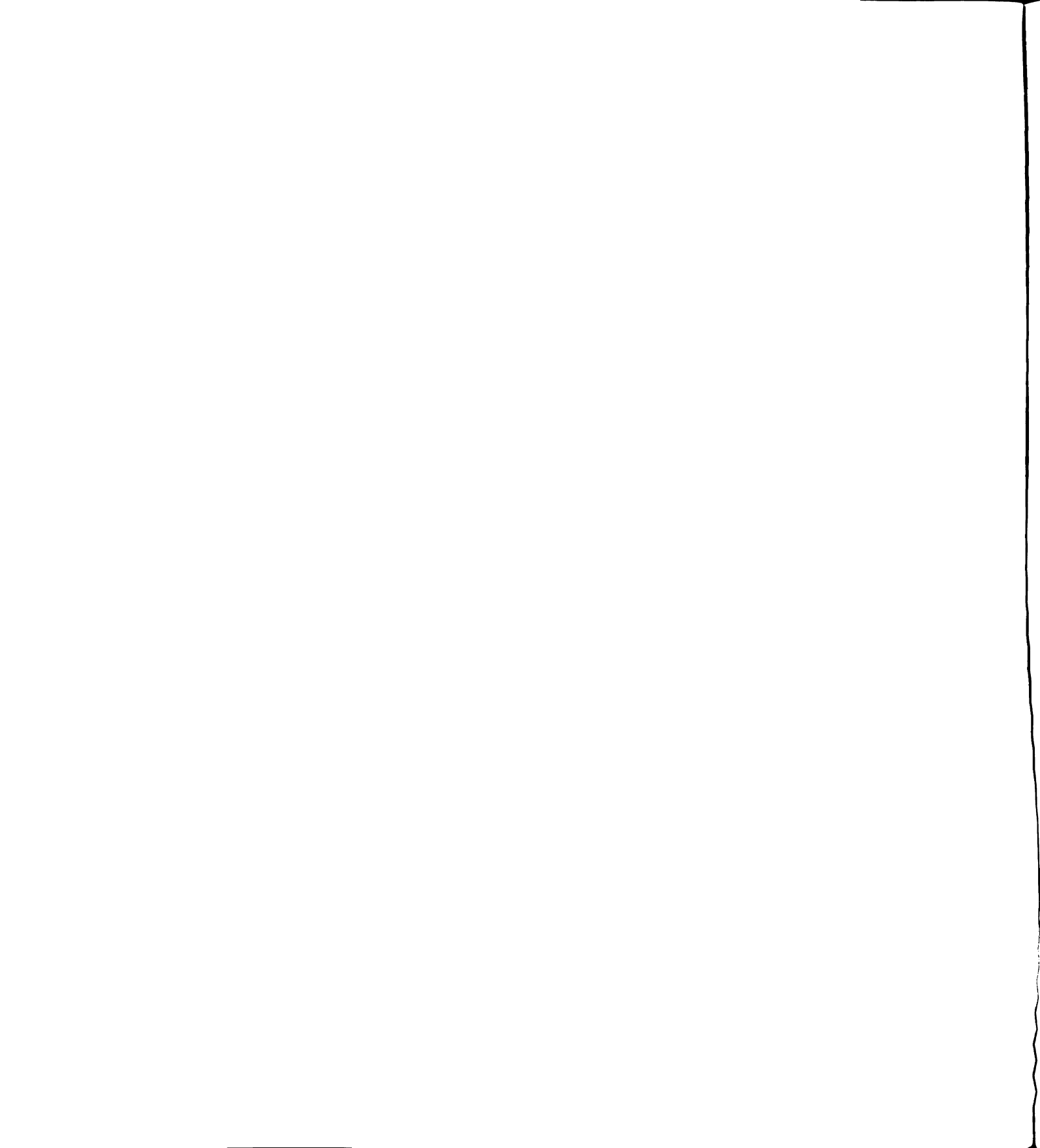
dipole moment, once using Gaussian98 and a second time using equation (1). These results are listed in Table 2 where μ is the dipole moment and $V(YXY)$ is the potential energy difference between the unperturbed and distorted methane molecule.

Table 2. Dipole and Potential from Molecular Distortion in the CH₄-N₂ Linear Approach				
distance (Å)	Gaussian 98 μ (a.u.)	Quack et al ¹⁴ μ (a.u.)	Gaussian 98 $V(YXY)$ (H)	Quack et al ¹⁴ $V(YXY)$ (H)
5.00	2.9356E-04	2.E-04	5.E-07	4.07070E-07
4.00	6.2890E-04	4.7E-04	2.0E-06	1.86641E-06
3.50	-8.9378E-04	-6.7E-04	4.0E-06	3.96732E-06
3.25	-4.2071E-03	-3.1E-03	8.79E-05	9.78689E-05
3.00	-1.2189E-02	-9.01E-03	7.014E-04	7.03584E-04

Table 2 shows that the potential energy differences due to the distortion of the methane molecule are of the same magnitude. For the Marquardt potential energy surface and Gaussian98, the difference between the values is less than 20 percent. These results seem reasonable considering that the Marquardt potential is based on a MRD-CI potential energy surface calculated using CC-PVDZ basis sets for carbon and hydrogen and that the Gaussian98 values are only converged to 1×10^{-7} Hartrees. The difference between the dipole moment values is more noticeable; however, the simple bond-dipole model provides a good approximation to the actual dipole.

5.2.2 Perpendicular Approach

Using the same procedure as used for the linear approach, we performed the same collection of calculations for the perpendicular approach of the N₂ molecule to the CH₄ molecule.



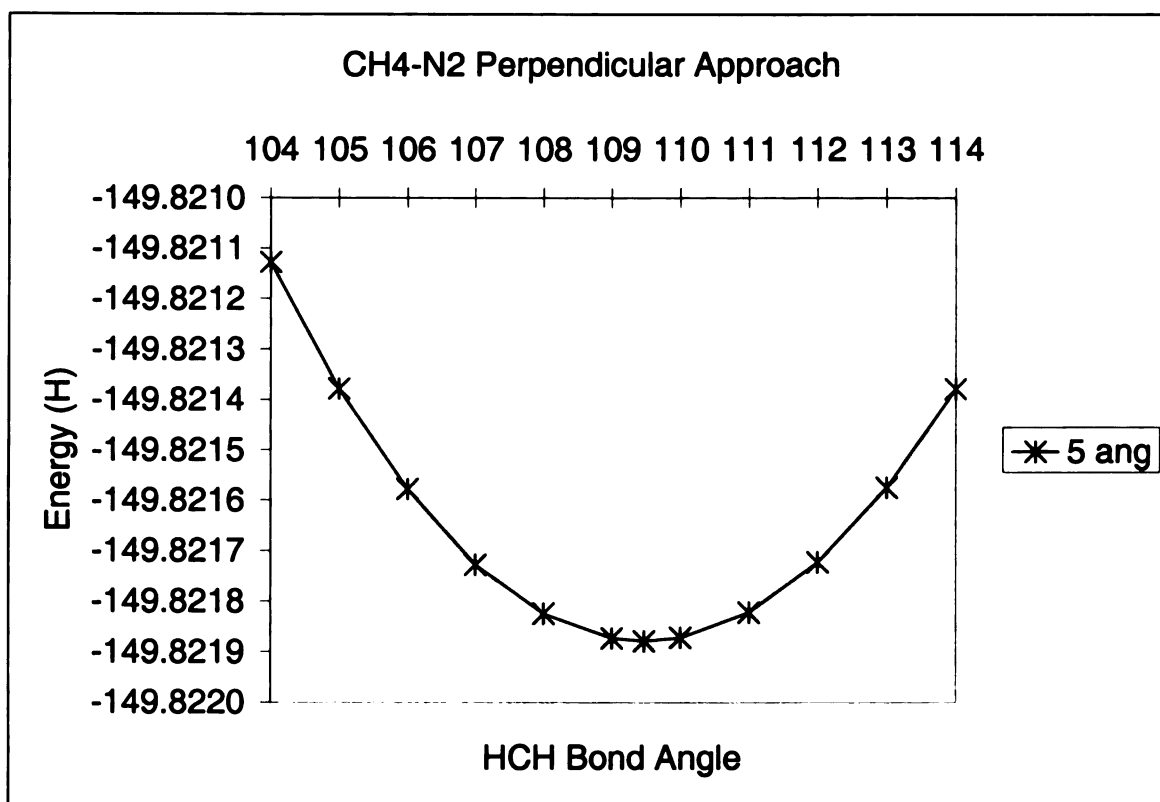


Figure 11: Energy as a Function of Bond Angle at 5.0 Å Separation for Methane-Nitrogen: Perpendicular Approach

At 5Å separation, N₂ has very little effect on the geometry of the CH₄ molecule. The optimized angle is 109.48⁰, which is only a hundredth of a degree different from the magnitude of the equilibrium bond angle. In contrast, the magnitude of the equilibrium bond angle of CH₄ changed by 0.13⁰ for the linear approach of N₂ at 5Å.

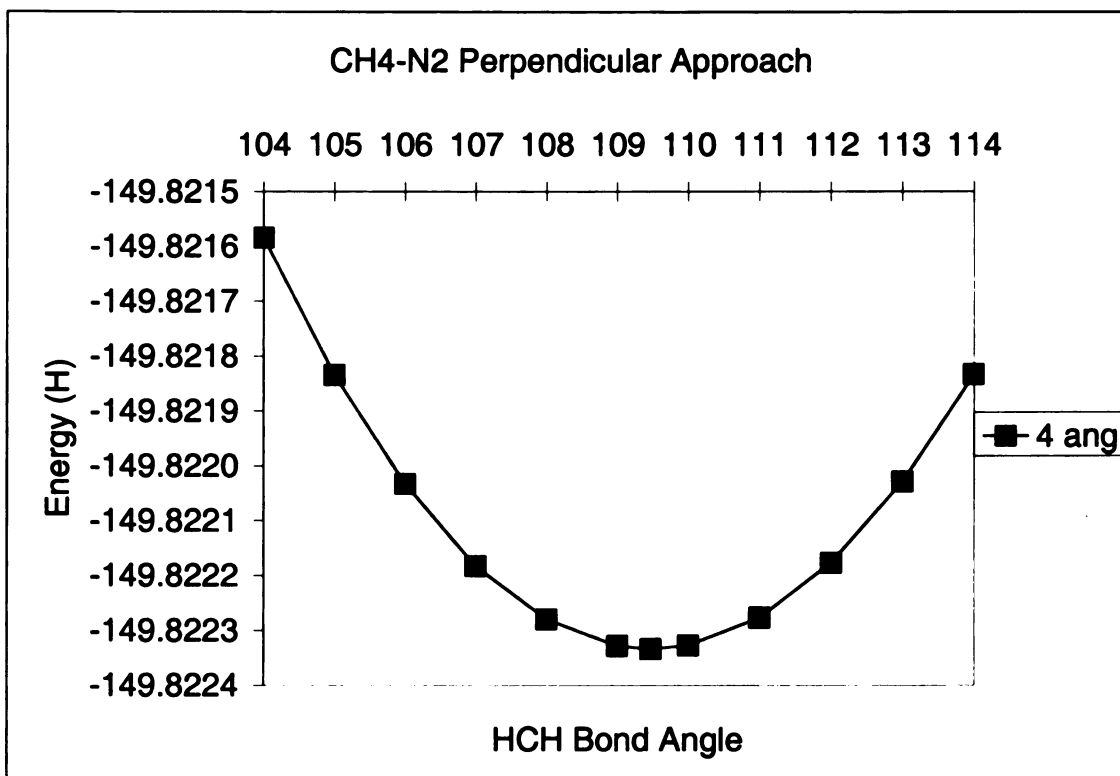


Figure 12: Energy as a Function of Bond Angle at 4.0 Å Separation for Methane-Nitrogen: Perpendicular Approach

In fact, when the distance is decreased to 4.0 Å, the magnitude of the minimized bond angle is almost equivalent to the magnitude of the tetrahedral angle, at 109.47° , which suggests that the bond angle is essentially unaffected by the N₂ molecule at this distance.

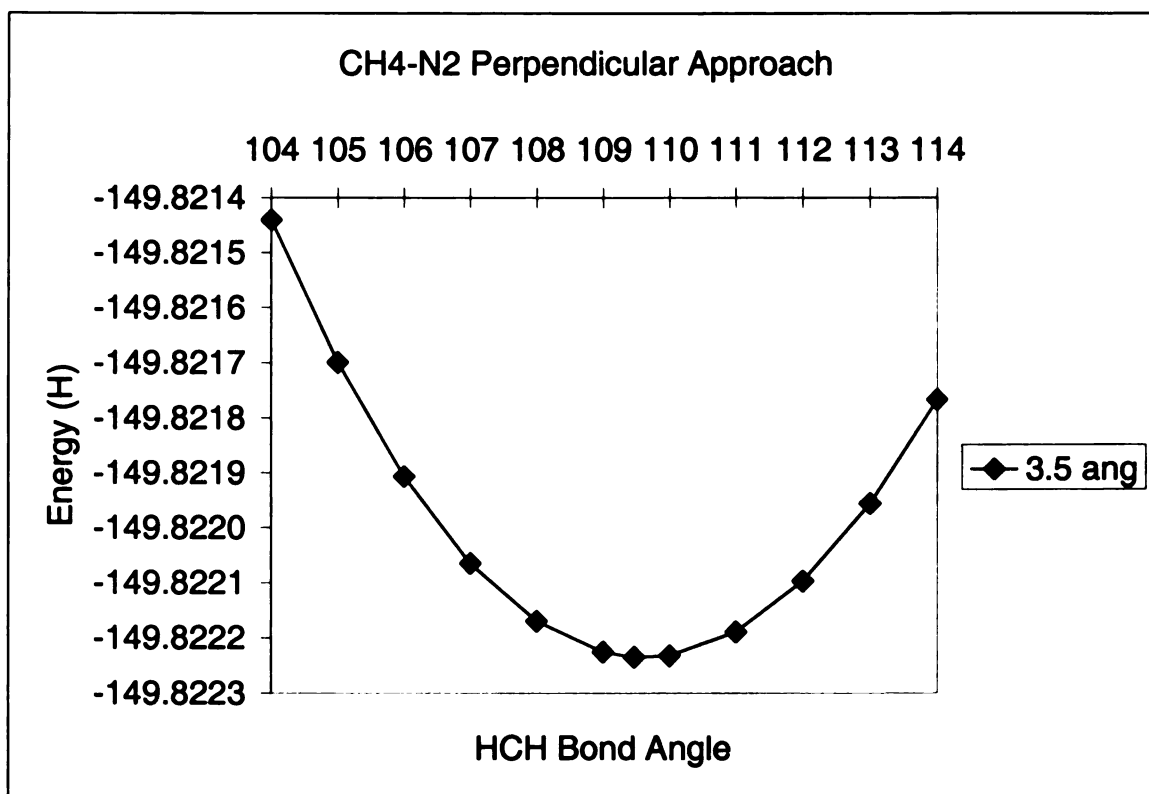


Figure 13: Energy as a Function of Bond Angle at 3.5 Å Separation for Methane-Nitrogen: Perpendicular Approach

It is not until the distance is decreased to 3.5 Å that the H-C-H angle expands to 109.68°.

