# LONG RANGE INTERACTION ENERGY BETWEEN ATOMS AND MOLECULES

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By

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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 ' ' ' tion 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 Walls 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 moments 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 $H_2 - H_e$ interactions respectively. Results obtained are compared with published results. In particular it is to be noted that published results use only the first three terms of the expansion of the interaction potential 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 $H_2$ are stated because approximate wave functions of these systems are used in Section 5.

## The Schrodinger 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 Schrodinger as

$$H\Psi = -i\hbar \frac{\partial \Psi}{\partial t},$$ 
2.1

$$H\Psi = E\Psi .$$ 
2.2

2.1 is called the time dependant equation, and 2.2 the stationary state equation which is applicable when the state of the system does not change with time. 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

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad 2.3$$

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 pertubation 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 $H_2$. How-
ever, 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 flexi-
ble function which has no readily available physical repre-
sentation but contains all the necessary variables in a form
easily handled.

The correctness of the wave function is not made cer-
tain 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 re-
sults 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 pertubation 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 pertubation 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 pertubation gives an upper bound. The theory of pertubations 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 pertubation 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 pertubation 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[1] 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 pertubation 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 $e^{-Z(r_1+r_2)}$ giving a 6% error in the energy. The first order function is $e^{-Z(r_1+r_2)}$ and with $Z$ minimized to $27/16$ gives an

error in energy of less than 2%. The next major step which
resulted in the correct energy was taken by Hylleraas[1] who
introduced the electron separation $r_{12}$ into the wave
function with the form

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

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 reason-
able 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 proceedure
was followed. The first wave function developed by Heitler
and London[2] took account of electron exchange and had the
form

$$N \left( e^{-(r_1 + r_2)} + e^{-(r_{a1} + r_{b1})} \right) \left( \alpha(1)\beta(2) - \alpha(2)\beta(1) \right)$$

Subsequent workers improved upon this as the basic form
by introducing parameters to account for screening, polar-
ization, 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 experi-
mental value. Also each type was based upon a physical

picture. The most successful attack was made not using a picture guide, but merely stragetically placing parameters in a simple functional combination. This is the aforementioned James and Coolidge[4] 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.

1. Born and Oppenheimer: Ann. der Phy. 84, 457, (1927).

2. Hylleraas: Z. f Phy. 65, 209, (1930).

3. Heitler and London: Z. f Phy.44, 455, (1927).

4. H. M. James and A. S. Coolidge:Journal of Chemical Physics 1, 825, (1933).

## 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, $C_n^{\nu}(z)$,[*] for integral values of n, is defined as the coefficient of $h^n$ of the termwise expansion of the generating function

$$\left(1 - 2hz + z^2\right)^{-\gamma}$$

This coefficient has the form

$$C_n^{\nu}(z) = \sum_{s=0}^{\leq n/2} (-1)^s \frac{\overline{|n+\gamma-s}}{\overline{|\gamma}\ s!\ (n-2s)!} (2z)^{n-2s} \qquad 3.1$$

Bateman, 176,9

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

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

$$= \sum_{n=0}^{\infty} C_n^{\gamma}\left[\cos(r_\circ, R_\circ)\right]\frac{R^n}{r^{n+2\gamma}} \quad , \quad |R| < |r| \qquad 3.2$$

[*] 1. "Higher Transcendal Functions", Bateman Manuscript Project, Vol.1, pp. 175-179 (McGraw-Hill, 1953). 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 $\left| \underline{R} - \underline{r_1} + \underline{r_2} \right|^{-2\nu}$ may be expressed by a double series of the Gegenbauer Polynomials.

$$\left| \underline{R} - \underline{r_1} + \underline{r_2} \right|^{-2\nu} = \sum_{n=0}^{\infty} C_n^{\nu}(-\cos X) \frac{r_2^n}{\left| R - r_1 \right|^{n+2\nu}} \quad , \quad |r_2| < |R - r_1|$$

$$= \sum_{n=0}^{\infty} C_n^{\nu}(-\cos X) r_2^n \sum_{K=0}^{\infty} C_K^{\frac{n+2\nu}{2}}(\cos\theta_1) \frac{r_1^K}{R^{n+K+2\nu}} \qquad 3.3$$

$$= \sum_{n=0}^{\infty} C_n^{\nu}(+\cos y) r_1^n \sum_{K=0}^{\infty} C_K^{\frac{n+2\nu}{2}}(\cos\theta_2) \frac{r_2^K}{R^{n+K+2\nu}} \quad , \qquad 3.4$$

$$|r_1| < |R| , |r_2| < |R| .$$

where $(\theta_1, \phi_1)$ and $(\theta_2, \phi_2)$ are the polar angles of $\underline{r_1}$ and $\underline{r_2}$ referred to $\underline{R}$ as polar as shown in Fig. 3.1.
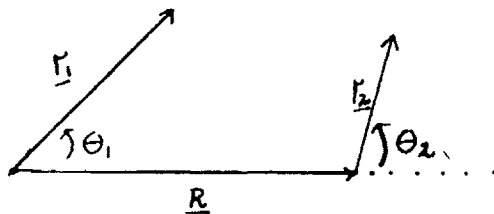


Fig. 3.1

$$\cos X = \frac{\cos\theta_2 (\underline{R} - r_1 \cos\theta_1) + r_1 \sin\theta_2 \sin\theta_1 \cos(\phi_1 - \phi_2)}{|\underline{R} - r_1|} \qquad 3.5$$

$$\cos y = \frac{\cos\theta_1 (\underline{R} + r_2 \cos\theta_2) + r_2 \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)}{|\underline{R} + r_2|} \qquad 3.6$$

Using 3.5 it will be proved that

$$\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} C_n^\nu(-\cos X)\, C_\kappa^{\frac{n+1}{2}\nu}(\cos\theta_1)\, \sin\theta_2 \, d\theta_2 \, d\phi_1 \, d\phi_2$$

$$= \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} C_n^\nu(-\cos\theta_2)\, C_\kappa^{\frac{n+1}{2}\nu}(\cos\theta_1)\, \sin\theta_2 \, d\theta_2 \, d\phi_1 \, d\phi_2 \qquad 3.7$$

Proof of 3.7.

$$\cos^n X = \sum_{s=0}^n \frac{n!}{(n-s)! s!} \frac{(\cos\theta_2)^{n-s}\, a^{n-s}\, \sin^s\theta_2 \cos^s(\phi_1-\phi_2)\, b^s}{|\underline{R}-\underline{r}_1|^n} \qquad 3.8$$

where $a = (\underline{R} - r_1\cos\theta_1)$, $b = r_1\sin\theta_1$

$$\int_0^{2\pi} \int_0^{2\pi} \cos^s(\phi_1-\phi_2)\, d\phi_1 \, d\phi_2$$

$$= \left(\frac{1}{2}\right)^s \int_0^{2\pi} \int_0^{2\pi} \left[ e^{i(\phi_1-\phi_2)} + e^{-i(\phi_1-\phi_2)} \right]^s \, d\phi_1 \, d\phi_2$$

$$= \sum_{v=0}^s \left(\frac{1}{2}\right)^s \frac{s!}{(s-v)!(v)!} \int_0^{2\pi} \int_0^{2\pi} e^{i(s-2v)(\phi_1-\phi_2)} \, d\phi_1 \, d\phi_2$$

$$= 0 \qquad \text{if} \qquad s-2v \neq 0$$

$$\int_0^{2\pi}\int_0^{2\pi} \cos^s(\phi_1-\phi_2)\, d\phi_1\, d\phi_2 = 0 \qquad s \neq 2\nu$$

$$= \left(\tfrac{1}{2}\right)^s \frac{s!}{\frac{s}{2}!\,\frac{s}{2}!} \int_0^{2\pi}\int_0^{2\pi} d\phi_1\, d\phi_2$$

if $S$ is even      3.9

$$\int_0^{\tau} \cos^\alpha\theta \sin^\beta\theta\, d\theta = \frac{(\alpha-1)}{(\alpha+\beta)} \int_0^{\tau} \cos^\alpha\theta \sin^{\beta-2}\theta\, d\theta$$

By repeated application with $\beta$ odd this reduces to

$$\frac{(\alpha+1)!!\,(\beta-1)!!}{(\alpha+\beta)!!} \int_0^{\tau} \cos^\alpha\theta \sin\theta\, d\theta$$

Therefore

$$= 0 \qquad \text{if} \quad \alpha \quad \text{odd}$$

$$= \frac{(\alpha-1)!!\,(\beta-1)!!}{(\alpha+\beta)!!} \int_0^{\tau} \sin\theta\, d\theta \qquad \text{if} \quad \alpha \quad \text{even}$$

$$\int_0^{\pi} \cos^{n-s}\theta \sin^{s+1}\theta\, d\theta \qquad \text{with} \quad S \quad \text{even}$$

$$\text{requires} \quad n \quad \text{even}$$

$$= \frac{(n-s-1)!!\,S!!}{(n+1)!!} \int_0^{\tau} \sin\theta\, d\theta = \frac{(n-s-1)!!\,S!!}{(n-1)!!} \int_0^{\tau} \cos^n\theta \sin\theta\, d\theta \quad 3.10$$

Place 3.9 and 3.10 in 3.8 and integrating gives

$$\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \sum_{s=0}^{n} \frac{n!}{(n-s)!s!} \left(\frac{1}{2}\right)^s \frac{s!}{\frac{s}{2}!\frac{s}{2}!} \frac{(n-s-1)!!s!!}{(n-1)!!} \frac{a^{n-s}b^s}{|\underline{R}-\underline{r}_1|^n} \cos^n\theta_2 \sin\theta_2 d\theta_2 d\phi_1 d\phi_2$$

$$= \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \sum_{s=0}^{n} \frac{n!!}{(n-s)!!} \frac{1}{s!!} \frac{a^{n-s}b^s \cos^n\theta_2 \sin\theta_2 d\theta_2 d\phi_1 d\phi_2}{|\underline{R}-\underline{r}_1|^n}$$

$$= \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \sum_{\frac{s}{2}=0}^{\frac{n}{2}} \frac{\frac{n}{2}!}{(\frac{n}{2}-\frac{s}{2})!\frac{s}{2}!} \frac{(a^2)^{\frac{n-s}{2}}(b^2)^{\frac{s}{2}} \cos^n\theta_2 \sin\theta_2 d\theta_2 d\theta_2 d\phi_1 d\phi_2}{|\underline{R}-\underline{r}_1|^n}$$

$$= \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \cos^n\theta_2 \sin\theta_2 d\theta_2 d\phi_1 d\phi_2 \qquad\qquad 3.11$$

$$= 0 \quad \text{for } n \text{ odd} \qquad\qquad 3.12$$

With $C_n^{\nu}(-\cos\chi)$ expanded as in 3.1 and using 3.12

$$\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} C_n^{\nu}(-\cos\chi) C_k^{\frac{n+2\nu}{2}}(\cos\theta_1) \sin\theta_2 d\theta_2 d\phi_1 d\phi_2$$

$$= \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} C_n^{\nu}(-\cos\theta_2) C_k^{\frac{n+2\nu}{2}}(\cos\theta_1) \sin\theta_2 d\theta_2 d\phi_1 d\phi_2$$

which is the required proof of 3.7 .

