Second Buckingham-effect virial coefficients of non-dipolar molecules

by

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Abstract

A molecular-tensor theory of the second electric-field-gradient-induced birefringence (EFGIB) virial coefficient B_Q, which describes the effects of molecular pair interactions on the molar Buckingham constant $_mQ$, is developed for non-dipolar molecules with axial and higher symmetry.

The resulting expressions for contributions to B_Q are evaluated numerically for the molecules CO_2, C_2H_4 and C_2H_6. These molecules were chosen since previously developed molecular-tensor theories of the second light-scattering virial coefficient B_ρ and the second Kerr-effect virial coefficient B_K have yielded calculated values for these species which are in close agreement with the available measured data.

The B_Q values calculated for CO_2, C_2H_4 and C_2H_6 reveal that, for the fluids behaving as gases, the pair-interaction contributions to $_mQ$ are generally at or below the threshold of resolution of the EFGIB apparatus, so that the measured $_mQ$ values reported in the literature have not been contaminated by pair-interaction effects. In addition, it is seen that if the precision of measured $_mQ$ data can be increased by around an order of magnitude, it should in principle become possible to resolve B_Q contributions, particularly for higher gas densities.

Declaration

I, Verlan Moodley, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.

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I hereby certify that this statement is correct.

Signed . . . .

V W Couling

Supervisor

Dedication

I dedicate this thesis to my late father, Yagumburam Moodley who sadly passed in January of 2016, shortly before I had decided to proceed with this research. He raised me with kindness and taught me patience and humility. He supported and advised me in all my decisions, never uttering a discouraging word. He always told me that I am solely in charge of my future but the key to a great future begins with educating one's self, by this he didn't just mean a traditional university degree, but more than that, he wished for his children to educate themselves about life, the world, and people. His greatest attribute was the kindness he had for people. I will forever thank him for teaching me that there is more to life than material wealth, it is more important to be wealthy in love, kindness, compassion and health. Though he may no longer be in my life, the morals and values he instilled in me will remain forever. Rest well Dad.

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Chapter 1

Review and Introduction

1.1 Review

The permanent multipole moments of a molecule, such as its electric dipole, quadrupole and octopole moments, are fundamental properties which describe the molecular charge distribution [1–3]. For molecules which are far apart compared to the molecular dimensions, it is these permanent electric moments which determine the intermolecular energy of interaction, called the electrostatic energy. The polarizabilities describe the distortion of the molecular charge distribution either by external applied fields or the fields arising from the permanent moments of the neighbouring molecules. Accurate and precise knowledge of the permanent multipole moments and polarizabilities is necessary for a detailed understanding of molecular structure and intermolecular forces.

1.1.1 The multipole expansion

A full description of two interacting molecules is a many-body problem, requiring consideration of the dynamic interaction of all charges on each other. Such a description is not readily tractable, and simplifications become necessary. Ignoring the

internal motion of the molecule's electrons as well as the motion of the molecule as a whole allows for the application of electrostatic theory. If the separation of the molecules is sufficiently large, it becomes possible to expand the electrostatic potential of a molecule about an arbitrarily chosen origin which is close to the charges. This gives rise to a series of moments of charge, knowledge of which allows for useful characterization of the molecule.

Consider a distribution of charges q_i in a vacuum. Let the charges have displacement vectors $\mathbf{r}_i$ from an arbitrary origin O which is close to, or within, the distribution. The electrostatic potential ϕ produced by this distribution at some arbitrary point P with displacement vector $\mathbf{R}$ from the origin, where $R > r_i$, is given by

$$\phi(\mathbf{R}) = \frac{1}{4\pi\varepsilon_0} \sum_i \frac{q_i}{|\mathbf{R} - \mathbf{r}_i|} \ . \tag{1.1}$$

Invoking the binomial theorem to expand the denominator of this summation yields

$$\phi(\mathbf{R}) = \frac{1}{4\pi\varepsilon_0} \left[\frac{1}{R} \sum_i q_i + \frac{R_\alpha}{R^3} \sum_i q_i\, r_{i\alpha} + \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{2R^5} \sum_i q_i\, r_{i\alpha} r_{i\beta} + \cdots \right] \ . \tag{1.2}$$

The Greek subscripts α, β, $\cdots$, denote tensor components (a vector being a first-rank tensor), and can be equal to the Cartesian components x, y or z. Using the Einstein summation convention, a repeated Greek subscript denotes a summation over all three Cartesian components. $\delta_{\alpha\beta}$ is the Kronecker delta tensor, $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, $\delta_{\alpha\beta} = 0$ if $\alpha \neq \beta$. The various moments of electric charge of the distribution are as follows:

the total charge

$$q = \sum_i q_i , \tag{1.3}$$

the electric dipole moment

$$\mu_\alpha = \sum_i q_i \, r_{i\alpha} , \tag{1.4}$$

and the (primitive) electric quadrupole moment

$$Q_{\alpha\beta} = \sum_i q_i \, r_{i\alpha} r_{i\beta} . \tag{1.5}$$

The higher-order moments are the octopole, hexadecapole, $\cdots$, however, since their contributions to the electrostatic potential of molecules which have a permanent electric quadrupole moment are successively smaller, they will not be considered in this work. The definition of the electric quadrupole moment in equation (1.5) is known as the primitive, or traced, quadrupole moment. An alternative, and often more useful, definition is the traceless quadrupole moment, which describes the departure from spherical symmetry of the charge distribution, and is given by [4]

$$\Theta_{\alpha\beta} = \frac{1}{2} \left(3Q_{\alpha\beta} - Q_{\gamma\gamma}\delta_{\alpha\beta} \right) = \frac{1}{2} \sum_i q_i \left(3r_{i\alpha}r_{i\beta} - r_i^2 \delta_{\alpha\beta} \right) . \tag{1.6}$$

The name "traceless" arises because $\Theta_{\alpha\alpha} = 0$.

The electrostatic potential of the charge distribution can be recast in terms of the moments of charge, namely

$$\phi(\mathbf{R}) = \frac{1}{4\pi\varepsilon_0} \left[\frac{1}{R} q + \frac{R_\alpha}{R^3} \mu_\alpha + \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{3R^5} \Theta_{\alpha\beta} + \cdots \right] . \tag{1.7}$$

Here, the contributions arising from terms for successively higher multipole mo-

ments are successively diminished by a factor of the order $\frac{1}{R}$. Hence, the leading non-vanishing moment provides a reasonably accurate description of the electrostatic potential ϕ at point P provided the distance R is sufficiently large. Since the contribution to the expanded property arising from each of the multipole moments depends only on the displacement $\mathbf{R}$ of point P from O, the multipole moments are considered to be located at the origin O.

If an electrostatic field $\mathbf{E}$ is applied to the charge distribution, the distribution will experience a net force $\mathbf{F}$ given by

$$F_\alpha = \sum_i q_i E_{i\alpha} = q(E_\alpha)_0 + \mu_\beta(\nabla_\beta E_\alpha)_0 + \frac{1}{3}\Theta_{\beta\gamma}(\nabla_\gamma\nabla_\beta E_\alpha)_0 + \cdots . \qquad (1.8)$$

Here, the field and its derivatives are determined at the origin O about which the Taylor expansion of the field has been taken. From equation (1.8), it can be shown that a quadrupolar charge distribution will experience a torque in a region of uniform field gradient. Equation (1.8) can be used to determine the potential energy U of the charge distribution in the presence of the applied field [3, 5]:

$$U = -\int_{r_1(\mathbf{E}=0)}^{r_2(\mathbf{E}=\mathbf{E})} F_\alpha \, dr_\alpha = q\phi - \int_0^{\mathbf{E}} \mu_\alpha \, dE_\alpha - \frac{1}{3}\int_0^{\mathbf{E}} \Theta_{\alpha\beta} \, d(\nabla_\beta E_\alpha) - \cdots . \qquad (1.9)$$

For a rigid charge distribution, it is only the permanent multipole moments which will contribute to equation (1.9), giving

$$U = q\phi - \mu_\alpha^{(0)} E_\alpha - \frac{1}{3}\Theta_{\alpha\beta}^{(0)}\nabla_\beta E_\alpha - \cdots , \qquad (1.10)$$

where the permanent multipole moments have the superscript $^{(0)}$.

For an axially symmetric charge distribution, each multipole moment is determined by a single scalar quantity, namely q, μ, Θ, $\cdots$; for example, the quadrupole moment

$\Theta_{\alpha\beta}$ has principal components $\Theta_{zz} = \Theta$, $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta$.

The effect of a change of origin on a quadrupole moment can be established by moving O by $\mathbf{r}'$ to O'. The quadrupole moment Θ' relative to the new origin O' is

$$\Theta'_{\alpha\beta} = \frac{1}{2}\sum_i q_i \left(3r'_{i\alpha}r'_{i\beta} - (r'_i)^2\delta_{\alpha\beta}\right) \tag{1.11}$$

which becomes

$$\Theta'_{\alpha\beta} = \Theta_{\alpha\beta} - \frac{3}{2}\mu_\alpha r'_\beta - \frac{3}{2}\mu_\beta r'_\alpha + \mu_\gamma r'_\gamma \delta_{\alpha\beta} + \frac{1}{2}q\left\{3r'_\alpha r'_\beta - (r')^2\delta_{\alpha\beta}\right\} \ . \tag{1.12}$$

The quadrupole moment is seen to be independent of the choice of origin if and only if both q and μ_α are zero. Indeed, it can be shown that in general, only the leading non-zero electric multipole moment is independent of the choice of origin. For a dipolar molecule, the quadrupole moment will depend on the location of the origin. In this work, only non-dipolar molecules will be considered.

1.1.2 Direct experimental determination of molecular electric quadrupole moments

As described in the preceding section, a non-uniform electric field will exert a torque on a quadrupolar molecule. In a gas of such molecules, the electric field will result in partial alignment of the molecules, causing the gas to become anisotropic and hence birefringent. This electric-field-gradient-induced birefringence (EFGIB), now known as the Buckingham effect, when described by a suitable molecular-tensor theory, yields a direct means for the determination of the electric quadrupole moment of a molecule. This method was first proposed by Buckingham in 1959 [6], and the experiment was first successfully demonstrated by Buckingham and Disch on

the CO_2 molecule in 1963 [7]. Since then, a number of researchers have performed EFGIB experiments on a range of non-dipolar as well as dipolar molecules, as described in two recent review articles [8, 9].

Buckingham's initial theory [6] is applicable only to non-dipolar molecules. The quadrupole moment of a dipolar molecule will depend on the origin to which these moments are referred. Hence, in 1968, Buckingham and Longuet-Higgins developed a new theory of EFGIB for dipolar molecules based upon the forward scattering of light-wave radiation by the molecules when in the presence of an applied non-uniform electric field [10].

In 1991, Imrie and Raab published a new theory of EFGIB using eigenvalue theory of wave propagation, based on Maxwell's equations [11]. Their theory used the primitive electric quadrupole moment, and their derived expression for the induced birefringence was shown to be origin independent, as required. However, when using the traceless quadrupole moment in their theory, they obtained an origin-dependent result for the birefringence of dipolar molecules which differed from the Buckingham Longuet-Higgins theory. In an attempt to resolve this discrepancy, accurate *ab initio* calculations of the dipolar molecules CO, N_2O and OCS were undertaken by Rizzo, Coriani, Halkier and co-workers [12, 13], whose results favoured the Longuet-Higgins theory. Raab and de Lange eventually brought a definitive resolution to the controversy through a revision of the Imrie-Raab theory, re-obtaining exactly the original Buckingham and Longuet-Higgins result [3, 14, 15].

Experimental measurement of EFGIB has been used to determine the electric quadrupole moments of a range of small molecules including H_2, O_2, N_2, Cl_2, CO_2, CS_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_4H_6, C_6H_6, C_6F_6, CO, OCS, N_2O and CH_3F [7, 16–30]. In all of these experiments it has been assumed that the contribution to the EFGIB

arising from molecular pair interactions is negligible.

There exists a range of alternative methods for measuring the electric quadrupole moments of molecules, these methods often relying on the study of molecular interactions, such as through collision-induced absorption in far-infrared spectra [4]. Most of these methods are indirect, and are dependent on the model used to describe the intermolecular interaction potential. Consequently, these data are not considered to be particularly reliable [4].

Ab initio quantum mechanical calculations of molecular properties such as the molecular electric quadrupole moment are becoming increasingly sophisticated and accurate. A good review of present state-of-the-art techniques is available [31]. To attain highly accurate *ab initio* calculations of the electric quadrupole moment is a non-trivial task, and requires the use of large basis sets and the inclusion of electron correlation effects and vibrational averaging, making the calculations computationally intensive. Accurate experimental determinations of quadrupole moments provide the quantum computationalists with useful benchmarks against which to assess the effects arising from refinements in their high-level *ab initio* methods.

1.2 The EFGIB of interacting molecules

A number of electromagnetic properties of gases are proportional to the number density of the constituent molecules, and for ideal gases, this proportionality is exact since each molecule is treated as an independent system, there being no interactions between the molecules. For real gases, in which molecules do interact with their neighbours, the electromagnetic properties will display a non-linear dependence on the number density of the molecules.

In 1956, Buckingham and Pople demonstrated how these intermolecular interaction effects can be accounted for through the use of a virial-type expansion [32]. In general, they represented any measurable molecular-optic property of a real gas by the parameter Q, and provided as examples of particular properties the refractive index, the dielectric constant, the Kerr effect and the Cotton-Mouton effect. The molecular-optic property which is the subject of this investigation is the Buckingham effect, for which the property Q is the molar Buckingham constant $_\mathrm{m}Q$. Q can be expressed as a virial expansion in inverse powers of the molar volume V_m as follows:

$$Q = A_Q + \frac{B_Q}{V_\mathrm{m}} + \frac{C_Q}{V_\mathrm{m}^2} + \cdots , \qquad (1.13)$$

where the first virial coefficient A_Q provides the ideal gas contribution to Q, while B_Q is the second virial coefficient describing the contribution to Q arising from the interaction of molecular pairs, and C_Q is the third virial coefficient, accounting for the contribution arising from interacting triplets. These virial coefficients are functions of the temperature alone, or for optical phenomena, of temperature and optical frequency alone [32].

If Q is a macroscopic property of a mole of ideal-gas molecules, and q is the microscopic contribution to this property arising from a single molecule, then Q will be the sum of the N_A mean contributions $\overline{q}$ of the individual isolated molecules, namely

$$Q = A_Q = N_\mathrm{A}\, \overline{q} . \qquad (1.14)$$

For higher gas densities, there are times when a representative molecule 1 is interacting with a neighbouring molecule 2, their relative configuration being described by the collective symbol τ, and their contribution to Q at any given instant being $q_{12}(\tau)$. (The interaction configuration τ is described in detail following equation (2.48)). Molecule 1 must be treated as half of an interacting pair, so that its contribution to

Q at a given instant is $\frac{1}{2}q_{12}(\tau)$. Neglecting any triplet or higher-order interactions, Q becomes [32]

$$Q = N_A \left\{ \bar{q} + \int_\tau \left[\frac{1}{2}q_{12}(\tau) - \bar{q} \right] P(\tau)\,d\tau \right\} , \tag{1.15}$$

where $P(\tau)\,d\tau$ is the probability that molecule 1 has a neighbour in the range $(\tau, \tau + d\tau)$. The relationship between the intermolecular potential energy $U_{12}(\tau)$ and the probability function is provided by

$$P(\tau) = \frac{N_A}{\Omega V_{\mathrm{m}}} e^{-U_{12}(\tau)/kT} , \tag{1.16}$$

where $\Omega = V_{\mathrm{m}}^{-1} \int_\tau d\tau$. From equation (1.13),

$$B_Q = \lim_{V_{\mathrm{m}} \to \infty} (Q - A_Q)\,V_{\mathrm{m}} , \tag{1.17}$$

which combined with equations (1.14) to (1.16) yields

$$B_Q = \frac{N_A^2}{V_{\mathrm{m}}} \int_\tau \left[\frac{1}{2}q_{12}(\tau) - \bar{q} \right] e^{-U_{12}(\tau)/kT} d\tau . \tag{1.18}$$

This general expression for B_Q can be applied to the particular molecular-optic property Q under consideration. In this work, it will be applied to EFGIB for interacting pairs of non-dipolar molecules.

In 2003, Marchesan, Coriani and Rizzo published a paper presenting a computational *ab initio* investigation of the density dependence of EFGIB for gases of the noble atoms helium, neon and argon [33]. The second EFGIB virial coefficient was computed for each of these gases over a range of temperature. These atoms do not possess permanent quadrupole moments, being spherically symmetric. For interacting pairs, the dimers do however exhibit a small quadrupole moment. By computing

the internuclear dependence of the molecular quadrupole moment and the dipole-dipole-quadrupole and dipole-magnetic dipole-dipole hyperpolarizabilities of the van der Waals dimers, they were able to successfully determine the second EFGIB virial coefficients for these species. The pair-interaction contributions to the EFGIB were found to be of the order of a few tens of parts per million for helium and neon, and of the order of a few parts per thousands for argon at standard experimental conditions, and hence would not be detectable with the presently available experimental apparatus.

We are not aware of any other theoretical studies of the density dependence of EFGIB in the literature.

1.3   The aim of this project

1.3.1   The relevance of molecular electric quadrupole moments

Multipole theory in electrostatics, magnetostatics and electrodynamics has often been very successful in relating various macroscopic electromagnetic phenomena in matter to the microscopic structure of individual molecules (for gases) or of unit cells (for crystals) [1–3]. For molecules which have no permanent electric dipole moment, and for which the electric quadrupole moment is the leading moment of charge, accurate and precise knowledge of the quadrupole becomes essential to the description of a range of thermodynamic, structural and spectral properties.

Take CO_2 for example. CO_2 is a greenhouse gas, and its release into the atmosphere via the burning of fossil fuels is contributing to global climate change. Post-combustion capture of this molecule is presently an extremely active field of research. The quadrupole moment of CO_2 is relatively large, and this can be exploited since

the molecule can bind preferentially to adsorbents compared to the nitrogen and oxygen in the atmosphere, these molecules both having comparatively rather small quadrupole moments [34–38]. The quadrupole moment of CO_2 is also relevant to atmospheric and space physics, such as in the measurement and modelling of radiative transfer in planetary atmospheres, which includes significant effects from collision-induced absorption involving CO_2 and other molecules. [39]

For those dipolar molecules which have relatively small dipole moments, such as CO, N_2O and OCS, their quadrupole moments can play a significant role in various phenomena. N_2O is also a major greenhouse gas as well as an ozone-depleting gas, and the quadrupole moment is essential to understanding, for example, its adsorption and desorption as a means to suppressing its emission from soil [40]. CO is an important biological gas, and knowledge of its molecular quadrupole moment has proven useful in, for example, the modelling of the migration of the CO molecule in myoglobin via molecular dynamics simulations [41]. CO is also the second most abundant gas-phase molecule in the interstellar medium. It is present in the solid phase in dense molecular clouds, and recent quantum-mechanical simulations of solid CO show how the quadrupolar character of the molecule accounts for the energetics of the CO-H_2O ice interaction [42].

1.3.2 Accounting for pair-interaction contributions to EFGIB

Measurement of EFGIB in gases is clearly a very useful route to determining molecular electric quadrupole moments. What is assumed in these experiments is that contributions arising from molecular pair interactions are sufficiently small at typical experimental pressures and temperatures that they can be ignored. The essential aim of this project is to develop a molecular-tensor theory of second Buckingham-

effect virial coefficients B_Q, and to use it to calculate B_Q for some typical small molecules. This will allow for a quantitative assessment of the relative contributions of pair-interaction effects to the measured EFGIB for a range of gases. Such knowledge can guide experimentalists in future attempts to measure B_Q, since the gas densities at which pair interactions should become discernible using present EFGIB apparatus will be known. Knowledge of B_Q will also reveal the extent to which the measured EFGIB data in the literature have been contaminated by pair-interaction contributions.

Section 2.1 of Chapter 2 reviews the theory of the Buckingham effect in ideal gases, while Section 2.2 presents the new molecular-tensor theory for the Buckingham effect accounting for pair-interaction contributions in dense gases comprised of non-dipolar molecules. Chapter 3 presents the calculated second EFGIB virial coefficients for gases of pure CO_2, C_2H_4 and C_2H_6, and includes comprehensive discussion of the implications of the results, both for existing measured EFGIB data and for any future experimental determinations of EFGIB data.

Chapter 2

The Theory of the Buckingham Effect

2.1 Non-interacting molecules

The approach initially adopted by Buckingham to derive a theory of the EFGIB effect, or Buckingham effect, for the special case of non-dipolar molecules [6] is similar to that used by Buckingham and Pople to obtain theories of the Kerr electro-optic effect [43] and the Cotton-Mouton magneto-optic effect [44].

Consider a neutral molecule in the presence of an external electrostatic field $\mathbf{E}$ and field gradient $\boldsymbol{\nabla}\mathbf{E}$. The orientation and position of the molecule is given by the variable τ. For all but the lightest of molecules at typical experimental temperatures (*ca.* 300 K to 500 K) the rotational energy levels are sufficiently close together that the orientation may be considered to vary continuously, and hence be treated classically rather than quantum mechanically.