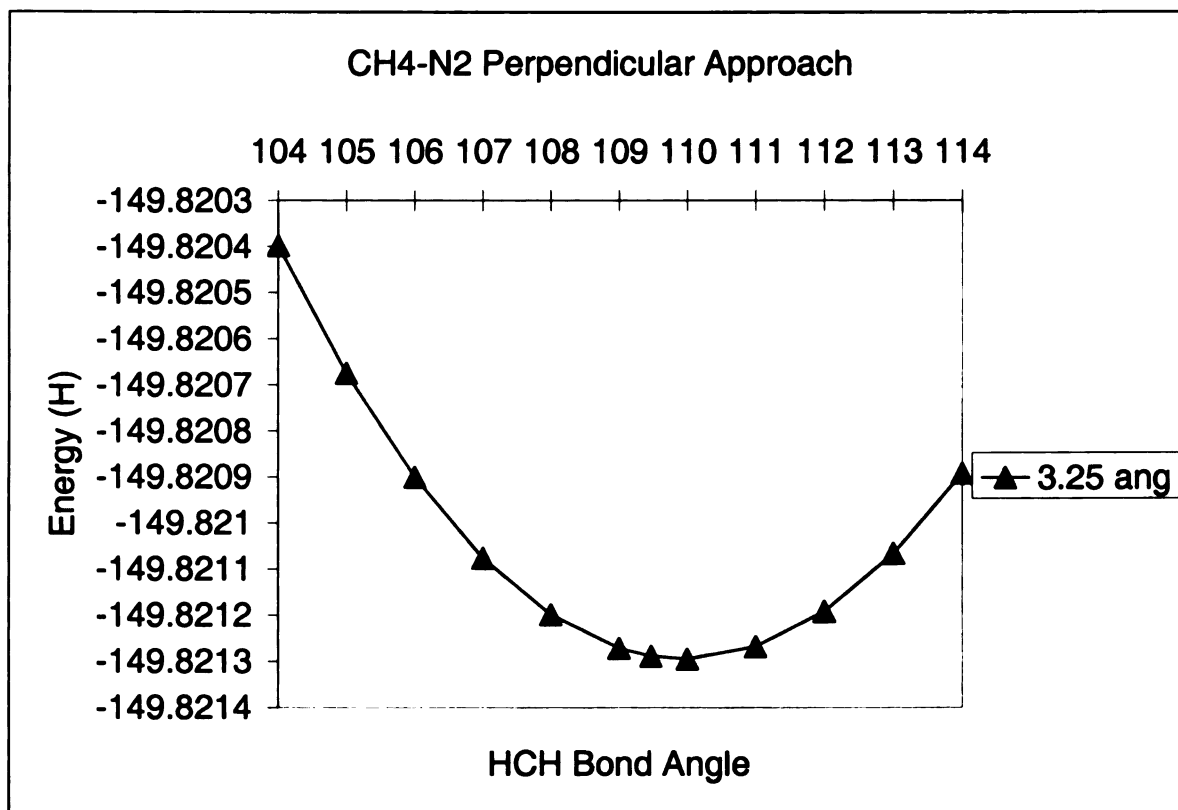


Figure 14: Energy as a Function of Bond Angle at 3.25 Å Separation for Methane-Nitrogen: Perpendicular Approach

At 3.25 Å the H-C-H angle is disturbed to 109.96°, which becomes noticeable as shown in Figure 14.

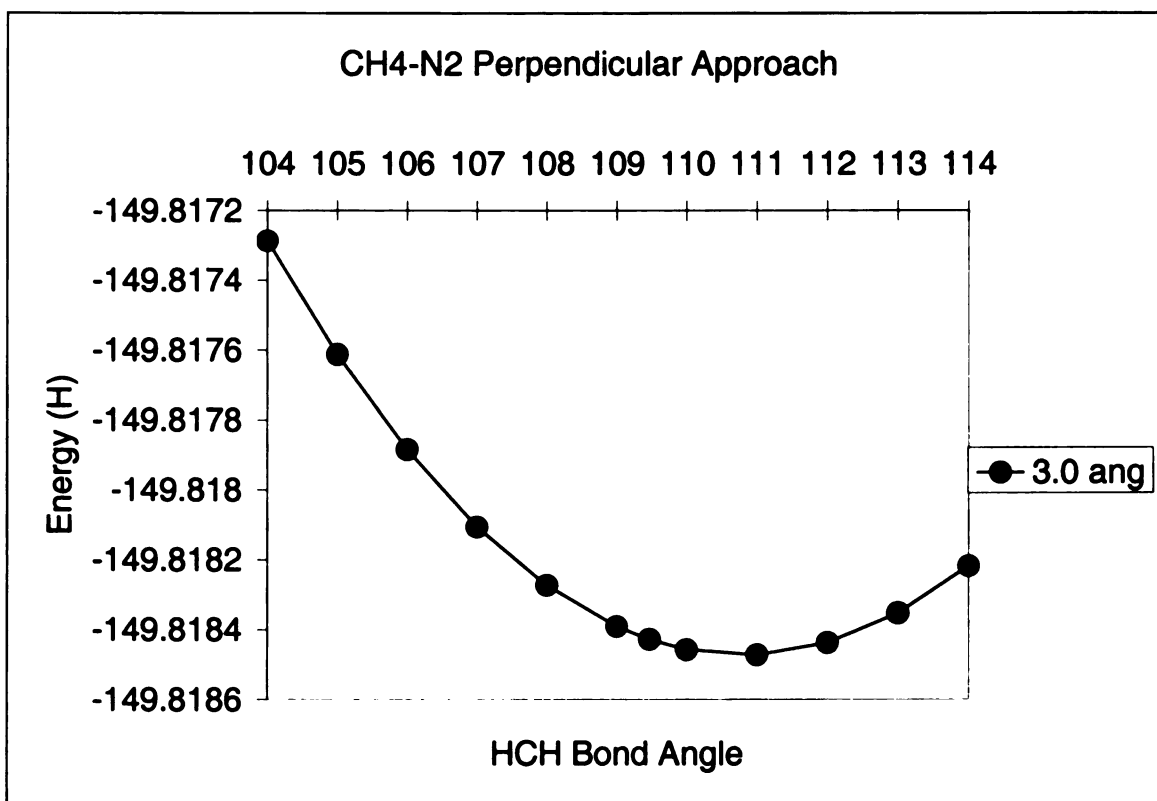


Figure 15: Energy as a Function of Bond Angle at 3.0 Å Separation for Methane-Nitrogen: Perpendicular Approach

Finally, at 3.0 Å, the distortion angle is 110.81°. In contrast to the distortion on the linear approach, the bond angle distortion for the perpendicular approach is less extreme. Also, squeezing of the bond angle as the N₂ first approaches is seen in the linear approach but not in the perpendicular approach. Listed in Table 3 are the N₂-CH₄ distances and the distortion angles at these distances.

Table 3. CH₄-N₂ Perpendicular Approach	
distance (Å)	distorted bond angle
5.00	109.48 ⁰
4.00	109.47 ⁰
3.50	109.63 ⁰
3.25	109.96 ⁰
3.00	110.81 ⁰

Listed in Table 4 are the dipoles and potential differences calculated using Gaussian98 and the Marquardt potential surface.

Table 4. Dipole and Potential from Molecular Distortion in the CH₄-N₂ Perpendicular Approach				
distance (Å)	Gaussian 98 μ (a.u.)	Quack et al ¹⁴ μ (a.u.)	Gaussian 98 V(YXY) (H)	Quack et al ¹⁴ V(YXY) (H)
5.00	0.E+00	-1.9699E-05	0.0000000	3.07966E-09
4.00	0.E+00	2.6861E-06	0.0000000	1.28879E-09
3.50	-3.E-04	-3.5564E-04	7.E-07	5.95173E-07
3.25	-8.3E-04	-1.0958E-03	5.9E-06	5.84582E-06
3.00	-2.2E-03	-3.0091E-03	4.42E-05	4.43188E-05

Table 5 shows that the potential values agree more closely between methods than the dipole moments. It is also noticeable that for the 5.0 Å and 4.0 Å values that the magnitudes of the dipole and potential difference for Gaussian98 are so small that they are reported as zero.

5.3 CH₄-H₂

For this portion of the study, again, the experimental geometry of methane was used, $R_{CH} = 1.087$ Å with all the HCH bond angles equal to 109.4712° except for the H1-C-H2 bond angle, which is described below. For molecular hydrogen, the geometry used was $R_{HH} = 0.7414$ Å. These geometries are provided by the *CRC Handbook of Chemistry and Physics*²¹. Using these parameters, two sets of single-point energy calculations were again performed: single-point energy values from the linear approach and single-point energy values from the perpendicular approach. The linear approach is discussed first.

5.3.1 Linear Approach

The separation between the H₂ center of mass and the CH₄ center of mass was set to distances of 4.0 Å, 3.5 Å, 3.25 Å, and 3.0 Å, 2.75 Å, 2.50 Å, and 2.25 Å. At each distance, the H1-C-H2 bond angle was varied from 104° to 114° in increments of 1° , also including the angle 109.4712° . The minimum of the curve in each slice is the optimized

H1-C-H2 bond angle for the respective hydrogen-methane separations. Our results are listed in Table 5.

Table 5. CH₄-H₂ Linear Approach	
distance (Å)	distorted bond angle
4.00	109.53 ⁰
3.50	109.62 ⁰
3.25	109.77 ⁰
3.00	110.12 ⁰
2.75	110.88 ⁰
2.50	112.48 ⁰
2.25	115.53 ⁰

Table 5 shows that as the H₂ molecule approaches the CH₄ molecule, the bond angle under investigation widens. Table 6 lists the potential differences and dipoles of the distorted CH₄ molecule.

Table 6. Dipole and Potential from Molecular Distortion in CH₄-H₂ Linear Approach				
distance (Å)	Gaussian98 μ (a.u.)	Quack et al ¹⁴ μ (a.u.)	Gaussian98 V(YXY) (H)	Quack et al ¹⁴ V(YXY) (H)
4.00	-8.E-05	-1.3164E-04	1.E-07	8.27122E-08
3.50	-2.E-04	-3.3323E-04	6.E-07	5.22746E-07
3.25	-5.1E-04	-6.6946E-04	2.2E-06	2.10298E-06
3.00	-1.1E-03	-1.4552E-03	1.04E-05	1.03475E-05
2.75	-2.4E-03	-3.1671E-03	4.90E-05	4.90498E-05
2.50	-5.04E-03	-6.7967E-03	2.224E-04	2.23087E-04
2.25	-1.02E-02	-1.3809E-02	8.952E-04	8.97715E-04

Agreement of the distortion potential energy differences is very good. The bond-dipole model is useful as a first approximation, but it is not very accurate.

5.3.2 Perpendicular Approach

Using the same procedure as for the linear approach, similar sets of data were calculated and collected for the perpendicular approach of the H₂ molecule toward the CH₄ molecule. Table 7 lists the bond angle at each of the H₂-CH₄ separations.

Table 7. CH₄-H₂ Perpendicular Approach	
distance	distorted bond angle
(Å)	(degrees)
4.00	109.4 ⁰
3.50	109.36 ⁰
3.25	109.38 ⁰
3.00	109.51 ⁰
2.75	109.92 ⁰
2.50	111 ⁰
2.25	113.39 ⁰

Again, we see a shrinking of the bond angle as the diatomic first approaches CH₄, but at 3.00 Å, the angle begins to expand.

Table 8. Dipole and Potential from Molecular Distortion in the CH₄-H₂ Perpendicular Approach				
distance (Å)	Gaussian98 μ (a.u.)	Quack et al ¹⁴ μ (a.u.)	Gaussian98 V(YXY) (H)	Quack et al ¹⁴ V(YXY) (H)
4.00	1.E-04	1.59341E-04	2.E-07	1.21E-07
3.50	1.E-04	2.48828E-04	2.E-07	2.24E-05
3.25	2.E-04	2.04088E-04	2.E-07	1.97E-07
3.00	-8.E-05	-8.68616E-05	1.E-07	3.67E-08
2.75	-7.5E-04	-1.00600E-03	5.0E-06	4.96E-06
2.50	-2.6E-03	-3.43816E-03	5.76E-05	5.78E-05
2.25	-6.57E-03	-8.87631E-03	3.764E-04	3.78E-04

In Table 8, there is a stray value at 3.50 Å separation which might be due to some mathematical error in the potential energy surface. Otherwise, the potentials are close in value and the dipoles are of the same magnitude.

5.4 CH₄-He

For this portion of the study, again, the experimental geometry of methane was used, $R_{CH} = 1.087 \text{ \AA}$ with all the H-C-H bond angles equal to 109.4712° except for the H1-C-H2 bond angle, which is varied as described below. This geometry is provided by the *CRC Handbook of Chemistry and Physics*²¹. Using these parameters we calculated the energies for separations between the He atom and the methane center of mass of 4.0 $\text{\AA}$, 3.5 $\text{\AA}$, 3.25 $\text{\AA}$, and 3.0 $\text{\AA}$, 2.75 $\text{\AA}$, 2.50 $\text{\AA}$, and 2.25 $\text{\AA}$. At each distance, the H1CH2 bond angle was varied from 104° to 114° in increments of 1° also including the angle 109.4712° . The minimum of the curve in each slice is the optimized H1-C-H2 bond angle for the respective helium-methane separation. The results are listed in Table 9.

Table 9. CH₄-He Approach	
distance ($\text{\AA}$)	distorted bond angle (degrees)
4.00	109.46°
3.50	109.46°
3.25	109.47°
3.00	109.55°
2.75	109.81°
2.50	110.55°
2.25	112.35°

The potential differences and dipole moments are shown in Table 10.

Table 10. Dipole and Potential from Molecular Distortion in CH₄-He				
Approach				
distance (Å)	Gaussian98 μ (a.u.)	Quack et al ¹⁴ μ (a.u.)	Gaussian98 V(YXY) (H)	Quack et al ¹⁴ V(YXY) (H)
4.00	0.E+00	2.50696E-05	0.E+00	4.21E-09
3.50	0.E+00	2.50696E-05	0.E+00	4.21E-09
3.25	0.E+00	2.68611E-06	0.E+00	1.29E-09
3.00	-1.E-04	-1.76431E-04	2.E-07	1.48E-07
2.75	-5.5E-04	-7.59173E-04	3.E-06	2.70E-06
2.50	-1.8E-03	-2.42282E-03	3.E-05	2.87E-05
2.25	-4.80E-03	-6.50056E-03	2.E-04	2.04E-04

Again, Gaussian98 is not sensitive enough to measure the smaller potential differences and dipoles. The values are of the same magnitude and the potential energies agree more closely than the dipole values.

5.5 Discussion

We have proven that frame distortion occurs as N₂, H₂, or He approaches a CH₄ molecule. The change in the equilibrium bond angle produces a dipole moment on methane, thus proving an additional mechanism for absorption in the far-IR or IR by compressed gas mixtures containing methane. This is the principal conclusion from our work.

In addition, we have found that the methane H1-C-H2 bond angle first narrows and then widens as N₂ approaches in the “linear” configuration shown in Figure 2 and Figure 3. At the separations of 4 Å and 5 Å, the bond angle decreases in magnitude from the tetrahedral angle. This behavior may be due to the interaction of the negative quadrupole of nitrogen and the slightly positive charge of the hydrogen atoms in the methane molecule. In the presence of N₂ at 3.5 Å, 3.25 Å, and 3.0 Å, the methane bond angle widens, probably due to steric effects associated with electron repulsion. On the

perpendicular approach of N_2 , we have found that the bond angle simply increases as the intermolecular distance decreases.

However, this behavior does not mirror the methane-hydrogen approaches. The reverse is seen. On the perpendicular approach, we find first a slight closing and then the reopening of the bond angle, while the linear approach shows only a widening of the bond angle. This behavior would follow since in the linear conformation the positive portion of the hydrogen quadrupole is facing the CH_4 molecule; while in the perpendicular conformation, the negative portion of the H_2 quadrupole moment can interact with the partially positively charged H nuclei in CH_4 . At shorter range, steric effects predominate.

