HIGH ORDER MULTIPOLe LONG RANGE INTERACTIONS
BETWEEN RARE GAS ATOMS
WITH APPLICATIONS TO THE CRYSTALLINE STATE

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fulfilment of the requirements for the degree of Doctor of
Philosophy.

by

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ABSTRACT

Long range interactions between the atoms in a rare gas crystal are developed in a many-body multipole series formalism. The various interaction terms are expressed as the product of a geometric part, which depends only upon the lattice structure, and a multipole interaction constant appropriate to the atomic species.

The interaction constants for Neon, Argon, Krypton and Xenon are calculated by means of time-dependent Brueckner-Goldstone perturbation theory and provide results of a higher expected accuracy than previous calculations and in many cases provide results previously unavailable.

Lattice summations are performed for the geometric part of the interactions. To overcome the slow convergence of the triple-dipole lattice summation, the finite summation range is extended, and extrapolation to infinite range is accomplished analytically by means of a continuum model for the crystal.

The contributions to the various properties of the rare gas crystals of three-body multipole long range interactions are calculated. In particular the lattice energy, the harmonic zero point vibrational energy, the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ and the bulk modulus are evaluated for each of the rare gas crystals at the absolute zero. The effects of the high order multipole terms are shown to be not negligible. The quantity $\delta = (C_{44} - C_{12})/C_{12}$, which is always positive when calculated with only two-body forces, is reduced when three-body interactions are included. In the cases of A, Kr and Xe, $\delta$ in fact becomes negative.
For the only experimental data available $\delta$ is found to be negative for Argon providing strong evidence for the existence of three-body forces.

In the final chapter a number of points arising from the thesis are discussed and some indication is given of the possible direction of future developments in this area of research.

The research on which this thesis is based was carried out at the University of Surrey between October 1969 and October 1972. Some portions of this work have been discussed in the following publications:

Doran M.B. and Zucker I.J. (1971); J. Phys. C 4 307 (Chapter Three)
Barker J.A., Klein M.L., Bobetic M.V., Zucker I.J., Doran M.B.
and Chell G.G. (1971); J. Phys. C 4 L355 (Chapters Four and Five)
Zucker I.J. and Doran M.B. (1972); to be published in J. Phys. C (Chapter Four)
Doran M.B. (1972); to be published in J. Phys. C (Chapter Two).
To my late Father
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# CONTENTS

<table>
<thead>
<tr>
<th>FOREWORD</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHAPTER 1</strong></td>
<td><strong>HIGH ORDER NONADDITIVE VAN DER WAALS FORCES</strong></td>
</tr>
<tr>
<td>Introduction</td>
<td>4</td>
</tr>
<tr>
<td>Justification for Perturbation Theory</td>
<td>6</td>
</tr>
<tr>
<td>Reaction-field Description of Long-range Interatomic Forces</td>
<td>9</td>
</tr>
<tr>
<td>Conclusion</td>
<td>15</td>
</tr>
<tr>
<td><strong>CHAPTER 2</strong></td>
<td><strong>THE CALCULATION OF THE VAN DER WAALS MULTIPOLe INTERACTION COEFFICIENTS</strong></td>
</tr>
<tr>
<td>Introduction</td>
<td>18</td>
</tr>
<tr>
<td>Time-dependent Brueckner Goldstone Perturbation Theory</td>
<td>23</td>
</tr>
<tr>
<td>Single Particle States and Evaluation of Diagrams</td>
<td>32</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>36</td>
</tr>
<tr>
<td><strong>CHAPTER 3</strong></td>
<td><strong>THE CONTRIBUTION OF THE HIGH ORDER MULTIPole 3-BODY VAN DER WAALS INTERACTIONS TO THE STATIC LATTICE ENERGY AND ZERO POINT ENERGY OF THE RGC AT ABSOLUTE ZERO</strong></td>
</tr>
<tr>
<td>Introduction</td>
<td>43</td>
</tr>
<tr>
<td>Static Lattice Energy</td>
<td>46</td>
</tr>
<tr>
<td>Zero Point Vibrational Energy</td>
<td>52</td>
</tr>
<tr>
<td>Appendix</td>
<td>57</td>
</tr>
</tbody>
</table>
FOREWORD

Before beginning the thesis proper, this is perhaps an appropriate point at which to briefly mention the motivation behind the present research and prepare the reader for the manner of its presentation in this thesis.

Many-body phenomena in solids has been an active area of theoretical research for many years now. It is only recently however that efforts have been made to add many-body interactions to the existing two-body description of some solids. An important question arises as to what is the relative magnitude of various many-body interactions and to what extent should they be incorporated into an atomistic description of solids bearing in mind the feasibility of performing lattice dynamical calculations? The object of this thesis is to attempt to answer these two questions, at least in part, for the simplest of all solids - the rare gas crystals (RGC) - and to perhaps provide some stimulation in this area of research.

The main reason for the simplicity of the RGC is that they are made up of neutral atoms with spherically symmetric charge distributions, removing the complications of interatomic coulomb interactions. Also the electronic energy of these solids is in the ground-state and therefore the adiabatic approximation may be used. From this standpoint, in Chapter One we attempt to develop and justify a multipole perturbation expansion for the interatomic interactions in the RGC in a many-body context. The main point to emerge here is that the total interaction can be expressed in terms of the lattice structure and an interaction
constant appropriate to the atomic species.

The significant lack of accurate data for the atomic interaction constants that we required, prompted their arduous quantum mechanical evaluation in Chapter Two.

With the various many-body interactions well defined we can now move on to evaluate some of the thermo-elastic properties of the RGC. The lattice energy and the harmonic zero-point energy are examined in Chapter Three, and the elastic constants defined by the theory of Homogeneous Deformations are evaluated in Chapter Four.

The use of pair potentials is often unavoidable in these last two chapters, and despite the lack of a very accurate potential, we have used throughout a Lennard Jones potential in which zero-point effects have been incorporated. Fortunately the conclusions of these chapters are not too sensitive to the particular form of the pair-potential chosen, so that this choice would not appear critical.

A problem that arises with the leading many-body term, the triple-dipole interaction, is the slow convergence of the corresponding summations. Extrapolation procedures in the past seemed unsatisfactory so that Chapter Five has been devoted to applying an analytic continuum model to the triple-dipole interactions in the RGC to extend the finite summations to the infinite crystal. Relations also emerge which check the accuracy of the finite sums.

The final Chapter is not specifically a summary of the foregoing chapters; it has been used as a vehicle for any thoughts and
ideas relevant to the theme of the thesis but which could not be incorporated in the body of the thesis for reasons of continuity.

Wherever possible the mathematics involved in derivations is placed at the end of each chapter. It is hoped that this will provide for more fluent reading.
High Order Nonadditive Van Der Waals Forces

Introduction

The usual derivation of the long range Van der Waals forces in the theory of intermolecular forces is well known and well defined; see for example Margenau and Kestner (1971). It is based on the Rayleigh-Schrödinger perturbation theory. The unperturbed Hamiltonian $H_0$ for a diatomic system of separation $R$ is taken to be the sum of the two Hamiltonians $H_A$ and $H_B$ of the non-interacting neutral atoms $A$ and $B$. The interaction Hamiltonian is given by

$$V_{AB} = H - (H_A + H_B) \tag{1.1}$$

where $H$ is the total Hamiltonian of the system. If there is no overlap between the atoms then $V_{AB}$ is just the classical electrostatic interaction between the charge distributions on each atom. The perturbed wavefunction $\phi_{AB}$ for the system is just the simple product of the unperturbed wavefunctions $\phi_A$ and $\phi_B$ of atoms $A$ and $B$ at infinite separation. This approach may then be generalised to a system of $N$ non-overlapping atoms interacting through pairwise potentials $V$, with unperturbed wavefunction $\phi = \prod_{i=1}^{N} \phi_i$.

On applying perturbation theory the energy of interaction $E$ may be written as the sum of contributions from the different orders of perturbation $E_n$

$$E = \sum_{\ell_1 \ell_2} E(\ell_1 \ell_2) + \sum_{\ell_1 \ell_2} E(\ell_1 \ell_2^2) + \sum_{\ell_1 \ell_2 \ell_3} \{E(\ell_1 \ell_2 \ell_3) + E(\ell_1 \ell_2 \ell_3^2) + \ldots \}$$

$$\tag{1.2}$$
Here we have introduced a bipolar expansion of $V$

$$V = \sum_{1,2} V(I_1 I_2)$$  \hspace{1cm} (1.3)

where $I_1 = 1,2,3 \ldots$ represent multipoles of order $2^{I_1} = 1,2,3 \ldots$ i.e. dipoles (D), quadrupoles (Q), octupoles (O) \ldots situated on atoms i.

The notation $I_1 = 1,2,3 \ldots$ or D,Q,O \ldots will be used interchangeably.

The first term on the right in equation (1.2) is found to be zero since it is just the average of $V$ over the systems ground state. The second term is found to be the sum of pairwise additive multipole-multipole interactions given more explicitly by

$$E(I_1 I_2)_2 = \sum_p \frac{\langle \psi_0 | V(I_1 I_2) | \phi_p \rangle <\psi_p | V(I_1 I_2) | \phi_0 \rangle}{E_0 - E_p}$$  \hspace{1cm} (1.4)

where the primed summation is over all excited states $p \neq 0$. The leading term in $E_2$ is $E(I1)_{2}$ or $E(DD)_{2}$ the dipole-dipole interaction first studied by Eisenschitz and London (1930). Higher order terms of $E_2$ such as $E(DQ)_{2}$, $E(QQ)_{2}$ and $E(DD)_{2}$ have also been studied - Margenau and Kestner (1971). All these factors were negative implying that attractive forces acted between neutral atoms to second order. Pair interactions occur again in the third order term $E_3$. Although $E(DD)_{3}$ is found to vanish little else is known about these terms despite investigations by Dalgarno and Lewis (1956) and by Chan and Dalgarno (1965) in the case of Hydrogen.

However, more interestingly we find three-body nonadditive factors appearing in $E_3$ of the form

$$E(I_1 I_2 I_3)_3 = \sum_{p,p',p''} \frac{\langle \psi_0 | V(I_1 I_2 I_3) | \phi_p \rangle \langle \phi_p | V(I_2 I_3) | \phi_{p'} \rangle \langle \phi_{p'} | V(I_3 I_1) | \phi_0 \rangle}{(E_0 - E_p)(E_0 - E_{p'})}$$  \hspace{1cm} (1.5)
where the primed summations are over excited states \( p, p' \neq 0 \). We are thus concerned here with triplets of atoms where all three pair interactions are coupled together providing a truly nonadditive quantum mechanical many-body effect. The lowest order three body factor \( E(DDD)_3 \) was first studied by Axilrod and Teller (1943) and Muto (1943). Ayres and Tredgold (1956) have given an expression for \( E(DDQ)_3 \). Bell (1970) has obtained a general expression for \( E(D_1D_2D_3)_3 \). His explicit result for \( E(DDQ)_3 \) disagrees with that of Ayres and Tredgold. All the terms \( E(D_1D_2D_3)_3 \) were found to be positive and thus produce a repulsive force between neutral atoms.

The fourth order energy term in equation (1.2) would be made up of two, three and four-body interactions. This term has been studied by Bade (1957) for dipole interactions only in the Drude model. He found that the three body factor \( E(DDD)_4 \) made up over 90% of the total dipole contribution to \( E_4 \). It was negative in sign and hence produced an attractive force.

The perturbational treatment of long range intermolecular forces outlined above involves a number of assumptions about the nature of the interaction between two or more atoms. In particular, in the next section, we must look carefully at the applicability of the perturbation expansion in the case of the rare gas atomic interaction.

Justification for Perturbation Theory

The interaction energy of a system of atoms may be defined as the difference between the total energy of the interacting atoms and the energy of the system at infinite distance. Since for long intermolecular
distances this involves the small difference of two large numbers it has been common practice to calculate this difference directly by perturbation theory rather than indirectly by variational methods. However, the use of perturbation theory in the simple form described in the previous section immediately raises a number of questions with regard to its applicability:

(1) In order that a simple product wavefunction may be taken as the zeroth order wavefunction of the system and that a bipolar expansion of $V$ may be valid then overlap of the atomic wavefunction must be zero or negligible at the interatomic separations considered. This point has been discussed in relation to theoretical calculations on helium by Margenau and Kestner (1971). They found that the multipole expansion should provide accurate results at the Van der Waals minimum and beyond. Overlap would also appear to be negligible at the Van der Waals minimum for the heavier rare gases since typically for example the radius of maximum radial charge density for the outermost orbital of argon is calculated by Herman and Skillman (1963) to be $0.657 \text{"A}$. whereas the nearest neighbour distance in crystalline argon is $3.755 \text{"A}$. We can feel confident then that the overlap criteria is satisfactorily met in the case of the rare gas interatomic forces in the crystalline state.

(2) Further problems arise from the use of the simple product zeroth wave-function. The perturbation procedure above is unable to exhibit short-range repulsive terms, which are necessary in order to ensure the existence of a minimum of the interatomic energy curve at the correct distance, and which are obviously missing in a perturbation series dominated by the leading second-order
attractive term. The necessary repulsive terms would arise from a properly antisymmetrized zeroth wave-function. However very great difficulties arise here in the construction of the corresponding unperturbed Hamiltonian which would give the correct energy for the system of atoms at infinite separation. Since we are interested here in the long-range part of the interaction we need not be too concerned about this problem and assume it can be handled in a more convenient way, perhaps variationally, and the results connected to the long-range results by interpolation.

However, the symmetry of the simple unperturbed Hamiltonian, $H_0 = H_A + H_B$, is lower than the symmetry of the perturbed Hamiltonian $H$. This symmetry change under perturbation means that as the perturbation is switched on gradually to full strength it is by no means certain that the true physical eigenstates of $H$ are continuously connected with the perturbed states derived from $H_0$. This problem has been examined recently by Claverie (1971) for the 2-body Van der Waals interaction and concludes on group-theoretical grounds that for this interaction which slowly varies with range, the difference between the perturbation energy and the true energy of interaction should decrease exponentially with range. Therefore, the perturbation theory above will give an increasingly better approximation of the true interaction energy as $R$ increases. In particular for the rare gas interatomic interactions at the Van der Waals minimum and beyond, the perturbation method should be adequate. We should also expect these results to hold for all many-body interactions between rare gas atoms.

(3) To be at all useful for our purposes the perturbation series must converge quickly. The question of convergence is discussed by
Margenau and Kestner (1971) who conclude that the series can be used with confidence. Lucas (1967) and Huller (1971) have examined the whole expansion for linear $E(\ell_1 \ell_2 \ldots \ell_n)$ many-dipole ($\ell_i = 1$) interactions only, in the Drude model and found that the terms of the series oscillated in sign and decreased in absolute size with increasing order $n$.

Recently Malrieu (1971) has performed an infinite diagrammatic summation of the dipole-dipole interaction terms $E(DD)_n$ for all orders $n$. He finds that the series converges if $\alpha^2/R^6 < 1$ where $\alpha$ is the static polarizability of the atomic species considered. This inequality is easily satisfied by the rare gas atoms for the Van der Waals distances, and the corrections due to the high orders of the perturbation expansion remain very small.

We conclude this section by saying that on all counts the present perturbation method appears to be a satisfactory treatment of the long range interatomic interactions between the rare gas atoms.

Reaction-field Description of Long-range Interatomic Forces

Reaction field theory can provide us with a physically intuitive semi-classical understanding of the long range many-body forces in a system of interacting atoms. Consider the total interaction energy of a close-packed crystal of $N$ non-overlapping spherically neutral atoms interacting through their instantaneous zero-point multipole moments. To simplify the problem we need only look at the interactions of one atom at the origin, say, and all the other $N-1$ atoms in the surrounding medium. The total interaction energy of the crystal can then be trivially obtained by multiplying each $n$-body result by the number of such distinct interactions.
involving any of the other N-1 atoms chosen as origin since each atom has an identical environment in a close-packed crystal structure. The following treatment parallels closely the linear response theory used by Linder (1967) and McLachlan (1963a).

We consider first the diatomic interactions of atom i at the origin with the other atoms j. An instantaneous fluctuating multipole moment \( M^j_i(\omega) \) of order \( 2^j_i \) on atom i produces a \( 2^j_i \) multipole radiation field \( E_j^j_i(\omega) \) at the site of a neighbouring atom j given by

\[
E_j^j_i = -T^j_i \cdot M^j_i
\]

(1.6)

where \( T^j_i \) is the radiation field susceptibility associated with \( M^j_i \). We have used a single dot notation to signify a general tensor product. The order of a susceptibility tensor \( T \) is \( l + 1 \) and that of a moment \( M \) is \( l \).

The field \( E_j^j_i \) induces a moment \( M^j_j \) on atom j given by

\[
M^j_j = \alpha^j_j \cdot E_j^j_i
\]

(1.7)

where \( \alpha^j_j \) is the frequency dependent atomic susceptibility of j which in turn produces a reaction field \( E_i^j_j \) at i

\[
E_i^j_j = -T^j_j \cdot M^j_j
\]

(1.8)

substituting equation (1.6) and (1.7) into (1.8) we obtain

\[
E_i^j_j = T^j_j \cdot \alpha^j_j \cdot T^j_i \cdot M^j_i
\]

(1.9)

This can be written as
is the change of field susceptibility in the presence of atom \( j \). According to McLachlan (1963b) the interaction energy of \( i \) and \( j \) is just the self-energy change of atom \( i \) given by

\[
\Delta E = -\frac{1}{2\pi} \int_0^\infty \alpha^i(i\omega) \beta^i j j(i\omega) \, d\omega
\]

where \( \alpha \) and \( \beta \) are the susceptibility of atom \( i \) and the change in field susceptibility respectively evaluated at complex frequency.

\( \Delta E \) is just a general second order two-body interaction \( E(\mathcal{L}_i, \mathcal{L}_j) \) discussed previously. It can be rewritten more usefully on substituting for \( \beta \)

\[
E(\mathcal{L}_i, \mathcal{L}_j) = -\frac{1}{2\pi} I:(T^j \cdot T^i) \int_0^\infty \alpha^i(i\omega) \alpha^j(i\omega) \, d\omega
\]

where we have assumed the atomic susceptibilities to be isotropic, so that these tensors can be replaced by scalars times their idemfactors. \( I \) is the resulting idemfactor and the double dot notation signifies a general scalar product.

