

John Dawson Ph.D. 1956

ABSTRACT

John M. Dawson, M. S. 1954 (Ph. D. University of Maryland)

Title of Thesis: Distortions of Atoms and Molecules in Dense Media

Thesis directed by Z. I. Slawsky

~~Department of Physics~~  
**DISTORTIONS OF ATOMS AND MOLECULES  
IN DENSE MEDIA**

Pages in thesis, 89. Words in abstract, 406.

This thesis deals with the distortions which are produced by molecular interactions in the electronic structure and vibrational motions of a molecule. The following are the main topics considered.

I. A method for attacking such problems is developed. The method combines both the variational and perturbation methods of Quantum Mechanics.

II. The effect of intermolecular interactions on the electronic kinetic energy within the molecules is discussed. The discussion is based on the application of the virial theorem to the problem of molecular interactions. The results are quite general and apply to all molecular interactions which are not violent as to produce electronic excitation.

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are considered.

(a) The effect of the London dispersion force between

**ABSTRACT**

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The effect of intermolecular forces between a hydrogen atom and its neighbors on its electronic structure.

Thesis directed by Z. I. Slawsky

Major: **Physics**

Minor: **Mathematics**

Pages in thesis, 89 . Words in abstract, 466.

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I. A method for attacking such problems is developed. The method combines both the variational and perturbation methods of Quantum Mechanics.

II. The effect of intermolecular interactions on the electronic kinetic energy within the molecules is discussed. The discussion is based on the application of the virial theorem to the problem of molecular interactions. The results are quite general and apply to all molecular interactions which are not so violent as to produce electronic excitation.

III. The effects of intermolecular forces on the electronic structure of hydrogen are calculated. Here three main problems are considered.

(a) The effect of the London dispersion force between form A P II P<sup>+</sup> on the internuclear spacing and vibrational

two hydrogen atoms on their electronic structure is calculated.

(b) The effect of embedding a hydrogen atom in a dielectric media is considered. This problem is intended to give a model for determining the average effect of the attractive forces between a hydrogen atom and its neighbors on its electronic structure.

(c) The effect of a perturbing potential of the form  $A P r^3$  on the electronic structure of hydrogen and helium is determined. It is assumed that the effects of such a potential are similar to the average effects produced by pressure. A comparison of the results for helium and experimental results is given.

IV. The effects of intermolecular forces on the internuclear spacing and vibrational frequencies of  $H_2^+$  are calculated. Here also three problems are considered.

(a) The effect of the Van der Waals force between an  $H_2^+$  molecule and a second molecule on the internuclear spacing and vibrational frequency of  $H_2^+$  are calculated.

(b) The effect of embedding an  $H_2^+$  molecule in a dielectric is investigated. As with hydrogen this is meant to be a model for a molecule in a dense gas or liquid. A shift in the vibrational frequency of about one per cent towards lower frequency is found when a reasonable value for the dielectric constant is taken. This is of the same order of magnitude as the shifts found for molecules in a liquid.

(c) The effects of a perturbing potential of the form  $A P R r^3$  on the internuclear spacing and vibrational

frequency of  $H_2^+$  are calculated. These effects are assumed to be similar to those produced by pressure. It is found that pressures of the order of 100,000 atmospheres are required to produce appreciable effects.

V. The effect of caging on the vibrational energy levels of a diatomic molecule is calculated. It is assumed that in a dense gas or liquid the neighboring molecules to a given molecule form a cage in which the molecule is confined. The calculation gives an estimate of this effect on the vibrations of a molecule. It is found that the effect is small.

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L. Jansen and J. M. Dawson, "On Intermolecular Forces and Crystal Structures of Rare Gases", *J. Chem. Phys.* 21, 1619-1620, 1953.

L. Jansen and J. M. Dawson, "On Intermolecular Forces and the Crystal Structures of the Rare Gases", *J. Chem. Phys.* 23, 482-486, 1955.

E. W. Castle, J. M. Dawson and L. Jansen, "Effect of Orientational Forces on Second Virial Coefficients", *J. Chem. Phys.* 23, 1730, 1955.

A. Michels, T. Paschendorf, G. J. Wolkers and J. M. Dawson, "Thermo-dynamic Properties of Xenon as a Function of Density up to 550 Amagat and as a Function of Pressure up to 2000 Atmospheres at Temperatures Between 0°C and 150°C", *Physica* 22, 17-24, 1956.

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DISTINCTIONS OF ATOMS AND MOLECULES

Publications

IN DENSE LIQUIDS  
B. J. Castle, L. Jansen and  
J. M. Dawson, "On the Second  
Virial Coefficients for Assem-  
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Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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## CHAPTER I

### GENERAL INTRODUCTION

When an atom or molecule is imbedded in a dense medium, its structure is altered by perturbing forces resulting from the presence of neighboring molecules. These perturbing forces distort the electronic structures of atoms and molecules and for molecules they also change the vibrational frequencies and internuclear distances. In some cases the distortions may be very large as in the following examples.

The Disturbance of the Outer Electrons in Metals. Here the perturbations are so large that the outer electrons can no longer be considered attached to any one atom, but must be thought of as more or less free to move around in the metal as a whole.

The Dissociation of Ionic Compounds Dissolved in an Electrolite. In this case the ions which form the molecule are pulled apart. The molecule as a unit ceases to exist.

The Distortions of the Molecules of any Material when it is Subjected to Very High Pressures. At very high pressures the electronic structure of an atom can be completely altered. In fact, for high enough pressures it no longer makes sense to speak of atoms or molecules. At such pressures the electrons are no longer bound to particular nuclei but are free to move about in the material as a whole. The substance must therefore be thought of as a collection of nuclei and electrons. The atoms of a material in such a condition may be thought of

## CHAPTER II

as crushed. It seems likely that matter in such a state would be a very good conductor of electricity, or in other words, it would be metallic in nature. Some calculations have been made

The variation method is often used to find approximate ground state wave functions for quantum mechanical systems. Through its use an upper bound for the ground state energy exists in such a metallic state. He found that pressures in excess of 250,000 atmospheres would be required.

The first two of these examples have been extensively studied and are fairly well understood. The third has received some theoretical and experimental attention. However, the pressures necessary to produce large distortions (the crushing of atoms) cannot be readily achieved in the laboratory at present.

In addition to these large effects, there are the weak distortions produced in the gaseous state by Van der Waals interactions. This type of distortion has received very little consideration.

In this thesis I am mainly concerned with these small effects, although the third example given above will receive considerable attention.

The first two chapters deal with general methods and results while the remainder of the thesis is devoted to the application of these methods to particular problems.

and variational methods for approximating solutions to the Schrödinger equation. It differs from the variation perturbation method recently proposed by Cohen<sup>(5)</sup>. His method applies only to one-dimensional problems whereas the method presented here can be applied to problems in any number of dimensions. This method and that of Cohen, however, have some similar features.

## CHAPTER II

### A VARIATION PERTURBATION METHOD

The variation method is often used to find approximate ground state wave functions for quantum mechanical systems. Through its use an upper bound for the ground state energy is determined. By choosing a function with a large number of adjustable parameters a very close approximation to this energy can usually be obtained. However, the method gives no indication of the error made. Several authors<sup>(2,3,4)</sup> have devised methods for determining a lower bound for this energy, but these methods are usually tedious to apply. In addition, the variation method suffers from the fact that there is no systematic method for determining the trial variation function. One must usually rely on physical intuition when choosing such a function. Since the accuracy of the results depends on the choice of this function, this is not a satisfactory situation.

A method is presented here for improving a chosen variation function and for estimating the error made by the use of such a function. This method combines both the perturbation and variational methods for approximating solutions to the Schrodinger equation. It differs from the variation perturbation method recently proposed by Cohen<sup>(5)</sup>. His method applies only to one-dimensional problems whereas the method presented here can be applied to problems in any number of dimensions. This method and that of Cohen, however, have some similar features.

is given by AN APPROXIMATE PERTURBATION METHOD

Suppose a Hamiltonian  $H_0$  is given for which the eigenvalues and eigenfunctions are known. If the  $k^{\text{th}}$  eigenvalue is  $E_k$  and its corresponding eigenfunction is  $U_k$  then

$$H_0 U_k = E_k U_k .$$

It will be assumed in what follows that the ground state is not degenerate.

If one has a slightly different Hamiltonian  $H$  with

$$H = H_0 + H'$$

then it is a well known result of perturbation theory that the ground state wave function for  $H$  is given to first order terms in  $H'$  by

$$\Psi_0 = U_0(r) + \sum_{k \neq 0} \frac{H'_{k0} U_k(r)}{E_0 - E_k} \quad (1)$$

An expression closely related to this was obtained by

Here  $r$  stands for all the variables on which the  $U$ 's depend. If the major contribution to the sum comes from terms with almost the same  $E_0 - E_k$  then an approximation to  $\Psi_0$  can be obtained by factoring out an average  $E_0 - E_k$ . When this is done equation (1) becomes

$$\begin{aligned} \Psi_0 &\approx U_0(r) + \frac{1}{\epsilon} \sum_{k \neq 0} H'_{k0} U_k(r) = \\ &= U_0(r) \left[ 1 - \frac{H'_{00}}{\epsilon} \right] + \frac{1}{\epsilon} \sum_k H'_{k0} U_k(r) \end{aligned} \quad (2)$$

where  $\epsilon$  is some kind of average value for  $E_0 - E_k$ .  $H'_{k0}$

is given by THE VARIATION PERTURBATION METHOD

Suppose one is able to find the ground state wave function corresponding to a given Hamiltonian  $H_0$ . One may try to approximate it by applying the variation method to a trial

Substituting this in (2) gives

$$\Psi_0 \approx U_0(r) \left[ 1 - \frac{H'_{oo}}{\epsilon} \right] + \frac{1}{\epsilon} \sum_k U_k(r) \int U_k^*(r') H'(r') U_0(r') d\tau' \quad (3)$$

value of the energy. In general  $\Psi_0$  will not be equal to  $E_0$  with  $E_0$  given by

Interchanging the order of summation and integration gives

$$\begin{aligned} \Psi_0 &\approx U_0 \left[ 1 - \frac{H'_{oo}}{\epsilon} \right] + \frac{1}{\epsilon} \int \sum_k U_k(r) U_k^*(r') H'(r') U_0(r') d\tau' \\ &= U_0 \left[ 1 - \frac{H'_{oo}}{\epsilon} \right] + \frac{1}{\epsilon} \int \delta(r-r') H'(r') U_0(r') d\tau' \quad (4) \\ &= U_0 \left[ 1 - \frac{H'_{oo}}{\epsilon} \right] + \frac{H'(r) U_0(r)}{\epsilon} = U_0 \left[ 1 - \frac{H'_{oo}}{\epsilon} + \frac{H'}{\epsilon} \right] \end{aligned}$$

Here use has been made of the fact that  $\sum_k U_k(r) U_k^*(r') = \delta(r-r')$

An expression closely related to this was obtained by

Lennard-Jones<sup>(6)</sup>.