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APPENDIX A
CHAPTER 2 RAW DATA

Table 1. Heats of Formation of Atoms and Molecules				
	ΔH_f	De	Do	ΔH_{atm}
H	52.103			
Li	38.074			
C	171.29			
F	18.975			
Na	25.645			
Cl	28.991			
HCCH	54.18	408	392	393
FCCF	1.01	388	379	380
ClCCl	52.37	355	348	348
Linear LiCCLi	88.29	335	331	330
Planar Li2C2	80.47	342	337	338
Linear NaCCNa	97.96	300	296	296
Planar Na2C2	87.51	310	305	306

Table 2. HCCCH Energies, De, and Do Values							
CCSD(T)	Mol. Energy	C Atm. Ener.	H Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pVDZ	-77.1091296	-37.7603079	-0.4992784	0.58996	370.20	0.56417	354.02
cc-pVTZ	-77.1875575	-37.7805485	-0.4998098	0.62684	393.35	0.60105	377.16
cc-pVQZ	-77.2092861	-37.7863026	-0.4999456	0.63679	399.59	0.61100	383.41
cc-pV5Z	-77.2157569	-37.7879925	-0.4999945	0.63978	401.47	0.61399	385.29
cc-pV6Z	-77.2179548	-37.7885099	-0.4999992	0.64094	402.19	0.61515	386.01
aug-cc-pVDZ	-77.1195588	-37.7647609	-0.4993343	0.59137	371.09	0.56558	354.91
aug-cc-pVTZ	-77.1916091	-37.7815947	-0.4998212	0.62878	394.56	0.60299	378.38
aug-cc-pVQZ	-77.2109605	-37.7867431	-0.4999483	0.63758	400.09	0.61179	383.90
aug-cc-pV5Z	-77.2164590	-37.7881355	-0.4999948	0.64020	401.73	0.61441	385.55
aug-cc-pV6Z	-77.2183947	-37.7886249	-0.4999993	0.64115	402.33	0.61536	386.14
d-aug-cc-pVDZ	-77.1204996	-37.7648673	-0.4993347	0.59210	371.55	0.56630	355.36
d-aug-cc-pVTZ	-77.1924876	-37.7816432	-0.4998213	0.62956	395.05	0.60377	378.87
d-aug-cc-pVQZ	-77.2112038	-37.7866576	-0.4999484	0.63799	400.35	0.61220	384.16

Table 3. Extrapolated HCCH Energies, De, Do Values							
CCSD(T)	Mol. Energy	C Atm. Ener.	H Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
feller							
cc-pvXz (DTQ56)	-77.2183847	-37.7886753	-0.5000042	0.64103	402.25	0.61523	386.07
cc-pvXz (Q56)	-77.2190853	-37.7887382	-0.4999997	0.64161	402.62	0.61582	386.43
aug-cc-pvXz (DTQ56)	-77.2186776	-37.7888204	-0.5000044	0.64103	402.25	0.61524	386.07
aug-cc-pvXz (Q56)	-77.2194467	-37.7888902	-0.4999998	0.64167	402.65	0.61588	386.47
schwarz2							
cc-pvXz (DTQ56)	-77.2224086	-37.7897452	-0.5000279	0.64286	403.40	0.61707	387.22
cc-pvXz (Q56)	-77.2197361	-37.7888670	-0.5000001	0.64200	402.86	0.61621	386.68
aug-cc-pvXz (DTQ56)	-77.2220571	-37.7898167	-0.5000273	0.64237	403.09	0.61658	386.91
aug-cc-pvXz (Q56)	-77.2200575	-37.7890441	-0.5000001	0.64197	402.84	0.61618	386.66
schwarz4							
cc-pvXz (DTQ56)	-77.2194711	-37.7889119	-0.5000158	0.64162	402.62	0.61582	386.44
cc-pvXz (56)	-77.2202666	-37.7890541	-0.5000042	0.64215	402.96	0.61636	386.77
aug-cc-pvXz (DTQ56)	-77.2200851	-37.7888840	-0.5000134	0.64229	403.04	0.61650	386.86
aug-cc-pvXz (56)	-77.2204308	-37.7891397	-0.5000040	0.64214	402.95	0.61635	386.77
schwarz6							
cc-pvXz (DTQ56)	-77.2216037	-37.7895166	-0.5000250	0.64252	403.19	0.61673	387.00
cc-pvXz (56)	-77.2202647	-37.7890536	-0.5000042	0.64215	402.95	0.61636	386.77
aug-cc-pvXz (DTQ56)	-77.2215643	-37.7895452	-0.5000238	0.64243	403.13	0.61664	386.94
aug-cc-pvXz (56)	-77.2204291	-37.7891392	-0.5000040	0.64214	402.95	0.61635	386.77

Table 4. Core-Valence and Extrapolated Core-Valence HCCH Energies, De, Do, Values with Unfrozen Core							
In these calculations excitations are allowed from the 1s core							
CCSD(T)	Mol. Energy	C Atm. Ener.	H Atm. Ener.	De	Do	Do	
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-77.1874641	-37.7979616	-0.4992784	0.59298	372.10	0.56719	355.92
cc-pCVTZ	-77.2897810	-37.8299103	-0.4998098	0.63034	395.54	0.60455	379.36
cc-pCQZ	-77.3194044	-37.8394847	-0.4999456	0.64054	401.95	0.61475	385.76
cc-pCV5Z	-77.3280094	-37.8421645	-0.4999945	0.64569	403.92	0.61790	387.74
Feller(TQ5)	-77.3315326	-37.8432063	-0.5000000	0.64512	404.82	0.61933	388.63
Schwartz(TQ5)	-77.3340899	-37.8439591	-0.5000000	0.64617	405.48	0.62038	389.29
Schwartz4(Q5)	-77.3349968	-37.8443405	-0.5000000	0.64632	405.57	0.62052	389.39
Schwartz6(Q5)	-77.3349838	-37.8443365	-0.5000000	0.64631	405.57	0.62052	389.38

Table 5. Core-Valence and Extrapolated Core-Valence HCCH Energies, De, Do, Values with Frozen Core							
In these calculations excitations are notallowed from the 1s core							
CCSD(T)	Mol. Energy	C Atm. Ener.	H Atm. Ener.	De	Do	Do	
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-77.1130478	-37.7616572	-0.4992784	0.59118	370.97	0.56539	354.78
cc-pCVTZ	-77.1902761	-37.7816584	-0.4998098	0.62734	393.66	0.60155	377.48
cc-pCQZ	-77.2103957	-37.7868046	-0.4999456	0.63690	399.66	0.61110	383.47
cc-pCV5Z	-77.2162312	-37.7881963	-0.4999945	0.63985	401.51	0.61406	385.33
Feller(TQ5)	-77.2186154	-37.7887122	-0.5000000	0.64119	402.35	0.61540	386.17
Schwartz(TQ5)	-77.2203454	-37.7890840	-0.5000000	0.64218	402.97	0.61639	386.79
Schwartz4(Q5)	-77.2209696	-37.7893264	-0.5000000	0.64232	403.06	0.61653	386.88
Schwartz6(Q5)	-77.2209608	-37.7893242	-0.5000000	0.64231	403.06	0.61652	386.87

Basis	SCF Optimized Geometries			CCSD(T) Optimized Geometries		
	RCC (ang)	RCF (ang)	Energy (H)	RCC (ang)	RCF (ang)	Energy (H)
cc-pVDZ	1.17092	1.27352	-274.47767	1.20969	1.30039	-275.12228
cc-pVTZ	1.16111	1.26488	-274.56960	1.19277	1.28859	-275.39160
cc-pVQZ	1.15976	1.26333	-274.59158	1.18918	1.28586	-275.47589
cc-pV5Z	1.15976	1.26300	-274.59730	1.18857	1.28512	-275.50418
aug-cc-pVDZ	1.17123	1.27280	-274.49432	1.21157	1.30594	-275.17825
aug-cc-pVTZ	1.16085	1.26428	-274.57370	1.19280	1.28948	-275.41192
aug-cc-pVQZ	1.15988	1.26304	-274.59263	1.18951	1.28613	-275.48396
aug-cc-pV5Z	1.15979	1.26287	-274.59748	1.18868	1.28524	-275.50741
d-aug-cc-pVDZ	1.17087	1.27180	-274.49649	1.21109	1.30440	-275.18297
d-aug-cc-pVTZ	1.16061	1.26422	-274.57451	1.19257	1.28935	-275.41477
d-aug-cc-pVQZ	1.15988	1.26303	-274.59290	1.18944	1.28603	-275.48514
d-aug-cc-pV5Z	1.15979	1.26287	-274.59750			

CCSD(T)	Mol. Energy	C-Atom Energ.		F-Atom Energ.		De		Do	
		Hartrees	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
Basis sets									
cc-pVDZ	-275.1222805	-37.7603079	-99.5275188	0.54663	343.01	0.53338	334.70		
cc-pVTZ	-275.3915977	-37.7805485	-99.6202156	0.59007	370.27	0.57682	361.96		
cc-pVQZ	-275.4758860	-37.7863026	-99.6500779	0.60313	378.47	0.58988	370.16		
cc-pV5Z	-275.5041820	-37.7879925	-99.6604344	0.60733	381.10	0.59408	372.79		
aug-cc-pVDZ	-275.1782473	-37.7647609	-99.5499697	0.54879	344.37	0.53554	336.06		
aug-cc-pVTZ	-275.4119244	-37.7815947	-99.6276085	0.59352	372.44	0.58027	364.13		
aug-cc-pVQZ	-275.4839582	-37.7867431	-99.6527181	0.60504	379.67	0.59179	371.35		
aug-cc-pV5Z	-275.5074120	-37.7881355	-99.6614698	0.60820	381.65	0.59496	373.34		
d-aug-cc-pVDZ	-275.1829664	-37.7848673	-99.5502582	0.55272	346.83	0.53947	338.52		
d-aug-cc-pVTZ	-275.4147700	-37.7816432	-99.6279403	0.59560	373.75	0.58236	365.44		
d-aug-cc-pVQZ	-275.4851379	-37.7866576	-99.6528383	0.60615	380.36	0.59290	372.05		
d-aug-cc-pV5Z	-275.5079363	-37.7881479	-99.6615430	0.60855	381.87	0.59531	373.56		

Table 8. Extrapolated FCCF Energies, De, and Do Values							
CCSD(T)	Mol. Energy	C Atm. Ener.	F Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
feller							
cc-pvXz (DTQ5)	-275.5163300	-37.7886412	-99.6650791	0.60889	382.08	0.59564	373.77
cc-pvXz (TQ5)	-275.5184825	-37.7886953	-99.6659328	0.60923	382.30	0.59598	373.98
aug-cc-pvXz (DTQ5)	-275.5173727	-37.7888247	-99.6654164	0.60889	382.08	0.59565	373.77
aug-cc-pvXz (TQ5)	-275.5187353	-37.7886518	-99.6661521	0.60913	382.23	0.59588	373.92
d-aug-cc-pvXz (DTQ5)	-275.5172988	-37.7887867	-99.6653747	0.60898	382.14	0.59573	373.83
d-aug-cc-pvXz (TQ5)	-275.5188643	-37.7887782	-99.6654236	0.61046	383.07	0.59722	374.76
schwartza							
cc-pvXz (DTQ5)	-275.5435210	-37.7901684	-99.6752946	0.61259	384.41	0.59935	376.10
cc-pvXz (TQ5)	-275.5291592	-37.7892060	-99.6700780	0.61059	383.15	0.59735	374.84
aug-cc-pvXz (DTQ5)	-275.5397500	-37.7902601	-99.6740789	0.61107	383.45	0.59783	375.14
aug-cc-pvXz (TQ5)	-275.5271247	-37.7890239	-99.6696871	0.60970	382.59	0.59646	374.28
d-aug-cc-pvXz (DTQ5)	-275.5386712	-37.7902115	-99.6738776	0.61049	383.09	0.59725	374.78
d-aug-cc-pvXz (TQ5)	-275.5269488	-37.7892371	-99.6697583	0.60896	382.13	0.59571	373.82
schwartz4							
cc-pvXz (DTQ5)	-275.5104719	-37.7888105	-99.6621062	0.60864	381.93	0.59539	373.61
cc-pvXz (Q5)	-275.5271584	-37.7893647	-99.6688438	0.61074	383.25	0.59750	374.93
aug-cc-pvXz (DTQ5)	-275.5136774	-37.7887625	-99.6628094	0.61053	383.12	0.59729	374.80
aug-cc-pvXz (Q5)	-275.5264566	-37.7892662	-99.6685762	0.61077	383.27	0.59753	374.95
d-aug-cc-pvXz (DTQ5)	-275.5145992	-37.7887339	-99.6629507	0.61123	383.55	0.59798	375.24
d-aug-cc-pvXz (Q5)	-275.5264486	-37.7893581	-99.6686112	0.61051	383.10	0.59726	374.79
schwartz6							
cc-pvXz (DTQ5)	-275.5308461	-37.7897353	-99.6699953	0.61138	383.65	0.59814	375.34
cc-pvXz (Q5)	-275.5271157	-37.7893622	-99.6688282	0.61073	383.24	0.59749	374.93
aug-cc-pvXz (DTQ5)	-275.5300598	-37.7897557	-99.6695217	0.61150	383.73	0.59826	375.41
aug-cc-pvXz (Q5)	-275.5264212	-37.7892641	-99.6685629	0.61077	383.26	0.59752	374.95
d-aug-cc-pvXz (DTQ5)	-275.5299036	-37.7897052	-99.6694948	0.61150	383.72	0.59826	375.41
d-aug-cc-pvXz (Q5)	-275.5264142	-37.7893558	-99.6685981	0.61051	383.10	0.59726	374.79

Table 9. Core-Valence and Extrapolated Core-Valence FCCF Energies, De, Do, Values with Unfrozen Core
In these calculations excitations are allowed from the 1s core.

CCSD(T)	Mol. Energy	C Atm. Ener.	F Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-275.2831823	-37.7979616	-99.5694181	0.54842	344.14	0.53518	335.83
cc-pCVTZ	-275.6173127	-37.8299103	-99.6815311	0.59443	373.01	0.58118	364.70
cc-pCVQZ	-275.7158902	-37.8394847	-99.7147153	0.60749	381.21	0.59424	372.89
cc-pCV5Z	-275.7470728	-37.8421645	-99.7254231	0.61190	383.97	0.59865	375.66
Feller(TQ5)	-275.7614997	-37.8432063	-99.7305243	0.61404	385.32	0.60079	377.00
Schwartzaa(TQ5)	-275.7721231	-37.8439591	-99.7342958	0.61561	386.30	0.60237	377.99
Schwartz4(Q5)	-275.7723932	-37.8443405	-99.7341178	0.61548	386.22	0.60223	377.91
Schwartz6(Q5)	-275.7723462	-37.8443365	-99.7341016	0.61547	386.21	0.60222	377.90
aug-cc-pCVDZ	-275.3405576	-37.8024758	-99.5919977	0.55161	346.14	0.53837	337.83
aug-cc-pCVTZ	-275.6365667	-37.8309189	-99.6888934	0.59694	374.59	0.58370	366.28
aug-cc-pCVQZ	-275.7234599	-37.8398090	-99.7173172	0.60921	382.28	0.59596	373.97
aug-cc-pCV5Z	-275.7501359	-37.8423047	-99.7264454	0.61264	384.43	0.59939	376.12
Feller(TQ5)	-275.7619538	-37.8432790	-99.7307631	0.61387	385.21	0.60062	376.90
Schwartzaa(TQ5)	-275.7706036	-37.8439832	-99.7339529	0.61473	385.75	0.60149	377.44
Schwartz4(Q5)	-275.7717969	-37.8443313	-99.7338575	0.61542	386.18	0.60217	377.87
Schwartz6(Q5)	-275.7717566	-37.8443275	-99.7338437	0.61541	386.18	0.60217	377.87

Table 10. Core-Valence and Extrapolated Core-Valence FCCF Energies, De, Do, Values with Frozen Core							
Differences between frozen and unfrozen core calculations							
CCSD(T)	Mol. Energy	C Atm. Ener.	F Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-275.1316983	-37.7616572	-99.5311034	0.54618	342.73	0.53293	334.42
cc-pCVTZ	-275.4050561	-37.7816584	-99.6254833	0.59077	370.72	0.57753	362.40
cc-pCVQZ	-275.4820770	-37.7868046	-99.6526520	0.60316	378.49	0.58992	370.18
cc-pCV5Z	-275.5068488	-37.7881963	-99.6615467	0.60736	381.13	0.59412	372.81
Feller(TQ5)	-275.5185023	-37.7887122	-99.6658762	0.60942	382.41	0.59617	374.10
Schwartz4(TQ5)	-275.5272703	-37.7890840	-99.6690883	0.61093	383.36	0.59768	375.05
Schwartz4(Q5)	-275.5269636	-37.7893264	-99.6687692	0.61077	383.27	0.59753	374.95
Schwartz6(Q5)	-275.5269262	-37.7893242	-99.6687558	0.61077	383.26	0.59752	374.95
aug-cc-pCVDZ	-275.1876256	-37.7660709	-99.5535215	0.54844	344.15	0.53520	335.84
aug-cc-pCVTZ	-275.4239587	-37.7826520	-99.6328323	0.59299	372.11	0.57974	363.80
aug-cc-pCVQZ	-275.4896011	-37.7871281	-99.6552590	0.60483	379.53	0.59158	371.22
aug-cc-pCV5Z	-275.5098975	-37.7883361	-99.6625707	0.60808	381.58	0.59484	373.27
Feller(TQ5)	-275.5189813	-37.7887826	-99.6661074	0.60920	382.28	0.59596	373.97
Schwartz4(TQ5)	-275.5256409	-37.7891044	-99.6687290	0.60997	382.76	0.59673	374.45
Schwartz4(Q5)	-275.5263784	-37.7893170	-99.6685078	0.61073	383.24	0.59748	374.93
Schwartz6(Q5)	-275.5263476	-37.7893151	-99.6684967	0.61072	383.24	0.59748	374.92