The electric field $\mathbf{E}$ can be written in tensor notation as E_α, while the field gradient $\boldsymbol{\nabla}\mathbf{E}$ can be written as $\nabla_\beta E_\alpha$, or as $E_{\alpha\beta}$. Buckingham's EFGIB apparatus comprises

a gas cell which is a conducting metal cylinder down the length of which run two thin parallel wires, which are separated by a small distance and which are equidistant from the cylinder's axis [7]. The cylinder is earthed, while the wires are held at the same potential relative to the cylinder, such that the axis experiences zero electric field but a high field gradient. If the space-fixed laboratory frame $O(x, y, z)$ is fixed in the quadrupole cell such that z is along the axis of the cylinder and in the direction of propagation of the light beam (which is parallel to, and centred on, the cell's axis), while the wires lie in the $yz-$plane, then the electric field-gradient tensor in the region between the wires is given by [6, 7]

$$\nabla_\beta E_\alpha = E_{\alpha\beta} = \begin{pmatrix} E_{xx} & 0 & 0 \\ 0 & E_{yy} = -E_{xx} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \qquad (2.1)$$

Here, the Greek subscripts pertain to the laboratory frame.

For a fixed position and orientation τ, the energy of a molecule in the field is $U(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})$. This energy can be written as a power-series expansion [1]

$$U(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) = U^{(0)} - \mu_i^{(0)} E_i - \frac{1}{2}\alpha_{ij}^{(0)} E_i E_j - \frac{1}{6}\beta_{ijk}^{(0)} E_i E_j E_k$$

$$- \frac{1}{24}\gamma_{ijkl}^{(0)} E_i E_j E_k E_l - \frac{1}{3}\Theta_{ij}^{(0)} E_{ij} - \frac{1}{3}A_{ijk}^{(0)} E_i E_{jk} \qquad (2.2)$$

$$- \frac{1}{6}B_{ijkl}^{(0)} E_i E_j E_{kl} - \frac{1}{6}C_{ijkl}^{(0)} E_{ij} E_{kl} + \cdots ,$$

where the terms $\mu_i^{(0)}$ and $\Theta_{ij}^{(0)}$ are the permanent electric dipole and quadrupole moments respectively, while the second-rank tensor $\alpha_{ij}^{(0)}$ is the static polarizability and

the third- and fourth-rank tensors $\beta_{ijk}^{(0)}$ and $\gamma_{ijkl}^{(0)}$ are the first- and second-order static hyperpolarizabilities of the molecule. These (hyper)polarizability tensors, together with the static polarizability tensors $A_{ijk}^{(0)}$, $B_{ijkl}^{(0)}$ and $C_{ijkl}^{(0)}$, arise from the distortion of the charge distribution of the molecule by the applied field E_α and field gradient $E_{\alpha\beta}$. Each of these polarizability tensors is unique, resulting from a particular combination of applied electric field and/or field gradient. Note that all tensors with Roman subscripts refer to the molecule-fixed axes $O(1, 2, 3)$.

For a gas of non-dipolar molecules, which is the focus of this project, the energy reduces to

$$U(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) = U^{(0)} - \frac{1}{2}\alpha_{ij}^{(0)} E_i E_j - \frac{1}{24}\gamma_{ijkl}^{(0)} E_i E_j E_k E_l$$

$$- \frac{1}{3}\Theta_{ij}^{(0)} E_{ij} - \frac{1}{6}B_{ijkl}^{(0)} E_i E_j E_{kl} - \frac{1}{6}C_{ijkl}^{(0)} E_{ij} E_{kl} + \cdots . \tag{2.3}$$

For a dilute gas, the oscillating dipole moment μ_i of a molecule arises solely due to the polarizing action of the oscillating electric field $\mathscr{E}_i$ of the light wave, and it is this oscillating dipole which primarily determines the refractive index. The optical-frequency polarizability tensor α_{ij} is modified by the applied non-uniform field so that the induced dipole moment for a non-dipolar diamagnetic molecule becomes [1]

$$\mu_i = \alpha_{ij}\mathscr{E}_j + \frac{1}{3}B_{ijkl}\mathscr{E}_j E_{kl} + \cdots . \tag{2.4}$$

The differential polarizability π_{ij} is defined as [1]

$$\pi_{ij} = \frac{\partial\mu_i}{\partial\mathscr{E}_j} = \alpha_{ij} + \frac{1}{3}B_{ijkl}E_{kl} + \cdots . \tag{2.5}$$

Buckingham's method to measure the molecular electric quadrupole moment of a gas molecule [6, 7] uses a technique whereby the gas sample is placed in the presence

of an applied non-uniform electric field, which partially orients the molecules. The resulting anisotropy in the refractive index, induced by the applied field and field gradient, is then measured ellipsometrically. This difference between the refractive indices of the gas for light travelling along the $z-$axis with electric vectors in the x and y directions, $n_x - n_y$, is given as [1]

$$n_x - n_y = \frac{2\pi N_{\mathrm{A}}}{(4\pi\varepsilon_0)V_{\mathrm{m}}}\overline{\pi} \ . \tag{2.6}$$

Here N_{A} is Avogadro's number, ε_0 is the permittivity of free space, V_{m} is the molar volume of the gas sample, and $\overline{\pi}$ is the orientational average of π, where π is the difference between the differential polarizabilities for a specific molecular configuration τ, namely

$$\pi = \pi(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) = \pi_{xx} - \pi_{yy} = \pi_{ij}\left(a_i^x a_j^x - a_i^y a_j^y\right) \ . \tag{2.7}$$

Here, a_i^x is the direction cosine between the x space-fixed and i molecule-fixed axes, while a_i^y is the direction cosine between the y space-fixed and i molecule-fixed axes.

Since the molecule is tumbling in space, the overbar in $\overline{\pi}$ denotes the orientational average of π over all configurations in the presence of the biasing influence of the applied non-uniform electric field. To proceed, it is assumed that the rapidly oscillating field of the incident light wave is sufficiently weak that it does not affect the orientation of the molecule, that the orientational variable τ is continuous, and that a Boltzmann-type weighting factor can be used to determine the orientational average required [3]. $\overline{\pi}$ can then be written as

$$\overline{\pi} = \frac{\int \pi(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})e^{-U(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})/kT}d\tau}{\int e^{-U(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})/kT}d\tau} \ . \tag{2.8}$$

The biased average in equation (2.8) can be converted into isotropic averages, i.e. the much more straightforward orientational averages for zero field and field gradient. This is achieved through a Taylor-series expansion of $\overline{\pi}$ in powers of both the field and field gradient, which yields

$$\overline{\pi} = AE_{xx} + BE_x^2 + CE_{xx}^3 + \cdots \tag{2.9}$$

where

$$A = \left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)_{E_x=E_{xx}=0} \quad , \quad B = \frac{1}{2} \left(\frac{\partial^2 \overline{\pi}}{\partial E_x^2} \right)_{E_x=E_{xx}=0} \quad , \quad C = \frac{1}{3!} \left(\frac{\partial^3 \overline{\pi}}{\partial E_{xx}^3} \right)_{E_x=E_{xx}=0} . \tag{2.10}$$

$\overline{\pi}$ is seen to be an even function of the electric field and an odd one in the electric field gradient. It can be shown that for molecules in the presence of a typical experimental electric field gradient of $E_{xx} < 10^9 \ \mathrm{V\,m^{-2}}$, $\overline{\pi}$ can be reduced to the first term in equation (2.9) as the subsequent terms are negligible when working in the dipole approximation [45]. Therefore

$$\overline{\pi} = AE_{xx} = \left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)_{E_x=E_{xx}=0} E_{xx} \tag{2.11}$$

where $\left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)$ is evaluated with both the field and the field gradient being zero. Differentiating equation (2.8) yields

$$\left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)_{E_x=E_{xx}=0} = \left\langle \frac{\partial \pi}{\partial E_{xx}} \right\rangle - \frac{1}{kT} \left\langle \pi \left(\frac{\partial U}{\partial E_{xx}} \right) \right\rangle . \tag{2.12}$$

The angular brackets in (2.12) denote an isotropic average over all possible orientations τ of the molecule. For molecular property X,

$$\langle X \rangle = \frac{\int X(\tau,0)e^{-U(\tau,0)/kT}d\tau}{\int e^{-U(\tau,0)/kT}d\tau} . \tag{2.13}$$

Substituting equation (2.12) back into equation (2.11) gives an expression for $\bar{\pi}$ as

$$\bar{\pi} = \left\{ \left\langle \frac{\partial \pi}{\partial E_{xx}} \right\rangle - \frac{1}{kT} \left\langle \pi \left(\frac{\partial U}{\partial E_{xx}} \right) \right\rangle \right\} E_{xx} \; . \tag{2.14}$$

To solve for $\bar{\pi}$ in equation (2.14), two expressions need to be evaluated, namely $\left(\frac{\partial \pi}{\partial E_{xx}} \right)$ and $\left(\pi \frac{\partial U}{\partial E_{xx}} \right)$.

It is useful to first obtain the transformation of the electric field gradient from the laboratory frame of space-fixed axes into molecule-fixed axes. This is achieved by means of the direction cosines, so that

$$E_{ij} = a^i_\alpha a^j_\beta E_{\alpha\beta} \; . \tag{2.15}$$

Since the electric field gradient $E_{\alpha\beta}$ has only two non-zero components, namely E_{xx} and $E_{yy} = -E_{xx}$ (see equation (2.1)), E_{ij} becomes

$$E_{ij} = a^i_x a^j_x E_{xx} + a^i_y a^j_y E_{yy} = \left(a^i_x a^j_x - a^i_y a^j_y \right) E_{xx} \; , \tag{2.16}$$

which is equivalent to

$$E_{ij} = \left(a^x_i a^x_j - a^y_i a^y_j \right) E_{xx} \; . \tag{2.17}$$

In order to obtain $\pi(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})$, the term $\left(\frac{\partial \pi}{\partial E_{xx}} \right)$ needs to be evaluated. From equation (2.7),

$$\left(\frac{\partial \pi}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} = \frac{\partial}{\partial E_{xx}} \left[\pi_{ij} \left(a^x_i a^x_j - a^y_i a^y_j \right) \right]_{E_x = E_{xx} = 0} \; . \tag{2.18}$$

Therefore, by differentiating equation (2.5) with respect to the field gradient com-

ponent E_{xx}, the following is obtained

$$\left(\frac{\partial \pi}{\partial E_{xx}}\right)_{E_x = E_{xx} = 0} = \left[\frac{\partial}{\partial E_{xx}}\left(\alpha_{ij} + \frac{1}{3}B_{ijkl}E_{kl} + \cdots\right)\left(a_i^x a_j^x - a_i^y a_j^y\right)\right]. \qquad (2.19)$$

Making use of the result in equation (2.17) yields

$$\left(\frac{\partial \pi}{\partial E_{xx}}\right)_{E_x = E_{xx} = 0} = \left[\frac{\partial}{\partial E_{xx}}\left(\alpha_{ij} + \frac{1}{3}B_{ijkl}\left(a_k^x a_l^x - a_k^y a_l^y\right)E_{xx} + \cdots\right)\left(a_i^x a_j^x - a_i^y a_j^y\right)\right].$$
$$(2.20)$$

Hence,

$$\left\langle\frac{\partial \pi}{\partial E_{xx}}\right\rangle = \frac{1}{3}B_{ijkl}\left\langle\left(a_i^x a_j^x - a_i^y a_j^y\right)\left(a_k^x a_l^x - a_k^y a_l^y\right)\right\rangle. \qquad (2.21)$$

This expands to

$$\left\langle\frac{\partial \pi}{\partial E_{xx}}\right\rangle = \frac{1}{3}B_{ijkl}\left\langle a_i^x a_j^x a_k^x a_l^x - a_i^x a_j^x a_k^y a_l^y - a_i^y a_j^y a_k^x a_l^x + a_i^y a_j^y a_k^y a_l^y\right\rangle. \qquad (2.22)$$

The isotropic averages of direction cosines are discussed in detail in [2], which provides the relationships

$$\left\langle a_i^x a_j^x a_k^x a_l^x\right\rangle = \left\langle a_i^y a_j^y a_k^y a_l^y\right\rangle, \qquad (2.23)$$

$$\left\langle a_i^x a_j^x a_k^y a_l^y\right\rangle = \left\langle a_i^y a_j^y a_k^x a_l^x\right\rangle. \qquad (2.24)$$

Substituting these results into equation (2.22) yields

$$\left\langle\frac{\partial \pi}{\partial E_{xx}}\right\rangle = \frac{2}{3}B_{ijkl}\left\langle a_i^x a_j^x a_k^x a_l^x - a_i^x a_j^x a_k^y a_l^y\right\rangle. \qquad (2.25)$$

The terms in equation (2.25) are evaluated by invoking the following standard results

of isotropic averages [2, 43]:

$$\left\langle a_i^x a_j^x a_k^x a_l^x \right\rangle = \frac{1}{15} \left(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} \right) \;,\tag{2.26}$$

$$\left\langle a_i^x a_j^x a_k^y a_l^y \right\rangle = \frac{1}{30} \left(4\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right) \;.\tag{2.27}$$

Substituting the results in equations (2.26) and (2.27) into equation (2.25) yields

$$\left\langle \frac{\partial \pi}{\partial E_{xx}} \right\rangle = \frac{1}{45} B_{ijkl} \left[-2\delta_{ij}\delta_{kl} + 3\delta_{ik}\delta_{jl} + 3\delta_{il}\delta_{jk} \right] \;,\tag{2.28}$$

while contracting over the subscripts yields

$$\left\langle \frac{\partial \pi}{\partial E_{xx}} \right\rangle = \frac{1}{45} \left[-2B_{iijj} + 3B_{ijij} + 3B_{ijji} \right] \;.\tag{2.29}$$

Equation (2.29) can be further reduced since the B-tensor is traceless [1], so that $B_{iijj} = 0$. Together with the result $B_{ijij} = B_{ijji}$ [1], equation (2.29) can be written as

$$\left\langle \frac{\partial \pi}{\partial E_{xx}} \right\rangle = \frac{1}{45} \left[6B_{ijij} \right] = \frac{6}{45} B_{ijij} \;.\tag{2.30}$$

The second term in equation (2.14) still needs to be evaluated. This expression, $\left(\pi \frac{\partial U}{\partial E_{xx}} \right)$, is evaluated with the field and the field gradient being zero. By using equations (2.5) and (2.7) this term becomes

$$\left(\pi \frac{\partial U}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} = \alpha_{ij} \left(a_i^x a_j^x - a_i^y a_j^y \right) \left(\frac{\partial U}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} \;.\tag{2.31}$$

The term $\left(\frac{\partial U}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0}$ is obtained through differentiation of equation (2.2) with

respect to the E_{xx} component of the electric field gradient, which yields

$$\left(\frac{\partial U}{\partial E_{xx}}\right)_{E_x = E_{xx} = 0} = -\frac{1}{3}\Theta_{ij}^{(0)}\left(a_i^x a_j^x - a_i^y a_j^y\right) \ . \tag{2.32}$$

Hence,

$$\left\langle \pi \frac{\partial U}{\partial E_{xx}} \right\rangle = -\frac{1}{3}\alpha_{ij}\Theta_{kl}^{(0)}\left\langle \left(a_i^x a_j^x - a_i^y a_j^y\right)\left(a_k^x a_l^x - a_k^y a_l^y\right)\right\rangle \tag{2.33}$$

$$= -\frac{1}{3}\alpha_{ij}\Theta_{kl}^{(0)}\left\langle a_i^x a_j^x a_k^x a_l^x - a_i^x a_j^x a_k^y a_l^y - a_i^y a_j^y a_k^x a_l^x + a_i^y a_j^y a_k^y a_l^y \right\rangle \ .$$

As before, use is made of the results for isotropic averages contained in equations (2.23) and (2.24), which leads to

$$\left\langle \pi \frac{\partial U}{\partial E_{xx}} \right\rangle = -\frac{2}{3}\alpha_{ij}\Theta_{kl}^{(0)}\left\langle a_i^x a_j^x a_k^x a_l^x - a_i^x a_j^x a_k^y a_l^y \right\rangle \ . \tag{2.34}$$

This can be further simplified by substitution of the results from equations (2.26) and (2.27), yielding

$$\left\langle \pi \frac{\partial U}{\partial E_{xx}} \right\rangle = -\frac{1}{45}\alpha_{ij}\Theta_{kl}^{(0)}\left\langle -2\delta_{ij}\delta_{kl} + 3\delta_{ik}\delta_{jl} + 3\delta_{il}\delta_{jk} \right\rangle \ . \tag{2.35}$$

Contracting over the subscripts yields

$$\left\langle \pi \frac{\partial U}{\partial E_{xx}} \right\rangle = -\frac{1}{45}\left[-2\alpha_{ii}\Theta_{kk}^{(0)} + 3\alpha_{ij}\Theta_{ij}^{(0)} + 3\alpha_{ij}\Theta_{ji}^{(0)} \right] \tag{2.36}$$

$$= -\frac{1}{45}\left[-2\alpha_{ii}\Theta_{kk}^{(0)} + 6\alpha_{ij}\Theta_{ij}^{(0)} \right] \ .$$

The quadrupole tensor $\Theta_{ij}^{(0)}$ is traceless, that is the components along the diagonal

sum to zero, therefore $\Theta_{kk}^{(0)} = 0$. Consequently, equation (2.36) reduces to

$$\left\langle \pi \frac{\partial U}{\partial E_{xx}} \right\rangle = -\frac{6}{45} \alpha_{ij} \Theta_{ij}^{(0)} \ . \tag{2.37}$$

The two terms required in equation (2.14) have been evaluated, and the expression for $\overline{\pi}$ becomes

$$\overline{\pi} = \frac{6}{45} \left[B_{ijij} + \frac{\alpha_{ij} \Theta_{ij}^{(0)}}{kT} \right] E_{xx} \ . \tag{2.38}$$

Equation (2.38) can then be substituted into equation (2.6) to give

$$n_x - n_y = \frac{2\pi N_{\mathrm{A}}}{(4\pi\epsilon_0) V_{\mathrm{m}}} \overline{\pi}$$

$$= \frac{2\pi N_{\mathrm{A}}}{(4\pi\epsilon_0) V_{\mathrm{m}}} \cdot \frac{6}{45} \left[B_{ijij} + \frac{\alpha_{ij} \Theta_{ij}^{(0)}}{kT} \right] E_{xx} \tag{2.39}$$

$$= \frac{N_{\mathrm{A}} E_{xx}}{15\epsilon_0 V_{\mathrm{m}}} \left[B_{ijij} + \frac{\alpha_{ij} \Theta_{ij}^{(0)}}{kT} \right] \ .$$

Equation (2.39) is an expression for the birefringence induced in the gas by the applied inhomogeneous electric field expressed in terms of the microscopic molecular properties of an individual molecule. The molar Buckingham constant $_{\mathrm{m}}Q$ is defined to be [6, 46]

$$_{\mathrm{m}}Q = \frac{6n(3\varepsilon_r + 2)}{5\varepsilon_r(n^2 + 2)^2} \lim_{E_{xx} \to 0} \left(\frac{n_x - n_y}{E_{xx}} \right) V_{\mathrm{m}} \ . \tag{2.40}$$

Substituting equation (2.39) into equation (2.40) gives an expression for the molar Buckingham constant in the limit of infinite dilution as

$$_{\mathrm{m}}Q = \frac{2N_{\mathrm{A}}}{45\varepsilon_0} \left[B_{ijij} + \frac{\alpha_{ij} \Theta_{ij}^{(0)}}{kT} \right] \ . \tag{2.41}$$

In the EFGIB experiment, a monochromatic beam of linearly-polarized laser light travels along the $z-$axis, which is chosen to coincide with the axis of the gas cell. The long, fine, parallel wires used to establish the inhomogenous electric field define the yz plane, and the laser beam is polarized at $45°$ to this plane so that as it enters the cell, it may be resolved into two components with orthogonal electric vectors $\mathscr{E}_x$ and $\mathscr{E}_y$ which will experience different refractive indices n_x and n_y as they travel through the birefringent medium. The beam will emerge from the cell elliptically polarized, since the two components will now have a relative phase difference δ of

$$\delta = \frac{2\pi l}{\lambda}\left(n_x - n_y\right) \ ,\tag{2.42}$$

where l is the pathlength of the medium, and λ is the wavelength of the light. The azimuth of this elliptically-polarized beam will still be $45°$ to the yz plane, and passing it through a quarter-wave plate with fast axis set at an azimuth of $45°$, the light will emerge linearly polarized but rotated from the initial $45°$ plane of polarization by an angle $\delta/2$ radians. The optical retardation δ is the observable property in the experiment, and from equation (2.42) it yields $(n_x - n_y)$, which together with knowledge of the refractive index and relative permittivity of the gas, its temperature and density, and the strength of the applied electric field gradient, allows for the calculation of $_\mathrm{m}Q$ via equation (2.40).