One may determine the best value of  $\epsilon$  by applying the variation principle to this function. It should be noted that  $\Psi_0$  is not normalized. The result of such a calculation gives the same energy as second order perturbation theory if the second order perturbation energy  $E_0^{(2)}$  is approximated by

$$\begin{aligned} E_0^{(2)} &= \sum_{k \neq 0} \frac{H'_{ok} H'_{ko}}{E_0 - E_k} \approx \frac{1}{\epsilon} \left[ \sum_k H'_{ok} H'_{ko} - (H'_{oo})^2 \right] \\ &= \frac{1}{\epsilon} \left[ (H')_{oo}^2 - (H'_{oo})^2 \right] \end{aligned}$$

## THE VARIATION PERTURBATION METHOD

Suppose one wishes to find the ground state wave function corresponding to a given Hamiltonian  $H_0$ . One may try to approximate it by applying the variation method to a trial function  $\Psi_0^{(0)}$  which has several adjustable parameters. These parameters are varied so as to minimize the expectation value of the energy. In general  $H_0 \Psi_0^{(0)}$  will not be equal to  $\overline{E_0^{(0)}} \Psi_0^{(0)}$  with  $\overline{E_0^{(0)}}$  given by

$$\overline{E_0^{(0)}} = \frac{\int \Psi_0^{(0)*} H_0 \Psi_0^{(0)} d\tau}{\int \Psi_0^{(0)*} \Psi_0^{(0)} d\tau}$$

The trial function  $\Psi_0^{(0)}$  is however, the ground state wave function for some Hamiltonian  $H$ .  $H$  is in fact given by

$$H = H_0 + \overline{E_0^{(0)}} - \frac{H_0 \Psi_0^{(0)}}{\Psi_0^{(0)}} \quad (5)$$

as can be seen from the equation

$$\begin{aligned} H \Psi_0^{(0)} &= \left[ H_0 + \overline{E_0^{(0)}} - \frac{H_0 \Psi_0^{(0)}}{\Psi_0^{(0)}} \right] \Psi_0^{(0)} = H_0 \Psi_0^{(0)} + \overline{E_0^{(0)}} \Psi_0^{(0)} - H_0 \Psi_0^{(0)} \\ &= \overline{E_0^{(0)}} \Psi_0^{(0)} \end{aligned}$$

If  $\Psi_0^{(0)}$  is a good approximation to the ground state wave function for  $H_0$  then  $\overline{E_0^{(0)}} - \frac{H_0 \Psi_0^{(0)}}{\Psi_0^{(0)}}$  will be small and  $E_0 - E_0^{(0)}$  by an average value  $\epsilon$  will be a good one or little can be treated as a perturbation. I have been unable

Let  $\overline{E}_o^{(0)} - \frac{H_o}{\Psi_o^{(0)}} \Psi_o^{(0)} = -v_o$

to establish a criterion for the adequacy of the approximation. If  $v_o$  has singularities of such order that the integral

$$\text{Then } H_o = H + v_o$$

Applying the results of the previous section one may obtain a better approximation by choosing the function  $\Psi_o^{(1)}$  defined by

$$\Psi_o^{(1)} = \Psi_o^{(0)} \left[ 1 + \frac{v_o}{\epsilon_1} \right] \quad (6)$$

For this case

It should be noted that the process can only lead to improvement since  $(v_o)_{\infty} = \int \Psi_o^{(0)*} v_o \Psi_o^{(0)} d\tau = 0$ . The accuracy of the results at any stage can be estimated from the rate of convergence of  $\epsilon_1$  and the size of  $v_o$  for the final iteration.

The parameter  $\epsilon_1$  is then determined by means of the variation method. The whole process may be repeated using  $\Psi_o^{(1)}$

in place of  $\Psi_o^{(0)}$  to obtain an even better approximation

$\Psi_o^{(2)}$ . The function  $\Psi_o^{(2)}$  is given by

$$\Psi_o^{(2)} = \Psi^{(1)} \left[ 1 + \frac{v_1}{\epsilon} \right] = \Psi_o^{(0)} \left[ 1 + \frac{v_o}{\epsilon_1} \right] \left[ 1 + \frac{v_1}{\epsilon_2} \right]$$

with

$$v_1 = \overline{\overline{E}_o^{(1)} - \frac{H_o}{\Psi_o^{(1)}} \Psi_o^{(1)}} , \quad \overline{\overline{E}_o^{(1)}} = \frac{\int \Psi_o^{(1)*} H_o \Psi_o^{(1)} d\tau}{\int \Psi_o^{(1)*} \Psi_o^{(1)} d\tau}$$

This process may be repeated until any desired accuracy is obtained. At each step the approximation of replacing  $E_o - E_k$  by an average value  $\epsilon$  must be a good one or little improvement will result from iteration. I have been unable

to establish any general criterion for the adequacy of the approximation. If  $v_e$  has singularities of such order that the integral

Before applying methods mentioned above to the calculation of the distortion of molecules due to the near presence is infinite, then the process cannot be continued. A case where this difficulty arises is considered in Chapter IV. A modification of this method is given in Appendix III which eliminates this difficulty. However, the modification is not as easy to use as the method presented here.

It should be noted that the process can only lead to improvement since the variation process is employed. The accuracy of the results at any stage can be estimated from the rate of convergence of  $\bar{E}$  and the size of  $v_e$  for the final iteration.

Here  $\bar{K}$  is the time average of the total kinetic energy of the system,  $\bar{F}_i$  is the force acting on the  $i^{\text{th}}$  particle and  $\bar{r}_i$  is the position vector of the  $i^{\text{th}}$  particle. The bar over the sum indicates its time average is to be taken. This formula holds in both classical and quantum mechanics. However, for a quantum mechanical system the time averages may be replaced by expectation values if the system is assumed to be in a stationary state, so that the expectation value does not change with time. A quantum mechanical derivation of (7) is given in Appendix I.

One may consider the force on the  $i^{\text{th}}$  particle as consisting of two components, an internal component and an

external component. The internal component is due to the interaction of the  $i^{\text{th}}$  particle with the other particles of the system while the external component is due to its interaction with material outside the system. When such a decomposition is made,  $\bar{K}$  takes the form

Before applying the methods presented above to the calculation of the distortion of molecules due to the near presence of other molecules, I shall discuss the virial method. The proper application of the virial theorem to an aggregate of molecules or atoms will give macroscopic information on the changes in the internal motions of the molecules and atoms, due to changes in external forces. According to this theorem the total kinetic energy of a system of particles is related to the forces acting on these particles. The relation is given by the formula

$$\bar{K} = - \sum_i \overrightarrow{F}_i \cdot \overrightarrow{r}_i \quad (7)$$

Here  $\bar{K}$  is the time average of the total kinetic energy of the system,  $\overrightarrow{F}_i$  is the force acting on the  $i^{\text{th}}$  particle and  $\overrightarrow{r}_i$  is the position vector of the  $i^{\text{th}}$  particle. The bar over the sum indicates its time average is to be taken. This formula holds in both classical and quantum mechanics. However, for a quantum mechanical system the time averages may be replaced by expectation values if the system is assumed to be in a stationary state, so that the expectation value does not change with time. A quantum mechanical derivation of (7) is given in Appendix I.

One may consider the force on the  $i^{\text{th}}$  particle as consisting of two components, an internal component and an

external component. The internal component is due to the interaction of the  $i^{\text{th}}$  particle with the other particles of the system while the external component is due to its interaction with material outside the system. When such a decomposition is made, equation (7) takes the form

$$2 \bar{K} = - \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - \sum_{\substack{i,j \\ i \neq j}} \overrightarrow{F}_{ij} \cdot \overrightarrow{r}_{ij} \quad (8)$$

Adding equations (10) and (11) and dividing by 2, one obtains

for  $2 \bar{K}$

In this equation  $\overrightarrow{F}_i^e$  is the external force on the  $i^{\text{th}}$  particle while  $\overrightarrow{F}_{ij}$  is the force on the  $i^{\text{th}}$  particle due to the  $j^{\text{th}}$  particle.