Table 11. Optimized Geometries of ClCCCl						
Basis	SCF Optimized Geometries			CCSD(T) Optimized Geometries		
	RCC (ang)	RCCl (ang)	Energy (H)	RCC (ang)	RCCl (ang)	Energy (H)
cc-pVDZ	1.18527	1.65074	-994.64344	1.22442	1.66458	-995.20934
cc-pVTZ	1.17577	1.64300	-994.69909	1.20872	1.64891	-995.43413
cc-pVQZ	1.17429	1.64066	-994.71265	1.20530	1.64339	-995.50320
cc-pV5Z	1.17438	1.63835	-994.71660	1.20506	1.63965	-995.52631
aug-cc-pVDZ	1.18522	1.65254	-994.64843	1.22560	1.66890	-995.24511
aug-cc-pVTZ	1.17528	1.64309	-994.70031	1.20889	1.64883	-995.44864
aug-cc-pVQZ	1.17424	1.64040	-994.71294	1.20551	1.64339	-995.50875
aug-cc-pV5Z	1.17434	1.63830	-994.71668	1.20533	1.63970	-995.52918

Table 12. ClCCCl Energies, De, Do Values							
CCSD(T)	Mol. Energy	C Atm. Ener.	Cl Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pVDZ	-995.2074680	-37.7603079	-459.5988318	0.48919	306.97	0.47846	300.24
cc-pVTZ	-995.4338556	-37.7805485	-459.6716172	0.52952	332.28	0.51880	325.55
cc-pVQZ	-995.5031076	-37.7863026	-459.6930524	0.54440	341.61	0.53367	334.88
cc-pV5Z	-995.5262854	-37.7879925	-459.6996677	0.55097	345.74	0.54024	339.00
aug-cc-pVDZ	-995.2428273	-37.7647609	-459.6121264	0.48905	306.89	0.47832	300.15
aug-cc-pVTZ	-995.4483663	-37.7815947	-459.6760177	0.53314	334.55	0.52241	327.82
aug-cc-pVQZ	-995.5086652	-37.7867431	-459.6944813	0.54622	342.76	0.53549	336.02
aug-cc-pV5Z	-995.5291477	-37.7881355	-459.7004921	0.55189	346.32	0.54116	339.59
d-aug-cc-pVDZ	-995.2476158	-37.7648673	-459.6129585	0.49196	308.71	0.48124	301.98
d-aug-cc-pVTZ	-995.4508026	-37.7816432	-459.6763463	0.53482	335.61	0.52410	328.88
d-aug-cc-pVQZ	-995.5097185	-37.7866576	-459.6946236	0.54716	343.35	0.53643	336.61
d-aug-cc-pV5Z	-995.5298591	-37.7881479	-459.7005969	0.55237	346.62	0.54164	339.89

Table 13. Extrapolated CIOCCl Energies, De, Do Values

CCSD(T)	Mol. Energy	Ci Atm. Ener.	Cl Atm. Ener.	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
feller						
cc-pvXz (DTQ5)	-995.5357186	-37.7886412	-459.7023054	0.55383	347.53	340.80
cc-pvXz (TQ5)	-995.5379436	-37.7886953	-459.7026202	0.55531	348.46	341.73
aug-cc-pvXz (DTQ5)	-995.5365350	-37.7888247	-459.7026613	0.55356	347.37	340.63
aug-cc-pvXz (TQ5)	-995.5396857	-37.7886518	-459.7033938	0.55559	348.64	341.91
d-aug-cc-pvXz (DTQ5)	-995.5368564	-37.7887867	-459.7027311	0.55382	347.53	340.80
d-aug-cc-pvXz (TQ5)	-995.5403196	-37.7887782	-459.7027077	0.55735	349.74	343.01
schwartz2a						
cc-pvXz (DTQ5)	-995.5573624	-37.7901684	-459.7084039	0.56022	351.54	344.81
cc-pvXz (TQ5)	-995.5466448	-37.7892060	-459.7047841	0.55866	350.57	343.84
aug-cc-pvXz (DTQ5)	-995.5545511	-37.7900260	-459.7079432	0.55814	350.24	343.51
aug-cc-pvXz (TQ5)	-995.5475786	-37.7890239	-459.7055434	0.55844	350.43	343.70
d-aug-cc-pvXz (DTQ5)	-995.5542660	-37.7902115	-459.7079568	0.55793	350.11	343.37
d-aug-cc-pvXz (TQ5)	-995.5481721	-37.7892371	-459.7056471	0.55840	350.40	343.67
schwartz4						
cc-pvXz (DTQ5)	-995.5321860	-37.7888105	-459.7021790	0.55021	345.26	338.53
cc-pvXz (Q5)	-995.5451059	-37.7893647	-459.7050394	0.55630	349.08	342.35
aug-cc-pvXz (DTQ5)	-995.5352547	-37.7887625	-459.7026397	0.55245	346.67	339.94
aug-cc-pvXz (Q5)	-995.5457796	-37.7892662	-459.7053730	0.55650	349.21	342.48
d-aug-cc-pvXz (DTQ5)	-995.5360734	-37.7887339	-459.7027288	0.55315	347.11	340.37
d-aug-cc-pvXz (Q5)	-995.5462134	-37.7893581	-459.7054472	0.55660	349.27	342.54
schwartz6						
cc-pvXz (DTQ5)	-995.5479636	-37.7897353	-459.7062697	0.55595	348.87	342.13
cc-pvXz (Q5)	-995.5450702	-37.7893622	-459.7050290	0.55629	349.08	342.34
aug-cc-pvXz (DTQ5)	-995.5476347	-37.7897557	-459.7061166	0.55589	348.83	342.09
aug-cc-pvXz (Q5)	-995.5454749	-37.7892641	-459.7053635	0.55649	349.20	342.47
d-aug-cc-pvXz (DTQ5)	-995.5478119	-37.7897052	-459.7061576	0.55609	348.95	342.22
d-aug-cc-pvXz (Q5)	-995.5461822	-37.7893558	-459.7054378	0.55659	349.27	342.54

Table 14. Core-Valence and Extrapolated Core-Valence C1CC1 Energies, De, Do, Values with Unfrozen Core

In these calculations excitations are allowed from the 2s,2p core.							
CCSD(T)	Mol. Energy	C Atm. Ener.	Cl Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-995.7218472	-37.7979616	-459.8155090	0.49491	310.56	0.48418	303.83
cc-pCVTZ	-996.2223104	-37.8299103	-460.0122802	0.53793	337.56	0.52720	330.82
cc-pCVQZ	-996.4117453	-37.8394847	-460.0907070	0.55136	345.98	0.54063	339.25
Feller(DTQ)	-996.5271187	-37.8435822	-460.1426767	0.55460	348.02	0.54387	341.29
Schwartz4(DTQ)	-996.6571622	-37.8478235	-460.2031283	0.55526	348.43	0.54453	341.70
Schwartz4(TQ)	-996.5210802	-37.8450107	-460.1359721	0.55911	350.85	0.54839	344.12
Schwartz6(TQ)	-996.5205131	-37.8449822	-460.1357366	0.55908	350.83	0.54835	344.09

Table 15. Core-Valence and Extrapolated Core-Valence C1CC1 Energies, De, Do, Values with Frozen Core

In these calculations excitations are not allowed from the 1s,2s,2p core.							
CCSD(T)	Mol. Energy	C Atm. Ener.	Cl Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-995.2184893	-37.7616572	-459.6018018	0.49157	308.47	0.48084	301.73
cc-pCVTZ	-995.4472661	-37.7816584	-459.6750883	0.53377	334.95	0.52304	328.22
cc-pCVQZ	-995.5114789	-37.7868046	-459.6954890	0.54689	343.18	0.53616	336.45
Feller(DTQ)	-995.5365382	-37.7885876	-459.7033587	0.55265	346.79	0.54192	340.06
Schwartz4(DTQ)	-995.5621745	-37.7903940	-459.7114021	0.55858	350.52	0.54785	343.78
Schwartz4(TQ)	-995.5485403	-37.7897747	-459.7072635	0.55446	347.93	0.54374	341.20
Schwartz6(TQ)	-995.5483380	-37.7897592	-459.7071971	0.55443	347.91	0.54370	341.18

Table 16. Optimized Geometries for Linear Li_2C_2						
SCF Optimized Energies			CCSD(T) Optimized Energies			
Basis	C//C ang.	C/Li ang	Energy Hartree	C//C ang.	C/Li ang	Energy Hartree
cc-pVDZ	1.24084	1.91335	-90.56181	1.27647	1.92548	-90.84990
cc-pVTZ	1.22918	1.88590	-90.58814	1.25774	1.89386	-90.93000
cc-pVQZ	1.22814	1.88563	-90.59374	1.25403	1.89388	-90.95306
5Z : QZ	1.22809	1.88631	-90.59469	1.25324	1.89411	-90.95949
6Z : QZ	1.22814	1.88644	-90.59488	1.25305	1.89419	-90.96199
aug-cc-pVDZ	1.24164	1.89593	-90.57045	1.27798	1.91654	-90.86928
aug-cc-pVTZ	1.22960	1.88715	-90.58975	1.25839	1.89809	-90.93690
aug-cc-pVQZ	1.22837	1.88657	-90.59403	1.25459	1.89571	-90.95553
aug(5Z : QZ)	1.22821	1.88623	-90.59482	1.25354	1.89479	-90.96086
aug(6Z : QZ)	1.22821	1.88611	-90.59493	1.25324	1.89452	-90.96283

Table 17. Extrapolated Geometries of Linear Li_2C_2			
	C//C ang.	C/Li ang	
Feller(DTQ)	1.2531	1.8939	
Schwartz4(DTQ)	1.2522	1.8939	
Schwartz4(DTQ)	1.2515	1.8876	
Schwartz4(TQ)	1.2519	1.8939	
Schwartz6(DTQ)	1.2520	1.8963	
Schwartz6(TQ)	1.2519	1.8939	
Used	1.2531	1.8943	

Table 18. Linear Li ₂ C ₂ Energies, De and Do Values								
CCSD(T)	Mol. Energy	C Atm. Ener.	Li Atm. Ener.	De	De	Do	Do	
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol	
cc-pVDZ	-90.8498966	-37.7603079	-7.4324199	0.46444	291.44	0.45704	286.80	
cc-pVTZ	-90.9299969	-37.7805485	-7.4326789	0.50354	315.98	0.49614	311.33	
cc-pVQZ	-90.9530636	-37.7863026	-7.4326951	0.51507	323.21	0.50767	318.57	
cc-(5Z-QZ)	-90.9594919	-37.7879925	-7.4326951	0.51812	325.12	0.51072	320.48	
cc-(6Z-QZ)	-90.9619854	-37.7885099	-7.4326951	0.51958	326.04	0.51218	321.40	
aug-cc-pVDZ	-90.8692826	-37.7647609	-7.4324253	0.47491	298.01	0.46751	293.37	
aug-cc-pVTZ	-90.9368984	-37.7815947	-7.4326814	0.50835	318.99	0.50095	314.35	
aug-cc-pVQZ	-90.9555288	-37.7867431	-7.4326955	0.51665	324.20	0.50925	319.56	
aug(5Z-QZ)	-90.9608586	-37.7881355	-7.4326955	0.51920	325.80	0.51180	321.16	
aug(6Z-QZ)	-90.9628328	-37.7886249	-7.4326955	0.52019	326.43	0.51279	321.78	

Table 19. Extrapolated Linear Li ₂ C ₂ Energies, De and Do Values								
CCSD(T)	Mol. Energy	C Atm. Ener.	Li Atm. Ener.	De	De	Do	Do	
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol	
feller								
cc-pvXz (DTQ)	-90.9623924	-37.7885879	-7.4326962	0.51982	326.19	0.51243	321.55	
schwartz2a								
cc-pvXz (DTQ)	-90.9719784	-37.7909315	-7.4326977	0.52472	329.27	0.51732	324.62	
schwartz4								
cc-pvXz (DTQ)	-90.9617190	-37.7885136	-7.4327418	0.51921	325.81	0.51181	321.17	
cc-pvXz (TQ)	-90.9663769	-37.7896236	-7.4327045	0.52172	327.38	0.51432	322.74	
schwartz6								
cc-pvXz (DTQ)	-90.9681228	-37.7900397	-7.4326906	0.52266	327.98	0.51526	323.33	
cc-pvXz (TQ)	-90.9663083	-37.7896063	-7.4327044	0.52169	327.36	0.51429	322.72	

Table 20. Core-Valence and Extrapolated Core-Valence Linear Li_2C_2 Energies, De, Do, Values with Unfrozen Core									
In these calculations excitations are allowed from the 1s core.									
CCSD(T)	Mol. Energy	C Atm. Ener.	Li Atm. Ener.	De	De	Do	Do		
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol		
cc-pCVDZ	-90.9959549	-37.7979616	-7.4660245	0.46798	293.66364	0.46058	289.02095		
cc-pCVTZ	-91.1166298	-37.8299103	-7.4742476	0.50831	318.97190	0.50092	314.32921		
cc-pCVQZ	-91.1512709	-37.8394847	-7.4763674	0.51957	326.03305	0.51217	321.39037		
cc-(QZ-5Z)	-91.1597739	-37.8421645	-7.4763674	0.52271	328.00554	0.51531	323.36285		
Feller(DTQ)	-91.1652172	-37.8435822	-7.4771037	0.52385	328.71788	0.51645	324.07519		
Schwartz4(DTQ)	-91.1795413	-37.8478235	-7.4813317	0.52123	327.07740	0.51383	322.43471		
Schwartz4(TQ)	-91.1712645	-37.8450107	-7.4775908	0.52606	330.10849	0.51866	325.46581		
Schwartz6(TQ)	-91.1711621	-37.8449822	-7.4775845	0.52603	330.08792	0.51863	325.44523		

Table 21. Core-Valence and Extrapolated Core-Valence Linear Li_2C_2 Energies, De, Do, Values with Frozen Core									
In these calculations excitations are not allowed from the 1s core.									
CCSD(T)	Mol. Energy	C Atm. Ener.	Li Atm. Ener.	De	De	Do	Do		
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol		
cc-pCVDZ	-90.8543096	-37.7616572	-7.4324199	0.46616	292.52	0.45876	287.87		
cc-pCVTZ	-90.9336587	-37.7816584	-7.4326793	0.50498	316.88	0.49758	312.24		
cc-pCVQZ	-90.9543836	-37.7868046	-7.4326953	0.51538	323.41	0.50799	318.77		
cc-(QZ-5Z)	-90.9601286	-37.7881963	-7.4326953	0.51835	325.27	0.51095	320.62		
Feller(DTQ)	-90.9617108	-37.7885876	-7.4326963	0.51914	325.77	0.51174	321.12		
Schwartz4(DTQ)	-90.9691449	-37.7903940	-7.4327116	0.52293	328.15	0.51554	323.50		
Schwartz4(TQ)	-90.9663452	-37.7897747	-7.4327045	0.52139	327.18	0.51399	322.53		
Schwartz6(TQ)	-90.9662834	-37.7897592	-7.4327043	0.52136	327.16	0.51396	322.51		