Although this project focuses on non-dipolar molecules, there is an important consequence of the Buckingham-Longuet Higgins (BLH) theory of dipolar molecules [10] for non-dipolar species, which is now examined. The BLH theory of EFGIB for dipolar molecules is based on the forward scattering of radiation by the molecules in the birefringent medium. Unlike equation (2.4), which is to electric dipole order, the BLH theory is applied to electric quadrupole-magnetic dipole order, so that the moments induced in a non-dipolar molecule in the presence of the incident light-wave

fields $\mathscr{E}_i$ and $\mathscr{B}_i$ are [3, 10, 14]

$$\mu_i = \alpha_{ij}\mathscr{E}_j + \frac{1}{3}B_{ijkl}\mathscr{E}_j\nabla_l E_k + \frac{1}{3}\mathscr{B}_{iljk}\left(\nabla_k\mathscr{E}_j\right)E_l + \frac{1}{\omega}J'_{ijk}\dot{\mathscr{B}}_j E_k \ , \tag{2.43}$$

$$\Theta_{ij} = \mathscr{B}_{klij}\mathscr{E}_k E_l \ , \tag{2.44}$$

and

$$m_i = -\frac{1}{\omega}J'_{jik}\dot{\mathscr{E}}_j E_k \ , \tag{2.45}$$

where ω is the frequency of the radiation. The BLH forward-scattering theory of EFGIB has been presented in thorough detail by Raab and de Lange [3, 14], and will not be reproduced here, it being sufficient for present purposes to simply provide the end result, namely

$$_{\mathrm{m}}Q = \frac{2N_{\mathrm{A}}}{45\varepsilon_0}\left[\frac{15}{2}b + \frac{\alpha_{ij}\Theta_{ij}^{(0)}}{kT}\right] \ . \tag{2.46}$$

In equation (2.41), $\frac{15}{2}b = B_{ijij}$, but in equation (2.46),

$$\frac{15}{2}b = B_{ijij} - \mathscr{B}_{ijij} - 5\omega^{-1}\varepsilon_{ijk}J'_{ijk} \ , \tag{2.47}$$

where ε_{ijk} is the Levi-Civita tensor. Equation (2.46) has two terms, indicating that in EFGIB, the anisotropy in the refractive index of the fluid arises from two distinct contributions. The source of the temperature-independent term is the distortion of the molecular charge distribution by the applied field gradient, while that of the temperature-dependent term is the orientational effect of the electric field gradient on the molecular quadrupole moments. Nearly all of the earlier EFGIB experiments were performed at a single (ambient) temperature, hence avoiding the challenges in recording measurements at higher temperatures. The temperature-independent

term was then assumed to make a negligible contribution to $_mQ$, so that setting $\frac{15}{2}b = 0$ in equation (2.46) allowed for the quadrupole moment to be extracted provided the polarizability tensor α_{ij} was known. Since 1997, there have been several temperature-dependent investigations of EFGIB for smaller molecules, and these have revealed the extent to which the electronic-distortion term contributes to the induced birefringence: 3% for CO_2 [22, 27], -5% for CS_2 [22], -9% for C_6H_6 [25], 7% for C_6F_6 [25], 10% for N_2 [26], 5% for N_2O [28] and 7% for CO [29]. These contributions, though often small, are clearly not negligible, especially since the aim of the EFGIB experiment is to extract precise and accurate values of the molecular quadrupole moments, with combined experimental uncertainties typically around 2 to 3%.

For the purposes of the present investigation, the contribution of the electronic-distortion tensors in equation (2.47) to the second EFGIB virial coefficient B_Q will be ignored. The reasons for this are twofold. Firstly, the individual tensor components for these polarizabilities are not known (either experimentally or computationally) even for small molecules, and so at present it is not feasible to calculate their contribution to B_Q, and secondly it seems reasonable to expect that their contribution to B_Q will be of the same order as for A_Q, namely around 10% or lower.

The new molecular-tensor theory for B_Q of non-dipolar molecules is now presented. It follows the formalism of Buckingham's original theory of EFGIB for non-interacting molecules [6] as has been presented in this section.

2.2 Non-dipolar interacting molecules

For higher gas densities, the methodology of Buckingham and Pople [32] for the treatment of intermolecular interaction effects via a virial expansion, as outlined in

general in Section 1.2 of Chapter 1, is followed.

Recall from equation (2.6) that in the limit of infinite dilution, the refractive index difference $n_x - n_y$ of a gas in the presence of an applied non-uniform electric field is

$$n_x - n_y = \frac{2\pi N_A}{(4\pi\varepsilon_0)V_m}\overline{\pi} \qquad (2.48)$$

where $\overline{\pi}$ is the average over all configurations τ of the quantity $\pi_{ij}\left(a_i^x a_j^x - a_i^y a_j^y\right)$ of a representative *isolated* molecule in the presence of the biasing influence of the applied non-uniform electric field.

For higher gas densities, the contribution of a representative molecule 1 to $n_x - n_y$ is not always given by equation (2.48), since there are times when molecule 1 has to be treated as half of an interacting pair. When molecule 1 is in the presence of a neighbouring molecule 2, the relative configuration of which is specified by τ, then the instantaneous contribution of molecule 1 to the induced birefringence becomes

$$\frac{1}{2}\left\{\frac{2\pi N_A}{(4\pi\varepsilon_0)V_m}\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})\right\} \qquad (2.49)$$

where

$$\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) = \pi^{(12)} = \pi_{ij}^{(12)}(a_i^x a_j^x - a_i^y a_j^y) \ . \qquad (2.50)$$

Here, $\pi_{ij}^{(12)}$ is the differential polarizability of the interacting pair, an expression for which will need to be derived explicitly. To obtain the biased orientational average $\overline{\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})}$, the molecular pair is allowed to rotate as a rigid whole (in the fixed configuration τ) in the presence of the biasing influence of the field and field gradient, E_α and $\nabla_\beta E_\alpha$ respectively. This biased average can then be converted into isotropic averages through a Taylor expansion in powers of $\mathbf{E}$ and $\boldsymbol{\nabla}\mathbf{E}$. Just as in the analysis

of an isolated molecule provided in equations (2.9) to (2.11), the leading term is

$$\overline{\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})} = \left(\frac{\partial \overline{\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} E_{xx} \tag{2.51}$$

where

$$\left(\frac{\partial \overline{\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} = \left\langle \frac{\partial \pi^{(12)}}{\partial E_{xx}} \right\rangle - \frac{1}{kT} \left\langle \pi^{(12)} \frac{\partial U^{(12)}}{\partial E_{xx}} \right\rangle , \tag{2.52}$$

yielding

$$\overline{\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})} = \left\{ \left\langle \frac{\partial \pi^{(12)}}{\partial E_{xx}} \right\rangle - \frac{1}{kT} \left\langle \pi^{(12)} \frac{\partial U^{(12)}}{\partial E_{xx}} \right\rangle \right\} E_{xx} . \tag{2.53}$$

Here, $U^{(12)} = U^{(12)}(\tau, 0, 0)$, the potential energy of the interacting pair of molecules in the absence of the applied field and field gradient. The quantities inside the angular brackets are initially referred to the molecule-fixed axes $O(1, 2, 3)$. The tensor product in $O(1, 2, 3)$ is fixed for a given interaction configuration τ. As the pair rotates as a rigid whole in the laboratory frame $O(x, y, z)$, the average projection of the pair properties, referred to $O(1, 2, 3)$, is averaged into $O(x, y, z)$ over all orientations. Averaging over the pair-interaction parameters τ can then be performed.

The density dependence of the molar Buckingham constant $_\mathrm{m}Q$ can be expressed as the virial expansion

$$_\mathrm{m}Q = A_Q + \frac{B_Q}{V_\mathrm{m}} + \frac{C_Q}{V_\mathrm{m}^2} + \cdots , \tag{2.54}$$

where A_Q, B_Q and C_Q are the first, second and third Buckingham-effect virial coefficients. From equation (2.40), the molar Buckingham constant $_\mathrm{m}Q$ in the limit of

infinite dilution is

$$A_Q = \lim_{V_{\mathrm{m}} \to \infty} ({}_{\mathrm{m}}Q) = \lim_{V_{\mathrm{m}} \to \infty} \left\{ \frac{6n(3\varepsilon_r + 2)\,(n_x - n_y)\,V_{\mathrm{m}}}{5\varepsilon_r(n^2 + 2)^2 E_{xx}} \right\}_{E_{xx} \to 0}$$

(2.55)

$$= \frac{2}{3} \cdot \frac{2\pi N_{\mathrm{A}}}{(4\pi\varepsilon_0)} \left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} .$$

Extrapolating this expression to higher densities yields

$$_{\mathrm{m}}Q = A_Q + \int_\tau \frac{4\pi N_{\mathrm{A}}}{3(4\pi\varepsilon_0)} \left\{ \frac{1}{2} \left(\frac{\partial \overline{\pi^{(12)}}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} - \left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} \right\} P(\tau) d\tau ,$$

(2.56)

where $P(\tau)d\tau$ is the probability of molecule 1 having a neighbour in the range $(\tau, \tau + d\tau)$, with $P(\tau)$ given in equation (1.16). Comparing equation (2.56) with equation (2.54), B_Q is seen to be

$$B_Q = \frac{4\pi N_{\mathrm{A}}^2}{3\Omega(4\pi\varepsilon_0)} \int_\tau \left\{ \frac{1}{2} \left(\frac{\partial \overline{\pi^{(12)}}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} - \left(\frac{\partial \overline{\pi}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} \right\} e^{-\frac{U_{12}(\tau)}{kT}} d\tau .$$

(2.57)

The relative configuration τ of two molecules of general symmetry may be expressed by seven variables, namely the separation R of the two molecular centres, the Euler angles α_1, β_1 and γ_1 used to define the direction cosines a_i^α between the laboratory frame $O(x, y, z)$ (referred to by $\alpha, \beta, \gamma \cdots$) and the molecule-fixed axes $O(1, 2, 3)$ of molecule 1 (referred to by $i, j, k \cdots$), and the Euler angles α_2, β_2 and γ_2 defining the direction cosines $a_{i'}^\alpha$ between the laboratory frame and the molecule-fixed axes $O(1', 2', 3')$ of molecule 2 (referred to by $i', j', k' \cdots$). These variables are described in full by Couling and Graham [47, 48], together with the evaluation of the normalization constant, which is $\Omega = (8\pi^2)^2$. The explicit expressions for the direction cosine tensors are

$$a_i^\alpha = \begin{bmatrix} \cos\gamma_1 & \sin\gamma_1 & 0 \\ -\sin\gamma_1 & \cos\gamma_1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos\beta_1 & 0 & -\sin\beta_1 \\ 0 & 1 & 0 \\ \sin\beta_1 & 0 & \cos\beta_1 \end{bmatrix} \begin{bmatrix} \cos\alpha_1 & \sin\alpha_1 & 0 \\ -\sin\alpha_1 & \cos\alpha_1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} \cos\alpha_1\cos\beta_1\cos\gamma_1 - \sin\alpha_1\sin\gamma_1 & \sin\alpha_1\cos\beta_1\cos\gamma_1 + \cos\alpha_1\sin\gamma_1 & -\sin\beta_1\cos\gamma_1 \\ -\cos\alpha_1\cos\beta_1\sin\gamma_1 - \sin\alpha_1\cos\gamma_1 & -\sin\alpha_1\cos\beta_1\sin\gamma_1 + \cos\alpha_1\cos\gamma_1 & \sin\beta_1\sin\gamma_1 \\ \cos\alpha_1\sin\beta_1 & \sin\alpha_1\sin\beta_1 & \cos\beta_1 \end{bmatrix},$$

$$(2.58)$$

and

$$a_{i'}^\alpha = \begin{bmatrix} \cos\alpha_2\cos\beta_2\cos\gamma_2 - \sin\alpha_2\sin\gamma_2 & \sin\alpha_2\cos\beta_2\cos\gamma_2 + \cos\alpha_2\sin\gamma_2 & -\sin\beta_2\cos\gamma_2 \\ -\cos\alpha_2\cos\beta_2\sin\gamma_2 - \sin\alpha_2\cos\gamma_2 & -\sin\alpha_2\cos\beta_2\sin\gamma_2 + \cos\alpha_2\cos\gamma_2 & \sin\beta_2\sin\gamma_2 \\ \cos\alpha_2\sin\beta_2 & \sin\alpha_2\sin\beta_2 & \cos\beta_2 \end{bmatrix}.$$

$$(2.59)$$

Equation (2.57) becomes

$$B_Q = \frac{2N_\mathrm{A}^2}{24\pi^2(4\pi\varepsilon_0)} \int_{R=0}^\infty \int_{\alpha_1=0}^{2\pi} \int_{\beta_1=0}^{\pi} \int_{\gamma_1=0}^{2\pi} \int_{\alpha_2=0}^{2\pi} \int_{\beta_2=0}^{\pi} \int_{\gamma_2=0}^{2\pi}$$

$$\times \left\{ \frac{1}{2}\left(\frac{\partial\overline{\pi^{(12)}}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0} - \left(\frac{\partial\overline{\pi}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0} \right\} \exp(-U_{12}(\tau)/kT) \quad (2.60)$$

$$\times R^2 \sin\beta_1 \sin\beta_2 \, dR \, d\alpha_1 \, d\beta_1 \, d\gamma_1 \, d\alpha_2 \, d\beta_2 \, d\gamma_2 \, .$$

Evaluation of B_Q by integrating over the pair interaction coordinates in equation (2.60) requires the intermolecular potential $U_{12}(\tau)$. In addition, the expression $\frac{1}{2}\left(\frac{\partial\overline{\pi^{(12)}}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0}$ needs to be evaluated, which requires the differential polarizabil-

ity $\pi_{iw}^{(12)}$ for interacting molecular pairs:

$$\pi_{iw}^{(12)} = \frac{\partial \mu_i^{(12)}}{\partial \mathscr{E}_w} \tag{2.61}$$

where $\mu_i^{(12)}(\mathscr{E}_w)$ is the total oscillating dipole moment induced on the interacting pair by the incident light-wave field $\mathscr{E}_w$. In order to proceed it becomes neccessary to make an assumption about the molecules, namely that they always retain their separate identities. While this will hold true in the long-range limit, at very short ranges, the charge distributions of the molecules will begin to overlap, a situation which will require high-level *ab initio* calculations for definitive description. Such calculations are extremely demanding and computationally intensive even for inter-acting atoms, but especially so for interacting molecules. Treating the molecules as if they retain their separate identities even in the region of overlap has proven profitable in the explication of molecular interactions for Rayleigh light-scattering [47, 49–51] and the Kerr effect [48, 52–54], where agreement between measured and calculated second virial coefficients can be achieved to within 10% or better, providing a measure of justification for the simplifying assumption, which allows equation (2.61) to be written as

$$\pi_{iw}^{(12)} = \frac{\partial(\mu_i^{(1)} + \mu_i^{(2)})}{\partial \mathscr{E}_w} \ . \tag{2.62}$$

Substituting this into equation (2.50), the difference between the differential polar-izabilities of an interacting pair in a specific configuration τ in the presence of the

applied field and field gradient is found to be

$$\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) = \pi_{iw}^{(12)}(a_i^x a_w^x - a_i^y a_w^y)$$

$$= \left(\frac{\partial \mu_i^{(1)}}{\partial \mathscr{E}_w} + \frac{\partial \mu_i^{(2)}}{\partial \mathscr{E}_w}\right)(a_i^x a_w^x - a_i^y a_w^y) \tag{2.63}$$

$$= \left(\pi_{iw}^{(1)} + \pi_{iw}^{(2)}\right)(a_i^x a_w^x - a_i^y a_w^y)$$

$$= \pi^{(1)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) + \pi^{(2)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) \ .$$

Now the dipole moment of molecule 1, $\mu_i^{(1)}$, is induced not exclusively by the oscillating light-wave field $\mathscr{E}_j$, but also partly by the field $\mathscr{F}_j^{(1)}$ which arises at molecule 1 due to the oscillating moments on molecule 2, so that

$$\mu_i^{(1)}\left(\mathscr{E}_j\right) = \left(\alpha_{ij}^{(1)} + \frac{1}{3}B_{ijkl}^{(1)}E_{kl} + \cdots\right)\left(\mathscr{E}_j + \mathscr{F}_j^{(1)}\right) \ . \tag{2.64}$$

With the aid of the second-rank $T-$tensor [1], $\mathscr{F}_j^{(1)}$ has the form

$$\mathscr{F}_j^{(1)} = T_{jm}^{(1)}\mu_m^{(2)} \tag{2.65}$$

where

$$\mu_m^{(2)}\left(\mathscr{E}_n\right) = \left(\alpha_{mn}^{(2)} + \frac{1}{3}B_{mnab}^{(2)}E_{ab} + \cdots\right)\left(\mathscr{E}_n + \mathscr{F}_n^{(2)}\right) \ , \tag{2.66}$$

where, in turn,

$$\mathscr{F}_n^{(2)} = T_{np}^{(2)}\mu_p^{(1)} \ . \tag{2.67}$$

Note that

$$T^{(1)} = (-1)^n \, T^{(2)} \, , \tag{2.68}$$

where n is the rank of the $T-$tensor [1]. If equations (2.66) and (2.67) are substituted into equation (2.65), followed by successive substitutions of $\mathscr{F}_j^{(1)}$ and $\mathscr{F}_n^{(2)}$, a series of terms contributing to the net field $\mathscr{F}_j^{(1)}$ in equation (2.65) is obtained, which, when substituted into equation (2.64), yields the required expression for the total oscillating dipole moment induced on molecule 1 by the light-wave field in the presence of the neighbouring molecule 2:

$$
\begin{aligned}
\mu_i^{(1)} \left(\mathscr{E}_w \right) = \; & \alpha_{iw}^{(1)} \mathscr{E}_w + \alpha_{ij}^{(1)} T_{jk} \alpha_{kw}^{(2)} \mathscr{E}_w + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(1)} \mathscr{E}_w \\[2ex]
& + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pw}^{(2)} \mathscr{E}_w + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rw}^{(1)} \mathscr{E}_w \\[2ex]
& + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rs}^{(1)} T_{st} \alpha_{tw}^{(2)} \mathscr{E}_w + \cdots \\[2ex]
& + \frac{1}{3} B_{iwkl}^{(1)} E_{kl} \mathscr{E}_w + \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} B_{kwmn}^{(2)} E_{mn} \mathscr{E}_w + \frac{1}{3} B_{ijkl}^{(1)} E_{kl} T_{jm} \alpha_{mw}^{(2)} \mathscr{E}_w \\[2ex]
& + \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} B_{mwpq}^{(1)} E_{pq} \mathscr{E}_w + \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} B_{klmn}^{(2)} E_{mn} T_{lp} \alpha_{pw}^{(1)} \mathscr{E}_w \\[2ex]
& + \frac{1}{3} B_{ijkl}^{(1)} E_{kl} T_{jm} \alpha_{mn}^{(2)} T_{np} \alpha_{pw}^{(1)} \mathscr{E}_w + \cdots \, .
\end{aligned}
\tag{2.69}
$$

Performing the operation $\frac{\partial}{\partial \mathscr{E}_w}$ on equation (2.69) yields the expression for the polarizability of molecule 1 in the presence of both the applied inhomogeneous field and a neighbouring molecule 2 in a specific relative configuration τ:

$$\pi_{iw}^{(1)} = \frac{\partial \mu_i^{(1)}}{\partial \mathscr{E}_w} = \alpha_{iw}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kw}^{(2)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pw}^{(2)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rw}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rs}^{(1)} T_{st} \alpha_{tw}^{(2)} + \cdots$$

$$+ \frac{1}{3} B_{iwkl}^{(1)} E_{kl} + \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} B_{kwmn}^{(2)} E_{mn} + \frac{1}{3} B_{ijkl}^{(1)} E_{kl} T_{jm} \alpha_{mw}^{(2)}$$

$$+ \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} B_{mwpq}^{(1)} E_{pq} + \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} B_{klmn}^{(2)} E_{mn} T_{lp} \alpha_{pw}^{(1)}$$

$$+ \frac{1}{3} B_{ijkl}^{(1)} E_{kl} T_{jm} \alpha_{mn}^{(2)} T_{np} \alpha_{pw}^{(1)} + \cdots .$$

$$(2.70)$$

This equation can be generalized to a differential polarizability $\pi_{iw}^{(p)}$ of a molecule p in the presence of the non-uniform field and a neighbouring molecule q. In addition, use of equation (2.19) allows the field gradient E_{ij} to be expressed as $E_{ij} = E_{xx}(a_i^x a_j^x - a_i^y a_j^y)$. The result is

$$\pi_{iw}^{(p)} = \alpha_{iw}^{(p)} + \alpha_{ij}^{(p)} T_{jk} \alpha_{kw}^{(q)} + \alpha_{ij}^{(p)} T_{jk} \alpha_{kl}^{(q)} T_{lm} \alpha_{mw}^{(p)}$$

$$+ \alpha_{ij}^{(p)} T_{jk} \alpha_{kl}^{(q)} T_{lm} \alpha_{mn}^{(p)} T_{np} \alpha_{pw}^{(q)} + \alpha_{ij}^{(p)} T_{jk} \alpha_{kl}^{(q)} T_{lm} \alpha_{mn}^{(p)} T_{np} \alpha_{pq}^{(q)} T_{qr} \alpha_{rw}^{(p)}$$

$$+ \alpha_{ij}^{(p)} T_{jk} \alpha_{kl}^{(q)} T_{lm} \alpha_{mn}^{(p)} T_{np} \alpha_{pq}^{(q)} T_{qr} \alpha_{rs}^{(p)} T_{st} \alpha_{tw}^{(q)} + \cdots$$

$$+ \frac{1}{3} B_{iwkl}^{(p)} E_{xx}(a_k^x a_l^x - a_k^y a_l^y) + \frac{1}{3} \alpha_{ij}^{(p)} T_{jk} B_{kwmn}^{(q)} E_{xx}(a_m^x a_n^x - a_m^y a_n^y)$$

$$\text{(2.71)}$$

$$+ \frac{1}{3} B_{ijkl}^{(p)} T_{jm} \alpha_{mw}^{(q)} E_{xx}(a_k^x a_l^x - a_k^y a_l^y)$$

$$+ \frac{1}{3} \alpha_{ij}^{(p)} T_{jk} \alpha_{kl}^{(q)} T_{lm} B_{mwpq}^{(p)} E_{xx}(a_p^x a_q^x - a_p^y a_q^y)$$

$$+ \frac{1}{3} \alpha_{ij}^{(p)} T_{jk} B_{klmn}^{(q)} T_{lp} \alpha_{pw}^{(p)} E_{xx}(a_m^x a_n^x - a_m^y a_n^y)$$

$$+ \frac{1}{3} B_{ijkl}^{(p)} T_{jm} \alpha_{mn}^{(q)} T_{np} \alpha_{pw}^{(p)} E_{xx}(a_k^x a_l^x - a_k^y a_l^y) + \cdots .$$

