THE CALCULATION OF VANDER WAALS' CONSTANT BY THE EXTENDED HARTREE-FOCK WAVE FUNCTION

JWE-SON KUO

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THE CALCULATION OF VAN DER WAALS CONSTANT
BY THE EXTENDED H-F WAVE FUNCTION

by

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A THESIS

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ABSTRACT

A recently developed wave function, the extended H-F wave function, is used to test its effectiveness in the calculation of the long-range interaction between atomic systems. A better numerical value of the van der Waals interaction constant is obtained.
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
</tr>
<tr>
<td>II. THEORY</td>
</tr>
<tr>
<td>III. RESULT AND DISCUSSION</td>
</tr>
<tr>
<td>REFERENCES AND NOTE</td>
</tr>
<tr>
<td>APPENDIX A</td>
</tr>
<tr>
<td>APPENDIX B</td>
</tr>
<tr>
<td>COMPUTER PROGRAM</td>
</tr>
</tbody>
</table>
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CHAPTER I

INTRODUCTION

The forces that exist between atoms are basically of two kinds; attractive when atoms or molecules are far part, and repulsive if the distance between them is small. When these forces are balanced, atoms can form into a stable molecule or a molecular complex. For purposes of discussion the terms long-range forces and short-range forces are normally used to describe the attractive forces and the repulsive forces respectively. The existence of these two different types of forces can be inferred from experiments and has long been known\(^1\): It is however, very difficult to construct an unique theory such that a potential gives rise to both these forces. This paper will describe an attempt to calculate the long-range force between Hydrogen and Helium atoms using a version of the extended Hartree-Fock technique.

There have been many calculations about the long-range forces between atoms. Particularly, the calculations of the leading term, the dipole-dipole interaction energy, have been reported. These reports are focused either on the applications of the values of the oscillator strength\(^2\) or on double perturbation technique\(^3\). Despite these efforts, the variation-perturbation theory is still a very effective tool, provided that the proper atomic wave function are given\(^4\). In recent years, a new type of wave function, the extended H-F wave function has been developed. Its effectiveness has been shown, for example, in the calculation of hyperfine structure constant of Li\(^5\). It is the purpose of this paper to compare the effectiveness of different types of wave function within the framework of the H-F method, through the calculation
of the long-range forces.

The Hartree-Fock method or H-F method is based on the independent particle model. In this model each electron of the system is assumed to move in a static potential arising from the presence of the remaining charges. To satisfy the Pauli exclusion principle the total wave function can be written as:

$$
\Psi = \frac{1}{\sqrt{N}} \sum_{\lambda} (-1)^{\lambda} P (\phi_1, \ldots, \phi_N),
$$

where $P$ is a permutation operator. This form alone does not constitute the exact solution of Schrödinger equation for a many electron atom; the variation of with respect to any arbitrary orbital will lead us to an approximation for the exact solution. Thus, after we take the first order variation, we obtain an integrodifferential equation:

$$
\left( -\frac{1}{2} \mathbf{\sigma} \cdot \frac{\mathbf{r}}{r^2} \right) \Phi_i (\mathbf{r}) + \sum_{j \neq i} \left( 2 J_{ij} (\mathbf{r}) - K_{ij} (\mathbf{r}) \right) \Phi_j (\mathbf{r}) = \sum_j \Phi_j (\mathbf{r}) \mathbf{\lambda}_j \cdot \mathbf{r}_j,
$$

where $J_{ij} (\mathbf{r}) \Phi_i (\mathbf{r}) = \langle \Phi_j (\mathbf{r}) | \lambda_{ij} | \Phi_i (\mathbf{r}) \rangle \Phi_i (\mathbf{r})$ and $K_{ij} (\mathbf{r}) \Phi_i (\mathbf{r}) = \langle \Phi_j (\mathbf{r}) | \lambda_{ij} | \Phi_i (\mathbf{r}) \rangle \Phi_j (\mathbf{r})$

$\mathbf{\lambda}_j \cdot \mathbf{r}_j$ is the coordinate of electron $j$.

This equation for the orbital $\Phi_i (\mathbf{r})$ is called the Hartree-Fock equation or H-F equation, the solution to which yields an optimum value for the orbital $\Phi_i (\mathbf{r})$. As $\mathbf{\lambda}$ is a Hermitian matrix, the above equation may be written as follows:
Several methods based on iteration techniques to obtain solutions to these equations have been suggested. Modifications due to Roothaan and others have produced reasonable numerical values for the total energy of atomic systems.

Although the H-F method is a good approximate method for calculating the wave functions of many-electron atoms it has some deficiencies within itself. The physical picture this method presents is that each electron is assumed to move under the influence of the average potential of other electrons. Apart from the Pauli exclusion principle, this method disregards the correlation of the motion of other electrons. Thus it cannot preclude the possibility of the two electrons with anti-parallel spins from occupying the same coordinate space. This can be illustrated by the example of two electrons in the configuration $1s^2$.

For the singlet case, the wave function will be:

$$
\psi_s = [\phi_{1s}^{111} \phi_{2s}(2) + \phi_{1s}^{111} \phi_{1s}(1)] [\gamma_1 \beta_2 - \beta_2 \gamma_1]
$$

while for the triplet case it will be:
\[ 4_T = \{ \phi_{1s} \phi_{2s} \phi_{2s} \phi_{2s} \} \{ \alpha_1 \beta_0 + \beta_0 \alpha_1 \} \]

As \( Y_1 \to Y_2 \), this implies that

\[ 4_S \neq 0 \quad 4_T = 0. \]

Hence, by asking that \( \bar{\psi} \) satisfy the Pauli exclusion principle we find a zero possibility for two electrons with the same spin occupying the same coordinate space while a non-zero possibility for electrons with different spin to be found at the same space. This is an undesirable description in that the coulomb interaction should keep pairs of electrons separated regardless of their spin states.

Further, since the H-F method uses the variational principle, it is assumed that the H-F energy value will be higher than the exact energy value. That is, the formula

\[ E_{corr} = E_{exact} - E_{H-F} \]

will be negative, where \( E_{corr} \) is the correlation energy. However, according to the virial theorem which is

\[ \langle H \rangle = -\langle K.E \rangle = \frac{1}{2} \langle P.E \rangle, \]

where \( K.E \) is kinetic energy and \( P.E \) is potential energy, the correlation energy can be rewritten as follows:
\[ E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \]
\[ = \langle H \rangle_{\text{exact}} - \langle H \rangle_{\text{HF}} \]
\[ = \frac{1}{2} \langle PE \rangle_{\text{exact}} - \frac{1}{2} \langle PE \rangle_{\text{HF}} \]

The negative value of \( E_{\text{corr}} \) will imply that the electrons in the H-F method are under the influence of a potential which is stronger than the actual potential within a many-electron atomic system.

On the other hand, the use of H-F wave functions in the calculation of different physical constants has pointed out the weakness of the H-F wave function. For example, though the H-F wave function can approach values for the total energy within a magnitude of a few percent of the experimental value, it cannot be used to calculate the binding energy of a molecule. The reason is simply that the value of the binding energy is of the order of a tenth of a percent of the total energy. Another example is the calculation of the hyperfine structure constant. Here the H-F wave function has shown a considerably poor value for the electron density within the nucleus. Thus, the theoretical values disagree widely from the experimental values. Because of these failures, some modifications to the H-F method have been suggested.

Suggested Modification of the Hartree-Fock Method

(A) Configurations interaction: In the traditional H-F method, only one configuration of atomic system is treated. That is
\[ \Psi = \frac{1}{\sqrt{N!}} \sum_{\Pi} (-1)^{\Pi} \prod_{S, \Pi} S(N) \]
where the choice of the orbitals in $S_1(1) \ldots S_n(N)$ represents a particular configuration. To improve upon the result for the total energy, the above configuration may be changed to $S_1'(1) \ldots S_n'(N)$. Here the choice of the new configuration is arbitrary provided that the associated new wave function $\Psi'$ is orthogonal to $\Psi$. Finally if we choose $K$ configurations, the total wave function will have the form:

$$\Psi_{total} = \Psi_0 + \sum_{i=1}^{K} \Psi_i \alpha_i.$$

By using the variation principle, we may now calculate the value of the expansion coefficients $\alpha_i$.

(B) Spin-polarized wave function: Slater has proposed that instead of using the same radial wave function (orbital) for the different spins, that different orbitals be used for the different spins. For example, in the case of Helium the completely anti-symmetric, traditional H-F wave function is given by:

$$\Psi = \begin{vmatrix}
\phi_1(1) \alpha(1) & \phi_1(2) \beta(1) \\
\phi_2(1) \alpha(2) & \phi_2(2) \beta(2)
\end{vmatrix},$$

while the introduction of spin-polarized orbitals would yield a wave function of the form:

$$\Psi = \begin{vmatrix}
\phi_1'(1) \alpha' \alpha(1) & \phi_1'(2) \beta' \beta(1) \\
\phi_2'(1) \alpha' \alpha(2) & \phi_2'(2) \beta' \beta(2)
\end{vmatrix}.$$
(C) Unrestricted H-F method: A wave function constructed to be simultaneously an eigenfunction of the Hartree-Fock Hamiltonian (energy), the total spin, $S^z$ and the z-component of the total spin $S_z$ that is also restricted to the form of a single determinant is called "a restricted H-F wave function". It describes a closed shell configuration. For non-closed shell configuration a single determinantal wave function may be used. In this case the wave function is not an eigenfunction of $S^z$ and $S_z$. This type of single determinant Hartree-Fock wave function is termed the "unrestricted Hartree-Fock wave function".

Extended Hartree Fock Method

Although these modifications may improve some particular energy value, they also may violate some basic assumptions of the H-F theory. First, the configuration interaction method destroys the single-particle approach to the extent that it would be difficult to obtain a simple explanation of the periodic table. Secondly, spin-polarized and unrestricted H-F wave functions fail to explain the coupling of electron spins of an atomic system with an odd number of electrons. Hence, a further modification of the traditional Hartree-Fock approach is necessary so as to include both the single-particle approach and the property of being an eigenfunction of spin operator. This modification of the wave function is called the "Extended H-F wave function."

As in the case of the usual Hartree-Fock method, the extended H-F method will follow the independent particle approach. For this approach, each orbital will be represented by two parts; a spatial part $\phi$ and a spin part $\chi$. These orbitals will be governed by an operator $G$, which also contains two parts. Thus, $G = O \omega$, where $O$ governs the spatial orbital, and $\omega$ governs the spin orbitals.
illustration, we give the Helium wave function as an example. There are
two orbitals in Helium: \( \phi_{a_1} \) and \( \phi_{b_1} \). The total wave function
can then be written as:

\[
\Psi = G(\phi_{a_1} \phi_{b_1})
\]

The operators \( O \) and \( \omega \) are the linear combination of permutation
operators. That is,

\[
O = \epsilon + (12)
\]

\[
\omega = \epsilon - (12)
\]

where \( \epsilon \) is an identity permutation operator and \( (12) \) is an exchange
permutation operator.

The next important property along this approach to a wave func-
tion is the need to satisfy the Pauli's exclusion principle or to possess
the antisymmetric property. By defining the operator \( G \) as the product
of an antisymmetric operator and a symmetric operator, we preserve the
antisymmetric property. For the example mentioned above,

\[
G = O \omega
\]

\[
= (\epsilon + (12))(\epsilon - (12))
\]

where \( O \) is symmetric and \( \omega \) is antisymmetric. Therefore \( G \) is an anti-
symmetric operator. However, the operators are generated from Young's
tableaux (see Reference 5). That is:
In other words, the operator $G$ is the product of one tableau, which generates a symmetric operator, and another associated tableau, which generates an anti-symmetric operator. Symbolically, it can be written as

$$G = \begin{bmatrix} 1 \end{bmatrix} \times \begin{bmatrix} \end{bmatrix}$$

which refers to a singlet case (symmetric in space, antisymmetric in spin). The other combination of tableaux,

$$G' = \begin{bmatrix} -1 \end{bmatrix} \times \begin{bmatrix} 1 \end{bmatrix}$$

which describes a triplet case (antisymmetric in space, symmetric in spin).

After the total wave function is generated through the anti-symmetric operator, the wave function may be written as:

$$\Psi = G (\Phi \chi)$$

where $\Phi$ represents the spatial part and $\chi$ represents the spin part. This wave function is then used to minimize the total energy with respect to a specific orbital $\Phi_i$.

In comparing the extended H-F wave function with the traditional H-F wave function, the former is much more flexible than the later. The extended H-F wave function may be an eigenfunction of the total spin operator for an atomic system with either an even or an odd number
of electrons. The traditional H-F wave function on the other hand is an
eigenfunction of the spin operator only for an even number of electrons
and a \( \Sigma \) state. In addition, in an extended H-F wave function, the
spatial orbital for a doubly occupied orbit can be different. Accord­
ingly, there are two sets of equations for the different orbitals which
are solved using an optimization technique. These extra equations will
provide us with one more degree of freedom to gain better numerical values.
The traditional H-F method does not provide this advantage. In our cal­
culation of the long-range interaction between atoms this type of wave
function will be used to study its effectiveness relative to the more
familiar Hartree-Fock wave function.

