ON THE DETERMINATION

of

INTERMOLECULAR POTENTIALS

by

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To the best of my knowledge this thesis contains no material published by another person, except where due reference is made in the text.

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ABSTRACT

The definition and computational aspects of the intermolecular potential energy function (hereafter simply called the intermolecular potential or the potential) are discussed. A very convenient method of determining the intermolecular potential by direct quantum mechanical calculation is developed and illustrated by application to the interaction of two ground state helium atoms.

A summary is also presented of the relationship between the intermolecular potential and the bulk properties of a gas to facilitate the investigation of the semi-empirical method of determining the potential. This approach is applied to the pair interactions of CH_4, CF_4 and SF_6 molecules.

Both the semi-empirical and quantum mechanical methods are then applied to the question of the non-additivity of the intermolecular potential.

TABLE OF CONTENTS

NOTE ON NOTATION

So as not to needlessly clutter the text many symbols are not defined in the text but the definitions of all symbols are collected in this section.

CHAPTER 2

P = number of nuclei

M_k = mass of a nucleus, k

N = number of electrons

m = mass of an electron, e = charge of an electron

M = number of separated molecules

H = a Hamiltonian, Ψ = a wavefunction

X = a wavefunction which is a product of separated molecule wavefunctions

A, B = wavefunctions of separated molecules

V = interaction part of the Hamiltonian

Q = symmetrization operator

T_1, P_1 = operators defined by (2.4.2) and (2.4.3)

$\hat{X}$ = an operator

V_{tr}, V_{tr}', S_{tr}' = matrix elements defined by

$$V_{tr} = \langle X_t \mid V \mid X_r \rangle$$

$V_{tr}' = \langle X_t | V | P_{ij} X_r \rangle$

$S_{tr}' = \langle X_t | P_{ij} X_r \rangle$

X_o = $A_o B_o$

A_o, B_o = ground state wavefunctions of separated molecules

A and B

W = a matrix element

E is an energy

e.g.

$E_o = \langle X_o | H_o | X_o \rangle$

$E_t = \langle X_t | H_o | X_t \rangle$

E_i = the i^{th} order energy

$X^{(i)}$ = the i^{th} order wavefunction

α, β = elementary spin functions

A_{hf}, B_{hf} = Hartree-Fock wavefunctions

A_c, B_c = correlation functions

B_{ci}, B_{cj} = orbitals on B

C_i = a coefficient in a linear sum

CHAPTER 3

Section 3.2

Z_n = canonical partition function

P = pressure, V = volume, T = temperature

μ = Chemical potential, bj = a coefficient

z	= number density, ρ = density
k	= Boltzmann constant, N_o = Avogradro's number
R	= gas constant
B, C, D	= second, third, fourth virial coefficients
U	= a potential energy function
U_o	= a central potential energy function
v	= a non-central potential energy function
f_{ab}	= an Ursell-Mayer function
X_l	= a phase shift
$\hat{k}$	= a wave number
l	= angular momentum quantum number
s	= a spin
β	$= kT^{-1}$
B_o, C_o	= central, classical second and third virial coefficients,
C_{add} & C_{nonadd}	= additive and non-additive third virial coefficients
d_n, D_n	= coefficients arising from angle integrations
H_n, I_n	= radial integrals (both the above are involved in C for angle dependent potentials)

Section 3.3

J = a flux, X = a gradient, L = a transport coefficient

α_t = thermal diffusion factor

α_o = reduced thermal diffusion factor

k_t = thermal diffusion ratio

R_t = thermal separation ratio

M_1, M_2, m_1, m_2 = molecular weights and masses of molecules,

F_i = an external force

$f^{(i)}$ = i^{th} order distribution function

g = relative velocity of two molecules

χ = angle of deflection

μ = shear viscosity coefficient

λ = thermal conductivity coefficient

D_{11} = self diffusion coefficient

$\Omega_{l,s}$ = a collision integral

$S^{(n)}$ = the collision cross-section

I_{el} = the elastic collision cross-section

I_{in} = the inelastic collision cross-section

γ^2 = $\frac{1}{2}m_{12}g^2/kT$

r_m = the distance of closest approach

m_{12} = reduced mass

λ_{int} = internal heat conductivity

λ_{tr} = translational heat conductivity

C_{int} = internal heat capacity

C_v = heat capacity at constant volume

K = coefficient of bulk viscosity

CHAPTER 4

Section 4.2

C_6, C_8, C_{10} = dispersion coefficients

σ = the zero of the potential function

ε = the depth of the potential well

r_o = the position of the potential minimum

U = the total potential

U_o = the central potential

v = the orientation dependent potential

U_{ss} = the spherical shell potential

d = the size of the spherical shell

r_o^* = r_o/d

Ω = the octopole moment, Φ = the hexadecapole moment, α = the polarisability

Additional Comments and Units used

In Chapter 2 the use of B_1 for a general wavefunction and B_{c1} for an orbital for He should not be confused. Throughout the thesis the symbol ∇^2 is used for the gradient operator and $\sum_{t=0}$ or $\sum_t'$ mean the sum over all states excluding the ground state.

In Chapter 3 a, b, c are used to denote molecules rather than 1, 2, 3. More details of notation for Chapter 3 will be found in Appendix C.

The units used throughout are, energies 10^{-5} a.u., C_6, C_8, C_{10} a.u. second virial coefficients $cm^3/mole$, third virial coefficients $cm^6/mole^2$, viscosities 10^{-7} poise, self diffusion coefficients $cm^2.sec.^{-1}$, octopole moments 10^{-34} e.s.u. cm^3, hexadecapole moments 10^{-42} e.s.u. cm^4 and polarizabilities 10^{-25} cm^3.

1. INTRODUCTION

Intermolecular potentials are of great interest and importance in many branches of chemistry, physics and biology.[1-7] For example, they are intimately involved in the molecular interpretation of the equilibrium and transport properties of matter,[1,5,6,7] the explanation of crystal structures,[2] the mechanisms of chemical reactions and the conformation of macromolecules.[2,4] In short, the problem of determining the intermolecular potential is one of the key problems which must be solved if we are to describe the observable bulk properties of matter in terms of its constituent molecules.[1-7] The other major problem is to relate these potential functions to the bulk properties.

Basically, the intermolecular potential may be determined in two ways

(a) by direct calculation using quantum mechanics,[2,3,4] and

(b) indirectly from an analysis of the bulk properties of matter.[1,2,3,6]

In the next Chapter the problem of defining and calculating the intermolecular potential in quantum mechanics will be discussed.

The intermolecular potential for the interaction of closed shell systems is an extremely small quantity. This means that if the normal variational solution of the Schrodinger equation is used the potential is obtained by taking the difference of two large nearly equal numbers.

Thus methods have been sought which determine the potential directly. One such method is perturbation theory in terms of separated molecule wavefunctions and this method is investigated in Chapter 2. Several questions related to this theory remain to be answered, they are

(a) as the perturbation expansion is not unique can one find a suitable expansion?

(b) as the theory is developed in terms of exact, unknown ground state wavefunctions of the separated molecules what can be learnt from approximate wavefunctions? and

(c) as the required exact, complete sets of excited state functions of the separated molecules are also unknown can good second order energies be obtained from truncated variational approximations to this set?

After a definition of the intermolecular potential these problems are investigated with particular reference to a widely discussed problem, the interaction of two ground state helium atoms.

In recent years very accurate semi-empirically determined potentials have been obtained for inert gas interactions [123-127], using the relationship between the properties of a gas and the intermolecular potential. After a discussion of the relationship between the interaction potential and the equilibrium and transport properties for both atoms and molecules in Chapter 3 an attempt is made in Chapter 4 to extend

this procedure to simple polyatomic molecule interactions and some of the additional problems encountered are discussed.

The last Chapter contains a discussion of the non-additivity of the many-body intermolecular potential. This Chapter further emphasises the utility of the perturbation theory of the intermolecular potential.

2. THE INTERMOLECULAR POTENTIAL

In the introductory chapter it was pointed out that there are two distinct parts to the problem of describing the bulk properties of matter in terms of the constituent molecules. It is the first of these problems, that of the intermolecular potential that will be investigated in this Chapter.

2.1 Definition of the Intermolecular Potential

Consider a system of P nuclei of mass M_k and charge $Z_k e$ and N electrons of mass m and charge e. We define the separated system as a system of M molecules each with a certain number of nuclei and electrons.

The Schrodinger equation for this system using a spin-free, non-relativistic Hamiltonian operator, H_t is[4,8,9]

$$H_t \Psi_t(r,R) = E_t \Psi_t(r,R) \qquad (2.1.1)$$

where Ψ_t is the total wavefunction and E_t the total energy of the system. The collection of co-ordinates required to specify the electrons and nuclei being denoted by r and R respectively.

Explicitly,

$$H_t = -\sum_{k=1}^{P} \frac{\hbar^2}{2M_k} \nabla_k^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + V_{ee}(r) + V_{en}(r,R) + V_{nn}(R) \qquad (2.1.2)$$

$$\text{where } V_{nn}(R) = \tfrac{1}{2} \sum_{k,l=1}^{P\,\prime} Z_k Z_l e^2 \, | R_k - R_l |^{-1}$$

$$V_{en}(r,R) = \sum_{k=1}^{P} \sum_{i=1}^{N} Z_k e^2 \, | R_k - r_i |^{-1} \qquad (2.1.3)$$

$$\text{and} \quad V_{ee}(R) = \tfrac{1}{2} \sum_{i,j=1}^{N\,\prime} e^2 \, | r_i - r_j |^{-1}$$

Equation (2.1.1) describing the combined system of all nuclei and electrons is usually simplified since it is unnecessarily complex.

The usual definition of the intermolecular potential is based on the assumed separation of nuclear and electronic motion which was first suggested by Born and Oppenheimer.[4,8,9,10]

2.2 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation assumes that we may write[8,9]

$$\Psi_t(r,R) = \Psi_n(R) \cdot \Psi_e(r,R) \qquad (2.2.1)$$

where $\Psi_n(R)$ depends on R only and $\Psi_e(r,R)$ depends on r and only parametrically on R.

Also implicit in the usual definition of the intermolecular potential is the adiabatic approximation in the Ehrenfest sense.[1,8] This states that the molecular aggregate, e.g. He_2 can be characterised by a set of quantum numbers e.g. $^1\Sigma_g^+$ which do not change during the collision. Thus for each set of these quantum numbers there is a potential energy surface which determines the motion of the nuclei.

If we substitute (2.2.1) in (2.1.1) then

$$\left\{-\sum_{k=1}^{N}\frac{\hbar^2}{2M_k}\nabla_k^2-\sum_{i=1}^{P}\frac{\hbar^2}{2m}\nabla_i^2+V_{ee}(r)+V_{en}(r,R)+V_{nn}(R)\right\}\Psi_n(R)\,\Psi_e(r,R)$$

$$=E_t\,\Psi_n(R)\,\Psi_e(r,R),$$

$$\text{i.e}\left\{-\sum_{i=1}^{P}\frac{\hbar^2}{2m}\nabla_i^2+V_{ee}(r)+V_{en}(r,R)\right\}\Psi_e(r,R)\,\Psi_n(R)$$

$$+\left\{\sum_{k=1}^{N}\frac{\hbar^2}{2M_k}\nabla_k^2+V_{nn}(R)\right\}\Psi_n(R)\,\Psi_e(r,R)$$

$$-\Psi_n(R)\sum_{k=1}^{N}\frac{\hbar^2}{2M_k}\nabla_k^2\,\Psi_e(r,R)-\sum_{k=1}^{N}\frac{\hbar^2}{2M_k}\nabla_k\,\Psi_n(R)\cdot\nabla_k(\Psi_e(r,R)$$

$$=E_t\,\Psi_n(R)\Psi_e(r,R) \qquad (2.2.2)$$

The last two terms on the left hand side of (2.2.2) involve differentiation of Ψ_e with respect to R and must be neglected since it was assumed that Ψ_e depends only parametrically on R. Thus (2.2.2) becomes an equation with one term dependent on R and one on r and R and may be separated into two equations,

$$H_e(r,R)\,\Psi_e(r,R) = E_e(R)\,\Psi_e(r,R) \qquad (2.2.3)$$

and $$H_n(R)\,\Psi_n(R) = E_t\,\Psi_n(R) \qquad (2.2.4)$$

where

$$H_e = -\sum_{i=1}^{P} \frac{\hbar^2}{2m} \nabla_i^2 + V_{ee}(r) + V_{en}(r,R) \qquad (2.2.5)$$

$$H_n = -\sum_{k=1}^{N} \frac{\hbar^2}{2M_k} \nabla_k^2 + V_{nn}(R) + E_e(R) \qquad (2.2.6)$$

and the separation constant, $E_e(R)$ is the electronic energy.

The equation (2.2.3), usually called the electronic Schrodinger equation, describes the motion of the electrons for a fixed set of nuclear co-ordinates and must be solved for each set of these co-ordinates. The equation (2.2.4) for the nuclear motion contains the electronic energy as a potential term. The nuclei thus move in an effective potential that is the sum of the nuclear coulomb repulsion, $V_{nn}(R)$ and the potential of the average force exerted on the nuclei by the electrons, $E_e(R)$

i.e. $V_{(R)} = V_{nn}(R) + E_e(R)$ (2.2.7)

Equation (2.2.4) is usually modified slightly by adjusting the energy of the system so that the potential energy is zero when the molecules are infinitely separated,[4] i.e.

$$\left(-\sum_{k=1}^{N} \frac{\hbar^2}{2M_k} \nabla_k^2 + \Delta V_{(R)}\right)\Psi_n(R) = E_t \Psi_n(R) \qquad (2.2.8)$$

where $\Delta V_{(R)} = V_{(R)} - \sum_{l=1}^{M} E_l$

E_l being the energy of the l^{th} separated molecule.

The Born-Oppenheimer approximation thus reduces the problem of the intermolecular potential to that of solving (2.2.3). The rationalization of this approximation is that the electrons are much lighter than the nuclei and move very much more rapidly.[8,9] It has been tested numerically for H_2 in the ground state[8] and found to be entirely adequate and should be even better for heavier systems.[9]

More elaborate approximations to the full Schrodinger equation involve including terms dropped from (2.1.1) by using (2.2.1) or by including spin and relativistic terms in the Hamiltonian.

These corrections may be summarised by the following equation,[8]

$$E-E_{bo} = E_{mp} + E_{rel} + E_r + E_c + E_{en} \qquad (2.2.9)$$

where E_{mp} is the correction due to mass polarisation, E_{rel} is due to relativistic corrections, E_r corresponds to the radial motion, E_c to the centrifugal forces and E_{en} to the coupling of electronic and nuclear motions. These terms are all small for the type of interactions that we shall discuss[8] and they will thus be neglected.

2.3 Solution of the Electronic Schrodinger Equation

To solve (2.2.3) exactly for all but the simplest systems is prohibitively difficult and thus approximate solutions must be sought. The most commonly used method for finding these approximate solutions

is by use of the variational principle and a trial wavefunction $\tilde{X}$ with adjustable parameters.[11] The lowest energy is obtained by minimising the expectation value of the Hamiltonian with respect to these adjustable parameters since by the variational principle

$$E \leq \frac{\langle \tilde{X} | H | \tilde{X} \rangle}{\langle \tilde{X} | \tilde{X} \rangle} \qquad (2.3.1)$$

This method has been very successful for interactions of the chemical bonding type e.g. H_2, Li_2, LiH, CO[11,12] if a carefully chosen trial wavefunction is used. However, only the total energy and not the intermolecular potential is determined directly by this method. Thus the potential for the interaction of the non-bonding type is obtained as a very small difference between two very large numbers, as illustrated in Table 1. Furthermore, the upper bound property of the variational method does not apply to this energy difference.

TABLE 1
Energies for He_2

R	E Total	E Atoms	E Interaction
5.0	-5.72335531	-5.72335924	0.00000393
5.4	-5.72338912	"	-0.00002988
5.5	-5.72339136	"	-0.00003212
5.6	-5.72339231	"	-0.00003307
6.0	-5.72338917	"	-0.00002993
7.0	-5.72337396	"	-0.00001473
8.0	-5.72336592	"	-0.00000662
9.0	-5.72336245	"	-0.00000321
10.0	-5.72336090	"	-0.00000166

E Total = E Atoms + E Interaction
Variationally determined, reference 71

Hence we will turn to a method which allows the intermolecular potential to be determined directly. This is perturbation theory in terms of separated molecule wavefunctions.

The use of simple products of separated molecule wavefunctions and Rayleigh-Schrodinger perturbation theory has long been applied to obtain the long range potential between two non-overlapping molecules,[13]

$$\text{i.e. } \Psi = X_o + \sum_{t \neq o} C_t X_t \qquad (2.3.2)$$

$$H = H_o + V \qquad (2.3.3)$$

$$E = E_o + E_1 + E_2 + \ldots\ldots \qquad (2.3.4)$$

where $E_o = \sum_{i=1}^{M} E_{oi}$, the sum of the separated molecule energies,

$H_o = \sum_{i=1}^{M} H_{oi}$, the sum of the separated molecule Hamiltonians,

V = interaction part of the Hamiltonian,

$X_t = \prod_{i=1}^{M} A_t$, the product of separated molecule wavefunctions, A_t

$$E_1 = \langle X_o \mid V \mid X_o \rangle$$

$$E_2 = \sum_{t \neq o} \langle X_o \mid V \mid X_t \rangle^2 / (E_o - E_t)$$

Here E_1 is the electrostatic energy and E_2 the second order energy of induction and dispersion.[13]

However, although the potential is obtained directly by this method the wavefunction (2.3.2) cannot satisfy (2.2.3) as it does not have the full symmetry of H_e. For example, for the interaction of two ground state helium atoms this wavefunction is not antisymmetric to exchange of electrons between the two atoms. This incorrect symmetry is usually called neglect of exchange or neglect of overlap. Generally, let Q be a projection operator which projects from an arbitrary wavefunction a function of the correct symmetry then [17,25,40] $HQ = QH$ and a solution X of (2.2.3) must satisfy $QX = X$. If Q commutes with H_o then the above R-S treatment leads to the correct result.

However, in our case $QH_o \neq H_oQ$ and X_o does not have the correct symmetry and the R-S procedure cannot be used.

Thus a perturbation theory must be developed in terms of QX_o and $\{QX_t\}$ which do have the correct symmetry. This leads to two problems,

1. QX_o is not an eigen function of H_o [25], and
2. although the set of simple products of excited state functions, $\{X_t\}$ is complete the set of correctly symmetrized products $\{QX_t\}$ is overcomplete. [14,16] The second point leads to a non-unique expansion of the wavefunction (and thus the energy) in terms of these functions.

Many different schemes have been developed to treat this perturbation theory problem corresponding to different choices of the expansion coefficients.[14-43] The energy expressions generally give a first order term which is the Heitler-London value but differ in higher order terms due to these different choices of expansion coefficients. The methods used have been,

1. more or less direct extensions of the R-S procedure with a particular arbitrary choice of expansion coefficients,[14-16,34,37-41]
2. methods related to degenerate perturbation theory,[18-21]
3. schemes based on transformations of the Hamiltonian[22-24] and
4. most commonly, projection operator techniques[25-33,35,36]

In the first mentioned methods it is difficult to justify a particular choice of expansion coefficients.[16] The degenerate perturbation theory methods are rather more complex than the other methods and rather hard to interpret.[18b] The third method leads to difficulties such as the possibility of the energy not being real.[23] Thus we will use the last mentioned method to study the problem.

2.4 Perturbation Theory of the Intermolecular Potential

It is usual to write[25, 31, 32]

$$\begin{aligned} \Psi &= WQ\, X_o \\ &= (1+T_1 H)\, QX_o \\ &= QX_o + T_1 H\, QX_o \end{aligned} \qquad (2.4.1)$$

It may be shown that if (2.4.1) is to satisfy the Schro dinger equation then,[32]

$$T_1 = (E - P_1 H P_1)^{-1} P_1 \tag{2.4.2}$$

where

$$\begin{aligned} P_1 &= Q - Q \mid X_o \rangle\langle X_o \mid Q \mid X_o \rangle^{-1} \langle X_o \mid Q \\ &= w^+ Q \\ &= Qw \end{aligned} \tag{2.4.3}$$

and

$$w = 1 - \mid X_o \rangle\langle X_o \mid Q \mid X_o \rangle^{-1} \langle X_o \mid Q \tag{2.4.4}$$

T_1 and P_1 have the following properties

$$\left.\begin{aligned} &T_1 = T_1^+,\ P_1 = P_1^+,\ T_1 X_o = P_1 X_o = 0 \\ &T_1 = QT_1 = T_1 Q = P_1 T_1 = T_1 P_1 = P_1 T_1 P_1 \\ &P_1 = QP_1 = P_1 Q = QP_1 Q \end{aligned}\right\} \tag{2.4.5}$$

and

$$T_1 = (1 - R_o w^+ V') R_o P_1 \tag{2.4.6}$$

where

$$R_o = \sum_t{}' \mid X_t \rangle\langle X_t \mid / (E_o - E_t) \tag{2.4.7}$$

and

$$V' = V - (E - E_o) \tag{2.4.8}$$

Thus

$$\Psi = Q X_o + T_1 Q H X_o \quad (QH = HQ)$$

$$= QX_o + T_1 HX_o \qquad (T_1 Q = T_1)$$

$$= QX_o + T_1 H_o X_o + T_1 VX_o$$

$$= QX_o + E_o T_1 X_o + T_1 VX_o \quad (H_o X_o = E_o X_o)$$

$$= QX_o + T_1 VX_o \quad (T_1 X_o = 0) \qquad (2.4.9)$$

The energy is then given by

$(E-H)\,\Psi = 0$ (from 2.2.3)

Thus

$$\langle X_o \mid E - H \mid \Psi \rangle = 0,$$

$$E = \langle X_o \mid H(QX_o + T_1 VX_o) \mid X_o \rangle \,/\, \langle X_o \mid Q \mid X_o \rangle$$

(since $\langle X_o \mid \Psi \rangle = \langle X_o \mid Q \mid X_o \rangle$)

$$= (\langle X_o \mid H_o Q X_o \rangle + \langle X_o \mid VQX_o \rangle$$

$$+ \langle X_o \mid H_o T_1 VX_o \rangle + \langle X_o \mid VT_1 V \mid X_o \rangle) / \langle X_o \mid Q \mid X_o \rangle$$

$$= (E_o \langle X_o \mid Q \mid X_o \rangle + \langle X_o \mid VQX_o \rangle$$

$$+ E_o \langle X_o \mid T_1 VX_o \rangle + \langle X_o \mid VT_1 V \mid X_o \rangle)$$

$$/ \langle X_o \mid Q \mid X_o \rangle \quad (H_o^+ = H_o)$$

$$= (E_o \langle X_o \mid Q \mid X_o \rangle + \langle X_o \mid VQX_o \rangle$$

$$+ 0 + \langle X_o \mid VT_1 V \mid X_o \rangle) / \langle X_o \mid QX_o \rangle \quad (T_1^+ = T_1, \langle X_o \mid T_1^+ = 0)$$

$$E = E_o + \langle X_o \mid VQX_o \rangle / \langle X_o \mid QX_o \rangle + \langle X_o \mid VT_1 V \mid X_o \rangle / \langle X_o \mid QX_o \rangle$$

(2.4.10)

Perturbation expansions may be obtained by expanding T_1 in a power series e.g. using the operator identity[32]

$$T = (1-B)^{-1} \times C = \tfrac{1}{2}(C^{+}+C) + \tfrac{1}{2}(BC^{+} + CB^{+}) + BTB^{+} \qquad (2.4.11)$$

then

$$T_1 = (1 - R_o w^{+} V^{1})^{-1} R_o P_1$$

$$= \tfrac{1}{2}(R_o P_1 + P_1 R_o) + \tfrac{1}{2}(R_o w^{+} V^{1} P_1 R_o + R_o P_1 V^{1} w R_o) + R_o w^{+} V^{1} T_1 V^{1} w R_o$$

Thus

$$T_1 = \tfrac{1}{2}(R_o P_1 + P_1 R_o) + \tfrac{1}{2}(R_o w^{+} V^{1} w R_o + R_o w^{+} Q V^{1} w R_o)$$

$$+ R_o w^{+} V^{1} T_1 V^{1} w R_o \quad (P_1 = w^{+} Q = Q w)$$

therefore

$$T_1 = \tfrac{1}{2}(R_o P_1 + P_1 R_o) + R_o w^{+} V_q^{1} w R_o + R_o w^{+} V^{1} T_1 V^{1} w R_o \qquad (2.4.12)$$

where

$$V_q^{1} = \tfrac{1}{2}(V^{1} Q + Q V^{1})$$

From $P_1 T_1 P_1 = T_1$

$$T_1 = \tfrac{1}{2}(P_1 R_o P_1 + P_1 R_o P_1) + P_1 R_o w^{+} V_q^{1} w R_o P_1 + P_1 R_o w^{+} V^{1} T_1 V^{1} w R_o P_1 \quad (P_1^2 = P_1)$$

Therefore

$$T_1 = P_1 R_o P_1 + P_1 R_o w^{+} V_q^{1} w R_o P_1 + P_1 R_o w^{+} V^{1} T_1 V^{1} w R_o P_1 \qquad (2.4.13)$$

Equation (2.4.13) is equivalent to

$$T_1 = P_1 (1 - R_o w^{+} V^{1} P_1)^{-1} R_o P_1$$

$$= P_1 \sum_{k=o}^{\infty} (R_o w^{+} V^{1} P_1)^{k} R_o P_1 \qquad (2.4.14)$$

Using (2.4.5) many other expansions of T_1 are possible and thus many different perturbation expressions could be obtained.

All these schemes will be equivalent to infinite order but will not be if the expansions of T_1 are truncated to low order.[32,33,34, 40]

The two most widely used schemes are the Murrell-Shaw-Musher-Amos formalism (MS-MA)[25,39,a,b] which corresponds to using (2.4.12) and the Eisenschitz-London-Hirschfelder-van der Avoird formalism[14,17,31] (EL-HAV) which uses (2.4.13).

The MS-MA scheme gave good results for the energy of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 at large separations[18 b,d] and reasonable results for the ground state of He_2[25 d,e] and $Li^+ - LiH$[28] were obtained using approximate wavefunctions. In all cases the energy was calculated to second order i.e. using the wavefunction to first order.

The principle disadvantage of the method is that the wavefunction does not have the correct symmetry order by order.[18,25,32,33] This means that the expectation value of the Hamiltonian is poor,[18 b,d] and the total wavefunction cannot be used variationally, as has been shown numerically for H_2.[18 b,d] This incorrect symmetry means that some terms may be missing from the energy expression.[31b] It may also mean that expectation values of other operators are as poor as the expectation value of the Hamiltonian.

The EL-HAV scheme does give a wavefunction of the correct symmetry order by order[31] but it does not give satisfactory energies to second order for the systems so far studied.[18] Also the long range limit of the second order energy in this scheme, unlike the MS-MA second order energy, does not have the correct behaviour i.e. does not approach (2.3.4) for these systems.[18,33] This is because the third order energy is not negligible compared to the second order energy.[18] Thus the concept of each order of perturbation being of very much smaller magnitude than the preceeding order is lost in this scheme. Methods to overcome this deficiency e.g. transformations of the Hamiltonian or calculation of the third order energy make the method much more complex than the MS-MA scheme for results of comparable accuracy.[18a,33] The use of the variational principle with the total wavefunction is not of much help either as we then only determine the total energy and not the intermolecular potential.[33] Thus it is preferable to develop a modification of the MS-MA scheme which gives a wavefunction of correct symmetry order by order than to correct the EL-HAV scheme.

This symmetrization is very easily accomplished since

$$\begin{aligned}\Psi &= Q X_o + T_1 V X_o \\ &= Q X_o + \tfrac{1}{2}(R_o P_1 + P_1 R_o) V X_o + \ldots. \\ &= Q X_o + X_m^{(1)} + \ldots..\end{aligned} \qquad (2.4.15)$$

But

$$
\begin{aligned}
Q\,\Psi &= \Psi \\
&= Q(QX_o + T_1 VX_o) \\
&= Q.QX_o + QX_m^{(1)} + \ldots \quad (Q^2 = Q) \\
&= QX_o + QX_m^{(1)} + \ldots \qquad (2.4.16) \\
&= QX_o + X^{(1)} + \ldots
\end{aligned}
$$

or alternatively the fact that

$$T_1 = QT_1 = \tfrac{1}{2}(QR_oP_1 + QP_1R_o) + \ldots \qquad (2.4.17)$$

may be used to develop a symmetrized expansion.

Thus although the MS-MA expansion of the wavefunction, (2.4.15) does not have the correct symmetry order by order the expansion (2.4.16) does since for example,

$$X^{(1)} = QX_m^{(1)}$$

and,

$$T_1 = QT_m^{(1)} + QT_m^{(2)} + \ldots \qquad (2.4.18)$$

and in general

$$X^{(n)} = QX_m^{(n)} \qquad (2.4.19)$$

However, since Q may be written as

$$Q = N(1+P_{ij}) \qquad (2.4.20)$$

where N is chosen so that $Q^2 = Q$ and P_{ij} is the operator which permutes the electron co-ordinates between the two sets and combines them in such a way as to produce a function of the correct symmetry, it is easily seen that the above expansion does not have the correct long range limit i.e. it does not approach (2. 3. 2.) at large distances. This is because of the extra factor N which has been introduced upon symmetrization i.e. by multiplying (2.4.15) by Q. This fault is easily corrected by making a Feenberg transformation[18a] of the Hamiltonian which enables us to write,

$$E = E_o + E_1 + cE_2 + \ldots. \qquad (2.4.21)$$

where c is an arbitrary constant. If c is chosen to be N^{-1} then the second order energy has the correct long range limit. A similar technique has been used by Certain and Hirschfelder[18a] to correct the long range behaviour in the EL-HAV scheme. However, they made an arbitrary choice of c (which gave the correct result for the systems studied) the significance of which they were unable to explain.