Now suppose \( i \) has two neighbours, \( j \) and \( k \). The reaction field produced at \( i \) will then consist of two terms similar to the ones above, but in addition, new terms will arise of the form

\[
E^j \mathcal{L}_k = - T^j \cdot \alpha^j \cdot T^k \cdot \alpha^k \cdot T^i \cdot M^i
\]
The latter is the field produced at \( i \) by \( k \) which results from the polarization of \( k \) by \( j \), which in turn was polarized by \( i \). This term plus its equivalent complementary term \( E^{jk}_i \) gives rise to the general third order 3-body energy term analogous to the 2-body term of equation (1.12)

\[
E(\mathbf{L}_i, \mathbf{L}_j, \mathbf{L}_k) = \frac{1}{\pi} \mathbf{I} : (\mathbf{T}_i \cdot \mathbf{T}_j \cdot \mathbf{T}_k) \int_0^\infty a_l(\omega) a_j(\omega) a_k(\omega) \, d\omega
\]

(1.14)

This process may be continued so as to include all \( N-1 \) neighbours of \( i \). In this way total interaction energy for the crystal of \( N \) atoms becomes

\[
E = \sum_{l_i, l_j, ..., l_k} \sum_{i=1}^{N-1} \sum_{j,k,...=1}^{N-1} \left\{ E(l_i, l_j) + E(l_i, l_j, l_k) + \ldots \right\}
\]

(1.15)

where the primed summations include only distinct interactions between the multipoles \( l_i, l_j, ..., l_k \) on atoms \( i, j, k, ... \) and the general interaction energy term is

\[
E(l_1, l_2, l_3, ..., l_n) = \frac{(n-1)!}{2\pi} \mathbf{I} : (\mathbf{T}_1 \cdot \mathbf{T}_2 \cdot \mathbf{T}_3 \cdot \ldots \cdot \mathbf{T}_n) \int_0^\infty a_1(\omega) a_2(\omega) a_3(\omega) \ldots a_n(\omega) \, d\omega
\]

(1.16)

This result takes a simple form for dipole (\( l=1 \)) interactions only where \( T_{ij}^D \) is the dyadic \((l=3, \mathbf{e}_{ij} \cdot \mathbf{e}_{ij})/R_{ij}^3\) and \( \mathbf{I} \) is the unit dyadic and \( \mathbf{e}_{ij} \) the unit vector pointing from \( i \) to \( j \)

\[
E(DDD...) = \frac{(n-1)!}{2\pi} \text{Tr}(T^D \cdot T^D \cdot T^D \ldots) \int_0^\infty \{a_i(\omega)\}^n \, d\omega
\]

(1.17)
In particular we obtain the well known results

$$E(DD)_2 = -\frac{3}{\pi R_{ij}^6} \int_0^\infty \left\{ a_D(i\omega) \right\}^2 \, dw$$

$$E(DDD)_3 = \frac{3(3 \cos \theta_{ij} \cos \theta_{jk} \cos \theta_{ki} + 1)}{\pi R_{ij}^3 R_{jk}^3 R_{ki}^3} \int_0^\infty \left\{ a_D(i\omega) \right\}^3 \, dw$$

Equation (1.18) shows the dipole-dipole term of Eisenschitz and London (1930), and in equation (1.19) we have the Axilrod-Teller (1943) triple-dipole interaction.

The total series of equation (1.15) has been summed for dipole interactions only by Lucas (1967) and with greater accuracy by Huller (1971) using the Drude model. In this approximation the atoms are linearly polarizable and can be represented by harmonic oscillators of equivalent polarizability, and the atoms interact only through the harmonic dipole-dipole coupling. In effect this model replaces the integrals over the polarizabilities evaluated in the complex frequency plane, by a single frequency approximation which stands outside the summation for all orders of interaction. From this approach we can form a reasonable opinion of the convergence of the perturbation series as we have already discussed.

It is important to realize at this stage that the total energy summation of equation (1.15) contains only linear terms in harmony with the original assumption that the reaction field $E_1$ and the moment $M_1$ are linearly dependent. This simplification is achieved by excluding from the summation those reaction-field components which correspond to multiple excitations. Such terms would be non-linear and are not rigorously expressible in terms of the ordinary susceptibilities but
involve susceptibilities of mixed frequencies. These terms are
included in the Rayleigh-Schrodinger perturbation expansion; for
example, the fourth-order dipole-dipole term. The neglect of the non-
linear terms does not seem to be important for our purposes since they
seem to be negligible compared to the leading linear terms; see for
example, Malrieu (1971).

The restriction to linear terms provides a great simplification:
all the linear interaction terms can be written as the product of a
purely geometric term \(W\) and an interatomic interaction term \(Z\) (the Van
der Waals coefficient) so that we have in general

\[
E(\ldots) = Z(\ldots) W(\ldots) \quad (1.20)
\]

We have, for example, for the triple dipole term of equation (1.19)
\(E(DDD)_3\) where

\[
Z(DDD)_3 = \frac{1}{\pi} \int_0^\infty \{\alpha^D(i\omega)\}^3 d\omega
\]

\[
W(DDD)_3 = \frac{3(3 \cos \theta_{ij} \cos \theta_{jk} \cos \theta_{ki})}{R_{ij}^3 R_{jk}^3 R_{ki}^3} \quad (1.21)
\]

where \(R_{ij}, R_{jk}, R_{ki}\) are the sides of a triangle of atoms \(ijk\)
and \(\theta_{ij}, \theta_{jk}, \theta_{ki}\) the internal angles.

The geometric factor \(W\) depends only on the lattice structure, and
any linear interaction can be summed over the lattice independently of
the interaction constant \(Z\). The latter term is a property of the atomic
species concerned and may be obtained from a quantum mechanical calculation
of the complex dynamical polarizabilities, or an experimental determination
of a related quantity: the oscillator strengths of those atoms. The formulation of \( Z \) in terms of the dynamic polarizabilities very conveniently reduces the original many-centred problem to that of a single-centred integral in the complex frequency plane. A simple transformation has been applied directly to the perturbation series, for example Dalgarno (1967), to obtain the single-centred result and this will be described in a later chapter.

Conclusion

The Rayleigh Schrodinger perturbation method is seen to be a reasonable way of examining the long range interactions of spherically neutral atoms and should be particularly suited to examining the long range interactions in rare gas crystals at the absolute zero temperature.

A great simplification is made on considering only linear multipole interactions and any loss of accuracy, albeit small, is more than offset by the computational simplicity of the interaction described in terms of the product of a geometric factor which may be evaluated exactly for a given lattice structure, and an interaction constant which is expressed in terms of the properties of the individual atoms.

Due to the largely self-cancelling nature of the convergent perturbation series for dipole interactions beyond the third-order triple-dipole term, observed by Lucas (1967) and Huller (1971), we felt that to a very good approximation the effects of many body multipole terms in general might be essentially described by considering only the 3-body terms of third-order.

The general formulation of \( W \) has been made by Bell (1970) for all third-order 3-body interactions. In particular we are interested
in the following explicit results, where for convenience we have placed the odd multipole on the third atomic site of a triplet of atoms forming a triangle of sides $R_{12}$, $R_{23}$ and $R_{31}$ with interior angles $\theta_1$, $\theta_2$ and $\theta_3$:

$$W(DDD)_3 = 3R_{12}^{-3}R_{23}^{-3}R_{31}^{-3}(1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3)$$

$$W(DDQ)_3 = \frac{3}{16} R_{12}^{-3}R_{23}^{-4}R_{31}^{-4}[(\cos \theta_3 - 25 \cos 3 \theta_3) + 6 \cos(\theta_1 - \theta_2) \times (3 + 5 \cos 2 \theta_3)]$$

$$W(QQD)_3 = \frac{15}{64} R_{12}^{-5}R_{23}^{-5}R_{31}^{-5}[3(\cos \theta_3 + 5 \cos 3 \theta_3)$$

$$+ 20 \cos(\theta_1 - \theta_2)(1 - 3 \cos 2 \theta_3) + 70 \cos 2(\theta_1 - \theta_2) \cos \theta_3$$

$$W(QQQ)_3 = \frac{15}{128} R_{12}^{-5}R_{23}^{-5}R_{31}^{-5}[-27 + 220 \cos \theta_1 \cos \theta_2 \cos \theta_3$$

$$+ 490 \cos 2 \theta_1 \cos 2 \theta_2 \cos 2 \theta_3 + 175(\cos 2(\theta_1 - \theta_2)$$

$$+ \cos 2(\theta_2 - \theta_3) + \cos 2(\theta_3 - \theta_1))]$$

$$W(DDO)_3 = \frac{5}{32} R_{12}^{-3}R_{23}^{-5}R_{31}^{-5}[9 + 8 \cos 2 \theta_3 - 49 \cos 4 \theta_3$$

$$+ 6 \cos(\theta_1 - \theta_2)(9 \cos \theta_3 + 7 \cos 3 \theta_3)]$$ \hspace{1cm} (1.22)$$

Apart from a numerical factor of three which has been transferred from the $Z$ constant, $W(DDD)_3$ agrees with the result of Axilrod and Teller (1943). However $W(DDQ)_3$ does not agree with Ayres and Tredgold (1956). Our own investigation of $W(DDQ)_3$ agrees with Bell and we believe his general results to be correct.
In the following chapters we shall use the ZW description of the higher order multipole 3-body interactions to evaluate their contribution to the static thermo-elastic properties of the RGC.
The first attempt at formulating the Van der Waals long range interaction was made by Eisenschitz and London (1930). The non-retarded second-order energy between two spherically symmetric ground-state atoms A and B was expressed as a power series of the inverse of the distance R between A and B. The leading term in this expansion is

\[ E(DD)_2 = - \frac{C_{AB}}{R^6} \quad (2.1) \]

where the Van der Waals coefficient \( C_{AB} \) was expressed in terms of the dipole oscillator strengths \( f^A_m \) and \( f^B_m \) by

\[ C_{AB} = \frac{3}{2} \sum \sum f^A_m f^B_m / \varepsilon^A_m \varepsilon^B_m (\varepsilon^A_m + \varepsilon^B_m) \quad (2.2) \]

where \( \varepsilon^A_m \) and \( \varepsilon^B_m \) are the corresponding excitation energies of A and B.

The analogous leading third-order interaction between three atoms A, B and C yields the energy expression

\[ E(DDD)_3 = 3Z(DDD)_3 \frac{(3 \cos \theta_A \cos \theta_B \cos \theta_C + 1)}{(R^A_R^B_R^C)^3} \quad (2.3) \]

where \( \theta_A, \theta_B \) and \( \theta_C \) are the internal angles of the triangle ABC. The triple-dipole interaction coefficient is given by

\[ Z(DDD)_3 = \frac{1}{2} \sum \sum \sum \frac{f^A_m f^B_n f^C_n}{\varepsilon^A_m \varepsilon^B_m \varepsilon^C_n} \cdot \frac{\varepsilon^A_m + \varepsilon^B_m + \varepsilon^C_n}{(\varepsilon^A_m + \varepsilon^B_m)(\varepsilon^B_m + \varepsilon^C_n)(\varepsilon^C_n + \varepsilon^A_m)} \quad (2.4) \]
Since equations (2.2) and (2.4) require the detailed knowledge of all excited states, including those in the continuum, a direct evaluation is very difficult. It has therefore been necessary, in the past, to resort to many different approximate methods to circumvent the problem. See, for example, Margenau and Kestner (1971). The usual approximation made is to assume that the interaction coefficients are dominated by a single oscillator strength. At best these methods can only be expected to give an order of magnitude estimate.

In recent years, active research in the quantitative determination of the interaction coefficients has been stimulated by the development of the semi-empirical methods. The use of these methods has been restricted to the many-dipole interactions i.e. \( C_{AB} \) and \( Z(DDD)_3 \) defined above.

In its simplest form the method substitutes the available theoretical and experimental oscillator strengths into equations (2.2) and (2.4). However, for only very few atomic systems are all the oscillator strengths that contribute significantly to \( C_{AB} \) and \( Z(DDD)_3 \) reliably known. The lack of data can be partly remedied and the accuracy of the data controlled by the use of the oscillator strength sum rules.

Improvements have been made to the semi-empirical method by Bell and Kingston (1966). Their method does not require an explicit oscillator strength distribution. Instead the known oscillator strengths are fitted to an assumed functional which is adjusted so as to reproduce the experimental refractive indices and Verdet constants as well as to satisfy the sum rules. Inaccuracies in the method, as in all the previous methods, arise from the use of uncertain experimental data taken from different frequency regions with differing accuracies.
Despite this however, Bell and Kingston's results for $C_{AB}$ and $Z(DDD)_3$ for the rare gases are believed to be accurate to within 10% and have been widely used in the literature.

An important complication of the methods discussed so far is that they are multi-centred i.e. they involved double or triple summations over the excited states of the two or three atoms involved. Recently, attention has been given to an alternative, though closely related, expression for the multipole interaction coefficients in terms of an integral over the imaginary frequency of products of dynamic polarisabilities $\alpha^j(i\omega)$ of the interacting atoms with multipoles of order $2^j$, i.e.

$$C(L_1L_2)_2 = \frac{(2L_1 + 2L_2)!}{4(2L_1)! (2L_2)!} \cdot \frac{2}{\pi} \int_0^\infty \alpha^{L_1}(i\omega) \alpha^{L_2}(i\omega) \, d\omega \quad (2.5)$$

$$Z(L_1L_2L_3)_3 = \frac{1}{\pi} \int_0^\infty \alpha^{L_1}(i\omega) \alpha^{L_2}(i\omega) \alpha^{L_3}(i\omega) \, d\omega \quad (2.6)$$

The change of notation here to a more general form is obvious. The more familiar dipole-dipole coefficient $C_{AB}$ would be given by $C(11)_2$ or $C(DD)_2$. The simpler form of the three-body coefficient arises from our preference to take the multipole factor into the geometric term $W(L_1L_2L_3)_3$ rather than the $Z(L_1L_2L_3)_3$ term.

The original form for the dipole-dipole coefficient can be regained from (2.5) by the substitution

$$\alpha(i\omega) = \sum_{n=1}^\infty \frac{f_n}{\epsilon_n^{2+} (i\omega)^2} \quad (2.7)$$

and performing the appropriate contour integration in the imaginary
complex plane using the identity relation

\[ \frac{2}{\pi} \int_{0}^{\infty} \frac{ab}{(a^2 + x^2)(b^2 + x^2)} \, dx = \frac{1}{a + b} \]

A similar result follows for \( Z(DDD)_3 \).

Although the formulation of the interaction coefficients by equations (2.5) and (2.6) is exact and has the advantage of being single-centred, a complete knowledge of the dynamic polarisabilities of the atoms is required. It has been usual to adopt a Padé approximant for the polarisability to reduce the infinite sum of equation (2.7) to a finite sum. For example the approximant

\[ \alpha'(i\omega) = \frac{\alpha(0)}{1 + (i\omega/\eta)^2} \]

is fitted to \( \alpha(i\omega) \) at the origin and at infinity. We then have \( \alpha(0) \) as the zero frequency (or static) polarisability and \( \eta = (N/\alpha(0))^{\frac{1}{3}} \) where \( N \) is the number of electrons contributing to the polarisability of the atom concerned.

This approximate method has been most usefully used by Tang (1969, 1971) and Langhoff and Karplus (1970) to obtain bounds on the many-dipole interaction coefficients and provides a check on more rigorous calculations.

In the present context it is important to have not only accurate values for \( Z(DDD)_3 \) for Ne, A, Kr and Xe, but also the three-body coefficients involving the higher order multipoles, i.e. quadrupoles and octupoles as well as dipoles. This necessarily requires accurate \( ab \text{ initio} \) methods since reliable experimental data is available only
for dipole interactions.

Theoretical investigations on the properties of atoms are normally based on the Hartree Fock (HF) approximation in which each electron is assumed to move independently in the spherically averaged potential of the other electrons. To evaluate the Van der Waals coefficients it has become usual to utilise the single-centre method with the approximation of equation (2.8) so that it remains necessary only to calculate the static multipole polarisabilities of the atoms concerned in the interaction. The HF method of calculating polarisabilities is described in detail by Dalgarno (1962) and falls broadly into two classes: the uncoupled HF (UCHF) and the coupled HF (CHF) approximation. The former case corresponds to the second order perturbation result while the latter case includes self-consistency between the perturbed atomic orbitals but neglects important interelectronic correlation effects. Neither method is satisfactory for our purposes. The UCHF approach produces serious overestimates for polarisabilities and the CHF method while being more accurate is very tedious, especially for large atoms, and suffers from the numerical inaccuracies attendant to variational methods.

It follows from the foregoing that a method is required that self-consistently accommodates the effect of the perturbation of a dynamic multipole field on the electronic structure of an atom (as in the CHF method), incorporates the important correlation effects between individual electrons in a physically transparent way and is tractable by reliable numerical methods. For weak dynamic multipole fields, a fast convergent time-dependent perturbation theory taken to sufficient order should satisfy these criteria evaluating directly, as it does, the effect of the perturbation.
A diagrammatic form of the time-dependent Rayleigh-Schrodinger perturbation theory is now described and finally used to evaluate the multipole dynamic polarizabilities and Van der Waals coefficients.

**Time dependent Brueckner Goldstone Perturbation Theory**

A many-body perturbation theory has been developed by Brueckner (1955) and Goldstone (1957) to investigate the properties of infinite nuclear structure and the infinite electron gas i.e. systems involving very large numbers of particles. Kelly (1963), however, has shown that the Brueckner Goldstone (BG) method can be applied with some success to finite systems like atoms, and in particular has investigated the problem of correlation energy and dynamic polarizability of beryllium and oxygen; (see Kelly (1968),(1969)). The BG method has further been extended to calculate various atomic properties of helium, lithium and neon by Chang et al (1968), Dutta et al (1970), (1971) and Matsubara et al (1970). A review of the applications to date is given by Kelly (1971).

The procedure is based upon Rayleigh-Schroedinger perturbation theory using the HF wave-functions as the zeroth order. Using the second quantization formalism one can associate Feynman-like diagrams to various orders of perturbation analogous to quantum electrodynamics. As with any perturbational method the important criterion here is the convergence in terms of orders of perturbation. It has been shown that for all applications to atomic systems made so far the convergence of this perturbation series is satisfactory with a judicious choice of zeroth wave-function.

The perturbational nature of the BG method means that one handles small quantities of the order of the difference between the actual and
HF Hamiltonian directly rather than the small difference of large numbers which occurs in variational methods. Perhaps the greater advantage of the BG method is that it provides a good conceptual picture of the nature of correlation effects. In particular one can utilize the diagrammatic technique to study the relative importance of various physical effects that contribute to the polarizability.

In the present problem we have seen that the calculation of the many-atom Van der Waals coefficients reduces to the evaluation of the linear response function \( \alpha'(i\omega) \) of each atom to an external time dependent electric multipolar field \( F(e^{i\omega t} + e^{-i\omega t}) \). The total Hamiltonian of an \( N \)-electron atom in the presence of this field becomes

\[
H = \sum_{i=1}^{N} T_i + \sum_{i<j}^{N} V_{ij} + H_{\text{ex}}(t) \tag{2.9}
\]

and the total wave-function is given by

\[
H\Psi = E\Psi \tag{2.10}
\]

where \( V_{ij} \) is the potential energy between electrons \( i \) and \( j \), and \( T_i \) is the sum of the kinetic energy operators for the \( i \)th electron and all one-body potentials acting on it. \( H_{\text{ex}}(t) \) is the external perturbation term due to the field.

A great simplification is achieved by splitting \( H \) into the sum of an unperturbed part

\[
H_0 = \sum_{i=1}^{N} (T_i + V_i) \tag{2.11}
\]
where the effect of \(N\) interacting electrons is approximated by a single-particle spherical potential \(V\), plus the perturbation Hamiltonian

\[
H_1 = \sum_{i<j} v_{ij} + H_{\text{ex}}(t) - \sum_{i=1}^{N} V_i
\]  

(2.12)

Since \(V\) is added and then subtracted one has complete freedom in its choice. This provides a method of controlling the convergence of the perturbation series, since \(V\) determines the basis set of zeroth wavefunctions.

In particular one normally chooses \(V\) to be hermitian and generates a complete orthonormal set of single particle orbitals \(\phi_n\) satisfying

\[
(T + V) \phi_n = \epsilon_n \phi_n \tag{2.13}
\]

and

\[
H_0 \phi_0 = E_0 \phi_0 \tag{2.14}
\]

For closed-shell states, \(\phi_0\) is a Slater determinant containing the \(N\) occupied ground-state solutions of equation (2.13) which are lowest in energy. The single-particle states are called unexcited if they are contained in \(\phi_0\) and excited if they are not.

The BG theory utilises the second-quantisation formalism with these single-particle orbitals as the basis states. The equations (2.11) and (2.12) are replaced by

\[
H_0 = \sum_{P} \epsilon_p a_P a_P^+ \tag{2.15}
\]

\[
H_1 = \sum_{pqrs} <pq|v|rs> a_p^+ a_q a_r a_s + \sum_{pq} <p| H_{\text{ex}} |q> a_p^+ a_q - \sum_{pq} <p|V|q> a_p^+ a_q \tag{2.16}
\]
The $a^+$ and $a$ are the usual fermion creation and destruction operators respectively. $\Phi_0$ is the vacuum state and any arbitrary configuration of the system is described by stating its relationship with $\Phi_0$. Vacancies in $\Phi_0$ are called holes and occupied states above $\Phi_0$ are called particles. So $\Phi_0$ is the state with no particles or holes and any other state can be specified by stating which particles and holes are present.