In the following chapters we include one chapter devoted to
theory, one chapter on the formulation for the specific calculation,
and a final chapter of discussion. Within the chapter on theory, the
variation-perturbation method and Goddard's G,1 method (a version of
the extended H-F method) will be reproduced. The reproduction of the
G,1 method will be confined to some small atoms and the reference to
the general method will be listed. Finally, a computer program will
be included for the particular calculation of the long-range inter­
action between He and H.
CHAPTER II
THEORY

In the preceding chapter, the differences in the formulation and
effectiveness between the traditional Hartree-Fock wave function and
the extended Hartree-Fock wave function were described in simple term.
We begin this chapter with a more formal quantum mechanical formulation
of the long-range interaction energy between two atomic systems. By
introducing the Born-Oppenheimer approximation the total Hamiltonian
can be separated into two parts: the exact Hamiltonian for the two
isolated systems and the electrostatic interaction energy between the
two atomic systems. At large distances, when the overlap of the elec­
tron clouds of the two atomic systems is small or negligible, this
interaction may be treated as a perturbation of the sum of the two exact
Hamiltonians for the two isolated atomic systems. Several alternatives
for the evaluation of the associated perturbation energy are discussed.

In section 2-2 one of the alternatives to be used in the calcu­
lation is given, namely the variation-perturbation theory. The major idea
behind this theory is that the first-order perturbed wave function is to
be treated as a trial function for a variational procedure. Thus, the
total wave function \( \psi \) is assumed to be the sum of the unperturbed wave
function \( \psi^0 \) and the first-order perturbed wave function \( \psi' \):
\[ \psi = \psi^0 + \psi' \]. Here \( \psi' \) is taken to be the product of a function of
position and the unperturbed wave function \( \psi = \psi^0 \), subject to the
orthogonality condition \( \langle \psi' | \psi^0 \rangle = 0 \). By utilizing a variational pro­
cedure the second-order perturbed energy can be written as follows:
Here, the energy \( E'' \) is a stationary function of the first-order perturbed wave function \( \psi' \). The stationary value of \( E'' \) implies the equality of the following two matrix elements:

\[
E'' = 2 \langle \psi' | \psi' \rangle + \langle \psi' | H^0 \psi' \rangle
\]

As a result, the exact second-order perturbed energy is given by

\[
E'' = \langle \psi' | \psi' \rangle \]

which is identical to the result from the Rayleigh-Schroedinger perturbation theory. The value of the variational formal for the second-order perturbed energy is that in the absence of the exact knowledge of the first-order correction to the wave function, \( \psi' \), the Rayleigh-Ritz procedure may be followed.

To use the above variational-perturbation theory, the unperturbed wave function for the isolated atomic systems should be known. For the atomic systems Hydrogen and the Helium, however, only the exact wave function for atomic Hydrogen is known -- the wave function for the isolated Helium atom must be approximated. The approximation to be used here is the extended Hartree-Fock wave function. The unperturbed wave function for the two-atom system, then, will be the product of the exact Hydrogen wave function and the extended Hartree-Fock wave function for Helium atom. In section 2-3 the numerical values of the extended Hartree-Fock wave function for the Helium atom will be summarized. For purposes of comparison, the numerical value for the traditional Hartree-Fock wave function for Helium will also be given.
In the final section we summarize the mathematical formulation basic to the numerical analysis. The details of this formulation are given in an appendix. Through the use of the variational-perturbation theory we obtain a stationary value for the van der Waals interaction energy which may be approximated by the familiar Rayleigh-Ritz procedure.
A quantum mechanical description of the interaction between atomic systems starts from the actual dynamics of the electrons and nuclei in the atomic systems. The nonrelativistic Hamiltonian for S atomic systems may be written as:

\[ H = \sum_{a=1}^{S} \frac{-1}{2} \frac{1}{m_a} \nabla_a^2 \psi_a + \sum_{i=1}^{N} \frac{-\frac{1}{2} \frac{1}{m_i} \nabla_i^2 \psi_i}{2} - \frac{2}{2} \sum_{a=1}^{S} \sum_{d=1}^{S} e^a e^d \frac{1}{r_{ad}} + \sum_{a \neq \beta} \frac{Z_a Z_{\beta}}{r_{ab}} + \sum_{i \neq j} \frac{e^i e^j}{r_{ij}} \]

where \( S \) is the number of nuclei, \( N \) is the number of electrons, and it is assumed that all nuclear and electronic coordinates have been referred to the center of mass. The first term of this Hamiltonian represents the kinetic energy of the nuclei; the second term represents the electron kinetic energy; the third term is the electron-nucleus-attractive potential; the fourth term is the nuclear mutual-repulsion energy; and the last term is the electron repulsion energy. The associated Schrödinger equation may be written as:

\[ H \psi(r,R) = E \psi(r,R) \]

where the wave function \( \psi(r,R) \) depends upon both the electronic coordinates \( r \) and the internuclear coordinates \( R \). This equation can be solved approximately by making a number of assumptions; the most important of which is called the Born-Oppenheimer approximation. This approximation rests upon the physical picture of massive nuclei moving so slowly relative to the electronic motions that the nuclear motion can be treated as the perturbation of the system. According to this approximation, the
total wave function may be written:

\[ \Psi (r, R) = \Psi_e (r) \phi (R) \]

where \( \Psi_e (r) \) is the electronic wave function and \( \phi (R) \) is the nuclear wave function. In this approximation the kinetic energy of the nuclei may be ignored. Then the new Hamiltonian in atomic units \(^8\) will be:

\[ H = \sum_{i=1}^{N} \frac{1}{2} \sigma_i^2 + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}} + \sum_{\alpha \neq \beta} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha \beta}} \]

Applied to the He-H system, this Hamiltonian reduces to:

\[ H = \frac{1}{2} \sigma_1^2 + \frac{1}{2} \sigma_2^2 + \frac{1}{2} \sigma_3^2 - \frac{1}{r_1} - \frac{2}{r_{He1}} - \frac{2}{r_2} - \frac{1}{r_{He2}} \]

\[ - \frac{2}{r_3} - \frac{1}{r_{He3}} + \frac{1}{r_{He2}} + \frac{1}{r_{H3}} + \frac{1}{r_{H2}} + \frac{2}{R} \]

where the coordinate are shown in Fig. I
We may rewrite the Hamiltonian as:

\[ H = \left( \frac{\hbar^2}{2m} \nabla^2 - \frac{1}{r_1} \right) + \left( \frac{\hbar^2}{2m} \nabla^2 - \frac{1}{r_2} - \frac{1}{r_3} \right) \]

or

\[ H = H_H + H_{He} + V \]

where \( H_H \) and \( H_{He} \) are the exact Hamiltonians of the Hydrogen and Helium atom respectively; and

\[ V = \left( \frac{2}{r_2} + \frac{1}{r_{12}} + \frac{1}{r_{23}} - \frac{2}{r_{He}} - \frac{1}{r_{He1}} - \frac{1}{r_{He2}} \right) \]

While no exact solution for this system exists, the long-range interaction, \( V \) is small enough in comparison to exact Hamiltonians of \( H \) and \( He \) that perturbation theory may be used. Briefly, the expression for the first- and second-order perturbation energy may be written as:

\[ E^{(\prime)} = \sum_{n} \frac{1}{\hbar^2} \left< \psi_n^{(1)} | V | \psi_n^{(1)} > \right> \]

\[ E^{(\prime\prime)} = \sum_{n} \frac{1}{\hbar^2} \left< \psi_n^{(1)} | V | \psi_n^{(1)} > \right> \left< \psi_n^{(1)} | V | \psi_n^{(1)} > \right> \]

where \( \psi_n^{(1)} > \) and \( E_n^{(0)} \) are the unperturbed eigenfunction and eigenvalue respectively. We note that the first order correction to the total energy, \( E^{(\prime)} \), vanishes for the He-H system. Therefore \( E^{(\prime\prime)} \) is the lowest order correction of the energy value for the \( n^{th} \) state, and is proportional to \( R^{-6} \). In the use of perturbation theory there are two difficulties which must be overcome: first, the calculation of the infinite
sum in the second-order perturbation; and second, the wave function of Helium atom must be known or approximated. In order to solve the first problem, Dalgarno and Lewis\textsuperscript{10} and Schwartz\textsuperscript{11} suggested the use of an auxiliary operator; the essence of which allows one to calculate the sum. For systems more complicated than atomic Hydrogen it is very difficult to solve the associated operator equation. Therefore, for the present problem the variation perturbation method will be used. By the use of this method, an estimate of the first order perturbed wave function may be found. The second-order perturbation energy can then be obtained directly through the formula:

$$E'' = <\psi' | V | \psi' >$$

which is identical to $E^{(2)}$ from Rayleigh-Schroedinger perturbation theory.

### 2-2 Variation-Perturbation Theory

It is a well known fact from perturbation theory that to calculate the second-order perturbed energy a knowledge of the complete set of wave functions for the unperturbed system is required. In general such a set is usually not accessible. To overcome this obstacle, an alternative method must be followed. One of such, which will be used in this paper, is the variation-perturbation theory.

For purposes of completeness, this theory will be discussed briefly. Details can be found in A. Dalgarno\textsuperscript{12} As we know from perturbation theory, a total wave function will be approximately equal to the sum of the unperturbed wave function and the first-order perturbed wave function $\psi'$. That is $\psi = \psi' + \psi$. To apply the variational principle, $\psi'$ can be taken equal to the product of a trial function $\psi'$.
and the unperturbed wave function $\psi^0$. Therefore

$$\psi = \psi^0 + \psi' = (1 + \kappa) \psi^0$$

Also, for convenience, we arrange that $$\langle \psi^0 \psi' \rangle = 0$$

Substituting the above formula into $\mathcal{E}$, we have

$$\mathcal{E} = \frac{\langle \psi^0 + \psi'H^0 + \psi' \psi^0 + \psi' \rangle}{\langle \psi^0 + \psi' \psi^0 + \psi' \rangle}$$

$$= \frac{\langle \psi^0 H^0 + \psi' \psi^0 + 2\langle \psi'H^0 \psi^0 \rangle + \langle \psi'H^0 \psi' \rangle \rangle}{1 + \langle \psi' \psi' \rangle}$$

if we ignore third and the higher order terms of $\kappa$. Here $\frac{H^0}{\sqrt{\alpha}}$ is assumed to be the order of $\kappa$. Using the above formula and $\mathcal{E} = \langle \psi'H^0 \psi^0 \rangle$, we have

$$\mathcal{E} = (\mathcal{E}^0 + \mathcal{E}' + 2\langle \psi'H^0 \psi^0 \rangle + \langle \psi'H^0 \psi' \rangle) (1 - \langle \psi'H^0 \psi' \rangle)$$

$$= \mathcal{E}^0 + \mathcal{E}' + 2\langle \psi'H^0 \psi^0 \rangle + \langle \psi'H^0 - \mathcal{E}^0 \psi' \rangle$$

or

$$\mathcal{E}' = 2\langle \psi'H^0 \psi^0 \rangle + \langle \psi'H^0 - \mathcal{E}^0 \psi' \rangle$$

if we continually neglect third and higher order term of $\kappa$ and $\frac{\mathcal{E}'}{\mathcal{E}^0}$ is assumed to be the order $\kappa$. For arbitrary variations of $\psi', \mathcal{E}'$ the condition that $\mathcal{E}'$ be stationary implies that

$$\mathcal{E}' = 2\langle \psi'H^0 \psi^0 \rangle + (H^0 \mathcal{E}^0) \psi' = \mathcal{E}' \psi^0$$
where the constraint \( \langle \psi' \psi^0 \rangle = 0 \) is imposed to the above variation and \( \zeta \) is a Lagrange multiplier. In other words,

\[
\langle \psi' \psi^0 \rangle + \langle \psi' H^0 - E^0 \psi \rangle = 0
\]

(2)

If we substitute equation (2) into equation (1) the stationary value for the second-order perturbed energy is given by

\[ E^{(n)} = \langle \psi' \psi^0 \rangle \]

which is identical to the result of perturbation theory.