The significance of the choice is probably that it cancels the extra factor N introduced by going from (2.4.12) i.e. the MS-MA scheme to (2.4.13) i.e. the EL-HAV scheme.

Before we obtain an expression for the second order energy it may be noted that

$$T_1 = (1 - R_o w^+ V')^{-1} R_o P_1$$
$$= R_o P_1 + R_o w^+ V' R_o P_1 + ... \qquad (2.4.22)$$

and this expansion leads to a second order energy expression identical to the second order MS-MA scheme, but enables the derivation of the expression to be made more easily. Thus we use

$$T_1 = R_o P_1 + R_o w^+ V' R_o P_1 + ...$$
$$= Q T_1$$
$$= Q R_o P_1 + Q R_o w^+ V' R_o P_1 + ... \qquad (2.4.23)$$

together with the Feenberg transformation (2.4.21) to obtain a wave-function of the correct symmetry and which gives a second order energy expression with the correct long range limit. This energy expressions are,

1st Order Energy

$$E_1 = \langle X_o | QV | X_o \rangle / \langle X_o | Q | X_o \rangle$$
$$= \langle X_o | N (1+P_{ij}) V | X_o \rangle / \langle X_o | N (1+P_{ij}) | X_o \rangle$$
$$= (\langle X_o | V | X_o \rangle + \langle X_o | V P_{ij} | X_o \rangle) / (\langle X_o | X_o \rangle + \langle X_o | P_{ij} | X_o \rangle)$$
$$= (V_{oo} + V_{oo'}) / (1+S_{oo'}) \qquad (2.4.24)$$
$$= V_{oo} - V_{oo} S_{oo'} + V_{oo'} \qquad (2.4.25)$$

(to first order in exchange)

The expression (2.4.25) is usually divided into coulomb and exchange parts i.e.

$$E_{coul} = V_{oo} + V_{nn} \tag{2.4.26}$$

$$E_{exch} = -V_{oo} S_{oo'} + V_{oo'} \tag{2.4.27}$$

where we have added the nuclear-nuclear coulomb repulsion energy, V_{nn} to V_{oo} to form the total coulomb energy of the system.

2nd Order Energy

$$E_2 = c \langle X_o | V Q R_o P_1 V | X_o \rangle / \langle X_o | Q | X_o \rangle$$

$$= \Sigma_t' (V_{ot}^2 + V_{ot} V_{ot'} + V_{ot} S_{ot'} E_1$$

$$+ V_{ot} V_{ot'} + V_{ot'} V_{ot'} + V_{ot'} S_{ot'} E_1) / (E_o - E_t)(1 - S_{oo'}) \tag{2.4.28}$$

$$= \Sigma_t' (V_{ot}^2 - V_{ot}^2 S_{oo'} + V_{ot} V_{ot'} + V_{ot} S_{ot'} E_1$$

$$+ V_{ot} V_{ot'}) / (E_o - E_t) \tag{2.4.29}$$

(to first order in exchange)

$$= E^2_{pol} + E^2_{exch} \tag{2.4.30}$$

where

$$E^2_{pol} = \Sigma_t' V_{ot}^2 / (E_o - E_t)$$

and $$E^2_{exch} = \Sigma_t' \{(V_{ot} V_{ot'} + V_{ot} S_{ot'} E_1 - V_{ot}^2 S_{oo'}) / (E_o - E_t) + V_{ot} V_{ot'} / (E_o - E_t)\} \tag{2.4.31}$$

Thus to first order in exchange the symmetrization of the MS-MA wavefunction leads to only a minor change in the energy expression. The extra term, $\sum_t' V_{ot} V_{ot'} / (E_o - E_t)$ should be very small for the interaction

of closed shell systems in the region of the vanderWaals minimum. This is because the integrals involved in the second-order exchange energy fall off exponentially with distance and the distances involved are large.

Little more can be learnt from the above expansion as to the magnitude of the various terms and the usefulness of the perturbation approach to the calculation of the intermolecular potential unless numerical applications to some typical systems are made. Since not even the exact ground state wavefunctions, A_o, B_o are known let alone the complete set of excited state functions A_t, B_t the equations presented so far appear to be of no use at all.

In the next sectionsthe problem of using the above formal basis in numerical applications will be discussed.

2.5 Wavefunctions for Closed shell Systems and the First Order Energy [18,31,33,34]

The model systems which have been treated so far e.g. two interacting spins in a magnetic field[34] or H_2^+ [31a,33b] have little in common with the interaction of closed shell systems, for which the perturbation theories were developed. Thus the success or failure of the various methods for these systems tells us little of which formalism or formalisms are suitable for calculating intermolecular potentials.

For electronic systems the exact wavefunction may be expanded in terms of antisymmetric products (or Slater determinants) of a complete set of one electron functions or orbitals, X_{ki} .[11,49]

Every selection of N one electron indices, $k_1 < k_2 < k_3 < \ldots < k_N$ is called a configuration, K and the function

$$\Psi_k(r) = (N!)^{\frac{1}{2}} \det (X_{k_1}, X_{k_2}, \ldots, X_{k_N}) \qquad (2.5.1)$$

is the normalised Slater determinant belonging to this configuration. The total wavefunction is then[11,48,49]

$$\Psi(r) = \Sigma_k C_k \Psi_k \qquad (2.5.2)$$

e.g. for a two electron system in a singlet state

$$\Psi(r) = \Psi(r_1, r_2)\,(\alpha(1)\beta(2) - \alpha(2)\beta(1))/\sqrt{2}$$

$$= \sum_{kl} C_{kl} X_k(r_1) X_l(r_2)\,(\alpha(1)\beta(2) - \alpha(2)\beta(1))/\sqrt{2} \qquad (2.5.3)$$

Where , r_1, r_2 are the space co-ordinates of electrons 1 and 2 and α, β are the elementary spin functions.

A special case of this method is the use of a single determinant, which is the Hartree-Fock (H.F.) wavefunction if the best possible single determinant is found.[11,49]

In practice the individual orbitals, X_{ki} are expanded in some truncated, complete set of basis functions e.g. Slater orbitals[11] (S.T.O.'s) or Gaussian orbitals[52] (G.T.O.'s). This enables the determination of the parameters in the wavefunction and properties from the wavefunction to be made analytically.

Although the exact, infinite series (2.5.2) has never been obtained for any system, very good approximations have been obtained for several atoms and some simple molecules and we feel that conclusions based on them should be valid for the complete wavefunction.

It is found that if the first determinant in (2.5.2) is the Hartree-Fock function or a close approximation to it, then the first coefficient, C_1 is very large compared to the other C_k.[48,49,50,51] Alternatively the wavefunction may be transformed into a form in which the first term is very close to the H-F function and for this expansion $C_1 \gg C_k$ e.g. the natural orbital transformation.[48,51] This is illustrated in Table 2.

TABLE 2
Multiconfiguration Wavefunctions for Some Molecules

System	C1	C2	C3	C4	Reference
Ne('S)	1.5275	-0.2647	-0.3516	-	162
Ne('S)*	0.98362	-	-	-	161
$Be('S)^+$	0.953188	-0.29863	-0.028595	-0.020816	50
$He('S)^+$	0.99599	-0.06160	-0.00768	-0.00165	50
$He('S)^+$	0.995996	-0.061646	-0.03569	-0.03086	163
$He('S)^+$	0.99598	-0.06191	-0.06163	-0.01265	51
He('S)	0.99596	-0.05671	-0.05010	-0.03086	49
$H_2('\Sigma_g^+)$	0.99029	-0.10242	-0.04478	-0.04478	164

This table gives the largest coefficients in expansion (2.5.2)
* Other $C_k < 0.1$
+ Natural orbital (N.O.) wavefunctions, 1st N.O. a very close approximation to H.F.

We may write the wavefunction as

$$A_o = C_1 A_1 + \sum_{i \neq 1} C_i A_i \qquad (2.5.4)$$

Where A_1 = the dominant configuration

or

$$A_o = C_{a_1} A_1 + d_a A_c \qquad (2.5.5)$$

and similarly for B_o

thus

$$X_o = A_o(i)\, B_o(j)$$

$$= (C_{a_1} A_1(i) + d_a A_c(i))\,(C_{b_1} B_1(j) + d_b B_c(j))$$

$$= C_{a_1} C_{b_1} A_1(i) B_1(j) + d_a C_{b_1} A_c(i) B_1(j)$$

$$+ d_b C_{a_1} A_1(i) B_c(j) + d_a d_b A_c(i) B_c(j) \qquad (2.5.6)$$

For the first order energy a general matrix element may be represented as,

$$W = \langle A_o(i)\, B_o(j) \mid \hat{X} \mid Y\, A_o(i)\, B_o(j) \rangle \qquad (2.5.7)$$

where $\hat{X} = V$ or 1, $Y = P_{ij}$ or 1,

$A_o(i) = C_{a_1} A_1(i) + d_a A_c(i)$

and $B_o(j) = C_{b_1} B_1(j) + d_b B_c(j)$

Then

$$W = C_{a1}^2\ C_{b1}^2 \langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_1 \rangle$$

$$+ C_{a1}^2\ C_{b1}\ d_b(\langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_c\rangle + \langle A_1B_c \mid \hat{X} \mid Y\, A_1B_1\rangle)$$

$$+ C_{a1}\ C_{b1}^2\ d_a(\langle A_1B_1 \mid \hat{X} \mid Y\, A_cB_1\rangle + \langle A_cB_1 \mid \hat{X} \mid Y\, A_1B_1\rangle)$$

$$+ C_{a1}\ C_{b1}\ d_ad_b(\langle A_1B_1 \mid \hat{X} \mid Y\, A_cB_c\rangle + \langle A_1B_c \mid \hat{X} \mid Y\, A_cB_1\rangle$$

$$+ \langle A_cB_1 \mid \hat{X} \mid Y\, A_1B_c\rangle + \langle A_cB_c \mid \hat{X} \mid Y\, A_1B_1\rangle)$$

$$+ C_{a1}\ d_ad_b^2(\langle A_1B_c \mid \hat{X} \mid Y\, A_cB_c\rangle + \langle A_cB_c \mid \hat{X} \mid Y\, A_1B_c\rangle)$$

$$+ C_{b1}\ d_a^2d_b(\langle A_cB_1 \mid \hat{X} \mid Y\, A_cB_c\rangle + \langle A_cB_c \mid \hat{X} \mid Y\, A_cB_1\rangle)$$

$$+ d_a^2d_b^2 \langle A_cB_c \mid \hat{X} \mid Y\, A_cB_c\rangle \qquad (2.5.8)$$

For closed shell systems, as was mentioned before $C_{a1}, C_{b1} \gg d_a, d_b$ and thus only terms of first order in d_a and d_b need be considered i.e.

$$W = \langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_1\rangle + (C_{a1}^2\ C_{b1}^2 - 1)\langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_1\rangle$$

$$+ d_b\ C_{a1}^2\ C_{b1}(\langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_c\rangle + \langle A_1B_c \mid \hat{X} \mid Y\, A_1B_1\rangle)$$

$$+ d_a\ C_{a1}^2\ C_{b1}(\langle A_1B_1 \mid \hat{X} \mid Y\, A_cB_1\rangle + \langle A_cB_1 \mid \hat{X} \mid Y\, A_1B_1\rangle)$$

(2.5.9)

For the homonuclear case (2.5.9) reduces to

$$W = \langle A_1B_1 \mid \hat{X} \mid Y\, A_1B\rangle + (C_{a1}^4 - 1)\langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_1\rangle$$

$$+ 2\, d_a\ C_{a1}^3(\langle A_1B_1 \mid \hat{X} \mid Y\, A_1B_c\rangle + \langle A_1B_c \mid \hat{X} \mid Y\, A_1B_1\rangle) \qquad (2.5.10)$$

$$= W_{11} + (C_{a1}^4 - 1) W_{11} + 2d_a C_{a1}^3 W_c \qquad (2.5.11)$$

where

$$W_{11} = \langle A_1 B_1 \mid \hat{X} \mid Y A_1 B_1 \rangle$$

$$W_c = (\langle A_1 B_1 \mid \hat{X} \mid Y A_1 B_c \rangle + \langle A_1 B_c \mid \hat{X} \mid Y A_1 B_1 \rangle)$$

The term $(C_{a1}^4 - 1) W_{11}$ may be termed a normalisation correction and the term W_c a correlation correction.

If B_c is expanded in a set of orthogonal, one-electron functions B_{ci} (as mentioned before) then for helium,

$$d_b B_c(3,4) = \sum_{ij} D_{ij} B_{ci}(3) B_{cj}(4) \frac{1}{\sqrt{2}} (\alpha(3)\beta(4) - \beta(3)\alpha(4)) \qquad (2.5.12)$$

For the coulomb energy

$$W_c = C_{a1}^3 \sum_{ij} D_{ij} \langle A_{c1}(1) A_{c1}(2) A_{c1}(1) A_{c1}(2) \mid V \mid B_{c1}(3) B_{c1}(4) B_{ci}(3) B_{cj}(4) \rangle$$

$$XS(1,2,3,4)$$

$$= C_{a1}^3 \sum_{ij} D_{ij} (2 \langle A_{c1} \mid R_b \mid A_{c1} \rangle \langle B_{c1} \mid B_{ci} \rangle \langle B_{c1} \mid B_{cj} \rangle$$

$$+ \langle B_{c1} \mid R_a \mid B_{ci} \rangle \langle B_{c1} \mid B_{cj} \rangle + \langle B_{c1} \mid R_b \mid B_{cj} \rangle \langle B_{c1} \mid B_{ci} \rangle$$

$$+ 2 \langle A_{c1} A_{c1} \mid B_{c1} B_{ci} \rangle \langle B_{c1} \mid B_{cj} \rangle$$

$$+ 2 \langle A_{c1} A_{c1} \mid B_{c1} B_{cj} \rangle \langle B_{c1} \mid B_{ci} \rangle)$$

$= 0$, due to orthogonality

(S (1,2,3,4) = an integral over spin functions)

Thus the first non-zero correction to the terms V_{oo} and $V_{oo}S_{oo}'$ are of second order in d and consequently very small.

Hence the only correction to the first order energy of order d is the correction to V_{oo}. For example for He_2 this term is,

$$W_c = \sum_{i,j} D_{ij} \left(\langle A_{c1}(1)\, A_{c1}(2)\, B_{c1}(3)\, B_{c1}(4) \mid V \mid P_{ij}\, A_{c1}(1)\, A_{c1}(2)\, B_{ci}(3)\, B_{cj}(4) \rangle \right.$$

$$\left. + \langle A_{c1}(1)\, A_{c1}(2)\, B_{ci}(3)\, B_{cj}(4) \mid V \mid P_{ij}\, A_{c1}(2)\, B_{c1}(3)\, B_{c1}(4) \rangle \right) S(1,2,3,4)$$

$$= \sum_{i,j} D_{ij} (W_1 + W_2) \qquad (2.5.13)$$

where S (1,2,3,4) is an integral over spin functions,

$$W_1 = -\left(\langle A_{c1} \mid B_{ci} \rangle \langle A_{c1} \mid B_{c1} \rangle \langle B_{c1} \mid R_a \mid B_{cj} \rangle + \langle A_{c1} A_{c1} \mid B_{c1} B_{cj} \rangle \right)$$

$$+ \langle A_{c1} \mid B_{c1} \rangle \langle A_{c1} \mid B_{cj} \rangle \langle B_{c1} \mid R_a \mid B_{ci} \rangle + \langle A_{c1} A_{c1} \mid B_{c1} B_{cj} \rangle \Big)$$

$$+ \langle A_{c1} \mid B_{ci} \rangle \langle A_{c1} B_{c1} \mid B_{c1} B_{cj} \rangle + \langle A_{c1} \mid B_{cj} \rangle \langle A_{c1} B_{c1} \mid B_{c1} B_{ci} \rangle \Big)$$

$$W_2 = -\left(\langle A_{c1} \mid B_{c1} \rangle \langle A_{c1} B_{ci} \mid B_{c1} B_{cj} \rangle + \langle A_{c1} B_{cj} \mid B_{c1} B_{ci} \rangle \right.$$

$$+ \langle A_{c1} \mid B_{c1} \rangle \langle A_{c1} \mid B_{ci} \rangle \langle B_{c1} \mid R_a \mid B_{cj} \rangle + \langle A_{c1} A_{c1} \mid B_{c1} B_{cj} \rangle \Big)$$

$$\left. + \langle A_{c1} \mid B_{c1} \rangle \langle A_{c1} \mid B_{cj} \rangle \langle B_{c1} \mid R_a \mid B_{ci} \rangle + \langle A_{c1} A_{c1} \mid B_{c1} B_{ci} \rangle \right) \Big)$$

i.e.

$$W_c = \sum_{i,j} D_{ij} \left(2 \langle A_{c1} \mid B_{c1} \rangle \langle A_{c1} \mid B_{ci} \rangle \langle B_{c1} \mid R_a \mid B_{cj} \rangle + \langle A_{c1} A_{c1} \mid B_{c1} B_{cj} \rangle \right)$$

$$+ 2 \langle A_{c1} \mid B_{c1} \rangle \langle A_{c1} \mid B_{cj} \rangle \langle B_{c1} \mid R_a \mid B_{ci} \rangle + \langle A_{c1} A_{c1} \mid B_{c1} B_{ci} \rangle \Big)$$

$$+ \langle A_{c1} \mid B_{c1} \rangle \{ \langle A_{c1} B_{ci} \mid B_{c1} B_{cj} \rangle + \langle A_{c1} B_{cj} \mid B_{c1} B_{ci} \rangle \}$$

$$+ \langle A_{c1} \mid B_{ci} \rangle \langle A_{c1} B_{c1} \mid B_{c1} B_{cj} \rangle + \langle A_{c1} \mid B_{cj} \rangle \langle A_{c1} B_{c1} \mid B_{c1} B_{ci} \rangle \}$$

(2.5.14)

where $R_a = -2/r_{1a}$ and $R_b = -2/r_{1b}$

If as is usual, we approximate the ground state wavefunctions by single determinants we shall call the result the "Single Determinant Separated Molecule" (S.D.S.M.) result. If the best single determinant or Hartree-Fock function is used the result will be called the "Hartree-Fock Separated Molecule" (H.F.S.M.) result.

2.6 Application to the $^1\Sigma g^+$ state of He_2

To gain more insight into the above equations for the first order energy the interaction of two ground state He atoms, the $^1\Sigma g^+$ state of He_2 will be considered. The S.D.S.M. results for He_2 are

$$E_{coul} = \{4[(aa|bb) - 2(a|R_b|a)] + 4/R\} \qquad (2.6.1)$$

$$E_{exch} = 2\{(a|b)^2 (3\,(aa|bb) - 4\,(a|R_b|a)) - 2(a|b)\,((aa|ab) - 2(a|R_b|b)) - (ab|ab)\} \qquad (2.6.2)$$

Where a and b are orbitals on atoms A and B respectively, R the distance between A and B and

$R_b = 1.0/r_{1b}$,

$(a|b) = \int a(1)\, b(1)\, d\tau_1$,

$(a|R_b|b) = \int a(1)\, r_{1b}^{-1}\, b(1)\, d\tau_1$

and

$(ab|cd) = \int\int a(1)\, b(1)\, r_{12}^{-1}\, c(2)\, d(2)\, d\tau_1\, d\tau_2$

Since the exact Hartree-Fock function is not known analytically, approximations in terms of a set of basis functions must be used. The best of these approximations are the S.T.O. expansions.[53-57] Murrell and Shaw[25 d,e] have previously used (2.6.1.) and (2.6.2.) together with an approximate H.F. function expanded in terms of S.T.O.'s, however, the function they used contained only two optimized non-linear parameters (orbital exponents) and thus their results may not be very close to the H.F.S.M. result.

To establish the H.F.S.M. result the equations (2.6.1) and (2.6.2) were solved using S.T.O. basis set of 1,2,3 and 4 functions (called n = 1,2,3,4 results respectively). The results for the coulomb, exchange and total first order energies may be seen in Tables 3,4, and 5. The n = 1 results are exceedingly poor but the n=2 results (particularly from the function determined by Clementi[53]) are quite close to the results the large basis sets. In fact the n = 2 results are in better agreement with the large basis sets results than the Murrell - Shaw results. Our n = 1

energies do not agree with those of Murrell and Shaw for the same function, however, we tested all the integrals involved against the tabulations of Hirschfelder and Linnett[44] and found agreement to at least 8 significant figures (see appendix B).

The n=3,4 results are almost identical except at very large distances where the first order energy is only a fraction of the total interaction energy anyway, making the differences of no importance. It is interesting to note how closely the coulomb energies for the n=3 and n=5 basis sets agree (the exchange energy for the n=5 basis set was not calculated as it would have been very time consuming). It is encouraging that the two n=3 and the two n=4 results are in good mutual agreement. This is because the second function in each case was determined by imposing constraints on the wavefunction which means that less non-linear parameters had to be optimised for the second function than for the first. This point is particularly relevant to the study of larger systems.

Also shown in Table 6,7 and 8 are the results for 1 s G.T.O. approximations to the H.F. function.[58] These results were obtained because,

(a) only G.T.O. wavefunctions are generally available for large, non-atomic systems,

(b) orientation dependent interactions are more easily calculated using G.T.O. than S.T.O. wavefunctions because of the greater ease of calculating the multicentre integrals over G.T.O.'s than S.T.O.'s,[62] and

(c) the G.T.O. wavefunctions give less accurate electron densities at large distances from the nuclei than do S.T.O. wavefunctions.[26]

The last point casts some doubt on the use of G.T.O. wavefunctions at the large distances involved in this type of work.

The first two points mean that if the perturbation method is to be of use for studying many-body and non-atomic interactions then the accuracy of G.T.O. wavefunctions must be tested for systems where the S.T.O. and G.T.O. results can be compared.

The G.T.O. results for n=8,9,10 are in good mutual agreement and in good agreement with the S.T.O. results except at very large distances where the exchange energy is very small and this will not lead to large errors in the total interaction energy. The coulomb energies for the smaller basis sets are better than the exchange energies. To obtain a good first order energy it seems that more than twice as many G.T.O.'s as S.T.O.'s are needed. This means that for the interaction of two atoms little advantage is gained in using the more easily integrable gaussians. However, for non-atomic and many-body interactions the advantage of easy integrability will be very great.

As the n=3 S.T.O. results are very close to the n=4 (and n=5 results for the coulomb energy) we then used this basis set to calculate the H.F.S.M. coulomb, exchange and first order energies over a greater range of distances in the region of the van der Waals minimum. These results are shown in Table 9. These results show that the electronic contribution to the coulomb energy is cancelled out by the coulomb repulsion of the nuclei at large distance i.e. when the atoms do not overlap appreciably. This is to be expected as the two separated atoms are electrically neutral. Similarly the exchange energy is only significant when the systems overlap appreciably. These points are seen by comparing E_{coul} and E_{exch} at distances where $S_{oo'}$ is significant to the values where $S_{oo'}$ is almost zero.

To obtain an estimate of the error involved by approximating A_o and B_o by single determinant wavefunctions the first order correction to the first order energy i.e. (2.5.11) was evaluated for two functions of the form,

$$A_o = N (A_{hf} + d\, A_c) \qquad (4.6.3)$$

where N is a normalising constant,

d is a "mixing coefficient",

A_{hf} an H.F. function and

A_c a "correlation" function. The correlation function allows for the

instantaneous correlations of the motions of the electrons (as opposed to the average interactions treated by A_{hf}) and it may be divided into two terms,

$$A_c = A_r + A_a \qquad (4.6.4)$$

the radical correlation function, A_r being expanded in terms of functions of r only and A_a, the angular correlation function depends on the angular as well as the radical electronic co-ordinates. For He radial correlation amounts to about 40% of the total correlation energy and the other 60% is angular correlation.[11]

Thus two functions were used one which obtains about 90% of the radial correlation and one which obtains about 85% of the angular correlation.[59,63] In both cases the effects are not large as can be seen from table 11.

2.7 Second Order Energy

Since the complete set of excited state wavefunctions is unknown (except for hydrogen) the variational method must be used to approximate this set i.e. one solves,[18d]

$$(H_o - E_o) X_1 + Q(V - E_1) X_o = 0 \qquad (2.7.1)$$

where X_1 is the first order wavefunction. Besides this the hydrogenic set needs the inclusion of continium functions to make the set complete and this leads to slow convergence.[18d,48] Thus Hirschfelder et al[18d]

in studying the $^1\Sigma g^+$ and $^3\Sigma u^+$ states of H_2 by different exchange perturbation methods used a basis set of elliptic co-ordinate functions to obtain good convergence. However, when a large basis set is used to solve (2.7.1) the set becomes practically linearly dependent and makes the variational method numerically unsatisfactory.[18b,d] Thus it seems preferable to use a scheme which is based on the variational principle but does not require the use of a large basis set and the consequent problems of near linear dependence and numerical instability.[18b] To do this the individual terms in (2.4.29) must be considered. At large distances the second order energy in the MS-MA scheme becomes equal to the non-exchange expression (2.3.4). This second order term, usually called the second order polarisation energy may be divided into two terms e.g. for two molecules,

$$E_2 = E_{disp} + E_{ind} \qquad (2.7.2)$$

$$E_{disp} = \Sigma'_t \langle A_o B_o \mid V \mid A_t B_t \rangle / (E_o - E_t)$$

$$E_{ind} = \Sigma'_t \langle A_o B_o \mid V \mid A_o B_t \rangle / (E_o - E_t)$$

$$+ \Sigma'_t \langle A_o B_o \mid V \mid A_t B_o \rangle / (E_o - E_t)$$

Thus the dispersion energy, E_{disp} arises from doubly excited configurations and the induction energy, E_{ind} arises from single excitations. The above terms are usually calculated by expanding V in a multipole series which is valid if the two systems do not overlap.[13] The result for the dispersion

energy is,[13]

$$E_{disp} = - C_6/r^6 - C_8/r^8 - C_{10}/r^{10} \ldots . \qquad (2.7.3)$$

where C_6, C_8, C_{10} are constants.

These terms may also be classified as dipole-dipole (C_6), dipole-quadrupole (C_8), quadrupole-quadrupole and dipole-octopole (C_{10}) because of the form of the terms which arise in the multipole expansion of V. The constants C_6, C_8 and C_{10} are usually calculated by relating them to oscillator strengths, refractive index data etc.[13a]

Quantum mechanical calculations have been made for simple atoms using elaborate wavefunctions and the variational method.[13a,c] However, Murrell et al[25b,63] have shown that a small basis set of S.T.O.'s can give good values of C_6, C_8 and the quadrupole-quadrupole part of C_{10} for H_2 (1% error) and C_6 for He_2 (best calculation 4% error). In each case the minimum possible number of basis functions were used. Similar results, using a different and somewhat larger basis set has been obtained for C_6 and C_8 for H_2 by Hirschfelder and Lowdin.[45] Murrell et al[25b, 63] do not use the variational principle directly to calculate E_{disp} but show that the finite sum,

$$E_1^2 = \Sigma'_t V_{o\,t}^2 / (E_o - E_t) \qquad (2.7.4)$$

is an upper bound to the second order polarisation energy if

(1) the basis states X_t are orthogonal to X_o and

(2) the matrix of H_o for the set X_t is diagonal. Here X_t is not

necessarily an eigenfunction of H_o but X_o is the ground state eigenfunction of H_o. They also show that

$$E_2^2 = \Sigma_t' \tilde{V}_{o\,t}^2 / (H_{oo} - E_t) \qquad (2.7.5)$$

where $\tilde{X}_o$ is an approximation to the true X_o and

$H_{oo} = \langle \tilde{X}_o | H_o | \tilde{X}_o \rangle$, gives a very good C_6 coefficient for He_2 e.g. a Hartree-Fock function gives an error of only 7%.

Thus if the second order exchange terms in (2.4.29) are not large one may use the same technique to obtain E_{disp} and calculate E^2_{exch} as a correction. To test this idea we took the approximate X_t which leads to C_6 for He_2 as determined by Murrell et al[25b] and calculated the second two terms of (2.4.31). These terms proved to be entirely neglible (see table 12) and the other two terms in (2.4.31) will be of similar magnitude. Thus for the second order energy we have calculated only the polarisation energy. Induction energies proved to be entirely negligible for an n=2 S.T.O.S.C.F. approximation to X_o and a one term (constructed from a 2p S.T.O.) excited state function even at the relatively short distance of 4.0 a.u. (see Table 12). The only remaining term is the dispersion energy. This may be calculated very simply by using (2.7.5) and S.T.O. S.C.F. approximations to X_o. We have calculated the C_6, C_8 and quadrupole-quadrupole part of C_{10} using excited states constructed from S.T.O.'s One S.T.O. proved

sufficient to obtain an accurate C_6 coefficient, two for the C_8 coefficient and one for the C_{10} coefficient. The overlap effects on the dispersion energy were then calculated by using the excited states which give the best long range coefficient and evaluating (2.7.5) over a range of distances around the van der Waals minimum. It might be argued that although these simple excited state functions give good second order energies at large distances this may not be true when exchange becomes significant. To test this a two term function was used to calculate C_6 and the overlap effect then calculated, the two results differ little, see table 13.

An interesting conclusion drawn from this work is that the finite sum.

$$E_3^2 = \Sigma_t {}' \tilde{V}_o^2 t / (E_o - E_t) \qquad (2.7.6)$$

gives a value of C_6 closer to the accepted value than does (2.7.5) For C_8 the two approximations are about equal with (2.7.5) slightly better than (2.7.6). The two approximations are once again about equally good for C_{10}. Only the results for the n=5 S.T.O. S.C.F. function are shown in the tables since the results using n=2,3,4,5 are almost identical.