We now develop BG time-dependent perturbation theory in the interaction representation. We assume that the final wave-function $\Psi$ is adiabatically derived from $\Phi_0$ by the perturbation $H_1$ multiplied by $e^{ait}$ where $a$ will be allowed to approach zero. Then we have

$$\Psi(t) = e^{-iH_0 t} U(t) \Phi_0$$  \hspace{1cm} (2.17)

where the evolution operator $U'(t)$ can be written

$$U'(t) = \sum_{n=0}^{\infty} (-i)^n \int_{t_1 > t_2 > \ldots > t_n} H_1(t_1) H_1(t_2) \ldots H_1(t_n) dt_1 dt_2 \ldots dt_n$$

and

$$H_1(t) = e^{iH_0 t} H_1 e^{-iH_0 t} e^{ait}$$ \hspace{1cm} (2.18)

The normalisation is chosen

$$\langle \Phi_0(t) | \Psi(t) \rangle = 1$$

which we obtain by dividing $\Psi$ by $\langle \Phi_0(t) | e^{-iH_0 t} U'(t) | \Phi_0 \rangle$ then

$$\Psi = \lim_{\alpha \to 0} \frac{e^{-iH_0 t} U'(t) \Phi_0}{\langle \Phi_0 | U'(t) | \Phi_0 \rangle}$$  \hspace{1cm} (2.20)
By the use of a theorem due to Wick (1950) \( U_a(t) \phi_0 \) becomes a sum of terms which may be represented by Feynman diagrams. In the graphical method of Goldstone (1957), which we shall adopt here, time is taken to flow upwards on the page. Each \( H_1(t) \) factor in equation (2.18) is called an interaction and is represented by a horizontal dotted line at the time co-ordinate \( t \). The intermediate state at a particular time is represented by drawing solid directed lines which go upwards to represent particles and downwards to represent holes.

Typical Goldstone graphs are shown in figures (2.1)a-c

\[
\begin{align*}
\langle \xi | v | k \rangle a_\xi^+ a_k | \phi_0 \rangle & \quad \langle qn | u | pn \rangle a_q^+ a_n^+ a_p a_n | \phi_0 \rangle & \quad \langle nq | u | pn \rangle a_n^+ a_q^+ a_p a_n | \phi_0 \rangle
\end{align*}
\]

A matrix element \( \langle \xi | v | k \rangle \) is represented in (a). This shows a hole in state \( \phi_\xi \) scattered into a hole state \( \phi_k \). In (b) an electron is scattered from the excited state \( \phi_p \) to the excited state \( \phi_q \) by the interaction \( \langle qn | u | pn \rangle \) with the unexcited state \( \phi_n \) which remains in the same state. An example of an exchange term is given in (c).

Any part of a graph which is completely disconnected from the rest of the graph and which has no external lines attached is called an unlinked part. Diagrams with no unlinked parts are called linked.
diagrams. According to Goldstone (1957), $U_\alpha(t)\phi_0$ may be factorized to become a product of linked terms times the sum of all possible unlinked terms. However, the latter sum is just $\langle \phi_0 | U_\alpha(t) | \phi_0 \rangle$. Hence, by considering only linked diagrams the denominator of equation (2.20) is cancelled. We have then, after performing the time integrations and taking the limit $\alpha \to 0$

$$\Psi = \sum_{n=0}^{\infty} \sum_{m=0}^{L} \exp(-i[E_0 + \omega]t) \left( \frac{1}{E_0 - H_0} H_c \right)^n \times \left( \frac{1}{E_0 - H_0 - \omega} V_{ex} \right) \left( \frac{1}{E_0 - H_0} H_c \right)^m \phi_0 \tag{2.21}$$

where we have summed only over linked diagrams $L$ and we have split the total perturbation $H_1$ into the correlation part

$$H_c = \sum_{i<j}^N u_{ij} - \sum_{i=1}^N V_i \tag{2.22}$$

and the external part, which we allow to only act once,

$$H_{ex}^\pm = V_{ex} \left(2\mathbb{I}\right)_{\pm i\omega t} \tag{2.23}$$

where a $2\mathbb{I}$-pole polarisation of the atom is produced by

$$V_{ex} \left(2\mathbb{I}\right) = F \sum_{i=1}^N r_i p_\lambda (\cos \theta_i) \tag{2.24}$$

$r_i$ being the radial distance of the $i$th electron and $F$ the amplitude of the applied field.

Since we are only interested in the linear response of an atom to $H_{ex}$, we then have in equation (2.21) a single interaction due to $H_{ex}$ and the number of correlation interactions $n + m$ are unrestricted.
The resulting wave-function may be written as $\psi_n^{(2l)}$. It is useful now to consider the total contribution to the energy of the perturbed HF atom from all linked diagrams with two interactions from $H_{ex}$ for the unperturbed but correlated state $\phi_n$, i.e. all correlations to $n$th order are included in $\phi_n$.

$$E^{(2)}_n = \int \sum_l <\phi_n|H_{ex}|\psi_n^{(2l)}>$$

$$= \int \sum_l <\phi_n|V_{ex}(2l)(e^{i\omega t} + e^{-i\omega t})|\psi_n^{(2l)}>$$

But the $2^L$-pole polarizability is defined by

$$\alpha^{(2l)}(\omega) = \frac{<\phi_n|\sum_l r_i P_l(\cos \theta_i)(e^{i\omega t} + e^{-i\omega t})|\psi_n^{(2l)}>}{<\phi_n|\phi_n>}(2.26)$$

This is then equivalent to

$$\alpha^{(2l)}(\omega) r^2 = E^{(2l)}_n$$

(2.27)

Therefore, to calculate the $2^L$-pole polarizability it is necessary only to write down and sum all linked diagrams in which there are two interactions with $V_{ex}^{(2l)}$ and as many correlation interactions as is felt to be necessary, i.e. until a further order of correlation produces no significant change to the polarizability on evaluating the diagrams.

All the necessary diagrams occurring in the $n$th order contribution to the energy $E_n^{(2l)}$ may now be written down following the usual prescription for drawing Goldstone graphs; see for example Day (1967).
The leading diagrammatic contribution to $E_{(2)}$ defined by equation (2.25) is given in figure (2.2). The heavy dot represents an interaction with $H_{\text{ex}}^\pm$. If the bottom interaction is with $H_{\text{ex}}^+$, then the top dot interaction is with $H_{\text{ex}}^-$. There are no correlation interactions at this order. This diagram gives rise to two terms contributing to $\alpha(\omega)$, i.e.

$$
\alpha_0^{(2\ell)}(\omega) = - \sum_{m, k} |<m|r_{\ell}^p(c_0)|k>|^2 |\left(\frac{1}{e_m - e_k - \omega}\right)^{-1} + \left(\frac{1}{e_m - e_k + \omega}\right)^{-1}|
$$

(2.28)

The summation over $k$ implies a regular summation over bound excited states and an integration over the continuum states.

In the present context we wish to calculate the dynamic polarizabilities for complex frequencies. The process of calculating $\alpha(i\omega)$ is exactly identical to that of $\alpha(\omega)$ with only a replacement of $\omega$ by $i\omega$ in all the energy denominators of perturbational expressions like equation (2.28). We then have the result

$$
\alpha_0^{(2\ell)}(i\omega) = - 2 \sum_{m, k} |<m|r_{\ell}^p(c_0)|k>|^2 \frac{e_m - e_k}{(e_m - e_k)^2 + \omega^2} 
$$

(2.29)

This lowest order contribution to $\alpha(i\omega)$ is equivalent to the UCHF result.

To include the self-consistency effects of a CHF scheme we go to the third-order diagrams of figure (2.3 a,b) and obtain the explicit results for (a) and (b) respectively

$$
\alpha_1^{(2\ell)}(i\omega)_a =
$$

$$
- 2 \sum_{mm', kk'} |<m|r_{\ell}^p(c_0)|k'><kk'|r_{12}^{-1}|mm'九龙>r_{\ell}^p(c_0)|m'>| \\
\times \frac{(e_m - e_k')(e_m - e_k') - \omega^2}{[(e_m - e_k')^2 + \omega^2][(e_m - e_k')^2 + \omega^2]} 
$$

(2.30)
\[ \alpha_1^{(2\ell)}(i\omega)_b = \]
\[ \sum_{mm'kk'} \langle m' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | k' > \langle m' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | k > \langle k' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | m' > \rangle \]
\[ \times \frac{(\varepsilon_m - \varepsilon_k)(\varepsilon_{m'} - \varepsilon_{k'}) - \omega^2}{[(\varepsilon_m - \varepsilon_k)^2 + \omega^2][(\varepsilon_{m'} - \varepsilon_{k'})^2 + \omega^2]} \quad (2.31) \]

The remaining correlation diagrams in third order are typified in figure (2.3 c,d) and are given explicitly by

\[ \alpha_1^{(2\ell)}(i\omega)_c = \]
\[ -2 \sum_{mm'kk'} \langle m | r \frac{\partial}{\partial \rho_y} (\cos \theta) | k' > \langle m' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | k > \langle k' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | m' > \rangle \]
\[ \times \frac{\varepsilon_m - \varepsilon_k}{(\varepsilon_m - \varepsilon_k + \varepsilon_{m'} - \varepsilon_{k'})[(\varepsilon_m - \varepsilon_k)^2 + \omega^2]} \quad (2.32) \]

and the exchange term

\[ \alpha_1^{(2\ell)}(i\omega)_d = \]
\[ 2 \sum_{mm'kk'} \langle m | r \frac{\partial}{\partial \rho_y} (\cos \theta) | k' > \langle m' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | k > \langle k' | r \frac{\partial}{\partial \rho_y} (\cos \theta) | m' > \rangle \]
\[ \times \frac{\varepsilon_m - \varepsilon_{k'}}{(\varepsilon_m + \varepsilon_{m'} - \varepsilon_k - \varepsilon_{k'})[(\varepsilon_m - \varepsilon_{k'})^2 + \omega^2]} \quad (2.33) \]

The HF single-particle energies are further modified in fourth order by the diagrams of figure (2.4 a-n). These diagrams introduce
second order correlation effects and are not included in a CHF calculation. If the sum of the contributions from these diagrams and even higher orders is large compared with the contribution of figures (2.2) and (2.3), then the BG perturbation theory is of doubtful use.

Certain higher order diagrams may often be summed to infinite order with no extra computational effort. For example the 4th order diagram (2.4 n) can be obtained from the diagram (2.3 a) by multiplying by a factor

\[ \frac{\langle k m' | r_{12}^{-1} | m k' \rangle}{(e_m + e_{m'} - e_k - e_{k'})} \]

Therefore the sum of all analogous diagrams to infinite order is obtained by multiplying the diagram (2.3 a) by the geometric series

\[ G(km' mk) = 1 + \frac{\langle k m' | r_{12}^{-1} | m k' \rangle}{(e_m + e_{m'} - e_k - e_{k'})} + \ldots \]

i.e.

\[ G(km' mk) = \left[ 1 - \frac{\langle k m' | r_{12}^{-1} | m k' \rangle}{(e_m + e_{m'} - e_k - e_{k'})} \right]^{-1} \]  \hspace{1cm} (2.34)

In practice one picks only the important correlations in figure (2.3) and sums them to infinity by multiplying by the appropriate factor \( G(km' mk) \).

**Single-Particle States and Evaluation of Diagrams**

In drawing the diagrams the initial single particle potential \( V \) is usually taken to be the HF potential \( V_{HF} \) and thus does not appear explicitly since to first order the energy of an atom is just the HF energy. Therefore the first-order correction is zero for \( V = V_{HF} \) and...
consequently the corresponding single-particle diagrams vanish. \( V_{HF} \) has the added advantage that for the rare-gas atoms in particular all the excited HF states lie in the continuum so that the sum over all the excited states appearing in the polarizability calculations just become integrals over k-space where \( E_k = k^2/2 \) is the energy of a particular continuum state. However, Kelly (1964) has demonstrated that \( V_{HF} \) does not produce a fast convergent perturbation series since it generates physically unrealistic excited states.

When we adopt the HF potential, the single-particle states are determined in the usual way (see e.g. Slater (1960)) by

\[
\begin{align*}
- \frac{\nabla^2}{2} \phi_n(r) &+ \frac{Z}{r} \phi_n(r) + \sum_{j=1}^{N} \int dr' \frac{\phi_j^*(r') \phi_j(r')}{|r - r'|} \phi_n(r) \\
- \sum_{j=1}^{N} \delta(m_s, m_{s_j}) \int dr' \frac{\phi_j^*(r') \phi_n(r')}{|r - r'|} \phi_j(r) = \epsilon_n \phi_n(r)
\end{align*}
\]

The unexcited states \((n \leq N)\) are calculated in the potential field of the nucleus and \(N-1\) other electrons because the direct and exchange terms in equation (2.35) cancel when \(j = n\) i.e. there is no self energy error. However, for the excited states \((n > N)\) generated by equation (2.35) there is no such cancellation and so the excited states are calculated in the field of the nucleus and \(N\) other electrons. Since excited electrons actually interact with \(N-1\) other electrons the \( V_{HF} \) generates a basis set of excited states which are not a good approximation to the real excited states and poor convergence is obtained in the perturbation series of equation (2.26). For example diagrams like figure (2.3 b) with \(m = m'\) occur when \( V_{HF} \) is used and are found to be large even though the true correlation effects are small.
To overcome these problems we follow the suggestion of Kelly (1964) to calculate all single-particle states in the HF field of the atom minus one of the outer electrons i.e. the potential $V_{HF}^{N-1}$. This potential may be chosen such that the corresponding outer unexcited states are HF states while the inner states are very closely approximated HF states. Errors arising from incomplete cancellation of the unexcited states with the single-particle potential $V_{HF}^{N-1}$ are corrected by the diagrams of figure (2.5) plus the corresponding exchange diagrams.

\[ \text{fig. (2.5)} \]

In this way we have generated a complete set of physically realistic basis states both excited and unexcited, all calculated in the field of the nucleus and N-1 electrons.

We are still left with a choice of which $V_{HF}^{N-1}$ to use depending upon which outer electron is removed in calculating the outer states from equation (2.35). This flexibility is utilised to the full in this calculation where the choice is made to make the more important transition matrix elements as accurate as possible. For example in the rare-gas atoms of ground-state outer electronic configuration $n(s^2p^6)$, $n \geq 2$, the important dipole transitions are np $\rightarrow$ md, $m \geq n$; so we choose $V_{HF}^{N-1}$ by calculating the excited d-states in the $V_{HF}$ field minus an np electron.

The use of a $V_{HF}^{N-1}$ potential has the complication that as well
as producing continuum excited states there is also an infinite set of bound excited states which must be summed individually. Kelly (1964) has developed a method for summing these states to infinity. The sums are carried out for a number, typically about ten, of the lowest excited bound states and then extrapolated to infinity by using the approximate result

\[ \lim_{n \to \infty} n^3 |<mn|u|ab>|^2 = \text{constant} \ C \] (2.36)

This result has been carefully checked numerically by Kelly (1964) and it is justified by an analysis of hydrogen-like atoms of large principal quantum number (see Kelly 1964). In practice we calculate about ten matrix elements then use equation (2.36) to go from \( n = 10 \) to \( n = N_f \) where \( N_f \) is typically about 20, and approximate the remainder by

\[ C \int_{N_f+1}^{\infty} n^{-3} dn = C/[2(N_f + 1)^2] \] (2.37)

The single-particle bound states, solutions of the HF \( N-1 \) equation (2.35), are square integrable and normalised to unity in the usual manner. Continuum states are labelled \( k, \ell, m, m_s \) where \( \epsilon = k^2/2 \) in equation (2.35) and have to be normalised in a different way by choosing them to have the usual asymptotic form for coulomb functions, i.e. we assume that the atom is enclosed in a large spherical volume of radius \( R_0 \) which tends to infinity. The asymptotic form of the radial wavefunction is

\[ \lim_{r \to \infty} R(k, \ell; r) = \cos[kr + \ell \pi/2] e^{-\kappa r} \] (2.38)
where \( V = q/r \) as \( r \to \infty \)

The normalisation factor for \( R \) of equation (2.38) is \((2/R_0)^{1/2}k\). Also, since \( R \) must vanish at the cut off \( r = R_0 \) we have,

\[
kR_0 + \delta_{\lambda+1} (q/k) \ln 2kR_0 - \frac{1}{2}(\lambda+1)\pi = (n+\frac{1}{2})\pi
\]  

(2.39)

where \( n \) is some integer. In the limit \( R_0 \to \infty \)

\[
\Delta n = (R_0/\pi)\Delta k \quad \text{and} \quad \sum_k n = (R_0/\pi) \int_0^\infty dk
\]

In calculating any observable, each single-particle state occurs twice and by dropping the normalisation factor \((2/R_0)^{1/2}\) from \( R(\lambda; r) \) we may replace \( \sum_k \) by \((2/R_0)^{1/2}\) \( \int_0^\infty dk \) and carry-out the \( k \)-integration for each set of \((\lambda, m, m_s)\) appearing in the diagrams.

With the techniques outlined above we can now generate a basis set of wave-functions, evaluate the diagrams in question, and find the multipole polarizabilities and hence the two and three-body Van der Waals coefficients.

Results and Discussion

We generated the basis sets of wave functions for all the rare gas atoms by a modified version of the Herman-Skillman (1963) computer program. The resulting wave functions are briefly called HSHFS (wave functions) since the HF equation (2.35) is solved self-consistently on replacing the exchange part of the HF potential by an averaged exchange potential due to Slater (1951) and modifying the resulting potential to have the correct behaviour at large distances. The HSHFS wave functions have been investigated extensively for a wide range of
atoms and are found to follow closely the exact HF wave-functions for those atoms for which HF wave-functions are available and predict the one-electron energies of atoms well beyond Xenon with good accuracy. For heavy atoms relativistic effects become significant for their innermost orbitals. No correction is made for this in the present calculations since we assume that only the outer orbitals are effectively polarized and contribute to the polarizability of the rare gas atoms.

The Herman-Skillman program was readily adapted to calculate bound and continuum excited states for a range of \( n \) and \( k \) values respectively. The HSHFS potential was modified to the particular \( V_{N-1}^{\text{HSHFS}} \) of our choice appropriate to the multipole polarization under consideration. The ground state radial wave-functions were checked against the usual \( V_{\text{HSHFS}} \) wave-functions and corresponded accurately for the orbital minus an electron, but differed slightly - as expected - for the inner orbitals. The excited states were thus retained and \( V_{\text{HSHFS}} \) ground state orbitals were subsequently used rather than diagrammatically correcting the \( N-1 \) orbitals. The continuum wave-functions were generated by a straightforward integration of equation (2.35) for positive energy values \( \varepsilon = \frac{1}{2} k^2 \). These functions were normalized by applying the result of equation (2.39).

In evaluating the diagrams, the continuum basis states have to cover the range \( k=0 \) to \( \infty \). This entire range is effectively included by the use of the Gauss-Laguerre quadrature method which also reduces the computing time significantly. In summing over bound states, for Neon, the ten lowest states for each angular momentum \( \ell \) were included explicitly and the contributions from the rest were included by the \( n^{-3/2} \) approximation of equation (2.36). For the heavier rare gas atoms it was necessary to increase \( n \) (the explicit summation) progressively for consistent accuracy.
Some exploratory calculations found that matrix elements corresponding to the closed shell core electrons were very small indicating that the core is hardly polarized at all by the external field. This fact plus the small degree of correlation between the outer (ns, mp) electrons and the core electrons led us to make the approximation that the polarizability of the rare gas atoms is due only to the outer (ns, mp) electrons and we can restrict subsequent computations to matrix elements involving only these electrons. This greatly simplifies the present calculations.