All matter is composed of electrons and nuclei. If one considers these as the fundamental particles of which any system is composed, then the forces between particles are coulombic in nature. Hence  $\overrightarrow{F}_{ij}$  is given by

The following relations were used in obtaining (12)

$$\overrightarrow{F}_{ij} = \frac{e_i e_j}{|r_{ij}|^3} \overrightarrow{r}_{ji} \quad (9)$$

where  $e_i$  and  $e_j$  are the charge on the  $i^{\text{th}}$  and  $j^{\text{th}}$  particles

and  $\overrightarrow{r}_{ji}$  is the vector distance from  $j$  to  $i$ . If (9) is substituted into (8) one obtains

$$2 \bar{K} = - \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - \sum_{\substack{i,j \\ i \neq j}} \frac{e_i e_j \overrightarrow{r}_{ji} \cdot \overrightarrow{r}_i}{|r_{ij}|^3} \quad (10)$$

for the form

$$2 \bar{K} = - \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - (\nabla + K) \cdot \sum_i \overrightarrow{r}_i - E \quad (11)$$

Now the value of the second term on the right hand side of equation (10) is not changed if  $i$  and  $j$  are interchanged. Thus  $2 \bar{K}$  is also given by the equation

$$2 \bar{K} = - \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - \sum_{\substack{i,j \\ i \neq j}} \frac{e_i e_j}{|r_{ij}|^3} \overrightarrow{r}_{ij} \cdot \overrightarrow{r}_j \quad (11)$$

One may apply equation (11) to a variety of systems. I shall apply it to the case of a gas confined to a container,

Adding equations (10) and (11) and dividing by 2, one obtains for  $2 \bar{K}$

$$2 \bar{K} = - \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e_i e_j}{|r_{ij}|} \quad (12)$$

For this case the only external forces are the pressure exerted on the surface of the container.

$$= \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - \bar{V}$$

The following relations were used in obtaining (12)

$$\overrightarrow{r}_{ij} = - \overrightarrow{r}_{ji}$$

by  $\int -P \hat{r} dA = \int \hat{r} \cdot \hat{dA}$ . The integral is

to be taken over the whole surface of the container. This integral may be converted into a volume integral by making

use of Green's theorem

$$\text{The quantity } \bar{V} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e_i e_j}{|r_{ij}|} \text{ in equation (12) is the}$$

total electrostatic potential energy of the system. If  $\bar{K}$  is subtracted from both sides of equation (12), the result has the form

$$\bar{K} = - \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - (\bar{V} + \bar{K}) = \sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i - \bar{E} \quad (13)$$

where  $\bar{E}$  is the average total internal energy of the system. Equation (13) gives a means for computing the total kinetic energy of a system when the external forces acting on it and its internal energy are known.

One may apply equation (13) to a variety of systems. I shall apply it to the case of a gas confined to a container, and the case of two interacting molecules.

#### THE PROBLEM OF A GAS IN A CONTAINER

For this case the only external forces are the pressure forces which the container exerts on the gas. The time average of the force exerted on the gas by an element  $A$  of the surface of the container is

in the electronic motions  $-P \int_A \vec{dA}$  one subtracts equation (14) for infinite volume and temperature  $T$  from equation (13) for finite  $P$  and temperature  $T$  one obtains the following relation where  $P$  is the pressure. Hence one may replace  $\sum_i \vec{F}_i \cdot \vec{r}_i$

by  $\int_A -P \vec{r} \cdot \vec{dA} = -P \int_V \vec{r} \cdot \vec{dA}$ . The integral is

to be taken over the whole surface of the container. This integral may be converted into a volume integral by making use of Green's theorem.

The left hand side is just the change in kinetic energy of the system  $\int_A \vec{r} \cdot \vec{dA} = P_{\text{from}} \int_V \vec{\nabla} \cdot \vec{r} dV = 3 P_{\text{from}}$  the terms on the right hand side are directly measurable since Substituting in (13), one obtains

$$\bar{K} = 3 PV - \bar{E} \quad (14)$$

This equation was first derived by Schottky<sup>(7)</sup>.

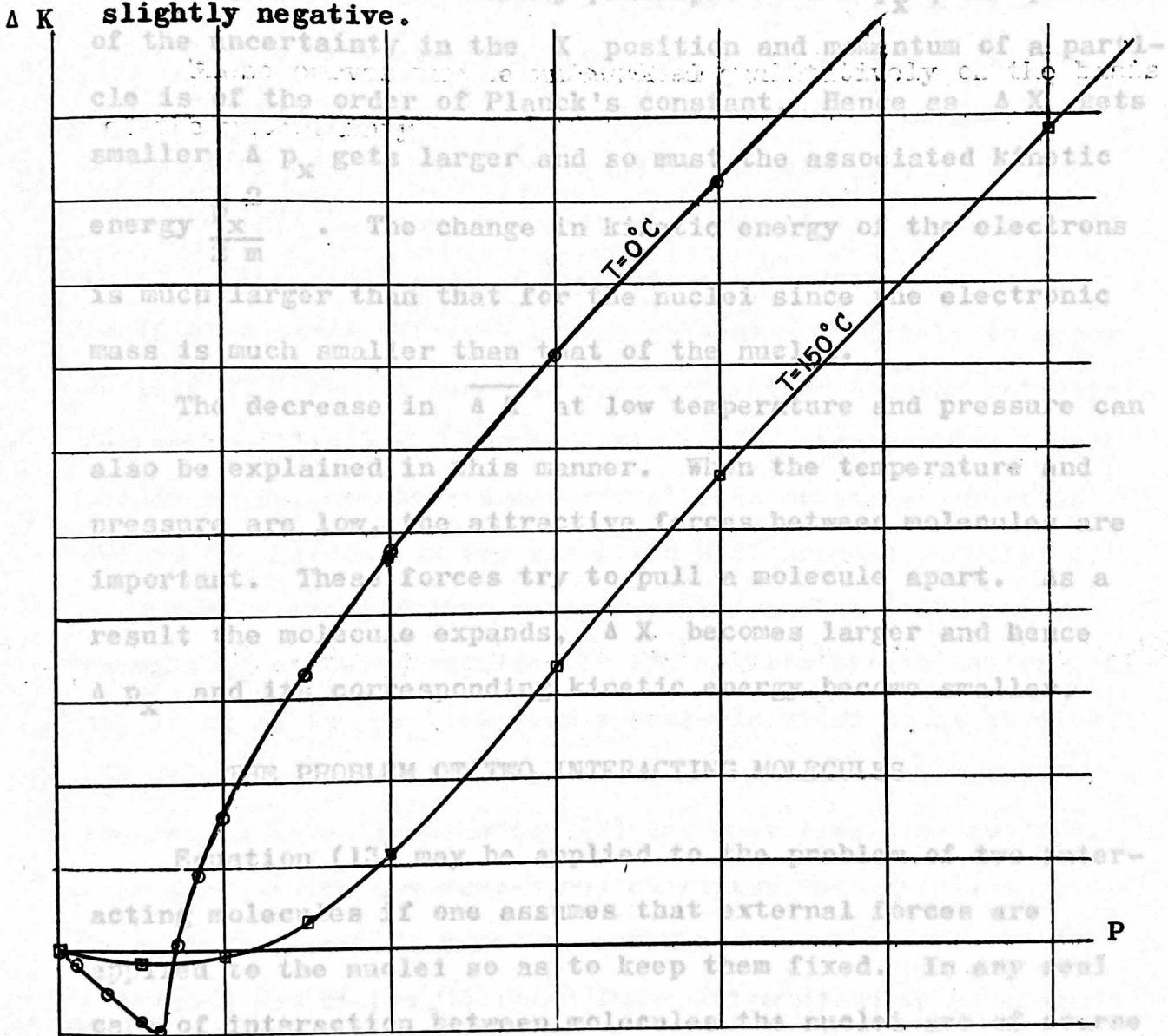
Suppose now that a gas in a very large container is compressed isothermally. It may be asked what happens to the kinetic energy of the system. Since the translational and rotational degrees of freedom of the molecules behave classically at ordinary temperatures, the kinetic energy of these motions will be  $\frac{1}{2} k T$  per degree of freedom and will not change in an isothermal compression. Hence any changes that do occur must come from changes in the electronic and vibrational motion. It may be argued that changes in vibrational kinetic energy must be small. Estimates of the size of such changes show that this is indeed the case (see Chapters V and VI). Hence any major changes in kinetic energy must be mainly due to changes in the electronic motions. If one subtracts equation (14) for infinite volume and temperature  $T$  from equation (14) for finite  $V$  and temperature  $T$  one obtains the following

$$\bar{K}_V - \bar{K}_{V=\infty} = 3 \left[ \frac{(PV)_V}{T=T} - \frac{(PV)_{V=\infty}}{T=T} \right] - \left[ \frac{\bar{E}_V}{T=T} - \frac{\bar{E}_{V=\infty}}{T=T} \right] \quad (15)$$

or 
$$\Delta \bar{K}_{T=T} = 3 \Delta \frac{PV}{T=T} - \Delta \frac{\bar{E}}{T=T}$$

The left hand side is just the change in kinetic energy of the system which results from the isothermal compression. The two terms on the right hand side are directly measurable since  $\Delta PV$  can be determined from pressure and volume measurements while  $\Delta \bar{E}$  is the change in total energy of the system and can

be obtained from thermodynamic considerations<sup>(8)</sup>. Michels and his coworkers<sup>(9,10,11,12)</sup> have determined  $\Delta K$  for several gases. Some typical curves of  $\Delta K$  vs pressure for xenon are shown in Figure I. The low temperature curve ( $T = 25^\circ C$ ) of  $\Delta K$  vs  $P$  first goes negative and then becomes positive, while the high temperature curve ( $T = 150^\circ C$ ) is positive, or very slightly negative.



$\Delta K$  vs  $P$  for  $Xe$ , Data taken from A. Michels, T. Wassenaar, G. J. Wolkers and J. Dawson. Physica XXII (1956) 17-28

Figure I

These curves may be understood qualitatively on the basis of the uncertainty principle. Consider a molecule imbedded in a dense gas. It will be pretty well confined to a small region of space by its neighbors. One may think of the neighbors as forming a cage in which the molecule (both nuclei and electrons) is confined. As the pressure is raised the cage contracts. According to the uncertainty principle  $\Delta x \Delta p_x$ , the product of the uncertainty in the  $X$  position and momentum of a particle is of the order of Planck's constant. Hence as  $\Delta X$  gets smaller  $\Delta p_x$  gets larger and so must the associated kinetic energy  $\frac{p_x^2}{2m}$ . The change in kinetic energy of the electrons is much larger than that for the nuclei since the electronic mass is much smaller than that of the nuclei.