14-16

It may be seen from tables ^ that the error incurred by using the multipole expansion for V is much larger for C_8 than C_6 and large for C_{10} than C_8. However, the error in the total second order energy is about the same as each successive term in (2.7.6.) gives a smaller contribution to the total second order energy.

From the above study, the overlap effects on the second order energies appear to come from the failure of the multipole expansion of V rather than from E^2_{exch} in (2.4.29) as can be seen from tables 12-16 These tables clearly show that in the vicinity of the van der Waals minimium the multipole expansion is excellent, even in the region of the zero of the potential energy it is reasonable. However, in the highly repulsive part of the potential the multipole expansion grossly overestimates the dispersion energy. This probably explains why joining an exponential repulsion term to the multipole dispersion term as is done in some semi-empirical work leads to to a spurious maximum in the potential.

2.8 Third Order Energy

Since the multipole expansion of the V is a good approximation in the region of the van der Waals minimum we shall base our conclusions on the third order energy calculated from this expansion. For two atoms

the third order energy is

$$E_3 = C/r'' + \ldots . \qquad (2.8.1)$$

where C is a constant,

and thus will be negligible at the distances we are considering.

As the third order exchange terms depend on products of similar integrals to the second order exchange terms they should be very small also.

2.9 Overall Potential Function

In this section the overall potential energy function for the $^1\Sigma_g^+$ state of He_2, and the individual contributions to it, will be discussed. These may be seen in table 17.

The total first order energy, which consists of the H.F.S.M. result, the normalisation correction and the correlation corrections (radial and angular) is repulsive at all distances. From table 11 it may be seen that the H.F.S.M. result is by far the biggest term. The radial correlation effect is much bigger than the angular effect but the normalisation term, for the radial function, is larger still. We have probably overestimated these corrections to the H.F.S.M. result since the radial and angular effects were calculated from separate wavefunctions. However, the error in the total potential will be small since they are small effects. In fact, more error is introduced by approximating the Hartree-Fock function by a small basis set expansion than by approximating the exact wavefunction by a Hartree-Fock function, see tables 3-8 and 11.

The second order energy, at various levels of approximation may be seen in table 17 . We have used formula (2.7.6) rather than (2.7.5) (which has been used previously[63]) since we feel that this is a more justifiable approximation to the true second order energy. This is because (2.7.6.) involves approximating V_{ot} by $\tilde{V}_{ot}$ rather than approximating

both V_{ot} and $(E_o - E_t)$ as is done in equation (2.7.5). The results shown for the second order energy in table 17 in successive columns are E_6, E_6+E_8, $E_6+E_8+E_{10}'$ where E_6 is the dipole-dipole, E_8 the dipole-quadrupole, E_{10} the quadrupole-quadrupole and E_{10}' the dipole-octopole dispersion energies respectively. E_{10}' was not calculated directly as this would involve solving some very complicated integrals over s, p and f S.T.O.'s and thus we obtained E_{10}' by scaling our E_{10} using the most accurately determined[13] values of the long range quadrupole-quadrupole (C_{10}'') and dipole-octopole dispersion coefficients (C_{10}')

i.e. $$E_{10}' = E_{10} \frac{C_{10}'}{C_{10}''} C_{10}''' \qquad (2.9.1)$$

where

$C_{10}' = 117.8$,

$C_{10}'' = 60.15$

$C_{10}''' = 59.05$ (our value of the quadrupole-quadrupole long range coefficient)

This approximation will lead to a small error in the final result as E_{10} and E_{10}' contribute little to the total potential.

As may be seen in table 17 the successive terms E_6, E_8, E_{10}' and E_{10} contribute less to the total second order energy than the preceeding terms in the region of the van der Waals minimum. As

mentioned before the error of approximating the full result by a multipole series is successively larger for each of the above terms.

We have not calculated normalisation and correlation corrections to the second order energy since the excellent values of the long range coefficients imply that the second order energy is quite accurate. The long rangecoefficients are, in fact, $C_6 = 1.491$ (1.465), $C_8 = 13.59$ (14.1), $C_{10}'' = 59.05$ (60.15) and $C_{10}' = 109.19$ (117.8), the values in parenteses being the best estimates of these coefficients.[13] The total potential has well depth of 3.570×10^{-5} a.u. at r = 5.60 a.u. and the zero of the potential occurs at 4.96 a.u. These values may be compared to the values from two recently variationally determined potentials and several recent semi-empirically determined potentials, see table 18 The agreement between all the results is good considering the difficulties of using the variational method (see section 2.3.) for this type of problem and the problems of obtaining a good semi-empirical potential (see chapter 4.)

It may be noted that the total potential using only $E_1 + E_6$ is poor but the potential using $E_1 + E_6 + E_8$ is very close to the full potential suggesting that at least an E_8 like term must be included in a semi-empirical potential for He_2.

Although there is agreement with the variationally determined

potentials the method used here has several advantages over the variational method,

(a) the variational wavefunctions have many more linear and non-linear parameters to be optimised, [70,71]

(b) the final energy is given as a sum of individual, physically interpretable contributions,

(c) extreme numerical accuracy does not have to be used since we are not taking the difference of two large numbers, and

(d) it is applicable to larger systems e.g. Ne and Ar.

The second point is very important since if the energy can be divided up into various effects then some minor contributions e.g. correlation corrections and higher order dispersion effects may be calculated to a lower accuracy but will cause little inaccuracy in the overall potential.

Furthermore, the potential being of this form is ideal for suggesting model potentials (Chapter 4) or for use in approximate calculations.

The method is extendable to larger systems since H.F. separated molecule wavefunctions give good results and G.T.O. wavefunctions are also accurate, if a sufficiently large basis set is used.

Lastly the results for one system may be related to the results of another system since the individual terms in the energy expansion may be compared.

2.10 Conclusions

It is apparent that perturbation theory in terms of separated molecule wavefunctions is an ideal tool for studying and calculating the intermolecular potential.

Accurate results are obtained for the interaction of two ground state He atoms. The final potential function is physically interpretable and the method is extendable to larger systems e.g. Ne, Ar interactions.

TABLE 3

Coulomb Energy for He_2, using S.T.O. S.C.F. Functions

R	n=1[1]	n=2[1]	n=2[2]	n=2[3]	n=3[4]	n=3[4]	n=4[1]	n=4[5]	n=5[1]
4.0	10.9966	28.0369	27.6181	27.5194	28.2802	28.1660	28.1435	28.1600	28.2866
5.0	0.5526	2.1927	2.1363	2.1233	2.2831	2.2454	2.2697	2.2687	2.2772
5.5	0.1206	0.6001	0.5812	0.5769	0.6395	0.6234	0.6398	0.6362	0.6366
5.7	-	0.3562	0.3442	0.3414	0.3837	0.3725	0.3858	0.3822	0.3817
6.0	0.0260	0.1624	0.1563	0.1550	0.1780	0.1717	0.1810	0.1778	0.1769
7.0	0.0012	0.0116	0.0110	0.0109	0.0136	0.0128	0.0151	0.0139	0.0135

TABLE 4

Exchange Energy for He_2, using S.T.O. S.C.F Functions

R	n=1[1]	n=2[1]	n=2[2]	n=2[3]	n=3[4]	n=3[4]	n=4[1]	n=4[5]	M-S[6]
4.0	61.6300	171.2703	168.1564	167.3953	175.2902	173.5587	174.3066	174.4773	167.33
5.0	3.3497	14.5891	14.1517	14.0519	15.6414	15.2158	15.7046	15.5920	13.92
5.5	0.7557	4.1444	3.9947	3.9606	4.5915	4.4134	4.7013	4.6011	3.903
5.7	-	2.4952	2.3988	2.3834	2.8049	2.6821	2.9099	2.8224	-
6.0	0.3226	1.1604	1.1114	1.1004	1.3378	1.2685	1.4239	1.3584	1.074
7.0	0.0079	0.0877	0.0831	0.0822	0.1110	0.1021	0.1411	0.1196	0.0777

[1] reference 53 , [2] reference 54 , [3] reference 56 , [4] reference 55b, [5] reference 55a, [6] reference 25d,e

TABLE 5

Total First Order Energies for He_2, using S.T.O. S.C.F. Functions

R	n=1[1]	n=2[1]	n=2[2]	n=2[3]	n=3[4]	n=3[4]	n=4[1]	n=4[5]	M-S [6]
4.0	50.6334	143.2334	140.5383	139.8759	147.0100	145.3927	146.1631	146.3173	139.77
5.0	2.7971	12.3964	12.0154	11.9286	13.3583	12.9704	13.4349	13.3233	11.80
5.5	0.6351	3.5443	3.4135	3.3837	3.9520	3.7900	4.0615	3.9649	3.329
5.7	-	2.1390	2.0546	2.0420	2.4212	2.3096	2.5241	2.4402	-
6.0	0.2966	0.9980	0.9551	0.9454	1.1598	1.0968	1.2429	1.1786	0.920
7.0	0.0067	0.0761	0.0721	0.0731	0.0975	0.893	0.1260	0.1057	0.0670

TABLE 6

Coulomb Energies for He_2, using G.T.O. S.C.F. Functions

R	10	9	8	7	6	5
4.0	28.380	28.349	28.183	28.737	28.322	24.769
4.5	8.129	8.152	8.093	8.281	7.671	5.870
5.0	2.352	2.329	2.299	2.304	1.949	1.292
5.5	0.702	0.663	0.653	0.616	0.478	0.266
5.7	0.407	0.348	0.363	0.304	0.221	0.107
6.0	0.234	0.190	0.189	0.160	0.105	0.043
6.5	0.115	0.092	0.056	0.042	0.023	0.009
7.0	0.060	0.025	0.021	0.004	0.010	0.001

reference 58, the number above the columns gives the number of basis functions used.

TABLE 7

Exchange Energies for He_2, using G.T.O. S.C.F. Functions

R	10	9	8	7	6	5
4.0	175.350	175.582	174.335	178.648	165.988	121.721
4.5	52.602	52.984	52.548	53.029	43.711	24.811
5.0	15.588	15.677	15.419	14.684	10.182	4.123
5.5	4.581	4.484	4.315	3.715	2.058	0.508
5.7	2.473	2.355	2.229	1.797	0.870	0.144
6.0	1.329	1.218	1.130	0.845	0.349	0.027
6.5	0.376	0.309	0.272	0.170	0.045	-0.008
7.0	0.102	0.072	0.060	0.029	0.002	-0.003

TABLE 8

Total First Order Energies for He_2, using G.T.O. S.C.F. Functions

R	10	9	8	7	6	5
4.0	146.970	147.233	146.152	149.911	137.666	96.952
4.5	44.473	44.832	44.455	44.748	36.040	18.941
5.0	13.236	13.348	13.120	12.380	8.233	2.831
5.5	3.879	3.821	3.662	3.099	1.580	0.242
5.7	2.066	2.007	1.866	1.493	0.649	0.037
6.0	1.095	1.028	0.941	0.685	0.244	-0.016
6.5	0.261	0.217	0.216	0.128	0.022	-0.017
7.0	0.042	0.047	0.039	0.025	-0.08	-0.004

TABLE 9

H.F.S.M. Results for He_2, 3 Term S.T.O. S.C.F. Function

R	E_{coul}	E_{exch}	E_1
4.0	28.2802	175.2902	147.0100
4.5	8.0817	52.7124	44.6307
4.8	3.7898	25.4654	21.6756
4.9	2.9420	19.9623	17.0203
5.0	2.2831	15.6414	13.3583
5.1	1.7711	12.2505	10.4794
5.2	1.3735	9.5908	8.2173
5.3	1.0649	7.5055	6.4406
5.4	0.8253	5.8716	5.0463
5.5	0.6395	4.5915	3.9520
5.6	0.4954	3.5891	3.0937
5.7	0.3837	2.8049	2.4212
5.8	0.2971	2.1913	1.8942
5.9	0.2300	1.7114	1.4814
6.0	0.1780	1.1378	0.9698
6.5	0.0493	0.3861	0.3368
7.0	0.0136	0.1111	0.0975
7.5	0.0037	0.0316	0.0279

Calculated from wavefunction table 1 reference 55b

TABLE 10

S.D.S.M. Results for He_2, 10 Term G.T.O. S.C.F. Function

R	E_{coul}	E_{exch}	E_1
4.0	28.380	175.350	146.970
4.5	8.129	52.602	44.473
4.85	3.391	22.472	19.081
4.95	2.660	17.611	14.951
5.0	2.352	15.588	13.236
5.1	1.806	12.210	10.404
5.2	1.452	9.562	8.110
5.3	1.133	7.485	6.352
5.4	0.893	5.857	4.964
5.5	0.702	4.581	3.879
5.6	0.554	3.581	3.027
5.7	0.450	2.798	2.348
5.8	0.369	2.185	1.816
6.0	0.234	1.329	1.095
6.5	0.115	0.376	0.261
7.0	0.060	0.102	0.042
7.5	0.042	0.026	-0.016

G.T.O. wavefunction parameters from table 8, 9 reference 58

TABLE 11 Correlation Corrections to First Order Energy

R	$-E_{corr}$ [1]	$-E_{corr}$ [2]	E_1 [3]
4.0	3.7503	0.4164	147.0100
4.5	1.1450	0.1006	44.6307
4.8	0.5540	0.0429	21.6756
4.9	0.4340	0.0323	17.0203
5.0	0.3397	0.0243	13.3583
5.1	0.2656	0.0183	10.4794
5.2	0.2075	0.0137	8.2173
5.3	0.1620	0.0103	6.4406
5.4	0.1264	0.0078	5.0463
5.5	0.0985	0.0058	3.9520
5.6	0.0767	0.0044	3.0937
5.7	0.0597	0.0033	2.4212
5.8	0.0465	0.0025	1.8942
5.9	0.0361	0.0019	1.4814
6.0	0.0281	0.0014	0.9698
6.5	0.0079	0.0003	0.3368
7.0	0.0022	0.0001	0.0975
8.0	0.0002	0.0000	0.0279
9.0	0.0000(1)		

[1] calculated from a radially correlated function, reference 59 normalisation correction to the energy = 3.1%.

[2] calculated from an angularly correlated function, reference 63 normalisation correction to the energy = 0.8%.

[3] calculated from a three term S.T.O. S.C.F. function, reference 55b

TABLE 12 Second Order Energy for He_2

R	E_{disp}	E_a	E_b	E_{ind}
4.0	29.7702	0.0533	0.0048	0.0219
4.5	16.2600	0.0098	0.0005	-
5.0	9.1003	0.0017	0.00005	0.0028
5.5	5.2672	0.0003	0.000005	0.0003
5.7	4.2757	0.0002	0.000002	0.0001
6.0	3.1614	0.0001	0.000001	0.00003
7.0	1.2630	0.000003	0.00000005	0.0000001

Calculated from a two term S.T.O. S.C.F. ground state wavefunction and a single excited state function

E_{disp} = dispersion energy

$E_a = V_{ot}^2 S_{oo}/(E_o - E_t)$

$E_b = V_{ot} S_{ot} E_1/(E_o - E_t)$

E_{ind} = induction energy

TABLE 13 Second Order Dipole-Dipole Energies for He_2, comparison of one and two term excited state functions

R	$-E_6^{1}$	$-E_6^{2}$	$-E_6^{3}$	$-E_6^{4}$
4.0	29.7097	31.7554	30.8309	32.9569
4.5	16.2460	16.7935	16.8590	17.4290
5.0	9.0985	9.2481	9.4418	9.5980
5.5	5.2680	5.3110	5.4668	5.5119
5.7	4.2768	4.3034	4.4381	4.4662
6.0	3.1625	3.1760	3.2819	3.2962
6.5	1.9667	1.9716	2.0409	2.0462
7.0	1.2636	1.2658	1.3113	1.3137
8.0	0.5679	0.5685	0.5893	0.5901
9.0	0.2802	0.2805	0.2907	0.2911

Dipole-dipole second order energies using a 5 term S.T.O. S.C.F. approximation to the ground state wavefunction

[1] formula (2.7.6), one excited state function

[2] formula (2.7.5), two excited state function

[3] formula (2.7.6), one excited state function

[4] formula (2.7.5), two excited state function

TABLE 14 Second Order Dipole-Dipole Energies for He_2

R	$-C_6^{1}$	$-C_6^{2}$	$-E_6^{3}$	$-E_6^{4}$
4.0	1.3007	1.3500	31.7554	32.9569
4.5	1.3945	1.4473	16.7935	17.4290
4.8	1.42873	1.4828	11.6816	12.1236
4.9	1.4374	1.4918	10.3851	10.7780
5.0	1.4450	1.4997	9.2481	9.5980
5.1	1.4516	1.5065	8.2494	8.5616
5.2	1.4573	1.5124	7.3710	7.6499
5.3	1.4622	1.5175	6.5972	6.8468
5.4	1.4665	1.5219	5.9144	6.1382
5.5	1.4701	1.5257	5.3110	5.5119
5.6	1.4732	1.5290	4.7769	4.9576
5.7	1.4759	1.5318	4.3034	4.4662
5.8	1.4782	1.5341	3.8830	4.0299
5.9	1.4802	1.5362	3.5091	3.6419
6.0	1.4818	1.5379	3.1760	3.2962
6.5	1.4870	1.5432	1.9716	2.0462
7.0	1.4892	1.5455	1.2658	1.3137
8.0	1.4904	1.5468	0.5685	0.5901
9.0	1.4906	1.5470	0.2805	0.2911
10.0	1.4906	1.5470	0.1491	0.1547

Second order dipole dipole energies, 5 term S.T.O. S.C.F. around state, 2 term excited state

Also reported are

$C_6 = E_6 r^6$ to show the deviation from the simple multipole result(2.7.3),

1, 3 formula (2.7.6.)

2, 4 formula (2.7.5.)

TABLE 15 Second Order Dipole-Quadrupole Energies for He_2

R	$-C_8^1$	$-C_8^2$	$-E_8^3$	$-E_8^4$
4.0	7.3551	7.6081	11.2230	11.6090
4.5	9.5706	9.8997	5.6916	5.8874
4.8	10.6332	10.9990	3.7734	3.9032
4.9	10.9384	11.3146	3.2914	3.4046
5.0	11.2193	11.6052	2.8722	2.9709
5.1	11.4768	11.8716	2.5076	2.5939
5.2	11.7118	12.1146	2.1908	2.2661
5.3	11.9252	12.3353	1.9154	1.9813
5.4	12.1183	12.5351	1.6761	1.7337
5.5	12.2923	12.7151	1.4680	1.5185
5.6	12.4486	12.8767	1.2871	1.3314
5.7	12.5884	13.0214	1.1297	1.1686
5.8	12.7132	13.1505	0.9927	1.0269
5.9	12.8242	13.2652	0.8734	0.9034
6.0	12.9225	13.3670	0.7694	0.7958
6.5	13.2646	13.7208	0.41628	0.4306
7.0	13.4391	13.9014	0.2331	0.2411
8.0	13.5634	14.0299	0.0808	0.0836
9.0	13.5889	14.0563	0.0316	0.0327
10.0	13.5936	14.0611	0.0136	0.0141

Second Order Dipole-Quadrupole Energies, using 5 term S.T.O. S.C.F. ground state function, and a 2 term excited state function,
1, 3 formula (2.7.6.)
2,4 formula (2.7.5.)

TABLE 16 Second Order Quadrupole-Quadrupole Energies for He_2

R	$-C_{10}^{1}$	$-C_{10}^{2}$	$-E_{10}^{3}$	$-E_{10}^{4}$
4.0	15.6658	16.1637	1.4940	1.5415
4.5	25.4384	26.2468	0.7471	0.7708
4.8	31.4442	32.4435	0.4843	0.4997
4.9	33.3804	34.4412	0.4183	0.4316
5.0	35.2632	36.3839	0.3611	0.3726
5.1	37.0825	38.2610	0.3115	0.3214
5.2	38.8300	40.0639	0.2686	0.2772
5.3	40.4985	41.7856	0.2316	0.2389
5.4	42.0832	43.4206	0.1996	0.2059
5.5	43.5803	44.9652	0.1721	0.1775
5.6	44.9874	46.4171	0.1483	0.1530
5.7	46.3037	47.7752	0.1279	0.1320
5.8	47.5300	49.0400	0.1103	0.1138
5.9	48.6660	50.2125	0.0952	0.0982
6.0	49.7152	51.2951	0.0822	0.0848
6.5	53.7707	55.4795	0.0399	0.0412
7.0	56.2274	58.0143	0.0199	0.0205
8.0	58.3560	60.2105	0.0054	0.0056
9.0	58.9181	60.7904	0.0017	0.0017
10.0	59.0458	60.9222	0.0006	0.0006

Second Order quadrupole-quadrupole energies, 5 term S.T.O. S.C.F. ground state function and a 1 term excited state function

1,3 formula (2.7.6)
2,4 formula (2.7.5)

TABLE 17 Total First Order, Second Order and Overall Potential for He_2

R	E_1	$-E_2$			U		
		1	2	3	4	5	6
4.0	138.3370	31.7554	42.9784	47.2505	106.5816	95.3586	91.0865
4.5	42.0170	16.7935	22.4851	24.6214	25.2235	19.5319	17.3956
4.8	20.4143	11.6816	15.4550	16.8398	8.7327	4.9593	3.5745
4.9	16.0323	10.3851	13.6765	14.8726	5.6472	2.3558	1.1597
5.0	12.5848	9.2481	12.1203	13.1529	3.3367	0.4645	-0.5681
5.1	9.8745	8.2494	10.7570	11.6477	1.6251	-0.8825	-1.7732
5.2	7.7442	7.3710	9.5618	10.3299	0.3732	-1.8176	-2.5857
5.3	6.0709	6.5972	8.5126	9.1749	-0.5263	-2.4417	-3.1040
5.4	4.7634	5.9144	7.5905	8.1613	-1.1510	-2.8271	-3.3979
5.5	3.7266	5.3110	6.7790	7.2711	-1.5844	-3.0524	-3.5451
5.6	2.9178	4.7769	6.0640	6.4880	-1.8591	-3.1462	-3.5702
5.7	2.2840	4.3034	5.4331	5.7988	-2.0194	-3.1491	-3.5148
5.8	1.7871	3.8830	4.8751	5.1911	-2.0959	-3.0886	-3.4040
5.9	1.3979	3.5091	4.3825	4.6548	-2.1112	-2.9846	-3.2569
6.0	0.9106	3.1760	3.9374	4.1111	-2.2654	-3.0268	-3.2005
6.5	0.3183	1.9716	2.3879	2.5020	-1.6533	-2.0696	-2.1837
7.0	0.0922	1.2658	1.4989	1.5558	-1.1736	-1.4867	-1.5436
8.0	-	0.5685	0.6493	0.6647	-0.5685	-0.6493	-0.6647
9.0	-	0.2805	0.3121	0.3169	-0.2805	-0.3121	-0.3169
10.0	-	0.1491	0.1627	0.1644	-0.1491	-0.1627	-0.1644

E_1 = total first order energy, E_2 = second order energy,

$^1E_6$, $^2E_6+E_8$, $^3E_6+E_8+E_{10}+E_{10}'$

U = total potential,

$^4E_1+E_6$, $^5E_1+E_6+E_8$, $^6E_1+E_6+E_8+E_{10}+E_{10}'$

TABLE 18 Potential Parameters for He_2

Method	σ (a.u.)	r_o (a.u.)	ε (10^{-5} a.u.)	ε/k (^oK)	ref
Variational M.C.S.C.F. wavefunction	5.037	5.659	3.321	10.48	71
Ditto, larger basis set	-	5.60	3.604	11.38	71
Variational, electron-pair wavefunction	-	5.58	3.81	12.0	70
Perturbation theory	4.96	5.650	3.570	11.25	this work
Ditto	4.999	5.615	3.381	10.65	25d,e
+Beck Potential	4.985	5.612	3.284	10.36	126
+MDD-1 Potential	5.00	5.66	3.84	12.24	84
+MDD-2 Potential	5.04	5.69	3.41	10.75	84
+Lennard-Jones 12-6 Potential	4.84	5.43	3.24	10.22	84

+semi-empirical potentials

3. BULK PROPERTIES AND THE INTERMOLECULAR POTENTIAL

3.1 Introduction

In the last chapter we considered the problem of computing the intermolecular potential. The purpose of this chapter is to show how these intermolecular potentials may be used to calculate the equilibrium and transport properties of a gas.

These bulk properties will be discussed and calculated by the method of statistical mechanics, the virial equation[6] being used for equilibrium properties and the Chapman-Enskog-Boltzmann method[5] for the transport properties.

The other purpose of this chapter is to provide the formulae and theoretical background for chapter 4.

3.2 Equilibrium Properties

Only the equation of state need be considered since this equation together with one of the heat capacities as a function of temperature determines all the equilibrium properties of a simple gas.[1] Heat capacities may be readily obtained from the equation of state and the properties of an ideal gas.[1,77]

The equation of state (appropriate for a moderately dense gas) in terms of the intermolecular potential is conveniently obtained from the grand partition function,[6] although other partition functions may be used.[1,77,78]

For a pure substance

$$\Xi = \sum_{n=0}^{\infty} Z_n \exp(n\mu/kT) \qquad (3.2.1)$$

$$pV = kT \ln \Xi$$

and

$$Z_n = (Z_1/V)^n Q_n/n!$$

To obtain an equation of state the assumed expansion

$$p = kT \sum_{i=1}^{\infty} b_i z^i \qquad (3.2.2)$$

is made which from (3.2.1) leads to

$$pV/RT = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots . \qquad (3.2.3)$$

where $\rho = 1/V$ is the density.

The temperature dependent coefficients, B,C,D,... are called the second, third, fourth, ... virial coefficients and the equation (3.2.3) is called the virial equation of state.

The expressions for B,C,D, etc. in terms of the intermolecular potential via Q_n (or Z_n) are given in references 1,6 and 77, which for B and C are,

$$B = -(N_o/2V)(Q_2 - Q_1^2),$$

$$C = -(N_o^2/3V^2)(V(Q_3 - 3Q_2Q_1 + 2Q_1^3) - 3(Q_2 - Q_1^{2,2})^2) \qquad (3.2.4)$$

The results in classical mechanics are

$$B = (N_o/2V\Omega^2) \iint_{(\tau)} f_{ab}\, d\tau_a\, d\tau_b, \qquad (3.2.5)$$

where $f_{ab} = \exp(-U_{ab}/kT) - 1$,

U_{ab} the two body, orientation dependent intermolecular potential between molecules a and b,

Ω is a normalising factor and τ a volume element.

To obtain an expression for C the three body potential U_{abc} is firstly written as

$$U_{abc} = U_{ab} + U_{bc} + U_{ca} + \Delta U_{abc} \qquad (3.2.6)$$

where ΔU_{abc} is the non-pairwise additive contribution.

Then

$$C_{add} = -(N_o^2/3V\Omega^3) \iiint_{(\tau)} f_{ab} f_{bc} f_{ca} \, d\tau_a \, d\tau_b \, d\tau_c \qquad (3.2.7)$$

and

$$C_{nonadd} = -(N_o^2/3V\Omega^3) \iiint_{(\tau)} (\exp(-\Delta U_{abc}/kT)-1) \exp(-(U_{ab} + U_{bc} + U_{ca})/kT) d\tau_a d\tau_b d\tau_c \qquad (3.2.8)$$

For the case of a spherically symmetric potential function i.e. one which depends on the distance between the molecules, R_{ij} but not on their relative orientations,

$$B = -2\pi N_o \int_o^\infty (\exp(-U_{ab}/kT) - 1) R^2 \, dR \qquad (3.2.9)$$

$$C_{add} = -(N_o^2/3V) \iiint_{(V)} f_{ab} f_{bc} f_{ca} dR_{ab} dR_{bc} dR_{ca}$$

$$= -(8(\pi N_o)^2/3) \iiint_{(\Delta)} f_{ab} f_{bc} f_{ca} R_{ab} R_{bc} R_{ca} \, d R_{ab} \, d R_{ac} \, d R_{bc} \qquad (3.2.10)$$

$$C_{nonadd} = -(N_o^2/3V) \iiint_{(V)} (\exp(-\Delta U_{abc}/kT)-1)$$

$$\exp(-(U_{ab} + U_{bc} + U_{ca})/kT)\, d R_{ab}\, d R_{bc}\, d R_{ca}$$

$$= -8(\pi N_o)^2/3) \iiint_{(\triangle)} \exp(-\Delta U_{abc}/kT)-1)$$

$$\exp(-(U_{ab} + U_{bc} + U_{ca})/kT)\, R_{ab}\, R_{bc}\, R_{ca}\, d R_{ab}\, d R_{bc}\, d R_{ca}$$

(3.2.11)

The full quantum mechanical result for B, assuming spherically symmetry is [79]

$$B = B_{direct} + B_{exch}$$

$$B_{direct} = -\sqrt{2}\, N_o \lambda^3 \left\{ \lambda^2/\pi^2 \int_o^\infty \hat{k}\, G_+(\hat{k}) \exp(-\lambda^2 \hat{k}^2/2\pi) d\hat{k} \right.$$

$$\left. + \sum_\ell (2\ell+1) \sum_n (\exp(-E_{n\ell}/kT)-1) \right\} \qquad (3.2.12a)$$

$$B_{exch} = \mp \sqrt{2}\, N_o \lambda^3/(2s+1) \left\{ \lambda^2/2\pi^2 \int_o^\infty \hat{k} G(\hat{k}) \exp(-\lambda^2 \hat{k}^2/2\pi) d\hat{k} \right.$$

$$\left. + \sum_\ell (-1)^\ell (2\ell+1) \sum_n (\exp(-E_{n\ell}/kT)-1) \right\} \mp N_o \lambda^2/2^{5/2}(2s+1)$$

(3.2.12b)

where $G_+(\hat{k}) = \sum_\ell (2\ell+1) X_\ell(\hat{k})$

and $G_-(\hat{k}) = \sum_\ell (-1)^\ell (2\ell+1) X_\ell(\hat{k})$

The term B_{exch} has been shown to be virtually zero at about $8^\circ K$ for He^3 and He^4 for several potential functions [79,84], and thus at higher temperatures one may develop a semi-classical expression for B from B_{direct} alone.