The potential of the interacting pair of molecules in the presence of the static applied inhomogeneous field is defined to be [3, 6]

$$U^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) = U^{(12)}(\tau, 0, 0) - \int_0^{E_i} \mu_i^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) \, dE_i$$

$$\text{(2.72)}$$

$$- \frac{1}{3} \int_0^{\nabla_j E_i} \Theta_{ij}^{(12)}(\boldsymbol{\tau}, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) \, d(\nabla_j E_i) .$$

The Kerr-effect terms from $\int_0^{E_x} \mu_i^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E}) \, a_i^x \, dE_x$ disappear when the potential

is differentiated with respect to the field gradient in equation (2.53). Since this is the only term in equation (2.53) which contains the potential, for our purposes it suffices to write the potential $U^{(12)}$ as

$$U^{(12)}(\tau, \mathbf{E}, \mathbf{\nabla E}) = U^{(12)}(\tau, 0, 0) - \frac{1}{3} \int_0^{E_{xx}} \Theta_{ij}^{(12)}(\boldsymbol{\tau}, \mathbf{E}, \mathbf{\nabla}E)(a_i^x a_j^x - a_i^y a_j^y) \, dE_{xx} \ ,$$

(2.73)

where, from equation (2.17), $\nabla_j E_i = E_{ij}$ has been written as $\left(a_i^x a_j^x - a_i^y a_j^y\right) E_{xx}$, and where $\Theta_{ij}^{(12)}$ is the total quadrupole moment of the pair in the presence of E_{xx}. As was argued for the dipole moment of the interacting pair, the quadrupole moment of each molecule is assumed to always retain its separate identity such that

$$\Theta_{ij}^{(12)} = \Theta_{ij}^{(1)} + \Theta_{ij}^{(2)} \ .$$

(2.74)

The potential becomes

$$U^{(12)}(\tau, \mathbf{E}, \mathbf{\nabla E}) = U^{(12)}(\tau, 0) + U^{(1)}(\tau, E_{xx}) + U^{(2)}(\tau, E_{xx}) \ .$$

(2.75)

$\Theta_{ij}^{(p)}$ is the total quadrupole moment (permanent and induced) of molecule p in the presence of the field and field gradient of a neighbouring molecule q, which can be written as [1]

$$\Theta_{ij}^{(p)} = \Theta_{0ij}^{(p)} + A_{0ijk}^{(p)}(E_k + F_k^{(p)}) + C_{0ijkl}^{(p)}(E_{kl} + F_{kl}^{(p)}) + \cdots \ .$$

(2.76)

Here, $\Theta_{0ij}^{(p)}$ is the permanent quadrupole moment of the molecule (now identified by the subscript zero), $A_{0ijk}^{(p)}$ and $C_{0ijkl}^{(p)}$ are static polarizability tensors (also denoted by the subscript zero), while $F_k^{(p)}$ and $F_{kl}^{(p)}$ are the static field and field gradient, respectively, arising at molecule p due to the permanent and induced multipole

moments of the neighbouring molecule q, which can be written as [1]

$$F_k^{(p)} = -\frac{1}{3}T_{klm}^{(p)}\Theta_{lm}^{(q)} \tag{2.77}$$

and

$$F_{kl}^{(p)} = -\frac{1}{3}T_{klmn}^{(p)}\Theta_{mn}^{(q)} \ . \tag{2.78}$$

For the non-dipolar molecules of this investigation, the static tensor $A_{0ijk}^{(p)}$ in equation (2.76) is equal to zero, so that the quadrupole moment for molecule p simplifies to

$$\Theta_{ij}^{(p)} = \Theta_{0ij}^{(p)} + C_{0ijkl}^{(p)}(E_{kl} + F_{kl}^{(p)}) \ . \tag{2.79}$$

Now,

$$F_{kl}^{(p)} = -\frac{1}{3}T_{klmn}^{(p)}\Theta_{mn}^{(q)} \tag{2.80}$$

requires

$$\Theta_{mn}^{(q)} = \Theta_{0mn}^{(q)} + C_{0mnpq}^{(q)}(E_{pq} + F_{pq}^{(q)}) \ , \tag{2.81}$$

where

$$F_{pq}^{(q)} = -\frac{1}{3}T_{pqrs}^{(q)}\Theta_{rs}^{(p)} \ . \tag{2.82}$$

Successive substitutions of $F_{kl}^{(p)}$ and $F_{pq}^{(q)}$ into equation (2.79) provide the series of

terms contributing to the total static quadrupole moment of molecule p:

$$\Theta_{ij}^{(p)} = \Theta_{0ij}^{(p)} + C_{0ijkl}^{(p)} E_{kl} - \frac{1}{3} C_{0ijkl}^{(p)} T_{klmn} \Theta_{0mn}^{(q)} + \frac{1}{9} C_{0ijkl}^{(p)} T_{klmn} C_{0mnpq}^{(q)} T_{pqrs} \Theta_{0rs}^{(p)} + \cdots .$$

(2.83)

Substituting equation (2.83) into equation (2.73), and bearing in mind equation (2.75), the expression for the potential energy of molecule p becomes

$$U^{(p)}(\tau, E_{xx}) = \left[-\frac{1}{3} \Theta_{0ij}^{(p)} + \frac{1}{9} C_{0ijkl}^{(p)} T_{klmn} \Theta_{0mn}^{(q)} + \cdots \right] (a_i^x a_j^x - a_i^y a_j^y) E_{xx} .$$

(2.84)

Armed with the explicit expressions for $\pi_{iw}^{(p)}$ in equation (2.71) and $U^{(p)}$ in equation (2.84), it is now possible to evaluate the term $\frac{1}{2} \left(\overline{\frac{\partial \pi^{(12)}}{\partial E_{xx}}} \right)_{E_x = E_{xx} = 0}$ in the expression for B_Q in equation (2.60). Recall equation (2.52):

$$\left(\overline{\frac{\partial \pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})}{E_{xx}}} \right)_{E_x = E_{xx} = 0} = \left\langle \frac{\partial \pi^{(12)}}{\partial E_{xx}} \right\rangle - \frac{1}{kT} \left\langle \pi^{(12)} \frac{\partial U^{(12)}}{\partial E_{xx}} \right\rangle .$$

(2.85)

Equation (2.63) yields

$$\left\langle \frac{\partial \pi^{(12)}}{\partial E_{xx}} \right\rangle = \left\langle \frac{\partial \pi^{(1)}}{\partial E_{xx}} \right\rangle + \left\langle \frac{\partial \pi^{(2)}}{\partial E_{xx}} \right\rangle ,$$

(2.86)

and since molecules 1 and 2 are identical, the isotropic averages of their molecular properties must be the same, so that

$$\left\langle \frac{\partial \pi^{(12)}}{\partial E_{xx}} \right\rangle = 2 \left\langle \frac{\partial \pi^{(1)}}{\partial E_{xx}} \right\rangle .$$

(2.87)

Similarly, and with the additional use of equation (2.75),

$$\left\langle \pi^{(12)} \frac{\partial U^{(12)}}{\partial E_{xx}} \right\rangle = \left\langle \left(\pi^{(1)} + \pi^{(2)} \right) \left(\frac{\partial U^{(1)}}{\partial E_{xx}} + \frac{\partial U^{(2)}}{\partial E_{xx}} \right) \right\rangle ,$$

(2.88)

which expands to

$$\left\langle \pi^{(12)} \frac{\partial U^{(12)}}{\partial E_{xx}} \right\rangle = \left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle + \left\langle \pi^{(1)} \frac{\partial U^{(2)}}{\partial E_{xx}} \right\rangle + \left\langle \pi^{(2)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle + \left\langle \pi^{(2)} \frac{\partial U^{(2)}}{\partial E_{xx}} \right\rangle$$

(2.89)

and, in turn, simplifies to

$$\left\langle \pi^{(12)} \frac{\partial U^{(12)}}{\partial E_{xx}} \right\rangle = 2 \left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle + 2 \left\langle \pi^{(1)} \frac{\partial U^{(2)}}{\partial E_{xx}} \right\rangle .$$

(2.90)

Hence,

$$\frac{1}{2} \left(\frac{\partial \overline{\pi^{(12)}(\tau, \mathbf{E}, \boldsymbol{\nabla}\mathbf{E})}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} = \left\langle \frac{\partial \pi^{(1)}}{\partial E_{xx}} \right\rangle - \frac{1}{kT} \left[\left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle + \left\langle \pi^{(1)} \frac{\partial U^{(2)}}{\partial E_{xx}} \right\rangle \right] .$$

(2.91)

The isotropic averages in equation (2.91) are now evaluated, beginning with $\left\langle \frac{\partial \pi^{(1)}}{\partial E_{xx}} \right\rangle$. Differentiating equation (2.71) with respect to the field gradient E_{xx} and setting the field gradient to zero yields

$$\left(\frac{\partial \pi_{iw}^{(1)}}{\partial E_{xx}} \right)_{E_x = E_{xx} = 0} = \left[\frac{1}{3} B_{iwnp}^{(1)} + \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} B_{kwnp}^{(2)} \right.$$

$$+ \frac{1}{3} B_{ijnp}^{(1)} T_{jm} \alpha_{mw}^{(2)}$$

$$+ \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} B_{mwnp}^{(1)} \qquad (2.92)$$

$$+ \frac{1}{3} \alpha_{ij}^{(1)} T_{jk} B_{klnp}^{(2)} T_{lm} \alpha_{mw}^{(1)}$$

$$\left. + \frac{1}{3} B_{ijnp}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(2)} + \cdots \right] (a_n^x a_p^x - a_n^y a_p^y) .$$

From equation (2.63),

$$\pi^{(1)} = \pi^{(1)}_{iw}(a_i^x a_w^x - a_i^y a_w^y) \tag{2.93}$$

so that

$$\left(\frac{\partial \pi^{(1)}}{\partial E_{xx}}\right)_{E_x = E_{xx} = 0} = \left[\frac{1}{3}B^{(1)}_{iwnp} + \frac{1}{3}\alpha^{(1)}_{ij}T_{jk}B^{(2)}_{kwnp}\right.$$

$$+ \frac{1}{3}B^{(1)}_{ijnp}T_{jm}\alpha^{(2)}_{mw}$$

$$+ \frac{1}{3}\alpha^{(1)}_{ij}T_{jk}\alpha^{(2)}_{kl}T_{lm}B^{(1)}_{mwnp}$$

$$+ \frac{1}{3}\alpha^{(1)}_{ij}T_{jk}B^{(2)}_{klnp}T_{lm}\alpha^{(1)}_{mw}$$

$$\left. + \frac{1}{3}B^{(1)}_{ijnp}T_{jk}\alpha^{(2)}_{kl}T_{lm}\alpha^{(2)}_{mw} + \cdots\right](a_n^x a_p^x - a_n^y a_p^y)(a_i^x a_w^x - a_i^y a_w^y) \ . \tag{2.94}$$

The isotropic average of equation (2.94) requires the isotropic average of the product of direction cosines, which has already been handled in equations (2.21) to (2.28). As already mentioned, there is a paucity of molecular B_{ijkl} tensor components in the literature, and so these terms will not be considered further. In any event, their expected contribution to B_Q is only a few percent. The BLH theory leads to additional interaction-induced contributions from $\mathscr{B}_{ijkl}$ and J'_{ijk}, which would need to be derived within the BLH theory [3, 10, 14], and which is beyond the scope of this project, though these tensor components are also not available in the literature. Fortunately, the combined contribution of these terms to B_Q should only be a few percent, so that their omission is not of serious concern. PhD student Mr

Siyabonga Ntombela, who is undertaking a project on EFGIB in the BLH formalism, is currently evaluating these terms as part of his project, as a means to verify these assumptions. This will require *ab initio* computation of the B_{ijkl}, $\mathscr{B}_{ijkl}$ and J'_{ijk} optical-frequency tensor components.

The remaining two isotropic averages in equation (2.91) are now evaluated. Initially, equation (2.84) is differentiated with respect to the field gradient, giving

$$\left(\frac{\partial U^{(p)}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0} = \left[-\frac{1}{3}\Theta_{0ij}^{(p)} + \frac{1}{9}C_{ijkl}^{(p)}T_{klmn}\Theta_{0mn}^{(q)} + ...\right](a_i^x a_j^x - a_i^y a_j^y) . \quad (2.95)$$

Then, $\left(\pi^{(1)}\right)_{E_x=E_{xx}=0}$ can be multiplied by the sum of the terms $\left(\frac{\partial U^{(1)}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0}$ and $\left(\frac{\partial U^{(2)}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0}$, hence providing the dominant contributions to B_Q. From equation (2.71)

$$\left(\pi^{(1)}\right)_{E_{xx}=E_x=0} = \left[\pi_{iw}^{(1)}(a_i^x a_w^x - a_i^y a_w^y)\right]_{E_x=E_{xx}=0}$$

$$= \left(\alpha_{iw}^{(1)} + \alpha_{ij}^{(1)}T_{jk}\alpha_{kw}^{(2)} + \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mw}^{(1)}\right.$$

$$+ \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pw}^{(2)} + \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rw}^{(1)}$$

$$\left.+ \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rs}^{(1)}T_{st}\alpha_{tw}^{(2)} + \cdots\right)(a_i^x a_w^x - a_i^y a_w^y) ,$$

$$(2.96)$$

while from equation (2.84)

$$\left(\frac{\partial U^{(1)}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0} = -\frac{1}{3}\Theta_{0ab}^{(1)}(a_a^x a_b^x - a_a^y a_b^y) \qquad (2.97)$$

wherein the $C-$tensor terms, the contributions of which are expected to be negligi-

ble, have been omitted. Thus $\left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle$ becomes

$$\left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle = -\frac{1}{3} \Big\{ \alpha_{iw}^{(1)} \Theta_{0ab}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kw}^{(2)} \Theta_{0ab}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(1)} \Theta_{0ab}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pw}^{(2)} \Theta_{0ab}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rw}^{(1)} \Theta_{0ab}^{(1)} \qquad (2.98)$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rs}^{(1)} T_{st} \alpha_{tw}^{(2)} \Theta_{0ab}^{(1)} + \cdots \Big\}$$

$$\times \ \left\langle (a_i^x a_w^x - a_i^y a_w^y)(a_a^x a_b^x - a_a^y a_b^y) \right\rangle .$$

The relevant results for isotropic averages contained in equations (2.21) to (2.28) are summarized here for convenience:

$$\left\langle (a_i^x a_w^x - a_i^y a_w^y)(a_a^x a_b^x - a_a^y a_b^y) \right\rangle = 2 \left\langle a_i^x a_w^x a_a^x a_b^x - a_i^x a_w^x a_a^y a_b^y \right\rangle$$

$$\qquad (2.99)$$

$$= \frac{1}{15} \left(-2\delta_{iw}\delta_{ab} + 3\delta_{ia}\delta_{wb} + 3\delta_{ib}\delta_{wa} \right) .$$

Application of these results to equation (2.98) yields

$$\left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle = -\frac{1}{45} \left\{ \alpha_{iw}^{(1)} \Theta_{0ab}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kw}^{(2)} \Theta_{0ab}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(1)} \Theta_{0ab}^{(1)} \right.$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pw}^{(2)} \Theta_{0ab}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rw}^{(1)} \Theta_{0ab}^{(1)}$$

$$\left. + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rs}^{(1)} T_{st} \alpha_{tw}^{(2)} \Theta_{0ab}^{(1)} + \cdots \right\}$$

$$\times \ \left(-2\delta_{iw}\delta_{ab} + 3\delta_{ia}\delta_{wb} + 3\delta_{ib}\delta_{wa} \right) \ .$$

$$(2.100)$$

Contracting over the subscripts gives

$$\left\langle \Pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle = -\frac{1}{45} \left[\left\{ -2\alpha_{ii}^{(1)}\Theta_{0aa}^{(1)} + 3\alpha_{iw}^{(1)}\Theta_{0iw}^{(1)} + 3\alpha_{iw}^{(1)}\Theta_{0wi}^{(1)} \right\} \right.$$

$$+ \left\{ -2\alpha_{ij}^{(1)}T_{jk}\alpha_{ki}^{(2)}\Theta_{0aa}^{(1)} + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kw}^{(2)}\Theta_{0iw}^{(1)} + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kw}^{(2)}\Theta_{0wi}^{(1)} \right\}$$

$$+ \left\{ -2\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mi}^{(1)}\Theta_{0aa}^{(1)} \right.$$

$$\left. + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mw}^{(1)}\Theta_{0iw}^{(1)} + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mw}^{(1)}\Theta_{0wi}^{(1)} \right\}$$

$$+ \left\{ -2\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pi}^{(2)}\Theta_{0aa}^{(1)} \right.$$

$$\left. + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pw}^{(2)}\Theta_{0iw}^{(1)} + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pw}^{(2)}\Theta_{0wi}^{(1)} \right\}$$

$$+ \left\{ -2\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{ri}^{(1)}\Theta_{0aa}^{(1)} \right.$$

$$+ 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rw}^{(1)}\Theta_{0iw}^{(1)}$$

$$\left. + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rw}^{(1)}\Theta_{0wi}^{(1)} \right\}$$

$$+ \left\{ -2\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rs}^{(1)}T_{st}\alpha_{ti}^{(2)}\Theta_{0aa}^{(1)} \right.$$

$$+ 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rs}^{(1)}T_{st}\alpha_{tw}^{(2)}\Theta_{0iw}^{(1)}$$

$$\left. \left. + 3\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rs}^{(1)}T_{st}\alpha_{tw}^{(2)}\Theta_{0wi}^{(1)} \right\} + \cdots \right].$$

$$(2.101)$$

Since the quadrupole moment is traceless, any quadrupole terms with a repeated subscript $\Theta_{0aa}^{(p)}$ are equal to zero and are eliminated from the equation. Also, the quadrupole moment tensor is symmetric in its subscripts, so that $\Theta_{0iw}^{(p)} = \Theta_{0wi}^{(p)}$. Hence,

$$\left\langle \pi^{(1)} \frac{\partial U^{(1)}}{\partial E_{xx}} \right\rangle = -\frac{6}{45} \Bigg[\alpha_{iw}^{(1)} \Theta_{0wi}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kw}^{(2)} \Theta_{0wi}^{(1)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(1)} \Theta_{0wi}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pw}^{(2)} \Theta_{0wi}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rw}^{(1)} \Theta_{0wi}^{(1)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rs}^{(1)} T_{st} \alpha_{tw}^{(2)} \Theta_{0wi}^{(1)} + \cdots \Bigg] .$$

$$(2.102)$$

A similar analysis yields

$$\left\langle \pi^{(1)} \frac{\partial U^{(2)}}{\partial E_{xx}} \right\rangle = -\frac{6}{45} \Bigg[\alpha_{iw}^{(1)} \Theta_{0wi}^{(2)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kw}^{(2)} \Theta_{0wi}^{(2)} + \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mw}^{(1)} \Theta_{0wi}^{(2)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pw}^{(2)} \Theta_{0wi}^{(2)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rw}^{(1)} \Theta_{0wi}^{(2)}$$

$$+ \alpha_{ij}^{(1)} T_{jk} \alpha_{kl}^{(2)} T_{lm} \alpha_{mn}^{(1)} T_{np} \alpha_{pq}^{(2)} T_{qr} \alpha_{rs}^{(1)} T_{st} \alpha_{tw}^{(2)} \Theta_{0wi}^{(2)} + \cdots \Bigg] .$$

$$(2.103)$$

The terms contributing to the integral for B_Q in equation (2.60) can be expressed

in condensed notation as

$$\left\{\frac{1}{2}\left(\frac{\partial\overline{\pi^{(12)}}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0} - \left(\frac{\partial\bar{\pi}}{\partial E_{xx}}\right)_{E_x=E_{xx}=0}\right\}$$

$$= \Theta_1\alpha_1 + \Theta_1\alpha_2 + \Theta_1\alpha_3 + \Theta_1\alpha_4 + \Theta_1\alpha_5 + \Theta_1\alpha_6 + \cdots$$

$$+ B_1\alpha_1 + B_1\alpha_2 + B_1\alpha_3 + \cdots .$$

$$(2.104)$$

The explicit expressions for $\Theta_1\alpha_1,\ \Theta_1\alpha_2,\ \cdots$ are

$$\Theta_1\alpha_1 = \frac{2}{15kT}\left\{\alpha_{iw}^{(1)}\Theta_{0wi}^{(2)}\right\}, \tag{2.105}$$

$$\Theta_1\alpha_2 = \frac{2}{15kT}\left\{\alpha_{ij}^{(1)}T_{jk}\alpha_{kw}^{(2)}\Theta_{0wi}^{(1)} + \alpha_{ij}^{(1)}T_{jk}\alpha_{kw}^{(2)}\Theta_{0wi}^{(2)}\right\}, \tag{2.106}$$

$$\Theta_1\alpha_3 = \frac{2}{15kT}\left\{\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mw}^{(1)}\Theta_{0wi}^{(1)}\right.$$

$$(2.107)$$

$$\left. + \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mw}^{(1)}\Theta_{0wi}^{(2)}\right\},$$

$$\Theta_1\alpha_4 = \frac{2}{15kT}\left\{\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pw}^{(2)}\Theta_{0wi}^{(1)}\right.$$

$$(2.108)$$

$$\left. + \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pw}^{(2)}\Theta_{0wi}^{(2)}\right\},$$

$$\Theta_1\alpha_5 = \frac{2}{15kT}\left\{\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rw}^{(1)}\Theta_{0wi}^{(1)}\right.$$

$$(2.109)$$

$$\left. + \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rw}^{(1)}\Theta_{0wi}^{(2)}\right\} ,$$

$$\Theta_1\alpha_6 = \frac{2}{15kT}\left\{\alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rs}^{(1)}T_{st}\alpha_{tw}^{(2)}\Theta_{0wi}^{(1)}\right.$$

$$(2.110)$$

$$\left. + \alpha_{ij}^{(1)}T_{jk}\alpha_{kl}^{(2)}T_{lm}\alpha_{mn}^{(1)}T_{np}\alpha_{pq}^{(2)}T_{qr}\alpha_{rs}^{(1)}T_{st}\alpha_{tw}^{(2)}\Theta_{0wi}^{(2)}\right\} .$$

The lowest-symmetry molecule treated in this project is C_2H_4, which is of D_{2h} symmetry. For this point group, the dynamic polarizability tensor $\alpha_{ij}^{(1)}$ has three independent components [1], namely

$$\alpha_{ij}^{(1)} = \alpha_{i'j'}^{(2)} = \begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix} . \qquad (2.111)$$

$\alpha_{ij}^{(2)}$ is the dynamic polarizability tensor of molecule 2 expressed in the molecule-fixed axes of molecule 1, which is provided by

$$\alpha_{ij}^{(2)} = a_\alpha^i a_\beta^j a_{i'}^\alpha a_{j'}^\beta \alpha_{i'j'}^{(2)} . \qquad (2.112)$$

For molecules of D_{2h} symmetry, the traceless quadrupole moment has two independent components [1], and is given by

$$\Theta_{0ij}^{(1)} = \Theta_{0i'j'}^{(2)} = \begin{bmatrix} \Theta_1 & 0 & 0 \\ 0 & \Theta_2 & 0 \\ 0 & 0 & -\Theta_1 - \Theta_2 \end{bmatrix} . \qquad (2.113)$$

Similarly,

$$\Theta_{0ij}^{(2)} = a_\alpha^i a_\beta^j a_{i'}^\alpha a_{j'}^\beta \Theta_{0i'j'}^{(2)} \; . \tag{2.114}$$

For axially-symmetric molecules, the polarizability tensor has two independent components ($\alpha_{11} = \alpha_{22}$ in equation (2.111)), while the quadrupole moment tensor has only one independent component ($\Theta_1 = \Theta_2$ in equation (2.113)). The second-rank $T-$tensor in space-fixed axes is [1]

$$T_{\alpha\beta} = \frac{1}{4\pi\varepsilon_0} \nabla_\alpha \nabla_\beta R^{-1} = \frac{1}{4\pi\varepsilon_0} \left(3R_\alpha R_\beta - R^2 \delta_{\alpha\beta} \right) R^{-5} \; . \tag{2.115}$$

In the molecule-fixed axes of molecule 1, $T_{ij} = a_\alpha^i a_\beta^j T_{\alpha\beta}$.