Since

$$\frac{d}{dz} C_{n+1}^{\nu-1} = 2(\nu-1) C_n^{\nu}(z) \qquad \text{Bateman 178,30}$$

then

$$\int_{-1}^{1} d C_{n+1}^{\nu-1}(x) = 2(\nu-1) \int_{-1}^{1} C_n^{\nu}(z)\, dz$$

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

$$= \frac{2\sqrt{n+2\nu-1}}{2(\nu-1)(n+1)!\sqrt{2(\nu-1)}} \qquad \text{Bateman 176,7}$$

$$= \frac{2\sqrt{n+2\nu-1}}{(n+1)!\sqrt{2\nu-1}} \qquad \text{if } n \text{ even} \left.\begin{array}{c} \\ \\ \\ \\ \end{array}\right\} 3.13$$

$$= 0 \qquad \text{if } n \text{ odd}$$

As a result

$$\nu=\tfrac{1}{2} \qquad \int_{-1}^{1} C_n^{\tfrac{1}{2}}(z)\, dz = \frac{2\sqrt{n}}{(n+1)!\sqrt{0}}$$

$$= 0 \qquad n \neq 0 \left.\begin{array}{c} \\ \\ \end{array}\right\} 3.14$$

$$= 2 \qquad n = 0$$

$$\nu = 1 \; ; \quad \int_{-1}^{1} C_n^1(z)\, dz \;=\; \frac{2\sqrt{n+1}}{(n+1)!\,\sqrt{1}}$$

$$= \; \frac{2}{(n+1)} \qquad \text{if } n \text{ even}$$

$$= \; 0 \qquad \text{if } n \text{ odd} \qquad\qquad 3.15$$

$$\nu = \frac{n+2}{2}\; ; \quad \int_{-1}^{1} C_K^{\frac{n+2}{2}}(z)\, dz \;=\; \frac{2\sqrt{K-1+n+2}}{(K+1)!\,\sqrt{n+2-1}}$$

$$= \; \frac{2\sqrt{K+n+1}}{(K+1)!\,\sqrt{n+1}}$$

$$= \; \frac{2\,(K+n)!}{(K+1)!\;n!} \qquad \text{if } K \text{ even}$$

$$= \; 0 \qquad\qquad \text{if } K \text{ odd} \qquad 3.16$$

With $\nu = \frac{1}{2}$ and $\gamma = 1$ in 3.2 using result 3.14 and 3.15 in 3.2 and with $\nu = \frac{1}{2}$, $\gamma = 1$, and $\nu = \frac{n+2}{2}$ using 3.14, 3.15, and 3.16 with 3.7 in 3.3 these results follow:

$$\int_{0}^{\pi} |R - r_1|^{-1} \sin\theta\, d\theta \;=\; \frac{2}{R} \qquad\qquad 3.17$$

$$\int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} |\underline{R} - \underline{r}_1 + \underline{r}_2|^{-1} \sin\theta_1 \, d\theta_1 \, \sin\theta_2 \, d\theta_2 \, d\phi_1 \, d\phi_2$$

$$= \frac{16\pi^2}{R} \qquad \begin{array}{l} |r_1| < |R| \\ |r_2| < |R| \end{array} \qquad \qquad 3.18$$

$$\int_0^\pi |R - \underline{r}_1|^{-2} \sin\theta \, d\theta = \sum_{n=0}^{\infty} \frac{2}{(n+1)} \frac{r_1^n}{R^{n+2}} \qquad |r_1| < R$$
$$\text{if } n \text{ even}$$

$$= \sum_{n=0}^{\infty} \frac{2}{(2n+1)} \frac{r_1^{2n}}{R^{2n+2}} \quad \text{all } n \qquad 3.19$$

$$\int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} |\underline{R} - \underline{r}_1 + \underline{r}_2|^{-2} \sin\theta_1 \, d\theta_1 \, \sin\theta_2 \, d\theta_2 \, d\phi_1 \, d\phi_2$$

$$= 16\pi^2 \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(k+n)!}{(k+1)!\,(n+1)!} \frac{r_1^k \, r_2^n}{R^{n+k+2}} \qquad \begin{array}{l} \text{if } k \text{ even} \\ \text{and } n \text{ even} \end{array}$$

$$= 16\pi^2 \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(2k+2n)!}{(2k+1)!\,(2n+1)!} \frac{r_1^{2k} \, r_2^{2n}}{R^{2n+2k+1}} \qquad 3.20$$

Since

$$\left| \underline{R} - \underline{r}_1 \right|^{-\nu_1} \cdot \left| \underline{R} - \underline{r}_2 \right|^{-\nu_2} = \left| \underline{R} - \underline{r}_1 \right|^{-(\nu_1 + \nu_2)}$$

then

$$\sum_{p=0}^{\infty} C_p^{\nu_1/2}(\cos\theta_1) \frac{r_1^p}{R^{p+1}} \cdot \sum_{s=0}^{\infty} C_s^{\nu_2/2}(\cos\theta_1) \frac{r_1^s}{R^{s+1}}$$

$$= \sum_{n=0}^{\infty} C_n^{\frac{\nu_1+\nu_2}{2}}(\cos\theta_1) \frac{r_1^n}{R^{n+2}} \qquad\qquad 3.21$$

and $C_n^{\frac{\nu_1+\nu_2}{2}}$ comes from $C_p^{\frac{\nu_1}{2}}$ $C_s^{\nu_2/2}$

where $p+s = n$ for all $0 \le p \le n, \ 0 \le s \le n$ .

as a result

$$\left| \underline{R} - \underline{r}_1 + \underline{r}_2 \right|^{-\nu_1} \cdot \left| \underline{R} - \underline{r}_1 \right|^{-\nu_2}$$

$$= \sum_{p=0}^{\infty} C_p^{\frac{\nu_1}{2}}(-\cos\chi) \, r_2^p \sum_{k=0}^{\infty} C_r^{\frac{\nu_1+p}{2}}(\cos\theta_1) \frac{r_1^k}{R^{p+k+\nu_1}} \cdot \sum_{s=0}^{\infty} C_s^{\nu_2/2}(\cos\theta_1) \frac{r_1^s}{R^{s+\nu_2}}$$

$$= \sum_{n=0}^{\infty} C_n^{\frac{\nu_1}{2}}(-\cos\chi) \, r_2^p \sum_{k=0}^{\infty} C_k^{\frac{\nu_1+\nu_2+p}{2}}(\cos\theta_1) \frac{r_1^k}{R^{n+k+\nu_1+\nu_2}} \qquad 3.22$$

Thus

$$\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} |\underline{R}-\underline{r_1}+\underline{r_2}|^{-1} |\underline{R}-\underline{r_1}|^{-1} \sin\theta_1 \sin\theta_2 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2$$

$$= 16\pi^2 \sum_{n=0}^{\infty} \frac{r_1^{2n}}{(2n+1)} \cdot \frac{1}{R^{2n+2}} \qquad\qquad 3.23$$

One more general angular result is needed.

$$C_n^{\nu}\left[z_1 z - (z_1^2-1)^{1/2}(z^2-1)^{1/2}\cos\phi\right]$$

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

$$\left. (z_1^2-1)^{\ell/2}(z^2-1)^{\ell/2} C_{n-\ell}^{\nu+\ell}(z_1) C_{n-\ell}^{\nu+\ell}(z) C_\ell^{\nu-1/2}(\cos\phi)\right]$$

Bateman 177,19

$$3.24$$

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

$$C_n^{1/2}\left[z_1 z - (z_1^2-1)^{1/2}(z^2-1)^{1/2}\cos\phi\right] = P_n(z) P_n(z_1)$$

$$+ \sum_{\ell=1}^{m} \frac{(n-\ell)!}{(n+\ell)!} P_n^\ell(z) P_n^\ell(z_1)\cos\ell\phi \qquad 3.25$$

For $\gamma = \psi$ the expansion is

$$C_n' \left[ z z_1 - (z_1^2 - 1)^{1/2} (z^2 - 1)^{1/2} \cos\phi \right]$$

$$= \sum_{\ell=0}^{n} 4^{\ell} \frac{(n-\ell)!}{(n+\ell+1)!} (\ell!)^2 (2\ell+1)(1-z^2)^{1/2}(1-z_1^2)^{1/2} \times$$

$$C_{n-\ell}^{\ell+1}(z_1) \, C_{n-\ell}^{\ell+1}(z) \, C_{\ell}^{1/2}(\cos\phi) \qquad\qquad 3.25$$