In general we found that correlation effects among the (mp) electrons were much more important than those among (ns) electrons or between (ns) and (mp) electrons. This is probably due to the fact that there is stronger overlap between p orbitals than between p and s or s and s orbitals.

A separate evaluation of the $\nabla_{\text{HHFS}}^{N-1}$ correction diagrams of fig. (2.5) found their contribution to be very small and were therefore left out of the calculations.

Particular excitation modes were found to be dominant for particular multipole fields; e.g. the major contribution to the dipole polarizability came from (mp) + $\ell$=2 states and $\ell$=0 states in order of importance. It was found that excitations into the continuum rather than to excitation bound states contributed by far the largest contribution to the polarizability. This gives a clue as to the inaccuracies of previous variational polarizability calculations where the trial functions adopted underestimated the contribution from the continuum states.
The important modes of excitation were pursued into fourth order
(second order in correlation) by the inclusion of the diagrams of
fig. (2.4). Also, repetitive diagrams like that of fig. (2.3a) were
summed to infinite order by the use of equation (2.34). The fourth
and higher order corrections were found to be small indicating a
strongly convergent perturbation series.

For the rare gas atoms Ne, A, Kr and Xe, the dipole, quadru-
pole and octupole dynamic polarizabilities were evaluated for an
adequate range of frequencies in the complex frequency plane. These
proved to be monotonically decreasing functions with increasing
frequency. For the purpose of comparison with existing theoretical
results our static (zero frequency) multipole polarizabilities are
presented in table (2.1) along with representative results (where
available) for the previous methods mentioned above.

We see immediately from table (2.1) that restriction to the
lowest order perturbation diagram of fig. (2.2), which corresponds to
the UCHF approximation, seriously overestimates the static polarizability
because of the choice of $V_{HF}^p$ and the neglect of correlation. Agree-
ment between the UCHF results and ours is noticeably better for the
heavier atoms in the case of the quadrupole polarizability. This is
presumably because the correlation modes for the rare gas atom (ns,mp)
configuration correspond to the important dipole excitation modes
but do not do so in the quadrupole case.

The CHF results somewhat underestimate the polarizability.
This arises through the choice of $V_{HF}^p$ and neglect of higher order
correlation diagrams included in the BG method.
Table (2.1) - The Static Multipole Polarizabilities for Ne, A, Kr and Xe
(atomic units)

<table>
<thead>
<tr>
<th></th>
<th>UCHF</th>
<th>CHF</th>
<th>PRESENT WORK</th>
<th>EXPT</th>
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</thead>
<tbody>
<tr>
<td>NEON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_D(0)$</td>
<td>2.809$^a$</td>
<td>2.362$^c$</td>
<td>2.603</td>
<td>2.672$^d$</td>
</tr>
<tr>
<td>$\alpha_Q(0)$</td>
<td>7.117$^a$</td>
<td>6.459$^c$</td>
<td>6.416</td>
<td></td>
</tr>
<tr>
<td>$\alpha_O(0)$</td>
<td>33.919$^b$</td>
<td>-</td>
<td>30.367</td>
<td></td>
</tr>
<tr>
<td>ARGON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_D(0)$</td>
<td>15.137$^a$</td>
<td>10.076$^c$</td>
<td>10.983</td>
<td>11.108$^d$</td>
</tr>
<tr>
<td>$\alpha_Q(0)$</td>
<td>49.189$^a$</td>
<td>47.164$^c$</td>
<td>48.237</td>
<td></td>
</tr>
<tr>
<td>$\alpha_O(0)$</td>
<td>523.025$^b$</td>
<td>-</td>
<td>449.720</td>
<td></td>
</tr>
<tr>
<td>KRYPTON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_D(0)$</td>
<td>23.505$^a$</td>
<td>-</td>
<td>16.634</td>
<td>16.776$^d$</td>
</tr>
<tr>
<td>$\alpha_Q(0)$</td>
<td>90.955$^a$</td>
<td>-</td>
<td>78.762</td>
<td></td>
</tr>
<tr>
<td>$\alpha_O(0)$</td>
<td>-</td>
<td>-</td>
<td>681.379</td>
<td></td>
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<tr>
<td>XENON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_D(0)$</td>
<td>40.559$^a$</td>
<td>-</td>
<td>26.847</td>
<td>27.324$^d$</td>
</tr>
<tr>
<td>$\alpha_Q(0)$</td>
<td>197.430$^a$</td>
<td>-</td>
<td>128.255</td>
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<tr>
<td>$\alpha_O(0)$</td>
<td>-</td>
<td>-</td>
<td>1104.76</td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES:

a Feiock F.D. and Johnson W.R. (1969)
b Langhoff P.W. and Hurst R.P. (1965); Phys. Rev. A139 1415
c Lahiri J. and Muckherji A. (1966); Phys. Rev. 141 428
   (1967); 153 386
   (1967); 155 24
The agreement between our results for the static dipole polarizability and the experimental results justified our choice of the $V_{\text{HSFPS}}$ potential which gave a strongly convergent perturbation series. The only previously published BG result is for Neon and is due to Matsubara et al (1970) who obtain a value of 2.672 a.n. for the static dipole polarizability. The difference between our result and theirs is probably due mainly to their inclusion of inner core correlation and polarization effects.

The required Van der Waals coefficients were obtained by numerical integration over the frequency in equations (2.5) and (2.6). The results are presented in tables (2.2) and (2.3). Comparison is made between our results and those of previous methods in table (2.4).

The semi-empirical results of Bell and Kingston (1966) have been regarded as the most reliable for C(DD)$_2$ and Z(DDD)$_3$ with an expected accuracy of better than 10% in all cases except possibly for Xenon. In fact our results do agree to this accuracy except for the triple-dipole coefficient of Xenon. Tighter theoretical bounds are provided by the continued factorization method of Tang (1971). Again our results agree very well except for Xenon where there is an inexplicably large discrepancy both for C(DD)$_2$ and Z(DDD)$_3$. This discrepancy did not exist in the earlier Padé approximant results of Tang (1969) for Xenon. Good agreement is again obtained with the BG calculation on Neon by Dutta (1971).

The good general agreement between our results and those for which data is available gives us confidence in our results for the other high order multipole Van der Waals coefficients.
### Table (2.2) - Two-Body Van der Waals Coefficients (atomic units)

<table>
<thead>
<tr>
<th>COEFFICIENT</th>
<th>COEFFICIENTS</th>
<th>NEON</th>
<th>ARGON</th>
<th>KRYPTON</th>
<th>XENON</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(DD)$_2$</td>
<td>C(DQ)$_2$</td>
<td>C(QQ)$_2$</td>
<td>C(DO)$_2$</td>
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</tr>
<tr>
<td>NEON</td>
<td>6.882</td>
<td>73.87</td>
<td>379.68</td>
<td>585.36</td>
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<tr>
<td>ARGON</td>
<td>66.89</td>
<td>1176.4</td>
<td>10180</td>
<td>19116.9</td>
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<tr>
<td>KRYPTON</td>
<td>135.11</td>
<td>2580.9</td>
<td>24275</td>
<td>41191</td>
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<tr>
<td>XENON</td>
<td>281.15</td>
<td>7033.5</td>
<td>83101</td>
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### Table (2.3) - Three-Body Van der Waals Coefficients (atomic units)

<table>
<thead>
<tr>
<th>COEFFICIENT</th>
<th>COEFFICIENTS</th>
<th>NEON</th>
<th>ARGON</th>
<th>KRYPTON</th>
<th>XENON</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Z(DDD)$_3$</td>
<td>Z(DDQ)$_3$</td>
<td>Z(QQQ)$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NEON</td>
<td>4.330</td>
<td>9.838</td>
<td>42.574</td>
<td>43.045</td>
<td>52.201</td>
</tr>
<tr>
<td>ARGON</td>
<td>176.74</td>
<td>675.77</td>
<td>2643.7</td>
<td>5988</td>
<td>10522</td>
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<tr>
<td>KRYPTON</td>
<td>537.48</td>
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<td>1809.4</td>
<td>9052</td>
<td>45409</td>
<td>92480</td>
<td>228389</td>
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### Table (2.4) - Comparison of Results

<table>
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<tr>
<th></th>
<th>SEMI-EMPIRICAL$^a$</th>
<th>CONTINUED FACTORIZATION$^b$</th>
<th>BG$^c$</th>
<th>PRESENT WORK</th>
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<tbody>
<tr>
<td>NEON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(DD)$_2$</td>
<td>6.35</td>
<td>6.94 ± 0.45</td>
<td>6.925</td>
<td>6.882</td>
</tr>
<tr>
<td>Z(DDD)$_3$</td>
<td>3.95</td>
<td>4.27 ± 1.7</td>
<td>4.347</td>
<td>4.330</td>
</tr>
<tr>
<td>ARGON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(DD)$_2$</td>
<td>65.3</td>
<td>68.3 ± 5.0</td>
<td>-</td>
<td>66.89</td>
</tr>
<tr>
<td>Z(DDD)$_3$</td>
<td>175.2</td>
<td>178 ± 6.0</td>
<td>-</td>
<td>176.74</td>
</tr>
<tr>
<td>KRYPTON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(DD)$_2$</td>
<td>130.35</td>
<td>138 ± 14.0</td>
<td>-</td>
<td>135.11</td>
</tr>
<tr>
<td>Z(DDD)$_3$</td>
<td>526.2</td>
<td>533.3 ± 23</td>
<td>-</td>
<td>537.48</td>
</tr>
<tr>
<td>XENON</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(DD)$_2$</td>
<td>268.25</td>
<td>414 ± 52.0</td>
<td>-</td>
<td>281.15</td>
</tr>
<tr>
<td>Z(DDD)$_3$</td>
<td>1761.7</td>
<td>2490 ± 183</td>
<td>-</td>
<td>1809.4</td>
</tr>
</tbody>
</table>

--

$^a$ Bell and Kingston (1966)  
$^b$ Tang (1971)  
$^c$ Dutta et al (1971)
CHAPTER 3

The Contribution of the Higher Order Multipole 3-body Van Der Waals Interactions to the Static Lattice Energy and Zero Point Energy of the RGC at the Absolute Zero

INTRODUCTION

Any attempt to calculate the binding energy of the RGC inevitably involves some consideration of their stability. The rare gases Ne, A, Kr and Xe solidify in face-centred cubic (FCC) lattices, but any reasonable pair potential for these materials leads to a lower energy and hence a greater stability for the hexagonal-close-packed (HCP) lattice. Explanations for this discrepancy between theory and experiment have a long history and are summarised for example by Jansen (1965). It would appear that any adequate explanation for FCC stability, by including an interatomic potential in addition to the pair potential, should satisfy two \textit{a priori} conditions:

1. The potential must be structure-sensitive i.e. it should emphasise the angular relationships between atoms in the FCC and HCP lattices.

2. The correction to the energy calculated on the basis of the pair potential must be large enough to overcome the existing stability barrier (typically about 0.01%) between the two structures by at least an order of magnitude.

This point has been discussed in some detail by Barron and Domb (1955) who concluded that the only plausible theoretical explanation was that many-body forces must be present in the RGC but they did not do any calculation on these forces. Certainly a consideration of many-body
forces shows that they satisfy the first of the criteria above, i.e. the many-body forces are structure-sensitive. To illustrate this we consider a central atom in the HCP and FCC structures and its 12 nearest neighbours. As far as pair-interactions are concerned the immediate neighbourhood of the atom in the two structures is, therefore, identical. Now consider all possible triplets of atoms formed by the central atom and any two of its twelve nearest neighbours. There are 66 such triplets in either structure; upon inspection it appears that 57 triplets in either structure are identical but 9 are different. From this we see that the two structures are already different for nearest neighbours if we consider triplet configurations. This example also illustrates the dramatic increases in the number of interactions to be considered in any finite summation of many-body interactions as, for example, going from pair-interaction to triplet-interaction.

The short-range, non additive 3-body interaction due to the electron exchange interaction of triplets of atoms was investigated by Jansen (1963) and (1964) and his collaborators on the basis of the Gaussian model for the charge distribution in the atom. The results of this investigation are of doubtful value. Graben et al (1966) found in their calculations of the third virial coefficient that Jansen's choice of $\beta$, the width parameter in the Gaussian charge distribution for a given atom, was far too large. Bullough et al (1966) performed calculations on the stacking fault energy of solid argon and found this to be 1/15th of the value given by Jansen and Zimering (1963). It has been pointed out by Swenberg (1967) that a more realistic choice of the value for $\beta$ would make the first-order 3-body exchange energy negligible. Finally, Present (1967) has determined the non-additive overlap energy of interaction between three atoms using the Thomas-Fermi-Dirac
approximation. He found that for Krypton, at a nuclear separation equal to the Van der Waals minimum, this energy correction was much smaller than Jansen's estimate and could certainly not explain the structure of solid Krypton.

Because of this uncertainty in the importance of short range many-body interaction we shall neglect this effect here. The stability problem was studied for long-range many-body Van der Waals interactions firstly by Axilrod (1951). He restricted his attention to the triple-dipole interaction of Axilrod and Teller (1943) and found, on the basis of this potential alone, the relative difference for the two lattices was 0.07% for a direct summation of triplets out to about four nearest neighbours distances. This difference favoured the FCC lattice but was somewhat too small to compensate the difference in two-body energy.

It should be noted that since the many-body interactions may each be written as the product of a purely geometric factor $W(l_1^{1/3}l_2^{1/3}l_3^{1/3})_3$ and an interaction constant $Z(l_1^{1/3}l_2^{1/3}l_3^{1/3})_3$, then the relative stability of the two lattice structures is calculated independently of the interaction constant. The geometric factor and hence the relative stability depends solely on the positions of the interacting atoms and may be established exactly. The Axilrod calculation has been repeated by Chell and Zucker (1968) and Huller (1971a). They found that his result for the relative $(DDD)_3$ stability was too large by a factor of 2.5 due to an error in his summation procedure. It was also demonstrated that because of the slow convergence of the summation, it was necessary to extend the range of summation beyond 4 nearest neighbour distances. A further improvement to the result of Chell and Zucker (1968) is reported in this chapter.

As mentioned in chapter 1 calculation of the many-dipole
contribution to the binding energy of the RGC has been summed to infinite order by Lucas (1967) and with greater accuracy by Huller. To achieve this result they use the Drude model as outlined by Badé (1957) where each atom of a RGC is replaced by an isotropic harmonic oscillator interacting via dipole-dipole forces. They found that the diminishing contributions from higher-order dipole terms alternate in sign and the resulting cancellations lead to only a small net effect in addition to the effect of the third order triple dipole term. Thus to a very good approximation this latter term is all that need be considered when dealing with many-body dipole interactions.

This leads us to consider whether higher order multipole 3-body terms of third order might be sufficient to describe all the effects of many-body multipole terms in general.

In this chapter we investigate the effects of \((DDD)_3\), \((DDQ)_3\), \((DQQ)_3\), \((DDO)_3\) and \((QQQ)_3\) on the binding energy of the RGC and hence the stability of the FCC and HCP structures and also the harmonic zero-point energy (ZPE) of the RGC.

**Static Lattice Energy**

In order to calculate the contribution of the factors \(\mathbf{I}_1\mathbf{I}_2\mathbf{I}_3\), given explicitly in chapter 1, to the lattice energy of a crystal of \(N\) atoms, all the triplet interactions of \(N\) atoms forming a given structure must be computed. Each geometric factor \(W(\mathbf{I}_1\mathbf{I}_2\mathbf{I}_3)\) thus has to be evaluated for every distinct triplet formed by the complete structure and added together. It was decided to adopt a different summation procedure to that of Chell and Zucker (1968). They summed \(W(DDD)_3\) over all the atoms inside cubes of increasing size out to a maximum
cube size of side 24a. They then extrapolated the result to the
infinite crystal.

We found that some improvement to convergence and to the extra­
polation could be achieved by summing out in spheres. This was done
by making one of the atoms the origin of a co-ordinate system. The
other two atoms were summed over spheres increasing in size by nearest
neighbour increments. The final lattice energy contribution is expressed
in terms of the half side 'a' of a unit cube in the close packed lattice
which is equal to $R_0/\sqrt{2}$ where $R_0$ is the nearest neighbour distance. The
pure numbers $T_0$ thus obtained were characteristic of the lattice and are
formally written in a slightly modified form

$$T_0 = \sum_{i \neq j} W(R_{ij}, R_{jk}, R_{ki}) \, a^{(p+3)}$$

$$p = 2Z_1 + 2Z_2 + 2Z_3$$

where $W(R_{ij}, R_{jk}, R_{ki})$ is the general 3-multipole geometric factor $W(\ell_1, \ell_2, \ell_3)$
for a triangle of sides $R_{ij}, R_{ik},$ and $R_{ki}$ with atoms at its vertices.
We have taken the kth atom as origin.

The summation $T_0$ was performed by computer. The number of triplets
to be summed increases dramatically with increasing radius: 9 million
triplets for a sphere of radius of $9R_0$, a range felt to be necessary
for the slowly convergent $W(DDD)_3$. To overcome, in some measure, the
time consuming number-crunching nature of this problem, the intrinsic
symmetry of the FCC and HCP lattices was taken into account in the
computer program. In effect only non-identical triplets were identified
and evaluated, and then were multiplied by their multiplicity factor.
The slowly convergent nature of $T_0$ for triple-dipole interaction in the
FCC and HCP lattices is demonstrated in table (3.1). There the values of $T_0$ for the FCC and HCP lattices are given together with the number of triplets evaluated as the summation was extended from first to sixth nearest neighbours. The inadequacy of summing to only nearest or next nearest neighbours in three-body terms is well illustrated. For the purposes of comparing $T_0$ for the FCC and HCP lattices we shall restrict the summation to $6R_0$ except in the case of $W(DDD)_3$ where the sum to infinity was estimated by integration after $6R_0$ by a procedure described later in chapter 5. The results are given in table (3.2).

The total lattice energy $E(l_1Z Z Z_3)$ of a crystal of $N$ atoms may be written in the general form

$$E = \frac{1}{3} cNZT_0 a^{-(p+3)}$$

(3.2)

where

$$\begin{cases} 
\sigma = 1 & \text{if } l_1 = l_2 = l_3 \\
\sigma = 3 & \text{if } l_1, l_2, l_3 \neq 0\
\end{cases}$$

Now in all the cases considered here at least two of the atoms carried the same multipole. In performing the summation the odd atoms were always made the origin. In eq.(3.2) atom 3 is placed at the origin. By allowing the other identical multipoles to take any lattice position all nonidentical triplets would be counted twice. The final result should therefore be divided by two, and in giving the values in table 3.2 this has in fact already been done, and in eq.(3.2) we then have $\sigma = 3$. But if all three atoms carried the same multipole all nonidentical triplets would be counted sixfold. In this case we put $\sigma = 1$ in eq.(3.2), and therefore effectively divide the sums by a further factor three.
It will be observed from table (3.2) that $T_0$ for the FCC lattice is always less than that for the HCP lattice. Now since the interaction constant $Z(Z_2, Z_3)_{3}$ is positive, all the terms $E(Z_1, Z_2, Z_3)_{3}$ contribute a repulsive energy to the net binding energy. The repulsive energy contributed by these terms in a FCC structure is less than in an HCP structure, and with these terms alone the FCC structure would be more stable. Axilrod (1951) had already deduced this, albeit inaccurately, for $(DDD)_3$ alone. But for $(DDQ)_3$, Ayres and Tredgold (1956) showed from their expression that the HCP structure was very much more stable. Thus there is conflict both with Ayres and Tredgold's explicit expression for $(DDQ)_3$ and their deduction concerning the relative stability of the two close-packed structures.