Although much work has been done, using a variety of techniques e.g. Wiener integrals, Landau's transport theory, many body scattering theory (e.g. the Faddeev equations) and the Lee and Yang binary expansion a fully satisfactory numerical method for the evaluation of C is not available.[80,81]

The Wiener integral approach of Fosdick and Jordan[82] appears very promising, as only increased computer time is needed to improve the results, however, it is a very time consuming method. Even for the second virial coefficient the use of equation (3.2.12) in actual computations can be very laborious since except for the simplest potentials, one has to obtain the phase shifts, X_ℓ by numerical integration of the radial, two-body Schrodinger equation.[1.6.79] This together with the fact that except for very light molecules at very low temperatures (e.g. He^4 around 10^oK) many phase shifts contribute significantly to B^6, makes the use of (3.2.12) very time consuming. Fortunately, the W.K.B., semi-classical or Wigner-Kirkwood approximation[6,83] has been shown to be in excellent agreement with the full quantum mechanical result for He^3 and He^4, using several potential functions,[79,84] above about 55^oK. The W.K.B. results have also been shown in excellent agreement with the Wiener integral results for C for a Lennard-Jones 12-6 potential right down to 20^oK.[82] These semi-classical results may be obtained by expanding Z_n or Q_n as a power series in h or $\hbar$.[1,6,83]

The results for a spherically symmetric potential are,[1,6]

$$B = B_o + wB^1 + w^2B^2 + w^3B^3 + \ldots . \qquad (3.2.13)$$

where

$$B_o = -2\,\pi N_o \int_o^\infty (\exp(-U/kT) - 1)\, r^2\, dr,$$

$$B^1 = (\pi N_o \beta^3/6) \int_o^\infty \exp(-U/kT)\,(U^1)^2\, r^2\, dr,$$

$$B^2 = -(\pi N_o \beta^4/6) \int_o^\infty \exp(-U/kT)\{(U'')^2/10$$

$$+ (U')^2/5\, r^2 + \beta(U')^3/9\, r - \beta^2 (U')^4/72\}\, r^2\, dr,$$

$$B^3 = (\pi N_o \beta^5/6) \int_o^\infty \exp(-U/kT)\{(U''')^2/140$$

$$+ 3(U'')^2/70\, r^2 + (U'')^3 \beta/126 + \beta (U')(U'')^2/30\, r$$

$$+ 2\beta (U')^3/315\, r^3 - \beta^2 (U')^2 (U'')^2/120 - \beta^2 (U')^4/1080\, r^2$$

$$- \beta^3 (U')^5/360\, r + \beta^4 (U')^6/4320\}\, r^2\, dr,$$

$m = M1\ M2/(M1 + M2)$,

$U^1 = dU/dr$, $U'' = d^2U/dr^2$, $U''' = d^3U/dr^3$,

$\beta = kT^{-1}$ and

$w = (\hbar^2/2m)$

The usual ideal gas contribution, B_{ideal} which comes from the type of statistics the molecules obey, has been omitted as it has been shown that the above semi-classical expansion is valid for B_{direct} in equation (3.2.12) but not for B_{exch}.[79] However, as B_{exch} is a rapidly vanishing function of temperature this expression, equation (3.2.13) should not contain the term B_{ideal}.

For C we have[6,83]

$$C = C_o + wC^1 + w^2C^2 + \ldots. \qquad (3.2.14)$$

where C_o is given by (3.2.10), (3.2.11)

$w = \hbar^2/m$,

m = mass of the molecule,

$$C = 8 B_o B^1 + (2(\pi N_o)^2 \beta^3/9) \iiint_{(\triangle)} (A_{ab} + A_{bc} + A_{ca})$$

$$R_{ab} R_{bc} R_{ca} \, d R_{ab} \, d R_{bc} \, d R_{ca}, \qquad (3.2.11)$$

and

$$A_{ab} = ((\partial U_{abc}/\partial R_{ab})^2 + \partial U_{abc}/\partial R_{bc} \cdot \partial U_{abc}/\partial R_{ca})$$
$$\exp(-(\quad U_{abc} \quad)/kT) - (U_{ab}^1)^2 \exp(-U_{ab}/kT)$$

with similar expressions for A_{bc} and A_{ac}

3.2.1. Experimental and Computational Aspects of the Virial Coefficients

Much work has been done on the establishment of the convergence of the virial equation, both theoretically[6] and numerically by comparing numerically generated equations of state with the virial series.[85] This latter work has been performed with hard and soft spheres and the gaussian potential[85] showing good agreement between the numerical and virial results in each case. However, no general convergence criteria have been found nor have more realistic potential been treated numerically. Experimental work[6] indicates that the range of usefulness of the virial equation as a means of representing compressibility data is up to the

saturated vapour for temperatures below the critical temperature (not for liquid densities, however) and above the critical temperature it starts to fail at about the critical density (200-300 times the density of an ideal gas at N.T.P.). If only a few terms are used in the series the maximum density is about one half the critical density with only useful quantitative representation to the critical density, however.

The experimental accuracy of the best B values is 1% or better but C is known to much lower accuracy, at best 5-10%[6,76]. In general the higher virial coefficients are of too low an accuracy to be of much value theoretically.[6]

Computationally the classical, central potential formula for B, (3.2.9), gives good agreement with experimental values for most substances at normal temperatures if the form of the potential and its parameters are carefully chosen.[1,6]

For gases consisting of light molecules e.g. He, H_2, CH_4, Ne quantum corrections are needed, particularly at low temperatures.[1,6,79] The full quantum mechanical treatment appears to be necessary only for He and H_2 isotopes at very low temperatures (below $50^{\circ}k$), however.[6,79] Non-spherical effects, shown by the difference between equations (3.2.5) - (3.2.8) and (3.2.9)-(3.2.11), contribute markedly for polar molecules but less so for molecules with only higher multipole moments.[89,90,91,140] Induction effects as well as these electrostatic, non-spherical effects

are also important if high accuracy is required.[89,91]

It appears that C is more sensitive to the accuracy of the two body potential than B and also no realistic additive potential alone can account for the experimental values indicating that non-additivity is important.[6,86]

However, the non-central and quantum corrections have less effect on C than B for those systems so far studied.[6,82]

The integrals for B and C have been solved analytically for only very simple potential forms and thus, in general numerical methods must be used to evaluate them.

The non-spherical integrals are very time consuming to evaluate since they are of large dimensions[87] e.g. for an axially symmetric polar molecule B is a 4 dimensional integral and C a 9 dimmensional integral.

Hence these integrations are usually carried out by expanding the exponential[88-95] e.g.

$$B = B_o - (N_o/2\Omega^2) \sum_{n=1} (1/n!)(-\beta)^n \iiint v^n \exp(-U_o/kT)\, d R_{ab}\, d w_a\, d w_b \qquad (3.2.16)$$

where

$$U_{ab} = U_o + v$$

and B_o is the expression (3.2.9) for a central potential.

Expressions of this type have been worked out for many types of orientation dependent potentials for B and to a lesser extent for C [88,89,91] [96,97,140].

The final results may be expressed in the form,

$$B^* = B_o^* + \sum_{n=1}^{\infty} d_n H_n(r^*, T^*) \qquad (3.2.17)$$

and

$$C^* = C_o^* + \sum_{n=1}^{\infty} D_n I_n(r^*, T^*) \qquad (3.2.18)$$

where

$$H_n(r^*, T^*) = r_o^{*(n-3)} \int_{o}^{\infty} r^{*(2-n)} \exp(-U_o/kT)\, dr^* \qquad (3.2.19)$$

and

$$I_n = \iiint_{(\triangle)} \exp(-U_{ab}/kT) f_{bc} f_{ca} R_{ab}^n R_{bc} R_{ca}\, d R_{ab}\, d R_{bc}\, d R_{ca} \qquad (3.2.20)$$

A program was written to integrate (3.2.9) for B central, (3.2.13) for the quantum corrections and (3.2.19) for the H functions. The program, which is based on adaptive Simpson's rule procedure will work for any potential form. It was checked against known values and found to be accurate (see appendix A).

The three dimensional integrals required for the third virial coefficient, (3.2.10), (3.2.11), (3.2.15) and (3.2.20) were numerically integrated by two methods.

The first program, adapted from one written by Spurling, Storvick and De Rocco, [140] is basically repeated applications of Simpson's rule to the three dimensional integral.

Secondly, a program was written based on the multidimensional integral formulae given by Hammer & Stroud[98] as used by Johnson and Spurling[87] for polar molecule third virial coefficients. This is very efficient and gives results of comparable accuracy to the first program but in about half the time.

These programs were tested against known values where possible and the results are collected in appendix A.

3.3 Transport Phenomena

In the previous section the properties of a gas in equilibrium were considered. If the system is not in equilibrium one or all of the state variables are functions of time, gradients in physical properties are present and transport phenomena occur as the system tends to equilibrium.[1,99] A spacial dependence of the state variables is associated with flux of some kind.

In this section we will consider non-equilibrium systems which can be described by the state variables and their linear derivatives, in particular by their gradients, i.e. when the system is "close to" equilibrium.

Thus

$$J = LX \qquad (3.3.1)$$

where X is a gradient, J is its conjugate flux and L a proportionality

constant. The rate at which the system approaches equilibrium is determined by L which is called the transport coefficient.

More generally,

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i=1,2,\ldots,n) \qquad (3.3.2)$$

for a system of n independent gradients with X_k a generalised gradient, J_i a generalised flux and L_{ik} a transport coefficient. The relationship between J_i and X_k is called thermodynamic coupling. Uncoupled transport processes are ones for which $L_{ik} = o$ for $i \neq k$ e.g. transport phenomena which arise from gradients in temperature, density or local macroscopic velocity i.e. heat conduction, diffusion and viscosity respectively.

Coupled transport processes arise if $L_{ik} \neq o$, the best known phenomena is this class being thermal diffusion.

The usual quantity reported for thermal diffusion is the thermal diffusion factor, α_t

i.e.

$$\alpha_t = \alpha_o (m_1 - m_2)/(m_1 + m_2)$$

$$\alpha_t = k_t / x_1 x_2 \qquad (3.3.3)$$

where m_1 and m_2 are the masses of the molecules and k_t the thermal diffusion ratio, α_o the reduced thermal diffusion ratio, and x_1 and x_2 mole fractions.

The problem of calculating these transport coefficients has been likened to an onion [100] in that it has three layers. The first is a kinetic theory layer which relates the transport coefficients to various molecular collision cross-sections or collision integrals, then the cross-section layer which is concerned with the determination of the cross-sections from the intermolecular potential and the core problem of determining the intermolecular potential.

The overall problem is concerned with the time evolution of the distribution function, $f^{(n)}$ which gives the state of the system at a particular time. For gases $f^{(1)}$ and $f^{(2)}$ are all that are needed since the system is dilute. [1,99] The equations which governs the time evolution of $f^{(1)}$ and $f^{(2)}$ are the Boltzmann integro-differential equation [1,5] and its generalisations. [1,99]

For a dilute monatomic gas the Boltzmann equation is sufficient [99] but for a dilute, polyatomic gas the Wang-Chang-Uhlenbeck-de Boer generalised Boltzmann equation, [1,101] is needed. Although a Boltzmann equation has been derived which takes into account three body collisions [99] no use will be made of it here as it is very hard to solve.

3.3.1 A Dilute, Monatomic Gas

The Boltzmann integro-differential equation is[1,5]

$$\frac{\partial f_i}{\partial t} = -v_i \cdot \nabla_{r_i} f_i - (F_i/m_i) \cdot \nabla_{v_i} f_i$$

$$+\iint (f_i' f_j' - f_i f_j)\, T\, dv_j \qquad (3.3.4)$$

where in classical mechanics

$$T = g\, b\, db\, d\varepsilon \qquad (3.3.5)$$

and in quantum mechanics (see appendix C)

$$T = \alpha(g,X)_{bs} \sin X\, dX\, d\varepsilon$$

and

$$\alpha(g,X) = (g/4K^2)\, |\Sigma_l\, (2l+1)\, (\exp(2i\, X_l) - 1)\, P_l(\cos X)|^2 \qquad (3.3.6)$$

where $\alpha(g,X)_{bs}$ is the quantum mechanical probability of deflection, $K = m_{12}\, g/\hbar$. The primed quantities indicate quantities after collision, unprimed before collision. The equation (3.3.4) is of the form

$$\frac{\partial f_i}{\partial t} = \frac{\partial f_i}{\partial t}\ \text{streaming} + \frac{\partial f_i}{\partial t}\ \text{collision} \qquad (3.3.7)$$

where by streaming is meant the natural motion of the molecules in absence of collisions.

Equation (3.3.4) shows that the equations in quantum and classical mechanics differ only in definition of the collision cross-section, thus the same will be true of the final expressions for the transport coefficients. The assumptions made in deriving the Boltzmann equation irrespective of the mechanics used are,[1,103]

(a) only binary collisions are important,

(b) the collisions are elastic,

(c) the potential is central,

(d) the molecules interact according to a single potential energy curve,

(e) the mean distance between the molecules is very much greater than the range of the intermolecular potential, and

(f) the assumption of "molecular chaos" i.e. the pre-collisional positions and momenta of colliding molecules are uncorrelated.[99]

Thus the equation strictly only applies to the interations of the inert gases in their ground state as even other atomic interactions although central and elastic may take place according to several possible energy curves.[18d] This latter point is easily overcome and the result is that the Boltzmann equation is solved for each potential energy curve and the resulting collision integrals averaged.[180]

The other points will be discussed in Section 3.3.2.

As only the macroscopic equations of transport concern us here only the normal solutions of the Boltzmann equation need be considered. These solutions, obtained by the Chapman-Enskog method(which is a perturbation approach), lead to expressions for the transport coefficients in terms of a set of collision integrals.[1,99] [5] [1,5]

In the first approximation the results for pure substances are,

$$(\mu)_1 = 266.93.10^{-7} \sqrt{MT}/(\sigma^2 \Omega^*_{22}) \qquad (3.3.8)$$

$$(\lambda)_1 = 1989.1.10^{-7} \sqrt{T/M}(\sigma^2 \Omega^*_{22}) \qquad (3.3.9)$$

$$(D_{11})_1 = 2.628.10^{-3} \sqrt{T^3/M} /(p \sigma^2 \Omega^*_{11}) \qquad (3.3.10)$$

and

$$(k_t)_1 = \frac{15(2A^* + 5)(6C^* - 5)(M_1 - M_2)}{2A^*(16A^* - 12B^* + 55)(M_1 + M_2)} x_1 x_2 \qquad (3.3.11)$$

where

$$\Omega_{ls} = \Omega^{(\ell,s)}(T) = \sqrt{kT/2\pi m_{12}} \int_0^\infty \exp(-z^2) z^{2s+3} S^{(l)} dz \qquad (3.3.12)$$

and all other quantities are defined in appendix C.

The only difference between classical and quantum mechanics is in the definition of the collision cross-section i.e. in classical mechanics,

$$S^{(l)} = 2\pi \int_0^\infty (1 - \cos^l \chi) b db \qquad (3.3.13)$$

where the angle of deflection of χ is given by

$$\chi(g,b) = \pi - 2b \int_{r_m}^{\infty} r^{-2}\, dr\, F(b,r) \qquad (3.3.14)$$

where

$$F(b,r) = \sqrt{1 - b^2/r^2 - 2U(r)/mg}$$

and $z^2 = mg^2/2kT$

and in quantum mechanics,

$$S^{(l)} = (2\pi/g)\int_0^{\infty} (1-\cos^l \chi)\, \alpha(g,\chi) \sin\chi d\chi \qquad (3.3.15)$$

where

$\alpha(g,\chi)_{b,s}$ is given by (3.3.6)

There are two schemes for higher approximations, one due to Chapman and Cowling[5] and one due to Kihara[1] but in both schemes,

$$(X) = f_X (X)_1 \qquad (3.3.17)$$

where X is a transport coefficient other than k_t and f_x is a correction factor. The Kihara second approximations are somewhat simpler and appear to be quite adequate in most common situations.[103] These are,

$$f_\mu = 1 + (3/49)(4\,\Omega^*_{23}/\Omega^*_{22} - 7/2)^2,$$

$$f_\lambda = 1 + (2/21)(4\,\Omega^*_{23}/\Omega^*_{22} - 7/2)^2, \qquad (3.3.18)$$

$$f_d = 1 + (6C^* - 5)^2/(16A^* + 40)$$

and $k_t^* = 59(6C^* - 5)/56A^*$. Detailed discussions as to the convergence of the two schemes may be found in references 103,188.

3.3.2.
Calculation of the Transport Coefficients

The full quantum solution is very laborious, as it is for the equilibrium properties because of the necessity of calculating many hundreds of phase shifts. Unfortunately, unlike the case of equilibrium properties no successful semi-classical formalism for calculating transport coefficients has been developed[1, 128].

However, for He^3 and He^4 above 100°K for several potentials the fully classical treatment is in excellent agreement with the quantum mechanical result[84,127,128].

Thus we will only use the classical mechanical solution. The computation of the transport coefficients in this case can be summarised by equations (3.3.12), (3.3.13) and (3.3.14). The problem of solving these equations numerically has been treated by several authors[105-107]. The only difficulties which arise are singularities in the integrands of (3.3.13) and (3.3.14). The program we have used was written by Munn and Smith[105] and overcomes these singularities by using Gauss-Mehler quadrature. The program has been fully tested and was further tested for the 12-6 spherical-shell potential against the program written by Barker et al[106] and four figure agreement was found. The program is faster than the Barker program and probably more accurate. Also it is a simple matter to modify to accommodate a different potential function.

3.3.3. A Dilute Polyatomic Gas

The assumptions (b) and (c) of the last section which are used in deriving the Boltzmann equation are not justified for a gas consisting of polyatomic molecules. This is because the potential energy of interaction of two polyatomic molecules depends on their orientations as well as their separation[3,4] and because of the existence of internal degrees of freedom in the molecule. The last point means that energy may be transferred upon collision by vibration and rotation of the molecules as well as by changes in translational energy. It is important to see how the treatment of the previous section must be modified, since we wish to use transport properties to obtain an estimation of the intermolecular potential. Thus we must find out which transport properties may be readily related to the potential and which properties are significantly affected by inelastic effects. A generalised Boltzmann equation which takes these extra effects into account has been derived by Wang-Chang and Uhlenbeck and independently by de Boer[101] by treating the translational degrees of freedom classically and the internal degrees of freedom quantum mechanically.

The equation is

$$\frac{\partial f_i}{\partial t} = -\left(v_i \cdot \frac{\partial}{\partial r_i} f_i\right) - \frac{F_i}{m_i} \cdot \frac{\partial f_i}{\partial v_i} + \sum_{j,k,\ell} \int\int\int (f'_k f'_\ell - f_i f_j)\, g\, I_{in}(g, \chi, \phi) \sin\chi \, d\chi \, d\phi \, d v_j, \tag{3.3.22}$$

Where I_{in} (g, χ, ϕ) is the inelastic collision cross-section for a collision of molecules initially in quantum states i and j and finally in quantum states k and l, the magnitude of the initial asymptotic relative velocity being g. Although further work, including fully quantum mechanical treatments have shown that the W-C-U-B formalism is not entirely general, it ignores spin anisotropy and internal degeneracy effects, it appears to be an adequate basis for discussing viscosity, diffusion and thermal conductivity.[109,100]

Equation (3.3.22) may be solved in an analogous manner to the normal Boltzmann equation and the results are,[1,101,110]

Shear Viscosity,

$$\mu^{-1} = \left\{8/5\,(\pi mkT)^{\frac{1}{2}}\right\} R_i \sum_{ijkl} (-\varepsilon_i - \varepsilon_j)$$

$$\int \left(\gamma^4 \sin^2\chi + {}^1/_3\,(\Delta\varepsilon)^2 - \tfrac{1}{2}(\Delta\varepsilon)^2 \sin^2\chi \right)^3 \exp(-\gamma^2)\, I_{in} \sin\chi\, d\chi\, d\chi\, d\phi\, d\gamma$$

Relaxation Time, τ and Bulk Viscosity, K

$$\tau^{-1} = (2nk/C_{int})(kT/\pi m)^{\frac{1}{2}} R_i \sum_{ijkl} (\Delta\varepsilon)^2$$

$$\exp(-\varepsilon_i - \varepsilon_j) \int (\gamma^3 \exp(-\gamma^2)\, I_{in} \sin\chi\, d\chi\, d\chi\, d\phi\, d\gamma\,, \qquad (3.3.24)$$

$$K = \tau(nk^2 T\, C_{int}/C_v^{\,2}) \qquad (3.3.25)$$

Coefficient of Heat Conductivity

$$\lambda = \lambda_{tr} + \lambda_{int} \qquad (3.3.26)$$

$$\lambda_{tr} = W\left\{(75kT^2/8m)\, X^{-1} + (15kT\, C_{int}/4m)\, Y/XZ\right\} \qquad (3.3.27a)$$

$$\lambda_{int} = W\left\{(3\, C_{int}^2\, T/2m)\, Z^{-1} + (15kT\, C_{int}/4m)\, Y/XZ\right\} \qquad (3.3.27b)$$

and Coefficient for the Diffusion of Internal energy, D

$$D^{-1} = -\left\{8p/3\,(\pi mkT)^{\frac{1}{2}}\right\} R_i \sum_{ijk\ell} (-\varepsilon_i - \varepsilon_j)$$

$$\gamma^5 \exp(-\gamma^2)\, I_{in}\, (1-\cos\chi)\sin\chi\, d\chi\, d\phi\, d\gamma \qquad (3.3.28)$$

where

$R_i = \left(\sum_i \exp(-\varepsilon_i)\right)^{-2}$

$\varepsilon_i = E_i/kt$,

E_i = energy of the i^{th} quantum state,

$\Delta\varepsilon = \varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j$,

n = molecular density in molecules/cm^3,

C_{int} = internal heat capacity/molecule,

λ_{tr} = translational heat conductivity

λ_{int} = internal heat conductivity

and X, Y, and Z are complicated integrals over γ, I_{in} etc. and are given in reference 110, $W = (1-Y^2/XZ)^{-1}$

3.3.4.
Approximations to the full results

Since the dynamics of a two body, inelastic collision are extremely complex we will discuss what can be learnt for approximate treatments.

If only elastic, central potentials are possible (3.3.23), (3.3.27) and (3.3.28) reduce to the classical, elastic collision results of section 3.2.1.[110] In the next approximation quasi-elastic collisions in which $\Delta\varepsilon$ is negligible compared to γ^2 and the translational and internal motions interact negligibly are considered. This means that I_{in} may be replaced by the elastic scattering cross-section I_{el} for the orientation dependent potential. Then as we are assuming translational and internal effects are independent,

$$\mu^{-1} = (8/5\ (\pi mkt)^{\frac{1}{2}})\ \int \gamma^7 \exp(-\gamma^7)\, I_{el} \sin^3 \chi\, d\chi\, d\phi\, d\gamma \quad (3.3.29)$$

This is just the normal elastic collision expression except that I_{el} must be calculated for a non-central potential. These cross-sections would still be very difficult to evaluate and thus many approximate models have been developed to treat this problem.[110a,111,113,114] The usual approximation is to assume that the distortion of the collision trajectories by the orientation dependent potential occurs mainly around the distance of closest approach of the colliding molecules and that in this region the relative orientations can be taken as fixed.[110a,111] This fixed orientation model thus reduces the problem to that of the kinetic theory of a gas with several potential energy curves, one for each relative orientation of the molecules.

It was mentioned before that this problem is easily solved.[180] The resulting collision integrals for each orientation are then averaged

over all orientations, equal weight being given to each orientation to obtain the final result. Reasonable results are obtained using this model for the viscosity of polar and quadrupolar gases,[110a,111] however, it probably overestimates the effect of the orientation dependent potential.[117] The effect of orientation dependent terms on the central potential parameters deduced from viscosity using this model is very small for polar molecules and barely significant for quadrupolar molecules.[110a,111] Thus the effect of an orientation dependent potential on the viscosity of octopolar and hexadecapolar gases will be expected to be entirely negligible. Viscosity then provides a good means of obtaining the central potential parameters for those types of gases.

Other models which have been proposed usually pre-average the potential[113,114] in some way to reduce the calculation to that of a central potential. Once again viscosity is relatively uneffected by an orientation dependent potential.

This insensitivity is not shown by thermal conductivity, however, since at this level of approximation,

$$\lambda^M/\mu = (^5/_2)\ C_{vtr} + (\rho D/\mu)\ C_{int} \qquad (3.3.30)$$

which is just the modified Eucken correction.[1,115]

The next step is to consider the full expression for μ

i.e.

$$\mu^{-1} = d\, R_i \sum_{ijk} \exp(-\varepsilon_i - \varepsilon_j) \left(\int\int \sin^2 \chi\, I_{in}\, d\theta + \frac{1}{3}\int (\Delta\varepsilon)^2\, I_{in}\, d\theta - \frac{1}{2}\int (\Delta\varepsilon)^2 \sin^2\chi\, I_{in}\, d\theta\right) \quad (3.3.31)$$

where d is a numerical factor

and $d\theta = \gamma^3 \exp(-\gamma^2) \sin\chi\, d\chi\, d\phi\, d\gamma$

The first integral on the right hand side is approximately equal to the normal elastic collision expression, the second term is related to τ by (3.3.24) but the term $(\Delta\varepsilon)^2 \sin^2\chi$ is more difficult as it couples the internal and translational motions. Mason and Monchick[110b] pointed out that if this last term is approximated by some sort of average value the last two terms nearly cancel e.g. using the rigid sphere value of 2/3 the cancellation is exact.

The cancellation has subsequently been confirmed by two model calculations. The first by Stevens[116] treats the collision of two methane molecules as the scattering of two rigid tetrahedra and the second by Clarke and Smith[117] who treat the problem of polar molecule interactions as the interaction of two rigid spheres with embedded point dipoles at their centres.

Stephens[116] finds viscosity very insensitive to inelastic effects, self-diffusion only slightly affected but thermal diffusion strongly dependent on these effects. He shows that self-diffusion would predict

a well depth which is too small and isotopic thermal diffusion would predict a well depth which is too large. Clark and Smith[117] find only approximately a 4% effect due to the dipole potential which they claim is an over estimation because their calculations were performed in two dimensions only. They also show that the fixed orientation model overestimates orientation dependent effects.

As thermal conductivity cannot be predicted by (3.3.30) over a substantial temperature range the full treatment in terms of orientation and inelastic effects is probably needed. Thus thermal conductivity cannot be used to obtain an estimate of the intermolecular potential. Similar conclusions have been made about thermal diffusion.[114b]

It is apparent from the previous discussion that only viscosity is suitable for the determination of potential parameters.

Stevens results indicate that self-diffusion may be of some use but only as a check on the reasonableness of the viscosity deduced parameters, however.

3.4 Conclusions

In this chapter we have summarised the relationship between the intermolecular potential and the bulk properties of a gas.

From the discussion it is apparent that the second virial coefficient and transport coefficients of a gas composed of atoms are readily calculated

from any intermolecular potential. However, for a gas composed of molecules the relationships are not as simple. Only second virial coefficients (when expansion (3.2.17) is valid and rapidly convergent) and viscosity are readily calculated.

Thus only second virial coefficients and viscosity coefficients are useful for determining the intermolecular potential of molecules from observed bulk properties of a gas. Third virial coefficients although readily calculated do not depend on the two body potential alone and are therefore not so useful.

4. SEMI-EMPIRICAL DETERMINATION OF INTERMOLECULAR POTENTIALS

4.1 Principles

In principle one may determine the complete intermolecular potential energy function by solving the Schrodinger equation as discussed in Chapter 2.

This is very time consuming for systems containing many electrons and so other strategies must be adopted to deal with these systems.

The usual strategies are

1. to approximate the exact equations by making some assumptions about the wavefunction or integrals appearing in the full result, or [26-30] [177]

2. to use the exact results for simple systems to suggest a model potential with adjustable parameters. [118-122] These adjustable parameters are then determined by comparing calculated and observed bulk properties. [1]

The first method is starting to be used more in recent years [26-30] since the formally exact theory is now known (exact in the sense discussed in Chapter 2) and appears to be very promising. The method is particularly useful for systems which are too complex for the use of the full quantum mechanical method but for which there is a lack of experimental data from which a model potential's parameters may be determined. [128]

The second method has been more extensively used and it is [118-122] this method that will be discussed in this chapter.

The method relies on several factors not the least of which is having a soundly based mathematical relationship between the bulk property and the intermolecular potential. Thus equilibrium and transport properties of gas have been extensively exploited using the formulae discussed in Chapter 3.

These properties have been shown to be sensitive to different [130-133] regions of the potential energy function and data in certain temperature [130] ranges is very insensitive to the overall potential form. This coupled with the fact that there appears to be no one-one relationship between the bulk property and the intermolecular potential means that several accurately measured properties over a wide temperature range [123-129] are needed to determine the model potential's parameters.

If the two body potential is required then the properties used should, strictly depend only on two body potentials. This strictly precludes the use of condensed phase properties such as the cohesive energy of crystals or the equation of state of liquids (as well as third virial coefficients) which, at least in principle depend on many body [6, 122] potentials. Indeed recent work has shown that the inclusion of three body potential energy terms are needed to obtain good agreement between [123,124] [134,135,159a] calculated and observed crystal properties, liquid properties and third [124] virial coefficients.

