LONG RANGE INTERACTION ENERGY BETWEEN ATOMS AND MOLECULES
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By

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Table of Contents

1. Introduction.

2. The Schrödinger Wave Equation and Approximate Solutions.

3. Some Mathematical Relations.


5. The Long Range Interaction Energy Between a Hydrogen Molecule and a Helium Atom.
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Section 1

Introduction

If the mass centres of two neutral systems are separated at a distance, $R$, which is large in comparison with atomic dimensions negative interaction energy exists and is responsible for the initial attraction between the systems. The effect of electron exchange between the systems is negligible when $R$ is large but becomes increasingly important as $R$ decreases. The interaction energy reaches a minimum value at some $R = R_0$ and finally becomes positive and strongly repulsive as $R$ decreases further. The magnitude of the interaction energy when $R = R_0$ compared to the combined unperturbed energies of the two systems is a function of the probability of their stable union, but a small minimum value of interaction energy can exist even when stable union is highly improbable. In this thesis the attractive forces for large values of $R$ will be considered.

This long range interaction energy is usually expressed in the form of a power series in $R^{-1}$ by expanding the interaction potential. The dynamic dipole-dipole interaction term proportional to $R^{-6}$ is called the Van der Waals energy. If neither system possesses permanent dipole or quadrupole moments this is the first term of the energy
expansion but terms of lower order in \( R^{-1} \) can exist when
the systems possess such permanent momenta and these terms
are due to static interactions.

In Section 3 of this thesis expansions are developed
for use in Sections 4 and 5, which Sections are concerned
with the calculation of long range interaction energy in the
cases \( H-H \) and \( H_{\alpha} - Ne \) interactions respectively. Results
obtained are compared with published results. In partic-
ular it is to be noted that published results use only the
first three terms of the expansion of the interaction poten-
tial in powers of \( R^{-1} \) whereas later terms are included in
the present treatment and can have a large effect on the
coefficients of the terms in the energy expansion. It should
also be noted that expansions of the potential in powers of
\( R^{-1} \) have been used in published treatments outside the
regions of convergence of these expansions. The consequences
of such treatments is considered.

Section 2 contains a survey of approximate methods
of solution of Schrödinger's stationary state equation, and
methods used to treat \( H_e \) and \( H_{\alpha} \) are stated because approx-
imate wave functions of these systems are used in Section 5.
Section 2

The Schrödinger Representation and Approximate Solutions

Application of the classical laws of physics to the phenomena of atomic structure led to erroneous results which could only be corrected by the addition of special restrictions. With De Broglie's hypothesis, and its subsequent verification for light particles, that every particle had associated with it a wave structure of definite wave length it was possible to set up a new branch of physics which described atomic phenomena and which included results of classical physics for macroscopic phenomena. The two laws which describe the atomic processes were given by Schrödinger as

\[ \hat{H}\psi = -\frac{i\hbar}{\hbar} \frac{\partial\psi}{\partial t} \]  
\[ \hat{H}\psi = E\psi \]  

2.1 is called the time dependent equation, and 2.2 the stationary state equation which is applicable when the state of the system does not change with time. \( \hat{H} \) is the Hamiltonian operator, \( E \) the energy, and \( \psi \) the probability amplitude of the system.

The simplest atomic problem, that of determining the stationary states of the hydrogen atom, has been solved only after making a number of simplifications. Relativistic
corrections being neglected, as well as the magnetic and
electric interactions of the spins of the electron and the
nucleus, reduces the problem to the solving of the differential equation

$$\nabla^2 \psi + \frac{e^2}{\hbar^2} m (E - V) \psi = 0$$  \hspace{1cm} 2.3

This can be solved exactly if the potential, \( V \), is
of the central field type permitting the separation of the
coordinate of the differential equation. Corrections for
the omission of the small terms in \( H \) can be made by means of
the classical perturbation theory. In this way it is possible
to get energy expressions for the hydrogen atom that are correct to better than one part in a million.

The equation 2.2 for a more complicated atomic system
than that of the hydrogen atom has not been solved exactly
and recourse is usually made to one or two approximate methods
to obtain a solution.

The first method is to assume a trial function which
is to represent the electron distribution. The trial function
contains parameters which are varied so as to minimize the
energy of the system. This variational method is generally
used to evaluate the ground state energy of the system.

The trial function is set up with as many parameters
as is desirable for flexibility. However it is possible to
use a large number of parameters and still obtain a poor
value of energy if the correct coordinates are not included.
A good example of this is the James and Coolidge function used for the hydrogen molecule problem. This function is in the form of a series and contains five parameters. It was possible by using thirteen terms of the series to get an answer that agrees to within the experimental error with the value of the ground state energy of \( H_2 \). However, the omission of a term dependant on the electron separation gives an energy value that is scarcely better than that obtained by Rösen with a simple trial function containing two parameters.

In general two types of wave functions are used. The one type depends on giving the trial function a form which is dictated by a physical picture of the system. Thus this method takes account of polarization by distorting unpolarized functions. The other method is to use a flexible function which has no readily available physical representation but contains all the necessary variables in a form easily handled.

The correctness of the wave function is not made certain by its giving the correct energy since many varied distributions can give the same minimum energy. As a result a function which gives the correct ground state energy by the variational principle can still lead to incorrect results for the next highest energy since the two distribu-
tions need not be members of an orthogonal set of functions.

The second method is to use perturbation theory. In this method the actual system is replaced by a similar though simpler one which is referred to as the unperturbed system and which must provide a complete set of orthogonal eigen functions. Where there is little difference in the description of the two systems the perturbation method gives a good answer with few terms being considered. With proper wave functions the variational method gives a lower bound to the energy while the perturbation gives an upper bound.

The theory of perturbations was developed by classical physicists to solve problems in astronomy involving more than two bodies.

The Hartree and Hartree-Fock treatments can be classified as perturbation and variational methods respectively. In applying this method the problem is simplified by replacing all the electrons but one by the central field obtained by averaging the electron distribution of all the electrons over the polar angles. The wave function obtained represents a first approximation and these functions are used to correct the central field potential by redetermining the average electron distribution. This process is repeated until further calculation yields no better result. Thus when numerical functions are used the method is similar
in principle to perturbation theory. If analytic wave functions are assumed the method has some similarity to the variational method.

Molecular problems are further complicated by the fact that a molecule possesses nuclear, vibrational and rotational energy in addition to electronic energy. Nuclear co-ordinates can be separated from the electronic ones provided the conditions required for a theorem by Born and Oppenheimer are satisfied. The electronic part must be solved by one of the above methods and the electronic energy, as a function of nuclear coordinates, placed in the equations for the vibration and rotation where it acts in the same way as the potential does in the electronic motion.

In all problems where two or more electrons are involved proper use must be made of the Pauli Principle when using approximate methods of solution. The perturbation method cannot be used unless all eigen functions of the unperturbed system are members of the same set.

The next simplest atom to hydrogen is the helium atom. Its ground state has been calculated by approximation methods. The simplest approximation to the exact ground state eigenfunction is the zeroth order function \( e^{-\frac{1}{2}(r + R)} \) giving a 6% error in the energy. The first order function is \( e^{-\frac{1}{2}(r + R)} \) and with minimized to \( \frac{27}{6} \) gives an
error in energy of less than 2%. The next major step which resulted in the correct energy was taken by Hylleraas who introduced the electron separation $r_{12}$ into the wave function with the form

$$[e^{-\alpha r_1 - \beta r_2} + e^{-(\beta r_1 + \alpha r_2)}]e^{-\gamma r_{12}}.$$ 

With this complicated function with three parameters he was able to get an energy value indistinguishable from that of experiment. This illustrated the manner in which a reasonable energy value can be obtained with a simple function and the extremes to which one must go in order to obtain a value approximating the experimental value.

For the hydrogen molecule much the same procedure was followed. The first wave function developed by Heitler and London took account of electron exchange and had the form

$$N \left(e^{-\alpha (r_1 + r_2)} + e^{-(\alpha r_1 + \beta r_2)} \right)(\alpha \psi(\Phi) - \alpha <\psi(\beta \Phi))$$

Subsequent workers improved upon this as the basic form by introducing parameters to account for screening, polarization, the shift of the centre of electron density from the nuclear centre, and ionic terms plus polarization. Each of these methods gave an improvement to the energy value obtained by calculation as compared to the experimental value. Also each type was based upon a physical
picture. The most successful attack was made not using a picture guide, but merely strategically placing parameters in a simple functional combination. This is the aforementioned James and Coolidge function.

Thus the best variational approach appears to be to introduce as many parameters as can be conveniently handled and at the same time to introduce into the function variables as they occur in the potential. Rosen's work with the hydrogen molecule seems to indicate that polarization of a system can be conveniently handled by assuming a distribution dependant in a linear manner on the interaction potential.

Section 3

Some Mathematical Relations.

Relations are developed in this section which are to be applied in sections 4 and 5. These are based on the properties of the Gegenbauer Polynomials.