It should be noted that the difference between the FCC and HCP lattice energy contribution of table (3.2) are in the third or fourth significant figures with one exception: $E(DDO)_3$. In this case $E(DDO)_3$ is smaller for the FCC than the HCP structure by more than 1%. The significance of this with regard to the overall stability problem must be examined by evaluating the absolute value of $E(DDO)_3$. This result is to be found in table (3.4) where the absolute values of all the various factors $E(Z_1, Z_2, Z_3)_{3}$ contributing to the energy of a crystal of $N$ atoms at the absolute zero are presented. The only experimentally measurable quantity, $H_0$, the heat of sublimation at the absolute zero, is also given for comparison. For convenience we reproduce here, in table (3.3) the values of $E(Z_1, Z_2, Z_3)_{3}$ transposed from table (2.3) with a change from atomic units to the more conventionally acceptable SI units. The experimental values of 'a' are taken from Glyde (1970) and are presented in Chapter Four.
### Table (3.1) - Convergence of $T_0$ for the Triple-Dipole Interaction

<table>
<thead>
<tr>
<th>DISTANCE</th>
<th>$1R_0$</th>
<th>$2R_0$</th>
<th>$3R_0$</th>
<th>$4R_0$</th>
<th>$5R_0$</th>
<th>$6R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FCC Triplets</strong></td>
<td>66</td>
<td>1431</td>
<td>15400</td>
<td>72010</td>
<td>292995</td>
<td>828828</td>
</tr>
<tr>
<td>$W(DDD)_3$</td>
<td>4.6622</td>
<td>7.0092</td>
<td>7.4568</td>
<td>7.5524</td>
<td>7.5911</td>
<td>7.6071</td>
</tr>
<tr>
<td><strong>HCP Triplets</strong></td>
<td>66</td>
<td>1540</td>
<td>12403</td>
<td>75078</td>
<td>289941</td>
<td>793170</td>
</tr>
<tr>
<td>$W(DDD)_3$</td>
<td>4.6649</td>
<td>7.0690</td>
<td>7.4377</td>
<td>7.5548</td>
<td>7.5932</td>
<td>7.6086</td>
</tr>
</tbody>
</table>

### Table (3.2) - $T_0$ for the General Three-Body interactions $(l_1l_2l_3)_3$

<table>
<thead>
<tr>
<th>INTERACTION</th>
<th>$W(DDD)_3$</th>
<th>$W(DDQ)_3$</th>
<th>$W(DQQ)_3$</th>
<th>$W(QQQ)_3$</th>
<th>$W(DDO)_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FCC</strong></td>
<td>7.6286</td>
<td>4.1029</td>
<td>4.6987</td>
<td>7.2314</td>
<td>1.0692</td>
</tr>
<tr>
<td><strong>HCP</strong></td>
<td>7.6301</td>
<td>4.1061</td>
<td>4.7045</td>
<td>7.2416</td>
<td>1.0814</td>
</tr>
</tbody>
</table>
### Table (3.3) - Three-Body Interaction Constants

<table>
<thead>
<tr>
<th>INTERACTION</th>
<th>Z(DDD)₃</th>
<th>Z(DDQ)₃</th>
<th>Z(DQQ)₃</th>
<th>Z(QQQ)₃</th>
<th>Z(DDO)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEON</td>
<td>6.1360</td>
<td>3.9001</td>
<td>2.5059</td>
<td>1.6228</td>
<td>4.7760</td>
</tr>
<tr>
<td>ARGON</td>
<td>250.47</td>
<td>267.90</td>
<td>293.47</td>
<td>327.12</td>
<td>664.48</td>
</tr>
<tr>
<td>KRYPTON</td>
<td>761.72</td>
<td>886.77</td>
<td>1054.4</td>
<td>1273.6</td>
<td>2128.6</td>
</tr>
<tr>
<td>XENON</td>
<td>2564.3</td>
<td>3589.1</td>
<td>5040.7</td>
<td>7100.2</td>
<td>10261.9</td>
</tr>
</tbody>
</table>

**UNITS:** \( J \times 10^{-10} \) \( J \times 10^{170} \) \( J \times 10^{150} \) \( J \times 10^{130} \) \( J \times 10^{110} \)

### Table (3.4) - The Three-Body FCC Lattice Energies (J mol⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>( H_0 )</th>
<th>E(DDD)₃</th>
<th>E(DDQ)₃</th>
<th>E(DQQ)₃</th>
<th>E(DDO)₃</th>
<th>E(QQQ)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEON</td>
<td>-1876</td>
<td>65.359</td>
<td>14.087</td>
<td>2.081</td>
<td>0.9025</td>
<td>0.1388</td>
</tr>
<tr>
<td>ARGON</td>
<td>-7746</td>
<td>584.34</td>
<td>143.00</td>
<td>25.440</td>
<td>13.107</td>
<td>2.0630</td>
</tr>
<tr>
<td>KRYPTON</td>
<td>-11212</td>
<td>1025.1</td>
<td>241.62</td>
<td>41.288</td>
<td>18.967</td>
<td>3.2100</td>
</tr>
<tr>
<td>XENON</td>
<td>-15818</td>
<td>1641.4</td>
<td>394.36</td>
<td>67.479</td>
<td>31.260</td>
<td>5.1875</td>
</tr>
</tbody>
</table>

From table (3.4) we see that \( E(DDD)₃ \) is quite large, being of the order of 10% of \( H_0 \) in the case of Xenon. The higher multipole terms are also seen to be significant decreasing fairly quickly in magnitude with increasing order. Despite the encouraging 1% difference in \( T_0(DDO)₃ \) between the FCC and HCP structures, the energy difference in the most favourable case, Xenon, is still only 0.351 J mol⁻¹. The FCC structure remains unstabilised by three-body terms.

The results for the FCC lattice energies of all the RGC will again be repeated, although to greater accuracy, in Chapter Four together with the Dude-model results of Huller (1971a) for the terms of perturbation order greater than three.
Zero Point Vibrational Energy

If a RGC of \( N \) atoms is assumed to be a collection of independent simple harmonic oscillators, then the harmonic zero-point energy of the crystal is given by

\[
ZPE = \frac{3}{2} h \nu_1
\]  

(3.3)

where \( \nu_1 \) is the first moment of the frequency distribution. Domb and Salter (1952) showed that \( \nu_1 \) could be written quite simply as

\[
\nu_1 = C \nu_2^{\frac{3}{2}}
\]

where \( \nu_2 \) is the second moment of the frequency distribution. For the FCC lattice we find from Domb and Salter (1952) and Isenberg (1962) that \( C = 0.9642 \). \( \nu_2 \) itself is easily computed in terms of the inter-atomic potentials. This is accomplished by means of the cell model described, for example, by Chell (1968a) where the fundamental assumptions are:

(1) The available volume is divided into identical cells with one particle per cell, the centres of which are on the classical lattice sites;

(2) The particles move in their cells independently of one another and in the mean field produced by all the other particles at rest on the cell centres. The total energy of a crystal is thus just the sum of the single particle energies, and correlation effects are neglected.

In the appendix a calculation of the potential energy, and hence \( \nu_2 \), of a typical atom due to its displacement \( \rho \) from its cell centre is given. The presentation differs from that of Chell (1968a) and Chell and Zucker (1968) in that they inadvertently assumed a certain non-zero
three-body term, (called here $T_8$) was in fact zero from symmetry considerations. The theory has also been generalised to accommodate higher multipole interactions.

We have then from the appendix the result that the contribution to $\mu_2$ and hence to the ZPE, from the pair potential and a multipole three-body potential may be expressed in terms of the lattice sums $P_2$ and $Q_2$ respectively. It should be noted that for clarity we have further expressed $Q_2$, in the appendix, in terms of the lattice sums $T_7$ and $T_8$.

$$Q_2 = 2aZ(T_7 + 2T_8) a^{-(p+5)} \quad (3.4)$$

The two-body ZPE, $\phi(2Z)$, is then just

$$\phi(2Z) = \frac{3}{2} \text{Ch} \left[ \frac{P_2}{3m} \right]^{\frac{1}{2}} \quad (3.5)$$

where the pair-potential contribution to $\mu_2$ is given by $P_2/12\pi^2m$.

If we now include the three-body interaction terms we have

$$\phi(2Z + 3Z) = \frac{3}{2} \text{Ch} \left[ \frac{P_2 + Q_2}{3m} \right]^{\frac{1}{2}} \quad (3.6)$$

The change in ZPE due to three-body terms is thus to a very good approximation

$$\phi(3Z) = \phi(2Z + 3Z) - \phi(2Z) = \frac{Q_2}{2P_2} \phi(2Z) \quad (3.7)$$

since $P_2 > Q_2$. 
It has been necessary here, for the purpose of comparison, to introduce a pair-potential. Unfortunately, whereas the forms of the three-body terms are known explicitly this is not so for the two-body potential. It is not our purpose here to discuss the various proposed pair potentials in use; instead we adopt here, and use consistently in the following chapters, the Lennard-Jones (12,6) potential. The use of this potential for RGC calculations is extensive and well documented; see for example Horton (1968) and Zucker (1968). It can be expected to give a fairly good two-body description of the RGC when its free parameters are derived from very low density gas data where three-body interactions are not expected to be significant.

\[ Q_2 \] was evaluated for all multipole three-body interactions by the lattice summations of \( T_7 \) and \( T_8 \) inside a sphere of radius \( 7R_0 \). The results of these calculations are presented in tables (3.5) and (3.6). The LJ(12,6) two-body \( P_2 \) values are bracketed indicating that improved theoretical values should be inserted when available. However calculations with other pair-potentials indicate that \( P_2 \) is unlikely to change by more than about 10%. Since \( Q_2 \ll P_2 \) the change in \( Q_2/2P_2 \), the relative size of \( \phi(3Z) \) to \( \phi(2Z) \), would be negligible in using different potentials.

From table (3.6) it can be seen that the contribution to \( Q_2 \) and hence to \( \phi(3Z) \) from the higher multipole three-body terms, 30\% in the case of \( \text{Xe} \), is not insignificant. The three-body terms increase the ZPE by 1\%-2\% of \( \phi(2Z) \). For \( \text{Ar}, \text{Kr}, \) and \( \text{Xe} \) this is of the same order as the anharmonic zero-point energy. The small change for \( \text{Ne} \) is because the multipole interaction coefficients for \( \text{Ne} \) are relatively smaller than for the other elements. The anharmonicity of \( \text{Ne} \) is also relatively larger. Chell and Zucker (1968) obtained a negative \( Q_2 \) for the triple-
dipole interaction suggesting a decrease in the ZPE; this was incorrect for the reason mentioned earlier.
### Table (3.5) - Lattice Sums $T_7$ and $T_8$

<table>
<thead>
<tr>
<th>INTERACTION</th>
<th>$(DDD)_3$</th>
<th>$(DDQ)_3$</th>
<th>$(DQQ)_3$</th>
<th>$(QQQ)_3$</th>
<th>$(DDO)_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_7$</td>
<td>-37.250</td>
<td>15.870</td>
<td>45.834</td>
<td>88.443</td>
<td>-34.873</td>
</tr>
<tr>
<td>$T_8$</td>
<td>30.930</td>
<td>-0.8766</td>
<td>2.5869</td>
<td>6.8517</td>
<td>20.668</td>
</tr>
</tbody>
</table>

### Table (3.6) - Two-Body ($P_2$) and Three-Body ($Q_2$) ZPE Terms

<table>
<thead>
<tr>
<th></th>
<th>$(DDD)_3$</th>
<th>$(DDQ)_3$</th>
<th>$(DQQ)_3$</th>
<th>$(DDO)_3$</th>
<th>$(QQQ)_3$</th>
<th>TOTAL $P_2$</th>
<th>$Q_2/2P_2 \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEON</td>
<td>0.044</td>
<td>0.009</td>
<td>0.004</td>
<td>0.001</td>
<td>0.001</td>
<td>0.059</td>
<td>(3.3)</td>
</tr>
<tr>
<td>ARGON</td>
<td>0.266</td>
<td>0.069</td>
<td>0.038</td>
<td>0.012</td>
<td>0.003</td>
<td>0.388</td>
<td>(12.74)</td>
</tr>
<tr>
<td>KRYPTON</td>
<td>0.414</td>
<td>0.102</td>
<td>0.055</td>
<td>0.014</td>
<td>0.005</td>
<td>0.59</td>
<td>(17.03)</td>
</tr>
<tr>
<td>XENON</td>
<td>0.561</td>
<td>0.143</td>
<td>0.077</td>
<td>0.020</td>
<td>0.008</td>
<td>0.809</td>
<td>(21.3)</td>
</tr>
</tbody>
</table>

* Obtained from the LJ potential of Barron and Klein (1965).
Appendix. The Potential Energy of a Particle Displaced from its Lattice Site: Two-Body Interactions

Let us consider a typical lattice point as the origin of a rectangular co-ordinate system (figure 3.1). Let \( \rho \) be the displacement of an atom from this point. The potential energy of the displaced atom with all the others at rest on their lattice points due to pair-wise interactions is

\[
\sum_{i \neq j} \phi(|R_{ij} - \rho|)
\]

Expanding as a Taylor series up to the quadratic term in \( \rho \) we have

\[
K(2) = \sum_{i \neq j} \phi(|R_{ij}|) - \rho \cdot R_{ij} \frac{\phi'}{R_{ij}}
\]

\[
+ \frac{1}{2} \rho^2 \frac{\phi'}{R_{ij}} + (\rho \cdot R_{ij})^2 \left( \frac{\phi''}{R_{ij}^2} - \frac{\phi'}{R_{ij}^3} \right)
\]

(A1)

The first term is simply the static lattice energy. The angular dependence of \( \rho \cdot R_{ij} = \rho R_{ij} \cos \theta \) can be removed by a spherical averaging method described by Chell (1968a). Terms involving odd powers of \( \cos \theta \) are shown to vanish. Hence the second term in (A1) is zero. However after averaging \( (\rho \cdot R_{ij})^2 \) is found to be \( \frac{1}{3} \rho^2 R_{ij}^2 \). Hence

\[
K(2) = \frac{\rho^2}{6} \sum_{i \neq j} \left( \phi'' + \frac{2\phi'}{R_{ij}} \right) = \frac{\rho^2}{6} \mu_2
\]

(A2)

where

\[
\mu_2 = \sum_{i \neq j} \left( \phi'' + \frac{2\phi'}{R_{ij}} \right)
\]

The second moment \( \mu_2 \) of the frequency distribution is then given, for
example, by Montroll E.W. (1943)

\[ \mu_2 = \frac{p^2}{12 \pi^2 m} \]  

(A3)

Three-Body Interactions

Let us consider the three-body interaction of the displaced atom with all the others at rest on their lattice sites (figure 3.2). This is

\[ \sum_{i \neq j \neq k} W(|R_{ij} - \rho|, |R_{ik} - \rho|, |R_{kj}|) \]

and again expanding in a Taylor series we have

\[ K(3) = \sum_{i \neq j \neq k} W(|R_{ij}|, |R_{ik}|, |R_{kj}|) \beta - \rho \left( \frac{R_{ij}}{R_{ij}} \frac{\partial W}{\partial R_{ij}} + \frac{R_{ik}}{R_{ik}} \frac{\partial W}{\partial R_{ik}} \right) 
+ \frac{1}{2} \beta^2 \left( \frac{1}{R_{ij}} \frac{\partial^2 W}{\partial^2 R_{ij}} + \frac{1}{R_{ik}} \frac{\partial^2 W}{\partial^2 R_{ik}} \right) + \frac{1}{2} (\beta \cdot R_{ij})^2 \left( \frac{1}{R_{ij}} \frac{\partial W}{\partial R_{ij}} - \frac{1}{R_{ik}} \frac{\partial W}{\partial R_{ik}} \right) 
+ \frac{1}{2} (\beta \cdot R_{ik})^2 \left( \frac{1}{R_{ik}} \frac{\partial^2 W}{\partial^2 R_{ik}} - \frac{1}{R_{ij}} \frac{\partial^2 W}{\partial^2 R_{ij}} \right) + 2(\beta \cdot R_{ij})(\beta \cdot R_{ik}) \frac{1}{R_{ij} R_{ik}} \frac{\partial^2 W}{\partial R_{ij} \partial R_{ik}} \] 

(A4)

The first term is again simply the lattice energy. The first order term again vanishes in the summation because of symmetry. The remaining terms with \( R_{ij} \) as variable in the summation are equivalent to those with \( R_{ik} \) as variable. We are left with

\[ K(3) = \beta^2 \sum_{i \neq j \neq k} 2 \left( W' + \frac{2}{R_{ij}} W' \right) + 4 \left( \frac{R_{ij} R_{ik}}{R_{ij} R_{ik}} \frac{\partial^2 W}{\partial R_{ij} \partial R_{ik}} \right) 
= 2(T_7 + 2T_8) \beta^2 \] 

(A5)
where
\[ T_7 = \sum_{i \neq j \neq k} \left( w_i w_j + \frac{2}{R_{ij}} w_j w_k \right) a^{(p+5)} \]

\[ T_8 = \sum_{i \neq j \neq k} \left( \frac{R_{ij} R_{ik}}{R_{ij}} \frac{\partial^2 W}{\partial R_{ij} \partial R_{ik}} \right) a^{(p+5)} \]

\[ P = 2I_1 + 2I_2 + 2I_3 \quad \text{for} \quad W = W(l_1 l_2 l_3) \]

If we write
\[ Q_2 = 2\sigma Z(T_7 + 2T_8) a^{-(p+5)} \quad (A6) \]

where
\[ \sigma = 1 \quad \text{if} \quad l_1 = l_2 = l_3 \]
\[ \sigma = 3 \quad l_1 = l_2 \neq l_3 \quad \ldots \text{etc.} \]

then the total potential energy for 2-body plus 3-body interactions is

\[ K = (P_2 + Q_2) \frac{\rho^2}{6} \]

The total second moment \( \mu_2 \) is given by

\[ \mu_2 = (P_2 + Q_2) / 12 \pi^2 m \quad (A8) \]
Fig. (3.1)

Fig. (3.2)
CHAPTER 4

The Contribution of High Order Multipole Three-body Forces to the Elastic Constants of the Rare Gas Crystals at the Absolute Zero

Introduction

Several authors - Goetze and Schmidt (1966), Zucker and Chell (1968), Huller, Goetze and Schmidt (1970), Barker, Klein and Bobetic (1970) - have investigated the effect of the Axilrod and Teller (1943) triple-dipole third-order perturbation of the Van der Waals long range interaction on the static lattice energy $E$, pressure $P$, elastic constants $C_{ij}$ and isothermal bulk modulus $K$, of the rare gas crystals. In particular a study of $\delta = (C_{44} - C_{12})/C_{12}$ was made, since with only 2-body forces $\delta$ was found to be always positive at the absolute zero. This result was obtained by including zero point effects (in the harmonic approximation) in the 2-body description, without which, the Cauchy relation $C_{12} = C_{44}$ would hold and $\delta = 0$. The inclusion of the Axilrod and Teller term was found to lead to a reduction in the theoretical value of $\delta$, and indeed $\delta$ may even become negative for $A$, $Kr$ and $Xe$.

Huller (1971) has evaluated $C_{ij}$ and $\delta$ with all orders of dipole interactions included. Surprisingly he found that the $C_{ij}$ were altered by very little and $\delta$ hardly at all from the values obtained with the third-order triple-dipole term alone. The reason for this was that higher order dipole interactions alternate in sign and the resulting cancellations lead to only a small net effect in addition to the effect of the third-order triple-dipole term. Thus to a very good approximation this latter term and perhaps the higher order multipole three-body terms
of third-order might be sufficient to describe all the effects of many body terms in general. It is the purpose of this chapter to investigate this suggestion in the case of the elastic constants and related thermoelastic properties of the RGC.