The choice of a trial function is rather arbitrary so long as the condition \( \langle \psi'' \psi^0 \rangle = 0 \) is satisfied. The simplest one will be

\[ \chi = A \tilde{\chi} \]

\[ \psi = (1 + A \tilde{\chi}) \psi^0 \]

where \( A \) is a constant

\[
E^{(n)} = 2A \langle \psi \tilde{\chi} \psi^0 \rangle + A^2 \langle \psi \tilde{\chi} H^0 - E^0 \chi \psi^0 \rangle
\]

\[
\frac{\partial E^{(n)}}{\partial A} = 0 \Rightarrow \langle \psi \tilde{\chi} \psi^0 \rangle + A \langle \psi \tilde{\chi} H^0 - E^0 \chi \psi^0 \rangle = 0
\]

\[ A = -\frac{\langle \psi \tilde{\chi} \psi^0 \rangle}{\langle \psi \tilde{\chi} H^0 - E^0 \chi \psi^0 \rangle} \]

\[ E^{(n)} = -\frac{\langle \psi \tilde{\chi} \psi^0 \rangle^2}{\langle \psi \tilde{\chi} H^0 - E^0 \chi \psi^0 \rangle} \]
Finally, we note that the lowest-order contribution to the second-order perturbation energy, $E''$ is actually the van der Waals energy:

$$E'' = C_{dd} \frac{1}{R^6} \cdot \frac{1}{R^6} \cdot \langle \Phi_+ | V_{dd} | \Phi_+ \rangle.$$ 

Therefore increasing the number of the variational parameters in $\Phi_+$ will increase the accuracy of the van der Waals constant $C_{dd}$.

2-3 Wave Function

In the preceding section, we have shown one way to evaluate the second-order perturbed energy without the knowledge of a complete set of unperturbed wave function. However, to apply it to a two-atom system it is necessary to know the wave function for the ground state of the two isolated systems; for the problem of interest, Hydrogen and Helium. For Hydrogen, we know the exact form of the wave function for its ground state; however, this is not the case for Helium, for which an approximate wave function must be used. For purposes of comparison both analytical traditional Hartree-Fock type and analytical extended Hartree-Fock type wave function will be used. By "analytical" is meant each orbital is expanded in a finite basis set.

To test the convergence of the calculation, two different bases sets for the isolated helium atoms will be used: a four bases set and a seven bases set. The values of the expansion coefficients for the two sets were found by Goddard. The energy value for seven bases set is $-2.877996$ while for four bases set, it is equal to $-2.877984$ in atomic unit. Their difference is only 12 parts of millionth. In addition, the electron densities at the nucleus are $3.6295$ and $3.6266$ for seven- and four-bases sets respectively. These numerical values for the
energy and the electron density are very close to the experimental value -2.903727 and 3.61489 respectively.\textsuperscript{14}

The extended H-F wave function for He contains two orbitals: $\phi_a(1s)\alpha_2$ and $\phi_b(1s)\beta_2$. Hence, the total wave function for Helium is given by

$$\Psi = \frac{1}{\sqrt{2}} C_{He} \left( \phi_a(1s) \phi_b(1s) + \phi_b(1s) \phi_a(1s) \right) \frac{1}{\sqrt{2}} \left( \alpha_2 \beta_2 - \alpha_1 \beta_1 \right),$$

where $C_{He} = \left( 1 + \left< \phi_a(1s) \phi_b(1s) \right> \right)^{1/2}$.

This is to be compared with the traditional Hartree-Fock wave function for Helium:

$$\Psi = \phi_1(1s) \phi_{1s} \left( \alpha_2 \beta_2 - \alpha_1 \beta_1 \right).$$

Inasmuch as an optimization technique for the finite bases set expansion technique has been used, each orbital can be presented as follows:

$$\begin{align*}
\phi_a &= \frac{1}{\sqrt{V_{He}}} \sum_{i,j} a_{ij} \sqrt{N_i^{-1}} e^{-a_i r} \\
\phi_b &= \frac{1}{\sqrt{V_{He}}} \sum_{i,j} b_{ij} \sqrt{N_i^{-1}} e^{-b_i r},
\end{align*}$$

For the four bases case the various parameters are given below:

\begin{align*}
\alpha_1 &= 3.30 & a_{11} &= 5.24636 & N_{11} &= 1 \\
\alpha_2 &= 1.433 & a_{12} &= 6.51141 & N_{12} &= 2 \\
& & a_{21} &= 1.13368 & N_{21} &= 1 \\
& & a_{22} &= 0.00247 & N_{22} &= 2 \\
\beta_1 &= 3.30 & b_{11} &= -1.57794 \\
\beta_2 &= 1.433 & b_{12} &= -4.91468 \\
& & b_{21} &= 4.42714 \\
& & b_{22} &= 0.00931
\end{align*}
For the seven bases case the parameters are given below:

\[
\begin{align*}
\alpha_1 &= 3.30 \\
\alpha_2 &= 1.433 \\
\beta_1 &= 3.30 \\
\beta_2 &= 1.433 \\
\end{align*}
\]

\[
\begin{align*}
\alpha_{11} &= 5.38232 \\
\alpha_{12} &= 6.27887 \\
\alpha_{13} &= -0.73604 \\
\alpha_{21} &= 1.00324 \\
\alpha_{22} &= 0.39236 \\
\alpha_{23} &= -0.16544 \\
\alpha_{24} &= 0.01891 \\
\beta_{11} &= -1.96987 \\
\beta_{12} &= -4.82171 \\
\beta_{13} &= 1.14920 \\
\beta_{21} &= 4.81726 \\
\beta_{22} &= -0.73235 \\
\beta_{23} &= 0.27076 \\
\end{align*}
\]

2-4 Mathematical Formulation

From the variational-perturbation theory, the second-order contribution to the perturbed energy is given by

\[
E^{(2')} = 2 \langle \psi' | V_1 \psi' \rangle + \langle \psi' | H_0 - E_0 | \psi' \rangle
\]

In the two-atom system, the Hamiltonian and the wave function for the isolated atomic systems are given respectively by
where we neglect the spin part as it does not come into the calculation.

The first-order wave function that takes into account the interaction between the two atoms is given by

$$\psi' = \int \psi$$

$$f = \sum_{N,K=1}^{N_0} \sum_{R^2}^{K_0} \sum_{m=-1}^{+1} C_{n}^{(m)} \left[ \alpha_{n}^{(m)}(k_0, l_0) \psi \right]$$

$$N_0 = K_0 = \text{designated number}$$

The functional form for this wave function depends on the angular nature of the dipole-dipole interaction. Substituting the formulas from $H^0$ to $V$ into the stationary expression for $E^{12'}$, we have

$$E^{12'} = \sum_{N,K} A_{n} \alpha_{C} (N,K) + \sum_{N,K} A_{n}^{K'} \alpha_{C} (N,K,N')$$

where

$$\alpha = \sum_{N,K} \left[ \frac{C_{n}^{(m)}}{R^6} \left( \frac{1}{\alpha_{n}} \right)^2 \frac{1}{C_{n}^{(m)}} \right]$$

$$\sum_{m=-1}^{+1} \alpha = \sum_{m=-1}^{+1} \left[ \frac{1}{C_{n}^{(m)}} \left( \frac{1}{\alpha_{n}} \right)^2 \left( \frac{\alpha_{n}}{q} \right)^{1+4+1} \right] = \left( \frac{1}{R^6} \right) \left[ \frac{1}{3} \right] \left( \frac{1}{C_{n}^{(m)}} \right)$$
The functional forms for both $C(N,K)$ and $F(NK,N'K')$ can be found in the appendix.

Taking the first-order variation of $E^{(0)}$ with respect to $A_{PQ}$, we obtain the following simultaneous equation:

$$\frac{\partial E^{(0)}}{\partial A_{PQ}} = \left( \frac{1}{R^6} \right) \left( \frac{2}{3} \right) \left( \frac{1}{C_{He}} \right) \left[ \sum_{N,K} A_{N,K} E(N,K) + \sum_{N',K'} A_{N',K'} E(N',K') \right] + \sum_{P,Q} F(P,Q,N,K) J = 0 .$$

For each value of $P,Q$

$$\sum_{N,K} A_{N,K} \left[ F(N,K,P,Q) + F(P,Q,N,K) \right] = -2 C(P,Q) .$$

After obtaining the value of $NK$ through solving the simultaneous equation above, the van der Waals constant can be found from the evaluation of the stationary value for the second-order perturbation energy:

$$E^{(2)} = \frac{1}{R^6} \left[ \frac{2}{3} \right] \left( \frac{1}{C_{He}} \right) \sum_{N,K} A_{N,K} C(N,K) + \sum_{N',K'} A_{N',K'} C(N',K') .$$

For this $\Psi'$, $F(N,K,N',K') = F(N,K,N,K)$

$$C(P,Q) = \sum_{N,K} A_{N,K} \left[ F(N,K,P,Q) + F(P,Q,N,K) \right] .$$

Substituting the above formula into the expression for $E^{(2)}$, we obtain the stationary value of the second order perturbation energy.

$$E^{(2)} = \frac{1}{R^6} \left[ \frac{2}{3} \right] \left( \frac{1}{C_{He}} \right) \sum_{N,K} A_{N,K} C(N,K) = \frac{C_{dd}}{R^6} ,$$

where

$$C_{dd} = \left[ \frac{2}{3} \right] \left( \frac{1}{C_{He}} \right) \sum_{N,K} A_{N,K} C(N,K) .$$

This expression is identical for $E^{(2)}$ to the second-order perturbation energy obtained from the perturbation theory.
CHAPTER III

RESULT AND DISCUSSION

The major intent of the present calculation is to test the effectiveness of the use of the extended Hartree-Fock wave functions through the calculation of the long-range interaction energy between atomic systems. The effectiveness is shown in the comparision of the numerical values of the van der Waals constants. For the present calculation, which focuses on the long-range interaction between Helium and Hydrogen, the extended Hartree-Fock wave function for the Helium atom will be used. The resulting numerical values of the van der Waals constant for two different expansion bases sets of the Helium wave function are each around 3.18. The numerical difference of these values due to the different number of variational parameters is small. In comparison to the semiempirical value, the present value is about 88% of it. Two other theoretical values, which were obtained through a similar method, are 2.81 by Davison and 3.02 by T. P. Das. The wave function Davison used includes both angular correlation and radial correlation. The actual wave function is so complicated that generalization to larger atomic systems is not obvious. Das, on the other hand, performed the calculation using the traditional H-F wave function of He. This approach lends itself to simple generalization to other atomic systems. The comparison of the different calculated van der Waals constants is shown in the following table.
Table I: The Comparison of the Calculated Van der Waals Constants

<table>
<thead>
<tr>
<th>No. of Variational Parameter</th>
<th>Present Calculation</th>
<th>Das(^a)</th>
<th>Davison(^b)</th>
<th>Semi-Empirical Value (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>-3.1752(^d)</td>
<td>-3.2104</td>
<td>-2.8163</td>
<td>-2.802</td>
</tr>
<tr>
<td>16</td>
<td>-3.1781(^d)</td>
<td>-3.1604</td>
<td>-2.8172</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>None</td>
<td>None</td>
<td>-3.0218</td>
<td>-2.8172</td>
</tr>
</tbody>
</table>

d. Four bases set.
e. Seven bases set.

From the above table, it is seen that the difference between the semi-empirical value and the values estimated by both the traditional H-F wave function and the extended H-F wave function are about 8\% and 12\% of the semi-empirical value respectively. However, we anticipate these discrepancies from the limitation of the traditional H-F approach for the calculation of the many-electron atomic wave function. The extended H-F wave function has relaxed one restriction in the traditional H-F wave function, namely that for a doubly occupied orbital, the spatial part should be the same. With this relaxation, we expect therefore, to have a better wave function. The van der Waals constant obtained from the restricted H-F wave function is about 3.02, while it is 3.18 when the extended H-F wave function is used. For functionally similar wave functions increasing the number of variation parameters will increase
will increase the numerical value of the van der Waals constant. This is illustrated by the above table. Convergence is also illustrated by the above table in which we see the improvement in the numerical value when the basis set for $\Phi_{ne}$ is changed and when the number of variational parameters is increased. The slight difference in value of the van der Waals constant as calculated with the four bases set for the unperturbed wave function of Helium as compared with the value for the seven bases set does not appear to be sufficient to justify the increase in time required for the numerical calculation.

A number of speculations appear to be in order. According to the variational principle, the value 3.022, 3.180 and 2.818 will be the approximate limit of the van der Waals constant using the traditional H-F wave function, the extended H-F wave function, and the correlated wave function respectively. In a similar sense, 3.18 is probably a better value than 3.02, as both types of wave function were expanded by the $s$-type Slater orbitals and no angular and radial correlations were added. It is our speculation that if these factors had been added, then the van der Waals constant would be around 2.80 for the extended H-F wave function. Hence, the value obtained through the traditional H-F wave function would be larger than -2.80. That is, in the absence of any contributions from angular correlations, we believe the van der Waals constant obtained from the most generalized H-F wave function approach would be smaller than -3.18, and the additional correlation effect will improve this value to -2.80.

In conclusion, the extended H-F wave function is an effective
wave function for the calculation of atomic interactions. This conclusion supplements the value shown for the H-F wave function in the calculation of the electron densities at the nucleus. In a practical sense, the analytical form of the extended H-F wave function is a better approximate solution for preserving the single particle approach of the many-electron atomic wave function.

Some comments should also be made for further calculations. Using methods similar to those illustrated above, an estimation of the short-range effect can be found by using the extended H-F wave function. With both the short-range and long-range interactions in hand, the pressure shift of the hyperfine structure constant can be calculated.