The Gegenbauer Polynomial, \( C_n^{(\lambda)} \), for integral values of \( n \), is defined as the coefficient of \( h^n \) of the termwise expansion of the generating function

\[
(1 - 2hx + x^2)^{-\lambda}
\]

This coefficient has the form

\[
C_n^{(\lambda)} = \sum_{s=0}^{n} (-1)^s \frac{n+s-\lambda}{s!} (2\lambda)^n s^n s!
\]

Bateman, 176,9

An inverse power of the distance \( |\mathbf{R} - \mathbf{r}| \), in terms of this polynomial, is then written

\[
|\mathbf{R} - \mathbf{r}|^{-2\lambda} = \sum_{n=0}^{\infty} C_n^{(\lambda)} \left[ \cos(\gamma, \rho) \right] \frac{R^n}{r^{n+2\lambda}}, \quad |\mathbf{R}| < |\mathbf{r}|
\]

\[
= \sum_{n=0}^{\infty} C_n^{(\lambda)} \left[ \cos(\gamma, \rho) \right] \frac{R^n}{\rho^{n+2\lambda}}, \quad |\mathbf{R}| < |\mathbf{r}|
\]

1. "Higher Transcendental Functions", Bateman


References to the results in this book will henceforth be labelled "Bateman" followed by the page on which it occurs and the number assigned to it therein.
The distance represented by $|R - r + r_2|^{-2\nu}$ may be expressed by a double series of the Gegenbauer Polynomials.

\[
|R - r + r_2|^{-2\nu} = \sum_{n=0}^{\infty} C_n^\nu(-\cos\theta) \frac{r_2^n}{|R - r_1|^{n+2\nu}}, \quad |r_2| < |R - r_1| 
\]

\[
= \sum_{n=0}^{\infty} C_n^\nu(-\cos\theta) r_2^n \sum_{k=0}^{\infty} C_k^{n+2\nu}(\cos\phi_r) \frac{r_k^K}{R^{n+k+2\nu}} 
\]

\[
= \sum_{n=0}^{\infty} C_n^\nu(\cos\theta) r_1^n \sum_{k=0}^{\infty} C_k^{n+2\nu}(\cos\phi_k) \frac{r_k^K}{R^{n+k+2\nu}} 
\]

where $(\theta_r, \phi_r)$ and $(\theta_k, \phi_k)$ are the polar angles of $r_1$ and $r_2$ referred to $R$ as polar as shown in Fig. 3.1.

\[
\cos X = \frac{\cos \theta_k (R - r_1 \cos \theta_r) + r_2 \sin \theta_k \sin \theta_r \cos (\phi_k - \phi_r)}{|R - r_1|} 
\]

\[
\cos Y = \frac{\cos \theta_k (R + r_2 \cos \theta_k) + r_1 \sin \theta_k \sin \theta_r \cos (\phi_k - \phi_r)}{|R + r_2|} 
\]

Fig. 3.1
Using 3.5 it will be proved that
\[
\begin{align*}
\int_{0}^{2\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} C_n^\nu (-\cos \theta_1)^{\nu \frac{n+1}{2}} (\cos \theta_2) \sin \theta_2 \sin \theta_3 d\theta_2 d\phi_1 d\phi_2 \\
= \int_{0}^{2\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} C_n^\nu (-\cos \theta_1)^{\nu \frac{n+1}{2}} (\cos \theta_2) \sin \theta_2 d\theta_2 d\phi_1 d\phi_2
\end{align*}
\]

3.7

Proof of 3.7.

\[
\cos^n X = \sum_{s=0}^{n} \frac{n!}{(n-s)!s!} (\cos \theta_2)^{n-s} a^{n-s} \sin^s \theta_2 \cos^s (\phi_1 - \phi_2) b^s
\]

3.8

where \( a = \left( R - r \cos \theta_2 \right) \), \( b = \frac{R}{r} \sin \theta_2 \).

\[
\begin{align*}
\int_{0}^{2\pi} \int_{0}^{2\pi} \cos^s (\phi_1 - \phi_2) d\phi_1 d\phi_2 \\
= \left( \frac{1}{2} \right)^s \int_{0}^{2\pi} \int_{0}^{2\pi} \left[ e^{i(\phi_1 - \phi_2)} + e^{-i(\phi_1 - \phi_2)} \right]^s d\phi_1 d\phi_2 \\
= \sum_{v=0}^{s} \left( \frac{1}{2} \right)^s \frac{s!}{(s-v)(v)!} \int_{0}^{2\pi} \int_{0}^{2\pi} e^{i(s-2v)(\phi_1 - \phi_2)} d\phi_1 d\phi_2 \\
= 0 \quad \text{if} \quad s - 2v \neq 0
\end{align*}
\]
\[
\int_0^{2\pi} \int_0^{2\pi} \cos^2(\theta - \phi) \, d\theta \, d\phi = 0 \quad \text{if } S \neq 2v
\]
\[
= \left(\frac{1}{2}\right)^S \frac{\pi}{\pi} \int_0^{2\pi} \int_0^{2\pi} \, d\theta \, d\phi
\]
if \( S \) is even \quad 3.9

\[
\int_0^{\pi} \cos^2 \theta \sin^2 \theta \, d\theta = \frac{(\alpha - 1)!}{(\alpha + \beta)!!} \int_0^{\pi} \cos^2 \theta \sin^\alpha \theta \, d\theta
\]
By repeated application with \( \beta \) odd this reduces to
\[
\frac{(\alpha + 1)!!}{(\alpha - 1)!!} \int_0^{\pi} \cos^2 \theta \sin^{\alpha - 1} \theta \, d\theta
\]
Therefore
\[
= 0 \quad \text{if } \alpha \text{ odd}
\]
\[
= \frac{(\alpha - 1)!!}{(\alpha + \beta)!!} \int_0^{\pi} \sin^\alpha \theta \, d\theta \quad \text{if } \alpha \text{ even}
\]

\[
\int_0^{\pi} \cos^n \theta \sin^m \theta \, d\theta \quad \text{with } S \text{ even}
\]
requires \( n \) even

\[
= \frac{\Pi - 1)!! \Pi}{(n + 1)!!} \int_0^{\pi} \sin^\Pi \theta \, d\theta = \frac{(n - 1)!! \Pi}{(n - 1)!!} \int_0^{\pi} \sin^\Pi \theta \, d\theta \quad 3.10
\]
Place 3.9 and 3.10 in 3.8 and integrating gives

\[
\int_{0}^{2\pi} \int_{0}^{\pi} \sum_{S=0}^{n} \frac{n!}{(n-S)!} \frac{(\frac{1}{2})^S}{S!} \frac{S!}{2!} \frac{(n-S-1)!}{(n-1)!} \frac{b^S}{(1-b)^n} \cos^{n-S-1} \theta_1 \sin^S \theta_2 \, d\phi_1 \, d\phi_2
\]

\[
= \int_{0}^{2\pi} \int_{0}^{\pi} \sum_{S=0}^{n} \frac{n!!}{(n-S)!!} \frac{1}{S!!} \frac{a^{n-S} b^S}{(1-b)^n} \cos^{n-S} \theta_1 \sin^S \theta_2 \, d\phi_1 \, d\phi_2
\]

\[
= \int_{0}^{2\pi} \int_{0}^{\pi} \sum_{\alpha_2=0}^{\frac{n}{2}} \frac{n!}{(n-2\alpha_2)! \alpha_2!} \frac{(a')^{\alpha_2} (b')^{n-2\alpha_2}}{(1-b)^n} \cos^{n-2\alpha_2} \theta_2 \sin^{2\alpha_2} \theta_2 \, d\phi_1 \, d\phi_2
\]

\[
= \int_{0}^{\pi} \int_{0}^{\pi} \cos^{n} \theta_2 \sin^2 \theta_2 \, d\phi_1 \, d\phi_2
\]

\[
= 0 \quad \text{for } n \text{ odd}
\]

With \( C_n^\nu (-\cos x) \) expanded as in 3.1 and using 3.12,

\[
\int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{2\pi} C_n^\nu (-\cos x) C_{\kappa}^{n\alpha \nu} (\cos \theta_1) \sin \theta_2 \, d\phi_1 \, d\phi_2
\]

\[
= \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{2\pi} C_m^\nu (-\cos \theta_2) C_{\kappa}^{n\alpha \nu} (\cos \theta_1) \sin \theta_2 \, d\phi_1 \, d\phi_2
\]

which is the required proof of 3.7.
Since
\[ \frac{d}{dz} C_{n+1}^{\nu} = 2(\nu-1)C_n^{\nu}(z) \]
Bateman 178,30

then
\[ \int_{-1}^{1} dC_{n+1}^{\nu}(z) = 2(\nu-1)\int_{-1}^{1} C_n^{\nu}(z) \, dz \]

\[ \int_{-1}^{1} C_n^{\nu}(z) \, dz = \frac{1}{2(\nu-1)} \left[ C_{n+1}^{\nu}(1) - C_{n+1}^{\nu}(-1) \right] \]

\[ = \frac{2 \sqrt{n+2\nu-1}}{2(\nu-1)(n+1)!} \frac{1}{2\nu-1} \]
Bateman 176,7

\[ = \frac{2 \sqrt{n+2\nu-1}}{(n+1)!} \frac{1}{2\nu-1} \quad \text{if } n \text{ even} \]

\[ = 0 \quad \text{if } n \text{ odd} \]

3.13

As a result

\[ \int_{-1}^{1} C_n^{\nu}(z) \, dz = \frac{2 \sqrt{n}}{(n+1)!} \frac{1}{10} \]

3.14

\[ = 0 \quad n \neq 0 \]

\[ = 2 \quad n = 0 \]
\[ \forall \nu = 1 \; ; \; \int_{-1}^{1} C_n'(z) \, dz = \frac{2 \sqrt{n+1}}{(n+1)!!} \]

\[ = \begin{cases} \frac{2}{(n+1)} & \text{if } n \text{ even} \\ 0 & \text{if } n \text{ odd} \end{cases} \tag{3.15} \]

\[ \forall \nu = \frac{n+2}{2} \; ; \; \int_{-1}^{1} C_{\frac{k+1}{2}}'(z) \, dz = \frac{2 \sqrt{k+1+n+2}}{(k+1)!! \sqrt{n+1}} \]

\[ = \frac{2 \sqrt{k+n+1}}{(k+1)!! \sqrt{n+1}} \]

\[ = \begin{cases} \frac{2 (k+n)!}{(k+1)! n!} & \text{if } k \text{ even} \\ 0 & \text{if } k \text{ odd} \end{cases} \tag{3.16} \]