The tensor manipulation facilities of the Macsyma algebraic manipulation package are indispensible in evaluating the expressions for the terms in equations (2.105) to (2.110), particularly as the expressions increase in complexity. Since these expressions become extremely large, often taking several pages to express, they are not explicitly reproduced here. These expressions are integrated (*i.e.* averaged) over the pair-interaction coordinates using equation (2.60), thereby establishing the contribution of each of the $\Theta_1\alpha_1$, $\Theta_1\alpha_2$, $\cdots$ terms to B_Q.

The integral in equation (2.60) requires an intermolecular potential $U_{12}(\tau)$. As previously [47, 48], use is made of the classical potential

$$U_{12}(\tau) = U_{LJ} + U_{\Theta,\Theta} + U_{\Theta,\text{ ind } \mu} + U_{\text{shape}} \tag{2.116}$$

where U_{LJ} is the Lennard-Jones 6:12 potential, $U_{\Theta,\Theta}$ is the electrostatic quadrupole-quadrupole interaction energy of the two molecules, and $U_{\Theta,\text{ ind } \mu}$ is the quadrupole-induced dipole interaction energy. U_{shape} accounts for the angular dependence of

short range repulsive forces for non-spherical molecules. Explicit expressions for each of these contributions to $U_{12}(\tau)$ for molecules of D_{2h} symmetry and higher have already been provided [47, 48]. It should be noted that evaluation of the induction energy $U_{\Theta,\,\text{ind}\,\mu}$ requires knowledge of the static molecular polarizability tensor $\alpha_{ij}^{(0)}$.

The integrals were evaluated by numerical integration using Gaussian quadrature, with the ranges of the orientation angles being divided into 16 intervals each, while the intermolecular separation R was given the range of 0.1 to 3.0 nm divided into 64 intervals. The technique of Gaussian quadrature has been used previously in evaluation of second light-scattering virial coefficients and second Kerr-effect virial coefficients, where the convergence of the integrals has been carefully tested to establish the necessary intervals for the angles and the range [47, 48]. Appendix A.1 provides an example Fortran program (for evaluation of the $\Theta_1\alpha_3$ contribution to B_Q). The programs were run in double precision on a personal computer with a dual-core processor using the Salford F90 compiler. Program run-times were typically of the order of 20 minutes each.

Chapter 3 presents the results for the computation of B_Q for the molecules CO_2, C_2H_4 and C_2H_6. These molecules were chosen since their static and dynamic molecular polarizabilities and molecular quadrupole moments have been well characterized in the literature, and the quadrupoles of CO_2 and C_2H_4 are relatively large, so that the contribution to $_mQ$ arising from B_Q for these species could also be expected to be relatively large. For example, the quadrupole moment of CO_2 is $\Theta = -14.27 \times 10^{-40}\,\text{C}\,\text{m}^2$ [27], while the N_2 molecule has $\Theta = -4.97 \times 10^{-40}\,\text{C}\,\text{m}^2$ [26], and the O_2 molecule $\Theta = -1.03 \times 10^{-40}\,\text{C}\,\text{m}^2$ [30]. The temperature-dependence of the second Kerr-effect virial coefficients B_K of these molecules have recently been calculated and found to be in good agreement with the available measured data [55], as

have the second light-scattering virial coefficients at room temperature [47, 49, 56].

Chapter 3

Results

3.1 Carbon Dioxide

The molecular data required to calculate B_Q for the axially-symmetric CO_2 molecule are presented in Table 3.1. As for the other molecules considered in this chapter, optimized values for the Lennard-Jones force constants R_0 and ε/k and the shape parameter D are obtained by fitting values of the second pressure virial coefficient $B(T)$ calculated according to

$$B(T) = \frac{N_A}{2\Omega} \int_\tau \left[1 - e^{-U_{12}(\tau)/kT} \right] d\tau \tag{3.1}$$

to the experimental data [57] over a range of temperature.

For axially-symmetric molecules, the two independent polarizability tensor components can be extracted from knowledge of the mean polarizability $\alpha = \frac{1}{3}\alpha_{ii} = \left(2\alpha_\perp + \alpha_\parallel\right)$ and the polarizability anisotropy $\Delta\alpha = \left(\alpha_\parallel - \alpha_\perp\right)$, where in equation (2.111), $\alpha_{33} = \alpha_\parallel$ and $\alpha_{11} = \alpha_{22} = \alpha_\perp$. All optical-frequency polarizabilities in this chapter are quoted for the Helium-Neon laser wavelength of $\lambda = 632.8$ nm. Tables 3.2 to 3.5 provide the relative magnitudes of the various contributions to B_Q calculated over the temperature span 250 K to 500 K.

Table 3.1: The molecular properties of CO_2 used in the calculation of B_Q.

Property	Value	Reference
R_0 (nm)	0.400	[58]
ε/k (K)	190.0	[58]
D_1	0.250^a	[56]
D_2	0.000	
$10^{40}\Theta_{11}(\mathrm{C\,m^2})$	$7.13_5 \pm 0.17$	[27, 56]
$10^{40}\Theta_{22}(\mathrm{C\,m^2})$	$7.13_5 \pm 0.17$	
$10^{40}\Theta_{33}(\mathrm{C\,m^2})$	-14.27 ± 0.33	
$10^{40}\alpha(\mathrm{C^2\,m^2\,J^{-1}})$	2.93141 ± 0.00021	[59]
$10^{40}\Delta\alpha(\mathrm{C^2\,m^2\,J^{-1}})$	2.356 ± 0.003	[56]
$10^{40}\alpha_{11}(\mathrm{C^2\,m^2\,J^{-1}})$	2.1461 ± 0.0012	
$10^{40}\alpha_{22}(\mathrm{C^2\,m^2\,J^{-1}})$	2.1461 ± 0.0012	
$10^{40}\alpha_{33}(\mathrm{C^2\,m^2\,J^{-1}})$	4.5021 ± 0.0012	
$10^{40}\alpha^{(0)}(\mathrm{C^2\,m^2\,J^{-1}})$	3.2402 ± 0.0004	[60, 61]
$10^{40}\Delta\alpha^{(0)}(\mathrm{C^2\,m^2\,J^{-1}})$	2.530 ± 0.009	[56, 62]
$10^{40}\alpha_{11}^{(0)}(\mathrm{C^2\,m^2\,J^{-1}})$	2.3969 ± 0.0034	
$10^{40}\alpha_{22}^{(0)}(\mathrm{C^2\,m^2\,J^{-1}})$	2.3969 ± 0.0034	
$10^{40}\alpha_{33}^{(0)}(\mathrm{C^2\,m^2\,J^{-1}})$	4.9269 ± 0.0064	

[a]Obtained by fitting to pressure virial coefficients reported in Ref. 57

Table 3.2: The relative magnitudes of the contributions to B_Q for CO_2 at $T = 250K$

Contributing Term	$10^{30} \times$ value ($C\,m^8 J^{-1} mol^{-2}$)	% contribution to B_Q
$\Theta_1 \alpha_1$	-1.55008	3311.43
$\Theta_1 \alpha_2$	2.12903	-4548.23
$\Theta_1 \alpha_3$	-0.62074	1326.08
$\Theta_1 \alpha_4$	-0.00326	6.96
$\Theta_1 \alpha_5$	-0.00172	3.67
$\Theta_1 \alpha_6$	-0.00004	0.09
B_Q	-0.04681	

Table 3.3: The relative magnitudes of the contributions to B_Q for CO_2 at $T = 300K$

Contributing Term	$10^{30} \times$ value ($C\,m^8 J^{-1} mol^{-2}$)	% contribution to B_Q
$\Theta_1 \alpha_1$	-0.93291	-726.11
$\Theta_1 \alpha_2$	1.54221	1200.34
$\Theta_1 \alpha_3$	-0.47679	-371.10
$\Theta_1 \alpha_4$	-0.00265	-2.06
$\Theta_1 \alpha_5$	-0.00135	-1.05
$\Theta_1 \alpha_6$	-0.00003	-0.02
B_Q	0.12848	

Table 3.4: The relative magnitudes of the contributions to B_Q for CO_2 at $T = 400K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	-0.45183	-258.54
$\Theta_1\alpha_2$	0.95879	548.63
$\Theta_1\alpha_3$	-0.32911	-188.32
$\Theta_1\alpha_4$	-0.00209	-1.20
$\Theta_1\alpha_5$	-0.00098	-0.56
$\Theta_1\alpha_6$	-0.00002	-0.01
B_Q	0.17476	

Table 3.5: The relative magnitudes of the contributions to B_Q for CO_2 at $T = 500K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	-0.26916	-178.32
$\Theta_1\alpha_2$	0.67652	$448,20$
$\Theta_1\alpha_3$	-0.25379	-168.14
$\Theta_1\alpha_4$	-0.00182	-1.21
$\Theta_1\alpha_5$	-0.00079	-0.52
$\Theta_1\alpha_6$	-0.00002	-0.01
B_Q	0.15094	

Table 3.6: A summary of the calculated B_Q values for CO_2

T (K)	$10^{30} \times B_Q$ ($\mathrm{C\,m^8 J^{-1} mol^{-2}}$)
250	-0.04681
300	0.12848
400	0.17476
500	0.15094

Table 3.6 summarizes the calculated B_Q temperature dependence. The usual range of experimental temperature for EFGIB measurements in the literature is 300 K to 500 K. CO_2 displays an unusual trend in that B_Q reaches a maximum value around 400 K, and diminishes both for higher temperatures and lower temperatures. The reason for this unusual behaviour arises from the $\Theta_1 \alpha_1$ term, which makes a negative contribution to B_Q, and which rapidly becomes large in magnitude as the temperature diminishes. At 250 K, B_Q has become negative. Whether this behaviour accurately describes the dependence of B_Q on temperature, or whether it is an artifact of the limitations of the long-range model, particularly at lower temperatures, could be investigated by experimental measurement of B_Q over an appropriate range of temperature. Such experimental investigation would only be feasible provided B_Q is large enough to be discernible by an EFGIB apparatus, which would have its particular limiting resolution for the measured optical retardance δ in equation (2.42). While the $\Theta_1 \alpha_2$ term is large and positive, the combined contribution to B_Q arising from the negative $\Theta_1 \alpha_1$ and $\Theta_1 \alpha_3$ terms is comparatively nearly as large in magnitude (indeed, for 250 K it is a little larger), so that no contribution substantially dominates the overall B_Q, these large contributions of opposite sign tending to cancel, yielding a relatively small net B_Q. The $\Theta_1 \alpha_4$ and higher-order terms rapidly

diminish as the series converges, contributing around 3% or less to B_Q for CO_2.

At 300 K, CO_2 has a measured $_mQ = (-25.33 \pm 0.37) \times 10^{-26}\,\mathrm{C\,m^5 J^{-1} mol^{-1}}$ [27], which was obtained for an experimental pressure of $P = 2.635$ MPa at a temperature of $T = 299.4$ K. Recalling equation (2.54), namely

$$_mQ = A_Q + \frac{B_Q}{V_\mathrm{m}} + \frac{C_Q}{V_\mathrm{m}^2} + \cdots \ , \tag{3.2}$$

it is now possible to calculate the B_Q/V_m pair-interaction contribution to $_mQ$. The molar volume is obtained by solving the equation

$$V_\mathrm{m} = \frac{RT}{P} \left(1 + \frac{B(T)}{V_\mathrm{m}} + \frac{C(T)}{V_\mathrm{m}^2} \right) \ , \tag{3.3}$$

using the appropriate second and third pressure virial coefficients from the tabulations of Dymond *et al.* [57]. For the experimental $P = 2.635$ MPa and $T = 299.4$ K, this yields $V_\mathrm{m} = 8.087 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}}$, which coupled with the calculated $B_Q = 0.12848 \times 10^{-30}\,\mathrm{C\,m^8 J^{-1} mol^{-2}}$ yields $B_Q/V_\mathrm{m} = 0.016 \times 10^{-26}\,\mathrm{C\,m^5 J^{-1} mol^{-1}}$. This is a contribution of only 0.063% to $_mQ$, and since $_mQ$ has a reported experimental uncertainty of 1.5%, this B_Q/V_m value is around two orders of magnitude too small to be measurable. While it is possible to measure $_mQ$ with greater precision by averaging a large number of measurements, this route is somewhat impractical since each measurement takes several hours to perform.

CO_2 has a critical temperature and pressure of $T_\mathrm{c} = 304.1$ K and $P_\mathrm{c} = 7.4$ MPa, respectively. For temperatures and pressures exceeding T_c and P_c, the CO_2 becomes a supercritical fluid, the phase behaviour of which becomes ambiguous, being neither a well-defined gas nor liquid. Under these conditions, the virial equation of state can become unreliable in calculating the the molar volume, and experimentally measured isotherms of the compressibility factor $Z = PV_\mathrm{m}/RT$ are used to obtain

reliable values for V_m, such as the CO_2 data of Holste *et al.* [63], Duschek *et al.* [64], Mantilla *et al.* [65] and Gomez-Osorio *et al.* [66]. Depending on the temperature and pressure, the supercritical fluid can tend to behave more like a gas or more like a liquid.

The relative contribution made to $_\mathrm{m}Q$ by interacting pairs of molecules in CO_2 is now assessed over the temperature range 250 to 500 K and the pressure range 1.7 to 10 MPa. Typical EFGIB measurements in the literature have been performed for pressures up to 4 MPa in the temperature range 300 to 500 K, though pressures up to 10 MPa should be accessible to our existing EFGIB apparatus, while temperatures down to 250 K could be achieved with suitable experimental modifications. Table 3.7 contains the CO_2 inverse molar volumes (or densities) V_m^{-1} for the temperatures 250 K, 300 K, 400 K and 500 K at the pressures 1.7 MPa, 4 MPa and 10 MPa. These V_m^{-1} data, combined with the B_Q data in Table 3.6, yield the calculated B_Q/V_m estimates listed in Table 3.8. For comparative purposes, Table 3.8 also contains the $_\mathrm{m}Q$ values interpolated from the EFGIB measurements of Chetty and Couling [27], together with their expected uncertainties. The largest value for B_Q/V_m of $0.062 \times 10^{-26} \, \mathrm{C \, m^5 J^{-1} mol^{-1}}$ (obtained at $P = 10$ MPa and $T = 400$ K) is 0.32% of $_\mathrm{m}Q$, which is almost an order of magnitude smaller than the experimental uncertainty limits and so is well below the presently available experimental limits of detection. Accumulating a large number of $_\mathrm{m}Q$ measurements at this temperature and pressure could reduce the experimental uncertainty by up to an order of magnitude, bringing B_Q contributions to the threshold of detectability. Unfortunately, at this temperature and pressure the supercritical CO_2 is probably behaving more like a liquid than a gas, so that triplet and higher-order interactions are probably making considerable contributions to $_\mathrm{m}Q$, thereby severely complicating the picture.

At $T = 400$ K and $P = 100$ MPa, $V_\mathrm{m}^{-1} = 21\,196 \, \mathrm{mol \, m^{-3}}$, so that $B_Q/V_\mathrm{m} =$

Table 3.7: Densities (inverse molar volumes) for gaseous CO_2 at relevant temperatures and pressures

T (K)	at $P = 1.7$ MPa, V_{m}^{-1} (mol m^{-3})	at $P = 4$ MPa, V_{m}^{-1} (mol m^{-3})	at $P = 10$ MPa, V_{m}^{-1} (mol m^{-3})
250	995.6[a]	$-$[b]	$-$
300	747.6	2095.8	$-$
400	527.2	1293.2	3563.2
500	413.8	987.4	2526.2

[a]At $T = 250$ K, $P = 1.7$ MPa is just under the saturation vapour pressure of 1.784 MPa

[b]The dash $-$ indicates temperatures and pressures for which the CO_2 is in the liquid phase

Table 3.8: Calculated B_Q/V_{m} contributions to $_{\mathrm{m}}Q$ for CO_2 at the temperatures and pressures in Table 3.7

T (K)	$10^{26}\,_{\mathrm{m}}Q$[a] (C m^{5}J^{-1}mol^{-1})	at $P = 1.7$ MPa, $10^{26}B_Q/V_{\mathrm{m}}$ (C m^{5}J^{-1}mol^{-1})	at $P = 4$ MPa, $10^{26}B_Q/V_{\mathrm{m}}$ (C m^{5}J^{-1}mol^{-1})	at $P = 10$ MPa, $10^{26}B_Q/V_{\mathrm{m}}$ (C m^{5}J^{-1}mol^{-1})
250	-30.22 ± 0.40	-0.005	$-$	$-$
300	-25.31 ± 0.40	0.010	0.027	$-$
400	-19.18 ± 0.40	0.009	0.023	0.062
500	-15.50 ± 0.40	0.006	0.015	0.038

[a]These $_{\mathrm{m}}Q$ values have been interpolated from the measured data in Ref. 27. The uncertainties are indicative of the experimental uncertainties in Ref. 27.

0.37×10^{-26} C m^{5}J^{-1}mol^{-1}. While at first glance this indicates a B_Q which should in principle be measurable (provided a large number of measurements are averaged

so as to reduce the uncertainty), at such a high pressure the supercritical CO_2 is clearly behaving more like a liquid, which explains the relatively high fluid density, so that each CO_2 molecule will have several closely-neighbouring molecules.

Some general conclusions can be drawn from the foregoing analysis. Our molecular-tensor theory of B_Q indicates that the measured EFGIB data for CO_2 reported in the literature have been obtained at pressures and temperatures for which molecular pair-interaction contributions are negligible, being an order of magnitude or more below the present limits of detectability. This is reassuring, since experimentalists have up to now been uncertain as to whether their EFGIB measurements have been contaminated by B_Q contributions, especially for higher pressures. The theory of B_Q also suggests that it will be very difficult to achieve measurements of B_Q for CO_2 since the contribution to $_mQ$ is below the threshold of detectibility for the existing EFGIB apparatus for those temperatures and pressures where the CO_2 fluid behaves as a gas.

3.2 Ethene

The molecular data required in the calculations of B_Q for C_2H_4 are presented in Table 3.9. Ethene is of D_{2h} symmetry, and as has been previously demonstrated, approximating the molecule to be of axial symmetry has led to poor agreement of calculated and measured second light-scattering virial coefficients B_ρ [67, 68] and second Kerr-effect virial coefficients B_K [69] of up to 40%. Taking the full symmetry of the molecule into account in the description of the molecular properties, which required extensive development of the molecular-tensor theories, brought the calculated B_ρ to within 3% of the measured value [47], and yielded good agreement between the measured and calculated B_K values over the full experimental temperature range of 202.4 K to 363.7 K [55].