Notes on the Numerical Calculation

All the numerical results have been performed with the aid of I.B.M. 360-50 at the University of New Hampshire. The computer programs are written in Fortran IV.

The program can be divided into two major parts; a program for calculating the various matrix elements and the program for solving the simultaneous equations. The general form for the set of simultaneous equations can be written as follows. For the index $P, Q$,

$$\sum_A a_{m,k}^N G(N, k, P, Q) = - c(P, Q)$$

The program for calculating the matrix elements consists of the numerical computation of the functions $F(N, K, P, Q)$ and $C(P, Q)$. This program has a main program and four function programs FA, FB, FC, FD.

After obtaining the values of $F(N, K, P, Q)$ and $C(P, Q)$, the data are transformed into the program for solving the simultaneous equations
for the variational parameters Ank. The double index (N,K) can be re­presented by one single index I. With a minimum effort, the van der Waals constant can be obtained through the product of the values of Ank and (CFQ) which can be checked in the formula in p. 14 section 2-4.

To check on the accuracy of the published values for the van der Waals constant, a separate calculation was made using the tradi­tional Hartree-Fock approach following T. P. Das et al. These values were reproduced exactly. As an indication of the relative numerical complexities involved, the calculation of the van der Waals constant using the traditional H-F approach consumed approximately 10 minutes of IBM 360-50 time, for a particular numbers of the variational parameters. The similar calculation using the extended H-F approach consumed 20 hours for the same number of variational parameters, Ank. The difference is largely due to the complexity of subfunction program FC and FD. The set of simultaneous equations can rather easily be solved by calling any conventional subprogram.
REFERENCES AND NOTE

Chapter I


Chapter 2

9. Atomic unit is defined as \( h = c = e = 1 \). From now on, every calculation will be in this unit.


13. See Reference 5.


Chapter 3

15. See Reference 5.
APPENDIX A

A-a Calculation of the second-order perturbed energy ... General remark.

From Sec. 2-2 it was shown that the second-order perturbed energy can be formulated as follows:

$$\varepsilon^{(2)} = 2\langle \psi' | H | \psi' \rangle + \langle \psi' | H_0 - E^0 | \psi' \rangle$$

For the present calculation, which focuses on the dipole-dipole interaction between H and He atomic systems, the following formulas will be substituted into the above formula.

A) Unperturbed wave function $\psi^0$

$$\psi^0 = \phi_{N \uparrow} \phi_{He(2 \uparrow 3 \downarrow)}$$

where

$$\phi_{N \uparrow} = \frac{1}{\sqrt{2}} \phi^2_h$$

$$\phi_{He(2 \uparrow 3 \downarrow)} = \frac{1}{\sqrt{2}} C_{He}$$

$$C_{He} = \sqrt{1 + 1 < \phi_a | \phi_b |^* | \phi_a >}$$

$$< \phi_a | \phi_a > = < \phi_b | \phi_b > = 1$$

$$< \phi_a | \phi_b > = < \phi_b | \phi_a >$$

B) First-order perturbed wave function $\psi'$

$$\psi' = \mathcal{A} \psi^0$$

+ The steps used in the calculation follow those of

Das et al, Phy. Rev. 174, 104 (1968)

where
\[ f = \sum_{N,k} \frac{A_{N,k}}{R^2} \sum_{m=1}^{2l+1} C_{N}^{(m)} Y_{l,m}^{(1)} \left[ V_3 Y_{l,m}^{(1)} \right] \]
\[ V_3 Y_{l,m}^{(1)} J \]
\[ C_{N}^{(m)} = (-1)^{-m} \left( 1 + \delta_{lm} \right) \times \frac{m^2}{3} \]

C) Unperturbed Hamiltonian \( H^0 \)
\[ H^0 = \left( \frac{-\hbar}{2} \nabla^2 - \frac{1}{r} \right) + \left( \frac{-\hbar}{2} \nabla^2 - \frac{1}{r} \nabla^2 - \frac{2}{r^2} - \frac{\hbar}{2} \nabla^2 \right) + \frac{1}{r} \]

D) Unperturbed Eigen value \( E^0 \)
\[ E^0 = E_{n}^0 + E_{n+1}^0 \]

E) Perturbation \( V^+ \)
\[ V = \sum_{N,k} \frac{1}{R^2} \sum_{m=1}^{2l+1} C_{N}^{(m)} Y_{l,m}^{(1)} \left[ V_3 Y_{l,m}^{(1)} + V_3 Y_{l,m}^{(1)} \right] \]

Before substituting the formulas from A) to E) into \( E^{(B)} \), some frequently used formulas will be introduced.

A—a—1 Frequently used formulas with Hydrogen orbital

\[ A) \quad \langle \phi_N \| \mathcal{V} \| \phi_N \rangle = \frac{1}{\hbar^2} \int \mathcal{V} e^{-2\hbar r^2} v^2 dV d\nu \]
\[ = \frac{C_0 (N+2)}{2^{N+1}} \]
\[ = \langle r^N \rangle_N \quad (A-10-1) \]

*Multipole expansion, see

R. J. Buehler and J. O. Hirschfelder, Phy. Rev. 83, 628 (1951)
B) \[ \langle \phi_H | Y_{l,m} Y_{l,m}^* | \phi_H \rangle = \frac{1}{4\pi} \int e^{-2\nu} \nu^n r^2 dr \times \int Y_{l,m}^* Y_{l,m} \, dn = \frac{1}{4\pi} < \nu >_H \quad (a-1-2) \]

C) \[ \langle \phi_H | \nu^n \frac{\partial^2}{\partial r^2} Y_{l,m} | \phi_H \rangle = \left[ (N-N')^2 - (N+N') - 2 \right] \times \frac{T(N+N' + 1)}{2N+N' + 1} \quad (a-1-3) \]

Where \( \frac{\partial^2}{\partial r^2} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \)

D) \[ \langle \phi_H | \nu^n Y_{l,m} \frac{\partial^2}{\partial r^2} Y_{l,m} | \phi_H \rangle = \frac{1}{4\pi} \langle \phi_H | \nu^n \frac{\partial^2}{\partial r^2} Y_{l,m} | \phi_H \rangle \quad (a-1-4) \]

A-e-2  Frequently used formulas with Helium orbital.

Let

\[ \phi_a = \frac{1}{\sqrt{2\pi}} \sum \frac{1}{\rho} C_p r^{\nu_p-1} e^{-\alpha_p r} \]
\[ \phi_b = \frac{1}{\sqrt{2\pi}} \sum \frac{1}{\rho} C_q r^{\nu_q-1} e^{-\alpha_q r} \]
\[ \phi_c = \frac{1}{\sqrt{2\pi}} \sum \frac{1}{\rho} C_s r^{\nu_s-1} e^{-\alpha_s r} \]
\[ \phi_d = \frac{1}{\sqrt{2\pi}} \sum \frac{1}{\rho} C_t r^{\nu_t-1} e^{-\alpha_t r} \]

A) \[ \langle \phi_a | Y_{l,m}^* Y_{l,m} | \phi_a \rangle \]
\[ = \frac{1}{4\pi} \sum \frac{1}{\rho} C_p C_p' \int r^n r^{(N_p+N_p' - 2)} e^{-(\alpha_p + \alpha_p') r^2} r^2 dr \times \int Y_{l,m}^* Y_{l,m} \, dn \]
\[ = \frac{1}{4\pi} F_A(a, N, a) \quad (a-2-1) \]
where FA will be defined in Appendix B

Note: \( \langle \phi_b | Y_{0,m}^* Y_{0,m} r^n | \phi_b \rangle = \frac{1}{4\pi} FA (b, n, b) \)

\( \langle \phi_a | Y_{0,m}^* Y_{0,m} r^n | \phi_a \rangle \)

B) \( \langle \phi_a | Y_{0,m}^* Y_{0,m} r^n | \phi_a \rangle \)

\[ = \frac{1}{4\pi} \sum_p \sum_q \sum C_p C_q \int V \, \eta^{p-1} e^{-\alpha v r} e^{-\frac{1}{2} \frac{\partial^2 V}{\partial r^2} (r \eta^{p-1} e^{-\alpha v r} \eta^{q-1} e^{-\alpha v r} j^r)} \]

\[ \times \int Y_{0,m}^* Y_{0,m} \, dV \]

\[ = \frac{1}{4\pi} FB (a, k, k'; b) \]

where FB will be defined in Appendix B

Note: \( \langle \phi_a | Y_{0,m}^* Y_{0,m} r^n | \phi_a \rangle = \frac{1}{4\pi} FB (a, k, k'; a) \)

\( FB (a, k, k'; b) = FB (a, k, k'; b) \) unless \( k = k' \)

C) \( \langle \phi_a | \phi_c (2) | \frac{1}{r_{12}} Y_{1,0}^* Y_{1,0} r_{1,2}^{-1} | \phi_b \rangle \)
\[
I = \left( \frac{1}{R} \right)^3 \sum_{\rho, \eta, \xi, \tau} C_\rho C_\eta C_\xi C_\tau \int \frac{1}{v_2} v_2^{(1+N_2+\nu-2)} \exp \left(-\frac{\rho^2 + \eta^2 + \xi^2 + \tau^2}{\nu_2^2} \right) \frac{1}{v_1} - (N_1+\mu-2) \exp \left(-\frac{\rho^2 + \eta^2 + \xi^2 + \tau^2}{\nu_1^2} \right) v_1^2 dv_1 \]

\[
= \frac{1}{\xi^n} F_C(a, k+k', b, c, d) \quad (A-2-3)
\]

where \( F_C \) will be defined in Appendix B.

Note: \( F_C(a, k+k', b, c, d) = F_C(b, k+k', a, c, b) \)

D) \( \langle \Phi_{111} \Phi_{22} \rangle \)

\[
I = \left( \frac{1}{R} \right)^3 \sum_{\rho, \eta, \xi, \tau} C_\rho C_\eta C_\xi C_\tau \int \frac{1}{v_2} v_2^{(1+N_2+\nu-2)} \exp \left(-\frac{\rho^2 + \eta^2 + \xi^2 + \tau^2}{\nu_2^2} \right) \frac{1}{v_1} - (N_1+\mu+\nu-2) \exp \left(-\frac{\rho^2 + \eta^2 + \xi^2 + \tau^2}{\nu_1^2} \right) v_1^2 dv_1 \]

\[
= \frac{1}{\xi^n} F_D(a, k, b, c, k', d) \quad (A-2-4)
\]

where \( F_D \) will be defined in Appendix B.
Note: \[ F_D(a, k, b, b, k'; a) = F_D(b, k, a, a, k, b) \]
\[ F_D(a, k, b, b, k'; a) + F_D(a, k', b, b, k, a) \]
\[ \text{Note: } K = K' \]

\[ E^{(2)} = 2 \langle \psi' | \nu | \psi^* > + \langle \psi' | H^* | E^0 | \psi^* > \]

A-b
\[ 2 \langle \psi' | \nu | \psi^* > \]

\[ \psi' = \frac{1}{2} \left[ \phi_H (1) + \sqrt{2} \phi_{\alpha(2)} \phi_{\alpha(3)} + \phi_{\beta(2)} \phi_{\alpha(3)} \right] \times \frac{1}{2} \left[ \sum_{m=-1}^{1} C_{m1} Y_{m1} \right] \]

\[ V = \sum_{m=-1}^{1} \frac{C_{m1}}{R^2} \left[ 2 \langle \nu, Y_{m1} | (V_0 Y_{m1} + V_2 Y_{m1}) \right] \]

\[ 2 \langle \psi' | \nu | \psi^* > = 2 \sum_{m=-1}^{1} \frac{A_{m1}}{R^6} \left[ \phi_H (1) Y_{m1} Y_{m1} \phi_H \right] \]

\[ \times \frac{1}{2} \left[ \phi_{\alpha(2)} \phi_{\alpha(3)} + \phi_{\beta(2)} \phi_{\alpha(3)} \right] \left( V_0 Y_{m1} + V_2 Y_{m1} \right) \]

\[ \times \left( V_0 Y_{m1} + V_2 Y_{m1} \right) \left( \phi_{\alpha(2)} \phi_{\alpha(3)} + \phi_{\beta(2)} \phi_{\alpha(3)} \right) \]

\[ = 2 \sum_{m=-1}^{1} \frac{A_{m1}}{R^6} \left[ \phi_H (1) Y_{m1} \phi_H \right] \left( V_0 Y_{m1} + V_2 Y_{m1} \right) \left( \phi_{\alpha(2)} \phi_{\alpha(3)} + \phi_{\beta(2)} \phi_{\alpha(3)} \right) \]
\[
V = 2 \sum_{n,k} \frac{A_{n,k}}{R_b^n \mathcal{C}_n(m)} \left( \frac{1}{q^n} \right)^2 \langle \gamma^{n+1} \rangle_n \times \frac{1}{2 C_h^2}
\]

\[\{ F_A(a, k+1, a) + F(a, k+1, b)\langle \phi_b \phi_a \rangle + F_A(b, k+1, a)\langle \phi_a \phi_b \rangle + F_A(b, k+1, b) + \text{all integrals contain } Y_3^{k+1} Y_{h,m}^{+13} Y_{l,m}^{11} \\]

are equal to the preceding four terms \[J\]

\[
= 2 \sum_{n,k} \frac{A_{n,k}}{R_b^n \mathcal{C}_n(m)} \left( \frac{1}{q^n} \right)^2 \langle \gamma^{n+1} \rangle_n \times \frac{1}{2 C_h^2}
\]

\[\{ F_A(a, k+1, a) + F_A(a, k+1, b)ba + F_A(b, k+1, a)ab + F_A(b, k+1, b) \}\]

where \[(i) \quad ab = \langle \phi_a \phi_b \rangle, \quad ba = \langle \phi_b \phi_a \rangle \quad \]