With \( \nu = \frac{1}{2} \) and \( \nu / \) in 3.2 using result 3.14 and 3.15 in 3.2 and with \( \nu = \frac{1}{2}, \nu /, \) and \( \nu = \frac{3}{4} \) using 3.14, 3.15, and 3.16 with 3.7 in 3.3 these results follow:

\[ \int_0^\pi |R - r|^{-1} \sin \phi \, d\phi = \frac{A}{R} \tag{3.17} \]
\[
\int \int \int \int \left| R - \frac{r_1}{R} \right|^{n-2} \sin \theta_1 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2 \\
= \frac{16\pi^2}{R} \int_{|r| > R1} \int_{|r| < R1} 3.18
\]

\[
\int_{0}^{2\pi} R - \frac{r_1}{R} \, d\theta_1 = \sum_{n=0}^{\infty} \frac{2}{(n+1)} \frac{R^n}{R^{n+2}} \text{ if } n \text{ even} 3.19
\]

\[
\int_{0}^{2\pi} \int_{0}^{2\pi} \left| R - \frac{r_1}{R} \right|^{n-2} \sin \theta_1 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2 \\
= 16\pi^2 \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(k+n)! \, R^{n-k} \, R^n}{(k+1)! \, (n+1)! \, R^{n+k+2}} \text{ if } k \text{ even and } n \text{ even} 3.20
\]

\[
= 16\pi^2 \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(2k+2\eta)! \, R^{2k} \, R^{2\eta}}{(2k+1)! \, (2\eta+1)! \, R^{2\eta+2k+1}} 3.20
\]
Since
\[ |R - r_i|^{-\nu_i} \cdot |R - r_j|^{-\nu_j} = |R - r_i|^{-\nu_i + \nu_j} \]
then
\[ \sum_{p=0}^{\infty} C_p^{\nu_p} (\cos \theta) \frac{r_i^p}{R^{n+p}} \cdot \sum_{s=0}^{\infty} C_s^{\nu_s} (\cos \theta) \frac{r_j^s}{R^{n+s}} = \sum_{n=0}^{\infty} C_n^{\nu_n} (\cos \theta) \frac{r_j^n}{R^{n+n}} \]
and \[ C_n^{\nu_n + \nu_j} \text{ comes from } C_p^{\nu_p} C_s^{\nu_s} \]
where \( p + s = n \) for all \( \theta \in \pi, \theta \in \pi \).
as a result
\[ |R - r_i + r_j|^n \cdot |R - r_i|^n \]
\[ = \sum_{p=0}^{\infty} C_p^{\nu_p} (-\cos \theta) \frac{r_i^p}{R^{n+p}} \cdot \sum_{k=0}^{\infty} C_k^{\nu_k} (\cos \theta) \frac{r_i^k}{R^{n+k}} \cdot \sum_{s=0}^{\infty} C_s^{\nu_s} (\cos \theta) \frac{r_j^s}{R^{n+s}} \]
\[ = \sum_{n=0}^{\infty} C_n^{\nu_n} (-\cos \theta) \frac{r_i^n}{R^{n+n}} \cdot \sum_{k=0}^{\infty} C_k^{\nu_k + \nu_j} (\cos \theta) \frac{r_i^k}{R^{n+n+k}} \] \[ \text{3.22} \]
Thus

\[
\sum_{n=0}^{\infty} \frac{1}{(2n+1)} R_{n+1}^2 \frac{1}{R^{2n+2}}
\]

One more general angular result is needed.

\[
C_n^{\nu} [z, \dot{z} - (z^2 - 1)^{\nu/2} (z \ddot{z})^{\nu/2} \cos \phi]
\]

\[
= \frac{12^{\nu-1}}{(\nu!)^2} \left[ \sum_{\ell=0}^{n} \left( \frac{4^{\nu}}{\sqrt{\nu+\ell}} \left( \frac{\Gamma(\nu+\ell+1)}{\Gamma(\nu+\ell+1)} \right) \left( \frac{(2n+2\ell+1)}{(2n+2\ell+1)} \right) \right) \right]
\]

For $\nu = \frac{1}{2}$, this becomes the Legendre double angle expansion in terms of the Associated Legendre Functions.

\[
C_n^{\nu/2} [z, \dot{z} - (z^2 - 1)^{\nu/2} (z \ddot{z})^{\nu/2} \cos \phi] = P_n(z) P_n(\dot{z})
\]

\[
+ \sum_{\ell=1}^{n} \frac{(n-\ell)!}{(n+\ell)!} P_n^{(\nu)}(x) P_n^{(\nu)}(\dot{x}) \cos \phi
\]

Bateman 177, 19

3.23

3.24

3.25
For \( \gamma = \gamma \) the expansion is

\[
C_n \left[ zz_r - (z_r^2 - 1) \frac{1}{2} (1 - z_r^2) \cos \phi \right]
\]

\[
= \sum_{l=0}^{n} \frac{4^l (n-l)!}{(n-2l)!} (2l+1) (1-z^2) \frac{1}{2} (1-z^2)^{\frac{1}{2}}
\]

An equivalent expansion for \( |\mathbf{R} - \mathbf{r}_1 + \mathbf{r}_2|^2 \) in the region \( |\mathbf{r}_1| < |\mathbf{r}_2| < |\mathbf{R}| \) is

\[
|\mathbf{R} - \mathbf{r}_1 + \mathbf{r}_2|^2 = \sum_{n=0}^{\infty} \frac{(-1)^n (\nabla \cdot \mathbf{r}_1)^n}{n!} \sum_{k=0}^{n} \frac{(\nabla \cdot \mathbf{r}_2)^k}{k!} \frac{1}{\mathbf{R}}
\]

\[
= \sum_{k=0}^{\infty} \sum_{n=0}^{\infty} C_k \frac{1}{2} (-\cos \phi) \frac{1}{2} (\cos \phi) \frac{1}{n} \frac{1}{2} \frac{1}{2} \frac{1}{R^{1+k+1}}
\]

where

\[
\Gamma_i = \hat{x} x_i + \hat{y} y_i + \hat{z} z_i
\]

\[
\mathbf{R} = i x_i + j y_i + k z_i
\]

\[
\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}
\]

\[
\nabla \mathbf{v} = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}
\]
Then
\[ (-1)^n \frac{(\nabla \cdot \mathbf{r})^n}{n!} \frac{1}{R} = C_n^k \frac{\cos \theta_i}{R^{n+1}} \]  
3.26

\[ \nabla_i (-1)^n \frac{(\nabla \cdot \mathbf{r})^n}{n!} \frac{1}{R} = - \nabla (-1)^{n-1} \frac{(\nabla \cdot \mathbf{r})^{n-1}}{(n-1)!} \frac{1}{R} \]
\[ = - \nabla \frac{C_{n-1}^k (\cos \theta_i) r_i^{n-1}}{R^n} \]  
3.27

And
\[ (\mathbf{r}_i \cdot \nabla_i) (-1)^n \frac{(\nabla \cdot \mathbf{r})^n}{n!} \frac{1}{R} = n (-1)^n \frac{(\nabla \cdot \mathbf{r})^n}{n!} \frac{1}{R} \]
\[ = n \frac{C_n^k (\cos \theta_i) r_i^n}{R^{n+1}} \]  
3.28

Also
\[ (\mathbf{r}_i \cdot \nabla_i) \left\{ \sum_{\beta=0}^{\infty} (-1)^\beta (\nabla \cdot \mathbf{r} \cdot \mathbf{r}_i)^\beta \frac{1}{n! R} \sum_{p=0}^{n} (-1)^p \frac{(\nabla \cdot \mathbf{r}_i)^p}{p!} \frac{1}{R} \right\} \]
\[ = \left\{ \sum_{n=0}^{\infty} (-1)^n (\nabla \cdot \mathbf{r} \cdot \mathbf{r}_i)^n \frac{1}{n! R} \sum_{p=0}^{n} (-1)^p \frac{(\nabla \cdot \mathbf{r}_i)^p}{p!} \frac{1}{R} \right\} \{ n + p \} \]
\[ = \sum_{\beta=0}^{\infty} \sum_{k=0}^{\infty} \beta C_\beta^k (\cos \theta_i) \frac{r_i^{\beta+k}}{R^{\beta+k+2}} \]  
3.29

So
\[ (\mathbf{r}_i \cdot \nabla_i) \left\{ \sum_{\eta=0}^{\infty} (-1)^\eta (\nabla \cdot \mathbf{r} \cdot \mathbf{r}_i)^\eta \frac{1}{n! R} \sum_{k=0}^{\infty} (-1)^k (\nabla \cdot \mathbf{r}_i)^k \frac{1}{k!} \frac{1}{R} \right\} \]
\[ = \sum_{\eta=0}^{\infty} \sum_{k=0}^{\infty} \eta C_\eta^k (-\cos \theta_i) \frac{C_{\eta+k}^k (\cos \theta_i) r_i^{\eta+k}}{R^{\eta+k+2}} \]  
3.30
Equivalent results are obtained in the co-ordinates of point two. These are obtained by replacing all subscripts 1 by 2 and vice versa.