4.2 Form of the Potential Function

The energy of interaction between two chemically saturated systems is attractive at large distances and for two spherically symmetric systems is of the form,

$$U(r) = -\{C_6/r^6 + C_8/r^8 + C_{10}/r^{10} + \ldots\} \qquad (4.2.1)$$

where C_6 and C_8 are constants. The energy is repulsive at short distances i.e. for two spherically symmetric systems of the form

$$U(r) = \sum_{i=1}^{m} C_i r^i \exp(-a_i r) \qquad (4.2.2)$$

Hence most models have been arrived at by adding these two terms e.g. the Lennard-Jones 12-6 potential,

$$U(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad (4.2.3)$$

Very simple potentials such as (4.2.3) are found to be useful for interpreting bulk properties only over a limited temperature range and that a set of parameters deduced from one property e.g. second virial coefficients[1,6], will not fit another property, e.g. viscosity.

A further illustration of the inflexibility of simple potentials is that the coefficient C_6 is usually about twice the accurate quantum mechanically derived value[6,120,137].

Attempts to increase the flexibility of the potential form have been made by introducing a third parameter e.g. the n-6 Lennard-Jones potential[133], the Kihara core potential[159] and the Morse potential[139]. These potentials are much more effective but still leave something to be

desired in obtaining full agreement with all the properties of simple gases e.g. Ar.[124]

Hence more elaborate potential functions have been devised and applied to the inert gases.[118-127] The reason for the emphasis on the inert gases being that the above-mentioned potential forms strictly only apply to atoms as the potential energy of interaction of two molecules depends on their relative orientation. Very good results have been obtained for the inert gases and in particular for Ar and He.[118-127,135] [123-125] [126,127,84]

Hence it is of interest to extend these model potential results to simple, almost spherical molecules e.g. CH_4.

However, there are two reasons for wishing to have a simpler, more physically interpretable potential for these molecular interactions than one derived from a generalisation of the very complex spherically symmetric potentials used for the inert gases.[135]

These reasons are

1. the potential depends on the mutual orientation of the molecules as well as their separation, thus making the number of potential parameters much larger than for atomic interactions, and
2. there are less properties which may be easily related to the intermolecular potential for molecules than for atoms as discussed in Chapter 3.

Thus in the next section a reasonably simple, physically interpretable potential function will be developed and applied to CH_4, CF_4 and SF_6.

4.3 The Interaction of Quasi-Spherical Molecules

The usual models for the interaction of polyatomic molecules divide the potential into two terms,[6,91]

$$U(r, \theta, \phi) = U_o(r) + v(r, \theta, \phi) \qquad (4.3.1)$$

where the central potential, $U_o(r)$ depends only on the separation of the molecules, r and the orientation dependent term, $v(r, \theta, \phi)$ depends on r and the collection of Euler angles (θ, ϕ) needed to specify the relative orientation of the two molecules.

4.3.1 The Central Potential

This is usually represented by the type of potential discussed in Section 4.2.

However, some potentials have been devised which average the interactions of the two molecules and obtain a central potential which takes into account the "size" and "shape" of the molecules and these seem preferable.

Examples are the Kihara core model, the De Rocco and Hoover spherical shell potential, the Hamman-Lambert potential and the Corner four centre model.[6]

The Kihara model gives quite a good fit to most properties but its "size" parameters are not physically meaningful[6] and it has the incorrect long range dispersion expression.[140c] The Hamann-Lambert model[141,142] gives good results but is very complex and can be well approximated by a Lennard-Jones 28-7 potential.[141] The Corner model is complex and more applicable to linear molecules than to the type of molecules we are considering.[6]

The De Rocco and Hoover model represents the two polyatomic molecules as interaction sites uniformly distributed over the surface of a sphere of diameter d. The form of the potential, averaged over all orientations, for 12-6 Lennard-Jones interaction sites is,

$$V_{ss}(r) = \frac{\varepsilon\left\{(3r_o^2 P_o^{(4)} + P_o^{(3)})P^{(9)} - (9r_o^2 P_o^{(10)} - P_o^{(9)})P^{(3)}\right\}}{(9P_o^{(10)}P_o^{(3)} - 3P_o^{(9)}P_o^{(4)})r} \qquad (4.3.2)$$

where $P^{(n)}_{(r)} = P^{(n)} = (r+d)^{-n} - 2r^{-n} + (r-d)^{-n}$

and $P_o^{(n)} = P^n(r_o)$

This model has been extensively used to interpret the equilibrium and transport coefficients of globular molecules,[140,143] including polar and quadrupolar molecules,[140b] with considerable success.

The model gives parameters consistent with liquid densities and molecular dimensions[140a] (for most molecules) and unlike the Kihara

core potential has the correct long range form i.e. (4.2.1)

However, although the optimum shell size, d deduced from B is in excellent agreement with the size of most molecules, (judged from known bond lengths) this is not so for molecules containing peripheral hydrogen atoms.[140]

The small values of d for these molecules has been attributed to the "softness" of the hydrogenic repulsions.[140b] Furthermore, the values of ε/k for Kr and Xe are in poor agreement with the values obtained from more elaborate potentials.[140,123] Finally, it has been claimed[146] that the potential is unable to fit recent high temperature viscosity data of CH_4, CF_4 and SF_6, although it works very well at moderate temperatures.[140e]

This indicates that the choice of Lennard-Jones 12-6 potential sites on the shell is quite arbitrary and not necessarily optimum. Recent work on the newest equilibrium and transport coefficients for the inert gases has shown that the n-6 Lennard-Jones potential and n-6-8 potential with $n \neq 12$ gives quite reasonable results.[133,138]

This suggests an obvious generalisation of the 12-6 Spherical Shell Potential to allow for different peripheral atoms in the molecules, that is a model with n-m Lennard-Jones interaction sites uniformly distributed over a spherical shell.

The potential then takes the form,

$$V_{ss}(r) = \frac{\varepsilon \left\{ (m-3)\, r_o^{\,} P_o^{(m-2)} + P_o^{(m-3)} \right) P^{(n-3)} - \left((n-3)\, r_o^{\,} P_o^{(n-2)} + P_o^{(m-3)} \right) P^{(m-3)} \right\}}{\left((n-3)\, P_o^{(n-2)} P_o^{(m-3)} - (m-3)\, P_o^{(m-2)} P_o^{(n-3)} \right) r} \qquad (4.3.3)$$

This is the form we shall use for the central potential.

4.3.2. The Orientation Dependent Potential

Models for the orientation dependent part of the potential are usually obtained from the formulae for long range electrostatic and induction forces between non-overlapping polarizable systems with permanent multipole moments.[1,13,89]

"Shape" factors or orientation dependent short range terms have been used[88,91] but the theoretical justification of these factors and their generalisation to other simple systems is difficult and thus for the quasi-spherical molecules considered here they will not be used.

For the orientation dependent term then we will use the leading electrostatic and induced moment long range terms. These terms for CH_4 and CF_4 are the octopole-octopole and octopole-induced dipole terms[89] and for SF_6 the hexadecapole-hexadecapole and hexadecapole-induced dipole terms. Anisotropies of the dispersion forces will be omitted since they are zero for these molecules.

4.4 Determination of the Potential Parameters

For a spherically symmetric system (e.g. Ar) viscosity coefficients, thermal conductivity coefficients, isotopic thermal diffusion coefficients, second virial coefficients, quantum mechanical calculations and beam scattering measurements may all be used to help determine the parameters of a model potential. However, for non-atomic molecules thermal conductivity and isotopic thermal diffusion are strongly affected by inelastic collisions(Chapter 3), self-diffusion coefficients are also significantly affected and thus none of these transport properties are reliable for obtaining potential parameters. Furthermore, quantum mechanical calculations of the short and long range potential are extremely difficult for molecules and beam scattering measurements are inaccurate.[144,145] Thus the only experimental data from which we may determine potential parameters are second virial coefficients and viscosity coefficients.

The only quasi-spherical molecules for which viscosity coefficients, μ and second virial coefficients, B have been measured accurately over a sufficiently wide enough temperature range to enable a meaningful determination of the potential parameters are CH_4, CF_4 and SF_6.

The best viscosity measurements for CH_4 obtained by several different workers,[146-153] using a variety of techniques, agree very well except for the very early high temperature measurements.[151-152] However, the data

obtained by these earlier workers for the inert gases has been shown by several recent studies[133,146,179] to be inaccurate and the same conclusion probable holds for CH_4. The second virial coefficients reported by several different workers for CH_4 are also in good agreement except at very low temperatures and here we have used the recommended values from reference 76.

Similarly, μ and B have been measured for CF_4 by several workers[146] and good agreement exists between these results. The data for SF_6[146] is reasonably good but the most recent measurements of μ seem to be the best.

Since we showed in Chapter 3 that the viscosity is relatively insensitive to the orientation dependent part of the potential and to inelastic collisions it may be used to determine the central potential parameters. These parameters together with the second virial coefficient may then be used to obtain the only other parameter, the first non-zero multipole moment of the molecule. These multipole moments are themselves of great value for testing the accuracy of approximate wavefunctions, being more sensitive to the accuracy of the wavefunction than the total energy, see Table 12.

Thus the procedure adopted for obtaining the potential parameters was as follows. A least mean square fit of calculated and observed viscosity data was made for fixed n and d to find the optimum ϵ and r_o.

Then d was changed and optimum ε and r_o were found for this d. This process was repeated until the optimum d, ε and r_o were found for a particular n. The same procedure was then followed for the next n until the optimum d, ε and r_o were found for each value of n.

The value of m was chosen to be 6 so as to obtain the correct long range behaviour for the potential i.e.

$$V_{ss} = (n-3)(n-2) A d^2 r^{-n} \left(1 + \frac{(n-1)n}{3.4} \left\{\frac{d}{r}\right\}^2 + \ldots\right)$$

$$- (m-3)(m-2) B d^2 r^{-m} \left(1 + \frac{(m-1)m}{3.4} \left\{\frac{d}{r}\right\}^2 + \ldots \right. \qquad (4.4.1)$$

$$V_{ss} \to - Bd^2 (m-3)(m-2) r^{-m} - Bd^4 \frac{(m-3)(m-2)(m-1)m}{3.4} r^{-m-2}$$

as $r \to \infty$, where A and B are constants dependant on d, ε and r_o.

if m=6,

$$V_{ss} \to -12Bd^2 r^{-6} - 60 d^4 r^{-8} B$$

The whole procedure was performed on a computer using a searching routine to find the optimum r_o and ε by minimising,

$$d\mu^2 = \frac{1}{n-1} \sum_{i=1}^{n} | \mu_i \text{ calc} - \mu_i \text{ observed} |^2 \qquad (4.4.2)$$

where

n = number of data points.

These parameters were then used together with the formulae below to obtain the multipole moments i.e.

for CH_4 and CF_4

$$B^* = B_o^* + aH_{14}(ro^*,T^*) + b\,H_{10}(ro^*,T^*) + \ldots. \qquad (4.4.3)$$

and for SF_6,

$$B^* = B_o^* + c\,H_{18}(ro^*,T^*) + g\,H_{12}(ro^*,T^*) + \ldots \qquad (4.4.4)$$

where

$$a = -(3^4.2^5.11/7.5^2)\Omega^{*2}T^{*-2}$$

$$= -162.95714\,\Omega^{*2}T^{*-2}$$

$$b = -(3^2.2^4/5)\Omega^*\alpha^*T^{*-1}$$

$$= -28.8\,\Omega^*\alpha^*T^{*-1}$$

$$c = -(2^5 \times 3 \times 11 \times 13 \times 10^3/5^2.7^2)\Phi^{*2}T^{*-2}$$

$$= -1.12065306.10^4\Phi^{*2}T^{*-2}$$

$$g = -(3^2.2^4.5/7)\Phi^*\alpha^*T^{*-1}$$

$$= -1.028571428.10^2\Phi^*\alpha^*T^{*-1}$$

$$\alpha^* = \alpha/r_o^3,\ \Omega^* = \Omega^2/\varepsilon\sigma_o^7,\ \Phi^* = \Phi^2/\varepsilon r_o^9$$

$$H_k(r_o^*,T^*) = r_o^{*(k-3)} \int_o^\infty \exp(-U_o/kT)\, r^{*-(k-2)}\, dr^*$$

α is the polarizability, Ω is the octopole moment and Φ is the hexadecapole moment of the molecule. These expressions were worked out from Kielich's papers[89] and the first term of (4.4.3) checked by direct evaluation.

It should be noted that the factor 11 in the coefficient was omitted in reference 140 f and the values of Ω reported there are thus in error.

The results of these fitting procedures may be seen in Tables 1 and 2. Tables 3, 4 and 5 show the actual viscosity values and the percentage deviation from experimental measurements. The second virial coefficients are shown in Tables 6, 7 and 8 for the best potential and the potential with n=12. A full breakdown of the second virial coefficient results into classical,quantum and non-central components may be found in appendix D.

The best potential for CH_4 is the one for which n=9, it gives the best fit to viscosity and second virial coefficients over the full temperature range and has a shell size of 2.15A which is very close to the shell size from structural parameters of 2.18A.

The potential with n=12 gives a very good fit to both viscosity and second virials, being inferior to n=9 only at high temperatures and in particular in the region of the Boyle temperature. However, it has a shell size of only 1.59A and the self diffusion coefficient, D_{11} for n=12 as not as good as for n=9. From Steven's work the elastic collision D_{11} should always be less than the true D_{11}, which is true for n=9 but not for n=12. These results show however, that although self-diffusion coefficients would give a much lowere ε/k than viscosity the inelastic effects on D_{11} are only a few percent.

For CF_4 n=15 gives the best fit to viscosity coefficients and has a shell size close to the physical shell size. Once again n=12 gives a

very good fit to both μ and B and in this case a very reasonable shell size also. In fact it fits B much better than the n=15 potential particularly in the region of the Boyle temperature. The potential with n=12 gives the best fit to μ for SF_6 and the best shell size .

The above results are not in agreement with the work of Dawe et al[146] who found that they could not fit their viscosity data for CH_4, CF_4 nor SF_6 to a spherical shell with n=12. However, we find a 1-2% error at worst in each case using this potential. It is possible that they did not find the optimum parameters for the potential. It must be remembered that to obtain optimum results d must be treated as a variable parameter, if this is not done a poorer fit is obtained especially for CH_4 . They also rely on the principle of corresponding states which our results indicate does not hold for these substances since at least three parameters are needed to fit the data. Also for CF_4 the best set of parameters is very hard to find and varies with the data used to find it. Many sets of parameters may be found which will give an almost identical fit to the data i.e. one may obtain local minima not the absolute minimum. The set we show for CF_4 were arrived at after using different data and different starting parameters in the search routine.

The results also show that a spherically symmetric potential (of the type used here anyway) cannot be expected to fit B and viscosity simultaneously with the same parameters because of the non-negligible contribution to B from the non-spherical part of the potential, especially for CF_4 as can be seen from Tables 3 and 4 appendix D.

The value of the octopole moment of CH_4 is in reasonable agreement with the best quantum mechanically derived result of 2.0, which is probably low judging by the trend of the results, see table 12.

The values of the dispersion coefficients are shown in Table 1 and for CH_4 there is only reasonable agreement between the value of C_6 and the best quantum mechanically derived value.

Previously determined values of the octopole moment of CF_4 are probably too low[140f] and the value derived in reference 140f is in error because of the factor of 11 missing from the octopole-octopole correction to B (see equation (4.4.3)). Thus the value for the n=12 potential is probably the most accurately determined to date.

The hexadecapole moment of SF_6 has not been determined previously and no comment can be made about the accuracy of our result. All that can be said is that due to experimental uncertainties and the insensitivity of the second virial coefficient to the hexadecapole moment it can only be said to lie in the range 26-28. This same uncertainty is present in the octopole moment values we have determined, a ±5% change in the octopole moment would have little effect on the second virial coefficient.

Another interesting point is that the quantum corrections to B for CH_4, which are usually neglected, are non-negligible as can be seen from tables 1 and 2 of appendix D.

4.5 Conclusions

We have shown that the use of a model potential containing both central and non-central terms gives an excellent fit to the second virial coefficients and viscosity coefficients of the quasi-spherical molecules, CH_4, CF_4 and SF_6. The worst fit is for CF_4 and even here the deviation from experiment is only 1-2% i.e. within experimental error. Furthermore, quite reasonable results were obtained for the self diffusion coefficients, long range coefficient, C_6 and octopole moment of CH_4.

The model potential's parameters in each case have a reasonable physical interpretation i.e. n indicates the "softness" or otherwise of the peripheral atom interactions and d indicates the "size" of the molecule. The results indicate that the interaction of the peripheral hydrogens in CH_4 is "softer" than the interaction of the peripheral fluorines in CF_4 and SF_6. The shell size, d for the optimum potential, as judged by fit to viscosity is in each case (and for the n=12 potential for CF_4) in good agreement with the "size" of the molecule (judged from known bond lengths). This last point means that if n is fixed and d is taken from known bond lengths only two parameters, ε and r_o need to be determined from viscosity, this means that a reasonable potential may be obtained when only a limited amount of experimental data is available.

These potentials should prove very useful for studying inelastic effects on transport properties, the properties of gas mixtures and the properties of liquids. This last point is particularly worthy of explanation since quite good results have been obtained for the equilibrium properties of liquid Ar.[134] The potentials are ideally suited to use in the perturbation theory of liquids since the non-central effects could be treated as a perturbation as were three-body effects in the study of Ar.[134]

TABLE 1. Parameters derived from viscosity

	CH_4			CF_4			SF_6		
n	8	9*	12	9	12	15*	9	12*	15
d	2.32	2.15	1.59	3.2	2.72	2.66	3.42	3.06	2.70
ε/k	237.2	232.0	222.8	309.5	320.9	318.8	418.3	418.6	423.4
r_o	3.854	3.840	3.848	4.465	4.456	4.425	5.91	5.088	5.066
C_6	102	95	113	111	173	151	473	526	624

* best fit to viscosity,
d, r_o in A, ε/k in °K, C_6, in a.u.,
d from structural parameters,
CH_4 2.18A, CF_4 2.65A, SF_6 3.16A

TABLE 2. Multipole Moments derived from B

	CH_4		CF_4		SF_6
n	9	12	12	15	12
Moment	3.0	2.9	7.9	10.0	26-28
α	26	26	40	40	62

Units, Ω for CH_4, CF_4 10^{-34} e.s.u. cm.^{3}
Φ for SF_6 10^{-42} e.s.u. cm.^{4}
and α 10^{-25} cm^3.

TABLE 3. Viscosity of CH_4

T	EXPT.	CALC.[1]	DIF	CALC.[2]	DIF	REF.
90.39	367	384	-4.6	378	-3.0	148
157.45	620	621	-0.16	618	0.32	148
200.06	776	774	0.26	774	0.26	148
246.1	939	936	0.32	935	0.45	149
293.0	1100	1092	0.73	1093	0.64	146
310.94	1163	1153	0.91	1152	1.0	149
377.6	1363	1367	-0.29	1362	0.074	149
403.0	1439	1441	-0.14	1437	0.14	146
444.27	1560	1560	0.0	1553	0.45	149
477.6	1651	1651	0.0	1647	0.24	149
497.0	1692	1701	-0.53	1699	0.42	146
601.0	1945	1964	-0.93	1963	-0.93	146
676.0	2113	2132	-0.90	2134	-1.00	146
749.0	2268	2289	-0.93	2297	-1.28	146
823.0	2426	2441	-0.62	2453	-1.11	146
900.0	2578	2590	-0.47	2606	-1.09	146
1050.0	2855	2865	-0.36	2889	-1.19	146

[1] n=9, [2] n=12,
DIF = ((EXPT. - CALC)/EXPT)×100
units for viscosity 10^{-7} poise.

TABLE 4. Viscosity of CF_4

T	EXPT.	CALC.[1]	DIF.	CALC.[2]	DIF.
293	1706	1730	-1.41	1691	0.88
323	1860	1867	-0.38	1830	1.61
348	1988	1979	0.45	1946	2.10
373	2105	2091	0.67	2060	2.14
400	2230	2211	0.86	2181	2.19
403	2243	2224	0.85	2194	2.18
423	2333	2310	0.99	2280	2.27
450	2458	2423	1.43	2394	2.60
473	2549	2517	0.87	2489	2.35
498	2640	2617	0.87	2590	1.89
523	2737	2715	0.81	2690	1.72
566	2904	2879	0.79	2858	1.58
573	2926	2905	0.72	2885	1.40
623	3107	3088	0.61	3074	1.06
673	3274	3266	0.25	3256	0.55
723	3441	3438	0.087	3433	0.23
773	3601	3604	-0.083	3603	-0.056
803	3699	3701	-0.054	3701	-0.054
823	3738	3764	-0.7	3766	-0.75
873	3807	3918	-2.92	3922	-3.03

[1] n=15

[2] n=12

experimental data from reference 146

TABLE 5. Viscosity of SF_6

T	EXPT.	CALC.[1]	DIF
293	1515	1532	-1.12
323	1653	1660	-0.43
348	1760	1764	-0.23
373	1869	1867	-0.17
400	1986	1976	0.50
403	1995	1988	0.35
423	2088	2069	0.91
450	2205	2178	1.22
473	2297	2270	1.18
498	2385	2369	0.67
523	2479	2465	0.57
566	2641	2626	0.57
573	2664	2651	0.49
623	2843	2831	0.42
673	3017	3006	0.36
723	3180	3178	0.63
773	3343	3345	-0.60
803	3437	3443	-0.17
823	3491	3507	-0.46
873	3660	3666	-0.16

[1] $n = 12$

$n = 12$

experimental values from reference 146

TABLE 6. Second Virial Coefficients for CH_4

T	B_{obs}	$B_{calc}{}^1$	$B_{calc}{}^2$
110	-344 ± 10	-363.16	-354.16
120	-284 ± 8	-299.49	-294.95
130	-248 ± 8	-253.79	-250.46
140	-217 ± 8	-217.73	-215.92
150	-191 ± 6	-189.16	-188.35
160	-169 ± 6	-166.01	-165.89
180	-133 ± 3	-130.79	-131.53
200	-107 ± 2	-105.33	-106.56
225	-84 ± 2	-82.03	-83.54
250	-67 ± 1	-64.78	-66.46
275	-53 ± 1	-51.52	-53.28
300	-42 ± 1	-41.02	-42.80
350	-27 ± 1	-25.49	-27.24
400	-15.5 ± 1	-14.55	-16.28
500	- 0.5 ± 1	- 0.16	- 1.89
523.16	1.49 ± 0.2	2.15	0.54
548.16	3.89 ± 0.2	4.50	2.90
573.16	5.98 ± 0.2	6.58	5.03
598.16	7.88 ± 0.2	8.48	6.94
600	8.5 ± 1	8.61	7.08
623.16	9.66 ± 0.2	10.20	8.68

^{1} n=9, ^{2} n=12

B_{obs}, experimental values from reference 76

TABLE 7. Second Virial Coefficients for CF_4

T	B_{obs}	$B_{calc}{}^1$	$B_{calc}{}^2$
273.16	-111.0	-124.44	-115.44
298.15	-88.3	-95.95	-90.82
303.15	-84.4	-91.12	-86.58
323.15	-70.4	-74.06	-71.50
348.15	-55.7	-56.78	-55.98
373.16	-43.5	-42.78	-43.24
398.17	-33.2	-31.26	-32.60
423.18	-24.4	-21.61	-23.58
448.20	-16.8	-13.41	-15.86
473.21	-10.1	-6.36	-9.18
498.23	-4.25	-0.26	-2.36
523.25	1.0	5.11	1.85
548.26	5.6	9.81	6.43
573.27	9.8	14.02	10.51
598.28	13.6	17.76	14.20
623.29	17.05	21.14	17.51
673.16	23.6	26.93	23.25

$^1{}_{n=15}$, $^2{}_{n=12}$

B_{obs}, experimental values from reference 76.

TABLE 8. Second virial coefficients of SF_6

T	B_{obs}	$B_{calc}{}^1$	$B_{calc}{}^2$	$B_{calc}{}^3$
280	-320 ± 10	-324.71	-334.89	-346.23
300	-277 ± 5	-274.59	-282.85	-292.06
325	-228 ± 5	-225.39	-231.94	-239.24
350	-190 ± 5	-186.75	-192.05	-197.99
375	-159 ± 5	-155.63	-160.04	-164.94
400	-135 ± 5	-130.08	-133.79	-137.92
440	-102 ± 3	-97.51	-100.41	-103.65
480	-76 ± 3	-72.26	-74.60	-77.22
520	-54 ± 3	-52.10	-54.04	-56.19

[1] hexadecapole moment = 26

[2] hexadecapole moment = 27

[3] hexadecapole moment = 28

B_{obs}, experimental values from reference 76

TABLE 9. Self Diffusion Coefficient for CH_4

T	EXPT.	CALC.[1]	CALC.[2]
90.0	266± 23	231	226
195.0	992± 6	996	969
273.0	2060± 50	1872	1878
298.2	2350± 10	2203	2138
353.6	3150± 10	3020	3152
382.6	3600± 10	3467	3711

[1] n=9, [2] n=12
units 10^{-4} cm^2 sec^{-1}
experimental data from reference 154

TABLE 10. Long Range Coefficient, C_6 for CH_4

Method	Value	Reference
L-J 12-6 potential parameters from B	265	137
Ditto parameters from μ	271	137
Exp-6 potential parameters from μ	214	137
London Formula	110 117	137
Slater-Kirkwood Formula	155	137
Kirkwood-Muller Formula	237	137
Refractive Index Data	150 ±10%	13
Spherical Shell Potential parameters from μ	95[1] 113[2] 102[3]	this work
Low Temperature Viscosity Data	150	147
Harmonic Oscillatar Model	117	H. Margenau, Rev. Mod. Phys. 11 1 (1939)

[1] n=9, [2] n=12, [3] n=8

TABLE 11. Semiempirically determined values of Ω for CH_4

Method	Value	Reference
Dielectric Second Virial Coefficient, L J 12-6 central potential	± 6	140f
Second Virial Coefficient L J 12-6 Central potential	± 5	140f
Phase Transition of solid heavy methane	± 1.6	140f
Second Virial Coefficient, spherical shell central potential, n=12	± 2.9	this
n= 9	± 3.0	work

TABLE 12. Quantum Mechanically derived Octopole Moment of CH_4

Wavefunction	Ω	E a.u.	Reference
Single Centre S.T.O.	5.3	-39.80	A.G. Turner, A.F. Saturno, P. Hauk and R.G. Parr, J. Chem. Phys. 33, 22 (1960) 40, 1919 (1964)
Minimum Basis S.T.O. S.C.F.	0.9354	-40.12827	R.M. Pitzer, J. Chem. Phys. 46, 4871 (1967)
Minimum Basis S.T.O. S.C.F.	2.8	-39.863	J.J. Sinai J. Chem. Phys. 39, 1575 (1963) 40, 3596 (1964)
S.T.O. S.C.F.	1.5	-40.1810	B.J. Woznick, J. Chem. Phys. 40, 2860 (1964)
Large Basis G.T.O. S.C.F.	1.8	-40.166	M. Krauss, J. Chem. Phys. 38, 564 (1963)
Approximate S.C.F.M.O.	5.7	-39.592	W.T. King, J. Chem. Phys. 39
Single Centre S.T.O.	4.46	-39.50	E.L. Albasiny and J.R.A. Cooper, Proc. Phys. Soc. (London) 82, 289 (1963)
S.T.O. S.C.G.F.	1.149	-39.607	M. Klessinger and R. McWeeny, J. Chem. Phys. 42, 3343 (1965)
S.T.O. S.C.F.	1.443	-39.644	
S.T.O. S.C.F.			G.P. Arrighini, C. Guidotti, M. Maestro, R. Moccia and O. Salvetti J. Chem. Phys. 49 2225 (1968)
39 S.T.O.	2.08	-40.20409	
34 S.T.O.	3.06	-40.1866	
27 S.T.O.	1.79	-40.19493	
22 S.T.O.	2.595	-40.17828	

5. NON-ADDITIVITY OF THE INTERMOLECULAR POTENTIAL

5.1 INTRODUCTION

In the previous chapters the two body intermolecular potential has been emphasised. However, to interpret the properties of even moderately dense gases, not to mention the properties of the condensed phases of matter,we need to know the potential energy of interaction of many molecules.

The usual approximation to the N-body potential, U_n is

$$U_n = \sum_{i=1}^{N} U_{ij} \qquad (5.1.1)$$

where U_{ij} is the two body potential for molecules i and j.

However, this additivity assumption has never been shown to be valid by quantum mechanical methods and semiempirical work on third virial coefficients and the equilibrium properties of liquids and crystals indicates that three body non-additive effects must be included to obtain good agreement with experiment. We will firstly investigate the problem from a quantum mechanical viewpoint since the abovementioned semi-empirical approach does not fully explore the problem for three reasons,

(a) the properties used to investigate non-additivity may have different sensitivity to different regions of the potential (as is the case with the two body potential),

(b) the inaccuracies in calculating the bulk properties may mask non-additive effects, as may inaccuracies in the experimental data, and

(c) the treatments use only approximate three body potentials.

However, in the last section the three-body non-additivity in CH_4, CF_4 and SF_6 is studied by considering the third virial coefficients to see if conclusions deduced for the inert gases hold for these quasi-spherical molecules.

5.2 A QUANTUM MECHANICAL APPROACH TO NON-ADDITIVITY

Three atom long range non-additivity in the absence of exchange has been extensively studied, however, higher order non-exchange effects have been studied by approximate models only. [13,165,173-176] [165,175]

Exchange or overlap three body effects have been studied by methods which do not give the correct two body potential or at such short distances as to be of little use in deciding the extent of non-additivity at distances appropriate for determining bulk properties. [26,168-172] [166,167] [166,167]

We will now discuss the problem using perturbation theory in terms of separated molecule wavefunctions as discussed in Chapter 2.