An equivalent expansion for $|\underline{R} - \underline{r_j} + \underline{r_2}|^{-1}$ in the region $|\underline{r_1}| \lessgtr |\underline{R}|$; $|\underline{r_2}| \lessgtr |\underline{R}|$ is

$$|\underline{R} - \underline{r_j} + \underline{r_2}|^{-1} = \sum_{n=0}^{\infty} (-1)^n \frac{(\nabla \cdot \underline{r_j})^n}{n!} \sum_{k=0}^{\infty} \frac{(\nabla \cdot \underline{r_2})^k}{k!} \cdot \frac{1}{R}$$

$$\equiv \sum_{k=0}^{\infty} \sum_{n=0}^{\infty} C_k^{1/2}(-\cos\chi) \, C_n^{k+1/2}(\cos\theta_1) \, \frac{r_2^k \cdot r_1^n}{R^{n+k+1}} \qquad 3.26$$

where 

$$\underline{r_j} = i\, x_i + j\, y_i + \kappa\, z_i$$

$$\underline{R} = i\, X_i + j\, Y + \kappa\, Z$$

$$\nabla = i\, \frac{\partial}{\partial x} + j\, \frac{\partial}{\partial y} + \kappa\, \frac{\partial}{\partial z}$$

$$\nabla_i = i\, \frac{\partial}{\partial x_i} + j\, \frac{\partial}{\partial y_i} + \kappa\, \frac{\partial}{\partial z_i}$$

Then

$$(-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{1}{R} = C_n^{\frac{1}{2}}(\cos\theta_i) \frac{r^n}{R^{n+1}} \qquad 3.26$$

$$\nabla_1 (-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{1}{R} = -\nabla (-1)^{n-1} \frac{(\nabla \cdot \vec{r})^{n-1}}{(n-1)!} \frac{1}{R}$$

$$= -\nabla C_{n-1}^{\frac{1}{2}}(\cos\theta) \frac{r_1^{n-1}}{R^n} \qquad 3.27$$

And

$$(\vec{r_1} \cdot \nabla_1)(-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{1}{R} = n (-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{1}{R}$$

$$= n C_n^{\frac{1}{2}}(\cos\theta_1) \frac{r_1^n}{R^{n+1}} \qquad 3.28$$

Also

$$(\vec{r_1} \cdot \nabla_1)\left\{ \sum_{n=0}^{\infty} (-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{1}{R} \cdot \sum_{p=0}^{\infty} (-1)^p \frac{(\nabla \cdot \vec{r_1})^p}{p!} \frac{1}{R} \right\}$$

$$= \left\{ \sum_{n=0}^{\infty} (-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{1}{R} \cdot \sum_{p=0}^{\infty} (-1)^p \frac{(\nabla \cdot \vec{r_1})^p}{p!} \frac{1}{R} \right\} \left\{ n+p \right\}$$

$$= \sum_{s=0}^{\infty} S C_s^{1}(\cos\theta_1) \frac{r_1^s}{R^{s+2}} \qquad 3.29$$

So

$$(\vec{r_1} \cdot \nabla_1)\left\{ \sum_{n=0}^{\infty} (-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \sum_{k=0}^{\infty} \frac{(\nabla \cdot \vec{r_2})^k}{k!} \frac{1}{R} \cdot \sum (-1)^p \frac{(\nabla \cdot \vec{r_1})^p}{p!} \frac{1}{R} \right\}$$

$$= \sum_{k=0}^{\infty} \sum n C_k^{\frac{1}{2}}(-\cos x) C_p^{\frac{k+2}{2}}(\cos\theta_1) \frac{r_1^p r_2^k}{R^{p+k+2}} \qquad 3.30$$

Equivalent results are obtained in the co-ordinates of point two. These are obtained by replacing all subscripts 1 by 2 and vise versa.

A furthur 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.

$$(\vec{r_1} \cdot \nabla_1) \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} (-1)^n \frac{(\nabla \cdot \vec{r_1})^n}{n!} \frac{(\nabla \cdot \vec{r_2})^k}{k!} \frac{1}{R} \cdot \sum_{s=0}^{\infty} \sum_{T=0}^{\infty} (-1)^s \frac{(\nabla \cdot \vec{r_1})^s}{s!} \frac{(\nabla \cdot \vec{r_2})^T}{T!} \frac{1}{R}$$

$$= \sum_{a=0}^{\infty} \sum_{b=0}^{\infty} b \, C_k^1(-\cos x) \, C_b^{\frac{k+1}{2}}(\cos \theta_1) \frac{r_1^b \, r_2^a}{R^{a+b+1}} \qquad 3.31$$

The radial integration of section 4 is of the type

$$\int_0^{\sigma} e^{-2r} r^{n+2} \, dr = \frac{1}{2^{n+3}} \int_0^{2\sigma} e^{-r} r^{n+2} \, dr = I_{n+3}(2\sigma)$$

$$I_{n+3}^{(2\sigma)} = \frac{1}{2^{n+3}} \left\{ \sqrt{n+3} - e^{-2\sigma} \sum_{a=0}^{n+2} \frac{(n+2)!}{(n+2-a)!} (2\sigma)^{n+2a-a} \right\} \qquad 3.32$$

These integrals are tabulated below for values of $2\sigma$

$2\sigma = 6, 8, 10, 12, 16, 20$ covering cases (1),(2) and (3) of Section 4.

Tabulation of $I_{n+3}(2\sigma)$

| $n$ | $\infty$ | 6 | 8 | 10 | 12 | 16 | 20 |
|---|---|---|---|---|---|---|---|
| 0 | ·250 | ·235 | ·247 | ·249 | ·250 | ·250 | ·250 |
| 1 | ·375 | ·318 | ·361 | ·371 | ·374 | ·375 | ·375 |
| 2 | ·750 | ·521, | ·676 | ·728 | ·744 | ·750 | ·750 |
| 3 | 1·875 | 1·000 | 1·519 | 1·749 | 1·837 | 1·872 | 1·875 |
| 4 | 5·625 | 2·095 | 4·065 | 4·895 | 5·392 | 5·603 | 5·624 |
| 5 | 19·6875 | 4·620 | 10·760 | 15·340 | 27·940 | 19·491 | 19·671 |
| 6 | 78·750 | 9·790 | 32·150 | 52·650 | 62·550 | 77·030 | 78·590 |

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 indioies in $\lambda_1, \lambda_2, u_1, u_2$ particular general results hold and these will be first investigated.

$$I = N^2 \iiint\limits_{1}^{0}\iiint\limits_{0}^{2\pi}\iiint\limits_{1}^{0}\iiint\limits_{-1}^{0}\iiint\limits_{0}^{2\pi} \left\{ e^{-zd(\lambda_1 + u_1 + \lambda_2 - u_2)} + e^{-zd(\lambda_1 - u_1 + \lambda_2 + u_2)} \right\}^2 \lambda_1^m u_1^p \lambda_2^n u_2^q$$

$$\times \frac{d^6}{8\cdot 8}(\lambda_1^2 - u_1^2)(\lambda_2^2 - u_2^2)\, d\lambda_1\, du_1\, d\phi_1\, d\lambda_2\, du_2\, d\phi_2 \qquad 3.33$$

where $\qquad N^2 = \dfrac{z^6}{2\pi^2(1+D^2)}$

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

$$zd = S = (1.166)(1.438) = 1.677$$

where $z$ is the value of the screening parameter and $d$ is the internuclear separation of the hydrogen atoms.

$$I = \frac{S^6}{32(1+D^2)}\iiint\limits_{1}^{0}\iiint\limits_{-1}^{1}\iiint\limits_{1}^{0}\iiint\limits_{-1}^{1}\left\{ e^{-S(\lambda_1 + u_1 + \lambda_2 - u_2)} + e^{-S(\lambda_1 - u_1 + \lambda_2 + u_2)} + 2e^{-S(\lambda_1 + \lambda_2)} \right\}$$

$$\times \left(\lambda_1^{m+2}u_1^p - \lambda_1^m u_1^{p+2}\right)\left(\lambda_2^{n+2}u_2^q - \lambda_2^n u_2^{q+2}\right) d\lambda_1\, du_1\, d\lambda_2\, du_2 \qquad 3.34$$

$$I(p \text{ and } q \text{ odd}) = \frac{S^6}{32(1+D^2)}\iiint\limits_{1}^{0}\iiint\limits_{-1}^{1}\iiint\limits_{1}^{\infty}\iiint\limits_{-1}^{1}\left\{ e^{-S(\lambda_1 + u_1 + \lambda_2 - u_2)} + e^{-S(\lambda_1 - u_1 + \lambda_2 + u_2)} \right\}$$

$$\times \left(\lambda_1^{m+2}u_1^p - \lambda_1^m u_1^{p+2}\right)\left(\lambda_2^{n+2}u_2^q - \lambda_2^n u_2^{q+2}\right) d\lambda_1\, du_1\, d\lambda_2\, du_2 \qquad 3.35$$