Note: \( ab = ba \)

A-b-2 \[E^0 \langle \psi' | \psi' \rangle\]

\[
E^0 \langle \psi' | \psi' \rangle = E^0 \sum_{n,k} \sum_{n', k'} \sum_{m} \frac{A_{n,k} A_{n', k'}}{R_b^n \mathcal{C}_n(m)} \langle \gamma^{n+1} \rangle_n \times \frac{1}{2 C_h^2}
\]

\[\langle \phi_h | Y_{h,m}^{+13} Y_{l,m}^{11} Y_{h,m}^{n+1} | \phi_h \rangle > \frac{1}{2 C_h^2} \langle \phi_a(1) \phi_a(3) + \phi_b(1) \phi_b(3) \rangle \]

\[
( Y_2^{k'} Y_{h,m}^{+13} + Y_2^{k'} Y_{l,m}^{11} ) ( Y_3^{k+1} Y_{h,m}^{11} + Y_3^{k+1} Y_{l,m}^{11} ) ( \phi_a(1) \phi_b(3) + \phi_b(1) \phi_b(3) ) \]

\[
= E^0 \sum_{n,k} \sum_{n', k'} \sum_{m} \frac{A_{n,k} A_{n', k'}}{R_b^n \mathcal{C}_n(m)} \langle \gamma^{n+1} \rangle_n \times \frac{1}{2 C_h^2}
\]

\[\times \frac{1}{C_h^2} \{ F_A(a, k+1, a) + F_A(a, k+1, b)ba + F_A(b, k+1, a)ab + F_A(b, k+1, b) + \text{all the integrals containing } Y_3^{k+1} Y_{h,m}^{+13} Y_{l,m}^{11} \text{ which are equal to the preceding four terms} \}\]
\[<\psi'|\psi'> = E_0 - \frac{Z_2}{np} \sum_{NN'} C_n^{(N)} \left( \frac{1}{h} \right) <\psi_1|\psi_2> \]

* \((FA(a, k+b) + FA(a, k+b)ba + FA(b, k+b)ab + FA(b, k+b)\)

Where we have used formula (a-1-1). We also note that the cross terms \(\gamma^+_n\) and \(\gamma^+_n\) vanish.
The last term:

\[
\left( -\frac{1}{2} \sigma_i^I - \frac{1}{\nu_i} \right) \Delta Y_{i,m} \langle \phi \rangle
\]

\[
= -\frac{1}{2} \left( \sigma_i^I Y_{i,m} \langle \phi \rangle \right) + \frac{1}{2} \left( \frac{1}{\nu_i^2} \Delta Y_{i,m} \langle \phi \rangle \right)
- \Delta Y_{i,m} \langle \phi \rangle
\]

\[
= -\frac{1}{2} \left( \sigma_i^I Y_{i,m} \langle \phi \rangle \right) + \frac{1}{2} \left( \frac{1}{(i+1)} \right) \Delta Y_{i,m} \langle \phi \rangle
- \Delta Y_{i,m} \langle \phi \rangle
\]

\[
= \left[ -\frac{1}{2} \left( \sigma_i^I Y_{i,m} \langle \phi \rangle \right) + \frac{1}{2} \left( \frac{1}{(i+1)} \right) \Delta Y_{i,m} \langle \phi \rangle \right]
+ \Delta Y_{i,m} \langle \phi \rangle
\]

\[
+ \left( -\Delta Y_{i,m} \langle \phi \rangle \right)
\]

Using (a-1-1) and (a-1-4)

\[
\langle \psi' | \hat{H}_N^0 | \psi' \rangle
\]

\[
= \sum_{K,K'} \sum_{m} \sum_{K,K'} \frac{A_{Km} A_{K'm}}{K} \frac{c_i^2}{c_{Km}} \left( \frac{1}{\phi_i} \right)^2 \left( \frac{1}{c^2_{Km}} \right)
\]

\[
x \left[ A_{Km} (a, K+K'; a) + A_{Km} (a, K+K'; b) + A_{Km} (a, K+K'; a) + A_{Km} (b, K+K'; b) \right]
\]

\[
x \left\{ -\frac{1}{2} \left[ (N-N')^2 - (N+N')^2 \right] - \frac{1}{2} \left( \frac{N+N'}{2} \right)^2 + \frac{1}{2} \left( \frac{N-N'}{2} \right)^2 \right\}
\]
B) $\langle \psi' | H_{He} | \psi' \rangle$

$$H_{He} = h_3 + h_4 + g_{23}$$

where

$$h_3 = \frac{-1}{2} v_3^2 - \frac{2}{\nu_3}$$

$$h_4 = \frac{-1}{2} v_4^2 - \frac{2}{\nu_4}$$

$$g_{23} = \frac{1}{\nu_{23}}$$

a) $\langle \psi' | h_3 | \psi' \rangle$

$$\sum_{n_{1}, n_{2}} \sum_{\alpha, \beta} \frac{A_{n_{1}} A_{n_{2}}}{\pi n_{1} n_{2}} C_{\pi_{1} m_{1}} \left( \frac{\phi_{2 n}}{\pi \phi_{2}} \right) < \psi_{2}^{\pi n_{1} m_{1}} > H \left( \frac{1}{2} \phi_{2} \right)$$

$$\langle \Phi_{a}(1) \phi_{b}(2) \phi_{a}(3) \rangle \left( \frac{1}{2} \phi_{2}^{3} - \frac{2}{\nu_{3}} \right)$$

$$\left( \frac{1}{2} \phi_{2}^{3} + \phi_{2}^{3} \phi_{a}(3) \right) \phi_{b}(3) \Phi_{a}(3) \Phi_{a}(3) \rangle$$

I. For the last term of $\left( \frac{1}{2} \phi_{2}^{3} - \frac{2}{\nu_{3}} \right)$, we have

$$\langle \Phi_{a}(1) \phi_{b}(2) \phi_{a}(3) \rangle \left( \phi_{2}^{3} \phi_{a}(3) + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{a}(3) \phi_{b}(3) + \phi_{b}(3) \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} \phi_{a}(3) + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} \phi_{a}(3) + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} \phi_{a}(3) + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} + \phi_{2}^{3} \phi_{a}(3) \right)$$

$$\left( \phi_{2}^{3} \phi_{a}(3) + \phi_{2}^{3} \phi_{a}(3) \right)$$
\[
\left( -2 \right) \left( \frac{d}{d_{\eta}} \right) \left\{ FA(a, k+k'1, a) + FA(a, k+k'1, b) b a + FA(b, k+k'1, a) \right. \\
\left. + FA(b, k+k'1, b) b a + FA(a, -l, a) FA(b, -l, b) + FA(a, -l, a) FA(b, k+k', a) + FA(b, -l, a) FA(a, k+k', b) + \\
FA(b, -l, b) FA(b, k+k', b) \right\}
\]

For the terms with \(-\frac{1}{2} v^2_{a} \)

\[-\frac{1}{2} v^2_{a} = \left( -\frac{1}{2} \right) \left[ v^2_{a} - \frac{L^2_{a}}{\nu^2_{a}} \right].\]

II. Angular part

\[
\left( + \frac{1}{2} \right) \frac{L^2_{a}}{\nu^2_{a}} \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right)
\]

\[
= \left( + \frac{1}{2} \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right)
\]

Note: \( L^2_{a} \phi_a(2) = L^2_{a} \phi_b(2) = 0 \) \( L^2_{a} Y_{l,m}(3) = 0 \)

\[
= \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right) \left( v^2_{a} Y_{l,m}(12) + v^2_{a} Y_{l,m}(13) \right)
\]

\[
= \left\{ FA(a, k+k'2, a) + FA(a, k+k'2, b) b a + FA(b, k+k'2, a) \right. \\
\left. + FA(b, k+k'2, b) b a + FA(b, k+k'2, b) \right\} \frac{1}{\eta}
\]
III. Radial part

\[
\begin{align*}
&= \langle \phi_a(12) \phi_b(13) + \phi_b(12) \phi_a(13) \rangle \left( \frac{1}{2} K_{Y_{1m}(2)} + \frac{1}{2} K_{Y_{1m}(13)} \right) \left( \frac{1}{2} \right) (D^2) \\
&\times \left( \frac{1}{2}\right) (\frac{1}{2}) \left\{ FB(a, k, k', a) + FB(a, k, k', b) b a + FB(b, k) a b + FB(b, k, k', b) + FB(a, 0, 0, a) FA(b, k+k', b) + FB(b, 0, 0, a) FA(a, k+k', b) + FB(b, 0, 0, b) FA(a, k+k', a) \right\}
\end{align*}
\]

\[
\langle \varphi | h_{\nu} | \varphi \rangle = \sum_{I} I + II + III
\]

\[
\times \sum_{a k} \sum_{b k'} \frac{A_{a k} A_{b k'}}{R^2} C_{\nu}^{(4)} \left( \frac{1}{4 \pi} \right)^2 \left( \frac{1}{2 C_{\nu}^2} \right) < \nu_{\nu''} + \nu'>
\]

where

1) \( \text{with } \left( \frac{1}{2} \right)^2 \)

III. Angular part

III. Radial part
b) \[ <\psi_1'h_3'\psi_1'> = <\psi_1'h_2'\psi_1'> \]

Therefore \[ <\psi_1'h_3'\psi_1'> = 2 <\psi_1'h_2'\psi_1'> \]

\[ = \sum_{\mathbf{m}} \sum_{\mathbf{m}'} \sum_{\mathbf{m}''} \frac{\text{Ank} \times \text{An}'}{R^6} \text{Clim} \left( \frac{1}{\text{Cm}} \right)^3 \left( \frac{1}{\text{Ch}_0} \right) <\psi_{\text{m}''}\psi_1'> \]

\[ \times \mathcal{I} + \mathcal{II} + \mathcal{III} \]

where \( \mathcal{I} + \mathcal{II} + \mathcal{III} \) are shown in \[ <\psi_1'h_2'\psi_1'> \]

c) \[ <\psi_1'g_{23}'\psi_1'> \]

\[ = \sum_{\mathbf{m}} \sum_{\mathbf{m}'} \frac{\text{Ank} \times \text{An}'}{R^6} \text{Clim} \left( \frac{1}{\text{Cm}} \right) <\psi_{\text{m}''}\psi_1'> \text{N} \left( \frac{1}{\text{Ch}_0} \right) \]

\[ <\phi_{a12} <\phi_{b13} + \phi_{b12} \phi_{a13} > \left( \frac{1}{\text{Cm}} \right)^2 \left( \frac{1}{\text{Ch}_0} \right) \]

\[ \left( \frac{1}{\text{Cm}} \right)^2 \left( \frac{1}{\text{Ch}_0} \right) \]

\[ \mathcal{I} = <\phi_{a12} \phi_{b13} + \phi_{b12} \phi_{a13} > \frac{1}{\text{Cm}} \text{Y}_{\text{em}(3)} \]

\[ + \frac{1}{\text{Cm}} \text{Y}_{\text{em}(2)} \frac{1}{\text{Cm}} \text{Y}_{\text{em}(1)} \]

\[ + \frac{1}{\text{Cm}} \text{Y}_{\text{em}(3)} \frac{1}{\text{Cm}} \text{Y}_{\text{em}(1)} \]

\[ \text{Using } \text{Function } FC \text{ and } FD. \]
\[
I = \frac{1}{4\pi} \left[ FC\left(a, k+k', a, b, o, b\right) + FC\left(a, k+k', b, b, o, a\right) + FC\left(b, k+k', a, o, a\right) + FC\left(b, k+k', b, o, a\right) + FC\left(a, o, a, b, k+k', b\right) + FC\left(a, o, b, b, k+k', a\right) + FC\left(b, o, a, a, k+k', a\right) + FC\left(b, o, b, a, k+k', a\right) \right] \\
+ \frac{1}{4\pi} \left[ FD\left(a, k', a, b, k', b\right) + FD\left(a, k', b, b, k, a\right) + FD\left(b, k', a, a, k, b\right) + FD\left(b, k', b, a, k, a\right) + FD\left(a, k, a, b, k', b\right) + FD\left(a, k, b, b, k, a\right) + FD\left(b, k, a, a, k, b\right) + FD\left(b, k, b, a, k, a\right) \right] \\
\times \frac{1}{2} \frac{\binom{A_{\mathbf{k}} A_{\mathbf{k}'}^*}{R^6}}{C_{\mathbf{h} b}} \left( \frac{1}{\frac{1}{4\pi R^6}} \right) < \nu^{n+m} >_H \]
Total Formula