Tables 3.10 to 3.13 provide the relative magnitudes of the contributing terms to B_Q calculated at intervals of temperature spanning 250 to 500 K, while Table 3.14 summarizes the calculated B_Q temperature dependence. C_2H_4 has a critical temperature of $T_c = 282.4$ K and a critical pressure of $P_c = 5.06$ MPa. The molar volume of C_2H_4 has been accurately determined as a function of temperature and pressure through experimentally measured isotherms of the compressibility factor Z [70, 71]. Table 3.15 contains the C_2H_4 inverse molar volumes V_m^{-1} for the temperatures 250 K, 300 K, 400 K and 500 K at the pressures 2 MPa, 4 MPa and 10 MPa. These V_m^{-1} data, combined with the B_Q data in Table 3.14, yield the calculated B_Q/V_m estimates listed in Table 3.16. For comparative purposes, Table 3.16 also contains the $_mQ$ values calculated via equation (2.46) using the measured room-temperature datum of $\alpha_{ij}\Theta_{ij}^{(0)} = (15.59 \pm 0.08) \times 10^{-80}\,\mathrm{C^3m^4J^{-1}}$ obtained by Imrie [5], the electronic distortion term b in equation (2.46) having been assumed to be zero.

Table 3.9: The molecular properties of C_2H_4 used in the calculation of B_Q.

Property	Value	Reference
R_0(nm)	0.4232	[47, 72]
ε/k(K)	190.0	[47, 72]
D_1	0.229650^a	[47]
D_2	0.213830^a	
$10^{40}\Theta_{11}$($C\,m^2$)	5.57 ± 0.63	[73]
$10^{40}\Theta_{22}$($C\,m^2$)	-10.54 ± 0.63	
$10^{40}\Theta_{33}$($C\,m^2$)	4.94 ± 0.33	
$10^{40}\alpha$($C^2\,m^2\,J^{-1}$)	4.71 ± 0.03	[69]
$10^{40}\Delta\alpha$($C^2\,m^2\,J^{-1}$)	1.92 ± 0.04	[69]
$10^{40}\alpha_{11}$($C^2\,m^2\,J^{-1}$)	4.41 ± 0.04	[69]
$10^{40}\alpha_{22}$($C^2\,m^2\,J^{-1}$)	3.79 ± 0.03	
$10^{40}\alpha_{33}$($C^2\,m^2\,J^{-1}$)	5.94 ± 0.02	
$10^{40}\alpha^{(0)}$($C^2\,m^2\,J^{-1}$)	4.73 ± 0.03	[69]
$10^{40}\Delta\alpha^{(0)}$($C^2\,m^2\,J^{-1}$)	1.63 ± 0.05	[69]
$10^{40}\alpha_{11}^{(0)}$($C^2\,m^2\,J^{-1}$)	4.30 ± 0.04	[69]
$10^{40}\alpha_{11}^{(0)}$($C^2\,m^2\,J^{-1}$)	4.09 ± 0.03	
$10^{40}\alpha_{11}^{(0)}$($C^2\,m^2\,J^{-1}$)	5.81 ± 0.02	

^{a}Obtained by fitting to pressure virial coefficients reported in Ref. 57

Table 3.10: The relative magnitudes of the contributions to B_Q for C_2H_4 at $T = 250K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	3.55966	-1381.16
$\Theta_1\alpha_2$	-4.38384	1700.94
$\Theta_1\alpha_3$	0.60739	-235.67
$\Theta_1\alpha_4$	-0.04288	16.64
$\Theta_1\alpha_5$	0.00289	-1.12
$\Theta_1\alpha_6$	-0.00095	0.37
B_Q	-0.25773	

Table 3.11: The relative magnitudes of the contributions to B_Q for C_2H_4 at $T = 300K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	1.56875	-674.24
$\Theta_1\alpha_2$	-2.22151	954.79
$\Theta_1\alpha_3$	0.43171	-185.54
$\Theta_1\alpha_4$	-0.01347	5.79
$\Theta_1\alpha_5$	0.00214	-0.92
$\Theta_1\alpha_6$	-0.00029	0.12
B_Q	-0.23267	

Table 3.12: The relative magnitudes of the contributions to B_Q for C_2H_4 at $T = 400K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	0.54615	-404.50
$\Theta_1\alpha_2$	-0.96629	715.66
$\Theta_1\alpha_3$	0.28485	-210.96
$\Theta_1\alpha_4$	-0.00119	0.88
$\Theta_1\alpha_5$	0.00149	-1.10
$\Theta_1\alpha_6$	-0.00003	0.02
B_Q	-0.13502	

Table 3.13: The relative magnitudes of the contributions to B_Q for C_2H_4 at $T = 500K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	0.27513	-361.44
$\Theta_1\alpha_2$	-0.57028	749.19
$\Theta_1\alpha_3$	0.21662	-284.58
$\Theta_1\alpha_4$	0.00120	-1.58
$\Theta_1\alpha_5$	0.00119	-1.56
$\Theta_1\alpha_6$	0.00002	-0.03
B_Q	-0.07612	

Table 3.14: A summary of the calculated B_Q values for C_2H_4

T (K)	$10^{30} \times B_Q$ ($C\,m^8\,J^{-1}mol^{-2}$)
200	-0.25773
300	-0.23267
400	-0.13502
500	-0.07612

Table 3.15: Densities (inverse molar volumes) for gaseous C_2H_4 at relevant temperatures and pressures

T (K)	at $P = 2$ MPa, V_m^{-1} (mol m^{-3})	at $P = 4$ MPa, V_m^{-1} (mol m^{-3})	at $P = 10$ MPa, V_m^{-1} (mol m^{-3})
250	1268.8	$-^a$	$-$
300	911.1	2187.2	11511.2^b
400	628.4	1315.3	3755.1
500	489.2	993.2	2565.7

^{a}The dash $-$ indicates temperatures and pressures for which the C_2H_4 is in the liquid phase
^{b}For this temperature and pressure, the supercritical phase closely resembles the liquid phase, having a high density

In Table 3.16, the second-largest value for B_Q/V_m of $-0.051 \times 10^{-26}\,C\,m^5\,J^{-1}mol^{-1}$ (obtained at $P = 10$ MPa and $T = 400$ K, as well as at $P = 4$ MPa and $T = 300$ K) is of the same order as the experimental uncertainty limits, and if a large number of $_mQ$ measurements were accumulated and averaged so as to reduce the statisti-

Table 3.16: Calculated B_Q/V_m contributions to $_mQ$ for C_2H_4 at the temperatures and pressures in Table 3.15

T (K)	$10^{26}\,{}_mQ^a$ ($C\,m^5J^{-1}mol^{-1}$)	at $P = 2$ MPa, $10^{26}B_Q/V_m$ ($C\,m^5J^{-1}mol^{-1}$)	at $P = 4$ MPa, $10^{26}B_Q/V_m$ ($C\,m^5J^{-1}mol^{-1}$)	at $P = 10$ MPa, $10^{26}B_Q/V_m$ ($C\,m^5J^{-1}mol^{-1}$)
250	13.65 ± 0.07	-0.032	$-$	$-$
300	11.38 ± 0.06	-0.021	-0.051	-0.27
400	8.53 ± 0.05	-0.009	-0.018	-0.051
500	6.83 ± 0.04	-0.007	-0.013	-0.035

^{a}These $_mQ$ values have been calculated from equation (2.46) using the measured room-temperature datum of $\alpha_{ij}\Theta_{ij}^{(0)} = (15.59 \pm 0.08) \times 10^{-80}\,C^3m^4J^{-1}$ in Ref. 5, and assuming $b = 0$

cal uncertainty, it would become possible in principle to resolve a measured value for B_Q. The largest value of $B_Q/V_m = -0.27 \times 10^{-26}\,C\,m^5J^{-1}mol^{-1}$ is obtained at $P = 10$ MPa and $T = 300$ K, where the supercritical phase is behaving much more like a liquid, higher-order molecular interactions having become significant, explaining the relatively high fluid density.

As was found in the case of the CO_2 molecule, our molecular-tensor theory of B_Q indicates that the EFGIB data for C_2H_4 measured by Imrie [5] at ambient temperature in the range $T = 294.8$ to 298.4 K, and for pressures in the range $P = 2.284$ MPa to 4.095 MPa, have been obtained at a temperature and pressures for which molecular pair-interaction contributions are negligible, being at or below the threshold of the present limits of detectability. This result clarifies that Imrie's EFGIB measurements have not been contaminated by B_Q contributions, especially for the higher experimental pressures around 4 MPa. The theory of B_Q also suggests that it will in

principle be possible to measure B_Q for C_2H_4 provided a large number of measurements are accumulated and averaged to reduce the statistical uncertainty in $_mQ$.

3.3 Ethane

Table 3.17 contains the molecular data required in the calculation of B_Q for the axially-symmetric C_2H_6 molecule. Both the quadrupole moment and the polarizability anisotropy of C_2H_6 are several times smaller than those of either CO_2 or C_2H_4, which might intuitively suggest that B_Q for C_2H_6 should be relatively small. Tables 3.18 to 3.21 provide the relative magnitudes of the contributing terms to B_Q calculated at intervals of temperature spanning 250 to 500 K, while Table 3.22 summarizes the calculated B_Q temperature dependence. What emerges is a B_Q that is in fact *larger* in magnitude than those for CO_2 and C_2H_4. The reason for this is the small and negative $\Theta_1\alpha_1$ and $\Theta_1\alpha_3$ term contributions, which do little to attenuate the relatively large and positive $\Theta_1\alpha_2$ term, this collision-induced contribution making by far the dominant contribution to B_Q.

The C_2H_6 fluid has a critical temperature of $T_c = 305.3$ K, and a critical pressure of $P_c = 4.87$ MPa. The molar volume of C_2H_6 has been accurately determined as a function of temperature and pressure through experimentally measured isotherms of the compressibility factor Z [70, 74]. Table 3.23 contains the C_2H_6 inverse molar volumes V_m^{-1} for the temperatures 250 K, 300 K, 400 K and 500 K at the pressures 1 MPa, 4 MPa and 10 MPa. These V_m^{-1} data, combined with the B_Q data in Table 3.22, yield the calculated B_Q/V_m estimates listed in Table 3.24. For comparative purposes, Table 3.24 also contains the $_mQ$ values interpolated from the measured data of Watson [45].

Table 3.17: The molecular properties of C_2H_6 used in the calculation of B_Q.

Property	Value	Reference
$R_0(\text{nm})$	0.4418	[58]
$\varepsilon/k(\text{K})$	230.0	[58]
D_1	0.200^a	
D_2	0.000	
$10^{40}\Theta_{11}(\text{C m}^2)$	1.25 ± 0.13	[45, 75]
$10^{40}\Theta_{22}(\text{C m}^2)$	1.25 ± 0.13	
$10^{40}\Theta_{33}(\text{C m}^2)$	-2.50 ± 0.26	
$10^{40}\alpha(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	4.96798 ± 0.00035	[59, 76]
$10^{40}\Delta\alpha(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	0.698 ± 0.056	[75]
$10^{40}\alpha_{11}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	4.735 ± 0.019	
$10^{40}\alpha_{22}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	4.735 ± 0.019	
$10^{40}\alpha_{33}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	5.433 ± 0.038	
$10^{40}\alpha^{(0)}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	4.9216 ± 0.0033	[60, 61]
$10^{40}\Delta\alpha^{(0)}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	$0.60_5 \pm 0.10$	[75]
$10^{40}\alpha_{11}^{(0)}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	4.72 ± 0.04	
$10^{40}\alpha_{11}^{(0)}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	4.72 ± 0.04	
$10^{40}\alpha_{11}^{(0)}(\text{C}^2\,\text{m}^2\,\text{J}^{-1})$	5.32 ± 0.07	

^{a}Obtained by fitting to pressure virial coefficients reported in Ref. 57

Table 3.18: The relative magnitudes of the contributions to B_Q for C_2H_6 at $T = 250K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	-0.10203	-7.68
$\Theta_1\alpha_2$	1.43597	108.22
$\Theta_1\alpha_3$	-0.01421	-1.07
$\Theta_1\alpha_4$	0.00674	0.51
$\Theta_1\alpha_5$	0.00033	0.02
$\Theta_1\alpha_6$	0.00006	0.00
B_Q	1.32686	

Table 3.19: The relative magnitudes of the contributions to B_Q for C_2H_6 at $T = 300K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	-0.06119	-7.07
$\Theta_1\alpha_2$	0.93717	108.36
$\Theta_1\alpha_3$	-0.01595	-1.84
$\Theta_1\alpha_4$	0.00448	0.52
$\Theta_1\alpha_5$	0.00022	0.03
$\Theta_1\alpha_6$	0.00004	0.00
B_Q	0.86477	

Table 3.20: The relative magnitudes of the contributions to B_Q for C_2H_6 at $T = 400K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	-0.02936	-6.27
$\Theta_1\alpha_2$	0.50984	108.92
$\Theta_1\alpha_3$	-0.01499	-3.20
$\Theta_1\alpha_4$	0.00250	0.53
$\Theta_1\alpha_5$	0.00011	0.02
$\Theta_1\alpha_6$	0.00002	0.00
B_Q	0.46812	

Table 3.21: The relative magnitudes of the contributions to B_Q for C_2H_6 at $T = 500K$

Contibuting Term	$10^{30} \times$ value $(C\,m^8J^{-1}mol^{-2})$	% contribution to B_Q
$\Theta_1\alpha_1$	-0.01727	-5.71
$\Theta_1\alpha_2$	0.3314	109.53
$\Theta_1\alpha_3$	-0.01330	-4.40
$\Theta_1\alpha_4$	0.00165	0.55
$\Theta_1\alpha_5$	0.00007	0.02
$\Theta_1\alpha_6$	0.00002	0.01
B_Q	0.30257	

Table 3.22: A summary of the calculated B_Q values for C_2H_6

T (K)	$10^{30} \times B_Q$ $(C\,m^8J^{-1}mol^{-2})$
250	1.32686
300	0.86477
400	0.46812
500	0.30257

Table 3.23: Densities (inverse molar volumes) for gaseous C_2H_6 at relevant temperatures and pressures

T (K)	at $P = 1$ MPa, V_m^{-1} (mol m^{-3})	at $P = 4$ MPa, V_m^{-1} (mol m^{-3})	at $P = 10$ MPa, V_m^{-1} (mol m^{-3})
250	563.6	$-^a$	$-$
300	434.6	2819.2[b]	$-$
400	309.7	1364.2	4197.5[b]
500	243.5	1009.9	2679.3

[a]The dash $-$ indicates temperatures and pressures for which the C_2H_6 is in the liquid phase
[b]For these temperatures and pressures, the supercritical phase closely resembles the liquid phase, having a high density

As seen in Table 3.24, the largest and second-largest values for B_Q/V_m of 0.24×10^{-26} $C\,m^5J^{-1}mol^{-1}$ (obtained at $P = 4$ MPa and $T = 300$ K) and of 0.20×10^{-26} $C\,m^5J^{-1}mol^{-1}$ (obtained at $P = 10$ MPa and $T = 400$ K), are under conditions of pressure and temperature where the supercritical phase is behaving much

Table 3.24: Calculated B_Q/V_{m} contributions to $_{\mathrm{m}}Q$ for C_2H_6 at the temperatures and pressures in Table 3.23

T (K)	$10^{26}\,_{\mathrm{m}}Q^a$ ($\mathrm{C\,m^5J^{-1}mol^{-1}}$)	at $P = 1$ MPa, $10^{26}B_Q/V_{\mathrm{m}}$ ($\mathrm{C\,m^5J^{-1}mol^{-1}}$)	at $P = 4$ MPa, $10^{26}B_Q/V_{\mathrm{m}}$ ($\mathrm{C\,m^5J^{-1}mol^{-1}}$)	at $P = 10$ MPa, $10^{26}B_Q/V_{\mathrm{m}}$ ($\mathrm{C\,m^5J^{-1}mol^{-1}}$)
250	-2.26 ± 0.09	0.075	–	–
300	-2.01 ± 0.09	0.038	0.24	–
400	-1.69 ± 0.08	0.015	0.064	0.20
500	-1.50 ± 0.08	0.007	0.031	0.081

^{a}These $_{\mathrm{m}}Q$ values have been interpolated from the measured data in Ref. 45. The uncertainties are indicative of the experimental uncertainties in Ref. 45.

more like a liquid, with higher-order molecular interactions having become significant, hence accounting for the relatively high fluid densities.

The next largest values are $B_Q/V_{\mathrm{m}} = 0.081 \times 10^{-26}\,\mathrm{C\,m^5J^{-1}mol^{-1}}$ (obtained at $P = 10$ MPa and $T = 500$ K) and $B_Q/V_{\mathrm{m}} = 0.075 \times 10^{-26}\,\mathrm{C\,m^5J^{-1}mol^{-1}}$ (obtained at $P = 1$ MPa and $T = 250$ K), and are at pressures and temperatures where the supercritical phase is behaving much more like a gas. Here, the B_Q contributions are, respectively, the same as and just smaller than the experimental uncertainties, suggesting that if a large number of $_{\mathrm{m}}Q$ measurements were to be undertaken, it would be possible to resolve measured values for B_Q.

What emerges from the analysis is that, as found for both CO_2 and C_2H_4, the molecular-tensor theory of B_Q indicates that the measured EFGIB data for C_2H_6 have been obtained at temperatures and pressures for which molecular pair interaction contributions are negligible, being at or below the threshold of the present limits of detectability. The theory of B_Q also suggests that it will in principle be

possible to measure B_Q for C_2H_6 provided a large-enough number of measurements are accumulated.

3.4 Concluding Remarks

A molecular-tensor theory has been developed to account for collision-induced contributions to EFGIB arising from molecular pair-interactions in the gas phase. The second EFGIB virial coefficient B_Q has been calculated for a range of temperature and pressure for the molecules CO_2, C_2H_4 and C_2H_6. These molecules have been chosen since there exist precise experimental measurements of $_mQ$, and the molecular properties required in the computation of B_Q are precisely known. In addition, previously developed molecular-tensor theories of the second light-scattering virial coefficient B_ρ and the second Kerr-effect virial coefficient B_K have yielded calculated values for CO_2, C_2H_4 and C_2H_6 which are in close agreement with the measured data.

The main conclusions to emerge from this project are firstly that the calculated B_Q values for CO_2, C_2H_4 and C_2H_6 indicate that collision-induced contributions to $_mQ$ are at or below the level of the experimental uncertainties, so that the measured $_mQ$ values reported in the literature have not been compromised by the presence of pair-interaction effects. Hence, the extracted molecular quadrupole moments are sound. Secondly, if the precision of measured $_mQ$ data can be increased by around an order of magnitude, it should begin to become possible to resolve B_Q contributions, particularly for higher gas densities, especially for C_2H_4 and C_2H_6. The calculated B_Q data can serve to guide experimentalists in their quest to measure B_Q, since the necessary experimental conditions and required limits of resolution are now made clear.

A future refinement to the theory will be the inclusion of the interaction-induced contributions to B_Q arising from the electronic distortion tensors B_{ijkl}, $\mathscr{B}_{ijkl}$ and J'_{ijk}. While we have assumed that these contributions will be of the order of 10% or smaller, this needs to be definitively established. Mr Ntombela, in his PhD project, is presently investigating these contributions in the BLH formalism of the EFGIB theory.