Table 22. Optimized Geometries for Planar Li ₂ C ₂									
	SCF Optimized Geometries				CCSD(T) Optimized Geometries				
	C//C	LI-(C//C)	C/Li	Energy	C//C	LI-(C//C)	C/Li	Energy	
basis	ang.	ang	ang.	Hartree	ang.	ang	ang	Hartree	
cc-pVDZ	1.25571	1.93143	2.03092	-90.57447	1.29316	1.93547	2.04062	-90.86490	
cc-pVTZ	1.24270	1.91073	2.00922	-90.59781	1.27300	1.90359	2.00719	-90.94303	
cc-pVQZ	1.24101	1.90927	2.00757	-90.60279	1.26858	1.90190	2.00488	-90.96523	
5Z : QZ	1.24082	1.90902	2.27684	-90.60366	1.26752	1.90164	2.28535	-90.97143	
6Z : QZ	1.24082	1.90902	2.27684	-90.60379	1.26719	1.90152	2.28508	-90.97383	
aug-cc-pVDZ	1.25601	1.92672	2.29996	-90.57884	1.29473	1.93307	2.32661	-90.87969	
aug-cc-pVTZ	1.24229	1.91073	2.27907	-90.59865	1.27289	1.90679	2.29262	-90.94851	
aug-cc-pVQZ	1.24101	1.90924	2.27713	-90.60293	1.26884	1.90282	2.28707	-90.96718	
aug(5Z : QZ)	1.24086	1.91008	2.27775	-90.60372	1.26775	1.90196	2.28575	-90.97252	
aug(6Z : QZ)	1.24086	1.91008	2.27775	-90.60383	1.26743	1.90152	2.28521	-90.97453	

Table 23. Extrapolated Geometries for Planar Li_2C_2			
	C//C	C/Li	
	ang.	ang.	
Feller(DTQ)	1.2673	2.0047	
Schwartz4(DTQ)	1.2661	2.0045	
Schwartz4(DTQ)	1.2660	1.9989	
Schwartz4(TQ)	1.2660	2.0036	
Schwartz6(DTQ)	1.2661	2.0053	
Schwartz6(TQ)	1.2660	2.0053	
Used	1.2673	2.0043	

Table 24. Planar Li ₂ C ₂ Energies, De and Do Values							
CCSD(T)	Mol. Energy	C Alm. Ener.	Li Alm. Ener.	De	Do	De	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pVDZ	-90.8649012	-37.7603079	-7.4324199	0.47945	300.86	0.47126	295.72
cc-pVTZ	-90.9430269	-37.7805485	-7.4326789	0.51657	324.15	0.50839	319.02
cc-pVQZ	-90.9652267	-37.7863026	-7.4326951	0.52723	330.84	0.51905	325.71
cc-(5Z-QZ)	-90.9714326	-37.7879925	-7.4326951	0.53006	332.62	0.52188	327.48
cc-(6Z-QZ)	-90.9738318	-37.7885099	-7.4326951	0.53142	333.47	0.52324	328.34
aug-cc-pVDZ	-90.8796879	-37.7647609	-7.4324253	0.48532	304.54	0.47713	299.41
aug-cc-pVTZ	-90.9485146	-37.7815947	-7.4326814	0.51996	326.28	0.51178	321.15
aug-cc-pVQZ	-90.9671815	-37.7867431	-7.4326955	0.52830	331.52	0.52012	326.38
aug-(5Z-QZ)	-90.9725242	-37.7881355	-7.4326955	0.53086	333.12	0.52268	327.99
aug-(6Z-QZ)	-90.9745328	-37.7886249	-7.4326955	0.53189	333.77	0.52371	328.63

Table 25. Planar Li ₂ C ₂ Energies, De and Do Values							
CCSD(T)	Mol. Energy	C Alm. Ener.	Li Alm. Ener.	De	Do	De	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pvXz (DTQ) schwarz4	-90.9740399	-37.7885879	-7.4326962	0.53147	333.50	0.52329	328.37
cc-pvXz (DTQ) schwarz4	-90.9830735	-37.7900315	-7.4326977	0.53582	336.23	0.52763	331.10
cc-pvXz (DTQ) cc-pvXz (TQ) schwarz6	-90.9737641 -90.9780396 -90.9780396	-37.7885136 -37.7896236 -37.7896236	-7.4327418 -7.4327045 -7.4327045	0.53125 0.53338 0.53338	333.37 334.70 334.70	0.52307 0.52520 0.52520	328.23 329.57 329.57
cc-pvXz (DTQ) cc-pvXz (TQ)	-90.9796422 -90.97979735	-37.7900397 -37.7896063	-7.4326906 -7.4327044	0.53418 0.53335	335.20 334.68	0.52600 0.52517	330.07 329.55

Table 26. Core-Valence and Extrapolated Core-Valence Planar Li_2C_2 Energies, De, Do, Values with Unfrozen Core									
In these calculations excitations are allowed from the 1s core.									
CCSD(T)	Mol. Energy	C Atm. Ener.	Li Atm. Ener.	De	De	Do	Do		
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol		
cc-pCVDZ	-91.0109577	-37.7979616	-7.4660245	0.48299	303.08	0.47480	297.94		
cc-pCVTZ	-91.1297649	-37.8299103	-7.4742476	0.52145	327.21	0.51327	322.08		
cc-pCVQZ	-91.1635923	-37.8394847	-7.4763674	0.53189	333.76	0.52371	328.63		
cc-pCV5Z	-91.1718102	-37.8421645	-7.4763674	0.53475	335.56	0.52657	330.42		
Feller(DTQ)	-91.1770591	-37.8435822	-7.4771037	0.53569	336.15	0.52751	331.02		
Schwartz4(DTQ)	-91.1908668	-37.8478235	-7.4813317	0.53256	334.18	0.52438	329.05		
Schwartz4(TQ)	-91.1831162	-37.8450107	-7.4775908	0.53791	337.55	0.52973	332.41		
Schwartz6(TQ)	-91.1830163	-37.8449822	-7.4775845	0.53788	337.53	0.52970	332.39		

Table 27. Core-Valence and Extrapolated Core-Valence Planar Li_2C_2 Energies, De, Do, Values with Frozen Core									
In these calculations excitations are not allowed from the 1s core.									
CCSD(T)	Mol. Energy	C Atm. Ener.	Li Atm. Ener.	De	De	Do	Do		
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol		
cc-pCVDZ	-90.8690464	-37.7616572	-7.4324199	0.48089	301.76	0.47271	296.63		
cc-pCVTZ	-90.9466382	-37.7816584	-7.4326793	0.51796	325.03	0.50978	319.89		
cc-pCVQZ	-90.9666219	-37.7868046	-7.4326953	0.52762	331.09	0.51944	325.95		
cc-pCV5Z	-90.9720883	-37.7881963	-7.4326953	0.53031	332.77	0.52212	327.64		
Feller(DTQ)	-90.9735551	-37.7885876	-7.4326963	0.53099	333.20	0.52281	328.07		
Schwartz4(DTQ)	-90.9805806	-37.7903940	-7.4327116	0.53437	335.32	0.52619	330.19		
Schwartz4(TQ)	-90.9781558	-37.7897747	-7.4327045	0.53320	334.59	0.52502	329.45		
Schwartz6(TQ)	-90.9780962	-37.7897592	-7.4327043	0.53317	334.57	0.52499	329.43		

Table 28. Optimized Geometries of Linear Na ₃ C ₂									
SCF Optimized Geometries				CCSD(T) Optimized Geometries					
Basis	C//C	C/Na	Energy	C//C	C/Na	Energy			
Set	ang.	ang.	Hartree	ang.	ang.	Hartree			
cc-pVDZ	1.24340	2.22622	-399.34639	1.27767	2.24266	-399.63932			
cc-pVTZ	1.23209	2.22580	-399.37736	1.25924	2.23728	-399.72359			
cc-pVQZ	1.23131	2.22649	-399.38480	1.25598	2.23783	-399.74826			
5Z : QZ	1.23126	2.22644	-399.38579	1.25518	2.23798	-399.75488			
6Z : QZ	1.23126	2.22758	-399.38599	1.25497	2.23953	-399.75742			
aug-cc-pVDZ	1.24566	2.23566	-399.35289	1.28117	2.25772	-399.65822			
aug-cc-pVTZ	1.23278	2.22703	-399.37936	1.26030	2.24116	-399.73142			
aug-cc-pVQZ	1.23149	2.22650	-399.38532	1.25638	2.23954	-399.75125			
aug(SZ : QZ)	1.23127	2.22544	-399.38624	1.25531	2.23797	-399.75662			
aug(6Z : QZ)	1.23112	2.22375	-399.38654	1.25498	2.23615	-399.75871			

Table 29. Extrapolated Geometries of Linear Na ₃ C ₂			
		C//C	C/Na
		ang.	ang.
Feller(DTQ)		1.2553	2.2376
Schwartz4(DTQ)		1.2546	2.2376
Schwartz4(DTQ)		1.2533	2.2366
Schwartz4(TQ)		1.2541	2.2382
Schwartz6(DTQ)		1.2544	2.2387
Schwartz6(TQ)		1.2541	2.2382
Used		1.2549	2.2341

Table 30. Linear Na ₂ C ₂ Energies, De and Do Values									
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	Do	Do	Do	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pVDZ	-399.6393178	-37.7603079	-161.8530266	0.41265	258.94	0.40605	254.80	0.40605	254.80
cc-pVTZ	-399.7235871	-37.7805485	-161.8579959	0.44650	280.18	0.43990	276.04	0.43990	276.04
cc-pVQZ	-399.7482583	-37.7863026	-161.8586765	0.45830	287.59	0.45170	283.45	0.45170	283.45
cc-(5Z-QZ)	-399.7548780	-37.7879925	-161.8586765	0.46154	289.62	0.45494	285.48	0.45494	285.48
cc-(6Z-QZ)	-399.7574232	-37.7885099	-161.8586765	0.46305	290.57	0.45646	286.43	0.45646	286.43
aug-cc-pVDZ	-399.6582177	-37.7647609	-161.8530441	0.42261	265.19	0.41601	261.05	0.41601	261.05
aug-cc-pVTZ	-399.7314156	-37.7815947	-161.8579977	0.45223	283.78	0.44564	279.64	0.44564	279.64
aug-cc-pVQZ	-399.7512493	-37.7867431	-161.8586766	0.46041	288.91	0.45381	284.77	0.45381	284.77
aug(5Z-QZ)	-399.7566165	-37.7881355	-161.8586766	0.46299	290.53	0.45640	286.39	0.45640	286.39
aug(6Z-QZ)	-399.7587091	-37.7886249	-161.8586766	0.46411	291.23	0.45751	287.09	0.45751	287.09

Table 31. Extrapolated Linear Na ₂ C ₂ Energies, De and Do Values									
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	Do	Do	Do	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol	Hartrees	kcal/mol
feller									
cc-pvXz (DTQ)	-399.7584706	-37.7885879	-161.8587844	0.46373	290.99	0.45713	286.85	0.45713	286.85
schwartz2									
cc-pvXz (DTQ)	-399.7689954	-37.7909315	-161.8588998	0.46933	294.51	0.46274	290.37	0.46274	290.37
schwartz4									
cc-pvXz (DTQ)	-399.7572351	-37.7885136	-161.8594533	0.46130	289.47	0.45471	285.33	0.45471	285.33
cc-pvXz (TQ)	-399.7624976	-37.7896236	-161.8590692	0.46511	291.86	0.45852	287.72	0.45852	287.72
schwartz6									
cc-pvXz (DTQ)	-399.7644701	-37.7900397	-161.8589252	0.46654	292.76	0.45994	288.62	0.45994	288.62
cc-pvXz (TQ)	-399.7624196	-37.7896063	-161.8590648	0.46508	291.84	0.45848	287.70	0.45848	287.70

Table 32. Core-Valence and Extrapolated Core-Valence Linear Na ₂ C ₂ Energies, De, Do, Values with Unfrozen Core									
In these calculations excitations are allowed from the 2s,2p core.									
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	De	Do	Do		
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol		
cc-pCVDZ	-400.1058631	-37.7979616	-162.0467489	0.41644	261.32	0.40985	257.18		
cc-pCVTZ	-400.4067758	-37.8299103	-162.1481008	0.45075	282.85	0.44416	278.71		
cc-pCVQZ	-400.5508986	-37.8394847	-162.2050837	0.46176	289.76	0.45517	285.62		
cc-pCV5Z	-400.5597264	-37.8421645	-162.2050837	0.46523	291.94	0.45863	287.80		
aug-cc-pCVDZ	-400.1277608	-37.8024758	-162.0470101	0.42879	269.07	0.42219	264.93		
aug-cc-pCVTZ	-400.4155459	-37.8309189	-162.1482401	0.45723	286.91	0.45063	282.78		
aug-cc-pCVQZ	-400.5541985	-37.8398090	-162.2051681	0.46424	291.32	0.45765	287.18		
aug-cc-pCV5Z	-400.5618683	-37.8423047	-162.2051681	0.46692	293.00	0.46033	288.86		
Feller(DTQ)	-400.6833598	-37.8435822	-162.2782776	0.43964	275.88	0.43304	271.74		
Schwartz4(DTQ)	-400.8665581	-37.8478235	-162.4139481	0.34301	215.25	0.33642	211.11		
Schwartz4(TQ)	-400.6340810	-37.8450107	-162.2379721	0.46812	293.75	0.46152	289.61		
Schwartz6(TQ)	-400.6336550	-37.8449822	-162.2378037	0.46808	293.73	0.46149	289.59		

Table 33. Core-Valence and Extrapolated Core-Valence Linear Na ₂ C ₂ Energies, De, Do, Values with Frozen Core							
In these calculations excitations are not allowed from the 1s,2s,2p core.							
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-399.64400	-37.76166	-161.85303	0.41462	260.18	0.40802	256.04
cc-pCVTZ	-399.72888	-37.78166	-161.85800	0.44957	282.11	0.44297	277.97
cc-pCVQZ	-399.75155	-37.78680	-161.85868	0.46059	289.02	0.45399	284.88
cc-pCV(QZ-5Z)	-399.75743	-37.78820	-161.85868	0.46369	290.97	0.45709	286.83
aug-cc-pCVDZ	-399.66288	-37.76607	-161.85305	0.42464	266.46	0.41804	262.33
aug-cc-pCVTZ	-399.73586	-37.78265	-161.85800	0.45455	285.24	0.44796	281.10
aug-cc-pCVQZ	-399.75419	-37.78713	-161.85868	0.46258	290.27	0.45598	286.13
aug-cc-pCV(QZ-5Z)	-399.75887	-37.78834	-161.85868	0.46484	291.69	0.45825	287.56
Feller(DTQ)	-399.75981	-37.78859	-161.85878	0.46506	291.83	0.45847	287.69
Schwartz2a(DTQ)	-399.76821	-37.79039	-161.85890	0.46962	294.69	0.46302	290.55
Schwartz4(TQ)	-399.76463	-37.78977	-161.85907	0.46695	293.01	0.46035	288.87
Schwartz6(TQ)	-399.76456	-37.78976	-161.85906	0.46691	292.99	0.46032	288.85

Table 34. Optimized Geometries of Planar Na ₃ C ₃									
Basis Set	SCF Optimized Geometries				CCSD(T) Optimized Geometries				
	C//C	Na-(C//C)	C/Na	Energy	C//C	Na-(C//C)	C/Na	Energy	
	ang.	ang	ang	Hartree	ang.	ang	ang	Hartree	
cc-pVDZ	1.26026	2.26431	2.35035	-399.36765	1.29583	2.27052	2.36115	-399.66005	
cc-pVTZ	1.24669	2.26164	2.34801	-399.39769	1.27612	2.26622	2.35433	-399.74313	
cc-pVQZ	1.24540	2.26057	2.34477	-399.40319	1.27161	2.26200	2.34965	-399.76666	
5Z : QZ	1.24521	2.26015	2.58047	-399.40406	1.27056	2.26154	2.59401	-399.77306	
6Z : QZ	1.24516	2.26043	2.58069	-399.40431	1.27019	2.26162	2.59390	-399.77560	
aug-cc-pVDZ	1.26065	2.27175	2.59809	-399.37122	1.29782	2.28525	2.62806	-399.67523	
aug-cc-pVTZ	1.24662	2.26058	2.58152	-399.39794	1.27563	2.26641	2.60074	-399.74931	
aug-cc-pVQZ	1.24540	2.25995	2.58038	-399.40350	1.27156	2.26232	2.59518	-399.76906	
aug(5Z : QZ)	1.24514	2.25962	2.57997	-399.40431	1.27048	2.26133	2.59379	-399.77443	
aug(6Z : QZ)	1.24514	2.25989	2.58020	-399.40444	1.27041	2.26197	2.59431	-399.77323	