\[ E^{(2)} = 2 \langle \psi' | V | \psi' \rangle + \langle \psi' | H^0 - E^0 | \psi' \rangle \]

\[ = \sum_{A=1}^{A_{\text{nic}}} \sum_{R=1}^{R_0} \sum_{b=1}^{R_b} \sum_{t=1}^{T_b} \frac{A_{\text{nic}}}{A_{\text{nic}}} \left( \frac{C_{\text{im}}}{C_{\text{im}}} \right) \left( \frac{C_{\text{im}}}{C_{\text{im}}} \right) \times 2 \langle \psi' | V^{\text{on}} | \psi' \rangle \times \left[ \mathcal{F} A (a_{k+1} \cdot a) + \mathcal{F} A (a_{k+1} \cdot b) + \mathcal{F} A (b_{k+1} \cdot a) + \mathcal{F} A (b_{k+1} \cdot b) \right] \]

\[-J \bigg( \sum_{n=0}^{N+N'^2} \sum_{m=0}^{N+N'^2} \bigg) - \frac{1}{2} \mathcal{F} A (a_{k+1} \cdot a) \mathcal{F} A (a_{k+1} \cdot b) - \frac{1}{2} \mathcal{F} A (b_{k+1} \cdot a) \mathcal{F} A (b_{k+1} \cdot b) \bigg] + \mathcal{F} A (a_{k+1} \cdot b) + \mathcal{F} A (b_{k+1} \cdot a) \]

\[ + \left( \frac{\mathcal{F} A (a_{k+1} \cdot a) + \mathcal{F} A (a_{k+1} \cdot b)}{2} \right) + \mathcal{F} A (a_{k+1} \cdot b) + \mathcal{F} A (b_{k+1} \cdot a) \]

\[ + \left( \frac{\mathcal{F} A (a_{k+1} \cdot a) + \mathcal{F} A (a_{k+1} \cdot b)}{2} \right) + \mathcal{F} A (a_{k+1} \cdot b) + \mathcal{F} A (b_{k+1} \cdot a) \]

\[ + \frac{1}{2} \mathcal{F} A (a_{k+1} \cdot a) \mathcal{F} A (a_{k+1} \cdot b) + \mathcal{F} A (b_{k+1} \cdot a) \mathcal{F} A (b_{k+1} \cdot b) \bigg] \]
A-c Simultaneous Equation

The general form in $E^{(2)}$ will be as follows

$$E^{(2)} = \sum_{n,k} A_{n,k} A_{n,k'} F(n,k, n'k') + \sum_{n,k} A_{n,k} F(n,k, p,q)$$

$$\frac{\partial E^{(2)}}{\partial \gamma_{pq}} = \sum_{n,k} A_{n,k} F(p,q, n,k') + \sum_{n,k} A_{n,k} F(n,k, p,q) + C(p,q)$$

then

$$\frac{\partial E^{(2)}}{\partial \gamma_{pq}} = 0 \Rightarrow \sum_{n,k} A_{n,k} [F(p,q, n,k') + F(n,k, p,q)] = -C(p,q)$$

Using above formula to get $A_{n,k}$, we have

$$\sum_{n,k} A_{n,k} F(n,k, p,q)$$

$$= \sum_{n,k} \left[ \begin{array}{c} \varepsilon F A(a, q, a+1, a) + F A(a, q+1, b) a + \ldots \\ + F A(b, q+1, b) \end{array} \right]$$

where

$$F(n,k, p,q) = \left\{ \begin{array}{ll} (-1)^{(N-P)^2-\nu} \frac{\Gamma(N+P+1)}{\Gamma(N+P+1)} a^{\nu P+N-2} a^\nu \end{array} \right\}$$

$$\nu = \left\{ \begin{array}{ll} 1 \nu P+N-2 > N \\ 2 \nu P+N-1 > N \end{array} \right\}$$

$$\nu \left\{ \begin{array}{ll} F A(a, a+1, a) + F A(a, a+1, b) a + \ldots \\ + F A(b, a+1, b) \end{array} \right\}$$
$$\frac{1}{2} \left( \sum \left( F_B (a, a, a) F_A (b, k+1, b) + \ldots + F_B (b, a, a) \right) F_A (a, k+1, a) \right)$$

$$+ (-\frac{1}{4}) \left( F_B (a, a, a) + F_B (a, a, k, b) + \ldots + F_B (b, a, a) \right)$$

$$+ (2) \left( F_A (a, k+2, a) + \ldots + F_A (b, k+2, b) \right)$$

$$+ (-\frac{1}{4}) \left( F_A (a, k+1, a) + \ldots + F_A (b, k+1, b) \right)$$

$$+ F_A (a, k, a) F_A (b, k+1, b) + \ldots + F_A (b, k, a) F_A (a, k+1, a)$$

$$+ 12 \left( F_C (a, k+a, a, b, b) + \ldots + F_C (b, k+a, b, a, a) \right)$$

$$+ \left( F_D (a, a, a, b, k, b) + \ldots + F_D (b, a, a, k, a) \right)$$

$$+ F_D (a, k, a, b, b) + \ldots + F_D (b, k, b, a, a)$$
The Formula for the van der Waals interaction constant

\[ E^{(d)} = \langle \psi' | V | \psi' \rangle = \langle \psi' | H - E^0 | \psi' \rangle \]

For this particular wave function \( \psi' \) and \( \psi'' \), when we substitute the stationary \( \alpha_{nk} \) into \( E^{(d)} \),

\[ E^{(d)} = \langle \psi' | V | \psi' \rangle = \sum_{mn} A_{mn} C_{\nu \mu} \left( \frac{1}{\sqrt{\alpha_n}} \right)^2 \left( \frac{1}{\sqrt{\alpha_m}} \right) \sum_{kk'} \alpha_{nk} \alpha_{nk'} \]

\[ \times \left[ F_{A} \left( a, k + 1, a \right) + F_{A} \left( a, k + 1, b \right) b a + \right. \]

\[ \left. \left. + F_{A} \left( b, k, b \right) \right] \right)

Therefore \[ C_{dd} = \sum_{nm} \sum_{kk'} A_{mn} C_{\nu \mu} \left( \frac{1}{\sqrt{\alpha_n}} \right)^2 \left( \frac{1}{\sqrt{\alpha_m}} \right) \sum_{kk'} \alpha_{nk} \alpha_{nk'} \]

\[ \times \left[ F_{A} \left( a, k + 1, a \right) + F_{A} \left( a, k + 1, b \right) b a + \right. \]

\[ \left. \left. + F_{A} \left( b, k, b \right) \right] \right)

because \[ C_{\nu \mu} = (-1)^{\nu + 1} \left( \frac{4\pi}{3} \right) \left( 1 + \delta_{\nu \mu, 0} \right) \]

\[ \sum_{\mu'} C_{\nu \mu} \left( \frac{4\pi}{3} \right)^2 \left( 1 + \mu' + 1 \right) = \frac{2}{3} \left( 4\pi \right)^2 \]
APPENDIX B

Closed Form for the Functions FA, FB, FC, FD.

B-a-1 Function FA

\[
FA(a, N, b) = \frac{2}{P} C_p C_q \int_0^\infty v^{N_p-1} e^{-N_q v} v^{-\sigma_f^2} dv
\]

where

\[
\sigma_f^2 = \frac{1}{\nu^2} \frac{\partial^2}{\partial \nu^2} - \frac{2}{\nu} \frac{\partial}{\partial \nu}
\]

\[
FB = \frac{2}{P} C_p C_q \int_0^\infty \left( N_p + N_q + 1 \right) e^{-\nu} v^{N_p-1} e^{-\nu} v^{-\sigma_f^2} dv
\]

Note: \( FA(a, N, b) = FA(b, N, a) \)

B-a-2 Function FB

\[
FB(a, k, k', b) = \frac{2}{P} C_p C_q \int_0^\infty v^{N_p-1} e^{-N_q v} v^{-\sigma_f^2} dv
\]

\[
\sigma_f^2 = \frac{1}{\nu^2} \frac{\partial^2}{\partial \nu^2} - \frac{2}{\nu} \frac{\partial}{\partial \nu}
\]

\[
FB = \frac{2}{P} C_p C_q \int_0^\infty \left( N_p + N_q + 1 \right) e^{-\nu} v^{N_p-1} e^{-\nu} v^{-\sigma_f^2} dv
\]

\[
\left\{ \left[ C \left( N_q + k' - 1 \right) \left( N_q + k' - 2 \right) \right] v^{N_p + k' + 2} e^{-\nu} + 2 (-\nu) C \left( N_q + k' - 1 \right) v^{N_p + k' + 1} e^{-\nu} \right\}
\]
\[ (+ \left(-d_{q}^2\right) R_{q+k'-1} - d_{q}) \]
\[ + \frac{2}{\nu} \int \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} + \left(-d_{q}\right) R_{q+k'-1} e^{-d_{q}r} \right) r^2 \, dr \]
\[ \times \int \, d\nu \]
\[ = \frac{2}{\rho} \frac{Z}{q} \sum \left( C_{p} C_{g} \int \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) x \right) \]
\[ \int \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} + \left(-d_{q}\right) R_{q+k'-1} e^{-d_{q}r} \right) r^2 \, dr \]
\[ = \frac{2}{\rho} \frac{Z}{q} \sum \left( C_{p} C_{g} \left\{ \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) \right\} \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) \right) \]
\[ + \left(-d_{q}\right) \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) \]
\[ + \left(-d_{q}\right)^2 \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) \left( R_{q+k'-1} R_{q+k-2} e^{-d_{q}r} \right) \]
\[ \text{Note: } \end{equation} \]
\[ F_{B} (a, k, k', b) + F_{B} (a, k', k, b) \text{ unless } k = k' \]
\[ FC(a, k+k', b, c, d) = \sum_{q} \frac{1}{4\pi} \int \frac{d^3 \mathbf{r}_1}{\mathbf{r}_1} \int \frac{d^3 \mathbf{r}_2}{\mathbf{r}_2} e^{-i(k+k' \cdot \mathbf{q})} \frac{1}{(\mathbf{r}_1 \cdot \mathbf{A})^2} \mathbf{r}_1 \cdot \mathbf{r}_2 \] 

where \( c' = \frac{1}{\sqrt{2 \omega}} \frac{\mathbf{A}}{\mathbf{r}_1} Y_{\ell_1 \ell_2}^m(\mathbf{r}_1, \mathbf{r}_2) \frac{\mathbf{r}_2}{\sqrt{2 \omega}} \frac{d^3 \mathbf{r}_1}{\mathbf{r}_1} \frac{d^3 \mathbf{r}_2}{\mathbf{r}_2} \)

Angular part

\[ \sum_{\ell_1, \ell_2} Y_{\ell_1 \ell_2}^m(\mathbf{r}_1, \mathbf{r}_2) \]
Therefore

\[ FC = \bar{z} c' \int r_i^{\kappa+\kappa'} r_i^{(\kappa+\nu-2)} e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_i \]

\[ \times \bar{z} \int r_0^{(\nu_0+\nu_0-2)} e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_0 \]

\[ \frac{1}{2\pi i} \oint_{\gamma_0} \oint_{\gamma_0'} \]

\[ = \bar{z} c' \int r_i^{\kappa+\kappa'} r_i^{(\kappa+\nu-2)} e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_i \]

\[ \times \int r_0^{(\nu_0+\nu_0-2)} e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_0 \]

Def \[ FC = FC_< + FC_> \]

\[ FC_< = \bar{z} c' \int_0^\infty r_i^{(\kappa+\nu+\nu_0)} e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_i \]

\[ \times \frac{1}{r_i} \int_0^\infty e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_0 \]

\[ FC_> = \bar{z} c' \int_0^\infty r_i^{(\kappa+\nu+\nu_0)} e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_i \]

\[ \int_0^\infty e^{-(\nu_0+\nu_0') / \nu_0} \, d\nu_0 \]

Using incomplete integrals.