The decrease in  $\overline{\Delta K}$  at low temperature and pressure can also be explained in this manner. When the temperature and pressure are low, the attractive forces between molecules are important. These forces try to pull a molecule apart. As a result the molecule expands,  $\Delta X$  becomes larger and hence  $\Delta p_x$  and its corresponding kinetic energy become smaller.

#### THE PROBLEM OF TWO INTERACTING MOLECULES

Equation (13) may be applied to the problem of two interacting molecules if one assumes that external forces are applied to the nuclei so as to keep them fixed. In any real case of interaction between molecules the nuclei are of course not held fixed. However, because of their large mass compared taking time averages and hence of direct application of the theorem. One may modify the theorem slightly so that it can

to that of the electrons, the nuclei respond much more slowly to forces than do the electronic clouds. For this reason in most cases of molecular interactions it is a good approximation to consider the electrons as always being in equilibrium with the instantaneous positions of the nuclei. That is, one assumes that one can calculate the electronic motion as if the nuclei were fixed. The nuclear motions are then calculated as if they took place in a potential which is the total electronic energy plus nuclear repulsion. This is the Born-Oppenheimer approximation<sup>(13)</sup> and it is good as long as the molecules are not thrown together at velocities comparable to those of the electrons. For collisions at such velocities ionization and excitation of the molecules is likely to occur so that it makes no sense to speak of intermolecular potentials for such collisions. For moderate interactions, where intermolecular potentials are meaningful, the electronic kinetic energy is the same as for the fixed nuclear configuration.

The external forces which hold the nuclei fixed may be thought of as being supplied by the inertia of the nuclei. If one looks at the problem from a semi-classical point of view, the situation is as follows. In order to apply the virial theorem as given in equation (7) one must take time averages over times which are long compared to the characteristic periods of the system. However, for the case of two interacting molecules one wishes to apply the theorem to an instantaneous nuclear configuration. This eliminates the possibility of taking time averages and hence of direct application of the theorem. One may modify the theorem slightly so that it can

be applied to this system. Instead of taking time averages since the nuclei are fixed the only kinetic energy in the system is due to the electrons. Now because of the relatively rapid motion of the electrons compared to that of the nuclei  $\Delta t$  may be long compared to the time it takes an electron to travel from one end of the molecule to the other, but be short compared to the motion of the nucleus. That is, the nuclei move so little in the time  $\Delta t$  that the time average of their motion is the same as their instantaneous motion while the electrons move so much in this time that the time average for them is a true average. The consideration of such an averaging process leads to the same results as keeping the nuclei fixed.

(16) For the case of two interacting atoms one has the situation shown in Figure II.

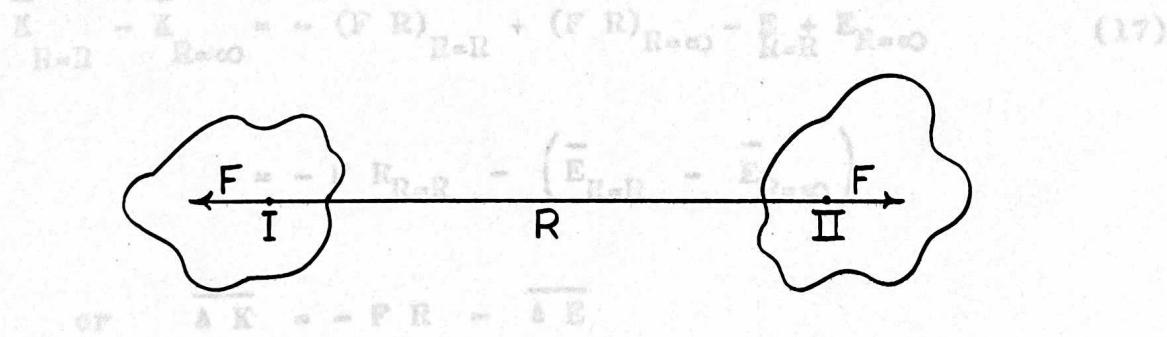


Figure II

Consider atoms I and II with internuclear separation  $R$ . A force must be applied to such nuclei to keep them fixed. By equation (13) the total kinetic energy of this system is given by the formula

$$\bar{K} = - \sum_i \vec{F}_i^e \cdot \vec{r}_i - \bar{E}$$

Since the nuclei are held fixed the only kinetic energy is electronic kinetic energy. The only external forces applied to the system are those which keep the nuclei fixed. Taking the origin at nucleus I, one obtains directly

Where  $\Phi = -\frac{e^2}{R}$  is the internucler or intermolecular potential.

$$\sum_i \overrightarrow{F}_i^e \cdot \overrightarrow{r}_i = F R$$

Hence  $\bar{K}$  is given by the expression

$$\bar{K} = -F R - \bar{E} \quad (16)$$

If equation (16) for an infinite separation is subtracted from (16) for a finite separation, a formula for the change in kinetic energy is found.

$$\bar{K}_{R=R} - \bar{K}_{R=\infty} = - (F R)_{R=R} + (F R)_{R=\infty} - \bar{E}_{R=R} + \bar{E}_{R=\infty} \quad (17)$$

$$= -F R_{R=R} - \left( \bar{E}_{R=R} - \bar{E}_{R=\infty} \right)$$

$$\text{or } \overline{\Delta K} = -F R - \overline{\Delta E}$$

Here it was assumed  $F R \rightarrow 0$  as  $R \rightarrow \infty$ .

Now  $-\overline{\Delta E}$  is just the change in total energy of the system and is therefore the nuclear potential given by the Born-Oppenheimer approximation. Furthermore  $F$ , the force required to hold the nuclei fixed, must be the negative of the derivative of  $\overline{\Delta E}$  with respect to  $R$ . A rigorous proof of this is given in Appendix II. Hence (17) may be written

in the form

$$\frac{\Delta K}{\Delta E} = R \frac{d\Phi}{dR} - \Phi \quad (18)$$

CHAPTER IV  
DISTORTION OF THE HYDROGEN ATOM

Where  $\Phi$  is the internuclear or intermolecular potential.

Hydrogen being the simplest of all atoms lends itself most readily to calculations of distortions produced in it by interactions with other atoms. Because of this these distortions can be calculated in greater detail and with more rigor than is possible when more complicated atoms are involved. For this reason calculations for hydrogen serve as a useful guide to understanding what happens in more complicated cases. Such calculations can even serve as a qualitative explanation for effects observed with other atoms.

As is well known, the explanation of Van der Waals forces and covalent binding are based on such analogies. To be sure when one wishes to make use of such analogies one must be certain that effects peculiar to hydrogen are not involved. However, by choosing appropriate idealized conditions hydrogen may often be used to indicate the properties of other atoms in situations where atomic hydrogen as such does not exist. To be more specific, one example of this is the change in the electronic kinetic energy of a highly compressed gas molecule.

As was stated in Chapter III, the electronic kinetic energy of any material increases when it is subjected to high pressure. One means of approximating this effect is to assume that the neighbors of any given molecule form a cage in which it is confined. As the pressure increases, the size of this cage

decreases. This approximation requires that one solve the Schrödinger equation for CHAPTER IV in a box. However, the

Schrödinger equation cannot be solved for complicated free atoms, let alone caged ones. Nevertheless, the problem of the

### DISTORTION OF THE HYDROGEN ATOM

BY INTERMOLECULAR INTERACTIONS

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decreases. This approximation requires that one solve the "Schrodinger equation for an atom in a box. However, the "Schrodinger equation cannot be solved for complicated free by atoms, let alone caged ones. Nevertheless, the problem of the caged hydrogen atom can be solved completely, and so if it is assumed that these results are similar to those that would be obtained in more complicated situations, some insight can be obtained into the behavior of highly compressed atoms. This is true even though highly compressed atomic hydrogen does not exist.

This Chapter will be divided into two parts. Part A deals with the distortions produced when two hydrogen atoms with large internuclear separations interact. For this case the interaction is that of the Van der Waals force between the atoms. This problem has received a considerable amount of attention<sup>(14)</sup>. This is particularly true of calculations of the energy. The distortion that these forces produce has been considered to a lesser extent. However, the main value of the calculations contained in this section is to indicate the validity of the methods employed. Part B of the Chapter will deal with the distortions produced in atoms under high pressure. The approach is a modification of the caged atom method. Instead of taking the effect of pressure to be one of caging, it is assumed that it can be approximated by a continuous potential. These calculations are applied to both hydrogen and helium. The line joining the two nuclei with the positive direction being that from nucleus I to nucleus II. The Hamiltonian for this system is given by