Theory

The heaviest rare gases Ne, A, Kr and Xe condense into FCC crystals. Because of their high symmetry cubic crystals have only three independent non-zero elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. Expressions for the elastic constants in terms of a pair potential function $\phi(r)$ have been derived by Born (1940) using the method of homogeneous deformations. The $C_{ij}$ obtained by this method obey the Cauchy relation $C_{12} = C_{44}$. This static lattice approximation was later improved by Barron and Klein (1965). They included the effects of zero point vibrations in the harmonic approximation which made $C_{44} > C_{12}$ at $T = 0^\circ K$, giving rise to a positive value for $\delta$. Their results were obtained for a Lennard Jones pair potential, which, despite an uncertain reliability, does provide us, for the purpose of comparison, with a consistent set of values for the $C_{ij}$ for the two-body interaction.

Using the method of homogeneous deformations Zucker and Chell (1968) have obtained expressions for the triple-dipole contribution to $E$, $P$ and $C_{ij}$ in terms of certain sums $T_0 - T_5$ evaluated for the geometric function $W(DDD)_3$ and its derivatives, for the FCC lattice. In the appendix of this chapter their results are generalised to include the higher order multipole three-body terms $W(L_1L_2L_3)_3$. A correction is also made to their results where a certain non-zero sum (called here $T_6$) was inadvertently omitted on the grounds of symmetry giving an incorrect
result for $C_{44}$.

The expressions for $P$ and $C_{ij}$ are now given as

$$E = \frac{1}{3} \sigma NZT_0 a^{-(p+3)}$$

$$P = -\frac{1}{2} \sigma Z T_1 a^{-(p+6)}$$

$$C_{11} = \frac{1}{2} \sigma Z (T_2 + 2T_3) a^{-(p+6)}$$

$$C_{12} = \frac{1}{2} \sigma Z (T_4 + 2T_5) a^{-(p+6)}$$

$$C_{44} = \frac{1}{2} \sigma Z (T_6 + 2T_7) a^{-(p+6)}$$

(4.1)

$$p = 2L_1 + 2L_2 + 2L_3$$

$$\begin{cases} 
\sigma = 1 & \text{if } L_1 = L_2 = L_3 \\
\sigma = 3 & \text{if } L_1 = L_2 \neq L_3 \ldots \text{ etc.} 
\end{cases}$$

The notation follows chapter 3 and the expression for the static lattice energy has been included for consistency.

Except in the case of $W(DDD)_3$ the lattice sums converged quite rapidly. The values given in Table (4.1) (apart from $W(DDD)_3$) are the values given by direct summation of all triangles formed by one atom at the origin and the other two atoms being anywhere within a sphere of radius seven nearest neighbours ($7R_0$) from the origin. The values of $T_0 - T_6$ for $W(DDD)_3$ given in table (4.1) are given by direct summation to $9R_0$ and are extrapolated to infinity by the integration method described in chapter 5.

In chapter 5 we find some general relations amongst the lattice sums. These are

$$mT_0 = 9T_1$$

$$(m-2)T_1 = T_2 + 2T_3 + 2T_4 + 4T_5$$

(4.2)
where \( m \) is the degree of homogeneity of \( W \), e.g., for \( W(DDD)_3 \), \( m = -9 \) and for \( W(DDQ)_3 \), \( m = 11 \). The second relation is in fact equivalent to the relation

\[
C_{11} + 2C_{12} + P = 3K \tag{4.3}
\]

which was formerly found to hold for a pairwise interaction description of the cubic crystals. It was later found to be satisfied in the triple-dipole case by Zucker and Chell (1968). As \( T_0-T_6 \) were all calculated independently of one another, equation (4.2) provides some check on the values of \( T_0-T_5 \) and also indirectly on \( T_6 \).

**Discussion**

The absolute values of the three-body elastic constants \( C_{11} \), \( C_{12} \) and \( C_{44} \) and the static lattice energy \( E \) and pressure \( P \) were thus evaluated for the FCC lattice using the equations (4.1). The bulk modulus \( K \) was also evaluated from equation (4.3). All the results are presented in tables (4.2a,b,c and d). Experimental data is quoted where available as a guide to the relative magnitude of the many-body results. Also included in the tables are the Drude-model results of Huller (1971b) for the total contribution from many-body dipole interactions of order greater than three (MBD)$_{4\rightarrow\infty}$ for the RGC of \( A \), \( Kr \) and \( Xe \).

The experimental values of 'a' are taken from Glyde (1970) and are as follows

<table>
<thead>
<tr>
<th>Ne</th>
<th>A</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>a:</td>
<td>2.23184</td>
<td>2.65554</td>
<td>2.82294</td>
</tr>
</tbody>
</table>
In table (4.3) values of $C_{12}^{12}$ are tabulated, first for triple-dipole interactions only, then the total for all three-body interactions and finally the total including the $(MBD)^{\infty}$ contribution. The two-body results are taken from the LJ potential of Barron and Klein (1965). Bracketed values again indicate that more accurate two-body results should be substituted when available. We finally obtain in the last column of table (4.3) the Cauchy deviation factor $\delta \times 100$.

It can be seen that the theoretical contribution of the high order multipole terms is not insignificant when compared with experiment. Their effect on $\delta$ is to make it more negative. Perhaps more interesting is the observation that in general the higher order multipole terms seem to cancel with the $(MBD)^{\infty}$ terms (although not so well for $C_{44}$). This leaves the triple-dipole term as the truly dominating many-body term. This simplifying assumption may justify the sole inclusion of this term in the sophisticated Barker-Pompe (1968) pair potential which attempts to accommodate many-body effects.
Table (4.1) - The Lattice Sums $T_0-T_6$

<table>
<thead>
<tr>
<th></th>
<th>$T_0$</th>
<th>$T_1$</th>
<th>$T_2$</th>
<th>$T_3$</th>
<th>$T_4$</th>
<th>$T_5$</th>
<th>$T_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(DDQ)$_3$</td>
<td>4.1033</td>
<td>-5.0151</td>
<td>21.895</td>
<td>2.5189</td>
<td>7.9867</td>
<td>5.5724</td>
<td>-1.3291</td>
</tr>
<tr>
<td>W(DQQ)$_3$</td>
<td>4.6987</td>
<td>-6.787</td>
<td>40.144</td>
<td>-0.2273</td>
<td>15.527</td>
<td>7.7663</td>
<td>-3.6514</td>
</tr>
<tr>
<td>W(QQQ)$_3$</td>
<td>7.2314</td>
<td>-12.052</td>
<td>65.842</td>
<td>5.7798</td>
<td>26.705</td>
<td>18.520</td>
<td>-4.7976</td>
</tr>
</tbody>
</table>

Table (4.2a) - Neon Lattice Energy and Elastic Constants

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>P</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DDD)$_3$</td>
<td>68.4</td>
<td>15.3</td>
<td>74.2</td>
<td>46.3</td>
<td>15.3</td>
<td>60.7</td>
</tr>
<tr>
<td>(DDQ)$_3$</td>
<td>14.1</td>
<td>3.85</td>
<td>20.7</td>
<td>14.8</td>
<td>4.10</td>
<td>18.1</td>
</tr>
<tr>
<td>(DQQ)$_3$</td>
<td>2.08</td>
<td>0.68</td>
<td>3.92</td>
<td>3.12</td>
<td>0.82</td>
<td>3.61</td>
</tr>
<tr>
<td>(DDO)$_3$</td>
<td>0.90</td>
<td>0.29</td>
<td>1.52</td>
<td>1.44</td>
<td>0.08</td>
<td>1.56</td>
</tr>
<tr>
<td>(QQQ)$_3$</td>
<td>0.14</td>
<td>0.05</td>
<td>0.33</td>
<td>0.24</td>
<td>0.08</td>
<td>0.29</td>
</tr>
<tr>
<td>TOTAL</td>
<td>85.62</td>
<td>20.17</td>
<td>100.67</td>
<td>65.9</td>
<td>20.38</td>
<td>84.26</td>
</tr>
<tr>
<td>EXPT.</td>
<td>-1876.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1120.0</td>
</tr>
</tbody>
</table>
### Table (4.2b) - Argon Lattice Energy and Elastic Constants

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>P</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₄₄</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DDD)₃</td>
<td>584.4</td>
<td>77.7</td>
<td>376.2</td>
<td>234.5</td>
<td>77.6</td>
<td>307.6</td>
</tr>
<tr>
<td>(DDQ)₃</td>
<td>143.0</td>
<td>23.3</td>
<td>124.8</td>
<td>88.7</td>
<td>24.7</td>
<td>108.1</td>
</tr>
<tr>
<td>(DQQ)₃</td>
<td>25.4</td>
<td>4.9</td>
<td>28.6</td>
<td>22.3</td>
<td>5.9</td>
<td>26.0</td>
</tr>
<tr>
<td>(DDO)₃</td>
<td>13.1</td>
<td>2.5</td>
<td>13.0</td>
<td>12.3</td>
<td>0.71</td>
<td>13.4</td>
</tr>
<tr>
<td>(QQQ)₃</td>
<td>2.10</td>
<td>0.5</td>
<td>3.0</td>
<td>2.5</td>
<td>0.7</td>
<td>2.8</td>
</tr>
<tr>
<td>(MBD₄→∞)</td>
<td>-145.0</td>
<td>-24.9</td>
<td>-161.0</td>
<td>-93.0</td>
<td>-56.0</td>
<td>-121.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>623.0</td>
<td>84.0</td>
<td>384.6</td>
<td>267.3</td>
<td>53.61</td>
<td>336.9</td>
</tr>
<tr>
<td>EXPT.</td>
<td>-7746.0</td>
<td>4390.0</td>
<td>1830.0</td>
<td>1640.0</td>
<td>2680.0</td>
<td>3450.0</td>
</tr>
</tbody>
</table>

### Table (4.2c) - Krypton Lattice Energy and Elastic Constants

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>P</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₄₄</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DDD)₃</td>
<td>1011.8</td>
<td>113.5</td>
<td>549.4</td>
<td>342.5</td>
<td>113.3</td>
<td>449.3</td>
</tr>
<tr>
<td>(DDQ)₃</td>
<td>241.6</td>
<td>32.7</td>
<td>175.5</td>
<td>124.7</td>
<td>34.7</td>
<td>152.5</td>
</tr>
<tr>
<td>(DQQ)₃</td>
<td>41.2</td>
<td>6.6</td>
<td>38.6</td>
<td>30.3</td>
<td>8.0</td>
<td>35.3</td>
</tr>
<tr>
<td>(DDO)₃</td>
<td>19.0</td>
<td>3.05</td>
<td>15.8</td>
<td>14.9</td>
<td>0.86</td>
<td>16.2</td>
</tr>
<tr>
<td>(QQQ)₃</td>
<td>3.2</td>
<td>0.5</td>
<td>3.8</td>
<td>3.1</td>
<td>0.8</td>
<td>3.5</td>
</tr>
<tr>
<td>(MBD₄→∞)</td>
<td>-310.0</td>
<td>-46.0</td>
<td>-290.0</td>
<td>-154.0</td>
<td>-98.0</td>
<td>-213.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1006.8</td>
<td>110.35</td>
<td>493.1</td>
<td>361.5</td>
<td>59.66</td>
<td>443.8</td>
</tr>
<tr>
<td>EXPT.</td>
<td>-11212</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table (4.2d) - Xenon Lattice Energy and Elastic Constants

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>P</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₄₄</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DDD)₃</td>
<td>1641.4</td>
<td>141.8</td>
<td>686.6</td>
<td>428.0</td>
<td>141.6</td>
<td>561.5</td>
</tr>
<tr>
<td>(DDQ)₃</td>
<td>394.3</td>
<td>41.6</td>
<td>223.7</td>
<td>158.9</td>
<td>44.2</td>
<td>194.4</td>
</tr>
<tr>
<td>(DQQ)₃</td>
<td>67.5</td>
<td>8.4</td>
<td>49.2</td>
<td>38.5</td>
<td>10.2</td>
<td>44.9</td>
</tr>
<tr>
<td>(DDO)₃</td>
<td>31.3</td>
<td>3.88</td>
<td>20.1</td>
<td>19.0</td>
<td>1.10</td>
<td>20.7</td>
</tr>
<tr>
<td>(QQQ)₃</td>
<td>5.2</td>
<td>0.80</td>
<td>4.80</td>
<td>3.90</td>
<td>1.0</td>
<td>4.50</td>
</tr>
<tr>
<td>(MBD₄→∞)</td>
<td>-598.0</td>
<td>-67.0</td>
<td>-400.0</td>
<td>-206.0</td>
<td>-139.0</td>
<td>-307.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1541.7</td>
<td>129.48</td>
<td>584.4</td>
<td>442.3</td>
<td>59.1</td>
<td>519.0</td>
</tr>
<tr>
<td>EXPT</td>
<td>-15818.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3590.0</td>
</tr>
</tbody>
</table>

### Table (4.3) - C₄₄ - C₁₂ and δ

<table>
<thead>
<tr>
<th></th>
<th>(DDD)₃ (l₁l₂l₃)₃ + (MBD)₄→∞</th>
<th>2-BODY</th>
<th>TOTAL</th>
<th>C₁₂</th>
<th>δ×100</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEON</td>
<td>- 31.0</td>
<td>- 45.52</td>
<td></td>
<td>(120)</td>
<td>( 74)</td>
</tr>
<tr>
<td>ARGON</td>
<td>-156.9</td>
<td>-250.69</td>
<td>-213.69</td>
<td>( 80)</td>
<td>(-134)</td>
</tr>
<tr>
<td>KRYPTON</td>
<td>-229.2</td>
<td>-357.84</td>
<td>-301.84</td>
<td>( 50)</td>
<td>(-252)</td>
</tr>
<tr>
<td>XENON</td>
<td>-286.4</td>
<td>-450.20</td>
<td>-383.20</td>
<td>( 40)</td>
<td>(-343)</td>
</tr>
</tbody>
</table>

The units of E are J mol⁻¹, the units of P, K and C_{ij} are MNm⁻²
APPENDIX

Elastic Constants by the Method of Homogeneous Deformations

Let \( W(R_{\lambda m}, R_{mn}, R_{nl}) \) be the 3-body multipole interaction function between three atoms \( \lambda, m \) and \( n \), whose position vectors in the undistorted crystal w.r.t. an arbitrary lattice site 0 as origin are \( \lambda \), \( m \) and \( n \) respectively (figure (4.1)). \( \lambda = (\lambda_1 a, \lambda_2 a, \lambda_3 a), m = (m_1 a, m_2 a, m_3 a) \) and \( n = (n_1 a, n_2 a, n_3 a) \), where the \( \lambda_i \)'s, \( m_i \)'s and \( n_i \)'s are integers characterising the lattice and \( a \) is half the side of a unit cube in the FCC lattice and is equal to \( R_0/\sqrt{2} \) where \( R_0 \) is the nearest neighbour distance. The total interaction energy of an undistorted crystal of \( N \) atoms is

\[
E = \frac{1}{3} \sigma Z \sum_{\lambda \neq m \neq n} W(|\lambda - m|, |m - n|, |n - \lambda|) \quad (A1)
\]

where we have put \( E = E(\lambda, \lambda, \lambda) \).

After a homogeneous deformation the interaction becomes

\[
E = \frac{1}{3} \sigma Z \sum_{\lambda \neq m \neq n} W\{(\lambda - m)^2 + 2\rho_{\lambda m}), (m - n)^2 + 2\rho_{mn}), (n - \lambda)^2 + 2\rho_{nl})\} \quad (A2)
\]

where \( 2\rho_{\lambda m} \) represents the change in the square of the separation of the two atoms \( \lambda \) and \( m \) after deformation and

\[
\rho_{\lambda m} = a^2 \sum_{i=1}^{3} \sum_{j=1}^{3} (\lambda_i - m_i)(\lambda_j - m_j) \eta_{ij}
\]

The \( \eta_{ij} \) are elements of the strain tensor and are given by
\[ \eta_{ij} = \frac{1}{2} \frac{a_{i} \cdot a_{j} - a^2 \delta_{ij}}{a^2} \]

where the \( a_{i} \) are the new elementary lattice vectors formed when a cube of side \( a \) is deformed into a parallelepiped. \( a^3 = \frac{1}{2} \nu \) where \( \nu \) is the volume per molecule for the FCC lattice.

If we expand \( (A2) \) in a Taylor series in \( \rho \) about the undistorted lattice positions,

\[
E^D = E + \frac{1}{3} \sigma NZ \sum_{m \neq n} \left\{ \sum_{i=1}^{3} (\rho_{i}D_{i} + \frac{1}{2} \sum_{j=1}^{3} \rho_{i} \rho_{j} D_{i} D_{j} + \ldots) W \right\} (A3)
\]

where the suffix \( \lambda m \) has been abbreviated to \( 1, \) \( m n \) to \( 2 \) and \( n \lambda \) to \( 3, \) and the operator \( D_{\lambda m} \) is \( \left( 1/|A_{\lambda} - m| \right) \left( \partial / \partial |A_{\lambda} - m| \right). \)

To simplify the summation procedure we take the odd multipole of the triplet as an origin in the crystal, i.e. we choose the \( \lambda \)th atom as origin. Therefore \( \lambda = 0 \) and \( (A3) \) becomes

\[
E^D = E + \frac{1}{3} \sigma NZ \sum_{m \neq n} \left\{ \sum_{i=1}^{3} (\rho_{i}D_{i} + \frac{1}{2} \sum_{j=1}^{3} \rho_{i} \rho_{j} D_{i} D_{j} + \ldots) W \right\} (A4)
\]

where \( E = \frac{1}{3} \sigma NZ \sum_{m \neq n} W. \)

Substituting for \( \rho \) and using the symmetry properties of cubic lattices we obtain

\[
E^D = E + \sigma NZ \left[ T_1 (\eta_{11} + \eta_{22} + \eta_{33}) + \frac{1}{2} (T_2 + 2T_3)(\eta_{11}^2 + \eta_{22}^2 + \eta_{33}^2) \right. \\
+ (T_4 + 2T_5)(\eta_{11} \eta_{22} + \eta_{22} \eta_{33} + \eta_{33} \eta_{11}) \\
+ 2(T_4 + 2T_6)(\eta_{12}^2 + \eta_{23}^2 + \eta_{31}^2) \left\} \right. a^{-p+3} \]

(A5)
\[ P = 2Z_1 + 2Z_2 + 2Z_3 \]

where \( T_1 \) - \( T_6 \) are pure numbers and are given by

\[
T_1 = \frac{1}{9} \sum_{m \neq n} (m_1^2 D_m^2 W + 8 \text{ other terms}) a^{(p+5)}
\]

\[
T_2 = \frac{1}{9} \sum_{m \neq n} (m_1^4 D_m^2 W + 8 \text{ other terms}) a^{(p+7)}
\]

\[
T_3 = \frac{1}{9} \sum_{m \neq n} (m_1^2 n_1^2 D_m^2 W + 8 \text{ other terms}) a^{(p+7)}
\]

\[
T_4 = \frac{1}{9} \sum_{m \neq n} (m_1^2 m_2^2 D_m^2 W + 8 \text{ other terms}) a^{(p+7)}
\]

\[
T_5 = \frac{1}{18} \sum_{m \neq n} (m_1^2 n_2^2 D_m^2 W + 17 \text{ other terms}) a^{(p+7)}
\]

\[
T_6 = \frac{1}{9} \sum_{m \neq n} (m_1 m_2 n_1 n_2 D_m D_n W + 8 \text{ other terms}) a^{(p+7)}
\]

Equation (A5) may be compared directly with the expression for the strained energy density obtained from elasticity theory for cubic lattices:

\[
\frac{E_D}{Nu} = \frac{E}{Nu} - P(n_{11} + n_{22} + n_{33}) + (C_{11}/2)(n_{11}^2 + n_{22}^2 + n_{33}^2)
\]

\[
+ C_{12}(n_{11}n_{22} + n_{22}n_{33} + n_{33}n_{11}) + 2C_{44}(n_{12}^2 + n_{23}^2 + n_{31}^2) + \ldots \]

Thus we have

\[
E = \frac{1}{3} \sigma N Z T_0 a^{-(p+3)}
\]

\[
P = -\frac{1}{2} \sigma Z T_1 a^{-(p+6)} \quad C_{11} = \frac{1}{2} \sigma Z (T_2 + 2T_3) a^{-(p+6)}
\]

\[
C_{12} = \frac{1}{2} \sigma Z (T_4 + 2T_5) a^{-(p+6)} \quad C_{44} = \frac{1}{2} \sigma Z (T_4 + 2T_6) a^{-(p+6)}
\]
CHAPTER 5

The Extension of Three-body Lattice Summations to Infinite Range by Continuum Integration

Introduction

The long-range nature of the three-body Van der Waals interactions is well illustrated by the computed lattice summations $T_0 - T_8$ for the calculation of the static lattice energy, zero point energy and the elastic constants. The effect is most marked in the more important triple-dipole interaction for which summations have been carried out to seven or nine nearest neighbour distances. In particular the sums $T_2$ and $T_3$ are found to be slowly convergent.