A further quantity which is required is given below for one of two situations. The second situation is obtained by using expansion 3.4 in place of 3.3. It is obtained in the same manner as 3.29 since it is the same thing multiplied by a constant as far as 1 is concerned.

\[
(N\cdot q_i) \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-1)^n (N\cdot q_i)^n}{n!} \frac{(N\cdot q_i)^k}{k!} \frac{1}{R} \sum_{s=0}^{\infty} \sum_{t=0}^{\infty} \frac{(-1)^s (N\cdot q_i)^s}{s!} \frac{(N\cdot q_i)^t}{t!} \frac{1}{R} \\
= \sum_{a=0}^{\infty} \sum_{b=0}^{\infty} b C_k^l (-\cos x) C_{l-1}^{(k)}(\cos a) \frac{R^b}{R^{a+b+1}} 3.31
\]
The radial integration of section 4 is of the type

\[ \int_0^\alpha e^{-2r} r^{n+2} dr = \frac{1}{2^{n+2}} \int_0^\alpha e^{-r} r^{n+2} dr = I_{n+2}(\alpha) \]

\[ I_{n+3}^{(\alpha)} = \frac{1}{2^{n+3}} \left\{ \frac{I_{n+1}^{(\alpha)} - \sum_{a=0}^{n+2} \frac{(\alpha)^{n+2}}{(n+2)!}} {2^{n+3}} \right\} \]

These integrals are tabulated below for values of \( \alpha = 0, 1, 2, 3 \) covering cases (1), (2) and (3) of Section 4.

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<th>( n+3 )</th>
<th>( \alpha = 0 )</th>
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<th>8</th>
<th>10</th>
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<td>0.209</td>
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<td>0.676</td>
<td>0.728</td>
<td>0.744</td>
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<td>4.065</td>
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<td>5.603</td>
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<td>9.790</td>
<td>32.150</td>
<td>52.650</td>
<td>62.550</td>
<td>77.020</td>
<td>78.590</td>
</tr>
</tbody>
</table>

| TABLE 3.1 |
The integrals which occur in section 5 may be written in the form given immediately below. For various powers \( s \) of the indices \( \Lambda_{1}, \Lambda_{2}, \Lambda_{3} \), particular general results hold and these will be first investigated.

\[
I = N^{2} \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} \left\{ e^{-s(\lambda_{1} + \alpha_{1} + \beta_{1})} + e^{-s(\lambda_{2} + \alpha_{2} + \beta_{2})} \right\} \lambda_{1}^{m_{1}} \lambda_{2}^{m_{2}} \lambda_{3}^{m_{3}} \times \left( \lambda_{1} - u_{1} \right) \left( \lambda_{2} - u_{2} \right) d\lambda_{1} du_{1} d\phi_{1} d\lambda_{2} du_{2} d\phi_{2}
\]

where

\[
N^{2} = \frac{\Xi^{6}}{2^{4} d^{4} (1 + d)}
\]

\[
D = e^{-zd} \left( 1 + zd + \left( \frac{zd}{3} \right)^{2} \right)
\]

\[zd = S = \left( \frac{1}{4\pi} \right) \left( 1.038 \right) = 1.677\]

where \( \Xi \) is the value of the screening parameter and \( d \) is the internuclear separation of the hydrogen atoms.

\[
I = \frac{S^{6}}{32(1 + d^{2})} \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} \left\{ e^{-s(\lambda_{1} + \alpha_{1} + \beta_{1})} + e^{-s(\lambda_{2} + \alpha_{2} + \beta_{2})} + 2d^{-s(\lambda_{1} + \lambda_{2})} \right\} \times \left( \lambda_{1} - \alpha_{1} - \beta_{1} \right) \left( \lambda_{2} - \alpha_{2} - \beta_{2} \right) d\lambda_{1} du_{1} d\phi_{1} d\lambda_{2} du_{2}
\]

\[
I(\text{pont}) = \frac{S^{6}}{32(1 + d^{2})} \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} \left\{ e^{-s(\lambda_{1} + \alpha_{1} + \beta_{1})} + e^{-s(\lambda_{2} + \alpha_{2} + \beta_{2})} \right\} \times \left( \lambda_{1} - \alpha_{1} - \beta_{1} \right) \left( \lambda_{2} - \alpha_{2} - \beta_{2} \right) d\lambda_{1} du_{1} d\phi_{1} d\lambda_{2} du_{2}
\]
By replacing $u_1$ by $-u$ and $u_2$ by $-u_2$, (3.35) becomes

\[
I = \frac{s^6}{16(1+b^2)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[ (1+i)^{\nu_1} \right] \left[ e^{-s(\lambda_1+\nu_1^{e_1}-\nu_2^{e_2})} + 2e^{-s(\nu_1^{e_1})} \right] \\
\times \left[ (\lambda_1^{e_1} u_2 - \lambda_2^{e_2} u_2) \chi_2 \lambda_2^{\nu_2}(\lambda_2^{e_2} u_2 - \lambda_2^{e_2} u_2) \right] \, du_1 \, du_2 \, du_2
\]

\[
= 0 \quad \text{if } p+q \text{ odd}
\]

\[
= \frac{s^6}{16(1+b^2)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-s(\lambda_1+\nu_1^{e_1}-\nu_2^{e_2})} \left( \lambda_1^{e_1} u_2 - \lambda_2^{e_2} u_2 \right) \chi_2 \lambda_2^{\nu_2} \lambda_2^{e_2} u_2 \lambda_2^{e_2} u_2 \, du_1 \, du_2 \, du_2
\]

\[
\quad \text{if } p+q \text{ even}
\]

\[
= \frac{s^6}{16(1+b^2)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{ e^{-s(\lambda_1+\nu_1^{e_1}-\nu_2^{e_2})} + e^{-s(\nu_1^{e_1})} \right\} \\
\times \left\{ (\lambda_1^{e_1} u_2 - \lambda_2^{e_2} u_2) \chi_2 \lambda_2^{\nu_2}(\lambda_2^{e_2} u_2 - \lambda_2^{e_2} u_2) \right\} \, du_1 \, du_2 \, du_2
\]

\[
\quad \text{if } p \text{ odd and } q \text{ odd}
\]

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-s\lambda_2(\lambda_2^{e_2} - \mu_2^{e_2})} \, d\lambda_2 \, d\mu = \frac{4}{s^3} D
\]

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-s(\lambda_2^{e_1} - \mu_2^{e_1})} \, d\lambda_2 \, d\mu_2 = \frac{4}{s^3}
\]
Particular cases desired:

\[ m = 2, n = 0, p = 0, q = 0 \quad I_1 \]
\[ m = 0, n = 0, p = 2, q = 0 \quad I_2 \]
\[ m = 2, n = 0, p = 2, q = 0 \quad I_3 \]
\[ m = 1, n = 1, p = 1, q = 1 \quad I_4 \]

Using 3.34, 3.39 and 3.40 with the even odd property of 3.36 the following is obtained,

\[ I_1 + I_2 = \frac{s^3}{4(1 + D^2)} \int \left( e^{s(\lambda + \mu)} + De^{-s^2} \right) (\lambda^2 + \mu^2) d\lambda, du, \]

\[ = \frac{s^3}{4(1 + D^2)} \left( \frac{8}{5^5} (s^5 + 6s^2 + 24s^3 + 24s^4 + 14s^5 + s^6) \right) \]

\[ = \frac{2}{5^5(1 + D^2)} \left( s^5 + 6s^2 + 24s^3 + 24s^4 + 14s^5 + s^6 \right) \]

\[ I_1 + I_2 = 6.472 \quad 3.41 \]
Using the same properties as for 3.41,

\[ I_3 = \frac{s^3}{4(1+D^2)} \int \int \int \left\{ e^{-s(\lambda_1 + \mu_1 I_1)} + De^{-sI_1} \right\} \left\{ \lambda_1^4 \mu_1 I_1^2 - \lambda_1^2 \mu_1^2 I_1^4 \right\} \, d\lambda_1 \, d\mu_1 \]

\[ = \frac{1}{s^2(1+D^2)} \left( \frac{s^2 + 4 + De^{-s}(s^2 + 7s^3 + 28s^4 + 60s^6)}{15} \right) \]

\[ = 2.239. \]

Using 3.37

\[ I_4 = \frac{s^6}{16(1+D^2)} \int \int \int \int \int \int e^{-s(\lambda_1 + \mu_1 + \lambda_2 + \mu_2 - \lambda_3 \mu_3)} (\lambda_1^3 \mu_1 - \lambda_1 \mu_1^3)(\lambda_2^3 \mu_2 - \lambda_2 \mu_2^3) \, d\lambda_1 \, d\mu_1 \, d\lambda_2 \, d\mu_2 \]

\[ = \frac{-s^6}{16(1+D^2)} \left[ \int \int e^{-s(\lambda_1 + \mu_1)} (\lambda_1^3 \mu_1 - \lambda_1 \mu_1^3) \, d\lambda_1 \, d\mu_1 \right]^2 \]

\[ = \frac{-s^6}{16(1+D^2)} \left[ - \frac{4s^3}{s^6} \right]^2 \]

\[ = \frac{-1}{(1+D^2)} \]

\[ = -0.685. \]
Section 4

The Long Range Interaction of Two Hydrogen Atoms.

A binary system consisting of two hydrogen atoms is described as in Fig. 4.1, where the atomic nucleus A and nucleus B have associated with them electrons 1 and 2 respectively.

![Diagram of two hydrogen atoms with associated electrons](image)

Fig. 4.1

Interparticle distances are denoted as in the figure. The polar angles \((\theta_1, \phi_1)\) of \(\mathbf{r}\) and \((\theta_2, \phi_2)\) of \(\mathbf{r}\) are referred to the internuclear distance \(R = AB\) as polar and an arbitrary plane through \(AB\). The \(Z\) axis of the Cartesian co-ordinates of A and B with origins at A and B respectively are taken in the direction of \(\mathbf{R}\).

In order to calculate the interaction energy for large values of \(R\) electron exchange between the atoms is neglected and the interaction energy is taken to be due to the perturbing effect of the Coulombic interaction,

\[
V(R) = \frac{1}{R} + \frac{1}{\mu \hbar_1^2} - \frac{1}{\mu \hbar_2^2} - \frac{1}{\mu \hbar_3^2}.
\]

4.1

Atomic units are used. At normal temperatures each of the
unperturbed atoms can be taken to be in its ground state because of the predominant statistical weighting of that state. The difference between the energies of the ground state and the first excited state of a hydrogen atom is so large that the probability of either atom being excited into a higher energy state as a result of the perturbation is negligible.