Table 35. Extrapolated Geometries for Planar Na ₃ C ₃		
	C//C	C/Na
	ang.	ang
Feller(DTQ)	1.2703	2.3394
Schwartz4(DTQ)	1.2689	2.2883
Schwartz4(DTQ)	1.2691	2.3498
Schwartz4(TQ)	1.2690	2.3470
Schwartz6(DTQ)	1.2690	2.3459
Schwartz6(TQ)	1.2690	2.3470
Used	1.2704	2.3473

Table 36. Planar Na ₂ C ₂ Energies, De and Do Values								
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	De	Do	Do	
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol	
cc-pVDZ	-399.6600509	-37.7603079	-161.8530266	0.43338	271.95	0.42659	267.69	
cc-pVTZ	-399.7431261	-37.7805485	-161.8579959	0.46604	292.44	0.45925	288.18	
cc-pVQZ	-399.7666633	-37.7863026	-161.8586765	0.47671	299.14	0.46992	294.88	
cc-(5Z-QZ)	-399.7730633	-37.7879925	-161.8586765	0.47973	301.03	0.47294	296.77	
cc-(6Z-QZ)	-399.7755974	-37.7885099	-161.8586765	0.48122	301.97	0.47444	297.71	
aug-cc-pVDZ	-399.6752329	-37.7647609	-161.8530441	0.43962	275.87	0.43283	271.61	
aug-cc-pVTZ	-399.7493127	-37.7815947	-161.8579977	0.47013	295.01	0.46334	290.75	
aug-cc-pVQZ	-399.7690602	-37.7867431	-161.8586766	0.47822	300.09	0.47143	295.83	
aug(5Z-QZ)	-399.7744311	-37.7881355	-161.8586766	0.48081	301.71	0.47402	297.45	
aug(6Z-QZ)	-399.7765111	-37.7886249	-161.8586766	0.48191	302.40	0.47512	298.14	

Table 37. Extrapolated Planar Na ₂ C ₂ Energies, De and Do Values								
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	De	Do	Do	
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol	
feller								
cc-pvXz (DTQ)	-399.7759672	-37.7885879	-161.8587844	0.48122	301.97	0.47443	297.71	
schwartz2a								
cc-pvXz (DTQ)	-399.7855028	-37.7909315	-161.8588998	0.48584	304.87	0.47905	300.61	
schwartz4								
cc-pvXz (DTQ)	-399.7757636	-37.7885136	-161.8594533	0.47983	301.10	0.47304	296.84	
cc-pvXz (TQ)	-399.7802482	-37.7896236	-161.8590692	0.48286	303.00	0.47607	298.74	
schwartz6								
cc-pvXz (DTQ)	-399.7819291	-37.7900397	-161.8589252	0.48400	303.71	0.47721	299.45	
cc-pvXz (TQ)	-399.7801735	-37.7896063	-161.8590648	0.48283	302.98	0.47604	298.72	

Table 38. Core-Valence and Extrapolated Core-Valence Planar Na₂C₂ Energies, De, Do, Values with Unfrozen Core

In these calculations excitations are allowed from the 2s,2p core.							
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-400.1264473	-37.7979616	-162.0467489	0.43703	274.24	0.43024	269.98
cc-pCVTZ	-400.4254844	-37.8299103	-162.1481008	0.46946	294.59	0.46267	290.33
cc-pCVQZ	-400.5689116	-37.8394847	-162.2050837	0.47977	301.06	0.47299	296.80
cc-pCV5Z	-400.5775819	-37.8421645	-162.2050837	0.48309	303.14	0.47630	298.88
Feller(DTQ)	-400.7011256	-37.8435822	-162.2782776	0.45741	287.03	0.45062	282.77
Schwartz6a(DTQ)	-400.8842318	-37.8478235	-162.4139481	0.36069	226.34	0.35390	222.08
Schwartz4(TQ)	-400.6516925	-37.8450107	-162.2379721	0.48573	304.80	0.47894	300.54
Schwartz6(TQ)	-400.6512685	-37.8449822	-162.2378037	0.48570	304.78	0.47891	300.52

Table 39. Core-Valence and Extrapolated Core-Valence Planar Na₂C₂ Energies, De, Do, Values with Frozen Core

In these calculations excitations are not allowed from the 1s,2s,2p core.							
CCSD(T)	Mol. Energy	C Atm. Ener.	Na Atm. Ener.	De	De	Do	Do
Basis sets	Hartrees	Hartrees	Hartrees	Hartrees	kcal/mol	Hartrees	kcal/mol
cc-pCVDZ	-399.6646692	-37.7616572	-161.8530309	0.43529	273.15	0.42850	268.89
cc-pCVTZ	-399.7478618	-37.7816584	-161.8579970	0.46855	294.02	0.46176	289.76
cc-pCVQZ	-399.7695989	-37.7868046	-161.8586765	0.47864	300.35	0.47185	296.09
cc-pCV5Z	-399.7752828	-37.7881963	-161.8586765	0.48154	302.17	0.47475	297.91
Feller(DTQ)	-399.7772884	-37.7885876	-161.8587842	0.48254	302.80	0.47576	298.54
Schwartz6a(DTQ)	-399.7850888	-37.7903940	-161.8588993	0.48650	305.28	0.47971	301.02
Schwartz4(TQ)	-399.7821448	-37.7897747	-161.8590686	0.48446	304.00	0.47767	299.74
Schwartz6(TQ)	-399.7820754	-37.7897592	-161.8590642	0.48443	303.98	0.47764	299.72

APPENDIX B
CHAPTER 3 RAW DATA

Table 1. SCF Quadrupoles of HCCH					
	Property Calculations	Field Gradient calculations			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	5.21121	5.21120	-76.82520	-76.82625	-76.82572
cc-pVTZ	5.41863	5.41865	-76.84884	-76.84993	-76.84938
cc-pVQZ	5.43455	5.43455	-76.85385	-76.85494	-76.85439
cc-pV5Z	5.44436	5.44435	-76.85497	-76.85606	-76.85551
cc-pV6Z	5.44423	5.44420	-76.85511	-76.85620	-76.85565
aug-cc-pVDZ	5.46892	5.46890	-76.82790	-76.82899	-76.82844
aug-cc-pVTZ	5.45771	5.45770	-76.84961	-76.85070	-76.85016
aug-cc-pVQZ	5.44559	5.44555	-76.85402	-76.85511	-76.85456
aug-cc-pV5Z	5.44453	5.44450	-76.85499	-76.85608	-76.85553
aug-cc-pV6Z	5.44352	5.44350	-76.85511	-76.85620	-76.85566
d-aug-cc-pVDZ	5.45567	5.45565	-76.82825	-76.82934	-76.82879
d-aug-cc-pVTZ	5.44564	5.44565	-76.84971	-76.85080	-76.85025

Table 2. CCSD(T) Quadrupoles of HCCH				
	Field Gradient Calculations			
Basis sets	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	4.50785	-77.10868	-77.10958	-77.10913
cc-pVTZ	4.80095	-77.18708	-77.18804	-77.18756
cc-pVQZ	4.84280	-77.20880	-77.20977	-77.20929
cc-pV5Z	4.86080	-77.21527	-77.21624	-77.21576
cc-pV6Z	4.86520	-77.21747	-77.21844	-77.21795
aug-cc-pVDZ	4.77215	-77.11908	-77.12004	-77.11956
aug-cc-pVTZ	4.84505	-77.19161	-77.19258	-77.19161
aug-cc-pVQZ	4.85700	-77.21048	-77.21145	-77.21096
aug-cc-pV5Z	4.86345	-77.21597	-77.21695	-77.21646
aug-cc-pV6Z	4.86615	-77.21791	-77.21888	-77.21839
d-aug-cc-pVDZ	4.75840	-77.12003	-77.12098	-77.12050
d-aug-cc-pVTZ	4.83335	-77.19201	-77.19297	-77.19249

Table 3. DFT(B3LYP) Quadrupoles of HCCH					
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	4.61713	4.61715	-77.28117	-77.28209	-77.28163
cc-pVTZ	4.90139	4.90140	-77.31166	-77.31264	-77.31215
cc-pVQZ	4.89813	4.89810	-77.31741	-77.31839	-77.31790
cc-pV5Z	4.90903	4.90915	-77.31933	-77.32031	-77.31982
cc-pV6Z	4.90791	4.91155	-77.31968	-77.32066	-77.32017
aug-cc-pVDZ	4.87387	4.87390	-77.28640	-77.28737	-77.28688
aug-cc-pVTZ	4.91726	4.91715	-77.31266	-77.31365	-77.31315
aug-cc-pVQZ	4.87216	4.87225	-77.31767	-77.31864	-77.31815
aug-cc-pV5Z	4.90775	4.90680	-77.31939	-77.32037	-77.31988
aug-cc-pV6Z	4.89025	4.89015	-77.31988	-77.32086	-77.32037
d-aug-cc-pVDZ	4.86497	4.86435	-77.28709	-77.28806	-77.28757
d-aug-cc-pVTZ	4.89342	4.89400	-77.31290	-77.31388	-77.31339
d-aug-cc-pVQZ	4.89071	4.88965	-77.31768	-77.31865	-77.31816

Table 4. Quadrupoles of FCCF					
	SCF Quadrpoles of FCCF				
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	-0.97258	-0.97255	-274.47696	-274.47676	-274.47686
cc-pVTZ	-0.84572	-0.84570	-274.56734	-274.56717	-274.56726
cc-pVQZ	-0.89863	-0.89860	-274.58903	-274.58885	-274.58894
cc-pV5Z	-0.92249	-0.92250	-274.59471	-274.59453	-274.59462
aug-cc-pVDZ	-1.03349	-1.03345	-274.49362	-274.49341	-274.49351
aug-cc-pVTZ	-0.94298	-0.94295	-274.57137	-274.57119	-274.57128
aug-cc-pVQZ	-0.91302	-0.91305	-274.59007	-274.58989	-274.58998
aug-cc-pV5Z	-0.91678	-0.91680	-274.59489	-274.59471	-274.59480
d-aug-cc-pVDZ	-0.85468	-0.85465	-274.49569	-274.49552	-274.49560
d-aug-cc-pVTZ	-0.90671	-0.90670	-274.57214	-274.57196	-274.57205
d-aug-cc-pVQZ	-0.91185	-0.91185	-274.59034	-274.59016	-274.59025
d-aug-cc-pV5Z	-0.91572	-0.91570	-274.59491	-274.59473	-274.59491
Basis sets	CCSD(T) Quadrpoles of FCCF				
cc-pVDZ		-0.40895	-275.12056	-275.12048	-275.12052
cc-pVTZ		-0.45690	-275.39150	-275.39141	-275.39145
cc-pVQZ		-0.58250	-275.47592	-275.47580	-275.47585
cc-pV5Z		-0.63430	-275.50423	-275.50410	-275.50416
aug-cc-pVDZ		-0.78600	-275.17600	-275.17585	-275.17592
aug-cc-pVTZ		-0.64850	-275.41182	-275.41169	-275.41176
aug-cc-pVQZ		-0.63565	-275.48398	-275.48386	-275.48392
aug-cc-pV5Z		-0.64005	-275.50746	-275.50733	-275.50739
d-aug-cc-pVDZ		-0.63670	-275.18089	-275.18076	-275.18082
d-aug-cc-pVTZ		-0.61565	-275.41468	-275.41455	-275.41461
d-aug-cc-pVQZ		-0.63315	-275.48517	-275.48504	-275.48510
d-aug-cc-pV5Z		-0.63885	-275.50798	-275.50785	-275.50791
Basis sets	DFT(B3LYP) Quadrpoles of FCCF				
cc-pVDZ	-0.05337	-0.05335	-275.64631	-275.64630	-275.646298
cc-pVTZ	-0.27828	-0.27830	-275.74266	-275.74261	-275.742634
cc-pVQZ	-0.44190	-0.44190	-275.76648	-275.76639	-275.766429
cc-pV5Z	-0.51039	-0.51080	-275.77397	-275.77386	-275.773912
aug-cc-pVDZ	-0.60025	-0.60045	-275.66684	-275.66672	-275.666775
aug-cc-pVTZ	-0.54044	-0.53910	-275.74753	-275.74742	-275.747474
aug-cc-pVQZ	-0.51631	-0.51800	-275.76799	-275.76789	-275.767939
aug-cc-pV5Z	-0.52176	-0.52450	-275.77428	-275.77417	-275.774224

Table 5. Quad rupoles of CCCCCI					
	SCF Quadrupoles of CCCCCI				
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	3.93167	3.93165	-994.64186	-994.64265	-994.64225
cc-pVTZ	3.93428	3.93425	-994.69678	-994.69756	-994.69716
cc-pVQZ	3.92530	3.92525	-994.71019	-994.71097	-994.71057
cc-pV5Z	3.93531	3.93520	-994.71417	-994.71496	-994.71455
aug-cc-pVDZ	4.05863	4.05860	-994.64677	-994.64758	-994.64716
aug-cc-pVTZ	3.85683	3.85675	-994.69794	-994.69871	-994.69832
aug-cc-pVQZ	3.87828	3.87815	-994.71048	-994.71126	-994.71086
aug-cc-pV5Z	3.89883	3.89875	-994.71425	-994.71503	-994.71463
d-aug-cc-pVDZ	3.93806	3.93790	-994.64829	-994.64908	-994.64868
d-aug-cc-pVTZ	3.82185	3.82175	-994.69831	-994.69907	-994.69868
d-aug-cc-pVQZ	3.86852	3.86840	-994.71062	-994.71139	-994.71099
d-aug-cc-pV5Z	3.90064	3.90050	-994.71427	-994.71505	-994.71465
CCSD(T) Quadrupoles of CCCCCI					
Basis sets					
cc-pVDZ		3.73365	-995.20710	-995.20785	-995.20747
cc-pVTZ		3.85235	-995.43348	-995.43425	-995.43386
cc-pVQZ		3.78920	-995.50274	-995.50350	-995.50311
cc-pV5Z		3.80535	-995.52592	-995.52668	-995.52629
aug-cc-pVDZ		3.77545	-995.24246	-995.24322	-995.24283
aug-cc-pVTZ		3.79695	-995.44800	-995.44876	-995.44837
aug-cc-pVQZ		3.75945	-995.50830	-995.50905	-995.50867
aug-cc-pV5Z		3.76720	-995.52878	-995.52954	-995.52915
d-aug-cc-pVDZ		3.66855	-995.24726	-995.24799	-995.24762
d-aug-cc-pVTZ		3.74915	-995.45044	-995.45119	-995.45080
d-aug-cc-pVQZ		3.74780	-995.50935	-995.51010	-995.50972
d-aug-cc-pV5Z		3.76825	-995.52949	-995.53025	-995.52986
DFT(B3LYP) Quadrupoles of CCCCCI					
Basis sets					
cc-pVDZ	4.10418	4.10370	-996.37300	-996.37382	-996.37341
cc-pVTZ	3.99562	3.99600	-996.43262	-996.43341	-996.43301
cc-pVQZ	3.91567	3.91670	-996.44733	-996.44811	-996.44771
cc-pV5Z	3.89775	3.89495	-996.45723	-996.45801	-996.45761
aug-cc-pVDZ	3.82461	3.82360	-996.38013	-996.38089	-996.38050
aug-cc-pVTZ	3.76884	3.76740	-996.43419	-996.43494	-996.43455
aug-cc-pVQZ	3.77873	3.77875	-996.44784	-996.44859	-996.44821
aug-cc-pV5Z	3.79085	3.79055	-996.45746	-996.45822	-996.45783