Appendix A

A.1 Fortran Program to calculate the $\Theta_1 \alpha_3$ contribution to B_Q.

```
        PROGRAM EFGIB_Q1A3

C PROGRAM TO CALCULATE TERM Q1A3 FOR CO2 USING GAUSSIAN INTEGRATION WITH
C 64 INTERVALS FOR THE RANGE, AND 10 INTERVALS FOR ALL ANGULAR VARIABLES
C (I.E. ALPHA1, BETA1, GAMMA1, ALPHA2, BETA2 AND GAMMA2).
C DOUBLE PRECISION IS USED THROUGHOUT.
C


C ----------------------
C SYSTEM INITIALIZATION:
C ----------------------

        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        COMMON COEF1,DCTC
        DIMENSION COEF2(64,2),COEF1(16,2),SEP(64),AL1(16),BE1(16),GA1(16)
     +  ,AL2(16),BE2(16),GA2(16),DCTC(9,16,16,16),FI(16,16,16,16,16),D1(6
     +  4),E1(16,16,16,16,16),F1(16,16,16,16,16),SE3(64),SE4(64),SE5(64),
     +  SE6(64),SE8(64),SE12(64),G1(16,16,16),DDP(16,16,16,16,16),DQP(16,
     +  16,16,16,16),DIDP(16,16,16,16,16)
        INTEGER X1,X2,X3,X4,X5,X6,X7


C
C MOLECULAR DATA FOR CO2 (632.8 nm):
C

        SS1=0.000000
        SS2=0.000000
        SS3=0.000000
        SS4=0.000000
        SS5=0.000000
        SS6=0.000000
        SS7=0.000000
```

```
        DIP=0.000
        A11=2.1461
        A22=2.1461
        A33=4.5021
        ALDYN=(A11+A22+A33)/3
        V11=2.3969
        V22=2.3969
        V33=4.9269
        ALSTAT=(V11+V22+V33)/3
        Q1=7.135
        Q2=7.135
        AMIN1=0.1000
        AMAX1=3.0000


C
C READ THE GAUSSIAN COEFFICIENTS FROM THE DATAFILE GAUSS64.DAT:
C
        OPEN(UNIT=10,FILE='GAUSS64.DAT')
          DO 10 ICTR1=1,64
            DO 20 ICTR2=1,2
              READ(10,1010,END=11)COEF2(ICTR1,ICTR2)
1010          FORMAT(F18.15)
20          CONTINUE
10        CONTINUE
11      CLOSE(UNIT=10)


C
C CALCULATE THE INTEGRATION POINTS FOR THE RANGE:
C
        SEP1=(AMAX1-AMIN1)/2
        SEP2=(AMAX1+AMIN1)/2
        DO 30 INDX=1,64
        SEP(INDX)=SEP1*COEF2(INDX,1)+SEP2
30      CONTINUE


C
C READ THE GAUSSIAN COEFFICIENTS FROM THE DATAFILE GAUSS16.DAT:
C
        OPEN(UNIT=11,FILE='GAUSS16.DAT')
          DO 100 ICTR1=1,16
            DO 110 ICTR2=1,2
              READ(11,6000,END=12)COEF1(ICTR1,ICTR2)
6000          FORMAT(F18.15)
110       CONTINUE
100     CONTINUE
12      CLOSE(UNIT=11)


C
```

```
C CALCULATE THE INTEGRATION POINTS FOR ALPHA1:
C
      AMIN=0.0
      AMAX=2.*3.14159265358979323846

      AL11=(AMAX-AMIN)/2.
      AL12=(AMAX+AMIN)/2.
      DO 120 INDX=1,16
        AL1(INDX)=AL11*COEF1(INDX,1)+AL12
120   CONTINUE


C
C CALCULATE THE INTEGRATION POINTS FOR BETA1:
C
      AMIN=0.0
      AMAX=3.14159265358979323846

      BE11=(AMAX-AMIN)/2.
      BE12=(AMAX+AMIN)/2.
      DO 121 INDX=1,16
        BE1(INDX)=BE11*COEF1(INDX,1)+BE12
121   CONTINUE


C
C CALCULATE THE INTEGRATION POINTS FOR GAMMA1:
C
      AMIN=0.0
      AMAX=2.*3.14159265358979323846

      GA11=(AMAX-AMIN)/2.
      GA12=(AMAX+AMIN)/2.
      DO 122 INDX=1,16
        GA1(INDX)=GA11*COEF1(INDX,1)+GA12
122   CONTINUE


C
C CALCULATE THE INTEGRATION POINTS FOR ALPHA2:
C
      AMIN=0.0
      AMAX=2.*3.14159265358979323846

      AL21=(AMAX-AMIN)/2.
      AL22=(AMAX+AMIN)/2.
      DO 123 INDX=1,16
        AL2(INDX)=AL21*COEF1(INDX,1)+AL22
123   CONTINUE


C
C CALCULATE THE INTEGRATION POINTS FOR BETA2:
```

```
C
      AMIN=0.0
      AMAX=3.14159265358979323846

      BE21=(AMAX-AMIN)/2.
      BE22=(AMAX+AMIN)/2.
      DO 124 INDX=1,16
        BE2(INDX)=BE21*COEF1(INDX,1)+BE22
124   CONTINUE

C
C CALCULATE THE INTEGRATION POINTS FOR GAMMA2:
C
      AMIN=0.0
      AMAX=2.*3.14159265358979323846

      GA21=(AMAX-AMIN)/2.
      GA22=(AMAX+AMIN)/2.
      DO 125 INDX=1,16
        GA2(INDX)=GA21*COEF1(INDX,1)+GA22
125   CONTINUE

C -------------
C MAIN PROGRAM:
C -------------

      OPEN(UNIT=4,FILE='BQ_q1a3_250K')

C
C INPUT MOLECULAR PARAMETERS FROM THE KEYBOARD:
C

C      WRITE(6,470)
C470   FORMAT(1X,'INPUT THE TEMPERATURE (IN KELVIN)')
C      READ(5,471)TEMP
C471   FORMAT(F10.5)
      TEMP=250.0
      TEMPK=TEMP*1.380622E-23

C      WRITE(6,472)
C472   FORMAT(1X,'INPUT R(0) (IN nm)')
C      READ(5,473)R
C473   FORMAT(F10.5)
      R=0.40

C      WRITE(6,474)
C474   FORMAT(1X,'E/K (IN K)')
C      READ(5,475)PARAM2
C475   FORMAT(F10.5)
```

```
      PARAM2=190.0

C       WRITE(6,476)
C476    FORMAT(1X,'SHAPE1 ')
C       READ(5,477)SHAPE1
C477    FORMAT(F10.5)
      SHAPE1=0.250

C       WRITE(6,478)
C478    FORMAT(1X,'SHAPE2 ')
C       READ(5,479)SHAPE2
C479    FORMAT(F10.5)
      SHAPE2=0.0




C
C CALCULATION OF THE LENNARD-JONES 6:12 POTENTIAL & STORAGE OF THE
C VALUES IN AN ARRAY:
C

      DO 61 X1=1,64

      D1(X1)=4.*PARAM2*1.380622E-23*((R/SEP(X1))**12-(R/SEP(X1))**6)
      SE12(X1)=SEP(X1)**12
      SE5(X1)=SEP(X1)**5
      SE8(X1)=SEP(X1)**8
      SE3(X1)=SEP(X1)**3
      SE4(X1)=SEP(X1)**4
      SE6(X1)=SEP(X1)**6

61    CONTINUE



C
C THE DIRECTION COSINE TENSOR COMPONENTS ARE STORED IN AN ARRAY:
C

      DO 66 X4=1,16
        DO 77 X3=1,16
          DO 88 X2=1,16

C
C DIRECTION COSINE TENSOR COMPONENTS:
C

      A1=COS(AL1(X2))*COS(BE1(X3))*COS(GA1(X4))-1.*SIN(AL1(X2))*SIN(GA1
    + (X4))
      A2=SIN(AL1(X2))*COS(BE1(X3))*COS(GA1(X4))+COS(AL1(X2))*SIN(GA1(X4
```

```
    + ))
      A3=-1.*SIN(BE1(X3))*COS(GA1(X4))
      A4=-1.*COS(AL1(X2))*COS(BE1(X3))*SIN(GA1(X4))-1.*SIN(AL1(X2))*COS
    + (GA1(X4))
      A5=-1.*SIN(AL1(X2))*COS(BE1(X3))*SIN(GA1(X4))+COS(AL1(X2))*COS(GA
    + 1(X4))
      A6=SIN(BE1(X3))*SIN(GA1(X4))
      A7=COS(AL1(X2))*SIN(BE1(X3))
      A8=SIN(AL1(X2))*SIN(BE1(X3))
      A9=COS(BE1(X3))

      DCTC(1,X2,X3,X4)=A1
      DCTC(2,X2,X3,X4)=A2
      DCTC(3,X2,X3,X4)=A3
      DCTC(4,X2,X3,X4)=A4
      DCTC(5,X2,X3,X4)=A5
      DCTC(6,X2,X3,X4)=A6
      DCTC(7,X2,X3,X4)=A7
      DCTC(8,X2,X3,X4)=A8
      DCTC(9,X2,X3,X4)=A9

88        CONTINUE
77       CONTINUE
66     CONTINUE


C
C THE MULTIPOLE INTERACTION ENERGIES ARE CALCULATED AND STORED
C IN ARRAYS:
C

      DO 939 X7=1,16
      WRITE(4,1000)X7
1000  FORMAT (1X, 'INDEX (IN RANGE 1 TO 16) IS CURRENTLY ',I2 )
      WRITE(6,1111)X7
1111  FORMAT (1X, 'Index (in range 1 to 16) is currently ',I2 )
        DO 40 X6=1,16

          DO 50 X5=1,16


C
C MOLECULE 2'S DIRECTION COSINE TENSOR COMPONENTS:
C

      B1=DCTC(1,X5,X6,X7)
      B2=DCTC(2,X5,X6,X7)
      B3=DCTC(3,X5,X6,X7)
      B4=DCTC(4,X5,X6,X7)
      B5=DCTC(5,X5,X6,X7)
```

```
      B6=DCTC(6,X5,X6,X7)
      B7=DCTC(7,X5,X6,X7)
      B8=DCTC(8,X5,X6,X7)
      B9=DCTC(9,X5,X6,X7)


          DO 60 X4=1,16
            DO 70 X3=1,16
              DO 80 X2=1,16

C
C MOLECULE 1'S DIRECTION COSINE TENSOR COMPONENTS:
C

      A1=DCTC(1,X2,X3,X4)
      A2=DCTC(2,X2,X3,X4)
      A3=DCTC(3,X2,X3,X4)
      A4=DCTC(4,X2,X3,X4)
      A5=DCTC(5,X2,X3,X4)
      A6=DCTC(6,X2,X3,X4)
      A7=DCTC(7,X2,X3,X4)
      A8=DCTC(8,X2,X3,X4)
      A9=DCTC(9,X2,X3,X4)


C
C CALCULATION OF THE DIPOLE-DIPOLE POTENTIAL:
C
      DDP(X2,X3,X4,X5,X6)=8.98758E-24*DIP**2*(-2*A9*B9+A6*B6+A3*B3)


C
C CALCULATION OF THE DIPOLE-QUADRUPOLE POTENTIAL:
C
      DQP(X2,X3,X4,X5,X6)=8.98758E-25*DIP*(Q2*(-2*A9*B9**2+(2*A6*B6+2*A
     + 3*B3+2*A9**2-2*A8**2-A6**2+A5**2-A3**2+A2**2)*B9+2*A9*B8**2+(-2*A
     + 6*B5-2*A3*B2)*B8+A9*B6**2+(2*A5*A8-2*A6*A9)*B6-A9*B5**2+A9*B3**2+
     + (2*A2*A8-2*A3*A9)*B3-A9*B2**2)+Q1*(-2*A9*B9**2+(2*A6*B6+2*A3*B3+2
     + *A9**2-2*A7**2-A6**2+A4**2-A3**2+A1**2)*B9+2*A9*B7**2+(-2*A6*B4-2
     + *A3*B1)*B7+A9*B6**2+(2*A4*A7-2*A6*A9)*B6-A9*B4**2+A9*B3**2+(2*A1*
     + A7-2*A3*A9)*B3-A9*B1**2))


C
C CALCULATION OF THE DIPOLE-INDUCED DIPOLE POTENTIAL:
C
      DIDP(X2,X3,X4,X5,X6)=-0.50*ALSTAT*8.07765E-27*DIP**2*(3*B9**2
     + +3*A9**2-2)



C
C CALCULATION OF THE QUADRUPOLE-QUADRUPOLE POTENTIAL:
```

```
C
      quad1=-16.*(a6*a9-a5*a8)*(b6*b9-b5*b8)-16.*(a3*a9-a2*a8)*(b3*b9-b
     + 2*b8)+4.*(2.*a9**2-2.*a8**2-a6**2+a5**2-a3**2+a2**2)*(b9-b8)*(b9+
     + b8)+(-4.*a9**2+4.*a8**2+3.*a6**2-3.*a5**2+a3**2-a2**2)*(b6**2-b5
     + **2)+4.*(a3*a6-a2*a5)*(b3*b6-b2*b5)+(-4.*a9**2+4.*a8**2+a6**2-a5**
     + 2+3.*a3**2-3.*a2**2)*(b3**2-b2**2)

      quad2=-16.*(a6*a9-a4*a7)*(b6*b9-b4*b7)-16.*(a3*a9-a1*a7)*(b3*b9-b
     + 1*b7)+4.*(2.*a9**2-2.*a7**2-a6**2+a4**2-a3**2+a1**2)*(b9-b7)*(b9+
     + b7)+(-4.*a9**2+4.*a7**2+3.*a6**2-3.*a4**2+a3**2-a1**2)*(b6**2-b4*
     + *2)+4.*(a3*a6-a1*a4)*(b3*b6-b1*b4)+(-4.*a9**2+4.*a7**2+a6**2-a4**
     + 2+3.*a3**2-3.*a1**2)*(b3**2-b1**2)

      quad3=4.*(4.*A9**2-2.*(A8**2+A7**2+A6**2+A3**2)+A5**2+A4**2+A2**2
     + +A1**2)*B9**2-16.*(2.*A6*A9-A5*A8-A4*A7)*B6*B9-16*(2.*A3*A9-A2*A8
     + -A1*A7)*B3*B9-4.*(2.*A9**2-2.*A7**2-A6**2+A4**2-A3**2+A1**2)*B8**
     + 2+16.*(A6*A9-A4*A7)*B5*B8+16.*(A3*A9-A1*A7)*B2*B8-4.*(2.*A9**2-2.
     + *A8**2-A6**2+A5**2-A3**2+A2**2)*B7**2+16.*(A6*A9-A5*A8)*B4*B7+16.
     + *(A3*A9-A2*A8)*B1*B7+(-8.*A9**2+4.*(A8**2+A7**2)+6.*A6**2-3.*(A5*
     + *2+A4**2)+2*A3**2-A2**2-A1**2)*B6**2+4.*(2.*A3*A6-A2*A5-A1*A4)*B3
     + *B6+(4.*A9**2-4.*A7**2-3.*A6**2+3.*A4**2-A3**2+A1**2)*B5**2-4.*(A
     + 3*A6-A1*A4)*B2*B5+(4.*A9**2-4.*A8**2-3.*A6**2+3.*A5**2-A3**2+A2**
     + 2)*B4**2-4.*(A3*A6-A2*A5)*B1*B4+(-8.*A9**2+4.*(A8**2+A7**2)+2.*A6
     + **2-A5**2-A4**2+6.*A3**2-3.*(A2**2+A1**2))*B3**2+(4.*A9**2-4.*A7*
     + *2-A6**2+A4**2-3.*A3**2+3.*A1**2)*B2**2+(4.*A9**2-4.*A8**2-A6**2+
     + A5**2-3.*A3**2+3.*A2**2)*B1**2

      E1(X2,X3,X4,X5,X6)=8.98758E-26*(1./3.)*(Q2**2*QUAD1+Q1**2*QUAD
     + 2+Q1*Q2*QUAD3)



C
C CALCULATION OF THE QUADRUPOLE-INDUCED DIPOLE POTENTIAL:
C

      QID1=Q2**2*(4.*A9**4+(-8.*A8**2+4.*A5**2+4.*A2**2)*A9**2+(-8.*A5*
     + A6-8.*A2*A3)*A8*A9+4.*A8**4+(4.*A6**2+4.*A3**2)*A8**2+A6**4+(-2.*
     + A5**2+2.*A3**2-2.*A2**2)*A6**2+A5**4+(2.*A2**2-2.*A3**2)*A5**2+A3
     + **4-2.*A2**2*A3**2+A2**4)+Q1**2*(4.*A9**4+(-8.*A7**2+4.*A4**2+4.*
     + A1**2)*A9**2+(-8.*A4*A6-8.*A1*A3)*A7*A9+4.*A7**4+(4.*A6**2+4.*A3*
     + *2)*A7**2+A6**4+(-2.*A4**2+2.*A3**2-2.*A1**2)*A6**2+A4**4+(2.*A1*
     + *2-2.*A3**2)*A4**2+A3**4-2.*A1**2*A3**2+A1**4)+Q1*Q2*(8.*A9**4+(-
     + 8.*A8**2-8.*A7**2+4.*A5**2+4.*A4**2+4.*A2**2+4.*A1**2)*A9**2+((-8
     + .*A5*A6-8.*A2*A3)*A8+(-8.*A4*A6-8.*A1*A3)*A7)*A9+(8.*A7**2+4.*A6*
     + *2-4.*A4**2+4.*A3**2-4.*A1**2)*A8**2+(8.*A4*A5+8.*A1*A2)*A7*A8+(4
     + .*A6**2-4.*A5**2+4.*A3**2-4.*A2**2)*A7**2+2.*A6**4+(-2.*A5**2-2.*
     + A4**2+4.*A3**2-2.*A2**2-2.*A1**2)*A6**2+(2.*A4**2-2.*A3**2+2.*A1*
     + *2)*A5**2+(2.*A2**2-2.*A3**2)*A4**2+2.*A3**4+(-2.*A2**2-2.*A1**2)
     + *A3**2+2.*A1**2*A2**2)
```

```
      QID2=Q2**2*(4.*B9**4+(-8.*B8**2+4.*B5**2+4.*B2**2)*B9**2+(-8.*B5*
     + B6-8.*B2*B3)*B8*B9+4.*B8**4+(4.*B6**2+4.*B3**2)*B8**2+B6**4+(-2.*
     + B5**2+2.*B3**2-2.*B2**2)*B6**2+B5**4+(2.*B2**2-2.*B3**2)*B5**2+B3
     + **4-2.*B2**2*B3**2+B2**4)+Q1**2*(4.*B9**4+(-8.*B7**2+4.*B4**2+4.*
     + B1**2)*B9**2+(-8.*B4*B6-8.*B1*B3)*B7*B9+4.*B7**4+(4.*B6**2+4.*B3*
     + *2)*B7**2+B6**4+(-2.*B4**2+2.*B3**2-2.*B1**2)*B6**2+B4**4+(2.*B1
     + *2-2.*B3**2)*B4**2+B3**4-2.*B1**2*B3**2+B1**4)+Q1*Q2*(8.*B9**4+(-
     + 8.*B8**2-8.*B7**2+4.*B5**2+4.*B4**2+4.*B2**2+4.*B1**2)*B9**2+((-8
     + .*B5*B6-8.*B2*B3)*B8+(-8.*B4*B6-8.*B1*B3)*B7)*B9+(8.*B7**2+4.*B6*
     + *2-4.*B4**2+4.*B3**2-4.*B1**2)*B8**2+(8.*B4*B5+8.*B1*B2)*B7*B8+(4
     + .*B6**2-4.*B5**2+4.*B3**2-4.*B2**2)*B7**2+2.*B6**4+(-2.*B5**2-2.*
     + B4**2+4.*B3**2-2.*B2**2-2.*B1**2)*B6**2+(2.*B4**2-2.*B3**2+2.*B1*
     + *2)*B5**2+(2.*B2**2-2.*B3**2)*B4**2+2.*B3**4+(-2.*B2**2-2.*B1**2)
     + *B3**2+2.*B1**2*B2**2)

      F1(X2,X3,X4,X5,X6)=-0.5*8.07765E-29*ALSTAT*(QID1+QID2)

C
C CALCULATION OF THE INTEGRATION ARGUMENT:
C

      T11=2.*A7**2-A4**2-A1**2
      T22=2.*A8**2-A5**2-A2**2
      T33=2.*A9**2-A6**2-A3**2
      T12=2.*A7*A8-A4*A5-A1*A2
      T13=2.*A7*A9-A4*A6-A1*A3
      T23=2.*A8*A9-A5*A6-A2*A3


      T111=2*A7**3-3*A4**2*A7-3*A1**2*A7
      T222=2*A8**3-3*A5**2*A8-3*A2**2*A8
      T333=2*A9**3-3*A6**2*A9-3*A3**2*A9
      T112=2*A7**2*A8-A4**2*A8-A1**2*A8-2*A4*A5*A7-2*A1*A2*A7
      T122=2*A7*A8**2-2*A4*A5*A8-2*A1*A2*A8-A5**2*A7-A2**2*A7
      T133=2*A7*A9**2-2*A4*A6*A9-2*A1*A3*A9-A6**2*A7-A3**2*A7
      T233=2*A8*A9**2-2*A5*A6*A9-2*A2*A3*A9-A6**2*A8-A3**2*A8
      T113=2*A7**2*A9-A4**2*A9-A1**2*A9-2*A4*A6*A7-2*A1*A3*A7
      T223=2*A8**2*A9-A5**2*A9-A2**2*A9-2*A5*A6*A8-2*A2*A3*A8