In the calculation of the long range interaction energy the usual method is to obtain a series representation of the interaction, \( V(R) \), in inverse powers of \( R \). This power series is then terminated at whatever stage is desired and the average value is calculated from this finite series. In doing the problem in this way three cases arise, depending upon the subsequent approximations which are made. The power series in \( R^{-1} \) is convergent in the region \( \frac{R}{\xi} < R, \xi < R \).

Case 1. If there is to be no overlap it is necessary that the atomic wave functions vanish for \( R \gg R_2, \frac{R_1}{R_2} \). This requires a renormalization of the wave function, and the series for the potential is valid.

Case 2. The atomic wave functions vanish for \( R_1 \gg R, \frac{R_2}{R} \). The wave functions extend over the complete region of space in which the expansion is a representation of the potential. There is a region in which the wave functions overlap and this overlap is neglected on the
assumption that the value added to the interaction energy by its inclusion is a very small percentage of the total non-overlap interaction energy at large separation of the mass centers. This approach also requires a renormalization of the wave function.

Case 3. The atomic wave functions extend throughout all space and the expansion of $V(R)$ in powers of $R^{-1}$ is used throughout - including the region where it does not converge. All overlap effects are neglected.

These three cases will now be considered in detail.

The unperturbed atoms are represented by the functions $\psi_{A1}(1)$ and $\psi_{B2}(2)$ centered on $A$ and $B$ respectively where

$$\psi_{A1}(1) = Ne^{-\frac{R}{\sigma_{A}}} , \psi_{B2}(2) = Ne^{-\frac{R}{\sigma_{B}}}$$

and

$$N^{-2} = \int \int \int e^{-2R}r_1^2dr_1sin\phi d\phi$$

where $\sigma_{A}, \sigma_{B}, \infty$ as for cases (1),(2) and (3) respectively.

Because $V(R)$ is small the distortion of the unperturbed binary system is taken to be linearly dependent on $V(R)$ and to be of the form

$$\psi = \psi_{A1}(1) \psi_{B2}(2) \left(1 + \lambda V\right)$$

where $\lambda$ is a parameter to be used to minimize the energy.
Using the variational principle the energy of the perturbed system is

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{I}{J} \quad \text{(4.4)}$$

where $H$ is the Hamiltonian of the system and integration is throughout the coordinate space of electrons 1 and 2.

Writing

$$\int \int \psi_{11}^{(1)} \psi_{22}^{(2)} f \psi_{11}^{(1)} \psi_{22}^{(2)} \, dt_1 \, dt_2 = \langle f \rangle \quad \text{(4.5)}$$

$$I = \langle (1+\lambda V)H(1+\lambda V) \rangle$$

$$J = \langle (1+\lambda V)^2 \rangle$$

where

$$H = H_0 + V$$

$$H_0 = H_{01} + H_{02} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + \frac{1}{r_1} - \frac{1}{r_2} \quad \text{(4.6)}$$

Using 3.2 and 3.3 is represented by

$$V(R) = \frac{1}{R} + \sum_{n=0}^\infty \sum_{\kappa=0}^\infty C^n_\kappa (-\cos \theta) L^n_\kappa C^{\kappa+1}_n \cos \theta \frac{R^{n+\kappa+1}}{R^{n+\kappa+1}}$$

$$- \sum_{n=0}^\infty C^n_\kappa \cos \theta \frac{R^{n+\kappa}}{R^{n+\kappa}} - \sum_{\kappa=0}^\infty C^{\kappa+1}_n \cos \theta \frac{R^{\kappa+1}}{R^{\kappa+1}}$$

$$= \sum_{n=1}^\infty \sum_{\kappa=1}^\infty C^n_\kappa (-\cos \theta) C^{\kappa+1}_n \cos \theta \frac{R^{n+\kappa+1}}{R^{n+\kappa+1}}$$

Therefore

$$\langle V(R) \rangle = 0 \quad \text{by 3.14} \quad \text{(4.7)}$$
\[ H V = H_0 V + V^2 \]

\[
H_0 V \psi_{B1}, \psi_{B2} = V H_0 \psi_{B1}, \psi_{B2} + \nabla \cdot \nabla \left( -\frac{1}{2} V^2 - \frac{1}{2} V^2 \right) V
\]

\[- \left( \nabla \cdot V \nabla + \nabla \cdot V \nabla \right) \psi_{B1}, \psi_{B2} \]

\[
= V H_0 \psi_{B1}, \psi_{B2} + \left( \frac{\nabla \cdot V + \frac{1}{r} \cdot \nabla \cdot V}{r} \right) \psi_{B1}, \psi_{B2}
\]

\[
= (V H_0 + S) \psi_{B1}, \psi_{B2}
\]

using 4.1 and 3.29 may be written in the form

\[
S = \sum_{n=1}^{\infty} \sum_{K=1}^{\infty} C_K \left( -\cos \theta \right) \frac{C_n^{N}}{R^{n+k+1}} \left\{ m n \cdot \frac{1}{r} + q n \cdot \frac{1}{r^2} \right\}
\]

\[
\langle S \rangle = 0 \quad \text{by} \quad 2.7 \quad \text{and} \quad 3.14
\]

\[
\langle H V \rangle = \langle H_0 V + V^2 \rangle = \langle V^2 + V H_0 + S \rangle = \langle V H + S \rangle
\]

\[
\langle V H V \rangle = \langle V^3 + V H_0 V \rangle
\]

\[
= \langle V^3 + V (V H_0 + S) \rangle = \langle V^3 + V^2 H_0 + V S \rangle = \langle V^2 H + V S \rangle
\]

\[
V S = \frac{1}{2} \left\{ \frac{\nabla \cdot V}{r} V^2 + \frac{\nabla \cdot V}{r^2} V^2 \right\}
\]
since \( V S \) is scalar.
\begin{equation}
\langle V^3 \rangle = \left\langle \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} C_k^{1/2} (-\cos x) C_n^{3/2} \frac{\kappa^2 \mu^2 \nu^2}{R^{n+2}} \right] \right\rangle^2 \end{equation}

Using the result 3.7 this may be written
\begin{equation}
\langle V^3 \rangle = \left\langle \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} C_k^{1/2} \cos \theta_n C_n^{3/2} \frac{\kappa^2 \mu^2 \nu^2}{R^{n+2}} \right] \right\rangle^2 \end{equation}

Using the expansion 3.1 this form will involve products of the angle \( \cos \theta_n \) as well as \( \cos \theta \), and the average values for \( k+k'+k'' = 1+1+2 \) are the first non zero cases.

As a result the lowest possible order to appear in \( \langle V^3 \rangle \) is at least of order \( R^{-11} \). Since this expansion is to be carried only to order \( R^{-10} \), \( \langle V \rangle \) does not appear.

Since \( \Psi \) is the solution of the Schrodinger equation
\begin{equation}
H \Phi_\nu \Psi_\nu = E \Phi_\nu \Psi_\nu \quad (\epsilon = \frac{1}{2})
\end{equation}
then
\begin{equation}
H \Phi_\nu \Psi_\nu = E \Phi_\nu \Psi_\nu \quad , \quad E_0 + E_0 + E = E
\end{equation}

Placing the results 4.8, 4.10 and 4.10 in \( \mathfrak{I} \) and \( \mathfrak{J} \) gives
\begin{equation}
\mathfrak{I} = \langle (1+\lambda V)H(1+\lambda V) \rangle = E_0 (1+\lambda^2 V^2) \lambda \langle V \rangle + 2 \lambda \langle V^3 \rangle
\end{equation}
\begin{equation}
\mathfrak{J} = \langle 1+\lambda^2 V^2 \rangle
\end{equation}
Placing $I$ and $J$ in 4.3 gives

$$\Delta E = E - E_0 = \frac{\lambda^2 \langle VS \rangle + 2\lambda \langle V^2 \rangle}{\langle 1 + \lambda^2 V^2 \rangle} \quad 4.11$$

A necessary condition for a minimum value of $\Delta E$
is that $\Delta E/\lambda = 0$ giving the following result

by neglecting terms of order less than $R^{-10}$. Since $\langle V^2 \rangle$
is of order $R^{-6}$ as is shown by 4.10.