A. The Van der Waals Interaction Between Two Hydrogen Atoms

(1) Calculation of the energy of interaction

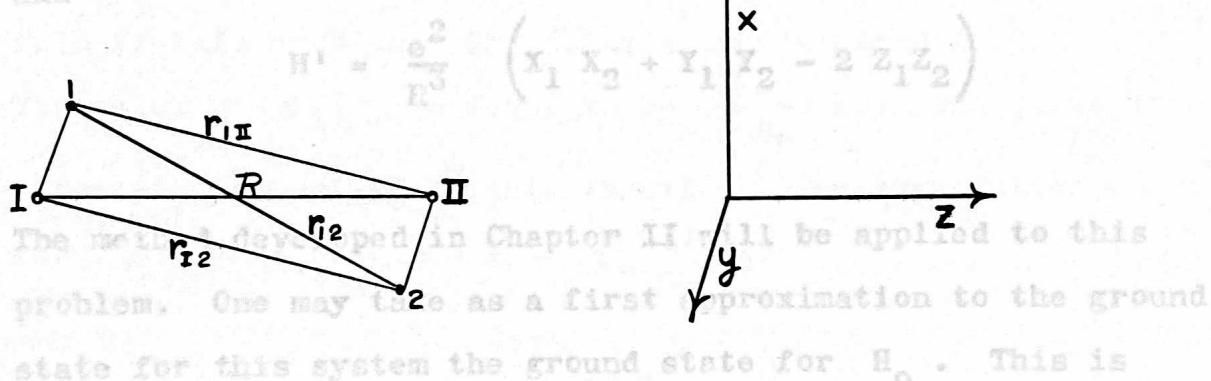
Suppose two hydrogen atoms interact when separated by a large internuclear distance. The situation is then that shown in Figure III

$$H = H_0 + H^* \quad (20)$$

with

$$H_0 = -\frac{e^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

and



The method developed in Chapter II will be applied to this problem. One may take as a first approximation to the ground state for this system the ground state for  $H_0$ . This is

$$\Psi_0^{(0)} = \frac{1}{\pi a_0^3} \left[ \exp \left( -\frac{r_1 + r_2}{a_0} \right) \right] \quad (21)$$

the product of the ground state wave functions for two isolated hydrogen atoms. The value for the energy obtained

when this function is used is the ground state energy. The nuclei of the two atoms are assumed to be fixed in space and separated by a distance  $R$ . The  $Z$  axis may be taken along the line joining the two nuclei with the positive direction being that from nucleus I to nucleus II. The Hamiltonian for this system is given by

$$H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1III}} - \frac{e^2}{r_{2II}} \quad (19)$$

For large  $R$ ,  $H$  may be approximated by

$$H = H_0 + H' \quad (20)$$

with

$$H_0 = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{e^2}{r_1} - \frac{e^2}{r_2} \quad (21)$$

This function has often been used to give an approximate solution to this problem. The value of  $\epsilon_1$  found to be when the variational principle is applied to this function, the expectation value

The method developed in Chapter II will be applied to this problem. One may take as a first approximation to the ground state for this system the ground state for  $H_0$ . This is

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the product of the ground state wave functions for two isolated hydrogen atoms. The expectation value for the energy obtained when this function is used is  $-\frac{e^2}{a_0}$ , the ground state energy of the free hydrogen atoms.

The variation perturbation method then gives for the first improved wave function

$$\Psi_0^{(1)} = \Psi_0^{(0)} \left( 1 + \frac{v_0}{\epsilon_1} \right)$$

$$-v_0 = \langle \bar{E} \rangle_{oo} - \frac{H \Psi_0^{(0)}}{\Psi} = -H' \quad (22)$$

or

The second approximation to the ground state wave function

$$\Psi_0^{(1)} = \left( \exp - \frac{r_1 + r_2}{a_0} \right) \left[ 1 + \frac{H'}{\epsilon_1} \right] \quad (23)$$

This function has often been used to give an approximate solution to this problem. The details can be found in Schiff<sup>(15)</sup>. The value of  $\epsilon_1$ , is found to be  $-\frac{e^2}{a_0}$  when the variational principle is applied to this function. The expectation value for the energy obtained from  $\Psi_0^{(1)}$  is

$$E_0^{(1)} = -\frac{e^2}{a_0} - 6 \frac{e^2 a_0^5}{R^6} \quad (24)$$

Subtracting the ground state energy for the isolated atoms from  $E_0^{(1)}$  gives an interaction energy of  $-6 \frac{e^2 a_0^5}{R^6}$ .

Carrying the variation perturbation method to the second degree of approximation one finds for  $v_1$

$$v_1 = \frac{6 e^2 a_0^5}{R^6} - \frac{\frac{H'}{\epsilon_1} \left[ \frac{e^2}{r_1} + \frac{e^2}{r_2} \right] + H' + \frac{H'^2}{\epsilon_1}}{1 + \frac{H'}{\epsilon_1}} \quad (25)$$

Retaining only terms of first order in  $H'$  gives

is found to be equal to  $-1.2 \frac{a_0}{R}$  and  $B$  to  $0.1716$

$$\text{with } v_1 = + \frac{e^2 a_0^5}{R^6} - H' - \frac{H'}{\epsilon_1} \left[ \frac{e^2}{r_1} + \frac{e^2}{r_2} \right] \text{ comes out to (26)}$$

The second approximation to the ground state wave function

$\Psi_0^{(2)}$  is given by

$$\text{if } \epsilon_1 \text{ is kept fixed at } -\frac{a_0}{R} \text{ and only } \epsilon_2 \text{ is allowed to vary} \quad (27)$$

$$\Psi_0^{(2)} = \Psi_0^{(1)} \left[ 1 + \frac{v_1}{\epsilon_2} \right] = \Psi_0^{(0)} \left( 1 + \frac{H'}{\epsilon_1} \right) \left\{ 1 + \frac{1}{\epsilon_2} \left[ -\frac{e^2 a_0^5}{R^6} + H' + \frac{H'}{\epsilon_1} \left( \frac{e^2}{r_1} + \frac{e^2}{r_2} \right) \right] \right\}$$

or to first order terms in  $H'$

$$\Psi_0^{(2)} = \Psi_0^{(0)} \left[ 1 - \frac{e^2 a_0^5}{R^6} + \left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right) H' + \frac{H'}{\epsilon_1 \epsilon_2} \left( \frac{e^2}{r_1} + \frac{e^2}{r_2} \right) \right] \quad (28)$$

Since equation (28) is not normalized it may be written equally

well as

$$\Psi_0^{(2)} = \Psi \left[ 1 + \left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \right) H' + \frac{H'}{\epsilon_1 \epsilon_2} \left( \frac{e^2}{r_1} + \frac{e^2}{r_2} \right) \right] \quad (29)$$

If  $\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2}$  is set equal to  $A$  and  $\frac{1}{\epsilon_1 \epsilon_2}$  is set equal to

B and the variation method is then applied to  $\Psi_0^{(2)}$ , A is found to be equal to  $-1.2 \frac{a_0}{e^2}$  and B to  $0.1714 \frac{a_0}{e^2}$ .

With these values of A and B the energy comes out to be

$$E_0^{(2)} = -\frac{e^2}{a_0} - 6.17 \frac{e^2 a_0^5}{R^6} \quad (30)$$

If  $\epsilon_1$  is kept fixed at  $-\frac{e^2}{a_0}$  and only  $\epsilon_2$  is allowed to

Since this function cannot be normalized, it is impossible to vary then  $\epsilon_2$  is found to be  $-0.143 \frac{a_0}{e^2}$  and the energy is

equal to  $-\frac{e^2}{a_0} - 6.16 \frac{e^2 a_0^5}{R^6}$ . The most accurate value for

the Van der Waals interaction between two hydrogen atoms has been obtained by Pauling and Beach<sup>(16)</sup>. They obtained a value

of  $-6.49903 \frac{e^2 a_0^5}{R^6}$  for this energy. This is considerably

lower than the value of  $-6.17 \frac{e^2 a_0^5}{R^6}$  obtained above. The

relatively small improvement in the interaction energy which was obtained from the second iteration of the variation perturbation method is due to the fact that assumptions made in this method are not accurate for this case. Attempts to carry the calculation to the third degree of approximation completely failed. This is because  $v_2$  has a term in it of the form

$$H' \left[ \left( \frac{a_0}{r_1} \right)^3 + \left( \frac{a_0}{r_2} \right)^3 \right] \quad (31)$$

When  $\Psi_o^{(3)}$  is calculated, it has a term of the form  
 must be added to the actual Hamiltonian to convert it into the  
 Hamiltonians for which  $\Psi_o^{(0)}$  and  $\Psi_o^{(2)}$  are the ground state wave functions. If the summations in the two equations  
 given above could be carried out then  $\Psi_o^{(2)}$  and  $\Psi_o^{(3)}$   
 and hence one of the form

$$\Psi_o^{(0)} H' \left[ \left( \frac{a_o}{r_1} \right)^3 + \left( \frac{a_o}{r_2} \right)^3 \right] \quad (33)$$

Since this function cannot be normalized, it is impossible to use it as an approximate wave function. The difficulty that arises here is due to the poor approximation which is made when  $E_o - E_k$  is replaced by an average energy in the expressions

$$\Psi_o^{(2)} = \Psi_o^{(1)} + \sum_{k \neq o} \frac{(v_1)_{ok} \Psi_k^{(1)}}{E_o^{(1)} - E_k^{(1)}} \quad (34)$$

approximating the sum in this manner is not good. One may take the poorness of the second and third approximations as an indication of this. A perhaps more convincing proof can be obtained by carrying out the sum for a particular case. Such a particular case is the following

$$\Psi_o^{(3)} = \Psi_o^{(2)} + \sum_{k \neq o} \frac{(v_2) \Psi_k^{(2)}}{E_o^{(2)} - E_k^{(2)}} \quad (35)$$

$\Psi_k$  is the  $k^{\text{th}}$  eigenfunction for hydrogen

Here  $E_k^{(1)}$  is the energy of the  $k^{\text{th}}$  eigenfunction  $\Psi_k^{(1)}$

of the Hamiltonian for which  $\Psi_o^{(1)}$  is the ground state.