Table 6. Quadrupoles of Linear Li ₂ C ₂					
SCF Quadrupoles of Linear Li ₂ C ₂					
Property calculations		Field Gradient Calculations.			
Basis sets	Property @	Field Grad @	0.0001	-0.0001	0
cc-pVDZ	35.92113	35.92090	-90.55783	-90.56501	-90.56142
cc-pVTZ	36.11907	36.11890	-90.58353	-90.59075	-90.58714
cc-pVQZ	36.36871	36.36855	-90.58902	-90.59630	-90.59266
cc-(5Z-QZ)	36.42224	36.42210	-90.58997	-90.59725	-90.59361
cc-(6Z-QZ)	36.48779	36.48765	-90.59016	-90.59745	-90.59380
aug-cc-pVDZ	36.65677	36.65660	-90.56656	-90.57389	-90.57022
aug-cc-pVTZ	36.51928	36.51915	-90.58514	-90.59245	-90.58879
aug-cc-pVQZ	36.50940	36.50925	-90.58933	-90.59663	-90.59297
aug(5Z-QZ)	36.50828	36.50820	-90.59010	-90.59740	-90.59375
aug(6Z-QZ)	36.50784	36.50770	-90.59021	-90.59751	-90.59385
CCSD(T) Quadrupoles of Linear Li ₂ C ₂					
Basis sets					
cc-pVDZ		34.77075	-90.84527	-90.85222	-90.84874
cc-pVTZ		35.19595	-90.92645	-90.93349	-90.92997
cc-pVQZ		35.49270	-90.94952	-90.95662	-90.95306
cc-(5Z-QZ)		35.57165	-90.95594	-90.96305	-90.95949
cc-(6Z-QZ)		35.64430	-90.95843	-90.96555	-90.96199
aug-cc-pVDZ		35.74955	-90.86463	-90.87178	-90.86820
aug-cc-pVTZ		35.65855	-90.93329	-90.94042	-90.93685
aug-cc-pVQZ		35.66620	-90.95196	-90.95910	-90.95552
aug(5Z-QZ)		35.67495	-90.95730	-90.96443	-90.96086
aug(6Z-QZ)		35.67865	-90.95927	-90.96641	-90.96283
DFT(B3LYP) Quadrupoles of Linear Li ₂ C ₂					
Basis sets					
cc-pVDZ	34.23046	34.22950	-91.11920	-91.12604	-91.12261
cc-pVTZ	34.54174	34.54115	-91.14847	-91.15537	-91.15191
cc-pVQZ	34.79379	34.79340	-91.15494	-91.16190	-91.15841
cc-(5Z-QZ)	34.84033	34.83875	-91.15668	-91.16365	-91.16016
cc-(6Z-QZ)	34.89727	34.89780	-91.15708	-91.16406	-91.16057
aug-cc-pVDZ	35.08634	35.08545	-91.12795	-91.13497	-91.13146
aug-cc-pVTZ	34.92038	34.91845	-91.15007	-91.15705	-91.15356
aug-cc-pVQZ	34.92334	34.92280	-91.15532	-91.16230	-91.15880
aug(5Z-QZ)	34.92483	34.92415	-91.15690	-91.16388	-91.16039
aug(6Z-QZ)	34.63372	34.91735	-91.15727	-91.16425	-91.16075

Table 7. Θ_{zz} Component of Planar Li_2C_2 Quadrupole					
SCF	SCF Θ_{zz} Component of Planar Li_2C_2 Quadrupole				
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	26.42364	26.42345	-90.57130	-90.57658	-90.57394
cc-pVTZ	26.26211	26.26195	-90.59421	-90.59946	-90.59683
cc-pVQZ	26.28749	26.28735	-90.59907	-90.60433	-90.60169
cc-(5Z-QZ)	26.30007	26.29995	-90.59991	-90.60517	-90.60254
cc-(6Z-QZ)	26.30757	26.30740	-90.60005	-90.60531	-90.60267
aug-cc-pVDZ	26.42695	26.42670	-90.57578	-90.58107	-90.57842
aug-cc-pVTZ	26.31244	26.31235	-90.59501	-90.60028	-90.59764
aug-cc-pVQZ	26.31155	26.31140	-90.59920	-90.60446	-90.60183
aug(5Z-QZ)	26.30941	26.30925	-90.59997	-90.60524	-90.60260
aug(6Z-QZ)	26.30894	26.30880	-90.60009	-90.60535	-90.60272
Basis sets	CCSD(T) Θ_{zz} Component of Planar Li_2C_2 Quadrupole				
cc-pVDZ		25.83225	-90.86111	-90.86628	-90.86369
cc-pVTZ		25.83985	-90.94040	-90.94557	-90.94298
cc-pVQZ		25.90455	-90.96264	-90.96782	-90.96522
cc-(5Z-QZ)		25.93655	-90.96884	-90.97403	-90.97143
cc-(6Z-QZ)		25.95380	-90.97124	-90.97643	-90.97383
aug-cc-pVDZ		26.04780	-90.87582	-90.88103	-90.87842
aug-cc-pVTZ		25.95015	-90.94588	-90.95107	-90.94847
aug-cc-pVQZ		25.95380	-90.96459	-90.96978	-90.96718
aug(5Z-QZ)		25.95645	-90.96993	-90.97512	-90.97252
aug(6Z-QZ)		25.95780	-90.97194	-90.97713	-90.97453
Basis sets	DFT(B3LYP) Θ_{zz} Component of Planar Li_2C_2 Quadrupole				
cc-pVDZ	25.37237	25.37200	-91.13161	-91.13668	-91.13414
cc-pVTZ	25.20428	25.20235	-91.15839	-91.16343	-91.16091
cc-pVQZ	25.26415	25.26320	-91.16484	-91.16989	-91.16736
cc-(5Z-QZ)	25.28720	25.28715	-91.16660	-91.17166	-91.16913
cc-(6Z-QZ)	25.30170	25.29990	-91.16696	-91.17202	-91.16948
aug-cc-pVDZ	25.41788	25.41980	-91.13640	-91.14148	-91.13893
aug-cc-pVTZ	25.29770	25.29675	-91.15965	-91.16471	-91.16217
aug-cc-pVQZ	25.30683	25.30675	-91.16516	-91.17022	-91.16768
aug(5Z-QZ)	25.30699	25.30540	-91.16674	-91.17180	-91.16926
aug(6Z-QZ)	25.30645	25.30510	-91.16710	-91.17216	-91.16963

Table 8. Θ_{yy} Component of Planar Li_2C_2 Quadrupole					
SCF	SCF Θ_{yy} Component of Planar Li_2C_2 Quadrupole				
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	-16.06928	-16.06925	-90.57555	-90.5723	-90.57394
cc-pVTZ	-16.18292	-16.18290	-90.59845	-90.59522	-90.59683
cc-pVQZ	-16.23168	-16.23165	-90.60332	-90.60007	-90.60169
cc-(5Z-QZ)	-16.26629	-16.26630	-90.60417	-90.60092	-90.60254
cc-(6Z-QZ)	-16.28308	-16.28310	-90.60431	-90.60105	-90.60267
aug-cc-pVDZ	-16.19942	-16.19945	-90.58004	-90.57680	-90.57842
aug-cc-pVTZ	-16.28427	-16.28430	-90.59927	-90.59602	-90.59764
aug-cc-pVQZ	-16.27610	-16.27615	-90.60346	-90.60020	-90.60183
aug(5Z-QZ)	-16.27387	-16.27395	-90.60423	-90.60098	-90.60260
aug(6Z-QZ)	-16.27356	-16.27365	-90.60435	-90.60109	-90.60272
CCSD(T) Θ_{yy} Component of Planar Li_2C_2 Quadrupole					
Basis sets					
cc-pVDZ		-15.87020	-90.86528	-90.86211	-90.86369
cc-pVTZ		-16.16610	-90.94460	-90.94137	-90.94298
cc-pVQZ		-16.26935	-90.96686	-90.96360	-90.96522
cc-(5Z-QZ)		-16.33000	-90.97307	-90.96980	-90.97143
cc-(6Z-QZ)		-16.36865	-90.97547	-90.97220	-90.97383
aug-cc-pVDZ		-16.33085	-90.88006	-90.87680	-90.87842
aug-cc-pVTZ		-16.37980	-90.95011	-90.94683	-90.94847
aug-cc-pVQZ		-16.37065	-90.96882	-90.96555	-90.96718
aug(5Z-QZ)		-16.36970	-90.97417	-90.97089	-90.97252
aug(6Z-QZ)		-16.36990	-90.97617	-90.97290	-90.97453
DFT(B3LYP) Θ_{yy} Component of Planar Li_2C_2 Quadrupole					
Basis sets					
cc-pVDZ	-15.40464	-15.40470	-91.13569	-91.13260	-91.13414
cc-pVTZ	-15.69964	-15.69950	-91.16248	-91.15934	-91.16091
cc-pVQZ	-15.81193	-15.81105	-91.16895	-91.16578	-91.16736
cc-(5Z-QZ)	-15.86851	-15.86735	-91.17072	-91.16754	-91.16913
cc-(6Z-QZ)	-15.90546	-15.90465	-91.17108	-91.16790	-91.16948
aug-cc-pVDZ	-15.83735	-15.83840	-91.14052	-91.13735	-91.13893
aug-cc-pVTZ	-15.91843	-15.91650	-91.16377	-91.16059	-91.16217
aug-cc-pVQZ	-15.91138	-15.90880	-91.16928	-91.16610	-91.16768
aug(5Z-QZ)	-15.90995	-15.91070	-91.17086	-91.16767	-91.16926
aug(6Z-QZ)	-15.90946	-15.91120	-91.17122	-91.16804	-91.16963

Table 9. Quadrupoles of Linear Na ₂ C ₂					
SCF Quadrupole of Linear Na ₂ C ₂					
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	47.51559	47.51435	-399.34140	-399.35091	-399.34615
cc-pVTZ	48.47527	48.47410	-399.37163	-399.38133	-399.37647
cc-pVQZ	48.69636	48.69525	-399.37900	-399.38874	-399.38386
cc-(5Z-QZ)	48.69327	48.69215	-399.37999	-399.38973	-399.38485
cc-(6Z-QZ)	48.70123	48.70010	-399.38019	-399.38993	-399.38505
aug-cc-pVDZ	49.04743	49.04625	-399.34785	-399.35766	-399.35275
aug-cc-pVTZ	48.85053	48.84945	-399.37366	-399.38343	-399.37853
aug-cc-pVQZ	48.70649	48.70540	-399.37953	-399.38927	-399.38439
CCSD(T) Quadrupole of Linear Na ₂ C ₂					
Basis sets					
cc-pVDZ		44.47110	-399.63410	-399.64299	-399.63852
cc-pVTZ		46.00460	-399.71897	-399.72817	-399.72356
cc-pVQZ		46.44525	-399.74362	-399.75291	-399.74825
cc-(5Z-QZ)		46.51530	-399.75024	-399.75954	-399.75487
cc-(6Z-QZ)		46.55900	-399.75278	-399.76209	-399.75742
aug-cc-pVDZ		46.45305	-399.65245	-399.66174	-399.65708
aug-cc-pVTZ		46.59030	-399.72672	-399.73603	-399.73136
aug-cc-pVQZ		46.56340	-399.74660	-399.75591	-399.75124
aug(5Z-QZ)		46.56630	-399.75197	-399.76128	-399.75661
aug(6Z-QZ)		46.54900	-399.75407	-399.76338	-399.75871
DFT(B3LYP) Quadrupole of Linear Na ₂ C ₂					
Basis sets					
cc-pVDZ	42.43210	42.42575	-400.59468	-400.60316	-400.59890
cc-pVTZ	43.29595	43.28935	-400.62965	-400.63831	-400.63396
cc-pVQZ	43.51357	43.50595	-400.64037	-400.64907	-400.64470
cc-(5Z-QZ)	43.52969	43.52410	-400.64239	-400.65109	-400.64672
cc-(6Z-QZ)	43.53921	43.52600	-400.64320	-400.65191	-400.64753
aug-cc-pVDZ	43.89563	43.88895	-400.60179	-400.61057	-400.60615
aug-cc-pVTZ	43.67435	43.66385	-400.63181	-400.64054	-400.63615
aug-cc-pVQZ	43.55906	43.55635	-400.64153	-400.65025	-400.64586

Table 10. Θ_{zz} Component of Planar Na_2C_2 Quadrupole					
SCF	SCF Θ_{zz} Component of Planar Na_2C_2 Quadrupole				
	Property calculations	Field Gradient Calculations.			
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	36.36619	36.36545	-399.36385	-399.37112	-399.36748
cc-pVTZ	36.42261	36.42180	-399.39214	-399.39942	-399.39577
cc-pVQZ	36.40388	36.40320	-399.39861	-399.40589	-399.40224
cc-(5Z-QZ)	36.39636	36.39570	-399.39946	-399.40674	-399.40309
cc-(6Z-QZ)	36.37383	36.37315	-399.39971	-399.40699	-399.40335
aug-cc-pVDZ	36.70472	36.70400	-399.36737	-399.37471	-399.37103
aug-cc-pVTZ	36.47252	36.47185	-399.39319	-399.40048	-399.39683
aug-cc-pVQZ	36.33939	36.37450	-399.39891	-399.40619	-399.40255
aug(5Z-QZ)	36.36187	36.36120	-399.39971	-399.40698	-399.40334
aug(6Z-QZ)	36.34475	36.34410	-399.39994	-399.40721	-399.40357
Basis sets	CCSD(T) Θ_{zz} Component of Planar Na_2C_2 Quadrupole				
cc-pVDZ		35.33375	-399.65565	-399.66272	-399.65917
cc-pVTZ		35.76320	-399.73951	-399.74666	-399.74308
cc-pVQZ		35.85585	-399.76308	-399.77026	-399.76666
cc-(5Z-QZ)		35.88545	-399.76948	-399.77666	-399.77306
cc-(6Z-QZ)		35.88460	-399.77202	-399.77919	-399.77560
aug-cc-pVDZ		36.03205	-399.67052	-399.67772	-399.67411
aug-cc-pVTZ		35.93175	-399.74568	-399.75287	-399.74927
aug-cc-pVQZ		35.87685	-399.76548	-399.77265	-399.76906
aug(5Z-QZ)		35.87775	-399.77085	-399.77803	-399.77443
aug(6Z-QZ)		35.86695	-399.77293	-399.78011	-399.77651
Basis sets	DFT(B3LYP) Θ_{zz} Component of Planar Na_2C_2 Quadrupole				
cc-pVDZ	33.46820	33.46450	-400.61235	-400.61904	-400.61568
cc-pVTZ	33.50279	33.49895	-400.64601	-400.65271	-400.64935
cc-pVQZ	33.51679	33.51595	-400.65617	-400.66287	-400.65950
cc-(5Z-QZ)	33.52760	33.52655	-400.65843	-400.66513	-400.66176
cc-(6Z-QZ)	33.53103	33.52985	-400.65922	-400.66593	-400.66256
aug-cc-pVDZ	33.89736	33.89145	-400.61673	-400.62351	-400.62011
aug-cc-pVTZ	32.97706	33.61345	-400.64765	-400.65437	-400.65099
aug-cc-pVQZ	33.45609	33.45060	-400.66397	-400.67066	-400.66730
aug(5Z-QZ)	33.52892	33.53235	-400.65924	-400.66594	-400.66257
aug(6Z-QZ)	33.52248	33.52465	-400.65974	-400.66645	-400.66308