The potential energy of interaction in the MS-MA scheme may be divided into the following terms, to third order in energy.

(a) 1st Order Terms,

(1) Coulomb Energy, $E_{coul} = V_{oo} + V_{nn}$,

(2) Exchange Energy, $E_{exch} = V_{oo}' S_{oo}' + V_{oo}'$

(b) 2nd Order Terms,

(1) Second Order Polarisation Energy of Induction and Dispersion, $E_o^2 = \sum_t^1 V_{ot}^2 / (E_o - E_t)$

(2) Second Order Exchange - Polarisation Energy,

$$E_1^2 = \sum_t^1 (V_{ot}' V_{ot} - S_{oo}' V_{ot} V_{ot} + V_{ot} S_{ot}' V_{oo}) / (E_o - E_t)$$

(c) 3rd Order Terms,

(1) Third Order Polarisation Energy

$$E_o^3 = \sum_{t,r}^1 V_{ot} V_{tr} V_{or} / (E_o - E_t)(E_o - E_r) - E^1 \sum_t^1 V_{ot}^2 / (E_o - E_t)^2$$

(2) Third Order Exchange - Polarisation Energy

$$E_1^3 = \left\{ \sum_{tr}' U_{ot} U_{tr} (U_{or} S_{oo}' + U_{or}' - S_{or}' U_{oo}) - U_{ot}' U_{tr} (U_{or} + U_{or}' - S_{or}' U_{oo}) \right\} / (E_o - E_t)(E_o - E_r)$$

The terms a(1), a(2) and b(1) are the only ones of importance for He_2 and this should be true of other closed shell interactions.

The coulomb energy is pairwise additive since,

$$E_{coul} = \langle A_i A_j \ldots A_N | \sum_{ij} V_{ij} | A_i A_j \ldots A_N \rangle + V_{nn}$$

$$= \sum_{ij} \langle A_i A_j | V_{ij} | A_i A_j \rangle + V_{nn} \qquad (5.2.1)$$

where A_i is the ground state wavefunction of the ith molecule..

The exchange energy has been shown to be very well approximated by using Hartree-Fock functions for A_i. Arguments were also advanced

to show that this will probably be so for other simple closed shell systems. Thus we will discuss the non-additivity of this term using Hartree-Fock, single determinant wavefunctions.

For an N molecule system for which each separated molecule wavefunction is a single determinant it has been shown that,

For two molecules A and B

$$E_{exch_{ab}} = \sum_{i=1}^{n} \sum_{j=1}^{m} \iint \rho_{ij}^{a}(1)\, r_{12}^{-1}\, \rho_{ij}^{b}(2)\, d\tau_{12} + S_{ij} \int \rho_{ij}^{a}(1)\, V^{b}(1)\, d\tau_1 + S_{ij} \int \rho_{ij}^{b}(1)\, V^{a}(1)\, d\tau_1 \quad (5.2.2)$$

where

$$\rho_{ij}^{a} = a_i b_j - \sum_{k=1}^{n} S_{kj}\, a_i a_k$$

$$\rho_{ij}^{b} = a_i b_j - \sum_{l=1}^{m} S_{il}\, b_j b_l$$

$$V^{a}(1) = -\sum_{j=1}^{p} Z_j / r_{1a} + \sum_{i=1}^{n} \int a_i^2(2)\, r_{12}^{-1}\, d\tau_2$$

$$V^{b}(1) = -\sum_{k=1}^{q} Z_k / r_{1b} + \sum_{j=1}^{m} \int b_i^2(2)\, r_{12}^{-1}\, d\tau_2$$

where molecule A has P nuclei of charge Z_j and n electrons, molecule B has q nuclei of charge Z_k and m electrons, a_i and b_i are spin orbitals, i.e.

$$A_o = (n!)^{-\frac{1}{2}} \det(a_1 a_2 \ldots a_n) \quad (5.2.3)$$

For N molecules,

$$E_{exch}{}_N = \sum_{pairs\ r,s} \iint \rho_{rs}(1)\, r_{12}^{-1}\, \rho_{rs}(2)\, d\tau_{12}$$
$$+ S_{rs} \int \rho^{r}_{rs} (V^T - V^r)\, d\tau + S_{rs} \int \rho^{s}_{rs} (V^T - V^s)\, d\tau$$

where r and s are spin-orbitals on different molecules R and S and

$$V^T = \sum_{i=1}^{N} V_i$$

In the case of three molecules,

$$E_{exch}{}_{ab} + E_{exch}{}_{ac} + E_{exch}{}_{bc} - E_{exch}{}_{abc}$$
$$= \sum_{ab} S_{ab} \int (\rho_{ab}{}^{a} + \rho_{ab}{}^{b})\, V^c\, d\tau$$
$$+ \sum_{bc} S_{bc} \int (\rho_{bc}{}^{b} + \rho_{bc}{}^{c})\, V^a\, d\tau$$
$$+ \sum_{ac} S_{ac} \int (\rho_{ac}{}^{a} + \rho_{ac}{}^{c})\, V^b\, d\tau \qquad (5.2.5)$$

It can be seen from these formulae that the exchange energy is, at most, three body non-additive.

Murrell et al[26] showed that if the Mulliken approximation is made for the integrals in the above formulae the exchange energy is pairwise additive. They also used an approximate Is S.T.O. wavefunction for He_3 and showed that the non-additivity was insignificant in this case also.

However, there are several approximations in their work,

(a) using a Is S.T.O. for the separated atom wavefunction which we have shown leads to a very poor two body potential,

(b) approximating the 1s S.T.O. by a linear combination of 1s G.T.O.'s.

Thus the first-order exchange non-additivity for He_3 was calculated using S.C.F. wavefunctions expanded, in terms of 1s G.T.O.'s.

The energy expression for this non-additivity is,

$$
\begin{aligned}
E_{nonadd} = {} & 4(a|b)\,\{\,(a|R_b|c) - (ab|cc)\,\} \\
& + 4(b|c)\,(\,(a|R_c|b) - (bc|aa)\,) \\
& + 4\,(a|c)\,(\,(b|R_a|c) - (ac|bb)\,) \\
& - 2\,(\,(a|b)^2 + (b|c)^2)\,(\,(a|R_c|a) \\
& - (aa|cc)\,) - 2(\,(a|b)^2 + (a|c)^2)\,(\,(b|R_c|b) - (bb|cc)\,) \\
& - (2\,(\,(b|c)^2 + (a|c)^2)\,(\,(a|R_b|a) - (aa|bb)\,\} \qquad (5.2.6)
\end{aligned}
$$

, notation as in Chapter 2. Only G.T.O. wavefunctions were used as they give excellent exchange energies for He_2 at all distances (compare tables 9 and 10 of Chapter 2) and furthermore the three centre integrals are far less time consuming for G.T.O.'s than for S.T.O.'s.

As with the first order energy for two He atoms the first-order energy using the various approximations to the Hartree-Fock functions was calculated to test the convergence of these functions to the true Hartree-Fock value for an equilateral triangle configuration. As can

be seen from table 1 the results are all quite consistent.

The non-additivity was then calculated for a linear array and for two isosceles triangle configurations for the 10 term G.T.O. S.C.F. function and the results may be seen in table 1 and 2 .

As can be seen the non-additivity is very small in the region of the potential which determines most of the physical properties of the substance i.e. 4-7 a.u.

The only second order term which is important for the interaction of two helium atom is the dispersion energy. This has been shown to be pairwise additive, on the assumption that V in V_{ot} can be expanded in a multipole series. This multipole result differs very little from the full second order dispersion energy for H_2 and He_2 in the region of the van der Waals minimum and thus the conclusion, at least for He and H interaction appears sound.

Second order induction effects may be shown to be non-additive, however. The contribution to the inductive energy arising from the excitation of molecule A from A_o to an excited state A_t is,

$$\left[\int \rho\,(A_o\, A_t)\, V^b\, d\tau\right]^2/(E_o - E_t) \qquad (5.2.6)$$

where $\rho\,(A_o A_t)$ is the transition density for the two states and V^b is the potential field due to B. For n molecules the corresponding contribution is

$$\left[\int \rho(A_o A_t)\,(V^b + \ldots + V^n)\, d\tau\right]^2/(E_o - E_t) \qquad (5.2.7)$$

Thus the induction energy will be non-additive since

$$\sum_{ij} E_{ind_{ij}} - E_{ind_n}$$

$$= \sum_{i,j,k}{}^{2}\ \rho(A_{io}\, A_{it})\, V^i\, V^k\, d\tau/(E_o - E_t) \qquad (5.2.8)$$

However, for non-polar molecules the induction energies are small, as shown for He_2 in Chapter 2, and thus this non-additive contribution will be negligible. This may not be so for polar molecule interactions e.g. for H_2O, however. The second order exchange energy is negligible for He_2 and this should be so for other closed shell systems and thus its non-additivity is unimportant. The same is probably true of the third order exchange energy. The only remaining term is the third order polarisation energy which is the same term which arises in the normal long range potential with no overlap. When the potential is expanded in a multipole series this term leads to the normal triple-dipole, dipole-dipole-quadrupole etc. potentials. As the multipole result is very close to the full result for E^2_o, this should be so for E^3_o. Thus we have calculated the non-additive E^3_o from the formulae given by Bell.[74]

TABLE 1 Percentage Deviation from Additivity of Exchange Energy of He_3, G.T.O. S.C.F. results.

R	n=10†	n=9†	n=8†	n=7†	n=10
2	5.579	5.580	5.579	5.579	-1.747
3	2.058	2.058	2.061	2.056	-0.242
4	0.604	0.603	0.602	0.606	-0.028
5	0.160	0.161	0.160	0.166	-0.003
6	0.041	0.0001	0.003	0.044	-
7	0.010	0.008	0.010	0.031	-

n= number of basis functions in G.T.O. S.C.F. function

† 1st 4 columns for an equilateral triangle configuration and last column for a symmetric linear array.

TABLE 2 Percentage Deviation from Additivity of Exchange Energy of He_3, G.T.O. S.C.F. results.

Θ	(r=3)	(r=5)
60	2.058	0.160
90	0.059	0.014
120	-0.006	-0.001
150	-0.022	-0.003
180	-0.242	-0.003

Results for an isosceles triangle ABC, $R_{ab} = R_{ac} = r$, $\angle BAC = \Theta$

TABLE 3 Comparison of Non-additive Exchange and Non-additive Third Order Polarisation Energies

R	E_{na}^{1}	E_{na}^{2}	E_{na}^{3}	E_{na}^{4}	E_{na}^{5}	E_{ad}
2.0	2873..	395.78	256.31	309.71	441.97	37575.
3.0	11.494	10.269	2.963	1.591	1.009	4686.
4.0	0.3194	0.771	0.125	0.038	0.014	273.26
5.0	0.075	0.104	0.011	0.003	0.0005	-1.704
6.0	0.002	0.020	0.0015	0.0002	0.00003	-9.602

Equilateral triangle configuration,

$E_{na_2}^{1}$ = exchange non-additive energy

$E_{na_3}^{2}$ = triple dipole energy

$E_{na_4}^{3}$ = dipole-dipole-quadrupole energy

$E_{na_6}^{4}$ = dipole-quadropole-quadrupole energy

E_{na}^{5} = triple-quadrupole energy

E_{ad} = total additive energy

TABLE 4 Comparison of Non-additive Energies

R	E_{na}^{1}	E_{na}^{2}	E_{na}^{3}	E_{na}^{4}	E_{na}^{5}	E_{ad}
2	-559.518	-71.777	-31.545	34.653	22.848	25141.
3	-8.802	-1.867	-0.365	0.178	0.052	3127
4	-0.098	-0.140	-0.015	0.004	0.0007	181.[illegible]
5	-0.001	-0.019	-0.001	0.0002	0.00003	-1.3[illegible]
6	—	-0.004	-0.0002	0.00002	0.000002	-6.454
7	—	-0.0009	-0.00003	0.000003	0.0000002	-3.108

Explanation of table same as for table 3 , except that here we have a symmetric linear array of He atoms.

This may be seen in table 3,4for He and it will be seen that it is at least an order of magnitude greater than the exchange non-additivity over the physically significant range of the potential.

It is apparent from the above discussion that the only major non-additive energy terms for helium interactions are the first order exchange energy, which is small and the third order polarisation energy which is readily predicted.

The same conclusions probably hold for other non-polar interactions. However, for polar molecules e.g. H_2O the inductive non-additivity may be large.

5.3 THIRD VIRIAL COEFFICIENT AND NON-ADDITIVITY

Several authors have shown that the additive third virial coefficient calculated on the basis of an accurately determined, semi-empirical, two-body potential gives very poor agreement with experiment. [86,124,140d,172] Thus three-body (the third virial coefficient depends on the interaction of three molecules) non-additivity has a pronounced effect on the third virial coefficient. It has also been shown that if the non-additive contribution to C (i.e. (3.2.8)) is calculated on the basis of the triple-dipole potential then the calculated and experimental values are in quite good agreement. [86,124]

Thus we have calculated the third virial coefficients of CH_4, CF_4 and SF_6 using the formulae and programs discussed in Chapter 3, the potentials used being those determined in Chapter 4. The non-additive potential used was the triple-dipole potential and the coefficient, C_{abc} appearing in the formula for this potential was calculated from,

$$C_{abc} = \tfrac{3}{4}\alpha C_6 \qquad (5.3.1)$$

where

α is polarizability of the molecule

and C_6 is the coefficient of the leading term in (4.2.1).

This formula has been shown to be within a few percent of the accurately determined value of C_{abc} in the case of Ar.[124] The results are shown in table 6-8 and are quite good for CH_4 but rather low for CF_4 and SF_6. The poor agreement for these molecules is probably due to the small value of C_6 predicted by the spherical-shell potential which was used in (5.3.1). since for CF_4 and SF_6 this is the only estimate of C_6 for these molecules. For CH_4 the value due to Dalgarno[13] was used. The results for SF_6 are, however, in better agreement with the data of Rowlinson et al than with those of MacCormack and Schneider.[76] This agreement would probably not be destroyed by using a larger C_6 coefficient.

TABLE 5 C for CH_4

T	C_{add}	C_{nadd}	$-C_o$	$-C_{od}$	C_t	C_{expt}		
						1	2	3
131	-8589	7577	319	50	-1381	-13600 ± 90%		
191	1702	2094	143	21	3632	4741 ± 10%		
200	1787	1849	133	20	3478	4351 ± 10%		
232	1953	1204	99	19	3039	-		
240	1704	1131	96	18	2721	3508 ± 3%		
273	1519	851	76	17	2277	2670 ± 3%	2620	2880
373	1177	474	37	13	1601		1834	2010
448	1083	353	28	12	1396		1585	
464	1082	300	27	11	1344		-	
548	1042	263	23	10	1272		1385	
573	1042	240	20	9	1253		1360	
623	1037	221	16	2	1240		1330	

C_{add} = additive C, C_{nadd} = non-additive C, C_o = octopole-octopole correction, C_{od} = octopole induced dipole correction,

C_t = total C,

[1] reference 181, [2] reference 182, [3] reference 183, $n = 9$ potential

TABLE 6 C for CF_4

T	C_{add}	C_{nadd}	$-C_o$	$-C_{od}$	C_t	C_{expt}[1]
273	4429	1134	892	120	4551	7100
373	3137	573	497	99	3114	4490
473	2776	376	311	82	2759	3660
573	2738	278	212	69	2735	3250
623	2799	221	154	59	2807	2563

[1] reference 182, n=12 potential

TABLE 7 C for SF_6

T	C_{add}	C_{nadd}	$-C_h$	$-C_{hd}$	C_t	C_{expt}[1]	C_{expt}[2]
273	10,673	6071	4960	59	11,725		101,130
307	11,307	4209	4033	56	11,427	19,920	
323	10,955	3650	3674	54	10,877	18,710	41,015
348	10,189	2995	3191	52	9,941	15,720	
370	9,479	2564	2801	51	9,191	13,910	
373	9,394	2517	2790	50	9,071		23,800
404	8,526	2087	2377	47	8,189	12,390	

C_h = hexadecapole-hexadecapole correction
C_{hd} = hexadecapole-induced dipole correction, $\Phi = 26 \times 10^{-42}$ e.s.u. cm^4, n = 12 potential

[1] reference 184

[2] reference 185

It is quite clear from the result that the additive third virial coefficient cannot account for the experimental results for these quasi-spherical molecules. The theoretical results for CH_4 (the most accurate of those determined here) indicate that non-additive effects other than the triple-dipole potential are quite small.

5.4 CONCLUSIONS

Both quantum-mechanical calculations on He and semi-empirical work on CH_4, CF_4 and SF_6 show that the major non-additive term in the three-body potential is the triple-dipole effect.

From the quantum mechanical results only three-body effects should be important which is in agreement with the results of previous studies of third virial coefficients, liquid and crystal properties.

CHAPTER 6 - CONCLUSIONS

In this chapter some overall conclusions are drawn from the work presented in this thesis.

The use of quantum mechanical perturbation theory, in terms of separated molecule wavefunctions, as a method of calculating intermolecular potentials has been investigated. The problem of finding a suitable perturbation expansion from the multitude of possible expansions was discussed. It was concluded that the Murrell-Shaw-Musher-Amos formalism is quite suitable. We showed that correcting the main defect of this theory i.e. the lack of correct symmetry of the first order wavefunction leads to only a minor change in the final energy expression.

For the interaction of closed shell systems a formalism was developed which shows that errors in the first order energy caused by approximating the ground state wavefunctions by Hartree-Fock functions should be small.

The problem of calculating the second order energy was also investigated and a method suitable for studying the interaction of closed shell systems was suggested.

A fairly complete solution, using the abovementioned method, was then obtained for the interaction of two closed shell He atoms. The results may be found in sections 2.6 to 2.10.
The overall potential agrees very well with those determined variationally and with empirically determined potentials.

The method should be applicable to larger systems such as Ne, Ar, Kr interactions since excellent results were obtained using Hartree-Fock separated molecule wavefunctions which are all that are available for these larger systems. Furthermore, G.T.O. wavefunctions proved to be just as accurate as S.T.O. wavefunctions. This is very important if application to larger, non-atomic (e.g. H_2O, N_2) systems is to be practical.

A further point (which was made in Chapter 2) is that the perturbation method unlike the variational method of obtaining the potential is physically interpretable and the results for one system may be related to those for another.

The same perturbation method when applied to the problem of non-additivity of the intermolecular potential, in Chapter 5 shows that this non-additivity is small. For three He atoms the major non-additive term is the well known triple dipole effect. This result agrees with the conclusions drawn from semi-empirical studies.

We have also determined (Chapter 4) as closely as possible the intermolecular potential for the interactions of pairs of CH_4, CF_4 and SF_6 molecules from an analysis of experimental viscosity and second virial coefficient data. The model potential used contains both central and non-central terms but still retains physical interpretability. An excellent fit to experimental viscosity and second virial coefficients was obtained in each case. Furthermore, reasonable values of the self-diffusion coefficient, octopole moment and dispersion coefficient (C_6) of CH_4 were also obtained. The potentials are simple enough for use in applications such as the study of the equilibrium properties of liquids. One such application was considered in Chapter 5 where the third virial coefficient, C of CH_4, CF_4 and SF_6 were calculated. Excellent results were obtained when the triple dipole non-additive potential was used to calculate the non-additive contribution to C for CH_4. The results for CF_4 and SF_6 were less satisfactory due to inaccuracy in the determination of the three-body coefficient, C_{abc}. However, the results do show that, in agreement with the work of Barker and Pompe on Ar and the theoretical results of section 5.2 that the major non-additive term is the triple-dipole effect.

APPENDIX A - VIRIAL COEFFICIENT PROGRAMS

In this appendix the programs used for computing the second and third virial coefficients are described and their accuracy is illustrated.

1. Second Virial Coefficient Program

As mentioned in section 3.2.2 the second virial coefficients were calculated by direct numerical integration using an adaptive Simpson's rule procedure. Since the intergrands for the quantum corrections and the H-functions become insignificant at large and small r the integrations were carried out between r_{max} and r_{min} the distances at which the integrands become less than a specified tolerance. A similar procedure was used for the classical central second virial coefficient, B_o except that at small r,

$$g(r) = 1 - \exp(-U(r)/kT) \to 1 \text{ as } r \to o \qquad (1)$$

and thus

$$B_o^* = (r_{min}/r_o^*)^3 + \int_{r_{min}}^{r_{max}} g(r)\, r^2\, dr \qquad (2)$$

where $B_o^* = B_o/b_o$, $b_o = 2/3\ \pi N_o r_o^3$

$r_o^* = r_o/d$, r_o and d are two distances characteristic of the potential function. The above scheme proved to be entirely satisfactory and accurate as can be seen from Table 1, where the results for

a Lennard-Jones 12-6 potential are compared to those obtained by a series expansion method.[79]

A listing of the program, second, may be found at the end of this appendix.

2. Third Virial Coefficient Programs

To evaluate the third virial coefficient a transformation from the variables r_{ab}^*, r_{bc}^* and r_{ca}^* to r_{ab}^*, x and y was made where

$$r_{ac}^* = r_{ab}^* (x+y)^{\frac{1}{2}}, \quad r_{bc}^* = r_{ab}^* ((1-x)+y)^{\frac{1}{2}}$$

and $r_{ij}^* = r_{ij}/d$

The various contributions to the third virial coefficient, defined in Chapter 3 then becomes,

$$C^*_{add} = -36\, r_o^{*-6} \int_o^\infty \int_o^{\frac{1}{2}} \int_o^{\alpha} f_{ab} f_{bc} f_{ca} r_{ab}^{*5} y \, dy \, dx \, dr_{ab}^* \quad (3)$$

$$C^*_{nad} = -36\, r_o^{*-6} \int_o^\infty \int_o^{\frac{1}{2}} \int_o^{\alpha} (f_{ab}+1)(f_{bc}+1)(f_{ca}+1) f_{abc}\, r_{ab}^{*5} y \, dy \, dx \, dr_{ab}^* \quad (4)$$

$$I_n^* = r_o^{*k} \int_o^\infty \int_o^{\frac{1}{2}} \int_o^{\alpha} f_{ac} f_{bc} (f_{ab}+1) r_{ab}^{*l} y \, dy \, dx \, dr_{ab}^* \quad (5)$$

and

$$C'^* = 8\, B'^* B_o^* + 3d^{-2} k^{-1} T^{-3} r_o^{*-6} \int_o^\infty \int_o^{\frac{1}{2}} \int_o^{\alpha} (A_{ab}+A_{bc}+A_{ca})\, r_{ab}^{*5} y \, dy \, dr \, dr_{ab}^* \quad (6)$$

where $f_{ij} = \exp(-U(r_{ij})/kT)$,

$f_{abc} = \exp(-\Delta U3/kT)$,

$\alpha = (1-(1-x)^2)^{\frac{1}{2}}$, $\quad k=n-6$ and $l=5-n$

and

$$A_{ab} = \left\{\left(\frac{\partial U_{abc}}{\partial r_{ab}}\right)^2 + \frac{\partial U_{abc}}{\partial r_{ac}} \cdot \frac{\partial U_{abc}}{\partial r_{bc}}\right\} \exp\left(-(U_{ab} + U_{bc} + \hat{U}_{ca}^{+\Delta U3})/kT\right)$$

$$-(U_{ab}')^2 \exp(-U_{ab}/kT), \text{etc.}$$

As mentioned in section 3.2.2 two schemes were used to evaluate these triple integrals,

a. repeated applications of Simpson's rule, and

b. multidimensional integral formulae.

The results for the 9-6 spherical shell potential may be seen in Table 2. Also shown are the results obtained by a hundred point non-adaptive Simpson's rule program written by Dr. J.A. Barker. It is clear from the table that methods (a) and (b) are equally accurate but the other program becomes inaccurate at low temperatures.

However, method (b) has several advantages over (a)

1. the number of integration points may easily be altered,

2. it is faster, and

3. it will give accurate results in a reasonable time on a small computer.

The first point is particularly relevant since, as can be seen from the tables results of about 10% accuracy may be obtained at a reduced temperature of about 2.0 using the minimum number of integration

points,(this takes 24 sec. on CDC 3200). Furthermore the program is so arranged that the temperature loop is innermost and the major computations are only performed once. Thus the time per integral decreases as the number of integrals increases.

Also the integration is performed over a number, n of sub-intervals e.g.

$$C^*_{add} = \int_0^{\infty}\int_0^{\frac{1}{2}}\int_0^{\alpha} g\, dydxd\, r^*_{12}$$

$$= \int_0^{\infty} hdR$$

$$= \frac{3}{8}\,(r_{min}/r_0^*)^6 + W_1 \int_{r_{min}}^{r1} hdR + W_2 \int_{r_1}^{r2} hdR + \ldots.$$

$$+ W_{n+1}\int_{r_n}^{r_{max}} hdR \qquad (7)$$

where the W_i are weighting factors dependent on r_{i-1} and r_i and are set up in the program. This allows the number and limits of the sub-integrals to be optimised for different potentials and different temperature ranges. The ones shown in the listing at the end of this appendix, are for a typical potential of the Lennard-Jones or spherical-shell[6,140] type.

TABLE 1. B For Lennard-Jones 12-6 Potential. $\sigma = 2.566$ Å, $\epsilon/k = 10.22^{\circ}K$

T ($^{\circ}K$)	BC_N	BC_S	BI_N	BI_S	$B2_N$	$B2_S$	$B3_N$	$B3_S$
20	-13.9839	-13.9820	15.7033	15.6904	-8.2928	-8.2775	9.8611	9.8322
50	4.8966	4.89797	3.6746	3.6714	-0.5684	-0.5672	0.2549	0.2541
100	9.6254	9.6283	1.4469	1.4456	-0.09697	-0.096768	0.02188	0.02182
500	10.7311	10.7344	0.2083	0.2081	-0.00253	-0.00253	0.00013	0.00013
1000	9.8079	9.8109	0.09456	0.09448	-0.000590	-0.000688	0.000016	0.000016
2000	8.7015	8.7043	0.04348	0.04344	-0.000143	-0.000142	0.000002	0.000002

Tolerances in Simpson's rule and r limit tests, 10^{-4}

N = by program SECOND (numerically)

S= by series expansion, reference 79

B in CC/mole

TABLE 2. C_{add} for a 9-6 Spherical Shell Potential

T	T*	C_{add}^{1}	C_{add}^{2}	C_{add}^{3}
191	0.824	875	1690	1701
200	0.863	1288	1775	1787
232	1.0	1757	1739	1746
348	1.5	1338	1240	1232
573	2.47	1045	1060	1038

$\epsilon/k = 232^{\circ}K$, $r_o = 3.84A$, $d = 2.15A$

1 Barker's program,
2 repeated Simpson's rule,
3 Stroud multidimensional integral formulae with DIV=3

TABLE 3. C* for a 9-6 Spherical Shell Potential by Stroud Method

T	T*	DIV=1	DIV=2	DIV=3	DIV=5
191	0.824	0.4923	0.4246	0.336	0.3207
232	1.0	0.4923	0.3829	0.3423	0.3402
348	1.5	0.2950	0.2494	0.24158	0.2417
404	2.0	0.23817	0.2124	0.2099	0.2102
573	2.47	0.2222	0.2045	0.2035	–
696	3.0	0.21701	0.2045	0.2040	–

DIV controls the number of points in the multidimensional integral formulae.

TABLE 4. C*, Lennard-Jones 12-6 Potential

T*	C* DIV=1	C* DIV=2	C* H.C.B.
1.0	0.08060	0.43315	0.42966
1.5	0.46170	0.54148	0.54339
2.0	0.40553	0.43611	0.43710
5.0	0.31923	0.31447	0.31508
10.0	0.28490	0.28631	0.28610
20.0	0.24349	0.24672	0.24643
100.0	0.14126	0.14235	0.14251

H.C.B., values from reference 1

APPENDIX B - QUANTUM MECHANICAL INTEGRALS

In this appendix the programs used to obtain the energy of the $^1\Sigma_g^+$ state of He_2 and of He_3 are discussed.

1. Integrals over Gaussian lobe functions

The energy integrals over gaussian lobe functions, X (or 1 s, G.T.O.'s centred anywhere in space.)

i.e.

$$X = N \exp(-ar^2) \qquad (1)$$

where $N = 1$, for unnormalised functions,

$= (\pi/2a)^{-3/4}$ for normalised functions,

are given in reference 52.

The only complicated integral appearing is

$$F_o(z) = \int_o^1 \exp(-zu^2)\, du \qquad (2)$$

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which is related to the error function and the incomplete gamma function. Many different ways of evaluating this function have been given but the most efficient appears to be to use the scheme suggested by Schwartz and Schaad[178] i.e.

$$F_o(z) = \exp(-z) \sum_{i=o}^{\infty} (2z)^i/(2i+1)!!, \quad z \leq 1.0 \qquad (3a)$$

$$= \tfrac{1}{2}(\pi/z)^{\frac{1}{2}} \operatorname{erf}(z^{1/2}), \quad z > 1.0 \qquad (3b)$$

$$\operatorname{erf}(z) = 1 - (a_o z^o + a_1 z^1 + \ldots + a_6 z^6)^{-16} \qquad (4)$$

or

$$\mathrm{erf}(z) = 1 - (a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5) \exp(-z^2) \qquad (5)$$

(the constants a_i and t being given in reference 186)

which we will call Hastings first and second approximations respectively.

Since the series 3(a) converges rapidly for $z \leq 1.0$ and erf(z)=1.0 to 8 figuresfor $z > 17.1$ this method is very efficient.