(Seen in Chapter II). The quantities  $E_k^{(2)}$  and  $\Psi_k^{(2)}$

are the corresponding  $k^{\text{th}}$  eigenenergy and  $k^{\text{th}}$  eigenfunction for the Hamiltonian having  $\Psi_o^{(2)}$  for its ground state wave

function. The functions  $v_1$  and  $v_2$  are potentials which must be added to the actual Hamiltonian to convert it into the Hamiltonians for which  $\Psi_o^{(1)}$  and  $\Psi_o^{(2)}$  are the ground state wave functions. If the summations in the two equations given above could be carried out then  $\Psi_o^{(2)}$  and  $\Psi_o^{(3)}$  would be good second and third approximations to the wave function for the system. However, in general the  $\Psi_{ko}^{(1)}$ 's  $\Psi_k^{(2)}$ 's and  $E_k^{(1)}$ 's and  $E_k^{(2)}$ 's are not known and so this is impossible. As was shown in Chapter II these summations can be carried out if the denominator is replaced by an average energy. This is true even though the individual terms in the sum are not known. If  $v$  has a peak in it, approximating the sum in this manner is not good. One may take the poorness of the second and third approximations as an indication of this. A perhaps more convincing proof can be obtained by carrying out the sum for a particular case. Such a particular case is the following

$$v = \frac{e}{r} - \Delta E \quad (30)$$

$\Psi_k$  is the  $k^{\text{th}}$  eigenfunction for hydrogen where  $\Delta E$  is the change in total kinetic energy,  $\Delta E$  is the eigenenergy of the  $k^{\text{th}}$  eigenstate for hydrogen. For this case the sum may also be calculated  $\sum_{k=0}^{\infty} \frac{v_{ko}}{E_o - E_k} \Psi_k$  approximate wave functions are used these two kinetic energies is equal to a constant times  $r \Psi_o$ . A proof of this is

given in Appendix III.

For this problem the variation perturbation method as presented in Chapter II breaks down after two iterations. The method may be modified to eliminate the difficulties encountered above. Such a modification is presented in Appendix III. Although the modification presented there is free from these difficulties it is not so easy to apply as the method of Chapter II.

(2) The change in the electronic kinetic energy and structure for two interacting hydrogen atoms with large internuclear separation

In the last section the Van der Waals interaction energy for two hydrogen atoms was calculated. Here the effect of this interaction on the electronic structure and kinetic energy will be determined.

In Chapter III it was shown that the change in total energy for two interacting atoms was related to the change in electronic kinetic energy by the equation

The interaction energies associated with these functions are

$$\Delta K = - R \frac{d\Delta E}{dR} - \Delta E \quad (36)$$

where  $\Delta K$  is the change in total kinetic energy,  $\Delta E$  is the change in total energy and  $R$  is the internuclear separation. From this formula and  $\Delta E$  it is possible to calculate the change in kinetic energy. The change in the kinetic energy may also be calculated from the perturbed wave function. When approximate wave functions are used these two kinetic energies need not agree. One may take the discrepancy between these

two values as an indication of the accuracy of the wave function. Agreement does not mean that the wave function is correct since both  $\Delta E$  and  $\Delta K$  can be wrong in such a way as to make this true. However, this does require that the total energy and the kinetic energy have the correct relation to each other. Since this is an additional requirement beyond that of minimum energy imposed by the variational principle, functions for which it is true will in general be more accurate than those for which it is not true.

The two approximate functions  $\Psi_o^{(1)}$  and  $\Psi_o^{(2)}$  given in the last section were

$$\Psi_o^{(1)} = \left\{ \exp \left( - \frac{\mathbf{r}_1 + \mathbf{r}_2}{a_0} \right) \right\} [1 + A H']$$

$$\Psi_o^{(2)} = \left\{ \exp \left( - \frac{\mathbf{r}_1 + \mathbf{r}_2}{a_0} \right) \right\} \left[ 1 + A H' + B H' \left\{ \frac{a_0 + a_0}{\mathbf{r}_1 \mathbf{r}_2} \right\} \right]$$

The interaction energies associated with these functions are

$$E_o^{(1)} - E_o^{(0)} = - \frac{6e^2 a_0^5}{R^6} \quad \text{for } \Psi_o^{(1)} \quad (40)$$

and

$$E_o^{(2)} - E_o^{(0)} = - 6.17 \frac{e^2 a_0^5}{R^6} \quad \text{for } \Psi_o^{(2)} \quad (41)$$

According to equation (36) the change in kinetic energy should be given by

$$\Delta K_o^1 = - R \frac{d}{dR} \left[ -6 \frac{e^2 a_0^5}{R^6} \right] + 6 \frac{e^2 a_0^5}{R^6} = - 30 \frac{e^2 a_0^5}{R^6} \quad (37)$$

for  $\Psi_o^{(1)}$  and by

$$\Delta K_o^{(2)} = -R \frac{d}{dR} \left[ -6.17 \frac{e^2 a_0^5}{R^6} \right] + 6.17 \frac{e^2 a_0^5}{R^6} = 30.85 \frac{e^2 a_0^5}{R^6} \quad (38)$$

for  $\Psi_o^{(2)}$

If however, one calculates  $\Delta K_o^{(1)}$  from the equation

$$\Delta K_o^{(1)} = \langle \Psi_o^{(1)} K \Psi_o^{(1)} \rangle - \langle \Psi_o^{(0)} K \Psi_o^{(0)} \rangle \quad (39)$$

where  $K$  is the kinetic energy operator

$$- \frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right)$$

one gets the very interesting result

$$\Delta K_o^{(1)} = 0 \quad (40)$$

The similar calculation for  $\Delta K_o^{(2)}$  yields

$$\Delta K_o^{(2)} = -1.3 \frac{e^2 a_0^5}{R^6} \quad (41)$$

There is a wide difference between these values and those given by the virial theorem. One does not have to search far to find the reason for this. As is well known the first order perturbed wave function is sufficient to give the second order perturbed energy. The energy is, however, the only operator for which this is true. For any other operator such as the kinetic energy

the first order wave function will give results which are good only to first order. The reason that the energy can be obtained to one higher order than the wave function used is that the solutions of the Schrödinger equation give stationary values for the energy. That is, small changes in the wave function do not change the expectation value of the energy. The change in the kinetic energy due to a slight change in the wave function is exactly balanced by an opposite change in potential energy.

~~noticed that contains second order terms in  $H'$ . The exact~~ It is interesting to compare the change in potential and kinetic energy with the change in total energy for  $\Psi_0^{(1)}$ .

These changes are

$$\Delta E = -6 \frac{e^2 a_0^5}{R^6} \quad (42)$$

$$\Delta K = 0$$

$$\Delta V = -6 \frac{e^2 a_0^5}{R^6}$$

According to the virial theorem the changes in  $K$  and  $V$  should be

$$\Delta K = -30 \frac{e^2 a_0^5}{R^6} \quad (43)$$

$$\Delta V = +24 \frac{e^2 a_0^5}{R^6}$$

$$\text{if } \Delta E \text{ is } -6 \frac{e^2 a_0^5}{R^6} \quad (43)$$

This is fairly close to the value of  $-30 \frac{e^2 a_0^5}{R^6}$  given by the virial theorem when  $\Delta E$  is taken as  $-6 \frac{e^2 a_0^5}{R^6}$ , the value

$\Delta K$  and  $\Delta V$  although  $\Delta E$  is very good compared to the correct value of  $-6.5 \frac{e^2 a_0^5}{R^6}$  the errors made in  $\Delta V$  and  $\Delta K$  are equal and opposite.

From what has just been said it is clear that to get the distortion or what is equivalent, the change in the wave functions of the interacting hydrogen atoms to the same accuracy as the interaction energy (second order in  $H'$ ) one must use a wave function that contains second order terms in  $H'$ . The exact perturbed wave function to second order in  $H'$  is given by equation (44)<sup>(15)</sup>.

$$\Psi = \Psi_0 + \sum_{k \neq 0} \frac{H'_{ko}}{E_0 - E_k} \Psi_k + \sum_{k \neq 0} \left\{ \left[ \sum_{n \neq 0} \frac{H'_{kn} H'_{no}}{E_0 - E_k E_0 - E_n} - \frac{H'_{ko} H'_{oo}}{(E_0 - E_k)^2} \right] \Psi_k - \frac{1}{2} \frac{\left| H'_{ko} \right|^2}{(E_0 - E_k)^2} \Psi_0 \right\} \quad (44)$$

If it is assumed as was done in the variation perturbation method for the first order wave function, that the denominators can be replaced by an average energy and if this average energy is taken to be  $E_0$  then one finds for

$$\Delta K = -24 \frac{e^2 a_0^5}{R^6} \quad (45)$$

This is fairly close to the value of  $-30 \frac{e^2 a_0^5}{R^6}$  given by the virial theorem when  $\Delta E$  is taken as  $-6 \frac{e^2 a_0^5}{R^6}$ , the value

obtained for the energy when this same approximation is made in the first order wave function. A perhaps more revealing approach to the problem is to try a variation function of the form or the so-called London dispersion forces between two molecules were considered. A classical picture of these forces is the following. At any instant in time the electrons of a given atom will have a definite configuration so that the mole-

where both  $a$  and  $A$  are adjustable parameters. When the variation method is applied to this function  $a$  is found to be equal to  $a_0 + \frac{15 a_0^7}{R^6}$  where  $a_0 = \frac{\hbar^2}{me^2}$ , the first Bohr radius for hydrogen, and  $A$  to  $-\frac{a_0}{e^2}$ . The energy and kinetic energy come out to be given by

$$\Delta E = -6 \frac{e^2 a_0^5}{R^6} \quad (47)$$

far as dispersion forces are concerned. If this is done, the results are found to be in agreement with the more rigorous quantum mechanical calculations.

$\Delta K = -30 \frac{e^2 a_0^5}{R^6}$

These values are in agreement with the virial theorem. It is interesting to notice that  $a$  is larger than  $a_0$ . Since  $a$  corresponds to the average distance of the electrons from their respective nuclei an increase in  $a_0$  is equivalent to an expansion of the atoms. It will be recalled that in the chapter on the virial theorem the cause of the negative portion of the  $\Delta K$  vs  $P$  curve was attributed to just such an expansion.

The calculation given above shows that the qualitative arguments given there are essentially correct.