Graphical extrapolation and curve-fitting methods have been used by Chell and Zucker (1968) and Barker et al (1971), but differences between the reported results indicate the inconsistency of these methods. Since $9R_0$ appears to be the limit of finite summation for reasonable computer time on a moderately fast computer using the maximum amount of crystal symmetry to reduce computer effort, it would be useful to develop an analytical method for extending the finite summation to infinite range.

A similar problem is encountered in the theory of liquids and a continuum integrational method is usually adopted; see for example Kestner and Sinanoglu (1970). This method seems to be appropriate to the long-range part of the crystal where finite sums would tend to a continuum integral as the range $nR_0$ was extended to infinity and the number of triplets summed increases very rapidly.
There follows the description of a continuum integrational technique for three-body interactions between atoms in a crystal outside a specified region of finite summation $nR_0$.

**Continuum Integration**

The regions of integration 1-6 are shown in figure (5.1). Two atoms, of separation $c$, are centred at A and B. 1 and 2 are regions of exclusion about A and B and have radii of $R_0/2$. We assume that a complete summation of all triplets in region 3 has been made i.e. within a sphere of radius $nR_0$.

Consider a small volume element at C, distances $a$ from B and $b$ form A. We adopt a bipolar cylindrical co-ordinate system (figure (5.2)) with centres at A and B. Then the number of atoms in the volume element at C is $\rho \frac{ab}{c} \, da \, db \, d\phi$ where $\rho$ is the number density of the crystal i.e. $\rho = \sqrt[3]{2/R_0}$ for close-packed crystals.

If $f(a,b,c)$ is the function to be integrated over the crystal, then the integrals for the various regions can now be written down bearing the following restrictions in mind.

1. C is excluded from regions 1 and 2
2. A is excluded from 3, the region previously summed
3. C is allowed in 3 where A is always outside
4. C is excluded from 4 to ensure $a \geq c$ outside of 3. This prevents summing the same triplet twice.
We thus obtain after performing the angular integrations,

\[ I_3 = 8\pi^2\rho^2 \int_{c-a}^{c+a} \int_{nR_0}^{nR_0/2} \int_{R_0/2}^{c+R_0/2} f(a,b,c) \, b \, db \, da \, dc \]  

(5.1)

\[ I_5 = 8\pi^2\rho^2 \int_{c-a}^{c+a} \int_{nR_0}^{c} \int_{c}^{R_0/2} f(a,b,c) \, b \, db \, da \]  

(5.2)

\[ I_6 = 8\pi^2\rho^2 \int_{c-a}^{c+a} \int_{nR_0}^{c+R_0/2} \int_{a-c}^{R_0/2} f(a,b,c) \, b \, db \, da \]  

(5.3)

The c integration was performed by considering the number of points in a shell of thickness \( dc \) and radius \( c \): \( 4\pi c^2 dc \). The final result is obtained by summing the integrals, i.e.

\[ I = I_3 + I_5 + I_6 \]  

(5.4)

For the correction to the triple-dipole \( T_0 \) sum and hence the static lattice energy we put \( f(a,b,c) = W(DDD)_3 \) and the integration above is straightforward giving the result

\[ \lim_{n \to \infty} \frac{1}{k} \Delta T_0 = \frac{1}{36n^3} - \frac{1}{128n^4} + \frac{1}{9216n^6} \]  

(5.5)

where \( k = 384\pi^2/2 \). \( \Delta T_0 \) is the infinite range correction to \( T_0 \) for the finite summation truncated at \( nR_0 \).

For the sums \( T_1 \ldots T_6 \) some care is required since here \( f(a,b,c) \) involves the products of the components of \( a \) and \( b \) and the derivatives of \( W(DDD)_3 \) w.r.t. \( a \) and \( b \).
Recalling the forms of $T_1$ -- $T_6$:

$$T_1 = \sum_{a \neq b} a_x^2 \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right) W$$

$$T_2 = \sum_{a \neq b} a_x^4 \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right)^2 W$$

$$T_3 = \sum_{a \neq b} a_x^2 a_y \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right) W$$

$$T_4 = \sum_{a \neq b} a_x^2 y \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right)^2 W$$

$$T_5 = \sum_{a \neq b} a_x^2 a_y \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right) W$$

$$T_6 = \sum_{a \neq b} a_x^2 a_y \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right) W$$

we can write for the symmetric function $W(DDD)_3$

$$T_1 = \frac{1}{3} \sum_{a \neq b} a \frac{\partial}{\partial a} W(DDD)_3$$

$$T_2 + 2T_4 = \frac{1}{3} \sum_{a \neq b} a_x^4 \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right)^2 W(DDD)_3$$

$$T_3 + 2T_5 = \frac{1}{3} \sum_{a \neq b} a_x^2 a_y \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right) W(DDD)_3 \quad (5.6)$$

Referring to figure (5.2) which shows a triplet with internal angles $\Psi_A$, $\Psi_B$ and $\Psi_C$ and orientation expressed in bipolar co-ordinates, we have

$$T_2 = \sum_{\text{continuum}} a^4 \sin^4 \Psi_B \cos^4 \phi \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right)^2 W(DDD)_3$$

$$T_3 = \sum_{\text{continuum}} a^4 \sin^4 \Psi_B \cos^4 \phi \left( \frac{1}{a} \frac{\partial}{\partial a} \frac{3}{3a} \right) W(DDD)_3$$
\[ T_4 = \sum_{\text{continuum}} a^4 \sin^4 \Psi \sin^2 \phi \cos^2 \phi \left( \frac{1}{a} \frac{3}{\partial a} \right)^2 W(DDD)_3 \]

\[ T_5 = \sum_{\text{continuum}} a^4 \sin^4 \Psi \sin^2 \phi \cos^2 \phi \left( \frac{1}{a} \frac{3}{\partial a} \frac{1}{b} \frac{3}{\partial b} \right) W(DDD)_3 \]

\[ T_6 = \sum_{\text{continuum}} a^4 \sin^4 \Psi \sin^2 \phi \cos^2 \phi \left( \frac{1}{a} \frac{3}{\partial a} \frac{1}{b} \frac{3}{\partial b} \right) W(DDD)_3 \]

Then, after performing the angular integrations, we have for the continuum limit

\[ \lim_{n \to \infty} \Delta T_2 = 3\Delta T_4 \]

(5.7)

\[ \lim_{n \to \infty} \Delta T_3 = 3\Delta T_5 = 3\Delta T_6 \]

By combining equation (5.7) with (5.6) we can now evaluate the corrections \( \Delta T_1 - \Delta T_6 \) by integrating only the functions

\[ f(a,b) = a \frac{3}{\partial a} W(DDD)_3, \quad a^4 \left( \frac{1}{a} \frac{3}{\partial a} \right)^2 W(DDD)_3 \quad \text{and} \quad a^2 b^2 \left( \frac{1}{a} \frac{3}{\partial a} \frac{1}{b} \frac{3}{\partial b} \right) W(DDD)_3 \]

using the integrals of equation (5.1), (5.2) and (5.3).

We obtain, with some tedium, the final result

\[ \lim_{n \to \infty} \frac{2}{k} \Delta T_1 = \frac{\log n}{12n^3} + \frac{\log 2}{18n^3} - \frac{17}{108n^3} + \frac{3}{128n^4} \]

\[ \lim_{n \to \infty} \frac{1}{k} \Delta T_2 = \frac{12}{k} \Delta T_4 = -\frac{3}{5n} + \frac{1}{60n^2} + \frac{\log n}{5n^3} + \frac{21\log 2}{18n^3} - \frac{185}{720n^3} - \frac{137}{1920n^4} \]

\[ \lim_{n \to \infty} \frac{1}{k} \Delta T_3 = \frac{12}{k} \Delta T_5 = \frac{12}{k} \Delta T_6 = \frac{3}{10n} - \frac{1}{120n^2} + \frac{\log n}{10n^3} - \frac{\log 2}{15n^3} + \frac{317}{1440n^3} + \frac{19}{1920n^4} \]

(5.8)

**Discussion**

The extrapolated results of Barker et al (1971) for \( T_1 - T_6 \) were obtained by assuming an \( nR_0 \) dependence of the form \( A + B/n^\gamma \) near
near the limit of finite summation. For \( T_1 \) \( \gamma \) was found to be close to three and for \( T_2 - T_6 \) slow convergence was indicated by a value for \( \gamma \) close to one. This essentially agrees with the continuum results of equation (5.8). The leading term for \( T_1 \) in the continuum method goes as \( \frac{\log n}{n^3} \) but this would show up in the numerical extrapolation as \( 1/n^3 \).

Continuum corrections to the elastic constants \( C_{ij} \) take a simple form using the \( T \)-sum relation for the elastic constants from the appendix of chapter 4.

\[
\lim_{n \to \infty} \Delta C_{11} = \Delta T_2 + 2\Delta T_3 = \frac{33}{20} \Delta T_0.
\]

\[
\lim_{n \to \infty} \Delta C_{12} = \Delta T_4 + 2\Delta T_5 = \frac{11}{20} \Delta T_0 \tag{5.9}
\]

In equations (5.9) there has been a surprising cancellation of the slowly convergent parts of equations (5.8) up to the \( 1/n^3 \) terms. On considering the leading \( 1/n^3 \) terms the above result follows.

These results are again essentially in agreement with Barker et al (1971) who find the corresponding zero stress \( c_{11} \) and \( c_{12} \) elastic constants have almost \( 1/n^3 \) dependence. However, their result of \( \gamma = 6 \) for the convergence of \( c_{44} \) is probably due to their method of finite summation where \( a, b, \) and \( c \leq nR_0 \).

We find, then, that the slowly convergent components of \( T_2 - T_6 \) add up to give zero contribution to \( C_{11}, C_{12} \) and \( C_{44} \). For this reason we can expect that the extrapolated values of \( T_2 - T_6 \), though of doubtful
accuracy, will produce accurate values of $C_{11}$, $C_{12}$ and $C_{44}$.

The final numerical results are presented in table (5.1). Our finite summations $T_0 - T_6$ are shown for spheres of radii $R_0$, $5R_0$, $8R_0$ and $9R_0$ with the corresponding values of the finite stress elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. The extrapolated values due to Barker et al (1971) and Zucker and Chell (1968) are also presented together with the continuum results.

The continuum result for $T_0$ (7.62955) is in very good agreement with the very accurate result of Huller (1970c) i.e. $7.62958 \pm 0.00013$. The continuum results for $T_1 - T_6$ seem to agree more with Zucker and Chell's results than Barker's. This is probably due to Barker's summation procedure over the region of intersection of two spheres rather than inside spheres or cubes concentric about the origin. The divergent nature of the correction to $T_2 - T_6$ suggests that the region of summation chosen is critical. However, as it is the elastic constants e.g. $T_2 + 2T_3$ etc., that we are interested in, and these go as $1/n^3$ then the region summed over is not that important.

**Further T-sum relations for three-body interactions**

The analysis of the previous section also produced some further relationships between the T-sums which should be obeyed by the finite sums, not only for the triple-dipole interaction but also for the other higher order multipole three-body sums to increasing accuracy with increasing order of the function $W(Z_1 Z_2 Z_3)_3$.

We can apply Euler's Theorem to the homogeneous function $W(DDD)_3$ of degree - 9 to obtain
\[
\left( a \frac{\partial}{\partial a} + b \frac{\partial}{\partial b} + c \frac{\partial}{\partial c} \right) W(\text{DDD})_3 = -9W(\text{DDD})_3
\]

From equation (5.6) we then find

\[
T_1 = -T_0 \quad (5.10)
\]

Applying Euler's Theorem again

\[
\left( a \frac{\partial}{\partial a} + b \frac{\partial}{\partial b} + c \frac{\partial}{\partial c} \right)^2 W(\text{DDD})_3 = 81W(\text{DDD})_3 \quad (5.11)
\]

Expressing the L.H.S. of equation (5.11) in terms of the T-sums

using equation (5.6) we get

\[
-11T_1 = T_2 + 2T_3 + 2T_4 + 4T_5 \quad (5.12)
\]

Equations (5.10) and (5.11) are exact for \(nR_\Sigma = \infty\). They are also exact for a spherically symmetric summation where triplets are summed with the restriction \(a, b \text{ and } c \leq nR_0\).

Similar relations are obtained for the other higher multipole interactions and we have the general result

\[
9T_1 = nT_0 \quad (n-2) T_1 = T_2 + 2T_3 + 2T_4 + 4T_5 \quad (5.13)
\]

where \(n\) is the degree of homogeneity of \(W(\mathcal{L}_1\mathcal{L}_2\mathcal{L}_3)_3\) e.g. for \(W(\text{DDD})_3\), \(n = -9\); for \(W(\text{DDQ})_3\), \(n = -11\) etc...

This result is very useful in that it enabled us to make an independent check on our finite summation \(T_0 - T_5\) both for analytic errors and for numerical accuracy. It also provided an indirect check on the derivatives of \(W(\mathcal{L}_1\mathcal{L}_2\mathcal{L}_3)_3\) used in the summations \(T_6 - T_8\).
It is of interest to make the comparison of equations (5.13) with relations from the elastic theory of cubic crystals. If the elastic constants of a cubic crystal are expressed in terms of a pairwise potential $\phi(R)$, we have for the bulk modulus

$$K^{(2)} = -\frac{V\partial p^{(2)}}{\partial V} = \frac{1}{3} \left[ c_{11}^{(2)} + 2c_{12}^{(2)} + p^{(2)} \right]$$

where $p^{(2)} = -\frac{\partial \phi}{\partial V}$ is the pressure and $V$ the volume.

On extending this result to the triple-dipole potential $W(DDD)$, Zucker and Chell (1968) found the following relations were obeyed

$$K^{(3)} = -\frac{V\partial p^{(3)}}{\partial V} = \frac{1}{3} \left[ c_{11}^{(3)} + 2c_{12}^{(3)} + p^{(3)} \right]$$  \hspace{1cm} (5.14)

where $p^{(3)} = -\frac{\partial W(DDD)}{\partial V}$  \hspace{1cm} (5.15)

which on converting to the T-sums become equations (5.10) and (5.12). Hence equations (5.14) and (5.15) appear to be general for all three-body interactions giving the relations of (5.13) on substituting for the T-sums.
Table (5.1) Tripole-dipole Lattice Sums to Infinite Range

<table>
<thead>
<tr>
<th>nR₀</th>
<th>1</th>
<th>5</th>
<th>8</th>
<th>9</th>
<th>B(∞)</th>
<th>Z &amp; C(∞)</th>
<th>CONT</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₀</td>
<td>4.6623</td>
<td>7.5911</td>
<td>7.6206</td>
<td>7.6233</td>
<td>7.62</td>
<td>7.62 ± 0.015</td>
<td>7.6295</td>
</tr>
<tr>
<td>T₁</td>
<td>-3.1641</td>
<td>-7.4739</td>
<td>-7.5846</td>
<td>-7.5969</td>
<td>-7.62</td>
<td>-7.62 ± 0.03</td>
<td>-7.5978</td>
</tr>
<tr>
<td>T₂</td>
<td>2.7012</td>
<td>-13.608</td>
<td>-17.265</td>
<td>-17.938</td>
<td>-23.4</td>
<td>-19.95 ± 0.3</td>
<td>-20.756</td>
</tr>
<tr>
<td>T₃</td>
<td>-0.6744</td>
<td>24.523</td>
<td>27.026</td>
<td>27.440</td>
<td>30.33</td>
<td>28.8 ± 0.3</td>
<td>28.854</td>
</tr>
<tr>
<td>T₄</td>
<td>1.3506</td>
<td>-5.5449</td>
<td>-6.7611</td>
<td>-6.9867</td>
<td>-9.69</td>
<td>-7.71 ± 0.06</td>
<td>-7.9260</td>
</tr>
<tr>
<td>T₅</td>
<td>1.1667</td>
<td>13.894</td>
<td>14.853</td>
<td>15.006</td>
<td>16.41</td>
<td>15.39 ± 0.06</td>
<td>15.4773</td>
</tr>
<tr>
<td>T₆</td>
<td>-0.5268</td>
<td>6.4008</td>
<td>7.1707</td>
<td>7.3023</td>
<td>8.64</td>
<td>---</td>
<td>7.7736</td>
</tr>
<tr>
<td>C₁₁</td>
<td>1.3524</td>
<td>35.438</td>
<td>36.787</td>
<td>36.941</td>
<td>37.26</td>
<td>37.65 ± 0.9</td>
<td>36.952</td>
</tr>
<tr>
<td>C₁₂</td>
<td>3.6840</td>
<td>22.244</td>
<td>22.944</td>
<td>23.025</td>
<td>23.13</td>
<td>23.07 ± 0.18</td>
<td>23.028</td>
</tr>
<tr>
<td>C₄₄</td>
<td>0.2970</td>
<td>7.2567</td>
<td>7.5803</td>
<td>7.6179</td>
<td>7.59</td>
<td>---</td>
<td>7.6212</td>
</tr>
</tbody>
</table>

B(∞): The extrapolated results of Barker et al (1971)
Z & C(∞): The extrapolated results of Zucker and Chell (1968)
CONT: The present results based upon the continuum model
CHAPTER 6

Further Comments on the Rare Gas Crystals

Introduction

The purpose of this, the final chapter, is not so much a summary of the previous chapters - an unnecessary repetition - but an opportunity to discuss topics which, although arising from the foregoing material, could not previously be included for reasons of consistency.

Inevitably, in the preparation of a thesis, numerous thoughts and ideas emerge which, though sometimes worthy of mention within the context of the thesis, are difficult to incorporate in any coherent and consistent manner. For this reason such material has been deferred until now and is tentatively presented as a series of subsections where some continuity is preserved by reference to the results and conclusions of previous chapters. In this way it is hoped that the main points already established may be reiterated and that some indication of the direction of future research might suggest itself.

The Dielectric Properties of the Rare Gases

In Chapter One a system of $N$ interacting rare gas atoms is given a many body description by equation (1.15). The total interaction energy is developed in a linear approximation as the sum of two-body, three-body etc. interactions. In practice the series can be interpreted as follows. The first term is a sum of two-body interactions in vacuo which as expected give good results for calculations on very low density gas properties.