By replacing $u_1$ by $-u_1$ and $u_2$ by $-u_2$ 3.35 becomes

$$I = \frac{S^6}{32(1+D^2)} \int_{1}^{\infty}\int_{-1}^{1}\int_{1}^{\infty}\int_{-1}^{1} \left[ \left(1+(-1)^{p+q}\right)\left\{ e^{-S(\lambda_1+u_1+\lambda_2-u_2)} \right\} + 2e^{-S(\lambda_1+\lambda_2)} \right]$$

$$\times \left[ \left(\lambda_1^{m+2}u_1^{p} - \lambda_1^{m}u_1 \right)\left(\lambda_2^{n+2}u_2^{q} - \lambda_2^{n}u_2^{q+2}\right) \right] d\lambda_1 du_1 d\lambda_2 du_2$$

$$= 0 \qquad p+q \text{ odd} \qquad\qquad 3.36$$

$$= \frac{S^6}{16(1+D^2)} \int_{1}^{\infty}\int_{-1}^{1}\int_{1}^{\infty}\int_{-1}^{1} e^{-S(\lambda_1+u_1+\lambda_2-u_2)}\left(\lambda_1^{m+2}u_1^{p}-\lambda_1^{m}u_1^{m+2}\right)\left(\lambda_2^{n+2}u_2^{q}-\lambda_2^{n}u_2^{q+2}\right)d\lambda_1 du_1 d\lambda_2 du_2$$

$$\begin{array}{c} p+q \quad \text{even} \\ p \text{ or } q \text{ odd} \end{array} \qquad 3.37$$

$$= \frac{S^6}{16(1+D^2)} \int_{1}^{\infty}\int_{-1}^{1}\int_{1}^{\infty}\int_{-1}^{1} \left\{ e^{-S(\lambda_1+u_1+\lambda_2-u_2)} + e^{-S(\lambda_1+\lambda_2)} \right\}$$

$$\times \left\{ \left(\lambda_1^{m+2}u_1^{p}-\lambda_1^{m}u_1^{p+2}\right)\left(\lambda_2^{n+2}u_2^{q}-\lambda_2^{n}u_2^{q+2}\right)\right\} d\lambda_1 du_1 d\lambda_2 du_2$$

$$\begin{array}{c} p+q \quad \text{even} \\ p \text{ and } q \text{ odd} \end{array} \qquad 3.38$$

$$\int_{1}^{\infty}\int_{-1}^{1} e^{-S\lambda_2}\left(\lambda_2^{2}-u_2^{2}\right)d\lambda_2 du_2 = \frac{4}{S^3}D \qquad 3.39$$

$$\int_{1}^{\infty}\int_{-1}^{1} e^{-S(\lambda_2-u_2)}\left(\lambda_2^{2}-u_2^{2}\right)d\lambda_2 du_2 = \frac{4}{S^3} \qquad 3.40$$

Particular cases desired:

$$m = 2, \quad n = 0, \quad p = 0, \quad g = 0 \qquad I_1$$

$$m = 0, \quad n = 0, \quad p = 2, \quad g = 0 \qquad I_2$$

$$m = 2, \quad n = 0, \quad p = 2, \quad g = 0 \qquad I_3$$

$$m = 1, \quad n = 1, \quad p = 1, \quad g = 1 \qquad I_4$$

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

$$I_1 + I_2 = \frac{S^3}{4(1+D^2)} \int_1^\infty \int_{-1}^1 \left( e^{-S(\lambda_1 + \mu_1)} + De^{-S\lambda} \right) \left( \lambda_1^4 - \mu_1^4 \right) d\lambda \, d\mu,$$

$$= \frac{S^3}{4(1+D^2)} \left( \frac{8}{S^5} (S^2+6) + \frac{2De^{-S}}{S^5} \left( S^4 + 4S^3 + 12S^2 + 24S + 24 - \frac{S^4}{5} \right) \right)$$

$$= \frac{2}{S^2(1+D^2)} \left( S^2 + 6 + 6D^2 + De^{-S} \left( \frac{S^4}{5} + S^3 + S^2 \right) \right)$$

$$I_1 + I_2 = 6.472 \qquad\qquad\qquad 3.41$$

Using the same properties as for 3.41,

$$I_3 = \frac{S^3}{4(1+D^2)} \iint\limits_{1}^{\infty}\int\limits_{-1}^{1} \left\{ e^{-S(\lambda_1 + u_1)} + De^{-S\lambda_1} \right\} \left\{ \lambda_1^4 u_1^2 - \lambda_1^2 u_1^4 \right\} d\lambda_1 \, du_1$$

$$= \frac{1}{S^2(1+D^2)} \left( S^2 + 4 + \frac{De^{-S}}{15} \left( S^4 + 7S^3 + 28S^2 + 60S + 60 \right) \right)$$

$$= 2.239.$$ 
<span style="float:right">3.42</span>

Using 3.37

$$I_4 = \frac{S^6}{16(1+D^2)} \iint\limits_{1}^{\infty}\int\limits_{-1}^{1}\iint\limits_{1}^{\infty}\int\limits_{-1}^{1} e^{-S(\lambda_1 + u_1 + \lambda_2 - u_2)} (\lambda_1^3 u_1 - \lambda_1 u_1^3)(\lambda_2^3 u_2 - \lambda_2 u_2^3) \, d\lambda_1 \, du_1 \, d\lambda_2 \, du_2$$

$$= \frac{-S^6}{16(1+D^2)} \left[ \iint\limits_{1}^{\infty}\int\limits_{-1}^{1} e^{-S(\lambda_1 + u_1)} (\lambda_1^3 u_1 - \lambda_1 u_1^3) \, d\lambda_1 \, du_1 \right]^2$$

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

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

$$= -0.685$$
<span style="float:right">3.43</span>

# 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.
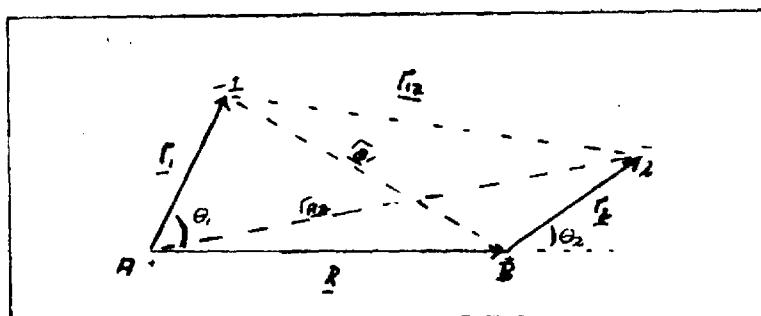


Fig. 4.1

Interparticle distances are denoted as in the figure. The polar angles $(\theta_1, \phi_1)$ of $\underline{r}$ and $(\theta_2, \phi_2)$ of $\underline{s}$ are referred to the internuclear distance $\underline{R} = AB$ 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 $\underline{R}$.

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,

$$V(R) = \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \qquad . \qquad 4.1$$

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 pertubation
is negligible.

In the calculation of the long range interaction
energy the usual method is to obtain a series representa-
tion 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 $r_1 < R, r_2 < R$.

Case 1. If there is to be no overlap it is
necessary that the atomic wave functions vanish for $r_1 \gg R/2$,
$r_2 \gg R/2$ . This requires a renormalization of the wave
function, and the series for the potential is valid.

Case 2. The atomic wave functions vanish for $r_1 \gg R$,
$r_2 \gg R$ . 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 renormal-
ization of the wave function.

. Case 3. The atomic wave functions extend through-
out 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 $\psi_{A_1}(1)$ and $\psi_{B_2}(2)$ centered on A and B respect-
ively where

$$\psi_{A_1}(1) = N e^{-r_1} \qquad , \qquad \psi_{B_2}(2) = N e^{-r_2}$$

and

$$N^{-2} = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} e^{-2r} r_1^2 \, dr_1 \, \sin\theta \, d\theta \, d\phi$$

where $\sigma, \rho_2, R, \infty$ as for cases (1),(2) and (3) respectively.

Because V(R) is small the distortion of the unper-
turbed binary system is taken to be linearly dependant on
V(R) and to be of the form

$$\psi = \psi_{A_1}(1) \, \psi_{B_2}(2) \left( 1 + \lambda V \right) \tag{4.3}$$

where $\lambda$ is a parameter to be used to minimize the energy.

Using the variational principle the energy of the perturbed system is

$$E = \int \psi^* H \psi \, d\tau \Big/ \int \psi^* \psi \, d\tau = I\big/J \qquad 4.4$$

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

$$\iint \psi_{A1}^{(1)} \psi_{B2}^{(2)} f \, \psi_{A1}^{(1)} \psi_{B2}^{(2)} \, d\tau_1 \, d\tau_2 = \langle f \rangle \qquad \text{in } 4.5$$

$$I = \left\langle (1+\lambda V) H (1+\lambda V) \right\rangle \quad ,$$

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

where

$$H = H_0 + V$$

$$H_0 = H_{01} + H_{02} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{r_1} - \tfrac{1}{r_2} \; .$$

Using 3.2 and 3.3  is represented by

$$V(R) = \frac{1}{R} + \sum_{n=0}^{\infty} \sum_{K=0}^{\infty} C_K^{\frac{1}{2}}(-\cos X) \, r_2^K \, C_n^{\frac{K+1}{2}}(\cos\theta_1) \, r_1^n \, \frac{1}{R^{n+K+1}}$$

$$- \sum_{n=0}^{\infty} C_n^{\frac{1}{2}}(\cos\theta_1) \frac{r_1^n}{R^{n+1}} - \sum_{K=0}^{\infty} C_K^{\frac{1}{2}}(\cos\theta_2) \frac{r_2^K}{R^{K+1}}$$

$$= \sum_{n=1}^{\infty} \sum_{K=1}^{\infty} C_K^{\frac{1}{2}}(-\cos X) \, C_n^{\frac{K+1}{2}}(\cos\theta_1) \, \frac{r_2^K r_1^n}{R^{n+K+1}} \qquad 4.6$$

Therefore

$$\langle V(R) \rangle = 0 \quad \text{by } 3.14 \qquad 4.7$$

$$HV = H_0 V \neq V^2$$

$$H_0 V \psi_{A1} \psi_{B2} = V H_0 \psi_{A1} \psi_{B2} + \psi_{A1}\psi_{B2}\left(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2\right) V$$

$$- \left(\nabla_2 V \cdot \nabla_2 + \nabla_1 V \cdot \nabla_1\right) \psi_{A1} \psi_{B2}$$

$$= V H_0 \psi_{A1} \psi_{B1} + \left(\frac{r_1 \cdot \nabla_1}{r_1} V + \frac{r_2 \cdot \nabla_2 V}{r_2}\right) \psi_{A1} \psi_{B2}$$

$$= \left(V H_0 + S\right) \psi_{A1} \psi_{B2}$$

using 4.1 and 3.2?  ?ay be written in the form

$$S = \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} C_k^{\tfrac{k}{2}}(-\cos x)\, C_n^{\tfrac{n}{2}}(\cos\theta_2) \left\{\frac{n\, r_1^{\,n-1} r_2^{\,k} + k\, r_1^{\,n} r_2^{\,k-1}}{R^{\,n+k+1}}\right\}$$