The results for the series expansion 3(a) are shown in Table 1 and for the Hastings approximations in Table 2. A comparison of the results using the ELLIOT 503 and CDC 3200 computers is given in Table 3. As can be seen at worst an accuracy of 2 or 3 parts in 10^{-7} is obtained and thus the above scheme is very satisfactory.

TABLE 1. Series Method

z	$F_o(z)$[1]	$\mathrm{erf}(z^{\frac{1}{2}})$[1]	$\mathrm{erf}(z^{\frac{1}{2}})$[2]
0.001	0.99996666	0.01128342	0.01128342
0.004	0.99986668	0.02256457	0.02256457
0.025	0.99916729	0.05637198	0.05637198
0.04	0.98682515	0.22270259	0.22270259
0.16	0.94913209	0.42839235	0.42839236
0.36	0.89192254	0.60385609	0.60385609
0.64	0.82203732	0.74210096	0.74210096
0.81	0.78471279	0.79690821	0.7960821
1.0	0.74682414	0.84270080	0.84270079

[1] by series expansion, ELLIOT 503

[2] from N.B.S. compilation, ref. 75

TABLE 2. Hastings Approximations

z	$F_o(z)^1$	$F_o(z)^2$	erf $(z^{\frac{1}{2}})^1$	erf$(z^{\frac{1}{2}})^2$	erf$(z^{\frac{1}{2}})^3$
1.21	0.70914687	0.70914675	0.88020520	0.88020506	0.88020507
1.44	0.67228729	0.67228735	0.91031397	0.91031404	0.91031398
1.96	0.60281463	0.60281489	0.95228486	0.95228527	0.95228512
2.56	0.54079133	0.54079143	0.97634828	0.97634846	0.97634838
4.0	0.44104081	0.44104064	0.99532252	0.99532214	0.99532227
6.25	0.35434644	0.35434648	0.99959286	0.99959298	0.99959305
9.0	0.29540240	0.29540245	0.99997774	0.99997790	0.99997791
10.24	0.27694422	0.27694424	0.99999388	0.99999397	0.99999397
12.25	0.25320750	0.25320751	0.99999923	0.99999926	0.99999926
13.69	0.23952075	0.23952075	0.99999983	0.99999984	0.99999983
16.0	0.22155673	0.22155673	0.99999999	0.99999999	0.99999998

[1] by Hastings first approximation
[2] by Hastings second approximation
} ELLIOT 503

[3] N.B.S. compilation, ref. 75

TABLE 3.

z	$F_o(z)^1$	$F_o(z)^2$
0.05	0.98358038	0.98358039
0.2	0.93715003	0.93715003
0.4	0.88125403	0.88125403
0.6	0.83140287	0.83140287
0.8	0.78681636	0.78681637
0.9	0.76628404	0.76628404
1.0	0.74682414	0.74682413
2.0	0.59814384	0.598143843
4.0	0.44104081	0.441040807
6.0	0.36160809	0.361608085
10.0	0.28024736	0.280247359

[1] ELLIOT 503
[2] CDC 3200

Slater Type Orbitals

The integrals required for the computation of the coulomb and exchange energies using Hartree-Fock functions expanded in terms of 1s S.T.O.'s were all calculated using analytic formulae[60] except for the exchange integrals. These were calculated by the Barnett-Coulson[61,62] method using Q.C.P.E. program 23 modified slightly to compute integrals over linear combinations of S.T.O.'s on the C.D.C. 3600 Computer. The accuracy was tested against standard results and the convergence of the series involved was also tested for typical integrals involved in He_2, see Table 5. Enough terms were always included to give at least 5 figure accuracy.

The integrals required for the calculation of the correlation corrections and the dispersion energy calculations were performed analytically or by use of the Miller-Browne[187] diatomic integral program.

TABLE 4 , Check of 1s S.T.O. Program

R	I_1	I_2	I_3	I_4	I_5	I_6*
6.0	0.047096291 (0.047096292)	0.017351265 (0.01735126)	0.166659498 (0.16665949)	0.015311456 (0.015311456)	0.166592680 (0.16659267)	0.000813980 (0.000814027)
8.0	0.010175700 (0.0101756997)	0.003019164 (0.00301916365)	0.124999873 (0.124999873)	0.002738738 (0.0027387379)	0.124997956 (0.124997956)	0.0000328957 (0.0000328960)
10.0	0.002012730 (0.0020127302)	0.000499399 (0.00049939923)	0.099999998 (0.099999977)	0.000461093 (0.00046109303)	0.099999947 (0.0999999472)	0.00000113833 (0.00000113835)
12.0	0.000374797 (0.0037479694)	0.000079875 (0.0000798748)	0.083333333 (0.083333333)	0.0000746590 (0.0000746586)	0.083333332 (0.083333332)	0. 000000035482 (0.000000354839)

I_1 = (a \| b), I_2 = (a \| Rb \| a), I_3 = (a \| Rb \| a), I_4 = (aa \| ab), I_5 = (aa \| bb), I_6 = (ab \| ab),
notation as in chapter 2, values in parentheses from reference 44

* 20 terms taken in the series' expansion of I_6.

TABLE 5 Convergence of Barnett-Coulson Method for Exchange Integrals

N	INTEGRAL
2	0.000025569
7	0.000027455
15	0.000027529
25	0.000027531
29	0.000027531

N = number of terms in series, results for a linear combination of 2,1 s S.T.O.'s at 5.5 a.u.

APPENDIX C -NOTE ON NOTATION FOR CHAPTER 3

In chapter 3 the role of statistics in the quantum mechanical calculation of B and transport coefficients has not been emphasized and in fact only cross-sections in Boltzmann statistics have been given .However the Fermi-Dirac and Bose-Einstein cases are readily obtained from these formulae ,see reference 1.

The form of the Boltzmann equation used in chapter 3 is only one of many ways of writing it ,however the one given there shows quite clearly the relation between the classical ,quantum and W-C-U-B cases.

A fuller discussion as to the dynamics of two body collisions and the definitions of the quantities used in chapter 3 ,sections (3.3.3) and (3.3.4) will be found in references 1 ,108-110. Furthermore definitions of the integrals A^*,B^* and C^* may be found in 1.

The units used for the transport coefficients in formulae (3.3.8),(3.3.9) and (3.3.10) are ,

viscosity gm.cm./sec. ,

thermal conductivity cal./cm.sec.^{o}K and

diffusion cm.^{2}/sec.

Finally in the formulae for the third virial coefficient the integration ranges are ,

τ,V ,all configuration space ,or

Δ,all triangles s.t. $r_{ab} \geqslant r_{bc}$ and $r_{ab} \geqslant r_{ac}$.

APPENDIX D - SECOND VIRIAL COEFFICIENTS

In this appendix the individual contributions to the total second virial coefficients for CH_4, CF_4 and SF_6 are shown. Only B_1 is shown for CF_4 and SF_6 since B_2 is negligible.

The notation is as follows,

B_{cl} = classical central B

B_1 = first quantum correction

B_2 = second quantum correction

B_o = total central B

B_{oc} = octopole-octopole correction

B_{ocd} = octopole-induced dipole correction

B_h = hexadecapole-hexadecapole correction

and B_{hd} = hexadecapole-induced dipole correction

TABLE 1. B for CH_4, n = 9

T	B_{cl}	B_1	B_2	B_o	B_{oc}	B_{ocd}
110	-336.97	11.72	-0.63	-325.88	-31.65	-5.63
120	-281.11	9.68	-0.41	-272.84	-23.15	-4.50
130	-238.90	6.68	-0.28	-232.50	-17.59	-3.70
140	-205.95	5.30	-0.19	-200.84	-13.77	-3.12
150	-179.60	4.32	-0.14	-175.42	-11.05	-2.69
160	-158.08	3.59	-0.11	-154.60	- 9.06	-2.35
180	-125.07	2.60	-0.07	-122.54	- 6.39	-1.86
200	-100.99	1.98	-0.04	- 99.05	- 4.75	-1.53
225	- 78.78	1.49	-0.03	- 77.32	- 3.46	-1.25
250	- 62.24	1.17	-0.02	- 61.09	- 2.63	-1.06
275	- 49.47	0.95	-0.01	- 48.53	- 2.08	-0.91
300	- 39.32	0.79	-0.01	- 38.54	- 1.68	-0.80
350	- 24.24	0.58	0	- 23.66	- 1.18	-0.65
400	- 13.59	0.45	0	- 13.14	- 0.87	-0.54
500	0.39	0.31	0	0.70	- 0.54	-0.42
523.16	2.74	0.29	0	3.03	- 0.49	-0.39
548.16	5.05	0.27	0	5.32	- 0.45	-0.37
573.16	7.10	0.25	0	7.35	- 0.41	-0.36
598.16	8.97	0.23	0	9.20	- 0.38	-0.34
600	9.09	0.23	0	9.32	- 0.37	-0.34
623.16	10.65	0.22	0	10.87	- 0.35	-0.32

TABLE 2. B for CH_4, n = 12

T	B_{c1}	B_1	B_2	B_o	B_{oc}	B_{ocd}
110	-332.33	10.08	-0.48	-322.73	-26.40	-5.03
120	-278.66	7.52	-0.31	-271.45	-19.45	-4.05
130	-237.85	5.82	-0.21	-232.24	-14.87	-3.35
140	-205.86	4.64	-0.15	-201.37	-11.71	-2.84
150	-180.14	3.79	-0.11	-176.46	- 9.44	-2.45
160	-159.05	3.16	-0.08	-155.97	- 7.77	-2.15
180	-126.56	2.31	-0.05	-124.30	- 5.52	-1.71
200	-102.75	1.77	-0.03	-101.01	- 4.13	-1.42
225	- 80.68	1.34	-0.02	- 79.36	- 3.02	-1.16
250	- 64.20	1.05	-0.01	- 63.16	- 2.32	-0.98
275	- 51.44	0.86	-0.01	- 50.59	- 1.84	-0.85
300	- 41.27	0.72	-0.01	- 40.56	- 1.49	-0.75
350	- 26.11	0.53	0	- 25.58	- 1.05	-0.61
400	- 15.39	0.41	0	- 14.98	- 0.78	-0.52
500	- 1.28	0.28	0	- 1.0	- 0.49	-0.40
523.16	1.11	0.26	0	1.37	- 0.45	-0.38
548.16	3.43	0.24	0	3.67	- 0.41	-0.36
573.16	5.51	0.23	0	5.74	- 0.37	-0.34
598.16	7.40	0.21	0	7.61	- 0.34	-0.33
600	7.53	0.21	0	7.74	- 0.34	-0.32
623.16	9.11	0.20	0	9.31	- 0.32	-0.31

TABLE 3. B for CF_4, n = 15

T	B_{cl}	B_1	B_o	B_{oc}	B_{ocd}
273.16	-73.86	0.50	-73.36	-45.70	-5.38
298.15	-55.86	0.41	-55.45	-35.88	-4.62
303.15	-52.72	0.39	-52.33	-34.29	-4.50
323.15	-41.45	0.34	-41.11	-28.90	-4.05
348.15	-29.68	0.29	-29.39	-23.79	-3.60
373.16	-19.88	0.25	-19.63	-19.92	-3.23
398.17	-11.61	0.22	-11.39	-16.94	-2.93
423.18	-4.54	0.19	-4.35	-14.58	-2.68
448.20	1.58	0.17	1.75	-12.69	-2.47
473.21	6.92	0.16	7.08	-11.15	-2.29
498.23	11.62	0.14	11.76	-9.88	-2.14
523.25	15.79	0.13	15.92	-8.81	-2.00
548.26	19.50	0.12	19.62	-7.92	-1.89
573.27	22.84	0.11	22.95	-7.15	-1.78
598.28	25.85	0.10	25.95	-6.50	-1.69
623.29	28.57	0.10	28.67	-5.93	-1.60
673.16	33.31	0.08	33.39	-5.00	-1.46

TABLE 4. B for CF_4, n = 12

T	B_{cl}	B_1	B_o	B_{oc}	B_{ocd}
273.16	-94.11	0.44	-93.67	-18.30	-3.47
298.15	-73.83	0.36	-73.47	-14.37	-2.98
303.15	-70.30	0.34	-69.96	-13.73	-2.89
323.15	-57.62	0.30	-57.32	-11.59	-2.60
348.15	-44.39	0.25	-44.14	- 9.53	-2.31
373.16	-33.39	0.22	-33.17	- 7.99	-2.08
398.17	-24.11	0.19	-23.92	- 6.80	-1.88
423.18	-16.18	0.17	-16.9	- 5.85	-1.72
448.2	- 9.32	0.15	- 9.17	- 5.10	-1.59
473.21	- 3.36	0.13	- 3.23	- 4.48	-1.47
498.23	1.92	0.12	2.04	- 4.03	-1.37
523.25	6.58	0.11	6.69	- 3.55	-1.29
548.26	10.73	0.10	10.83	- 3.19	-1.21
573.27	14.45	0.09	14.54	- 2.89	-1.14
598.28	17.81	0.09	17.90	- 2.62	-1.08
623.29	20.86	0.08	20.94	- 2.40	-1.03
673.15	26.14	0.07	26.21	- 2.02	-0.94

TABLE 5. B for SF_6, n = 12

T	B_{cl}	B_l	B_h	B_{hd}	B_h	B_{hd}	B_h	B_{hd}
280	-260.81	0.43	-60.65	-3.68	-70.54	-3.97	-81.58	-4.27
300	-222.59	0.36	-49.17	-3.19	-57.18	-3.44	-66.13	-3.70
325	-184.10	0.29	-38.85	-2.73	-45.19	-2.94	-52.26	-3.17
350	-153.14	0.24	-31.47	-2.38	-36.59	-2.56	-42.33	-2.76
375	-127.72	0.20	-26.01	-2.10	-30.25	-2.27	-34.98	-2.44
400	-106.50	0.17	-21.87	-1.88	-25.43	-2.03	-29.41	-2.18
440	-78.99	0.14	-17.05	-1.61	-19.83	-1.73	-22.94	-1.86
480	-57.28	0.11	-13.69	-1.40	-15.92	-1.51	-18.42	-1.63
520	-39.71	0.10	-11.25	-1.24	-13.09	-1.34	-15.14	-1.44

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      PROGRAM SECOND
C     CALCULATES THE CLASSICAL,CENTRAL SECOND VIRIAL COEFFICIENT
C         THE FIRST ,SECOND AND THIRD QUANTUM CORRECTIONS
C     AND NON-SPHERICAL CONTRIBUTIONS (VIA THE H-FUNCTION)
C
      INTEGER XX,YY,ZZ,VV
      REAL MASS,NO,PI
      DIMENSION T(50),OMEGA(50),KKP(50),HF(50)
      COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
      EXTERNAL G,GR,FQCINT,SQCINT,TQCINT,UKR
      DATA(BK=1,38054E-16) ,(NO=6,02252E23),(PI=3,14159265)
     1,(H=6,6256E-27)
      PRINT 100
C     READ POTENTIAL  PARAMETERS
      READ 1 ,RO ,D,EK,MASS,NN $READ 2 ,XX,YY,ZZ,VV ,NT
      PRINT  3 ,RO,D,EK,MASS,NN  $PRINT 4 ,XX,YY,ZZ,VV ,NT
      D=D*1,E-8$RO=RO*1,E-8  $PRINT 150
C     READ TEMPERATURES
      READ 5   ,(T(I),I=1,NT) $PRINT 6   ,(T(I),I=1,NT)
C     READ TOLERANCES FOR INTEGRATIONS
      READ 1000 ,TOLR,TOLI
      TOLR=TOLR*1,E-4$TOLI=TOLI*1,E-4  $PRINT 1001 ,TOLR,TOLI
C     SET UP CONSTANTS FOR AN ARBITARY  POTENTIAL FUNCTION
      ROS=RO/D $RO33=(RO**3) $BO=2,*PI*NO*RO33/3,0
      Q=H*H/(4,*PI*PI*MASS) *NO$RO3=3,/(ROS**3)
      C1=0,25*D/(RO33*BK)$C2=1,/(D*D*BK)$C3=C2*C2
      PRINT  7   ,BO,Q
C     SET UP INITIAL ESTIMATES OF RMAX AND RMIN
      RMIN0=1,8$RMIN1=1,8$RMIN2=RMIN3=1,8
      RMIN0=1,5$RMIN1=1,4
      RMAX0=RMAX1=RMAX2=RMAX3=20,0
C     SET UP CONSTANTS FOR A PARTICULAR POTENTIAL FUNCTION
      IF(YY,EQ,3) GOTO 15
      DO 8  I=1,NT
      TEMP=T(I) $TR=1,/TEMP$TSQR=TR*TR$TCUR=TR*TSQR$TFTHR=TR*TCUR
      CONST1=C1*TCUR$CONST2=TSQR*C3$BQUANT=B1=B2=B3=0,0
C     CLASSICAL VALUE
      RMIN0=FINDR(GR,-,1,RMIN0,TOLR)
      RMAX0=FINDR(G,1,0,RMAX0,TOLR)
      BCL=RO3*(SIMPSONF(RMIN0,ROS,TOLI,G) +SIMPSONF(ROS,RMAX0,TOLI,G)
     1+RMIN0**3/3,0) $IF(ZZ) 9,9,10                                    05F
C     QUANTUM CORRECTIONS FOLLOW
 10   RMIN1=FINDR(FQCINT,-,1,RMIN1,TOLR)
      RMAX1=FINDR(FQCINT,1,0,RMAX1,TOLR)
      B1=CONST1*(SIMPSONF(RMIN1,ROS,1,E-4,FQCINT)
     1+SIMPSONF(ROS,RMAX1,1,E-4,FQCINT)) $B1=Q*B1  $IF(ZZ-1) 9,9,11
 11   RMIN2=FINDR(SQCINT,-,1,RMIN2,TOLR)
      RMAX2=FINDR(SQCINT,1,0,RMAX2,TOLR)
      B2=-CONST1*C2*TR*(SIMPSONF(RMIN2,ROS,1,E-4,SQCINT)
     1+SIMPSONF(ROS,RMAX2,1,E-4,SQCINT)) $B2=Q*Q*B2$ IF(ZZ-2) 9,9,12
 12   RMIN3=FINDR(TQCINT,-,1,RMIN3,TOLR)
      RMAX3=FINDR(TQCINT,1,0,RMAX3,TOLR)
      B3=CONST1*(SIMPSONF(RMIN3,ROS,TOLI,TQCINT)+SIMPSONF(ROS,RMAX3,
     1TOLI,TQCINT))
      B3=Q*B3$B3=Q*B3$B3=Q*B3 $B3=CONST2*B3
 9    BQUANT=B1+B2+B3 $BTOTAL=BCL+BQUANT
```

```
      IF(VV,EQ,1) PRINT 200 ,RMIN0,RMAX0,RMIN1,RMAX1,RMIN2,RMAX2,
     1RMIN3,RMAX3  $IF(XX-1) 13,13,14
   13 BCL=B0*BCL$TEMP=EK*TEMP$B1=B0*B1$B2=B2*B0$B3=B3*B0
      BQUANT=B0*BQUANT$BTOTAL=B0*BTOTAL
   14 TEMP=TEMP/EK  $PRINT 300,TEMP,BCL,BQUANT,BTOTAL,B1,B2,B3
    8 CONTINUE
   15 IF(YY,EQ,1) GOTO 16    $PRINT 400
C     H-FUNCTION ROUTINE
C     READ NUMBER OF MULTIPOLE MOMENTS AND POLARIZABILITY
      READ 17  ,NOM,ALPHA  $ PRINT 18 ,NOM,ALPHA
C     READ MULTIPOLE MOMENTS
      DO 19   I=1,NOM
      READ 20   ,OMEGA(I)$OMEGA(I)=OMEGA(I)*1,E-34$PRINT 21,OMEGA(I)
   19 CONTINUE
C     SET UP INITIAL ESTIMATE OF RMIN AND RMAX
      RMINH=3,5$RMAXH=7,0  $RO7=RO**7$ALPHAS=ALPHA*1,E-25 /(RO**3)
      RMINH=1,65 $RMAXH=8,0
C     READ THE NO,OF AND TYPE OF H-FUNCTIONS REQUIRED
      READ 22   ,NKP $PRINT 23,NKP
      DO 24   I=1,NKP
      READ 22 , KKP(I) $PRINT 25  ,KKP(I)
   24 CONTINUE
      DO 26  I=1,NT
      TEMP=T(I)$TR=1,/TEMP
      DO 27    IK=1,NKP
      KP=KKP(IK)
      RMINH=FINDR(UKR,-0,1,RMINH,TOLR)
      RMAXH=FINDR(UKR,1,0,RMAXH,TOLR)
      IF(VV,EQ,1) PRINT 500,RMINH,RMAXH  $RMIN2=2,*RMINH
      IF(RMAXH,GT,RMIN2) GOTO 29
      HFUNC=SIMPSONF(RMINH,RMAXH,TOLI ,UKR) $GOTO 30
   29 HFUNC=SIMPSONF(RMINH,RMIN2,TOLI ,UKR)+SIMPSONF(RMIN2,RMAX ,TOLI,
     1UKR)
      HF(IK)=HFUNC
   30 CONTINUE
   27 CONTINUE
C     PRESENT VERSION FOR OCTOPOLE-OCTOPOLE AND OCTOPOLE-INDUCED DIPOLE
C     CORRECTIONS
      VO=HF(1)$VOD=HF(2)
      TR=EK*TR
      DO 31  J=1,NOM
      OMEGAS=OMEGA(J)*OMEGA(J)/(RO7*EK*BK)
      D1=OMEGAS*OMEGAS*TR*TR*B0*14,811428*11,0
      D2=28,8*TR*OMEGAS*ALPHAS*B0
      VIROCT=D1*VO$VIROID=D2*VOD
      PRINT 32  ,TEMP,OMEGA(J) ,VIROCT,VIROID
   31 CONTINUE
   26 CONTINUE
   16 CONTINUE
    1 FORMAT(4F10,0,I3)
    2 FORMAT(5I3)
    3 FORMAT(21H-POTENTIAL PARAMETERS,/,4H-RO=,F16,9,2X,2HD=,F16,9,2X,
     13HEK=,F16,9,5HMASS=,F16,9,/,4H-NN=,I3)
    4 FORMAT(16H-CONTROL NUMBERS, /,4H-XX=,I3,2X,3HYY=,I3,2X,3HZZ=,I3,2X
     1,3HVV=,I3,/,24H-NUMBER OF TEMPERATURES=,I3)
    5 FORMAT(F10,0)
```

```
  6     FORMAT(F16,9)
  7     FORMAT(4H-BO=,F16,9,5X,2HQ=,E16,9)
 17     FORMAT(I3,F16,9)
 18     FORMAT(5 H-NOM=,I3,/,16H-POLARIZABILITY=,F16,9)
 21     FORMAT(18H-MULTIPOLE MOMENT=,E16,9)
 20     FORMAT(F10,0)
 22     FORMAT(I3)
 23     FORMAT(5H-NKP=,I3)
 25     FORMAT(4H-KP=,I3)
 32     FORMAT(13H-TEMPERATURE=,F16,9,7HMOMENT=,E16,9,/
     1,19H-MOMENT CORRECTION=,E16,9,2X ,19HINDUCED CORRECTION=,E16,9)
100     FORMAT(34H-SECOND VIRIAL COEFFICIENT PROGRAM,/)
150     FORMAT(13H-TEMPERATURES,/)
200     FORMAT(27H-DISTANCES FOR INTEGRATIONS,/,8F16,9)
300     FORMAT(13H-TEMPERATURE=,F16,9,2X,/,4H-BO=,F16,9,2X,9HBQUANTUM=,
     1F16,9,2X,7HBTOTAL=,F16,9,/,4HBR1=,F16,9,2X,3HB2=,F16,9,2X,3HB3=,
     2F16,9)
400     FORMAT( 28 H-NON-SPHERICAL CONTRIBUTIONS,/)
500     FORMAT(7H-RMINH=,F16,9,2X,6HRMAXH=,F16,9)
1000    FORMAT(2F10,0)
1001    FORMAT(12H-TOLERANCES , /,7H-FOR R=,E16,9,2X,17HFOR INTEGRATIONS=,
     1E16,9)
        END
        FUNCTION G(X)
C       CALCULATES THE INTEGRAND FOR THE CLASSICAL,CENTRAL B I,E,G(X)
        COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
        POTENT=4,*EK*(X**(-12)-X**(-6))*TR
        G=(1,0-EXP(-POTENT))*X*X
        END
        FUNCTION GR(X)
C       FUNCTION GR(X)  =G(X)-X*X
        COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
        POTENT=4,*EK*(X**(-12)-X**(-6))*TR
        GR=(1,0-EXP(-POTENT))*X*X-X*X
        END
        FUNCTION FQCINT(X)
C       INTEGRAND FOR THE FIRST QUANTUM CORRECTION
        COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
        POTENT=4,*EK*(X**(-12)-X**(-6))*TR
        F=24,*EK*(-2,*(X**(-13)+X**(-7))
        F=F*EK $FQCINT=F*F*X*X*EXP(-POTENT)
        END
        FUNCTION SQCINT(X)
C       INTEGRAND FOR THE SECOND QUANTUM CORRECTION
        COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
        POTENT=4,*EK*(X**(-12)-X**(-6))*TR
        F=24,*EK*(-2,*(X**(-13)+X**(-7))
        F=F*EK $F2=F*F
        S=24,*EK*(26,*X**(-14)-7,*X**(-8))
        SQCINT=(0,1* S*S +,2*F2*W+0,1111111111*F2*F*TR*XR
     1-0,01388888*F2*F2*TSQR)*EXP(-POTENT)*X*X
        END
        FUNCTION TQCINT(X)
C       INTEGRAND FOR THE THIRD  QUANTUM CORRECTION
        COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
        POTENT=4,*EK*(X**(-12)-X**(-6))*TR
```

```
      F=24.*EK*(-2.*(X**(-13)+X**(-7))
      S=24.*EK*(26.*X**(-14)-7.*X**(-8))
      T=24.*EK*(-364.*X**(-15)+56.*X**(-9))
      F2=F*F$F4=F2*F2$S2=S*S$X2=X*X$T2=1./TEMP
      TX=1./(TEMP*X)$X2R=1./X2
      TQCINT=(0.00714286*T**2+0.04285714*X2R*S2+0.00793651*S2*S*TR
     1+0.0333333333*F*S2*TX +0.00634921*TX*X2R*F2*F
     2-0.008333333*F2*S2*T2-0.00092593*F4*T2*X2R
     3-0.002777777*F4*F*T2*TX     +0.00023148*F4*F2*T2*T2)*X2*EXP(-POTENT
     4)
      END
      FUNCTION UKR(X)
C     INTEGRAND FOR H-FUNCTION
      COMMON EK,TEMP,TR,TSQR,TCUR,TFTHR,ROS, KP
      POTENT=4.*EK*(X**(-12)-X**(-6))*TR
      POTENT=EK*(CC1*PSN-CC2*PS3)*XR*TR
      UKR=(ROS/X)**KP* (X*X/(ROS*ROS*ROST)*EXP(-POTENT )
      END
      FUNCTION   FINDR(PR,DX,RM,TOL)
C     FINDS THE MINIMIUM (IF DX.LT.0) OR MAXIMIUM (IF DX.GT.0) R
C     FOR THE INTEGRANDS
      X=RM$X=X-DX
 1    X=X+DX$TEST=ABS(PR(X))$IF(TEST-TOL) 2,2,1
 2    RG=X
      FINDR=RG
      END
      FUNCTION SIMPSONF(A,B,DELTA,FN)
C     ADAPTIVE SIMPSON S  RULE INTEGRATION
      REAL K
      X1=A$X2=B$K=X2-X1
      S1=FN(X1)$S0=S1=S1+FN(X2)
 2    S2=0.$H=0.5*K$X=X1+H
 4    S2=S2+FN(X)
      X=X+K$IF(X.GT.X2) 6,4
 6    S1=S1+4.*S2
      IF(H*ABS((S1-S0-S0)/ S1).LT.DELTA) 10,8
 8    S0=S1$S1=S1+S2-S2 $K=H$GOTO 2
 10   SIMPSONF=0.3333333333*H*S1$END
```