1) \[ I (K, a, \nu) = \int_0^\nu r^K e^{-\nu r} \, dr \]

\[ = \sum_{\kappa=1}^{K+1} \frac{\Gamma(K+1)}{a^{K+1}} - (\frac{1}{a})^\nu \int_0^{\nu} \frac{r^{K-\nu+1}}{\Gamma(K-\nu+2)} \, dr \]
2) \[ \mathcal{J}(K,\omega,v) = \int_{\nu=\nu_{K}}^{\infty} rK_{\omega}e^{-\nu v} d\nu \]

\[ = \sum_{t=1}^{K+1} \left( \frac{1}{\alpha_d} \right)^t r^{K-t+1} \frac{\Gamma(K+1)}{\Gamma(K-t+1)} e^{-\nu v} \]

\[ \mathcal{C}_c = \sum C'_s \int_{\nu=0}^{\infty} r_{i} (K+K'\mu+M'+N+1) e^{-(\omega+\nu v)} d\nu \]

\[ x \left\{ \frac{\Gamma(NL+M+1)}{(d_{L}+d_{L})N_{L}+M+1} - \sum_{t=1}^{N_{L}+L+1} \frac{1}{(d_{L}+d_{L})N_{L}+M+1} \frac{\Gamma(N_{L}+L+1)}{\Gamma(N_{L}+L+1-t)} \right\} \]

\[ = \sum C'_s \left\{ \frac{\Gamma(NL+M+1)}{(d_{L}+d_{L})N_{L}+M+1} \right\} \sum_{t=1}^{N_{L}+L+1} \frac{1}{(d_{L}+d_{L})N_{L}+M+1} \frac{\Gamma(N_{L}+L+1)}{\Gamma(N_{L}+L+1-t)} \]

\[ \mathcal{C}_g = \sum C'_s \int_{\nu=0}^{\infty} r_{i} (K+K'+M'+N+1) e^{-(\omega+\nu v)} d\nu \]

\[ x \left\{ \frac{\Gamma(NL+M+1)}{(d_{L}+d_{L})N_{L}+M+1} - \sum_{t=1}^{N_{L}+L+1} \frac{1}{(d_{L}+d_{L})N_{L}+M+1} \frac{\Gamma(N_{L}+L+1)}{\Gamma(N_{L}+L+1-t)} \right\} \]

\[ = \sum C'_s \left\{ \frac{\Gamma(NL+M+1)}{(d_{L}+d_{L})N_{L}+M+1} \right\} \sum_{t=1}^{N_{L}+L+1} \frac{1}{(d_{L}+d_{L})N_{L}+M+1} \frac{\Gamma(N_{L}+L+1)}{\Gamma(N_{L}+L+1-t)} \]

\[ \text{Where} \quad \omega = (N_{L}+N_{g}+N_{L}+N_{g}+1) \]
\[ F C = F C_c + F C_d \]
and \[ W = N_0 + N_1 + N_2 + N_3 + K + K' \]

\[ = \sum C_i \int \left[ \frac{\Gamma(N_3 + N_4 + 1)}{(\sigma s + \sigma d_s) N_3 + N_4 + 1} \times \frac{\Gamma(K + K' + N_p + N_q)}{(\sigma p + \sigma q) N_p + N_q + K + K'} \right] \]

\[ - \sum_{t=1}^{N_4+N_5+1} \left( \frac{1}{\sigma s + \sigma d_s} \frac{\Gamma(N_3 + N_4 + 1)}{\Gamma(N_3 + N_4 + t + 2)} \times \frac{\Gamma(W - t + 1)}{(\sigma p + \sigma q + \sigma d_s + \sigma d_f) W - t + 1} \right) \]

\[ + \sum_{t=1}^{N_4+N_5+1} \left( \frac{1}{\sigma s + \sigma d_s} \frac{\Gamma(N_3 + N_4 + 1)}{\Gamma(N_3 + N_4 + t - 2)} \times \frac{\Gamma(W - t + 1)}{(\sigma p + \sigma q + \sigma d_s + \sigma d_f) W - t + 1} \right) \]

\[ F C(a, K + K', b, b, a) = F C(b, K + K', a, a, b) \]

\[ F C(a, b, b, t + k; a) = F C(a, K + K'; b, b; a) \]

B-a-4 Function FD

\[ F D(a, K, b, c, k; d) \]

\[ = \frac{1}{4\pi} \sum C_i \int v_1 (N_0 + N_3 + K) e^{-(\sigma s + \sigma d_s)} dv_1 \int Y_{l_{min}}(1) dv_2 \]

\[ \times \int v_2 (N_2 + N_3 + K') e^{-(\sigma s + \sigma d_f)} \frac{1}{v_2} dv_2 \int Y_{l_{min}}(2) dv_{22} \]

where \[ C_i = C_p C_q C_s C_t \]

\[ \frac{1}{v_{10}} = \sum_{l=1}^{2} \frac{v_{10}}{v_{2l_{10}}} \frac{Y_{l_{min}}(1)}{Y_{l_{min}}(2)} \frac{\sum_{j=1}^{l} \frac{Y_{l}^{(v)}}{v_{2l_{10}}}}{v_{2l_{10}}} \]
Angular part

\[ \int Y_{\ell m}(\Omega) Y_{\ell' m'}^{*}(\Omega) \, d\Omega, \quad \int Y_{\ell m}(\theta) Y_{\ell' m'}^{*}(\theta) \, d\Omega \]

\[ = \delta_{\ell \ell'} \delta_{mm'} \]

\[ F_{D} = \frac{\Omega}{2} \frac{1}{4\pi} \int r_{i} \left( n_{\ell} + n_{\ell'} + k_{s} \right) e^{-i \left( p_{1} + p_{2} \right) r_{i}} \, dr_{i} \]

\[ \times \frac{4\pi}{3} \int r_{j} \left( n_{\ell} + n_{\ell'} + k_{s} \right) e^{-i \left( q_{1} + q_{2} \right) r_{j}} \frac{r_{j}^{3}}{r_{j}^{2}} \, dr_{j} \]

\[ F_{D} = F_{Dc} + F_{D\gamma} \]

\[ F_{Dc} = \frac{1}{3} \frac{\Omega}{2} \frac{1}{4\pi} \int r_{i} \left( n_{\ell} + n_{\ell'} + k_{s} \right) e^{-i \left( p_{1} + p_{2} \right) r_{i}} \, dr_{i} \]

\[ \frac{1}{r_{i}} \int r_{j} \frac{r_{j}^{3}}{r_{j}^{2}} \left( n_{\ell} + n_{\ell'} + k_{s} \right) e^{-i \left( q_{1} + q_{2} \right) r_{j}} \, dr_{j} \]

\[ F_{D\gamma} = \frac{1}{3} \frac{\Omega}{2} \frac{1}{4\pi} \int r_{i} \left( n_{\ell} + n_{\ell'} + k_{s} \right) e^{-i \left( p_{1} + p_{2} \right) r_{i}} \, dr_{i} \]

\[ \int r_{j} \frac{r_{j}^{3}}{r_{j}^{2}} \left( n_{\ell} + n_{\ell'} + k_{s} \right) e^{-i \left( q_{1} + q_{2} \right) r_{j}} \, dr_{j} \]

Using incomplete integral in Function FC

\[ I(k, d, r) \text{ and } J(k, d, r) \]
\[\text{FD } < = \frac{1}{3} \sum \mathcal{C}^t \int_0^{N_p+N_q+K-2} e^{-(\sigma p+\sigma q) \nu_1} \, d\nu_1 \times \int_0^{N_5+N_4+N^{(4)+1}} e^{-(\nu \sigma_5+\nu \sigma_4+\nu \sigma_6+\nu \sigma_7)} \, d\nu_2 \]

\[\times \sum_{t=1}^{K_5+N_4+K\cdot 2} \frac{\Gamma(N_5+N_4+K\cdot 2)}{\Gamma(N_5+N_4+K\cdot 1+1-t+1)} \]

\[\times \sum_{t=1}^{K_5+N_4+K\cdot 2} \frac{\Gamma(N_5+N_4+K\cdot 2)}{\Gamma(N_5+N_4+K\cdot 1+1-t+1)} \times \frac{\Gamma(N_p+N_q+K-1)}{(\sigma p+\sigma q)^{N_p+N_q+K-1}} \]

where \( \omega = N_p+N_q+N_5+N_4+K+K' \)

\[\text{FD } > = \frac{1}{3} \sum \mathcal{C}^t \int_0^{N_p+N_q+K+1} e^{-(\sigma p+\sigma q) \nu_1} \, d\nu_1 \times \int_0^{N_5+N_4+N^{(4)+2}} e^{-(\nu \sigma_5+\nu \sigma_4+\nu \sigma_6+\nu \sigma_7)} \, d\nu_2 \]

\[= \frac{1}{3} \sum \mathcal{C}^t \int_0^{N_5+N_4+K\cdot 2} e^{-(\nu \sigma_5+\nu \sigma_4+\nu \sigma_6+\nu \sigma_7)} \, d\nu_2 \]

\[\times \sum_{t=1}^{K_5+N_4+K\cdot 1} \frac{\Gamma(N_5+N_4+K\cdot 1)}{\Gamma(N_5+N_4+K\cdot 0+1-t)} \times \frac{\Gamma(N_p+N_q+K-1)}{(\sigma p+\sigma q)^{N_p+N_q+K-1}} \]
\[ \frac{1}{3} \sum C'_1 \sum_{x=1}^{N_0+N_1+N_2} \left( \frac{1}{v_x + c} \right)^t \frac{\Gamma(N_0+N_1+N_2)}{\Gamma(N_0+N_1+N_2 + t)} \]

\[ k \frac{\Gamma(C - t + 1)}{(d_0 + d_1 + d_2 + d_3) \omega - t + 1} \]

where \( \omega = N_0 + N_1 + N_2 + N_3 + N_4 + K + K' \)

\[ FD = FD > r \cdot FD < \]

\[ = \frac{1}{3} \sum C'_1 \left\{ \left[ \frac{\Gamma(N_0+N_1+N_2)}{(d_0 + d_1 + d_2) N_0 + N_1 + N_2 + 2} \right] \cdot \frac{\Gamma(N_0+N_1+N_2)}{(d_0 + d_1 + d_2) N_0 + N_1 + N_2 + 1} \right\} \]

\[ - \left[ \sum_{x=1}^{N_0+N_1+N_2} \left( \frac{1}{v_x + c} \right)^t \frac{\Gamma(N_0+N_1+N_2)}{\Gamma(N_0+N_1+N_2 + t)} \cdot \frac{\Gamma(C - t + 1)}{(d_0 + d_1 + d_2 + d_3) \omega - t + 1} \right] \]
PROGRAM TO CALCULATE INTERACTION BETWEEN H AND HE

THIS PART IS TO STORE ALL INFORMATION FROM GODDARD IN ARRAY

A(I), B(J).................. EXPONENTIAL COEFF. IN SLATER POLY.
C(I), D(J).................. EXPANSION COEFFICIENT
N(I), M(J).................. PRINCIPAL QUANTUM NO IN (N, L, M)

C

C IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION C(10), N(10), A(10), D(10), M(10), B(10), XN(10), XM(10)
DATA NNN/7/
WRITE (6, 46)
46 FORMAT (1H1)
READ (5, 5) (C(I), A(I), D(I), B(I), I = 1, NNN)
5 FORMAT (4(F10.5, 2X))
READ (5, 10) (N(I), M(I), I = 1, NNN)
10 FORMAT (2(I2, 2X))
AN = N(I)
BM = M(I)
XN(I) = DSQRT(2 * A(I))**(2 * AN + 1) / DSQRT(DGAMMA(2 * AN + 1.))
XM(I) = DSQRT(2 * B(I))**(2 * BM + 1) / DSQRT(DGAMMA(2 * BM + 1.))
C

C NOTE .................. NEW EXPANSION COEFF MUST BE EQUAL TO OLD
C EXPANSION COEFF TIME NORMALIZATION COEFF
DO 25 I = 1, NNN
AN = N(I)
BM = M(I)
C(I) = XN(I) * C(I)
25 D(I) = XM(I) * D(I)
WRITE (6, 30) (C(I), N(I), A(I), D(I), M(I), B(I), I = 1, NNN)
30 FORMAT (2(2X, F8.5, 3X, I2, 3X, F8.5, 6X))
C

C THIS PART IS FROM VARIATION PERTURBATION THEORY SUCH THAT THERE IS
C A SIMULTANEOUS EQUATION

ENERGY = 3.377984
AB = FA(C, N, A, O, D, M, B)
BA = FA(C, N, A, O, D, M, B)
1 READ (5, 105) NUMBER
105 FORMAT (I5)
IF(NUMBER.EQ.0) GO TO 100
READ (5, 45) IN, IK, IP, IQ
45 FORMAT (4(I2, 2X))
AIN = IN
AIK = IK
AIP = IP
AIQ = IQ
C

C AAAAAAAAAAAA
G LEVEL 19

MAIN

DATE = 70324 18/46/54

VOID=0.
ARGU=AIN+AIQ-2.
IF(ARGU) 60, 48, 49
48 ARGU=ARGU+1.
49 SAA=(AIN+AIQ-2.)*DGAMMA(ARGU)/(2.)*(AIN+AIQ-1.)
SAB=DGAMMA(AIN+AIQ+1.)/2.*&(IN+IP-1)
SAC=DGAMMA(AIN+AIQ+2.)/2.*&(IN+IP)
SAD=FB(C, N, A, IK+IQ, C, N, A)
SAE=FB(C, N, A, IK+IQ, D, M, B)
SAF=FB(D, M, B, IK+IQ, D, M, B)

ATIXA=((-1.)*SAA+2.*SAB*(-2.)*SAC)*(SAD+2.*SAE*BA+SAF)