$\langle S \rangle = 0$  by 3.7 and 3.14

$$\langle HV \rangle = \langle H_0 V + V^2 \rangle = \langle V^2 + V H_0 + S \rangle = \langle VH + S \rangle$$

$$\langle VHV \rangle = \langle V^3 + V H_0 V \rangle$$

$$= \langle V^3 + V(V H_0 + S)\rangle =$$

$$= \langle V^3 + V^2 H_0 + VS \rangle$$

$$= \langle V^2 H + VS \rangle$$

$$VS = \tfrac{1}{2}\left\{\frac{r_1 \cdot \nabla_1}{r_1} V^2 + \frac{r_2 \cdot \nabla_2}{r_2} V^2\right\} \qquad \text{since} \qquad \text{is scaler.}$$

4.9

$$\langle V^3 \rangle = \left\langle \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} C_k^{1/2}(-\cos x) C_n^{\frac{k+1}{2}}(\cos\theta_1) \frac{r_2^k r_1^n}{R^{n+k+1}} \right]^2 \right\rangle$$

Using the result 3.7 this may be written

$$= \left\langle \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} C_k^{1/2}(\cos\theta_2) C_n^{\frac{k+1}{2}}(\cos\theta_1) \frac{r_2^k r_1^n}{R^{n+k+1}} \right]^3 \right\rangle \qquad 4.10$$

Using the expansion 3.1 this form will involve products

of the angle $\cos\theta_2$ as well as $\cos\theta_1$ and the average values

for $\quad K+K'+K'' = 1+1+2$

$\quad n+n'+n'' = 1+1+2 \quad$ 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 $R^{-10} \langle V^3 \rangle$ does not appear.

Since $\mathbf{E}$ is the solution of the Schrodinger equation

$$H_{0i} \psi_{A1} \psi_{B2} = E_{0i} \psi_{A1} \psi_{B2} \qquad (i=1,2)$$

then $\quad H_0 \psi_{A1} \psi_{B2} = E_0 \psi_{A1} \psi_{B2} \quad , E_{01} + E_{02} = E$ .

Placing the results 4.6, 4.8 and 4.10 in $\mathbf{I}$ and $\mathbf{J}$ gives

$$\mathbf{I} = \langle (1+\lambda V) H (1+\lambda V) \rangle = E_0 (1+\lambda^2 V^2) \lambda^2 \langle VS \rangle + 2\lambda \langle V^2 \rangle ,$$

$$\mathbf{J} = \langle 1+\lambda^2 V^2 \rangle$$

Placing $I$ and $J$ in 4.3 gives

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

A necessary condition for a minimum value of $\Delta E$ is that $\partial \Delta E / \partial \lambda = 0$ 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 4.1

$$\text{therefore } 0 = \left[ \langle 1 \rangle + \lambda^2 \langle v^2 \rangle \right] \left[ \lambda \langle VS \rangle + \langle v^2 \rangle \right] - \left[ \lambda^2 \langle VS \rangle + 2\lambda \langle v^2 \rangle \right] \lambda^2 \langle v^2 \rangle$$

$$= \langle 1 \rangle \left[ \lambda \langle VS \rangle + \langle v^2 \rangle \right] \qquad .$$

Therefore

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

And

$$\lambda = - \frac{\langle v^2 \rangle}{\langle VS \rangle} \qquad . \qquad 4.12$$

Substitution of 4.12 into 4.11 gives

$$\Delta E = \frac{\dfrac{\langle v^2 \rangle^2}{\langle VS \rangle^2} \langle VS \rangle - 2 \dfrac{\langle v^2 \rangle^2}{\langle VS \rangle}}{\langle 1 \rangle + \dfrac{\langle v^2 \rangle^6}{\langle VS \rangle^2}}$$

$$\Delta E = - \frac{\langle V^2 \rangle^2}{\langle 1 \rangle \cdot \langle VS \rangle} \qquad 4.13$$

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

$$V^2 = -\frac{1}{R^2} + \frac{1}{r_{12}^2} + \frac{1}{r_{A2}^2} + \frac{1}{r_{B1}^2} - \frac{2}{r_{12}} \left( \frac{1}{r_{A2}} + \frac{1}{r_{B1}} \right) + \frac{2}{r_{A2} r_{B1}} + \frac{1}{R} V \qquad 4.14$$

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

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

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

$$= \left\langle \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!(2k+1)!} \frac{r_1^{2n} r_2^{2k}}{R^{2n+2k+2}} \right\rangle 16 \pi^2 . \qquad 4.15$$

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

$$\langle V^2 \rangle = 16 \pi^2 \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!(2k+1)!} \frac{I_{2n+3} I_{2k+3}}{R^{2n+2k+2}} . \qquad 4.16$$

$$\langle 1 \rangle = 16\pi^2 I_3 \cdot I_3 \qquad \text{4.17}$$

as given by 4.

$$\langle VS \rangle = \left\langle \frac{1}{2} \left\{ \frac{r_1 \cdot \nabla_1}{r_1} \left( \frac{1}{r_{12}^2} + \frac{1}{r_{B1}^2} - \frac{2}{r_{12}} \left[ \frac{1}{r_{A2}} + \frac{1}{r_{B1}} \right] + \frac{2}{r_{A2} r_{B1}} \right) \right. \right.$$
$$\left. \left. + \frac{r_2 \cdot \nabla_2}{r_2} \left( \frac{1}{r_{12}^2} + \frac{1}{r_{A2}^2} - \frac{2}{r_{12}} \left[ \frac{1}{r_{A2}} + \frac{1}{r_{B1}} \right] + \frac{2}{r_{A2} r_{B1}} \right) + S \right\} \right\rangle \qquad \text{4.18}$$

using the results of 3.26 to 3.31 permits the above
expression to take the form

$$\langle VS \rangle = \frac{1}{2} \left\{ \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{(n r_1^{n-1} r_2^k + k r_1^n r_2^{k-1})}{R^{n+k+2}} \left\{ C_k^1(-\cos X) C_n^{\frac{k+3}{2}}(\cos\theta_1) \right. \right.$$

$$+ 2 C_n^{\frac{1}{2}}(\cos\theta_1) C_k^{\frac{1}{2}}(-\cos\theta_2) - 2 C_k^{\frac{1}{2}}(-\cos X) C_n^{\frac{k+3}{2}}(\cos\theta_1)$$

$$\left. - 2 C_n^{\frac{1}{2}}(\cos y) C_k^{\frac{n+3}{2}}(\cos\theta_2) \right\}$$

$$\left. + \sum_{n=0}^{\infty} C_n^1(\cos\theta_1) \frac{n r_1^{n-1}}{R^{n+2}} + \sum_{k=0}^{\infty} C_k^1(-\cos\theta_2) \frac{k r_2^{k-1}}{R^{k+2}} \right\} \qquad \text{4.19}$$

With 4.8, 4.7, and 3.29, 3.30, 3.31 and the same in point two

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

$$\left. - \sum_{n=0}^{\infty} \langle n\, r_1^{2n-1} \rangle \frac{1}{(2n+1)} \frac{1}{R^{2n+1}} - \sum_{k=0}^{\infty} \langle k\, r_2^{2k-1} \rangle \frac{1}{(2k+1)} \frac{1}{R^{2k+1}} \right]$$

$$= 16\pi^2 \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!\,(2k+1)!} \cdot \frac{\langle n\, r_1^{2n-1} r_2^{2k} + k\, r_2^{2k-1} r_1^{2n} \rangle}{R^{2n+2k+2}} \right]$$

$$= 16\pi^2 \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!\,(2k+1)!} \left\{ \frac{n\,I_{2n+2}\,I_{2k+3} + k\,I_{2n+3}\,I_{2k+2}}{R^{2n+2k+2}} \right\} \quad 4.20$$

Then

$$\Delta E = - \frac{\left[ \sum_{n=0}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!\,(2k+1)!} \cdot \frac{I_{2n+3}\,I_{2k+3}}{R^{2n+2k+2}} \right]^2}{I_3^2 \left[ \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \frac{(2n+2k)!}{(2n+1)!\,(2k+1)!} \left\{ \frac{n\,I_{2n+2}\,I_{2k+3} + k\,I_{2n+3}\,I_{2k+2}}{R^{2n+2k+2}} \right\} \right]}$$

$$= - \frac{\left[ \frac{2}{3} \frac{I_5^2}{R^6} + 2 \frac{I_7 I_5}{R^8} + \frac{14}{5} \frac{I_7^2}{R^{10}} + \frac{8}{3} \frac{I_5 I_9}{R^{10}} \right]^2}{I_3^2 \left[ \frac{4}{3} \frac{I_4 I_5}{R^6} + \frac{4 I_5 I_6 + 2 I_4 I_7}{R^8} + \frac{56}{5} \frac{I_6 I_7 + 8 I_5 I_9 + \frac{8}{3} I_4 I_9}{R^{10}} \right]}$$