```
      PROGRAM THIRD
C     PROGRAM TO CALCULATE THE THIRD VIRIAL COEFFICIENT
C     BY EVALUATING THE TRIPLE INTEGRAL BY STROUD MULTIPLE INTEGRAL
C     FORMULAE ,THIS VERSION USES N SUBDIVISION AND A 7-TH, DEGREE
C     FORMULA
C     THIS VERSION IS SET UP TO CALCULATE THE ADDITIVE AND NON-
C     ADDITIVE THIRD VIRIAL COEFFICIENTS FOR A LENNARD-JONES 12-6
C     POTENTIAL
      DIMENSION T(50),GF1(40),GF2(40),GF3 (40), WT(40),WTA(20),WTB(20) ,
     1CONR1(20,10),CONR2(20,10),CONR3(20,10),CONR4(20,10),SUM1(20,10)
     2,SUM2(20,10),SUM3(20,10),SUM4(20,10)
      REAL MASS,NO,NU
      DATA (GNU=0,9258200998) ,(ETA=0,9258200998)
      DATA (GMU1=0,7341125288),(GMU2=0.4067031864)
      DATA (A1=0,2957475995),(B1=0,0941015089)
      DATA (CC1=0,2247031748),(CC2=0,4123338623)
      DATA(WTA=0,00,0,25,0,25,0,25,0,25,0,25,0,25,0,25,0,25,1.0,1,0,2,0,
     13,0,3,0)
      DATA(WTB=0,00,1,0,1,25,1,5,1,75,2,0,2,25,2,5,2,75,3,0,
     14,0,5,0,7,0,10,0)
      DATA(PI=3,141592653),(NO=6,02252E23),(BK=1,3805E-16)
     1,(H=6,6256E-27)
      PRINT 1
    1 FORMAT(33H-THIRD VIRIAL COEFFICIENT PROGRAM,//)
C     SET UP THE WEIGHTS FOR THE INTEGRATION FORMULA
      DO 21 L=1,6
   21 WT(L)=A1
      DO 22 L=7,18
   22 WT(L)=B1
      DO 23 L=19,26
   23 WT(L)=CC1
      DO 24 L=27,34
   24 WT(L)=CC2
C     SET UP THE POINTS  FOR THE INTEGRATION FORMULA
      DO 15 L=1,34
   15 GF1(L)=GF2(L)=GF3(L)=0,0
      GF1(1)=GF2(2)=GF3(3)=GNU
      GF1(4)=GF2(5)=GF3(6)=-GNU
      GF1(7)=GF2(7)=GF1(8)=GF2(9)=GF3(8)=GF3(9)=ETA
      GF1(10)=GF1(11)=GF2(12)=-ETA
      GF2(10)=GF3(11)=GF1(12)=ETA
      GF1(13)=GF2(13)=GF1(14)=GF3(14)=GF2(15)=GF3(15)=-ETA
      GF1(16)=GF2(17)=GF3(18)=ETA
      GF3(16)=GF3(17)=GF2(18)=-ETA
      GF1(19)=GF2(19)=GF3(19)=GF2(20)=GF3(20)=GF1(21)=GF1(22)=GF2(22)
     1 =GF3(21)=GMU1
      GF1(20)=GF2(21)=GF3(22)=-GMU1
      GF1(23)=GF2(23)=GF1(24)=GF2(25)=GF3(25)=GF1(26)=GF2(26)=GF3(26)
     1=GF3(24)=-GMU1
      GF3(23)=GF2(24)=GF1(25)=GMU1
      GF1(27)=GF2(27)=GF3(27)=GF2(28)=GF3(28)=GF1(29)=GF3(29)=GF1(30)
     1=GF2(30)=GMU2
      GF1(28)=GF2(29)=GF3(30)=-GMU2
      GF1(31)=GF2(31)=GF1(32)=GF3(32)=GF2(33)=GF3(33)=GF1(34)=GF2(34)=
     1GF3(34)=-GMU2
      GF3(31)=GF2(32)=GF1(33)=GMU2
```

```
C       READ THE POTENTIAL PARAMETERS AND THE MASS
        READ 2 ,RO,D,EK,NU,MASS  $PRINT 3 ,RO,D,EK,NU,MASS
 2      FORMAT(5F10,0)
 3      FORMAT(21H-POTENTIAL PARAMETERS,/,4H-RO=,F16,9,5X,2HD=,F16,9,5X,
       13HEK=,F16,9,//,4H-NU=,F16,9,//,22H-MASS OF THE MOLECULE=,F16,9,/)
        RO=RO*1,0E-8 $D=D*1,0E-8
C       READ TEMPERATURES
        READ 33,NT  $PRINT 4,NT
 33     FORMAT(I3)
 4      FORMAT(24H-NUMBER OF TEMPERATURES=,I3)
        PRINT 5
 5      FORMAT(13H-TEMPERATURES,/)
        DO 6 I=1,NT
        READ 7,TEMP $T(I)=TEMP$PRINT 8,T(I)
 7      FORMAT(F10,0)
 8      FORMAT(F16,9)
 6      CONTINUE
        ROS=RO/D $BO=2,*NO*PI*(RO**3)/3,$BO2=BO*BO  $NU=NU/(EK*BK*(D**9))
        Q=H*H*NO/(4,0*PI*PI*MASS)   $ROSM6=ROS**(-6)
        PRINT 115,ROS,BO,BO2,Q
 115    FORMAT(29H-DERIVED POTENTIAL PARAMETERS,/,5H-ROS=,F16,9,5X,
       13HBO=,F16,9,5X,6HBO*BO=,F16,9,/ ,3H-Q=,E16,9)
C       READ INTEGRATION PARAMETERS
        READ 9,DIV,RX,IREQ1,IREQ2,NN
 9      FORMAT(2F10,0,3I3)
        WTB(1)=RX$WTA(1)=1,0-RX
        DO 169 I=1,NN
        WTA(I)=WTA(I)*ROS $WTB(I)=WTB(I)*ROS
 169    CONTINUE
        RXX=WTB(1)*D *1,0E8 $PRINT 125,DIV,NN,RXX,IREQ1,IREQ2
 125    FORMAT(23H-INTEGRATION PARAMETERS,/,5H-DIV=,F16,9,5X,
       123H NUMBER OF R DIVISIONS=,I3,/,30H-LOWER LIMIT OF R INTEGRAT.  =
       2,F16,9,/,17H-REQUEST NUMBERS=,2I3)
        PRINT 120
 120    FORMAT(12H-TEMPERATURE,8X,21HCLASSICAL ADDITIVE C ,15H-NON-ADD
       1ITIVE C,//)
        NDIV=DIV $CENTRE=0,5/DIV$C=CENTRE$CDEL=2,*CENTRE
        DO 110 IL=1,NN $DO 110 IT=1,NT
 110    CONR1(IL,IT)=CONR2(IL,IT)=CONR3(IL,IT)=CONR4(IL,IT)=0,0
        DO 10 L=1,34 $DO 111 IL=1,NN$DO 111 IT=1,NT
 111    SUM1(IL,IT)=SUM2(IL,IT)=SUM3(IL,IT)=SUM4(IL,IT)=0,0
        C1=-CENTRE
        DO 11 I=1,NDIV
        C1=C1+CDEL $X1=GF1(L)*C+C1
        DO 11 IL=1,NN
        R=WTA(IL)*X1+WTB(IL) $RR=1,0/R$RR2=RR*RR
        RR3=RR2*RR$RR6=RR3*RR3$RR12=RR6*RR6$RR5=RR2*RR3
        C3=-CENTRE
        DO 11 K=1,NDIV
        C3=C3+CDEL $X3=GF3(L)*C+C3$X=X3/2,0
        OMX=1,0-X $OMXSQ=OMX*OMX$ROMOSQ=SQRT(1,0-OMXSQ)$XSQ=X*X$C2=-CENTRE
        DO 11 J=1,NDIV
        C2=C2+CDEL $X2=GF2(L)*C+C2$Y=X2*ROMOSQ$YSQ=Y*Y
        R13SQ=RR2/(XSQ+YSQ)   $RR13=1,0/SQRT(R13SQ)
        R136=R13SQ*R13SQ*R13SQ  $RR1312=R136*R136   $XR13=1,0/RR13
        R23SQ=RR2/(OMXSQ+YSQ) $RR23=1,0/SQRT(R23SQ)
```

```
      R236=R23SQ*R23SQ*R23SQ   $R2312=R236*R236   $XR23=1.0/RR23
      FACTORR=X2*(1.0-OMXSQ)/RR5
      DO 100 IT=1,NT
      TEMP=T(IT) $TR=1.0/TEMP
      IF(IREQ2.NE.1) GOTO 700
      IF(R.LE.1.0) GOTO  48
  700 CONTINUE
C     SET UP  U(R12)
      POT12=4.*EK*(RR**12-RR**6)*TR
      IF(POT12.GT.700.)48,49
   48 ER12=-1.0  $GOTO 50
   49 ER12=EXP(-POT12)-1.0
   50 CONTINUE
      IF(IREQ2.NE.1) GOTO 701
      IF(RR13.LE.1.0) GOTO 51
  701 CONTINUE
C     SET UP  U(R13)
      POT13=4.*EK*(XR13**12-XR13**6) *TR   $IF(POT13.GT.700.) 51,52
   51 ER13=-1.0 $ GO TO 53
   52 ER13=EXP(-POT13)-1.0
   53 CONTINUE
      IF(IREQ2.NE.1) GOTO 702
      IF(RR23.LE.1.0) GOTO 54
  702 CONTINUE
C     SET UP  U(R23)
      POT23=4.*EK*(XR23**12-XR23**6)  *TR  $IF(POT23.GT.700.) 54,55
   54 ER23=-1.0  $GOTO 56
   55 ER23=EXP(-POT23)-1.0
   56 CONTINUE
      PSUM1=ER12*ER13*ER23*FACTORR *WT(L)
      SUM1(IL,IT)=SUM1(IL,IT)+PSUM1
      R2=R*R$RR13SQ=RR13*RR13$RR23SQ=RR23*RR23
      IF(IREQ1.LT.1) GOTO 60
      IF(IREQ2.NE.1) GOTO 703
      IF(RR13.LE.1.0) GOTO 225   $IF(RR23.LE.1.0) GOTO 225
  703 CONTINUE
      CS1=0.5*(R2+RR13SQ-RR23SQ)/(RR13*R)
      CS2=0.5*(R2+RR23SQ-RR13SQ)/(R*RR23)
      CS3=0.5*(RR13SQ+RR23SQ-R2)/(RR13*RR23)
      POT123=POT12+POT13+POT23
      IF(POT123.GT.700)  GOTO 225  $GRH=EXP(-POT123)   $GOTO 2500
  225 GRH=0.0  $ GOTO 57
 2500 CONTINUE
      DELU3=NU*(R*RR13*RR23)**(-3)*(1.0+3.0*CS1*CS2*CS3)
      DELU3=DELU3*EK*TR     $IF(DELU3.GT.700.) 57,61
   57 ER123=-1.0   $GOTO 62
   61 ER123=EXP(-DELU3)-1.0
   62 CONTINUE
      PSUM2=GRH*ER123*FACTORR *WT(L)
      SUM2(IL,IT)=SUM2(IL,IT)+PSUM2
   60 CONTINUE
  100 CONTINUE
   11 CONTINUE
      DO 10 IT=1,NT  $DO 10 IL=1,NN
      CONR1(IL,IT)=CONR1(IL,IT)+SUM1(IL,IT)
      CONR2(IL,IT)=CONR2(IL,IT)+SUM2(IL,IT)
```

```
10    CONTINUE
      AAA=CDEL**3/8.0  $CONST=-18.0*ROSM6
      DO 58 IT=1,NT    $DO 58 IL=1,NN
      CONR1(IL,IT)=AAA*CONR1(IL,IT)
      CONR2(IL,IT)=AAA*CONR2(IL,IT)
58    CONTINUE
      DO 59 IT=1,NT
      CON1=CON2=CON3=CON4=0.0
      DO 599 IL=1,NN
      CON1=CON1+WTA(IL)*CONR1(IL,IT)
      CON2=CON2+WTA(IL)    *CONR2(IL,IT)
599   CONTINUE
      CON1=CON1*CONST*0.625*WTB(1)**6*ROSM6
      CON1=CON1*BO2$CON2=CON2*BO2*CONST
      PRINT 65,T(IT),CON1,CON2
65    FORMAT(F16.9,7X,F16.9,7X,F16.9)
59    CONTINUE
      STOP
      END
```

```
      PROGRAM GAUSLOBE
C     CALCULATES THE ENERGY INTEGRALS FOR LINEAR COMBINATIONS OF
C     GAUSSIAN LOBE FUNCTIONS (EITHER NORMALIZED OR UNNORMALIZED)
C
      REAL KEI,KEIC,NATI,NATIC,NN
      DIMENSION FXCD(5,10),FYCD(5,10),FZCD(5,10),RNORMC(5,10)
     1,COEF(5,10),CXCD(3),CYCD(3),CZCD(3),CHARGE(3),RNORMF(5)
     2,ALPHA(5,10)
      DIMENSION TGR(200),NX(10) ,NOC(10)
      DIMENSION ZETASQ(20)
      COMMON FXCD,FYCD,FZCD,RNORMC,COEF,CXCD,CYCD,CZCD,CHARGE,RNORMF
     1,ALPHA
      COMMON TGR,NX,NOC
      PRINT 1000
 1000 FORMAT(45H-ENERGY INTEGRALS FOR GAUSSIAN LOBE FUNCTIONS,//)
      READ 105,NOBS
  105 FORMAT(I3)
      PRINT 106   ,NOBS
  106 FORMAT(22H-NUMBER OF BASIS SETS=,I3)
      IB=0
  801 CONTINUE
      PRINT 1255
 1255 FORMAT(15H-NEXT BASIS SET,/)
      IB=IB+1
      PI2=6.2831853073
      PI75=0.423777208 $PI15=5.568327996
      READ 100, NOF ,NON
  100 FORMAT(2I3)
      PRINT 231,NOF,NON
  231 FORMAT(21H-NUMBER OF FUNCTIONS=,I3,/, 18H-NUMBER OF NUCLEI=,I3 /)
      PRINT 4000
 4000 FORMAT(32H-SCALING FACTOR FOR EACH ORBITAL)
      DO 5000 I=1,NOF
      READ 5001 ,ZETASQ(I)
 5001 FORMAT(F10.0)
      PRINT 5002 ,I,ZETASQ(I)
 5002 FORMAT(8H-ORBITAL,I3,5X,15HSCALING FACTOR=,F16.9)
 5000 CONTINUE
      DO 60 I=1,NOF
      READ 987,NV
  987 FORMAT(I3)
      NOC(I)=NV
      PRINT 978 ,I,NV
  978 FORMAT(9H-FUNCTION,I3,2X,18HNO. OF COMPONENTS=,I3)
   60 CONTINUE
      DO 70 I=1,NOF
      READ 837, NV
  837 FORMAT(I3)
      NX(I)=NV
      IF(NV) 839,838,839
  838 CONTINUE
      PRINT 840, I
  840 FORMAT( 9H-FUNCTION,I3,2X,34HCONSISTS OF UNNORMALIZED FUNCTIONS)
      GOTO 841
  839 CONTINUE
      PRINT 842 ,I
```

```
  842  FORMAT( 9H-FUNCTION,I3,2X,34HCONSISTS OF   NORMALIZED FUNCTIONS)
  841  CONTINUE
   70  CONTINUE
       PRINT 338
  338  FORMAT(30H-BASIS FUNCTION SPECIFICATIONS,/,9H-FUNCTION ,5X
      1,9HCOMPONENT,26X,8HPOSITION,17X,8HEXPONENT,9X,11HCOEFFICIENT)
       DO 1 I=1,NOF
       NK=NOC(I)
       DO 1 J=1,NK
       READ 101,X,Y,Z,W,V
  101  FORMAT(5F10.0)
       FXCD(I,J)=X$FYCD(I,J)=Y$FZCD(I,J)=Z$ALPHA(I,J)=W$COEF(I,J)=V
       ALPHA(I,J)=ALPHA(I,J)*ZETASQ(I)
       W=W*ZETASQ(I)
       PRINT 200,I,J,X,Y,Z,W,V
  200  FORMAT(I3,10X,I3,5X, 5F16.9)
    1  CONTINUE
       PRINT 355
  355  FORMAT(23H-NUCLEAR SPECIFICATIONS,/,7H-NUMBER,30X,8HPOSITION,17X,
      16HCHARGE,//)
       DO 2 I=1,NON
       READ 102,X,Y,Z,CC
  102  FORMAT(4F10.0)
       CXCD(I)=X $CYCD(I)=Y $CZCD(I)=Z $CHARGE(I)=CC
       PRINT  301,I,X,Y,Z,CC
  301  FORMAT(I3,5X,4F16.9)
    2  CONTINUE
       PRINT 222
  222  FORMAT(40H-NORMALIZING CONSTANTS OF THE COMPONENTS,/,
      19H-FUNCTION,5X,9HCOMPONENT,5X,8HCONSTANT,/)
       DO 3 I=1, NOF $NK=NOC(I) $M=NX(I) $DO 3 J=1,NK
       IF (M) 61,61,62
   61  X=1.0 $GOTO 63
   62  XC=ALPHA(I,J)$X=(XC+XC)**(0.75)*PI75
   63  CONTINUE
       RNORMC(I,J)=X*COEF(I,J)
       PRINT 333,I,J,X
  333  FORMAT(I3,11X,I3,7X,F16.9)
    3  CONTINUE
       PRINT 344
  344  FORMAT(39H-NORMALIZING CONSTANTS OF THE FUNCTIONS, /,
      19H-FUNCTION,11X,8HCONSTANT,/)
       DO 4 I=1,NOF
       AU=0.0
       NK=NOC(I)
       DO 5 J=1,NK  $ DO 5 K=1,NK
       A=ALPHA(I,J) $B=ALPHA(I,K)
       AX=FXCD(I,J) $BX=FXCD(I,K)
       AY=FYCD(I,J) $BY=FYCD(I,K)
       AZ=FZCD(I,J) $BZ=FZCD(I,K)
       APB=A+B
       ABSQ=(AX-BX)*(AX-BX) +(AY-BY)*(AY-BY)+(AZ-BZ)*(AZ-BZ)
       AW=RNORMC(I,J)*RNORMC(I,K)*(APB)**(-1.5)*EXP(-A*B*ABSQ/APB)*PI15
       AU=AU+AW
    5  CONTINUE
       XX=1.0/SQRT(AU)
```

```
      RNORMF(I)=XX
      PRINT 326,I,XX
  326 FORMAT(I3 ,12X,F16.9)
    4 CONTINUE
      PRINT 366
  366 FORMAT(23H-ONE ELECTRON INTEGRALS)
      DO 9 I=1,NOF $DO 9 J=1,NOF
      NN=RNORMF(I)*RNORMF(J)
      OLI=KEI=NATI=0.0
      NI=NOC(I) $NJ=NOC(J)
      TERM1=TERM2=0.0
      DO 10 K=1,NI  $ DO 10 L=1,NJ
      CN=RNORMC(I,K)*RNORMC(J,L)
      A=ALPHA(I,K) $B=ALPHA(J,L)
      APB=1.0/(A+B)
      ATB=A*B $PAB=PI15*(APB**1.5)
      AX=FXCD(I,K) $BX=FXCD(J,L)
      AY= FYCD(I,K) $ BY=FYCD(J,L)
      AZ=FZCD(I,K) $BZ=FZCD(J,L)
      ABS=(AX-BX)*(AX-BX) +(AY-BY)*(AY-BY)+( AZ-BZ)*(AZ-BZ)
      ADB=ATB*APB $ARG=(-ABS*ADB) $EXPARG=EXP(ARG)
      PAB=PAB*EXPARG
C     OVERLAP INTEGRAL CALCULATED
      OLIC=CN*PAB
      OLI=OLI+OLIC
C     KINETIC ENERGY INTEGRAL CALCULATED
      KEIC=CN*PAB*ADB*(3.0+ARG+ARG)
      KEI=KEI+KEIC
C     NUCLEAR ATTRACTION INTEGRALS CALCULATED
      PX=(A*AX+B*BX)*APB
      PY=(A*AY+B*BY)*APB
      PZ=(A*AZ+B*BZ)*APB
      NATIC=0.0
      DO 11 M=1,NON
      CX=CXCD(M) $CY=CYCD(M)$CZ=CZCD(M)
      CPS=(CX-PX)*(CX-PX)+(CY-PY)*(CY-PY)+(CZ-PZ)*(CZ-PZ)
      X=CPS/APB
C     CALCULATES THE FUNCTION
C     INTEGRAL OF EXP(-X*U**2)*DU FROM 0 TO 1
      FOX=1.0
      IF(X.EQ.0.0) GOTO 58
      ERFX=1.0 $XS=SQRT(X)
      IF(X.GT.17.1) GOTO 59
C     X LESS THAN OR EQUAL TO 1
      IF (X.GT.1.0) GOTO 55
      AR=0.5 $TERM=PTLSUM=2.0
      DO 53 JJ=2,50
   52 AR=AR+1.0
      TERM=TERM*X/AR
      PTLSUM=PTLSUM+TERM
      IF(TERM/PTLSUM-1.0E-7) 54,54,52
   53 CONTINUE
   54 FOX=0.5*PTLSUM*EXP(-X)
      GOTO 58
C     X GREATER THAN 1.0
   55 CONTINUE
```

```
      ERFX=1.0- ((((((4.30638E-5*XS+2.765672E-4)*XS+1,520143E-4)*XS
     1+9.2705272E-3)*XS+4,2282012E-2)*XS+7.0523078E-2)*XS+1.0)**(-16)
   59 FOX=ERFX*0.886226925/XS
   58 CONTINUE
      NATIC=NATIC-CN*CHARGE(M)*APB*EXPARG*FOX
   11 CONTINUE
      NATI=NATI+NATIC
   10 CONTINUE
      OLI=NN*OLI$KEI=NN*KEI$NATI=NN*NATI*PI2
      PRINT 500,I,J,OLI    ,KEI   ,NATI
  500 FORMAT(3H-FN,I3,2X,3HAND,2X,2HFN,I3,5X,8HOVERLAP=,F16.9,
     15X,14HK.E. INTEGRAL=,F16.9,5X,23HNUCL. ATTRAC. INTEGRAL=,F16.9)
    9 CONTINUE
      PRINT 458
  458 FORMAT(40H-INDIVIDUAL NUCLEAR ATTRACTION INTEGRALS,/)
      DO 99 I=1,NOF$DO 99 J=1,NOF
      NN=RNORMF(I)*RNORMF(J)
      DO 999 M=1,NON
      NATIC=NATI=0.0
      NI=NOC(I) $NJ=NOC(J)
      DO 9999 K=1,NI $DO 9999 L=1,NJ
      CN=RNORMC(I,K)*RNORMC(J,L)
      A=ALPHA(I,K) $B=ALPHA(J,L)
      APB=1.0/(A+B)
      ATB=A*B $PAB=PI15*(APB**1.5)
      AX=FXCD(I,K) $BX=FXCD(J,L)
      AY= FYCD(I,K) $ BY=FYCD(J,L)
      AZ=FZCD(I,K) $BZ=FZCD(J,L)
      ABS=(AX-BX)*(AX-BX) +(AY-BY)*(AY-BY)+( AZ-BZ)*(AZ-BZ)
      ADB=ATB*APB $ARG=(-ABS*ADB) $EXPARG=EXP(ARG)
      PAB=PAB*EXPARG
      PX=(A*AX+B*BX)*APB
      PY=(A*AY+B*BY)*APB
      PZ=(A*AZ+B*BZ)*APB
      CX=CXCD(M) $CY=CYCD(M)$CZ=CZCD(M)
      CPS=(CX-PX)*(CX-PX)+(CY-PY)*(CY-PY)+(CZ-PZ)*(CZ-PZ)
      X=CPS/APB
C     CALCULATES THE FUNCTION
C     INTEGRAL OF EXP(-X*U**2)*DU FROM 0 TO 1
      FOX=1.0
      IF(X.EQ.0.0) GOTO 158
      ERFX=1.0 $XS=SQRT(X)
      IF(X.GT.17.1) GOTO 159
C     X LESS THAN OR EQUAL TO 1
      IF (X.GT.1.0) GOTO 155
      AR=0.5 $TERM=PTLSUM=2.0
      DO 153 JJ=2,50
  152 AR=AR+1.0
      TERM=TERM*X/AR
      PTLSUM=PTLSUM+TERM
      IF(TERM/PTLSUM-1.0E-7) 154,154,152
  153 CONTINUE
  154 FOX=0.5*PTLSUM*EXP(-X)
      GOTO 158
C     X GREATER THAN 1.0
  155 CONTINUE
```

```
      ERFX=1.0- ((((((4.30638E-5*XS+2.765672E-4)*XS+1.520143E-4)*XS
     1+9.2705272E-3)*XS+4.2282012E-2)*XS+7.0523078E-2)*XS+1.0)**(-16)
  159 FOX=ERFX*0.886226925/XS
  158 CONTINUE
      NATIC=NATIC-CN*CHARGE(M)*APB*EXPARG*FOX
 9999 CONTINUE
      NATI=NATI+NATIC
      NATI=NN*PI2*NATI
      PRINT 409 ,I,J,M,NATI
  409 FORMAT(3H-I=,I3,5X,2HJ=,I3,5X,2HM=,I3,5X,5HNATI=,F16.9)
  999 CONTINUE
   99 CONTINUE
      PRINT 555
  555 FORMAT(23H-TWO ELECTRON INTEGRALS)
      NI=0
      DO 641 KP=1,NOF
      DO 641 KR=KP,NOF $DO 641 KS=KR,NOF
      NI=NI+1
      TGR(NI)=TELI(KP,KP,KR,KS)
      PRINT 150,NI,KP,KP,KR,KS,TGR(NI)
  150 FORMAT(4H-NI=,I5,2X,4H  I=,I5,2X,4H  J=,I5,2X,4H  K=,I5,2X,
     14H  L=,I5,5X,10H INTEGRAL=,F16.9)
  641 CONTINUE
      KPE=NOF-1
      DO 22 KP=1,KPE
      KQS=KP+1
      DO 22 KQ=KQS,NOF
      DO 22 KR=KP,NOF
      IF(KP-KR) 20,18,18
   18 DO 19 KS1= KQ,NOF
      NI=NI+1
      TGR(NI)=TELI(KP,KQ,KR,KS1)
      PRINT 110 ,NI,KP,KQ,KR,KS1,TGR(NI)
  110 FORMAT(4H-NI=,I5,2X,4H  I=,I5,2X,4H  J=,I5,2X,4H  K=,I5,2X,
     15H   L=,I5,5X,10H INTEGRAL=,F16.9)
   19 CONTINUE
      GOTO 22
   20 DO 21 KS2=KR,NOF
      NI=NI+1
      TGR(NI)=TELI (KP,KQ,KR,KS2)
      PRINT 111,NI,KP,KQ,KR,KS2,TGR(NI)
  111 FORMAT(4H-NI=,I5,2X,4H  I=,I5,2X,4H  J=,I5,2X,4H  K=,I5,2X,
     15H   L=,I5,5X,10H INTEGRAL=,F16.9)
   21 CONTINUE
   22 CONTINUE
      IF(IB-NOBS) 801,805,805
  805 CONTINUE
      STOP
      END
      FUNCTION TELI(I,J,K,L)
C     CALCULATES THE TWO ELECTRON INTEGRAL (IJ/KL)
      INTEGER P,Q
      REAL NN
      DIMENSION FXCD(5,10),FYCD(5,10),FZCD(5,10),RNORMC(5,10)
     1,COEF(5,10),CXCD(3),CYCD(3),CZCD(3),CHARGE(3),RNORMF(5)
     2,ALPHA(5,10)
```

```
      DIMENSION TGR(200),NX(10) ,NOC(10)
      COMMON FXCD,FYCD,FZCD,RNORMC,COEF,CXCD,CYCD,CZCD,CHARGE,RNORMF
     1,ALPHA
      COMMON TGR,NX,NOC
      PI25=17.493418326
      NN=RNORMF(I)*RNORMF(J)*RNORMF(K)*RNORMF(L)
      ERI=0.0
      N1=NOC(I)$N2=NOC(J)$N3=NOC(K)$N4=NOC(L)
      DO 13 M=1,N1  $ DO 13 N=1,N2
      DO 13 P=1,N3  $ DO 13 Q=1,N4
      AX=FXCD(I,M) $BX=FXCD(J,N)
      AY=FYCD(I,M) $BY=FYCD(J,N)
      AZ=FZCD(I,M) $BZ=FZCD(J,N)
      CX=FXCD(K,P) $DX=FXCD(L,Q)
      CY=FYCD(K,P) $DY=FYCD(L,Q)
      CZ=FZCD(K,P) $DZ=FZCD(L,Q)
      A=ALPHA(I,M) $ B=ALPHA(J,N)
      C=ALPHA(K,P) $D=ALPHA(L,Q)
      APB=A+B$CPD=C+D $ABCD=APB+CPD
      RAPB=1.0/APB $RCPD=1.0/CPD
      ABS=(AX-BX)*(AX-BX)+(AY-BY)*(AY-BY)+(AZ-BZ)*(AZ-BZ)
      CDS=(CX-DX)*(CX-DX)+(CY-DY)*(CY-DY)+(CZ-DZ)*(CZ-DZ)
      PX=(A*AX+B*BX )*RAPB $QX=(C*CX+D*DX)*RCPD
      PY=(A*AY+B*BY)*RAPB $QY=(C*CY+D*DY)*RCPD
      PZ=(A*AZ+B*BZ)*RAPB $QZ=(C*CZ+D*DZ)*RCPD
      PQS=(PX-QX)*(PX-QX)+(PY-QY)*(PY-QY)+(PZ-QZ)*(PZ-QZ)
      X=PQS*APB*CPD/ABCD
C     CALCULATES THE FUNCTION
C     INTEGRAL OF EXP(-X*U**2)*DU FROM 0 TO 1
      FOX=1.0
      IF(X.EQ.0.0) GOTO 8
      ERFX=1.0 $XS=SQRT(X)
      IF(X.GT.17.1) GOTO 10
C     X LESS THAN OR EQUAL TO 1
      IF (X.GT.1.0) GOTO 5
      AR=0.5 $TERM=PTLSUM=2.0
      DO 3 JJ=2,50
 2    AR=AR+1.0
      TERM=TERM*X/AR
      PTLSUM=PTLSUM+TERM
      IF(TERM/PTLSUM-1.0E-7) 4,4,2
 3    CONTINUE
 4    FOX=0.5*PTLSUM*EXP(-X)
      GOTO 8
C     X GREATER THAN 1.0
 5    CONTINUE
      ERFX=1.0- ((((((4.30638E-5*XS+2.765672E-4)*XS+1.520143E-4)*XS
     1+9.2705272E-3)*XS+4.2282012E-2)*XS+7.0523078E-2)*XS+1.0)**(-16)
 10   FOX=ERFX*0.886226925/XS
 8    CONTINUE
      CN=RNORMC(I,M)*RNORMC(J,N)*RNORMC(K,P)*RNORMC(L,Q)
      ERIC=(CN      *RAPB*RCPD)*(EXP(-ABS*A*B*RAPB-CDS*C*D*RCRD))*FOX
     1/(SQRT(ABCD))
      ERIC=ERIC+ERIC
      ERI=ERI +ERIC
 13   CONTINUE

TELI=ERI*NN*PI25
END
```