Moving to higher densities through liquids to solids the two-body approximation is corrected principally by the three-body terms. This term is repulsive and hence reduces the attraction between the atoms. This
may be viewed as the shielding of individual atoms by their environment leading to an effective atomic polarizability whose value is less than that of the free-atom. We are thus led to a non-polar dielectric description for the rare gases in which the dielectric constant \( \varepsilon \) or the refractive index \( n \) is related to the atomic polarizability \( \alpha \). According to the Lorentz local-field model such a relation is given by the Lorentz-Lorenz function

\[
\frac{(n^2-1)}{(n^2+2)} \rho = \frac{(\varepsilon-1)}{(\varepsilon+2)} \rho = \frac{4\pi Na}{3M} = F
\]

(6.1)

where \( \rho \) is the density of the medium, \( M \) the atomic weight and \( N \) is Avogadro's number.

Experimentally \( F \) is indeed found to be nearly independent of density as implied by equation (6.1), but small significant deviations do occur. Starting at low density \( F \) increases slowly with density, passes through a maximum, and then decreases rather more rapidly. The low density behaviour is fairly well understood in terms of the effect of statistical fluctuations on the induced dipole moment and the contribution of higher order multipole two-body forces with increasing density. However, at higher densities the rare gases solidify with the crystalline symmetry required of the Lorentz model and their dielectric behaviour should be described adequately by equation (6.1). The decreasing value of \( F \) with increasing density in the solid phase can only be explained by introducing a density dependence for the polarizability such that the polarizability of an atom in the crystalline environment is less than that of the free-atom. This is seen to be a many-body effect and as a first approximation can be attributed to the three-body term.
Sinnock and Smith (1969) found that at 78°K the polarizability of argon at 5461 Å decreased by about 1.5% from the free-atom value. On the basis of the oscillator model - Margenau (1938) - we can make a crude theoretical estimate for the many-body corrections to the dipole-dipole description using the results of Huller (1971a) to tenth order in perturbation.

For a crystal of N oscillators of classical frequency $\omega_0$, dipole polarizability $\alpha_0$ and atomic volume $v$, the oscillator model static lattice energy in the dipole approximation is given by Huller as

$$U = \frac{\pi \omega_0 N}{2} \sum_{n=2}^{\infty} b_n \left( \frac{10 \alpha_0}{v} \right)^n$$

(6.2)

where $n$ is the order of perturbation. The $b_n$ are the geometric coefficients. We can rearrange equation (6.2) as a two-body interaction ($n = 2$) corrected by the many-body interactions ($n > 2$) to obtain

$$U = \frac{\pi \omega_0 N}{2} b_2 \left( \frac{10 \alpha_0}{v} \right)^2 \left\{ 1 + \sum_{n=3}^{\infty} \frac{b_n}{b_2} \left( \frac{10 \alpha_0}{v} \right)^{n-2} \right\}$$

(6.3)

or alternatively giving the polarizability a molar density dependence

$$U = \frac{\pi \omega_0 N}{2} b_2 \left( \frac{10 \alpha}{v} \right)^2$$

(6.4)

where

$$\alpha = \left\{ 1 + \sum_{n=3}^{\infty} \frac{b_n}{b_2} (10N\alpha_0)^{n-2} \right\}^{\frac{1}{2}} \alpha_0$$

At 78°K, $\rho = 4.1 \times 10^4$ mol/m$^3$ and $\alpha_0 = 1.64 \times 10^{-30}$ m$^3$.

From Huller's coefficients $b_n$ we obtain a decrease in polarizability of 2.2%. In view of the approximations made in deriving this result the
agreement with the experimental result is acceptable. This simple example shows that many-body forces seem to play an important role in the dielectric theory of the RGC. It would thus seem desirable to develop a dielectric theory involving three-body forces at least. Some indication of how this may be done has been given by Linder (1967).

The Stability of the Rare Gas Crystals

We have seen that the introduction of multipole three-body terms to the static lattice interaction energy is unable to stabilise the FCC structure for the RGC. The calculations of Chapter Three have been recently repeated by Fowler and Graben (1972). Their results and conclusions are in complete agreement, although to lower accuracy. Assuming therefore that the stability of the FCC structure for the RGC cannot be resolved by the contribution of many-body effects to the static lattice energy we must look elsewhere for a possible solution. Three areas, hitherto little explored, appear worthy of consideration. Two of them involve many-body effects directly.

(1) Mechanical Stability

A necessary condition for the Thermodynamic stability of a crystal lattice is that the crystal be mechanically stable with respect to arbitrary small homogeneous deformations. Born (1940) derived mathematical expressions for these stability requirements for cubic lattices of the Bravais type on the assumption of central forces of a general type. It is trivial to extend these stability criteria to both FCC and HCP structures for non-central forces. This will enable us to include three-body terms and zero-point effects.
Briefly, in order for a simple crystal lattice to be mechanically stable, the quadratic form representing the strain energy function,

$$\frac{1}{2} \sum_{ij} C_{ij} \delta_i \delta_j$$

must be positive definite so that any combination of small strains \( \delta_i \) will result in an increase in energy. If we arrange the elastic constants \( C_{ij} \) above in the form of a \( 6 \times 6 \) matrix then the above quadratic form is positive definite if the principal minors of the matrix are all positive. A fuller treatment is available in Born and Huang (1954). Disregarding the Cauchy relation which only hold for central forces, we obtain the following stability conditions:

- **FCC**: \( C_{44} > 0 \) \( C_{12} > 0 \) \( C_{11} - C_{12} > 0 \)
- **HCP**: \( C_{44} > 0 \) \( C_{33} > 0 \) \( C_{11} - C_{12} > 0 \) \( C_{33}C_{12} > C_{13}^2 \)

These conditions are found to be satisfied for both lattices by purely central forces of the Lennard-Jones type. Pair potentials including zero-point effects have only been derived for the FCC structure - Barron and Klein (1965) - and together with the three-body elastic constant results of Chapter Four still satisfy the stability criteria. It remains therefore that a suitable pair-potential be derived for the HCP structure and together with the three-body terms a similar stability analysis be made. To this end we have provided in the Appendix to this chapter, the results of calculations, analogous to those of Chapter Four, of the triple-dipole T-sums appropriate to the HCP structure. It is hoped that at a later date when an accurate pair-potential becomes available for the HCP lattice, then the mechanical stability of FCC against HCP will be resolved.
(2) Stacking Fault Energy

For the close-packed FCC and HCP structures the interatomic forces are such that it is a fair approximation to regard the atoms as hard spherical balls held together by attractive forces. These structures are generated by stacking close-packed layers to obtain the familiar sequences of ...ABCABC... for the FCC structure and ...ABABAB... for the HCP structure. Incorrect stacking by the insertion or removal of a layer is called a stacking fault and leads to a general increase of lattice energy. The fault energy at 0°K can be represented by the number of pairs of separation $nR_0$ which are not in the proper stacking sequence, multiplied by the distortion energy $\psi_n$ per pair. This concept is explained in more detail for example by Hirth and Lothe (1968).

If it could be demonstrated that the FCC structure was much more stable to faulting than the HCP structure for the RGC this might well be the explanation for nature's preference for the FCC structure in these solids. Interestingly, for both structures, in the hard-ball central-force model, both first - and second - nearest-neighbour bonds do not contribute to the fault energies. Since the contribution to the two-body lattice energy from $3R_0$ out to infinity is typically only about 0.02% of the total two-body energy, then the non-central forces become very significant. In particular the relatively small contribution from the three-body interactions in favour of the FCC structure may well become dominant.

An attempt has been made previously to examine many-body effects in stacking fault energies of the RGC by Pliskin and Greenberg (1965) and Bullough et al (1966). Although they have used the questionable three-body exchange potential of Jansen, their methods could be used to calculate say the triple-dipole contribution to the stacking fault energy.
Again, accurate pair potentials for the rare gases are vital for a thorough analysis.

(3) Entropy

Usually, consideration of the thermodynamic stability of the RGC has in the past involved an examination of the cohesive energy of these crystals. In fact stability and metastability are determined by the relative free energies, and it is the phase of lowest free energy which is in Thermodynamic equilibrium.

The difference in Gibbs free energy between two phases at fixed temperature T and pressure P is expressed as

$$\Delta F = \Delta E + P\Delta V - T\Delta S$$

where $E$ is the internal energy, $V$ the volume and $S$ the entropy of the solid. In systems such as the RGC, the enthalpy difference between two phases is nearly zero, i.e.

$$\Delta E + P\Delta V \approx 0$$

It would therefore seem to be important to consider the full free energy at all finite temperatures. More explicitly, in such cases it is essential to include the entropy contribution to the free energy.

The entropy difference between the FCC and HCP phases in the RGC lies in the vibrational characteristics of the two lattices. One way of approximately calculating the entropy is from the frequency spectrum $D(\omega)$ of the lattice vibrations. An expression for the vibrational entropy
valid for the temperature range of interest (i.e. where quantum effects are negligible) is given by

\[ S(T) = k \int D(\omega) \left[ 1 + \ln \left( \frac{kT}{\hbar \omega} \right) \right] d\omega \]

where \( k \) is the Boltzmann's constant and \( D(\omega) \) is normalised to \( 3N \), the number of vibrational modes in a crystal of \( N \) atoms. The frequency spectrum can be obtained from a perturbational treatment of a harmonic analysis of the crystal - Wallace (1964) - or from a molecular dynamics simulation - Gibson et al (1960).

Recently a second method of calculating the entropy has been proposed by Esbjorn et al (1972). This method is derived from Boltzmann's H-theorem and is independent of any form of vibrational analysis. The entropy is found from phase space distribution functions which are measured directly in the course of a molecular dynamics simulation. Furthermore, this method can be used to monitor the progress of a simulation, so that thermodynamic averages are taken only in the equilibrised state of the system. Esbjorn et al find that this method increases the accuracy and reliability with which the entropy can be found.

An estimation of thermal entropy effects in the RGC has in fact been made by Barron and Domb (1965) using the lattice dynamic approach. Although they conclude that these effects are not significant, their approximations are such that further investigations into this important area would be justified.
Pair Potentials for the Rare Gases

A recurrent problem throughout this thesis has been the absence of accurate true pair potentials between the rare gas atoms. For a full evaluation of the effects of many-body forces in the solid or liquid state we require pair potentials in vacuo, i.e. pair potentials which are not derived from solid or liquid state data.

The evaluation of such potentials has, over the years, received much attention from both experimentalists and theorists alike. Currently much progress is being made in molecular beam experiments - Mueller et al (1971) - although fundamental problems in the uniqueness of the potential derived from the inversion of scattering data seem to bedevil this approach. The present approach of experimentalists - Robinson et al (1971) - appears to be the construction of pair potentials piecemeal from low and high-energy scattering data, spectroscopic data and transport and virial data. The danger here is that the procedure may degenerate into complicated curve fitting of little physical significance. One antidote for this malady is some guidance through the choice of a mathematical model for the potential. The efforts made in this direction are well documented by Margenau and Kestner (1971), in particular for the simpler interactions of H-H and He-He.

For the heavier atoms ab initio and even semi-empirical calculations are proving extremely difficult to perform with acceptable accuracy. This is particularly the case at the intermediate range where long-range forces in second-order perturbation with non-symmetrized wave functions become comparable with the short-range forces in first-order perturbation with symmetrized wave functions. It would be a dubious procedure simply to add them, inasmuch as they would have been obtained by mutually
inconsistent approximations.

At the moment the best way to tackle the intermediate range problem is probably to extend the long range theory to allow for small atomic overlap effects. In this way we construct the many-atomic wave functions from the wave functions of the separated atoms. In so doing we should find that the total energy should be given as a sum of independent terms each of which possesses a clear physical interpretation.

The difficulty that arises with this approach is how to obtain a properly antisymmetrized set of wave functions from the constituent atomic wave functions without ending up with a set of functions which are non-orthogonal, overcomplete and for which no acceptable zeroth Hamiltonian can be found? We shall conclude this chapter by mentioning an approach due to Boehm and Yaris (1971) which seems to circumvent the difficulties - somewhat suspiciously - and arrives at a solution which rather interestingly connects the intermediate-range forces with low energy inelastic electron-atom scattering data in the same way as the long-range forces are connected to oscillator strengths obtainable from optical spectra. Although Boehm and Yaris deliberately avoided a perturbational approach their results do in fact emerge more simply from a perturbational formalism and provide an interesting connection with the methods of Chapters One and Two. In essence, Boehm and Yaris have adopted a linear response approach - cf. Linder (1967) - to the intermediate region in the Martin-Schwinger Greens-functional formalism. Simple product wave functions are used; electron transfer states are neglected and so the number of electrons per atom (equal to the atomic number) is conserved in all atomic states. They treat interatomic electron exchange by introducing the HF exchange operator into the
interatomic potential energy operator. By taking the reference state
expectation value of the latter the correlation between two localized
electron density functions in the diatomic case is expressed by the
sum of four terms: dispersion interaction, polarization-exchange inter-
action, exchange-polarization interaction and exchange-exchange inter-
action.

This result has the physical interpretation that was expected,
but could be more simply obtained by recognizing that each of the four
terms corresponds, in the order written, to the second-order perturbation
diagrams:

![Diagram of perturbation diagrams](image)

(a) (b) (c) (d)

Fig. (6.1)

where we have taken a basis set of antisymmetrized products of eigen-
functions of the separate atoms:

$$
\psi_{mn} = \bigwedge A_m(i) B_n(j)
$$

for reasons stated earlier this approach is fraught with many imponderables
and therefore these pseudo second-order results must be carefully
interpreted.

A related method of Murrell and Shaw (1967) writes down the total
wave function as the sum of a zeroth order antisymmetrized wave function
and a linear combination of simple product functions.

$$
\psi = \psi_{00} + \sum_{m,n} C_{mn} A_m(i) B_n(j)
$$
The results obtained are similar to those above with the addition of scaled coulomb terms which would be small for the interactions of weakly overlapping spherically neutral atoms. Here again difficulties arise in formulating a unique perturbation expansion.

Moving to three-body interaction in the small overlap approximation we can immediately write down the linear three-body, third-order diagrams:

(a) (b) (c) (d)

Fig. (6.2)

In order, we have one three-body dispersion interaction (a), three exchange-exchange-polarization interactions (b), three polarization-polarization-exchange interactions (c), and one three-body exchange interaction (d). Eight terms in all; a result identical to that of Boehm and Yaris.

A further result of Boehm and Yaris (1971) is that the second and third-order small overlap terms can be further expressed in terms of Bethe-Salpeter amplitudes which occur in low energy inelastic electron-atom scattering theory as the components of the inelastic scattering matrix. Hence, in principle, the intermediate range interatomic energy terms above can be obtained from single-atom properties as can the long range energies.

Finally, in the limit of zero overlap, the exchange terms vanish and on writing out explicitly the two-body diagram of Fig. (6.1a) we
obtain the familiar long range result

$$E_{DIS} = - \sum' \sum' \frac{|<\psi_{mn}\rangle r_{ij}^{-1}|\psi_{00}\rangle|^2}{E_{mn} - E_{00}}$$

which can further be expanded in the usual multipolar series.

A similar result is obtained for the three-body diagram Fig. (6.2a).
APPENDIX

Elastic Constants of the H.C.P. Crystal Structure by the Method of Homogeneous Deformations

From equation (A4) of the Appendix to Chapter Four we have the distortion energy of the crystal

$$ E^D = E + \frac{1}{3} \sigma NZ \sum_{m \neq n} \left\{ \frac{3}{2} \sum_{i=1}^{3} \left[ r_{0i} \rho_i D_i + \frac{1}{2} \sum_{j=1}^{3} \rho_{ij} D_i D_j + \ldots \right] W^m \right\} $$  \hspace{1cm} (A1)

where

$$ E = \frac{1}{3} \sigma NZ \sum_{m \neq n} W = \frac{1}{3} \sigma NZ T_0 a^{-p+3} $$

Substituting for $\rho$ and using the symmetry properties of Hexagonal close-packed lattices we obtain

$$ E^D = E + \sigma NZ \left\{ T_1 (\eta_{11} + \eta_{22}) + T_2 \eta_{33} + \frac{1}{2} (T_3 + 2T_7) (\eta_{11}^2 + \eta_{22}^2) \right. $$

$$ + \frac{1}{2} (T_4 + 2T_8) \eta_{33}^2 + (T_5 + 2T_9) (\eta_{11} \eta_{33} + \eta_{22} \eta_{33}) $$

$$ + (T_6 + 2T_{10}) \eta_{11}^2 \eta_{22} + 2(T_5 + 2T_{11}) (\eta_{23}^2 + \eta_{13}^2) $$

$$ + 2(T_6 + 2T_{12}) \eta_{12}^2 a^{-p+3} \right\} $$  \hspace{1cm} (A2)

where $T_0 - T_{12}$ are pure numbers and are given by

$$ T_0 = \sum_{m \neq n} W a^{p+3} $$

$$ T_1 = \sum_{m \neq n} m_1^2 D_m W a^{p+5} $$
\[ T_2 = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+5)} \]

\[ T_3 = \sum_{m \neq n} m \cdot 4^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_4 = \sum_{m \neq n} m \cdot 3^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_5 = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_6 = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_7 = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_8 = \sum_{m \neq n} m \cdot 3^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_9 = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_{10} = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_{11} = \sum_{m \neq n} m \cdot 3^D \cdot m \cdot W \cdot a^{(p+7)} \]

\[ T_{12} = \sum_{m \neq n} m \cdot 2^D \cdot m \cdot W \cdot a^{(p+7)} \]

(A3)

Equation (A3) may be compared directly with the expression for the strained energy density obtained from elasticity theory for HCP structures.

\[ \frac{E_D}{Nv} = \frac{E}{Nv} - \{ C_{11}(\eta_{11} + \eta_{22}) + C_{33}\eta_{33}\} + \frac{1}{2} \{ C_{11}(\eta_{11}^2 + \eta_{22}^2) + (C_{33}\eta_{33})^2 \}

+ C_{13}(\eta_{11}\eta_{33} + \eta_{22}\eta_{33}) + C_{12}\eta_{12}\eta_{22}

+ 2 C_{44}(\eta_{23}^2 + \eta_{13}^2) + 2 C_{66}\eta_{12}^2 \]

(A4)
then

\[ p = -\frac{1}{4} \sigma z(T_1 + T_2) a^{-(p+6)} \]

\[ C_{11} = \frac{1}{2} \sigma z(T_3 + 2T_7) a^{-(p+6)} \]

\[ C_{23} = \frac{1}{2} \sigma z(T_4 + 2T_8) a^{-(p+6)} \]

\[ C_{33} = \frac{1}{2} \sigma z(T_5 + 2T_9) a^{-(p+6)} \]

\[ C_{44} = \frac{1}{2} \sigma z(T_5 + 2T_{11}) a^{-(p+6)} \]

\[ C_{66} = \frac{1}{2} \sigma z(T_6 + 2T_{12}) a^{-(p+6)} \]

(A5)

We have numerically evaluated the sums \( T_0 - T_{12} \) to \( 6R_0 \) for the triple-dipole interaction (\( \sigma = 1, p = 6 \)) and the results are presented in table (6.1). The value for \( T_0 \) is given in Chapter Three.

| Table (6.1) - The Triple-Dipole Sums \( T_1 - T_{12} \) for the HCP lattice |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( T_1 \)       | \( T_2 \)       | \( T_3 \)       | \( T_4 \)       | \( T_5 \)       | \( T_6 \)       |
| -7.5278         | -7.5397         | -16.633         | -17.156         | -5.0411         | -5.5443         |
| \( T_7 \)       | \( T_8 \)       | \( T_9 \)       | \( T_{10} \)    | \( T_{11} \)    | \( T_{12} \)    |

These results were checked by the use of a relation for the HCP lattice analogous to equation (4.2):

\[ 9K = 2C_{11} + C_{33} + 2C_{12} + 4C_{13} + 3P \]

(A6)

This relation was found to be satisfied to the expected accuracy.
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