Therefore

$$\langle 0 \rangle = \left[ (\langle 1 \rangle + \lambda^2 \langle V^2 \rangle) \left[ \lambda \langle VS \rangle + \langle V^2 \rangle \right] - \lambda^3 \langle VS \rangle + 2\lambda \langle V^2 \rangle \right] \lambda^2 \langle V^2 \rangle$$

$$= \langle 0 \rangle \left[ \lambda \langle VS \rangle + \langle V^2 \rangle \right]$$

Therefore

$$\lambda \langle VS \rangle + \langle V^2 \rangle = 0$$

And

$$\lambda = -\frac{\langle V^2 \rangle}{\langle VS \rangle} \quad 4.12$$

Substitution of 4.12 into 4.11 gives

$$\Delta E = \frac{\langle V^2 \rangle^3 \langle VS \rangle - 2 \langle V^2 \rangle^2}{\langle VS \rangle^2 \langle VS \rangle} \frac{1}{\langle 1 \rangle + \frac{\langle V^2 \rangle^6}{\langle VS \rangle^2}}$$
$$\Delta E = - \frac{\langle V^2 \rangle^2}{\langle i \rangle \cdot \langle VS \rangle}$$

These average values will now be calculated with the aid of the results of section 3.

$$\sqrt{\frac{2}{V}} = \frac{1}{R^2} + \frac{1}{R_1^2} + \frac{1}{R_2^2} + \frac{1}{R_3^2} - \frac{2}{R_1} \left( \frac{1}{R_1} + \frac{1}{R_3} \right) + \frac{2}{R_1 R_3} + \frac{1}{R}$$

using results 3.3, 3.7, 3.19, 3.20 and 3.23 along with 4.5

$$\langle V^2 \rangle = 16 \pi^2 \left( \frac{1}{R^2} + \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(2n+2k)!}{(2n+1)!(2k)!} \frac{r_1^{2n} r_2^{2k}}{R^{2n+2k+2}} \right)$$

$$- \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \frac{r_1^{2n}}{R^{2n+2}} - \sum_{k=0}^{\infty} \frac{1}{(2k+1)} \frac{r_2^{2k}}{R^{2k+2}}$$

$$= \left( \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!(2k)!} \frac{r_1^{2n} r_2^{2k}}{R^{2n+2k+2}} \right) / 16 \pi^2$$

The integration over $r_1$ and $r_2$ has been done in 3.34. In terms of these integrals there

$$\langle V^2 \rangle = 16 \pi^2 \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!(2k)!} \frac{I_{2n+2,2k}}{R^{2n+2k+2}}$$
\[ \langle 1 \rangle = 16 \pi^2 I_3 \cdot I_3 \] as given by 4.

\[ \langle VS \rangle = \left\{ \frac{1}{2} \left\{ \frac{1}{r_1} \left( \frac{1}{r_2} + \frac{1}{r_3} - \frac{2}{r_2 r_3} \left[ \frac{1}{r_1} + \frac{1}{r_3} \right] + \frac{2}{r_2 r_3 r_1} \right) \right. \\
\left. + \frac{r_2 r_3}{r_1} \left( \frac{1}{r_2} + \frac{1}{r_3} - \frac{2}{r_2 r_3} \left[ \frac{1}{r_1} + \frac{1}{r_3} \right] + \frac{2}{r_2 r_3 r_1} \right) + \right\} \right\} \\
\] using the results of 3.26 to 3.31 permits the above expression to take the form

\[ \langle VS \rangle = \frac{1}{2} \left\{ \sum_{n=0}^{\infty} \sum_{k=0}^{2n} \left( \frac{n r_1^{n-1} r_2^k + k r_1^n r_2^{k-1}}{r_1^{n+k+2}} \right) \left\{ C_\nu^k (-\cos \chi) C_{n+k}^m (\cos \theta) \\
+ 2 C_{\nu}^{n} (\cos \theta) C_{\nu+k}^{n+k} (-\cos \phi) - 2 C_{\nu}^{n} (\cos \chi) C_{n+k}^m (\cos \theta) \\
- 2 C_{\nu}^{n} (\cos \theta) C_{\nu+k}^{n+k} (\cos \phi) \right\} \right. \\
\left. + \sum_{n=0}^{\infty} C_\nu^k (\cos \theta) \frac{n r_1^{n-1}}{r_1^{n+k+2}} + \sum_{n=0}^{\infty} C_{\nu}^{n+k} (-\cos \phi) k r_3^{k-1} \frac{r_3^{k+1}}{r_3^{k+2}} \right\} \]
With 4.8, 1.7, and 3.29, 3.30, 3.31 and the same
in point two

\[
\langle VS \rangle = 16\pi^2 \left[ \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \left\{ \frac{\left<n r_{n}^{2n-1} r_{k}^{2k} \right>}{(2n)! (2k)!} \right\} \frac{(2n+2k)!}{2^{2n+2k+2}} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{\left<k r_{2k} \right>}{(2k+1)!} \frac{1}{R^{2k+1}} \right]
\]

\[
= 16\pi^2 \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)! (2k+1)!} \frac{\left<n r_{n}^{2n-1} r_{k}^{2k} + k r_{2k} \right>}{R^{2n+2k+2}} \right]
\]

Then

\[
\Delta E = - \left[ \frac{\sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(2n+2k)!}{(2n+1)! (2k+1)!} \frac{\left<n r_{n}^{2n-1} r_{k}^{2k} + k r_{2k} \right>}{R^{2n+2k+2}}}{I_3^2} \right]^2
\]

\[
I_3^2 \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)! (2k+1)!} \frac{\left<n n r_{n} r_{k} + k r_{2k} \right>}{R^{2n+2k+2}} \right]
\]

\[
= - \frac{\frac{2}{3} \frac{I_4^2}{R^6} + 2 \frac{I_5 I_5}{R^8} + \frac{14}{3} \frac{I_5^2}{R^{10}} + \frac{6}{3} \frac{I_5 I_9}{R^{10}}}{I_3^2} \left[ \frac{\frac{4}{3} \frac{I_4 I_6}{R^6} + \frac{4}{3} \frac{I_5 I_7}{R^8} + \frac{5}{3} \frac{I_6 I_7 + 2 I_5 I_9}{R^{10}}}{I_3} \right]^2
\]
Expanding by the binomial theorem

\[
\Delta E = -\frac{3R^6}{4I_3^2I_6} \left[ \frac{4I^4_5}{9R^{12}} + \frac{8I^2_5I^2_7}{3R^{14}} + \frac{4I^2_5I^2_7 + 4I^2_5I^2_7 + 4I^2_5I^2_7}{R^{16}} \right]
\]

\[
x \left[ 1 - \frac{3I^3_7 + \frac{3}{2}I^2_7}{R^2} - \frac{3I^3_7 + \frac{3}{2}I^2_7 + 6I^3_9 + 2I^3_7 - 9I^3_9}{R^4} \right.
\]

\[
- \frac{-9I^3_7 - 9I^3_7}{R^6} \right]
\]

Collecting in powers of \(R^{-1}\) to the order

\[
= -\left[ \frac{\frac{1}{R^6}}{\frac{1}{R^6}} + \frac{\frac{1}{R^8}}{\frac{1}{R^8}} + \frac{\frac{7}{20I_3^2I_4} + \frac{3}{20I_3^2I_4} - \frac{2I_3^2I_4 + 2I_3^2I_4 - 2I_3^2I_4}{R^{10}}} \right]
\]

\[
= -\frac{A}{R^6} - \frac{B}{R^8} - \frac{C}{R^{10}}
\]
\[
A = \frac{1}{3} \frac{I_5^3}{I_2 I_4} \quad \quad B = \frac{3I_4^2 I_7}{I_3^2 I_4} - \frac{I_5^2 I_6}{I_3 I_4^2} \\
C = \frac{7I_5 I_7^2}{20 I_3^2 I_4} + \frac{3I_5^2 I_8}{I_3^2 I_4^2} - \frac{2I_5^2 I_9}{I_3 I_4^2} + \frac{2I_4^2 I_8}{I_3 I_4} - \frac{9I_5 I_6}{I_3 I_4^2}
\]

<table>
<thead>
<tr>
<th>Table of Coefficients</th>
<th>( R = 6 )</th>
<th>( R = 8 )</th>
<th>( R = 10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A ) (2σ = R)</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>( A ) (2σ = 2R)</td>
<td>5.072</td>
<td>6.000</td>
<td>6.000</td>
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<tr>
<td>( A ) (2σ = 3R)</td>
<td>112.5</td>
<td>112.5</td>
<td>112.5</td>
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<tr>
<td>( B ) (2σ = R)</td>
<td>23.107</td>
<td>82.644</td>
<td>90.160</td>
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<tr>
<td>( B ) (2σ = 2R)</td>
<td>104.604</td>
<td>111.852</td>
<td>112.464</td>
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<tr>
<td>( C ) (2σ = R)</td>
<td>291.9375</td>
<td>291.9375</td>
<td>291.9375</td>
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<tr>
<td>( C ) (2 = R)</td>
<td>497.097</td>
<td>984.164</td>
<td>1736.383</td>
</tr>
<tr>
<td>( C ) (2 = 2R)</td>
<td>2384.367</td>
<td>2844.719</td>
<td>2922.702</td>
</tr>
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<td>$\frac{A}{R}$</td>
<td>$\frac{B}{R^2}$</td>
<td>$\frac{C}{R^6}$</td>
<td>$\frac{D}{R^4}$</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
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<td>-------------</td>
</tr>
<tr>
<td>(2e=10)</td>
<td>1.286 x 10^{-4}</td>
<td>2.264 x 10^{-5}</td>
<td>6.000 x 10^{-6}</td>
</tr>
<tr>
<td>(2e=R)</td>
<td>5.722 x 10^{-5}</td>
<td>1.913 x 10^{-5}</td>
<td>6.872 x 10^{-6}</td>
</tr>
<tr>
<td>(2e=2R)</td>
<td>1.259 x 10^{-4}</td>
<td>2.289 x 10^{-5}</td>
<td>6.000 x 10^{-6}</td>
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<td>(2e=3)</td>
<td>6.631 x 10^{-5}</td>
<td>6.906 x 10^{-6}</td>
<td>9.125 x 10^{-6}</td>
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<tr>
<td>(2e=2R)</td>
<td>13.610 x 10^{-6}</td>
<td>4.926 x 10^{-6}</td>
<td>9.026 x 10^{-7}</td>
</tr>
<tr>
<td>(2e=2R)</td>
<td>6.165 x 10^{-5}</td>
<td>6.667 x 10^{-6}</td>
<td>1.125 x 10^{-6}</td>
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<tr>
<td>(2e=2)</td>
<td>4.828 x 10^{-5}</td>
<td>3.719 x 10^{-6}</td>
<td>2.920 x 10^{-7}</td>
</tr>
<tr>
<td>(2e=2R)</td>
<td>8.222 x 10^{-6}</td>
<td>9.166 x 10^{-7}</td>
<td>1.736 x 10^{-7}</td>
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<tr>
<td>(2e=2R)</td>
<td>3.944 x 10^{-5}</td>
<td>2.649 x 10^{-6}</td>
<td>2.912 x 10^{-7}</td>
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<tr>
<td>$\Delta E$ (2e=∞)</td>
<td>2.362 x 10^{-4}</td>
<td>9.231 x 10^{-5}</td>
<td>7.417 x 10^{-6}</td>
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<tr>
<td>$\Delta E$ (2e=R)</td>
<td>7.906 x 10^{-5}</td>
<td>2.394 x 10^{-5}</td>
<td>6.497 x 10^{-6}</td>
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<tr>
<td>$\Delta E$ (2e=2R)</td>
<td>2.270 x 10^{-4}</td>
<td>3.220 x 10^{-5}</td>
<td>7.416 x 10^{-6}</td>
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The results obtained above are compared with those of other authors in the following table:

<table>
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<tr>
<th>Author</th>
<th>Wave function</th>
<th>Potential</th>
<th>Method</th>
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<tr>
<td>(i)</td>
<td>Ne^{-\mu-K(I+V)}</td>
<td>\sum_{i}^{\text{var}} \langle \psi_{i}^{+}</td>
<td>Var.</td>
</tr>
<tr>
<td>(ii)</td>
<td>Ne^{-\mu-K(I+AV)}</td>
<td>\langle \psi_{1}^{+} \psi_{1} \rangle = \langle H \rangle</td>
<td>Var.</td>
</tr>
<tr>
<td>(iii)</td>
<td>Ne^{-\mu-K(I+AV)}</td>
<td>\psi_{1}^{+}</td>
<td>Var.</td>
</tr>
<tr>
<td>(iv)</td>
<td>Ne^{-\mu-K(I+AV)}</td>
<td>\psi_{1}^{+}</td>
<td>Var.</td>
</tr>
<tr>
<td>(v)</td>
<td>Ne^{-\mu-K(I+AV)}</td>
<td>\psi_{1}^{+}</td>
<td>Var.</td>
</tr>
<tr>
<td>(vi)</td>
<td>Ne^{-\mu-K(I+AV)}</td>
<td>\psi_{1}^{+}</td>
<td>Var.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coeff. of R^{-6}</th>
<th>Coeff. of R^{-8}</th>
<th>Coeff. of R^{-10}</th>
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<tr>
<td>(i) -6</td>
<td>-1 3 5</td>
<td>- 1 4 1 6</td>
</tr>
<tr>
<td>(ii) -6</td>
<td>-1 3 5</td>
<td>- 1 4 1 7 5</td>
</tr>
<tr>
<td>(iii) -6</td>
<td>-2 6 5 7</td>
<td>- 1 0 6 9 1</td>
</tr>
<tr>
<td>(iv) -6</td>
<td>-1 1 2 5</td>
<td>- 1 0 2 9</td>
</tr>
<tr>
<td>(v) -6 4 9 9 0 3</td>
<td>-1 2 4 3 9 9</td>
<td>- 1 1 3 5 2 1</td>
</tr>
<tr>
<td>(vi) -6</td>
<td>-1 1 2 5</td>
<td>- 2 9 1 4 3 7 5</td>
</tr>
</tbody>
</table>
Graphs of the variation of coefficient with range of integration
Graphs of the variation of energy with distance for the three cases.
The graphs of section 4 show that although the coefficients are subject to very large deviations for case 1, case 2 and case 3 show very little difference at separations of greater than 7 atomic units. The actual total energy of the first three terms of the series can hardly be distinguished in cases 2 and 3, whereas case 1 showed as much error at a separation of 10 atomic units as case 2 at only 6 atomic units.

The individual coefficients become smaller as the separation distance decreases. The values obtained under case 3 may be looked upon as the maximum limiting values of these coefficients for any particular wave function used.

Thus the use of the interaction potential in the expanded form is justifiable from the point of view that little error is introduced at large separations of the nuclei. The reason for this is that the correction terms which give the value of the function in the convergent region are weighted by an exponentially decreasing function with distance. For the same reason there is actually a static interaction potential consisting of this correction factor and is so small that it can be properly put equal to zero. The average static interaction may thus be likened to a small quantity of the first order and treated as such in any development for interaction energies at long range.
The calculations of Pauling and Beach were made in order to improve a result obtained by Marginau. In particular the coefficient of $R^{-6}$ was considered to be too small and that of $R^{-8}$ and $R^{-10}$ too large. Their result (v) is derived by using many terms in the function of (v) of 4.23 and their result (iii) by using only ground state functions. They used the first three terms in the expansion of $V(R)$ only. With only these first three terms the present calculation gives the result (iv) in which the coefficients of $R^{-8}$ and $R^{-10}$ are slightly smaller than in (iii). In (iii) the trial function is of a different form from that used in (iv).

When the expansion of $V(R)$ is not terminated at the third term the present calculation shows that the coefficient of $R^{-10}$ is increased by about 200% because of contributions from the next two terms in $V(R)$ which are neglected by Pauling and Beach but which are found to be of considerable magnitude. If Pauling and Beach had used these additional terms their coefficient of $R^{-10}$ would have been increased similarly and it is felt that the value of the third coefficient would be around 3300.

Thus the conclusion reached is that in determining the series form of long range interaction energy that the improper use of $V(R)$ as in case 3 is justifiable provided all the contributing terms are included in the expansion.

Section 5

The Long Range Interaction Between A Hydrogen Molecule and a Helium Atom.

As in section 4 the long range interaction energy is determined by using the variational principle and is considered as arising from the coulombic interaction of the particles of the two systems.

Because it is shown in section 4 that the value of the interaction energy is not greatly affected when wave functions are not restricted to the region in which \( V(R) \) in powers of \( R^{-1} \) is valid wave functions will extend throughout all space and the interaction potential, \( V(R) \), will be developed in a series form valid in a restricted region - the expansions of section 3 being used for this purpose. Because the separation, \( R \), of the hydrogen molecule and the helium atom is large electron exchange will be neglected.

Section 4 also shows that when an LCAO method is used the interaction energy is increased slightly over values obtained by using a linearly distorted ground state function. Therefore only ground state functions of each system will be considered, and these will have desirable symmetry properties.

The hydrogen molecule, being of diatomic homonuclear
type will have cylindrical symmetry about its nuclear axis in virtue of the Paul principle. The helium atom will be assumed to be spherically symmetrical in its ground state. As stated in section 2 this introduces a 2% error in the ionization of the helium atom. The deviation from spherical symmetry due to the presence of two bound electrons is small and the co-ordinate will also be ignored in the wave function.

Massey and Buckingham, using a variational approach, obtained an expression for the long range interaction energy of two hydrogen molecules. The derivation makes use of the presence of cylindrical symmetry and the vanishing of the wave functions on their boundary. The result is correct to the second order of approximation. Since these same criteria are satisfied in this case the same energy expression may be used with proper modification of the wave function.

Writing the unperturbed wave functions as $\psi_H(1,2)$ for the hydrogen molecule and $\psi_e(3,4)$ for the helium atom then the perturbed wave function, $\psi$ for the complete system is given a form similar to that of section 4 and thus

$$\psi = N \psi_H(1,2) \psi_e(3,4) [1 + \lambda V]$$

$$N^{-2} = \int \psi_H^* \psi_e (\psi_H \psi_e) \, d^3 \tau$$
5.1 has the same form as the trial function of Massey and Buckingham. The interaction energy of such a system according to Massey and Buckingham is

\[
\Delta E = \langle V \rangle - \left[ \langle V \rangle - \frac{\langle \delta^2 V \rangle}{\langle \frac{\partial^2 V}{\partial x^2} \rangle} \right]^2
\]

where the symbols have the same significance as in section 4.

The binary system is described as shown in Fig. 5.1 where A, B are the nuclei of the hydrogen molecule and C is that of the helium atom. M is the mid-point of AB.

Electrons \( \epsilon = 1, 2 \) and \( \gamma = 3, 4 \) are assigned to the hydrogen molecule and the helium atom respectively. All particles are referred to \( M \epsilon = R \) as polar line, and the reference plane for the azimuthal angles \( \phi \) is the plane ABC. Particles of the hydrogen molecule referred to \( M \) as origin and particles of the helium atom referred to \( C \) as origin have polar co-ordinates

\[
A(r_1, \theta, \phi, 0), \ B(r_2, \theta, 0); \ i(r_i, \theta_i, \phi_i); \ j(r_j, \theta_j, \phi_j)
\]
Where

\[ r_A = r_B = \frac{\Omega}{2}, \quad \Theta_A = \pi - \alpha, \quad \Theta_B = \alpha \]

\[ V(R) = \sum_{n=0}^{\infty} \frac{\sum_{k=0}^{\infty} e^{-n} \left( \frac{(\nabla \cdot r_i)^n}{n! R} \right)}{R^n} \left( \frac{r_i^k}{k!} \right) \]

By 3.26

\[ V(R) = 2 \sum_{n=0}^{\infty} \frac{\sum_{k=1}^{\infty} e^{-n} \left( \frac{(\nabla \cdot r_i)^n}{n! R} \right)}{R^n} \left( \frac{r_i^k}{k!} \right) \]

\[ = -\sum_{n=0}^{\infty} \frac{\sum_{k=1}^{\infty} e^{-n} \left( \frac{(\nabla \cdot r_i)^n}{n! R} \right)}{R^n} \left( \frac{r_i^k}{k!} \right) \]

since the systems are neutral.