(3) Average effect of attractive forces on the electronic structure of hydrogen

In the previous section the Van der Waals attractive forces or the so-called London dispersion forces between two molecules were considered. A classical picture of these forces is the following: At any instant of time the electrons of a given atom will have a definite configuration so that the molecule will have an instantaneous dipole moment. This moment polarizes the neighboring molecules, inducing in them a dipole moment. These two dipoles interact in such a way as to give rise to a force of attraction. The dispersion force is the average of this force over all configurations of the electrons of the given molecule<sup>(17)</sup>.

On the basis of this explanation one should be able to replace a neighboring molecule by a polarizable sphere in so far as dispersion forces are concerned. If this is done, the results are found to be in agreement with the more rigorous quantum mechanical calculations. The effect of the dispersion forces of all the neighbors of a given molecule will be the same as that produced by surrounding it with a collection of dielectric spheres. The average effect on the given molecule will be similar to that produced by embedding it in a dielectric medium. Hence, the total effect may be approximated by placing the molecule in a spherical cavity in a dielectric medium. The radius of the cavity can be taken to be roughly a molecular diameter. An approximate solution to this problem will be given here for the case of hydrogen.

Figure IV illustrates this problem

The hydrogen atom is placed at the center of the cavity. The electron induces an image charge  $+q$  in the dielectric **image charge**. This charge attracts the electron and expands the atom. The proton also induces a charge on the sphere; but since it is uniformly distributed over the surface, it produces no field inside the cavity. The problem is to find the image charge and its distance from the center of the sphere. This problem is difficult to solve for an arbitrary position of the electron. However, if the distance of the electron from the center of the cavity is small compared to the diameter of the cavity, the problem is readily solved. For this case the electric potential inside the cavity is that due to the electron and the image charge and is given by the following expression

$$\Phi_I = -\frac{e}{r} \left( 1 + \frac{r}{\rho} \cos \theta \right) + \frac{q}{L} \left( 1 + \frac{\rho}{L} \cos \theta \right) \quad (48)$$

Here  $q$  is the magnitude of the image charge,  $L$  is the distance of the image charge from the center of the cavity,  $r$  is the distance from the center to the electron,  $\rho$  is the distance of the point at which the potential is taken from the center and  $\theta$  is the angle between the line joining the center with the electron and the line joining the center with the point at which the potential is taken. Outside the cavity the potential is given by the equation

$$\Phi_o = -\frac{e^l}{r^l} \left( 1 + \frac{r^l}{\rho} \cos \theta \right) \quad (49)$$

where  $e^l$  is the apparent charge on the electron as seen from the outside and  $r^l$  is its apparent distance from the center.

**Figure IV**

The hydrogen atom is placed at the center of the cavity. The electron induces an image charge  $+q$  in the dielectric. This charge attracts the electron and expands the atom. The proton also induces a charge on the sphere; but since this is uniformly distributed over the surface, it produces no field inside the cavity. The problem is to find the image charge and its distance from the center of the sphere. This problem is difficult to solve for an arbitrary position of the electron. However, if the distance of the electron from the center of the cavity is small compared to the diameter of the cavity, the problem is readily solved. For this case the electrical potential inside the cavity is that due to the electron and the image charge and is given by the following expression

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Here  $q$  is the magnitude of the image charge,  $L$  is the distance of the image charge from the center of the cavity,  $r$  is the distance from the center to the electron,  $\rho$  is the distance of the point at which the potential is taken from the center and  $\theta$  is the angle between the line joining the center with the electron and the line joining the center with the point at which the potential is taken. Outside the cavity the potential is given by the equation

$$\Phi_o = -\frac{e^1}{\rho} \left( 1 + \frac{r^1}{\rho} \cos \theta \right) \quad (49)$$

where  $e^1$  is the apparent charge on the electron as seen from the outside and  $r^1$  is its apparent distance from the center.

The quantities  $\rho$  and  $\theta$  have the same meaning as before. One must choose  $q$ ,  $L$ ,  $e^1$  and  $r^1$  so that the usual boundary conditions are satisfied at the walls of the cavity; that is, the potential and the normal component of  $D$  are continuous at the boundary. When these conditions are imposed, one finds that  $q$ ,  $L$ ,  $e^1$  and  $r^1$  are given by the following equations

$$\begin{aligned} e &= \epsilon e^1 & \frac{3e^2 a_0^2 (\epsilon - 1)}{R^3 (2\epsilon + 1)} \\ r^1 &= \frac{3r e}{2\epsilon + 1} \end{aligned} \quad (54)$$

while the change in proton-electron potential energy is

$$\begin{aligned} L &= \frac{R^2 (2\epsilon + 1)}{2\epsilon r} \\ q &= \frac{(\epsilon - 1)}{\epsilon^2} \frac{e R (2\epsilon + 1)}{2r} \end{aligned} \quad (55)$$

Here  $\epsilon$  is the dielectric constant.

The perturbing force on the electron is given by

$$F = -\frac{e q}{L^2} = -\frac{2e^2 r}{R^3 (2\epsilon + 1)} \frac{(\epsilon - 1)}{(2\epsilon + 1)} \quad (51)$$

Integrating this force from 0 to  $r$  gives the perturbing potential  $V$  which is equal to

$$V = -\frac{e^2 r^2}{R^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)} \quad (52)$$

Since the model is only approximate, this may be taken to be the total disturbance. The variation perturbation method gives as a first approximation to the perturbed wave function the function

the boundary condition that the wave function goes to zero at

$$\left( \exp - \frac{r}{a_0} \right) \left( 1 + A r^2 \right) \quad (53)$$

hydrogen and approximately for helium and argon by Ten Seldam (18).

Cottrell (19) gave an approximate solution for the hydrogen molecule ion. All these calculations appear to be in qualitative agreement with the theory of perturbation. The order of magnitude for the change in electronic kinetic energy is

The perturbation energy is equal to

$$\langle v \rangle = - \frac{3 e^2 a_0^2 (\epsilon - 1)}{R^3 (2\epsilon + 1)} \quad (54)$$

while the change in proton electron potential energy is

$$\left\langle \Delta - \frac{e^2}{r} \right\rangle = \frac{11.25 (\epsilon - 1) a_0^2 e^2}{R^3 (2\epsilon + 1)} \quad (55)$$

and the change in kinetic energy is equal to

$$\langle \Delta K \rangle = - \frac{11.25 (\epsilon - 1) a_0^2 e^2}{R^3 (2\epsilon + 1)} \quad (56)$$

(that is, by a soft cage) then, as will be shown later, perturbation theory may be applied. Furthermore, one may use such a method for calculating the effect of pressure.

### B. The Effect of Pressure on the Electronic Structure and Kinetic Energy of Atoms

Several authors have attempted to approximate the effect of pressure on atoms and molecules by considering it to be essentially an effect of caging by the neighboring atoms (9,18). As was stated earlier, they think of the neighbors as forming a rigid cage in which the given molecule is confined. The problem is then to solve Schrödinger equation for the atom with the boundary condition that the wave function goes to zero at

the cage walls. This problem has been solved exactly for hydrogen and approximately for helium and argon by Ten Seldam<sup>(18)</sup>. Cottrell<sup>(19)</sup> gave an approximate solution for the hydrogen molecule ion. All these calculations appear to give the right order of magnitude for the change in electronic kinetic energy of a molecule under high pressures. As would be expected, they fail at low pressures.

This caged atom model for the effect of pressure on an atom is only an approximation and one which is only valid at high pressures. In many cases it is difficult to apply. Rather paradoxically, it is just as difficult to solve the problem of an atom in a large cage as for an atom in a small one. This is contrary to the situation generally found in perturbation theory where a small disturbance is more easily handled than a large one. It therefore seems appropriate to turn to a perturbation method for calculating the effect of pressure.

If one replaces the rigid cage by a continuous potential (that is, by a soft cage) then, as will be shown later, perturbation theory may be applied. Furthermore, one may use such a potential at low pressures (10 to 100 atmospheres) since the effect of attraction between molecules may also be included. Of course, the use of either a continuous potential or of a cage, smooths out the random fluctuations that occur in the environment of a given atom. If these fluctuations are large, as is the case in a very dilute gas where a molecule is violently perturbed during collisions but is otherwise free from all forces, then no smooth potential can be expected to represent the situation.

Any potential which is to give the average effect of pressure should be one which rises rapidly with distance from the nucleus. The rigid cage is such a potential. It is zero out to a distance  $R$  and after that becomes infinite. The potential that will be used here is of the form

$$\Phi = A P r^3 \quad (57)$$

Here  $P$  is the pressure,  $r$  is the distance from the nucleus, and  $A$  is a parameter which relates the measured pressure to the force that the electron feels.  $A$  should be almost constant over a wide pressure range. It would be about  $\frac{4}{3} \pi$  if the pressure the electron had to support acted over an area given by  $4\pi r^2$ . Actually this is not the case. At low pressure, where the molecules are randomly distributed, the pressure acts over the surface of a sphere twice the size of a molecule. When the pressure becomes very high, the molecules are packed into some kind of lattice. If it is assumed that the molecules are spherical and the lattice is taken to be cubic closest packed, then any molecule must support the pressure force on a sphere of radius  $\sqrt{\frac{6}{2\pi}}$  times the radius of a molecule. Because of this packing, effect  $A$  is not strictly a constant, but depends somewhat on pressure. In this theory the value of  $A$  is determined by fitting the theoretical curve at one point of the experimental curve.