Expanding by the binomial theorem

$$\Delta E = \frac{-3R^6}{4 I_3^2 I_4 I_5}\left[\ \frac{4}{9}\frac{I_6^4}{R^{12}}\ +\ \frac{8}{3}\frac{I_6^3 I_7}{R^{14}}\ +\ \frac{4 I_6^2 I_7^2 + \frac{55}{5} I_6^2 I_7^2 + \frac{32}{9} I_5^3 I_9}{R^{16}}\ \right]$$

$$\times\left[\ 1\ -\ \frac{3\frac{I_6}{I_4} + \frac{3}{2}\frac{I_7}{I_5}}{R^2}\ -\ \frac{\frac{42}{5}\frac{I_6 I_7}{I_4 I_5} + 6\frac{I_8}{I_4} + 2\frac{I_9}{I_5} - 9\frac{I_6^2}{I_4^2}}{R^4}\right.$$

$$\left. -\ \frac{-9\frac{I_7^2}{4 I_5^2} - 9\frac{I_6 I_7}{I_5 I_4}}{R^4}\ \right]$$

Collecting in powers of $R^{-1}$ to the order $\quad\cdot$

$$= -\left[\ \frac{\frac{1}{3}\frac{I_5^3}{I_3^2 I_4}}{R^6}\qquad \frac{\frac{3}{2}\frac{I_5^2 I_7}{I_3^2 I_4} - \frac{I_5 I_6}{I_3^2 I_4}}{R^8}\right.$$

$$\left. \frac{\frac{71}{20}\frac{I_5 I_7^2}{I_3^2 I_4} + 3\frac{I_5^3 I_6^2}{I_3^2 I_4^3} - 2\frac{I_5^2 I_8}{I_3^2 I_4^2} + 2\frac{I_5^2 I_9}{I_3^2 I_4} - 29\frac{I_5^2 I_6 I_7}{5 I_3^2 I_4^2}}{R^{10}}\ \right] \qquad 4.21$$

$$= -\frac{A}{R^6} - \frac{B}{R^8} - \frac{C}{R^{10}} \qquad\qquad 4.22$$

$$A = \frac{1}{3}\frac{I_5^3}{I_2 I_4} \qquad\qquad B = \frac{3 I_6^2 I_7}{I_3^2 I_4} - \frac{I_5^3 I_6}{I_3^2 I_4^2}$$

$$C = \frac{71 I_5 I_7^2}{20 I_3^2 I_4} + \frac{3 I_5^3 I_6^2}{I_3^2 I_4^3} - \frac{2 I_5^2 I_8}{I_3^2 I_4^2} + \frac{2 I_4^2 I_9}{I_3^2 I_4} - \frac{29 I_5^2 I_6 I_7}{5 I_3^2 I_4^2}$$

Table of Coefficients

|  | $R=6$ | $R=8$ | $R=10$ |
|---|---|---|---|
| $A$ $(2\sigma=8)$ | 6 | 6 | 6 |
| $A$ $(2\sigma=R)$ | 2·669 | 4·753 | 5·591 |
| $A$ $(2\sigma=2R)$ | 5·872 | 6·000 | 6·000 |
| $B$ $(2\sigma=\infty)$ | 112·5 | 112·5 | 112·5 |
| $B$ $(2\sigma=R)$ | 23·107 | 82·644 | 90·160 |
| $B$ $(2\sigma=2R)$ | 101·604 | 111·852 | 112·464 |
| $C$ $(2\sigma=\infty)$ | 2919·375 | 2919·375 | 2919·375 |
| $C$ $(2=R)$ | 497·097 | 984·164 | 1736·383 |
| $C$ $(2=2R)$ | 2384·367 | 2844·719 | 2912·702 |

## Table of Energies

| | $R = 6$ | $R = 8$ | $R = 10$ |
|---|---|---|---|
| $\frac{A}{R^6}$ $(2\sigma = \infty)$ | $1.286 \times 10^{-4}$ | $2.289 \times 10^{-5}$ | $6.000 \times 10^{-6}$ |
| $\frac{A}{R^6}$ $(2\sigma = R)$ | $5.722 \times 10^{-5}$ | $2.813 \times 10^{-5}$ | $5.812 \times 10^{-6}$ |
| $\frac{A}{R^6}$ $(2\sigma = 2R)$ | $1.259 \times 10^{-4}$ | $2.289 \times 10^{-5}$ | $6.000 \times 10^{-6}$ |
| $\frac{B}{R^8}$ $(2\sigma = \infty)$ | $6.631 \times 10^{-5}$ | $6.706 \times 10^{-6}$ | $1.125 \times 10^{-6}$ |
| $\frac{B}{R^8}$ $(2\sigma = R)$ | $13.620 \times 10^{-6}$ | $4.926 \times 10^{-6}$ | $9.016 \times 10^{-7}$ |
| $\frac{B}{R^8}$ $(2\sigma = 2R)$ | $6.165 \times 10^{-5}$ | $6.667 \times 10^{-6}$ | $1.125 \times 10^{-6}$ |
| $\frac{C}{R^{10}}$ $(2\sigma = \infty)$ | $4.828 \times 10^{-5}$ | $2.719 \times 10^{-6}$ | $2.920 \times 10^{-7}$ |
| $\frac{C}{R^{10}}$ $(2\sigma = R)$ | $8.222 \times 10^{-6}$ | $9.166 \times 10^{-7}$ | $1.736 \times 10^{-7}$ |
| $\frac{C}{R^{10}}$ $(2\sigma = 2R)$ | $3.944 \times 10^{-5}$ | $2.649 \times 10^{-6}$ | $2.912 \times 10^{-7}$ |
| $\Delta E$ $(2\sigma = \infty)$ | $2.362 \times 10^{-4}$ | $3.231 \times 10^{-5}$ | $7.417 \times 10^{-6}$ |
| $\Delta E$ $(2\sigma = R)$ | $7.906 \times 10^{-5}$ 199% high | $2.394 \times 10^{-5}$ 34.8% high | $6.497 \times 10^{-6}$ 6.8% high |
| $\Delta E$ $(2\sigma = 2R)$ | $2.270 \times 10^{-4}$ 4% high | $3.220 \times 10^{-5}$ 0.4% high | $7.416 \times 10^{-6}$ 0.014% high |

The results obtained above are compared with those
of other authors in the following table'

| | Coeff. of $R^{-6}$ | Coeff. of $R^{-8}$ | Coeff. of $R^{-10}$ |
|---|---|---|---|
| (i) | -6 | -135 | -1426 |
| (ii) | -6 | -135 | -1417.5 |
| (iii) | -6 | -115.7 | -1069.1 |
| (iv) | -6 | -112.5 | -1029 |
| (v) | -6.49903 | -124.399 | -1135.21 |
| (vi) | -6 | -112.5 | -2914.375 |

| | Author | Wave function | Potential | Method |
|---|---|---|---|---|
| (i) | Margenau | $Ne^{-r_1-r_2}(1+v)$ | $\sum_i^{} \sum_i^{} (\frac{1}{r}(-\cos)(n(\cos)\frac{r_1^n r_2^t}{R^{n+t+1}}) = V_1^4$ | Pert. |
| (ii) | Bean | $Ne^{-r_1-r_2}(1+\lambda v)$ | $V_1^4$ ) $\langle VH \rangle = \langle HV \rangle$ | Var. |
| (iii) | Pauling and Beach | $N_1 N_2 e^{-k}e^{-k}$ | $V_1^4$ | Var. |
| (iv) | Bean | $Ne^{-r_1-r_2}(1+\lambda v)$ | $V_1^4$ | Var. |
| (v) | Pauling and Beach | $\sum\sum N_1 N_2 L_{n_1} Y_{l_1}^m L_{n_2} Y_{l_2}^m$ | $V_1^4$ | Var. |
| (vi) | Bean | $Ne^{-r_1-r_2}(1+\lambda v)$ | $V_1^6$ | Var. |