      T123=2*A7*A8*A9-A4*A5*A9-A1*A2*A9-A4*A6*A8-A1*A3*A8-A5*A6*A7-A2*A
     +   3*A7


      Z11 = A33*(A7**2*B9**2+(2*A4*A7*B6+2*A1*A7*B3)*B9+A4**2*B6**2+2*A
     +   1*A4*B3*B6+A1**2*B3**2)+A22*(A7**2*B8**2+(2*A4*A7*B5+2*A1*A7*B2
     +   )*B8+A4**2*B5**2+2*A1*A4*B2*B5+A1**2*B2**2)+A11*(A7**2*B7**2+(2
     +   *A4*A7*B4+2*A1*A7*B1)*B7+A4**2*B4**2+2*A1*A4*B1*B4+A1**2*B1**2)

      Z22 = A33*(A8**2*B9**2+(2*A5*A8*B6+2*A2*A8*B3)*B9+A5**2*B6**2+2*A
```

```
+    2*A5*B3*B6+A2**2*B3**2)+A22*(A8**2*B8**2+(2*A5*A8*B5+2*A2*A8*B2
+    )*B8+A5**2*B5**2+2*A2*A5*B2*B5+A2**2*B2**2)+A11*(A8**2*B7**2+(2
+    *A5*A8*B4+2*A2*A8*B1)*B7+A5**2*B4**2+2*A2*A5*B1*B4+A2**2*B1**2)

  Z33 = A33*(A9**2*B9**2+(2*A6*A9*B6+2*A3*A9*B3)*B9+A6**2*B6**2+2*A
+    3*A6*B3*B6+A3**2*B3**2)+A22*(A9**2*B8**2+(2*A6*A9*B5+2*A3*A9*B2
+    )*B8+A6**2*B5**2+2*A3*A6*B2*B5+A3**2*B2**2)+A11*(A9**2*B7**2+(2
+    *A6*A9*B4+2*A3*A9*B1)*B7+A6**2*B4**2+2*A3*A6*B1*B4+A3**2*B1**2)

  Z12 = A33*(A7*A8*B9**2+((A4*A8+A5*A7)*B6+(A1*A8+A2*A7)*B3)*B9+A4*
+    A5*B6**2+(A1*A5+A2*A4)*B3*B6+A1*A2*B3**2)+A22*(A7*A8*B8**2+((A4
+    *A8+A5*A7)*B5+(A1*A8+A2*A7)*B2)*B8+A4*A5*B5**2+(A1*A5+A2*A4)*B2
+    *B5+A1*A2*B2**2)+A11*(A7*A8*B7**2+((A4*A8+A5*A7)*B4+(A1*A8+A2*A
+    7)*B1)*B7+A4*A5*B4**2+(A1*A5+A2*A4)*B1*B4+A1*A2*B1**2)

  Z13 = A33*(A7*A9*B9**2+((A4*A9+A6*A7)*B6+(A1*A9+A3*A7)*B3)*B9+A4*
+    A6*B6**2+(A1*A6+A3*A4)*B3*B6+A1*A3*B3**2)+A22*(A7*A9*B8**2+((A4
+    *A9+A6*A7)*B5+(A1*A9+A3*A7)*B2)*B8+A4*A6*B5**2+(A1*A6+A3*A4)*B2
+    *B5+A1*A3*B2**2)+A11*(A7*A9*B7**2+((A4*A9+A6*A7)*B4+(A1*A9+A3*A
+    7)*B1)*B7+A4*A6*B4**2+(A1*A6+A3*A4)*B1*B4+A1*A3*B1**2)

  Z23 = A33*(A8*A9*B9**2+((A5*A9+A6*A8)*B6+(A2*A9+A3*A8)*B3)*B9+A5*
+    A6*B6**2+(A2*A6+A3*A5)*B3*B6+A2*A3*B3**2)+A22*(A8*A9*B8**2+((A5
+    *A9+A6*A8)*B5+(A2*A9+A3*A8)*B2)*B8+A5*A6*B5**2+(A2*A6+A3*A5)*B2
+    *B5+A2*A3*B2**2)+A11*(A8*A9*B7**2+((A5*A9+A6*A8)*B4+(A2*A9+A3*A
+    8)*B1)*B7+A5*A6*B4**2+(A2*A6+A3*A5)*B1*B4+A2*A3*B1**2)

  W11 = V33*(A7**2*B9**2+(2*A4*A7*B6+2*A1*A7*B3)*B9+A4**2*B6**2+2*A
+    1*A4*B3*B6+A1**2*B3**2)+V22*(A7**2*B8**2+(2*A4*A7*B5+2*A1*A7*B2
+    )*B8+A4**2*B5**2+2*A1*A4*B2*B5+A1**2*B2**2)+V11*(A7**2*B7**2+(2
+    *A4*A7*B4+2*A1*A7*B1)*B7+A4**2*B4**2+2*A1*A4*B1*B4+A1**2*B1**2)

  W22 = V33*(A8**2*B9**2+(2*A5*A8*B6+2*A2*A8*B3)*B9+A5**2*B6**2+2*A
+    2*A5*B3*B6+A2**2*B3**2)+V22*(A8**2*B8**2+(2*A5*A8*B5+2*A2*A8*B2
+    )*B8+A5**2*B5**2+2*A2*A5*B2*B5+A2**2*B2**2)+V11*(A8**2*B7**2+(2
+    *A5*A8*B4+2*A2*A8*B1)*B7+A5**2*B4**2+2*A2*A5*B1*B4+A2**2*B1**2)

  W33 = V33*(A9**2*B9**2+(2*A6*A9*B6+2*A3*A9*B3)*B9+A6**2*B6**2+2*A
+    3*A6*B3*B6+A3**2*B3**2)+V22*(A9**2*B8**2+(2*A6*A9*B5+2*A3*A9*B2
+    )*B8+A6**2*B5**2+2*A3*A6*B2*B5+A3**2*B2**2)+V11*(A9**2*B7**2+(2
+    *A6*A9*B4+2*A3*A9*B1)*B7+A6**2*B4**2+2*A3*A6*B1*B4+A3**2*B1**2)

  W12 = V33*(A7*A8*B9**2+((A4*A8+A5*A7)*B6+(A1*A8+A2*A7)*B3)*B9+A4*
+    A5*B6**2+(A1*A5+A2*A4)*B3*B6+A1*A2*B3**2)+V22*(A7*A8*B8**2+((A4
+    *A8+A5*A7)*B5+(A1*A8+A2*A7)*B2)*B8+A4*A5*B5**2+(A1*A5+A2*A4)*B2
+    *B5+A1*A2*B2**2)+V11*(A7*A8*B7**2+((A4*A8+A5*A7)*B4+(A1*A8+A2*A
+    7)*B1)*B7+A4*A5*B4**2+(A1*A5+A2*A4)*B1*B4+A1*A2*B1**2)

  W13 = V33*(A7*A9*B9**2+((A4*A9+A6*A7)*B6+(A1*A9+A3*A7)*B3)*B9+A4*
```

```
   +    A6*B6**2+(A1*A6+A3*A4)*B3*B6+A1*A3*B3**2)+V22*(A7*A9*B8**2+((A4
   +    *A9+A6*A7)*B5+(A1*A9+A3*A7)*B2)*B8+A4*A6*B5**2+(A1*A6+A3*A4)*B2
   +    *B5+A1*A3*B2**2)+V11*(A7*A9*B7**2+((A4*A9+A6*A7)*B4+(A1*A9+A3*A
   +    7)*B1)*B7+A4*A6*B4**2+(A1*A6+A3*A4)*B1*B4+A1*A3*B1**2)

     W23 = V33*(A8*A9*B9**2+((A5*A9+A6*A8)*B6+(A2*A9+A3*A8)*B3)*B9+A5*
   +    A6*B6**2+(A2*A6+A3*A5)*B3*B6+A2*A3*B3**2)+V22*(A8*A9*B8**2+((A5
   +    *A9+A6*A8)*B5+(A2*A9+A3*A8)*B2)*B8+A5*A6*B5**2+(A2*A6+A3*A5)*B2
   +    *B5+A2*A3*B2**2)+V11*(A8*A9*B7**2+((A5*A9+A6*A8)*B4+(A2*A9+A3*A
   +    8)*B1)*B7+A5*A6*B4**2+(A2*A6+A3*A5)*B1*B4+A2*A3*B1**2)


     Q11 = A7**2*B8**2*Q2+2*A4*A7*B5*B8*Q2+2*A1*A7*B2*B8*Q2+A4**2*B5
   1    **2*Q2+2*A1*A4*B2*B5*Q2+A1**2*B2**2*Q2+A7**2*B9**2*(-Q2-Q1)+2
   2    *A4*A7*B6*B9*(-Q2-Q1)+2*A1*A7*B3*B9*(-Q2-Q1)+A4**2*B6**2*(-Q2
   3    -Q1)+2*A1*A4*B3*B6*(-Q2-Q1)+A1**2*B3**2*(-Q2-Q1)+A7**2*B7**2*
   4    Q1+2*A4*A7*B4*B7*Q1+2*A1*A7*B1*B7*Q1+A4**2*B4**2*Q1+2*A1*A4*B
   5    1*B4*Q1+A1**2*B1**2*Q1

     Q22 = A8**2*B8**2*Q2+2*A5*A8*B5*B8*Q2+2*A2*A8*B2*B8*Q2+A5**2*B5
   1    **2*Q2+2*A2*A5*B2*B5*Q2+A2**2*B2**2*Q2+A8**2*B9**2*(-Q2-Q1)+2
   2    *A5*A8*B6*B9*(-Q2-Q1)+2*A2*A8*B3*B9*(-Q2-Q1)+A5**2*B6**2*(-Q2
   3    -Q1)+2*A2*A5*B3*B6*(-Q2-Q1)+A2**2*B3**2*(-Q2-Q1)+A8**2*B7**2*
   4    Q1+2*A5*A8*B4*B7*Q1+2*A2*A8*B1*B7*Q1+A5**2*B4**2*Q1+2*A2*A5*B
   5    1*B4*Q1+A2**2*B1**2*Q1

     Q33 = A9**2*B8**2*Q2+2*A6*A9*B5*B8*Q2+2*A3*A9*B2*B8*Q2+A6**2*B5
   1    **2*Q2+2*A3*A6*B2*B5*Q2+A3**2*B2**2*Q2+A9**2*B9**2*(-Q2-Q1)+2
   2    *A6*A9*B6*B9*(-Q2-Q1)+2*A3*A9*B3*B9*(-Q2-Q1)+A6**2*B6**2*(-Q2
   3    -Q1)+2*A3*A6*B3*B6*(-Q2-Q1)+A3**2*B3**2*(-Q2-Q1)+A9**2*B7**2*
   4    Q1+2*A6*A9*B4*B7*Q1+2*A3*A9*B1*B7*Q1+A6**2*B4**2*Q1+2*A3*A6*B
   5    1*B4*Q1+A3**2*B1**2*Q1

     Q12 = A7*A8*B8**2*Q2+A4*A8*B5*B8*Q2+A5*A7*B5*B8*Q2+A1*A8*B2*B8*
   1    Q2+A2*A7*B2*B8*Q2+A4*A5*B5**2*Q2+A1*A5*B2*B5*Q2+A2*A4*B2*B5*Q
   2    2+A1*A2*B2**2*Q2+A7*A8*B9**2*(-Q2-Q1)+A4*A8*B6*B9*(-Q2-Q1)+A5
   3    *A7*B6*B9*(-Q2-Q1)+A1*A8*B3*B9*(-Q2-Q1)+A2*A7*B3*B9*(-Q2-Q1)+
   4    A4*A5*B6**2*(-Q2-Q1)+A1*A5*B3*B6*(-Q2-Q1)+A2*A4*B3*B6*(-Q2-Q1
   5    )+A1*A2*B3**2*(-Q2-Q1)+A7*A8*B7**2*Q1+A4*A8*B4*B7*Q1+A5*A7*B4
   6    *B7*Q1+A1*A8*B1*B7*Q1+A2*A7*B1*B7*Q1+A4*A5*B4**2*Q1+A1*A5*B1*
   7    B4*Q1+A2*A4*B1*B4*Q1+A1*A2*B1**2*Q1

     Q13 = A7*A9*B8**2*Q2+A4*A9*B5*B8*Q2+A6*A7*B5*B8*Q2+A1*A9*B2*B8*
   1    Q2+A3*A7*B2*B8*Q2+A4*A6*B5**2*Q2+A1*A6*B2*B5*Q2+A3*A4*B2*B5*Q
   2    2+A1*A3*B2**2*Q2+A7*A9*B9**2*(-Q2-Q1)+A4*A9*B6*B9*(-Q2-Q1)+A6
   3    *A7*B6*B9*(-Q2-Q1)+A1*A9*B3*B9*(-Q2-Q1)+A3*A7*B3*B9*(-Q2-Q1)+
   4    A4*A6*B6**2*(-Q2-Q1)+A1*A6*B3*B6*(-Q2-Q1)+A3*A4*B3*B6*(-Q2-Q1
   5    )+A1*A3*B3**2*(-Q2-Q1)+A7*A9*B7**2*Q1+A4*A9*B4*B7*Q1+A6*A7*B4
   6    *B7*Q1+A1*A9*B1*B7*Q1+A3*A7*B1*B7*Q1+A4*A6*B4**2*Q1+A1*A6*B1*
```

```
7    B4*Q1+A3*A4*B1*B4*Q1+A1*A3*B1**2*Q1


  Q23 = A8*A9*B8**2*Q2+A5*A9*B5*B8*Q2+A6*A8*B5*B8*Q2+A2*A9*B2*B8*
1    Q2+A3*A8*B2*B8*Q2+A5*A6*B5**2*Q2+A2*A6*B2*B5*Q2+A3*A5*B2*B5*Q
2    2+A2*A3*B2**2*Q2+A8*A9*B9**2*(-Q2-Q1)+A5*A9*B6*B9*(-Q2-Q1)+A6
3    *A8*B6*B9*(-Q2-Q1)+A2*A9*B3*B9*(-Q2-Q1)+A3*A8*B3*B9*(-Q2-Q1)+
4    A5*A6*B6**2*(-Q2-Q1)+A2*A6*B3*B6*(-Q2-Q1)+A3*A5*B3*B6*(-Q2-Q1
5    )+A2*A3*B3**2*(-Q2-Q1)+A8*A9*B7**2*Q1+A5*A9*B4*B7*Q1+A6*A8*B4
6    *B7*Q1+A2*A9*B1*B7*Q1+A3*A8*B1*B7*Q1+A5*A6*B4**2*Q1+A2*A6*B1*
7    B4*Q1+A3*A5*B1*B4*Q1+A2*A3*B1**2*Q1




  term1=A33**2*(-Q2-Q1)*T33**2*Z33+A22**2*Q2*T23**2*Z33+A11**2*Q1
1    *T13**2*Z33+2*A33**2*(-Q2-Q1)*T23*T33*Z23+2*A22**2*Q2*T22*T23
2    *Z23+2*A11**2*Q1*T12*T13*Z23+A33**2*(-Q2-Q1)*T23**2*Z22+A22**
3    2*Q2*T22**2*Z22+A11**2*Q1*T12**2*Z22+2*A33**2*(-Q2-Q1)*T13*T3
4    3*Z13+2*A22**2*Q2*T12*T23*Z13+2*A11**2*Q1*T11*T13*Z13+2*A33**
5    2*(-Q2-Q1)*T13*T23*Z12+2*A22**2*Q2*T12*T22*Z12+2*A11**2*Q1*T1
6    1*T12*Z12+A33**2*(-Q2-Q1)*T13**2*Z11+A22**2*Q2*T12**2*Z11+A11
7    **2*Q1*T11**2*Z11


  term2=A33**2*Q33*T33**2*Z33+2*A22*A33*Q23*T23*T33*Z33+2*A11*A33
1    *Q13*T13*T33*Z33+A22**2*Q22*T23**2*Z33+2*A11*A22*Q12*T13*T23*
2    Z33+A11**2*Q11*T13**2*Z33+2*A33**2*Q33*T23*T33*Z23+2*A22*A33*
3    Q23*T22*T33*Z23+2*A11*A33*Q13*T12*T33*Z23+2*A22*A33*Q23*T23**
4    2*Z23+2*A22**2*Q22*T22*T23*Z23+2*A11*A33*Q13*T13*T23*Z23+2*A1
5    1*A22*Q12*T12*T23*Z23+2*A11*A22*Q12*T13*T22*Z23+2*A11**2*Q11*
6    T12*T13*Z23+A33**2*Q33*T23**2*Z22+2*A22*A33*Q23*T22*T23*Z22+2
7    *A11*A33*Q13*T12*T23*Z22+A22**2*Q22*T22**2*Z22+2*A11*A22*Q12*
8    T12*T22*Z22+A11**2*Q11*T12**2*Z22+2*A33**2*Q33*T13*T33*Z13+2*
9    A22*A33*Q23*T12*T33*Z13+2*A11*A33*Q13*T11*T33*Z13+2*A22*A33*Q
:    23*T13*T23*Z13+2*A22**2*Q22*T12*T23*Z13+2*A11*A22*Q12*T11*T23
;    *Z13+2*A11*A33*Q13*T13**2*Z13+2*A11*A22*Q12*T12*T13*Z13+2*A11
<    **2*Q11*T11*T13*Z13+2*A33**2*Q33*T13*T23*Z12+2*A22*A33*Q23*T1
=    2*T23*Z12+2*A11*A33*Q13*T11*T23*Z12+2*A22*A33*Q23*T13*T22*Z12
>    +2*A22**2*Q22*T12*T22*Z12+2*A11*A22*Q12*T11*T22*Z12+2*A11*A33
?    *Q13*T12*T13*Z12+2*A11*A22*Q12*T12**2*Z12+2*A11**2*Q11*T11*T1
@    2*Z12+A33**2*Q33*T13**2*Z11+2*A22*A33*Q23*T12*T13*Z11+2*A11*A
1    33*Q13*T11*T13*Z11+A22**2*Q22*T12**2*Z11+2*A11*A22*Q12*T11*T1
2    2*Z11+A11**2*Q11*T11**2*Z11


  TERM=term1+term2



  FI(X2,X3,X4,X5,X6)=(SIN(BE1(X3))*SIN(BE2(X6)))*TERM
```

```
C
C CALCULATION OF THE SHAPE POTENTIAL:
C

      G1(X3,X4,X6)=4.*PARAM2*1.380622E-23*R**12*(SHAPE1*(3.*COS(BE1(X3
     + )**2+3.*COS(BE2(X6))**2-2.)+SHAPE2*(3.*COS(GA1(X4))**2*SIN(BE1(X3
     + ))**2+3.*COS(GA2(X7))**2*SIN(BE2(X6))**2-2.))


80              CONTINUE
70            CONTINUE
60          CONTINUE
50        CONTINUE

c       WRITE(4,1444)term
c1444   FORMAT(1X,'term IS',E15.7)

40      CONTINUE

C
C THE INTEGRAL IS CALCULATED:
C

        SS6=0.00
        DO 940 X6=1,16
c       WRITE(6,1911)X6
c1911   FORMAT (1X, 'sub-index (in range 1 to 16) is currently ',I2 )
          SS5=0.00
          DO 950 X5=1,16
            SS4=0.00
            DO 960 X4=1,16
              SS3=0.00
              DO 970 X3=1,16
                SS2=0.00
                DO 980 X2=1,16
                  SS1=0.00
                  DO 990 X1=1,64


C
C SUMMATION OF THE ENERGY TERMS WITH SUBSEQUENT DIVISION BY (-kT):
C

      G3=-1.*(D1(X1)+E1(X2,X3,X4,X5,X6)/SE5(X1)+F1(X2,X3,X4,X5,X6)/SE8(
     + X1)+G1(X3,X4,X6)/SE12(X1)+DDP(X2,X3,X4,X5,X6)/SE3(X1)+DIDP(X2,X3,
     + X4,X5,X6)/SE6(X1)+DQP(X2,X3,X4,X5,X6)/SE4(X1))/TEMPK

      IF(G3.LT.-85) GO TO 5000
      G4=2.71828**G3
```

```
        GO TO 5010
5000    G4=0
C5010   SS1=SS1+(FI(X2,X3,X4,X5,X6)/(SEP(X1)**6))*G4*COEF2(X1,2)
5010    SS1=SS1+(FI(X2,X3,X4,X5,X6)/(SEP(X1)**4))*G4*COEF2(X1,2)
990               CONTINUE
        SS2=SS2+SS1*COEF1(X2,2)
C
C
980                CONTINUE
        SS3=SS3+SS2*COEF1(X3,2)
C
C
970              CONTINUE
        SS4=SS4+SS3*COEF1(X4,2)
C
C
960           CONTINUE
        SS5=SS5+SS4*COEF1(X5,2)
C
C
950          CONTINUE
        SS6=SS6+SS5*COEF1(X6,2)
C
C
940        CONTINUE
        SS7=SS7+SS6*COEF1(X7,2)


C
C
939     CONTINUE
        ANS=SS7*SEP1*AL11*BE11*GA11*AL21*BE21*GA21*6.022169**2*
      + 8.987552**3*1E-37/(TEMP*1.380622*90*3.14159265358979323846**2)



C
C THE INTEGRAL IS PRINTED TOGETHER WITH MOLECULAR DATA USED
C

        WRITE(4,2266)
2266    FORMAT(1X,'THE Q1A3 TERM CONTRIBUTION TO B_Q FOR CO2:')
        WRITE(4,2267)
2267    FORMAT(1X,'   ')
        WRITE(4,2269)
2269    FORMAT(1X,'   ')
        WRITE(4,1140)ANS
1140    FORMAT(1X,'THE INTEGRAL IS',E15.7)
        WRITE(4,2150)
2150    FORMAT(1X,'INPUT DATA:')
        WRITE(4,2155)TEMP
```

```
2155   FORMAT(1X,'TEMPERATURE:       ',F10.5)
       WRITE(4,9260)ALDYN
9260   FORMAT(1X,'MEAN DYNAMIC ALPHA:',F10.5)
       WRITE(4,9261)A11
9261   FORMAT(1X,'DYNAMIC ALPHA11:   ',F10.5)
       WRITE(4,9262)A22
9262   FORMAT(1X,'DYNAMIC ALPHA22:   ',F10.5)
       WRITE(4,9263)A33
9263   FORMAT(1X,'DYNAMIC ALPHA33:   ',F10.5)
       WRITE(4,9264)ALSTAT
9264   FORMAT(1X,'MEAN STATIC ALPHA: ',F10.5)
       WRITE(4,9961)V11
9961   FORMAT(1X,'STATIC ALPHA11:    ',F10.5)
       WRITE(4,9962)V22
9962   FORMAT(1X,'STATIC ALPHA22:    ',F10.5)
       WRITE(4,9963)V33
9963   FORMAT(1X,'STATIC ALPHA33:    ',F10.5)
       WRITE(4,2190)Q1
2190   FORMAT(1X,'THETA11:           ',F10.5)
       WRITE(4,2241)Q2
2241   FORMAT(1X,'THETA22:           ',F10.5)
       WRITE(4,2210)R
2210   FORMAT(1X,'R(0):                  ',F6.5)
       WRITE(4,2220)SHAPE1
2220   FORMAT(1X,'SHAPE FACTOR 1:    ',F10.5)
       WRITE(4,2221)SHAPE2
2221   FORMAT(1X,'SHAPE FACTOR 2:    ',F10.5)
       WRITE(4,2230)PARAM2
2230   FORMAT(1X,'E/K:               ',F9.5)
       WRITE(4,2235)AMIN1,AMAX1
2235   FORMAT(1X,'MIN AND MAX POINTS OF RANGE (64 INTERVALS):',2(F10.5,3
     + X))
       WRITE(4,2240)
2240   FORMAT(1X,'END BT')
       WRITE(4,2261)
2261   FORMAT(1X,'   ')
       WRITE(4,2262)
2262   FORMAT(1X,'   ')
       WRITE(4,2263)
2263   FORMAT(1X,'   ')
       WRITE(4,2264)
2264   FORMAT(1X,'   ')
       WRITE(4,2265)
2265   FORMAT(1X,'   ')
       CLOSE(UNIT=4)
       END
```

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