BBB BBB BBB
S=DGAMMA(AIN+AIQ+3.)/2.*&(IN+IP+1)
SRA=FB(C, N, A, IN, IP, C, N, A)
SBB=FB(C, N, A, IN, IP, D, M, B)*BA
SBC=FB(D, N, A, IN, IP, C, N, A)*AB
SBD=FB(D, M, B, IN, IP, D, M, B)
SDE=FB(C, N, A, IP, IN, C, N, A)
SBF=FB(C, N, A, IP, IN, D, M, B)*BA
SBG=FB(D, M, B, IN, C, N, A)*AB
SBH=FB(D, M, B, IP, IN, D, M, B)

HHHHHHHHHH
ATIXB=S*(-0.5)*(SBA+SBB+SBC+SBD+SBE+SBG+SBH)
SHA=FB(C, N, A, IK+IQ-2, C, N, A)
SHB=FB(C, N, A, IK+IQ-2, D, M, B)*BA
SHC=FB(D, M, B, IK+IQ-2, D, M, B)

ATIXC=S*(2.)*(SHA+2.*SHB+SHC)

CCCCCC
SCA=FB(C, N, A, 0, 0, C, N, A)
SCB=FB(C, N, A, 0, 0, D, M, B)
SCD=FB(D, M, B, 0, 0, D, M, B)
SCC=FB(D, M, B, 0, 0, C, N, A)

ATIXD=S*(-1.)*(SCA*SAF+SCB*SAE+SCC*SAE+SCD*SAD)

DDDDDDDDDD
SDA=FB(D, M, B, IK+IQ-1, D, M, B)
SDB=FB(C, N, A, IK+IQ-1, C, N, A)
SDB=FB(C, N, A, IK+IQ-1, D, M, B)

ATIXE=S*(-4.)*(SDA+2.*SDB*BA+SDE)

EEEEEEEEE
IV G·LEVEL 19

MAIN

DATE = 70324

18/46/54

SE4=FA(C,N,A,-1,C,N,A)
SEB=FA(C,N,A,-1,D,M,B)
SEC=FA(D,M,B,-1,D,M,B)

C

ATIXF=S*{-4.*}(SEA*SAF+2.*SEB*SAE+SEC*SAD)

C

SFA=FC(C,N,A,IK+IQ,C,N,A,D,M,B,D,M,B)
SFB=FC(C,N,A,IK+IQ,D,M,B,D,M,B,C,N,A)
SFC=FC(D,M,B,IK+IQ,D,M,B,C,N,A,C,N,A)

C

ATIXG=S*2.*{SFA+2.*SFB+SFC)

C

SGA=FD(C,N,A,IK+IQ,C,N,A,D,M,B,IK+IQ,D,M,B)
SGD=FD(C,N,A,IK+IQ,D,M,B,IK+IQ,D,M,B,C,N,A)
SGE=FD(D,M,B,IK+IQ,D,M,B,IK+IQ,C,N,A)
SGF=FD(D,M,B,IK+IQ,D,M,B,C,N,A,IK+IQ,C,N,A)

C

ATIXH=S*(SGA+2.*SGB+SGC+SGD+2.*SGE+SGF)

C

ATIXI=S*(-2.*ENERGY*(SAD+2.*SAE*BA+SAF)

C

ATR IX=ATIXA+ATIXB+ATIXC+ATIXD+ATIXE+ATIXF+ATIXG+ATIXH+ATIXI

C

WRITE(6,50) IN,IK,IP,IQ,ATRIX
WRITE(6,51) ATIXA,ATIXB,ATIXC,ATIXD,ATIXE,ATIXF,ATIXG,ATIXH,ATIXI

50 FORMAT(Ix,*MATRIX(*I2,I2,I2,I2,*')=*I1X,D12.5)
51 FORMAT(///,9(1X,D12.5///))

GO TO 1

60 WRITE(5,65) VOID
65 FORMAT(1X,*WRONG*,F8.5)

100 CALL EXIT

END
FUNCTION FA(C,N,A,K,D,M,B)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 C,A,D,B,FA
DIMENSION C(10),N(10),A(10),D(10),M(10),B(10)
DATA NNN/7/

C
FA = 0.
DO 100 I = 1, NNN
   DO 100 J = 1, NNN
      AK = K
      PN = N(I)
      QM = M(J)
      FA = FA + C(I)*D(J)*DGAMMA(PN+QM+AK+1.)/((A(I)+B(J))**(N(I)+M(J)+K+1))
 100 CONTINUE
RETURN
END
FUNCTION FB(C,N,A,K,KK,D,M,B)

IMPLICIT REAL*8(A-H,O-Z)

REAL*8 C,A,D,B,F

DIMENSION C(10),N(10),A(10),D(10),M(10),B(10)

DATA NNN/7/

FB = 0.

DO 200 I=1,NNN

DO 200 J=1,NNN

PN = N(I)

QM = M(J)

AK = K

RK = KK

AG = PN + QM + AK + BK

AE = A(I) + A(J)

IAG = N(I) + M(J) + K + KK

GA = (QM + BK) * (QM + BK - 1.) * DGAMMA(AG - 1.) / AE**(IAG - 1)

GB = (2. * B(J)) * (QM + BK) * DGAMMA(AG) / AE**(IAG)

GC = (B(J) * A(J)) * DGAMMA(AG + 1.) / AE**(IAG + 1)

200 FB = FB + C(I) * D(J) * (GA - GB + GC)

RETURN

END
FUNCTION FC(C, N, A, KK, D, M, B, C1, N1, A1, D1, M1, B1)
IMPLICIT REAL*8(A-H, O-Z)
REAL*3 C, A, D, B, C1, A1, D1, M1, B1, FC
DIMENSION C(10), N(10), A(10), D(10), M(10), B(10), C1(10), N1(10), A1(10)
1, D1(10), M1(10), B1(10)
DATA NNN/7/
C******************************************************************************
FC=0.
DO 370 I=1, NNN
DO 370 J=1, NNN
DO 370 K=1, NNN
DO 370 L=1, NNN
AA=A(I) +B(J)
AN=N(I)+M(J)
BB=A1(K)+B1(L)
BM=N1(K)+M1(L)
MM=N1(K)+M1(L)
AK=KK
IAN=N(I)+M(J)+KK
X=(1./AA**IAN-1./AA+BB)**IAN)*(DGMMA(BM+1.)*DGMMA(AN+AK)/BB**(
1MM+1))
Y=0.
DO 360 II=1, MM
AA=II
360 Y=Y+(1./BB**II)*(1-1II)*(DGMMA(BM)*DGMMAIAN+AK+BM-AM+1.)/(DGMMA
1(BM+2.-AM)*((AA+BB)**(IAN+MM-II+1)))
CONTINUE
370 FC=FC+C(I)*D(J)*C1(K)*D1(L)*(X+Y)
RETURN
END
FUNCTION FD(C,N,A,K1,D,M,B,C1,N1,A1,K2,D1,M1,B1)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 C,A,D,B,C1,A1,D1,B1,FD
DIMENSION C(10),N(10),A(10),D(10),M(10),B(10),C1(10),N1(10),A1(10)
DATA NNN/7/
FD=0.
DO 470 I=1,NNN
   DO 470 J=1,NNN
      DO 470 K=1,NNN
         DO 470 L=1,NNN
            AA=A(I)+B(J)
            AN=N(I)+M(J)
            BB=A1(K)+B1(L)
            BM=N1(K)+M1(L)
            MMM=N1(K)+M1(L)+K2-1
            CC=AA+BB
            AK=K1
            BK=K2
            AMM=MMM
            CN=AN+AK
            DM=BM+BK
            IAN=N(I)+M(J)+K1
            IBM=N1(K)+M1(L)+K2
            ICN=IAN+IBM
            UU=DGAMMA(AMM)*DGAMMA(AK+BNK+2.)/DGAMMA(AN+AK-1.)/BB**(IBM+2)*AA**IAN
            XX=(AA/AA+BB)**IAN
            YY=(BB/(AA+BB))*(AN+AK-1.)*(AA/AA+BB)**IAN
            ZZ=0.5*(BB*BB)/(CC*CC)*(AN+AK-1.)*(AN+AK)*(AA/CC)**IAN
            UUV=UUC*(1.-XX-YY-ZZ)
         61 IF(K2).EQ.61,62,61
            DO 480 IJ=1,MMM
               EM=IJ
               SS=DGAMMA(AMM)*DGAMMA(CN+DM-EM+1.)/DGAMMA(DM-EM+1.)*BB**IJ*CC**ICN
               TT=(DM+1.)*EM/(DM-EM+2.)*(DM-EM+1.)*(DM-EM)
            480 ZZZ=ZZZ+SS*(1.-TT)
            CONTINUE
         CONTINUE
         IF(K2).EQ.61,62,61
      62 ZZZ=0.
         FD=FD+C(I)*D(J)*C1(K)*D1(L)*YYYYZZZ*0.333333
      CONTINUE
   CONTINUE
   DO 470 K=1,NNN
      DO 470 L=1,NNN
         CONTINUE
      CONTINUE
   CONTINUE
CONTINUE
C THIS PROGRAM IS TO REPRODUCE THE RESULT OF DAS' ARTICLE.
C C(I) IS EXPANSION COEFF.
C N(I) IS S PRINCIPLE QUANTUM NO
C A(I) IS EXPONENTIAL COEFF. IN SLATER POLY.
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION C(10),N(10),A(10),D(10),M(10),B(10),XN(10)
III=5
WRITE(6,46)
46 FORMAT(1H1)
   READ(5,5) (C(I),A(I),I=1,5)
5 FORMAT(2(F10.5,2X))
   READ(5,10) (N(I),I=1,5)
10 FORMAT(I2)
   DO 15 I=1,5
   AN=N(I)
15 XN(I)=(DSQRT(2.*A(I))**(2.*AN+1.))/DSQRT(DGAMMA(2.*AN+1.))
   DO 25 I=1,5
25 C(I)=XN(I)*C(I)
WRITE(6,26) (C(I),N(I),A(I),I=1,5)
26 FORMAT(2X,F10.5,3X,I2,3X,F10.5):///)
   TEST=FA(C,N,A,0,C,N,A)
WRITE(6,27) TEST
27 FORMAT(IX,'TEST VALUE=',D12.5:///)
   DO 30 IP=1,III
   DO 30 IQ=1,III
   DO 30 IN=1,III
   DO 30 IK=1,III
   BP=IP
   BQ=IQ
   BN=IN
   BK=IK
   AAA=(-1.)*IP*IP+1.+IN*IN+1.)*DGAMMA(BN+BP+1.)/2.*IN+IP-1.)*FA(C,N,A,IK+IQ,C,N,A)
   BBB=(-1.)*IQ*I+IQ+1.+IQ+1.*DGAMMA(BN+BP+3.)/2.*IQ+IP+1.)*FA(C,N,A,IK+IQ-2,C,N,A)
   CCC=DGAMMA(BN+BP+1.)/2.*IQ+IP-3.)*FA(C,N,A,IK+IQ,C,N,A)
   DDD=DGAMMA(BN+BP+3.)/2.*IQ+IP-1.)*FA(C,N,A,IK+IQ-2,C,N,A)
   EEE=DGAMMA(BN+BP+1.)/2.*IQ+IP-2.)*FA(C,N,A,IK+IQ,C,N,A)*IN*IP
   FFF=DGAMMA(BN+BP+3.)/2.*IQ+IP-1.)*FA(C,N,A,IK+IQ-2,C,N,A)*IK*IQ
   GA=AAA+BBB+CCC+DDD
   GC=EEE+FFF+CCC+DDD
WRITE(6,41) IP,IQ,IN,IK,GC
41 FORMAT(IX,'DAS MATRIX=',I2,I2,I2,I2,I2,'=','D12.5/) WRITE(6,42) IP,IQ,IN,IK,GA
42 FORMAT(IX,'REAL MATRIX=',I2,I2,I2,I2,I2,'=','D12.5/) WRITE(7,39) GC
39 FORMAT(D12.5)
30 CONTINUE
DO 50 IP = 1, III
DO 50 IQ = 1, III
BP = IP
GB = (-4.) * (DGAMMA(BP + 4.) / 2. ** (IP + 2)) * FA(C, N, A, IQ + 1, C, N, A)
WRITE(7, 39) GB
50 WRITE(6, 60) IP, IQ, GB
60 FORMAT(1X, 'MATRIX', 12, 12, '= ', 12.5)
WRITE(7, 45) III
45 FORMAT(1X, 'MATRIX ELEMENT', 12)
CALL EXIT
END
FUNCTION FA(C,N,A,K,D,M,B)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 C,A,D,B,FA
DIMENSION C(10),N(10),A(10),D(10),M(10),B(10)
DATA NNN/7/

C
FA=0.
DO 100 I=1,NNN
DO 100 J=1,NNN
AK=K
PN=N(I)
QM=M(J)
100 FA=FA+C(I)*D(J)*DGAMMA(PN+QM+AK+1.)/(A(I)+B(J))**(N(I)+M(J)+K+1))
RETURN
END