Graphs of the variation of coefficient with range of integration



R.
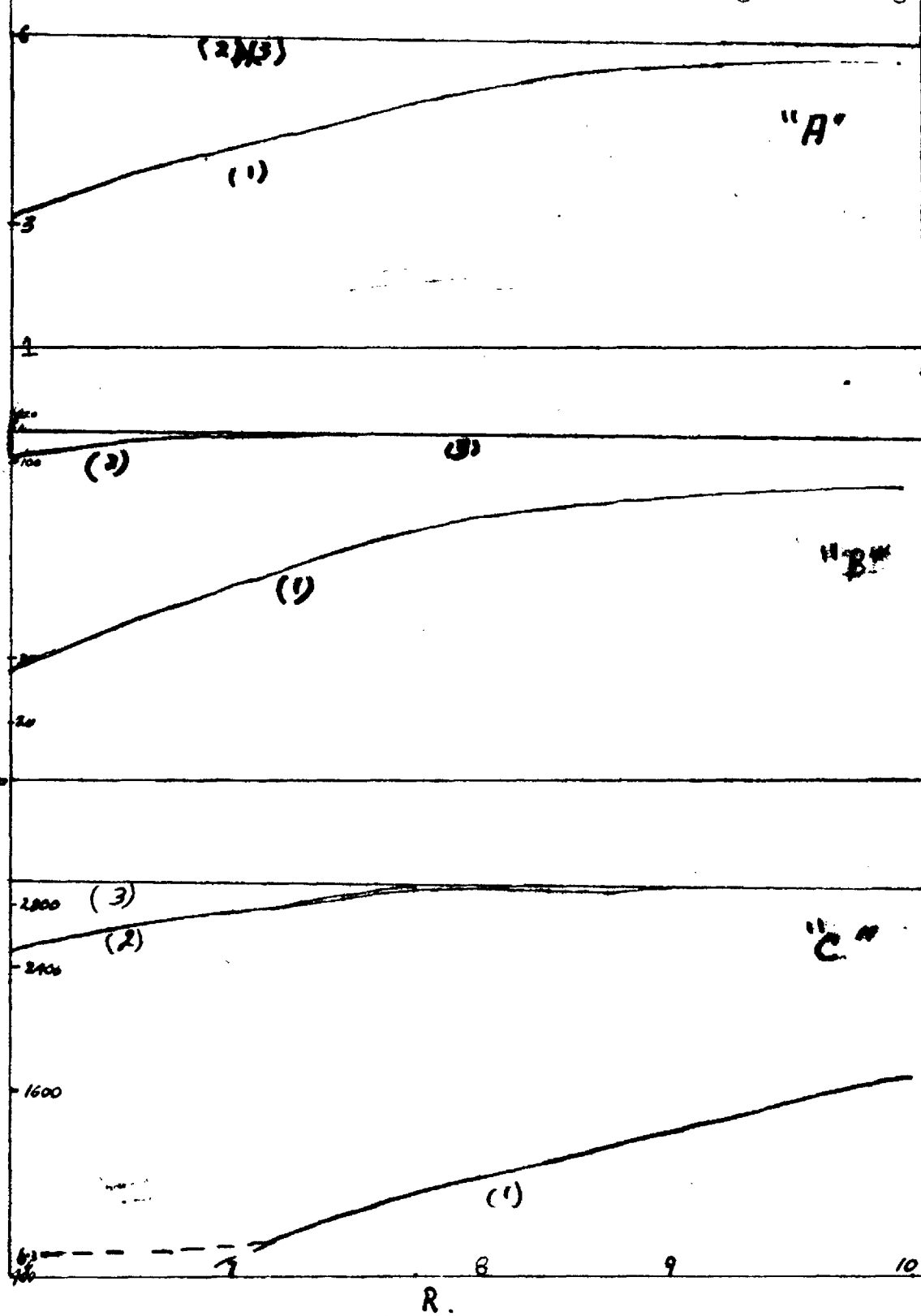
Graphs of the variation of energy with distance for the three
cases.
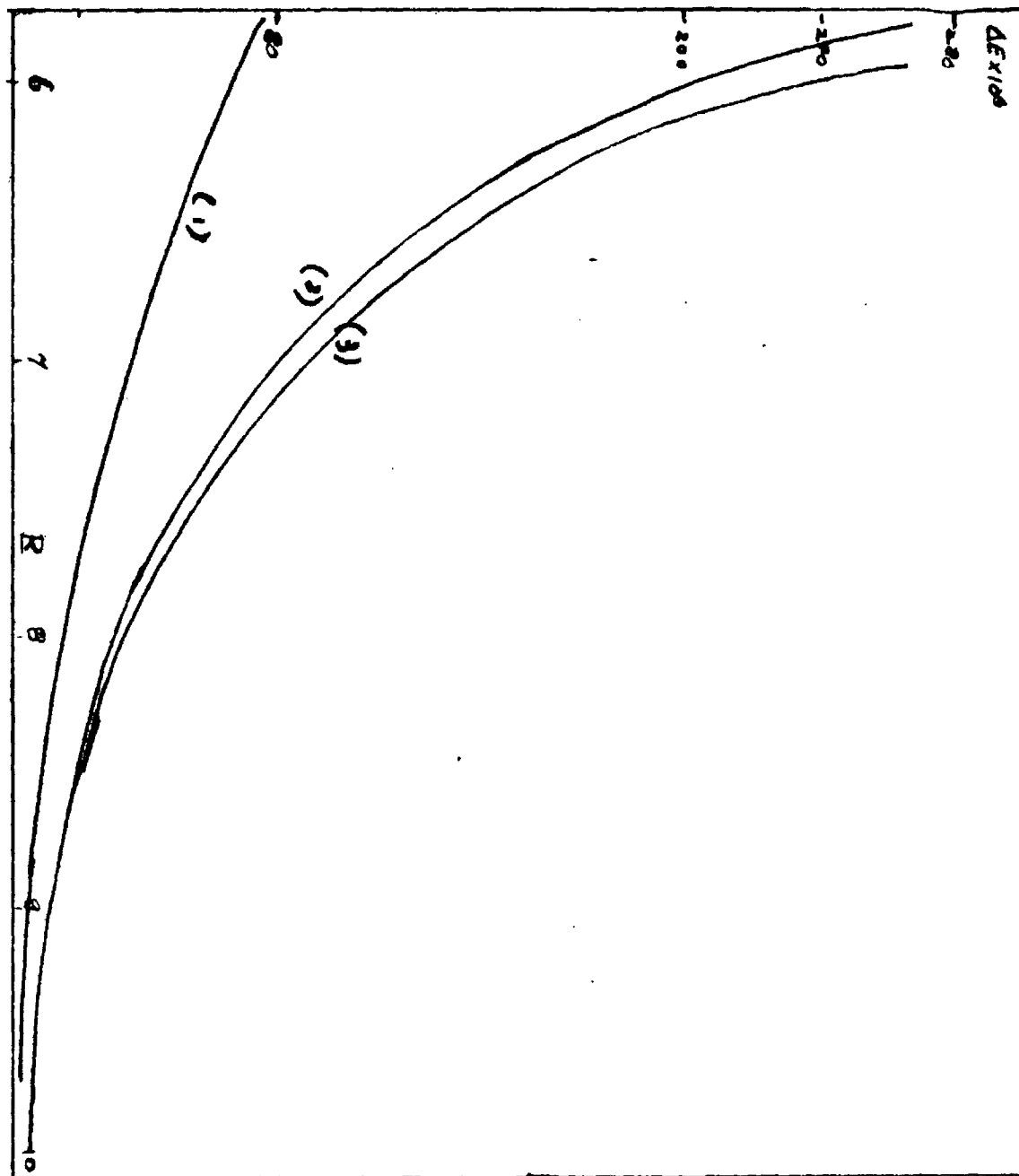
The graphs of section 4 show that although the
coefficients are subject to very large deviations for
case 1, case 2 and case 3 show very little difference at
separations of greater than 7 atomic units. The actual
total energy of the first three terms of the series can
hardly be distinguished in cases 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.

1. H. Margenau: Physical Review 38, 747, (1939).

2. L. Pauling and Beach: Physocal Review 47, 686, (1935).

## 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 caulombic 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

47

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 $\psi_{AB}(1,2)$ for the hydrogen molecule and $\psi_C(3,4)$ 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

$$\psi = N \psi_{AB}(1,2) \psi_C(3,4) [1 + \lambda V]$$

$$N^{-2} = \int (\psi_{AB}\psi_C)(\psi_{AB}\psi_C) \, d\tau$$

5.1

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

$$\Delta E = \langle V \rangle - \frac{\left[\langle V^2 \rangle - \frac{\langle V \rangle^2}{\langle 1 \rangle}\right]^2}{\langle \{\sum_{i,j} \nabla_{i,j} V\}^2 \rangle}$$

5.2

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.
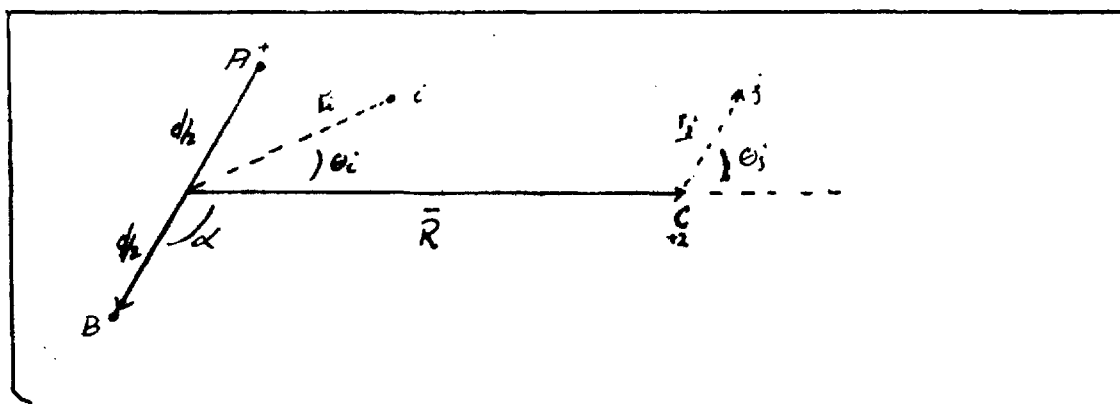


Electrons $i = 1,2$ and $j = 3,4$ are assigned to the hydrogen

molecule and the helium atom respectively. All particles

are referred to $MC = R$ 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

$$A(r_A, \Theta_A, 0), \quad B(r_B, \Theta_B, 0); \quad i(r_i, \Theta_i, \phi_i); \quad j(r_j, \Theta_j, \phi_j)$$

Where

$$r_A = r_B = d/2, \quad \Theta_A = \pi - \alpha, \quad \Theta_B = \alpha$$

$$V(R) = \frac{2}{r_{AC}} + \frac{2}{r_{BC}} - \frac{2}{r_{1C}} - \frac{2}{r_{2C}} - \frac{1}{r_{A3}} - \frac{1}{r_{A4}} - \frac{1}{r_{B3}} - \frac{1}{r_{B4}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} + \frac{1}{r_{14}} + \frac{1}{r_{24}} \qquad 5.3$$

By 3.26

$$V(R) = 2\sum_{n=0}^{\infty} e_i (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{1}{R} - \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} e_i (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{(\nabla \cdot r_j)^k}{k!} \frac{1}{R} ; \quad \left( \begin{array}{c} i = 4, 3, 4, 2 \\ j = 3, 4 \end{array} \right)$$

$$= -\sum_{n=0}^{\infty} \sum_{k=1}^{\infty} e_i (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{(\nabla \cdot r_j)^k}{k!} \frac{1}{R}$$

$$= -\sum_{n=0}^{\infty} \sum_{k=1}^{\infty} e_i (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{(\nabla \cdot r_j)^k}{k!} \frac{1}{R} \qquad 5.4$$

since the systems are neutral.