Table 11. Θ_{zz} Component of Planar Na_2C_2 Quadrupole					
	SCF Θ_{yy} Component of Planar Na_2C_2 Quadrupole				
	Property calculations		Field Gradient Calculations.		
Basis sets	Property Θ	Field Grad Θ	0.0001	-0.0001	0
cc-pVDZ	-21.35167	-21.35155	-399.36962	-399.36535	-399.36748
cc-pVTZ	-21.52509	-21.52495	-399.39793	-399.39362	-399.39577
cc-pVQZ	-21.58987	-21.58980	-399.40440	-399.40009	-399.40224
cc-(5Z-QZ)	-21.60388	-21.60385	-399.40526	-399.40094	-399.40309
cc-(6Z-QZ)	-21.59570	-21.59570	-399.40551	-399.40119	-399.40335
aug-cc-pVDZ	-21.68500	-21.68505	-399.37320	-399.36887	-399.37103
aug-cc-pVTZ	-21.65632	-21.65635	-399.39900	-399.39467	-399.39683
aug-cc-pVQZ	-21.57139	-21.58985	-399.40471	-399.40039	-399.40255
aug(5Z-QZ)	-21.58440	-21.58440	-399.40550	-399.40119	-399.40334
aug(6Z-QZ)	-21.57575	-21.57580	-399.40573	-399.40142	-399.40357
Basis sets	CCSD(T) Θ_{zz} Component of Planar Na_2C_2 Quadrupole				
cc-pVDZ		-20.86890	-399.66126	-399.65709	-399.65917
cc-pVTZ		-21.41470	-399.74522	-399.74094	-399.74308
cc-pVQZ		-21.60855	-399.76883	-399.76451	-399.76666
cc-(5Z-QZ)		-21.65005	-399.77523	-399.77090	-399.77306
cc-(6Z-QZ)		-21.66595	-399.77777	-399.77344	-399.77560
aug-cc-pVDZ		-21.70495	-399.67629	-399.67195	-399.67411
aug-cc-pVTZ		-21.71720	-399.75145	-399.74710	-399.74927
aug-cc-pVQZ		-21.67125	-399.77123	-399.76690	-399.76906
aug(5Z-QZ)		-21.67290	-399.77661	-399.77227	-399.77443
aug(6Z-QZ)		-21.66680	-399.77869	-399.77435	-399.77651
Basis sets	DFT(B3LYP) Θ_{zz} Component of Planar Na_2C_2 Quadrupole				
cc-pVDZ	-19.66378	-19.66335	-400.61765	-400.61372	-400.61568
cc-pVTZ	-20.01005	-20.00925	-400.65136	-400.64736	-400.64935
cc-pVQZ	-20.15104	-20.14980	-400.66153	-400.65750	-400.65950
cc-(5Z-QZ)	-20.17747	-20.17605	-400.66379	-400.65975	-400.66176
cc-(6Z-QZ)	-20.19390	-20.19765	-400.66459	-400.66055	-400.66256
aug-cc-pVDZ	-20.31136	-20.30910	-400.62215	-400.61808	-400.62011
aug-cc-pVTZ	-19.92045	-20.27225	-400.65303	-400.64898	-400.65099
aug-cc-pVQZ	-20.17168	-20.21010	-400.66286	-400.65882	-400.66083
aug(5Z-QZ)	-20.20684	-20.20820	-400.66460	-400.66056	-400.66257
aug(6Z-QZ)	-20.20483	-20.20495	-400.66511	-400.66107	-400.66308

APPENDIX C
CHAPTER 5 RAW DATA

Table 1. CH ₄ -N ₂ Perpendicular Approach using aug-cc-pvtz basis set for 5.0 and 4.0 Å Separations			
5.0 Å separation		4.0 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-149.821128	104	-149.821584
105	-149.8213782	105	-149.821834
106	-149.8215775	106	-149.822033
107	-149.8217278	107	-149.822183
108	-149.8218247	108	-149.82228
109	-149.8218733	109	-149.822328
109.4712	-149.821879	109.4712	-149.822334
109.48	-149.821879	109.47	-149.822334
110	-149.8218723	109.5	-149.822334
111	-149.821822	110	-149.822327
112	-149.8217228	111	-149.822276
113	-149.8215751	112	-149.822177
114	-149.8213791	113	-149.822029
		114	-149.821833

Table 2. CH ₄ -N ₂ Perpendicular Approach using aug-cc-pvtz basis set for 3.5 and 3.25 Angstrom Separations			
3.5 Å separation		3.25 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-149.8214405	104	-149.820398
105	-149.821699	105	-149.8206748
106	-149.8219064	106	-149.8209002
107	-149.8220646	107	-149.821076
108	-149.8221694	108	-149.8211983
109	-149.8222256	109	-149.8212715
109.4712	-149.8222348	109.4712	-149.8212886
109.6	-149.8222354	109.96	-149.8212946
109.63	-149.8222354	110	-149.8212946
110	-149.822232	111	-149.8212679
111	-149.822189	112	-149.8211917
112	-149.8220969	113	-149.8210665
113	-149.8219561	114	-149.8208925
114	-149.8217668		

Table 3. CH ₄ -N ₂ Perpendicular Approach using aug-cc-pvtz basis set for 3.0 Å Separations	
3.0 Å separation	
Angle	Energy
	Hartrees
104	-149.817287
105	-149.817612
106	-149.817884
107	-149.818105
108	-149.818273
109	-149.81839
109.4712	-149.818428
110	-149.818457
110.8	-149.818473
110.81	-149.818473
111	-149.818472
112	-149.818437
113	-149.818352
114	-149.818218

Table 4. CH ₄ -N ₂ Linear Approach using aug-cc-pvtz basis set for 5.0 and 4.0 Å Separations			
5.0 Å separation		4.0 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-149.8213045	104	-149.8212801
105	-149.8215469	105	-149.8215138
106	-149.8217386	106	-149.8216971
107	-149.8218813	107	-149.8218317
108	-149.821971	108	-149.8219141
109	-149.8220125	109	-149.8219483
109.34	-149.8220153	109.19	-149.8219493
109.4712	-149.8220148	109.2	-149.8219493
110	-149.8220045	109.4712	-149.8219474
111	-149.8219474	110	-149.8219335
112	-149.8218415	111	-149.8218698
113	-149.8216872	112	-149.8217576
114	-149.8214848	113	-149.8215973
		114	-149.8213892

Table 5. CH ₄ -N ₂ Linear Approach using aug-cc-pvtz basis set for 3.5 and 3.25 Å Separations			
3.5 Å separation		3.25 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-149.8172923	104	-149.8097708
105	-149.8175600	105	-149.8101183
106	-149.8177772	106	-149.8104143
107	-149.8179450	107	-149.8106596
108	-149.8180613	108	-149.8108530
109	-149.8181288	109	-149.8109963
109.4712	-149.8181435	109.4712	-149.8110463
109.87	-149.8181473	110	-149.8110891
109.9	-149.8181473	111	-149.8111318
110	-149.8181469	111.34	-149.8111350
111	-149.8181159	111.4	-149.8111350
112	-149.8180362	112	-149.8111248
113	-149.8179080	113	-149.8110682
114	-149.8177316	114	-149.8109623
		115	-149.8108076
		116	-149.8106042
		117	-149.8103525
		118	-149.8100529
		119	-149.8097056

Table 6. CH ₄ -N ₂ Linear Approach using aug-cc-pvtz basis set for 3.0 Å Separations	
3.0 Å separation	
Angle	Energy
	Hartrees
99	-149.7885192
100	-149.7893414
101	-149.7901081
102	-149.7908196
103	-149.7914759
104	-149.7920775
105	-149.7926245
106	-149.7931173
107	-149.7935562
108	-149.7939410
109	-149.7942725
109.4712	-149.7944103
110	-149.7945508
111	-149.7947763
112	-149.7949491
113	-149.7950697
114	-149.7951382
114.8	-149.7951558
114.83	-149.7951558
115	-149.7951551
116	-149.7951206
117	-149.7950350
118	-149.7948988
119	-149.7947122

Table 7. CH ₄ -H ₂ Perpendicular Approach using aug-cc-pvtz basis set for 4.0 and 3.5 Å Separations			
4.0 Å separation		3.5 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-41.6130504	104	-41.6130603
105	-41.6132963	105	-41.613304
106	-41.6134914	106	-41.613497
107	-41.6136375	107	-41.613641
108	-41.6137305	108	-41.6137321
109	-41.6137751	109	-41.6137749
109.4	-41.613779	109.36	-41.6137781
109.4712	-41.6137789	109.4	-41.6137781
110	-41.6137701	109.4712	-41.6137779
111	-41.613716	110	-41.6137682
112	-41.613613	111	-41.6137123
113	-41.6134615	112	-41.6136077
114	-41.6132618	113	-41.6134546
		114	-41.6132534

Table 8. CH ₄ -H ₂ Perpendicular Approach using aug-cc-pvtz basis set for 3.25 and 3.0 Å Separations			
3.25 Å separation		3.0 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-41.6127939	104	-41.6119134
105	-41.6130384	105	-41.6121644
106	-41.6132322	106	-41.6123647
107	-41.613377	107	-41.6125158
108	-41.6134691	108	-41.6126143
109	-41.6135127	109	-41.6126642
109.38	-41.6135163	109.4712	-41.6126705
109.4	-41.6135163	109.5	-41.6126706
109.4712	-41.6135162	109.51	-41.6126706
110	-41.613507	110	-41.6126646
111	-41.6134521	111	-41.6126159
112	-41.6133484	112	-41.6125184
113	-41.6131964	113	-41.6123723
114	-41.6129962	114	-41.612178

Table 9. CH ₄ -H ₂ Perpendicular Approach using aug-cc-pvtz basis set for 2.75 and 2.5 Å Separations			
2.75 Å separation		2.5 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-41.6095553	104	-41.6038628
105	-41.6098284	105	-41.6041942
106	-41.6100504	106	-41.6044737
107	-41.6102228	107	-41.6047025
108	-41.6103426	108	-41.6048783
109	-41.6104132	109	-41.6050039
109.4712	-41.6104289	109.4712	-41.6050445
109.9	-41.6104342	110	-41.6050789
109.92	-41.6104342	111	-41.6051035
110	-41.6104341	112	-41.6050781
111	-41.6104054	113	-41.605003
112	-41.6103277	114	-41.6048785
113	-41.610202		
114	-41.610027		

Table 10. CH ₄ -H ₂ Perpendicular Approach using aug-cc-pvtz basis set for 2.25 Å Separations	
2.25 Å separation	
Angle	Energy
	Hartrees
104	-41.5910364
105	-41.5915061
106	-41.5919218
107	-41.5922841
108	-41.5925918
109	-41.5928469
109.4712	-41.5929459
110	-41.5930493
111	-41.5931991
112	-41.5932968
113	-41.5933428
113.39	-41.5933468
113.4	-41.5933468
114	-41.5933373
115	-41.5932808

Table 11. CH ₄ -H ₂ Linear Approach using aug-cc-pvtz basis set for 4.0 and 3.5 Å Separations			
4.0 Å separation		3.5 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-41.613106	104	-41.6131301
105	-41.6133592	105	-41.6133881
106	-41.6135615	106	-41.6135952
107	-41.6137147	107	-41.613753
108	-41.6138145	108	-41.6138573
109	-41.6138659	109	-41.6139131
109.4712	-41.6138728	109.4712	-41.613922
109.5	-41.6138729	109.6	-41.6139227
109.53	-41.6138729	109.62	-41.6139227
110	-41.6138676	110	-41.6139191
111	-41.6138199	111	-41.6138757
112	-41.6137236	112	-41.6137832
113	-41.613578	113	-41.6136419
114	-41.6133844	114	-41.6134523

Table 12. CH ₄ -H ₂ Linear Approach using aug-cc-pvtz basis set for 3.25 and 3.0 Å Separations			
3.25 Å separation		3.0 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-41.6128024	104	-41.6117048
105	-41.6130687	105	-41.6119908
106	-41.6132838	106	-41.6122251
107	-41.6134495	107	-41.6124095
108	-41.6135615	108	-41.6125398
109	-41.6136247	109	-41.6126209
109.4712	-41.613637	109.4712	-41.6126411
109.77	-41.6136394	110	-41.6126516
109.8	-41.6136393	110.1	-41.6126519
110	-41.613638	110.11	-41.6126519
111	-41.6136017	110.12	-41.6126519
112	-41.6135161	111	-41.6126322
113	-41.6133816	112	-41.6125632
114	-41.6131985	113	-41.6124447
		114	-41.6122773

Table 13. CH ₄ -H ₂ Linear Approach using aug-cc-pvtz basis set for 2.75 and 2.5 Å Separations			
2.75 Å separation		2.5 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-41.6087869	104	-41.6018304
105	-41.6091178	105	-41.6022598
106	-41.6093959	106	-41.6026339
107	-41.6096231	107	-41.6029548
108	-41.6097951	108	-41.603218
109	-41.6099169	109	-41.6034289
109.4712	-41.6099554	109.4712	-41.6035074
110	-41.6099872	110	-41.6035862
110.88	-41.6100069	111	-41.6036904
110.89	-41.6100069	112	-41.6037419
110.9	-41.6100069	112.48	-41.603748
111	-41.6100066	112.49	-41.603748
112	-41.6099753	112.5	-41.603748
113	-41.6098937	113	-41.6037411
114	-41.6097622	114	-41.6036886

Table 14. CH ₄ -H ₂ Linear Approach using aug-cc-pvtz basis set for 2.25 Å Separations	
2.25 Å separation	
Angle	Energy
	Hartrees
104	-41.5864587
105	-41.5870911
106	-41.5876632
107	-41.5881776
108	-41.5886288
109	-41.5890235
109.4712	-41.589185
110	-41.5893603
111	-41.5896398
112	-41.5898626
113	-41.5900292
114	-41.5901403
115	-41.5901964
115.5	-41.590204
115.53	-41.5902041
116	-41.5901981
117	-41.590146

Table 15. CH ₄ -He Approach using aug-cc-pvtz basis set for 4.0 and 3.5 Å Separations			
4.0 Å separation		3.5 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-43.3408519	104	-43.3408727
105	-43.3411011	105	-43.3411217
106	-43.3412995	106	-43.3413198
107	-43.3414488	107	-43.3414688
108	-43.3415449	108	-43.3415646
109	-43.3415925	109	-43.3416121
109.46	-43.3415978	109.46	-43.3416172
109.4712	-43.3415978	109.4712	-43.3416172
109.5	-43.3415977	109.5	-43.3416171
110	-43.3415906	110	-43.3416099
111	-43.3415394	111	-43.3415584
112	-43.3414392	112	-43.3414581
113	-43.3412905	113	-43.3413092
114	-43.3410935	114	-43.341112

Table 16. CH ₄ -He Approach using aug-cc-pvtz basis set for 3.25 and 3.0 Å Separations			
3.25 Å separation		3.0 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-43.340777	104	-43.3403936
105	-43.3410267	105	-43.3406476
106	-43.3412256	106	-43.3408507
107	-43.3413754	107	-43.3410045
108	-43.3414721	108	-43.3411051
109	-43.3415203	109	-43.3411574
109.47	-43.3415258	109.4712	-43.3411647
109.4712	-43.3415258	109.5	-43.3411648
109.5	-43.3415258	109.55	-43.3411648
110	-43.3415189	110	-43.3411599
111	-43.3414682	111	-43.3411132
112	-43.3413686	112	-43.3410169
113	-43.3412204	113	-43.3408722
114	-43.3410239	114	-43.3406792

Table 17. CH ₄ -He Approach using aug-cc-pvtz basis set for 2.75 and 2.5 Å Separations			
2.75 Å separation		2.5 Å separation	
Angle	Energy	Angle	Energy
	Hartrees		Hartrees
104	-43.3392281	104	-43.3360642
105	-43.3394966	105	-43.3363742
106	-43.3397138	106	-43.3366321
107	-43.3398813	107	-43.3368391
108	-43.3399956	108	-43.3369924
109	-43.3400609	109	-43.3370956
109.4712	-43.3400741	109.4712	-43.3371257
109.8	-43.3400772	110	-43.3371478
109.81	-43.3400772	110.5	-43.3371549
110	-43.3400762	110.54	-43.337155
111	-43.3400419	110.55	-43.337155
112	-43.3399582	111	-43.3371495
113	-43.3398255	112	-43.3371009
114	-43.3396441	113	-43.3370025
		114	-43.3368546

Table 18. CH ₄ -He Approach using aug-cc-pvtz basis set for 2.25 Å Separations	
2.25 Å separation	
Angle	Energy
	Hartrees
104	-43.3280358
105	-43.3284556
106	-43.3288205
107	-43.3291319
108	-43.3293874
109	-43.32959
109.4712	-43.3296649
110	-43.3297394
111	-43.3298357
112	-43.329879
112.3	-43.3298825
112.34	-43.3298825
112.35	-43.3298825
113	-43.3298712
114	-43.329811



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