As in 3.3 and 3.4 with angles defined as in 3.5 and 3.6

\[ V = -\sum_{n=1}^{\infty} \frac{\sum_{k=1}^{\infty} C_k \left( -\cos \phi_j \right) C_n \left( \sin \phi_i \right) \frac{R^n r_i^k}{R^{n+k+1}}}{R^{n+k+1}} \]

Because of the cylindrical symmetry in \( H \) and the spherical symmetry in \( H_0 \), application of 3.7 to gives

\[ \langle V \rangle = -\left\langle \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} e^{-n} C_k \left( -\cos \phi_j \right) C_n \left( \sin \phi_i \right) \frac{R^n r_i^k}{R^{n+k+1}} \right\rangle = 0 \]

by 3.14.
Placing 5.6 in 5.2 yields

\[
\Delta E = - \frac{\langle v^2 \rangle^2}{\langle \{ \sum_{i,j} v_{ij} v \}^2 \rangle}
\]

5.7

Expressions for these two quantities will now be determined and the Van der Waals energy will be calculated.

From 5.4, by 3.27

\[
\sum_{i,j} \nabla_{i,j} V
\]

\[
= - \sum_{i,j} \nabla_{i,j} \sum_{n=1}^{\infty} \frac{e_{ij} (\nabla \cdot r_{ij})^n (\nabla \cdot r_{ij})^k}{n!} \frac{1}{R^n R^k}
\]

5.8

\[
= - \nabla \sum_{i,j} \sum_{n=1}^{\infty} c_{ij} \frac{k^2}{R^{n+k+1}}
\]

\[
+ \nabla \sum_{i,j} \sum_{n=1}^{\infty} c_{ij} \frac{k^2}{R^{n+k+1}}
\]

\[
= - 2 \nabla \sum_{n=1}^{\infty} \frac{e_{ij} (-1)^n (\nabla \cdot r_{ij})^n}{R^n} \]

\[
+ 2 \nabla \sum_{n=1}^{\infty} \frac{e_{ij} (\nabla \cdot r_{ij})^n}{R^{n+1}}
\]
\[
\sum_{i,j} \nabla e_{ij} \cdot V
\]
\[
= \sum_{n=0}^{\infty} \frac{2(n+1)}{R} \ e_{i} \ C_{n}^{1/2} \ \left([\cos e_{i}] \frac{R_{i}^{n}}{R^{n+1}} \right)
\]
\[
= \sum_{n=0}^{\infty} \frac{2(n+1)}{R} \ e_{i} \ (-1)^{n} (\nabla \cdot R_{i}) \frac{1}{n!} \ \frac{1}{R}
\]
\[
\left\{ \sum_{i,j} \nabla e_{ij} \cdot V \right\}^{2}
\]
\[
= \frac{4}{R^{2}} \left[ \sum_{n=0}^{\infty} \frac{(n+1)}{R} \ C_{n}^{1} \ \left([\cos e_{i}] \frac{R_{i}^{n}}{R^{n+1}} \right)
\right]^{2}
\]
\[
= \frac{4}{R^{2}} \left[ \sum_{n=0}^{\infty} \frac{(n+1)}{R} \ C_{n}^{1} \ \left([\cos e_{i}] \frac{R_{i}^{n}}{R^{n+1}} \right)
\right]^{2}
\]
\[
= \frac{4}{R^{2}} \left[ \sum_{n=0}^{\infty} \frac{(n+1)}{R} \ C_{n}^{1} \ \left([\cos e_{i}] \frac{R_{i}^{n}}{R^{n+1}} \right)
\right]^{2}
\]
\[+ 2 \sum_{n=0}^{\infty} \frac{(n+1)(n+k+1)}{R} \ C_{n}^{1} \ \left([\cos e_{i}] \frac{R_{i}^{n+k+2}}{R^{n+k+2}} \right)
\]

Using results 3.36 and the fact that \(d\eta = -d\eta\) only even \(R^{-1}\) can occur in the first expression—and in the same way as in 3.43 \(n+k\) must be even in the second expression.

As a result this denominator expression is even in powers of \(R^{-1}\).
The same type of considerations when applied to the $\langle v^2 \rangle$ reveals that in the same way as in the denominator the numerator expression must be even in powers of $R^{-1}$.

Thus the form of the interaction energy will be

$$\Delta E = \frac{-F(\alpha)}{R^6} - \frac{G(\alpha)}{R^8} - \frac{H(\alpha)}{R^{10}}$$

For the purpose of the calculation of the Van der Waals energy term it is simpler to use expressions 5.10 and 5.5 to obtain the dipole-dipole interactions.

The first term of the denominator is obtained from 5.10 and is

$$\frac{16}{R^6} \left[ \lambda_1^2 \cos^2 \theta_1 + \lambda_2^2 \cos^2 \theta_2 + 2 \lambda_1 \lambda_2 \cos \theta_1 \cos \theta_2 \right]$$

Using the double angle expansion stated in 3.28 and results 3.41, 3.42 and 3.43

$$\frac{32}{R^6} \frac{d^2}{4} \left[ \lambda_1^2 \mu_1^2 \cos^2 \chi + (\lambda_1^2 + \lambda_2^2 - 1) \sin^2 \chi \right]$$

$$= \frac{d^2}{R^6} \left[ 8 \cos^2 \chi (I_3 + I_4) + 4 \sin^2 \chi (I_1 + I_2 - I_3 - I_4) \right]$$

$$= \frac{12 \cdot 32 d^2}{R^6} \left[ 1 + \frac{500}{12 \cdot 432} \sin^2 \chi \right]$$

5.12
using 5.4 the numerator has for its first term the dipole-dipole term expressible as

\[ -(\nabla \cdot p_i)(\nabla \cdot r_j) \frac{1}{R^i} \]

\[ = \left[ (r_i \cdot r_j) - 3(r_i \cdot r_i)(r_j \cdot r_j) \right] \frac{1}{R^3} \]  

5.13

Since the spherical symmetry of system \( j \) implies the same general conditions for average values as section 4 then

\[ \langle x_j^2 \rangle = \langle y_j^2 \rangle = \langle x_j y_j \rangle = \langle \cos \phi_j \rangle = \langle \sin \phi_j \rangle = 0 \]

\[ \langle \cos^2 \phi_j \rangle = \langle \sin^2 \phi_j \rangle = \frac{1}{2} \]

Placing these results in 5.13 after squaring gives the following

\[
\left[ 2(r_i \cdot r_i)(r_j \cdot r_j) - (r_i \cdot r_j)^2 + (r_i \cdot r_j)^2 + \right. \\
2(r_i \cdot r_i)(r_j \cdot r_j) + (r_i \cdot r_j)^2 + (r_j \cdot r_j)^2 \\
- 6 \left\{ (r_i \cdot r_j) (r_i \cdot r_j) \right\} + 9(r_i \cdot r_j)^2 \left( r_i \cdot r_j \right)^2 \right] \frac{1}{R^6}
\]  

5.14
Collecting
\[
\left( \frac{1}{2\pi} \right) \left\{ 16 r_1^2 \cos^2 \theta_1, +16 r_2^2 \cos^2 \theta_2 + 2 r_1^2 \sin^2 \theta_1, \right\}
\]
\[
5.16
\]

Using the Wang function for the distribution and the double angle expansion of 3.25 along with the average values of these angles as determined in elliptical coordinates in 3.41, 3.42 and 3.43 the line 5.16 takes the numerical form
\[
d^2 \frac{\mu^6}{(2\pi)^2} \left\{ 8.219 + 3.84 \sin^2 \theta \right\}
\]
\[
5.17
\]

The Van der Waals energy term comes from 5.17 squared upon 5.12. This gives the numerical form given in the unaveraged form below

\[
\Delta E = -\left( \frac{d}{2\pi} \right)^4 \frac{(8.219)^2 \left\{ 1 + 0.097 \sin^2 \alpha \right\}^2}{16 \times 12 \times 432 \times \{ 1 + 0.04 \sin \alpha \}^2}
\]
\[ \Delta E = - \frac{2.395 \left( 1 + 0.97 \sin \alpha \right)^2}{\left( 1 + 0.40 \sin \alpha \right)^3} \]

\[ \approx - 2.395 \quad \text{for the average value.} \]

The first term of the interaction energy of two hydrogen atoms is 6 units. That of two hydrogen molecules is 15.01 units according to Massey and Buckingham. It would be expected that result for \( H_2 - He \) would fall somewhere between these results. This is not the case here and can be attributed to one of two reasons. The first of these is that the binding energy of both \( H_2 \) and \( He \) are fairly large. The interaction energy is small. Consequently an error in the initial energy is greatly amplified in the interaction energy. Since the Wang function is a rather poor representation and since

\[ \Delta E \propto \frac{\Psi_{H_2} \Psi_{He}}{\Psi_{H_2} \Psi_{He}}, \]

then the error in the energy may be up to as much as 50% low. The result should be at least in the right order of magnitude. The second reason is that the Massey and Buckingham result of 16.01 would appear to be much too large because of the statement that \( \langle (r \cdot \hat{r})(k \cdot \hat{k}) \rangle = \langle (r \cdot \hat{r})^2 \rangle \).
But \( \langle (\vec{r}_1 \cdot \vec{r}_2) \rangle \approx \frac{1}{10} \langle (\vec{r}_1 \cdot \vec{r}_2)^2 \rangle \). Since the numerator appears squared this error has greater affect in the numerator than in the denominator. This would decrease the average interaction which they obtained and bring it closer to the \( \alpha \alpha \) interaction value.

Because there is no permanent dipole in \( \text{H}_2 \) the interaction is expected to be less than \( \hbar \) as it is calculated to be. This same reason accounts for the drastic decrease of the interaction energy upon angular orientation of the nuclear axis of \( \text{H}_2 \). The variation in this case is negligible.

In conclusion it is felt that the energy value obtained in this section is of the correct order of magnitude but may be considerably increased by the use of more accurate representative functions of the unperturbed systems.