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

$$V = -\sum_{n=1}^{\infty} \sum_{k=1}^{\infty} e_i C_k^{1/2}(-\cos\theta_{ij}) C_n^{\frac{k+1}{2}}(\cos\theta_i) \frac{r_i^n r_j^k}{R^{n+k+1}} \qquad 5.5$$

Because of the cylindrical symmetry in H     and the spherical symmetry in He, application of 3.7 to      gives

$$\langle V \rangle = -\left\langle \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} e_i C_k^{1/2}(-\cos\theta_{ij}) C_n^{\frac{k+1}{2}}(\cos\theta_i) \frac{r_i^n r_j^k}{R^{n+k+1}} \right\rangle = 0 \qquad 5.6$$

by 3.14.

Placing 5.6 in 5.2 yields

$$\Delta E = -\frac{\langle V^2 \rangle^2}{\left\langle \left\{ \sum_{i,j} \nabla_{i,j} V \right\}^2 \right\rangle}$$

5.7

Expressions for these two quantities will now be determined and the Van der Waals energy will be calculated. From 5.6. by 5.27

$$\sum_{i,j} \nabla_{i,j} V$$

$$= -\sum_{i,j} \nabla_{i,j} \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} e_i \, (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{(\nabla \cdot r_j)^k}{k!} \frac{1}{R}$$

$$= -\nabla \sum_{i,j} \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} e_i C_{k-1}^{k_2}(-\cos\theta_j) \, C_n^{k_2}(\cos\theta_i) \frac{r_i^n \, r_j^{k-1}}{R^{n+k+1}}$$

$$+ \nabla \sum_{i,j} \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} e_i \, C_k^{k}(-\cos\theta_j) \, C_{n-1}^{k}(\cos\theta_i) \frac{r_i^{n-1} \, r_j^k}{R^{n+k+1}}$$

$$= -2\nabla \sum_{n=0}^{\infty} e_i \, (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{1}{R} \qquad ; (i = A, B, 1, 2)$$

$$= -2\nabla \sum_{n=0}^{\infty} e_i \, C_n^{k_2}(\cos\theta_i) \frac{r_i^n}{R^{n+1}}$$

5.8

$$\sum_{i,j} \nabla_{i,j} V$$

$$= +\sum_{n=0}^{\infty} 2\frac{(n+1)}{R} e_i \; C_n^{1/2} (\cos\theta_i) \frac{r_i^n}{R^{n+1}}$$

$$= +\sum_{n=0}^{\infty} 2\frac{(n+1)}{R} e_i \cdot (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{1}{R} \qquad 5.9$$

$$\left\{ \sum_{i,j} \nabla_{i,j} V \right\}^2$$

$$= \frac{4}{R^2} \left[ (n+1) e_i (-1)^n \frac{(\nabla \cdot r_i)^n}{n!} \frac{1}{R} \right]^2$$

$$= \frac{4}{R^2} \left[ \sum_{n=0}^{\infty} (n+1) C_n^1 (\cos\theta_i) \frac{r_i^n}{R^{n+2}} \right.$$
$$\left. + 2\sum_{n=0}^{\infty} \sum_{K=0}^{\infty} (n+1)(K+1) C_n^{1/2}(\cos\theta_i) C_K^{1/2}(\cos\theta_i) \frac{r_i^n r_i^{K}}{R^{n+K+2}} \right] \quad 5.10$$

Using results 3.36 and the fact that $d\theta = -d\theta$ 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

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

5.11

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

$$\frac{4}{R^2}\left[ +2\,C_1^{1/2}(\cos\theta_1)\frac{r_i}{R^2} + 2\,C_1^{1/2}(\cos\theta_2)\frac{r_2}{R^2} \right]^2$$

$$= \frac{16}{R^6}\left[ r_1^2\cos^2\theta_1 + r_2^2\cos^2\theta_2 + 2r_1 r_2\cos\theta_1\cos\theta_2 \right]$$

Using the double angle expansion stated in 3.25 and results 3.41, 3.42 and 3.43

$$\frac{32}{R^6}\,\frac{d^2}{4}\left\langle\left[ \lambda_1^2\mu_1^2\cos^2\alpha + \frac{1}{2}(\lambda_1^2+u_1^2 - \lambda_1^2 u_1^2)\sin^2\alpha \right.\right.$$
$$\left.\left. + \lambda_1\lambda_2 u_1 u_2\cos^2\alpha \right]\right\rangle$$

$$= \frac{d^2}{R^6}\left[ 8\cos^2\alpha\,(I_3+I_4) + 4\sin^2\alpha\,(I_1+I_2-I_3-1) \right]$$

$$= \frac{12.432\,d^2}{R^6}\left[ 1 + \frac{.500}{12.432}\sin^2\alpha \right]$$

5.12

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

$$-\langle \nabla \cdot \underline{r}_i \rangle (\nabla \cdot \underline{r}_j) \frac{1}{R} \qquad\qquad i = 1, 2; \quad j = 3, 4$$

$$= \left[ (\underline{r}_i \cdot \underline{r}_j) - 3(\underline{R}_o \cdot \underline{r}_i)(\underline{R}_o \cdot \underline{r}_j) \right] \frac{1}{R^3} \qquad\qquad 5.13$$

Since the spherical symmetry of system $j$ implies the same general conditions for average values of section 4 then

$$\langle x_j^2 \rangle = \langle y_j^2 \rangle = \langle z_j^2 \rangle = \frac{1}{Z_{He}^2}$$

$$\langle z_j x_j' \rangle = \langle z_j y_j' \rangle = \langle x_j y_j' \rangle = 0$$

$$\langle \cos\phi_j \rangle = \langle \sin\phi_j \rangle = 0$$

$$\langle \cos^2\phi_j \rangle = \langle \sin^2\phi_j \rangle = \frac{1}{2}.$$

Placing these results in 5.13 after squaring gives the following

$$\left[ 2(\underline{r}_1 \cdot \underline{r}_3)(\underline{r}_2 \cdot \underline{r}_3) + (\underline{r}_1 \cdot \underline{r}_3)^2 + (\underline{r}_2 \cdot \underline{r}_3)^2 + \right.$$
$$2(\underline{r}_3 \cdot \underline{r}_4)(\underline{r}_2 \cdot \underline{r}_4) + (\underline{r}_1 \cdot \underline{r}_4)^2 + (\underline{r}_2 \cdot \underline{r}_4)^2$$
$$-6\left\{ (r_1\cos\theta_1 + r_2\cos\theta_2)( \underline{r}_1 \cdot \underline{r}_3\, r_3\cos\theta_3 + \underline{r}_1 \cdot \underline{r}_4\, r_4\cos\theta_4 \right.$$
$$\left. + \underline{r}_2 \cdot \underline{r}_3\, r_3\cos\theta_3 + \underline{r}_2 \cdot \underline{r}_4\, r_4\cos\theta_4 )\right\} \qquad 5.14$$
$$\left. + 9(r_1\cos\theta_1 + r_2\cos\theta_2)^2 (r_3^2\cos^2\theta_3 + r_4^2\cos^2\theta_4). \right] \frac{1}{R^6}$$

$$= \left\langle \frac{1}{Z_{He}^2} \left\{ 4 r_1 r_2 \cos\theta_1 \cos\theta_2 + 4 r_1^2 \cos^2\theta_1 + 2 r_1^2 \sin^2\theta_1 \right. \right.$$

$$- 6\cdot 2 r_1^2 \cos^2\theta_1 - 6\cdot 2 r_2^2 \cos^2\theta_2 - 6 \times 4 r_1 r_2 \cos\theta_1 \cos\theta_2 \qquad 5.15$$

$$\left. \left. + 2 \times 9 \times 2\, r_1^2 \cos^2\theta_1 + 2 \times 9 \times 2\, r_1 r_2 \cos\theta_1 \cos\theta_2 \right\} \right\rangle$$

Collecting

$$\left\langle \frac{1}{Z_{He}^2} \left\{ 16\, r_1^2 \cos^2\theta_1 + 16\, r_1 r_2 \cos\theta_1 \cos\theta_2 + 2 r_1^2 \sin^2\theta_1 \right\} \right\rangle \qquad 5.16$$

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 co-
ordinates in 3.41, 3.42 and 3.43 the line 5.16 takes the
numerical form

$$d^2 \times \left(\frac{16}{27}\right)^2 \left\{ 8.219 + .384 \sin^2\alpha \right\} \qquad 5.17$$

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

$$\Delta E = \frac{ -\left( d \times \frac{16}{27} \right)^4 (8.219)^2 \left\{ 1 + .047 \sin^2\alpha \right\}^2 }{ \frac{16}{27} 12.432 d^2 \left\{ 1 + .040 \sin^2\alpha \right\} }$$

$$\Delta E = - \quad 2 \cdot 395 \frac{\{ 1 + \cdot 047 \, \sin\alpha \}^2}{\{ 1 + \cdot 040 \, \sin\alpha \}} \qquad\qquad 5.18$$

$$\doteq - 2 \cdot 395 \qquad\qquad \text{for the average value.}$$

The first term of the interaction energy of two hydrogen atoms is 6 units. That of two hydrogen molecules is 16.01 units according to Massey and Buckingham. It would be expected that the 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 $H_2$ $He$ 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

$$\Delta E \doteqdot \int \psi^* H \psi \, d\tau / \int \psi^* \psi \, d\tau,$$

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 $\langle (r_1 \cdot r_3)(r_2 \cdot r_3) \rangle = \langle (r_1 \cdot r_3)^2 \rangle$ .

But $\langle (r_1 \cdot r_3)(r_2 \cdot r_3) \rangle \simeq -\frac{1}{10} \langle (r_1 \cdot r_3)^2 \rangle$ . 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 HH interaction value.

Because there is no permanent dipole in $H_2$ the interaction is expected to be less than $H$ 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 $H_2$ . 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.

1. Massey and Buckingham :Proceedings of the Royal Irish Academy, 45, 31, 1938.

2. S. C. Wang: Pysical Review 31, 579, (1928).