When  $\Phi$  is added to the Hamiltonian for hydrogen, the new Hamiltonian is

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r} + A P r^3 \quad (58)$$

One may attempt to find the ground state for this problem by means of the variation perturbation method of Chapter II. As a first approximation, the ground state wave function for hydrogen may be used. The quantity  $-A P r^3$  is then  $v_0$  and the second approximation to this function is

Here  $\Delta E$  is the change in the electrostatic potential plus

$$\Psi_0^{(1)} = \Psi_0^{(0)} \left( 1 + \frac{A P r^3}{\epsilon} \right) = \left( \exp -\frac{r}{a_0} \right) \left( 1 + \frac{A P r^3}{\epsilon} \right) \quad (59)$$

is given by

Applying the variation method to this function with  $\epsilon$  adjustable, one finds  $\epsilon$  to be equal to

$$\frac{e^2}{202.5 \frac{a_0}{a_0}} - \frac{2362 A P a_0^3}{517.5}$$

This is in good agreement with the value obtained above.

In this problem the difficulties that were met with in the case of the two interacting hydrogen atoms do not arise. With this value for  $\epsilon$  the expectation value of the energy is given by

$$\langle E \rangle = -\frac{e^2}{2 a_0} + 7.5 A P a_0^3 - \frac{661.4 A^2 P^2 a_0^7}{e^2} \quad (60)$$

strong function of  $r$ . Some indication of the error made by

The change in the total kinetic energy turns out to be equal to

$$\Delta K = 23.0 A P a_0^3 \quad (61)$$

while the change in the electrostatic potential energy is given by

$$v_1 = A P r^3 \left\langle -\frac{e^2}{r} \right\rangle A P a_0^3 + \frac{e^2}{a_0} = -23.0 A P a_0^3 \quad (62)$$

to first order terms in  $P$ . The values of  $r^3$  and  $\frac{1}{r}$  for

When the virial theorem is applied to this problem, the following relation is found to hold in the limit of small pressures

$$\Delta K = 22.5 \times A P a_0^3 + \Delta E \quad (63)$$

Here  $\Delta E$  is the change in the electrostatic potential plus the electronic kinetic energy. For low pressure (low compared to those needed to crush an atom)  $\Delta E$  is zero. Hence  $\Delta K$  is given by

$$\Delta K = 22.5 A P a_0^3 \quad (64)$$

This is in good agreement with the value  $23 A P a_0^3$  obtained above. In this problem the difficulties that were met with in the case of the two interacting hydrogen atoms do not arise since here there is a first order change in energy and a first order perturbed wave function has been used.

One may ask if the use of perturbation methods are valid for this problem since the perturbing potential is such a strong function of  $r$ . Some indication of the error made by its use can be obtained from the value of  $v_1$

$$v_1 = \frac{H \Psi_o^{(1)} - \bar{E}_o^{(1)} \Psi_o^{(1)}}{\Psi_o^{(1)}}$$

Using the values for  $\epsilon$  and  $\bar{E}_o^{(1)}$  found above,  $v_1$  is given by

$$v_1 = A P r^3 - 7.5 A P a_0^3 - 7.68 A P a_0 r^2 + 15.36 A P a_0^2 r$$

this problem. Since approximating the effects of pressure by to first order terms in  $P$ . The values of  $r^3$  and  $\frac{v_1}{AP}$  for a continuous potential is rather crude, the exact form of the

$r$	$r^3$	$\frac{v_1}{AP}$	$\frac{H'}{AP} = r^3 - \frac{v_1}{AP}$
0.0	0	-7.5	7.5
0.5	.125	-1.62	1.75
1.0	1.0	+1.17	-.17
1.5	3.375	1.63	1.75
2.0	8	0.5	7.50
2.5	15.63	-1.46	17.09
3.0	27.0	-3.51	30.51
3.5	42.88	-4.89	47.77
4.0	64.00	-4.86	68.86
4.5	91.13	-2.66	93.79
5.0	125.00	2.45	122.55
6.0	216.00	24.42	191.58

Then  $H'$  taken as the perturbing potential, the calculations given above are exact. This is even for the energy differences.

As can be seen  $\frac{v_1}{AP}$  is quite small over a large range of  $r$ . Since  $v_1$  is the difference between the perturbing potential and the ground state wave function which gives the wave function

$$\Psi_o^{(1)} = \Psi_o \left( 1 + \frac{APr^3}{\epsilon} \right)$$

and the perturbing potential  $APr^3$ , this can be taken as an indication that the method is valid.

One may also take another point of view with respect to this problem. Since approximating the effects of pressure by a continuous potential is rather crude, the exact form of the

perturbing potential is not significant. It only needs to have the right shape. Hence one may take for this perturbing potential that perturbation which gives  $\Psi_0^{(1)}$ . This potential is given by  $A P r^3 - v_1$  and is equal to

$$H' = 7.5 A P a_0^3 + 7.68 A P a_0 r^2 - 15.36 a_0^4$$

When  $H'$  is taken to be the perturbing potential, the calculations given above are exact. This is true even for the energy since

the expectation value for the energy is given by

$$\int \Psi_0^{(1)} v_1 \Psi_0^{(1)} d\tau = 0.$$

A calculation similar to that given for hydrogen may be applied to helium. Let  $\Psi_0$  be the ground state wave function for undisturbed helium. If it is assumed that each of the electrons is acted on by a perturbing potential of the form  $A P r^3$  then the variation perturbation method gives for a first approximation to the perturbed wave function

$$\Psi_0^{(1)} = \Psi_0 \left[ 1 + \frac{A P r_1^3}{\epsilon} \right] \left[ 1 + \frac{A P r_2^3}{\epsilon} \right] \quad (65)$$

Applying

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + \frac{e^2}{r_{12}} - \frac{2e^2}{r_1} \frac{2e^2}{r_2} + A P r_1^3 + A P r_2^3$$

to  $\Psi_0^{(1)}$  gives

The exact wave function  $\Psi_0$  is not known for helium. However, there are some good variational wave functions which can

$$H \Psi_o^{(1)} = E_o \Psi_o^{(1)} - \frac{\hbar^2}{2m} \left[ 2 \left( \nabla_1 \Psi_o \cdot \nabla_1 \frac{APr_1^3}{\epsilon} \right) \left( 1 + \frac{APr_2^3}{\epsilon} \right) + 2 \left( \nabla_2 \Psi_o \cdot \nabla_2 \frac{APr_2^3}{\epsilon} \right) \left( 1 + \frac{APr_1^3}{\epsilon} \right) + \Psi_o \left( 1 + \frac{APr_2^3}{\epsilon} \right) \nabla_1^2 \frac{APr_1^3}{\epsilon} + \Psi_o \left( 1 + \frac{APr_1^3}{\epsilon} \right) \nabla_2^2 \frac{APr_2^3}{\epsilon} \right] + APR_1^3 \Psi_o^{(1)} + APR_2^3 \Psi_o^{(1)}$$

the calculations become identical with those given for hydrogen.

Here  $E_o$  is the ground state energy for helium. The expectation value for the energy is given by

$$\langle E \rangle = \int \frac{\Psi_o^{(1)} H \Psi_o^{(1)}}{\Psi_o^{(1)} \Psi_o^{(1)}} d\tau_1 d\tau_2 \quad (67)$$

Applying the variational method to this, one finds  $\langle E \rangle$  is equal which is equal to

$$E_o + \left[ - \frac{\hbar^2}{2m} \int \Psi_o \left( 1 + \frac{APr_1^3}{\epsilon} \right) \left( 1 + \frac{APr_2^3}{\epsilon} \right) \left\{ 2 \left( \vec{\nabla}_1 \Psi_o \cdot \vec{\nabla}_1 \frac{APr_1^3}{\epsilon} \right) \left( 1 + \frac{APr_2^3}{\epsilon} \right) \right. \right. \right. \\ \left. \left. \left. + 2 \left( \vec{\nabla}_2 \Psi_o \cdot \vec{\nabla}_2 \frac{APr_2^3}{\epsilon} \right) \left( 1 + \frac{APr_1^3}{\epsilon} \right) + \Psi_o \left( 1 + \frac{APr_2^3}{\epsilon} \right) \nabla_1^2 \frac{APr_1^3}{\epsilon} \right. \right. \\ \left. \left. + \Psi_o \left( 1 + \frac{APr_1^3}{\epsilon} \right) \nabla_2^2 \frac{APr_2^3}{\epsilon} \right\} d\tau_1 d\tau_2 + \int \Psi_o^2 \left( \frac{1+APr_1^3}{\epsilon} \right)^2 \left( \frac{1+APr_2^3}{\epsilon} \right)^2 x \right. \\ \left. \left( APr_1^3 + APr_2^3 \right) d\tau_1 d\tau_2 \right] \div \int \Psi_o^2 \left( \frac{APr_1^3}{1+\epsilon} \right)^2 \left( \frac{APr_2^3}{1+\epsilon} \right)^2 d\tau_1 d\tau_2 \quad (66)$$

The exact wave function  $\Psi_o$  is not known for helium. However, there are some good variational wave functions which can

be used. One such function is of the form

$$\Psi = \left[ \exp - \frac{r_1}{a} \right] \left[ \exp - \frac{r_2}{a} \right]$$

The quantity  $a$  is a variation parameter. When the variation principle is applied to this function,  $a$  is found to be

$\frac{16}{27} a_0$ . (15) When this is used in (66) to calculate the energy, the calculations become identical with those given for hydrogen. The energy turns out to be

$$\langle E \rangle = E_0 + 15 AP a^3 + 202.5 \frac{A^2 P^2 a^4 a_0^4 e^2}{\epsilon^2} + 1035 \frac{A^2 P^2 a^6}{\epsilon} \quad (67)$$

Applying the variational method to this, one finds  $\frac{1}{\epsilon}$  is equal to  $\frac{1035}{405} \frac{a^2}{a_0 e^2}$ . The first order perturbation energy is

$$+ 15 A P a^3$$

and  $\Delta K$  is given by

$$\Delta K = 46 A P a^3 \quad (68)$$

Figure V shows  $\Delta K$  vs  $P$  for helium. Curve I is an experimental curve obtained from the date of Bridgman, Curve II is the curve calculated from (68) with  $A = 50$ , Curve III is the curve calculated from (68) with  $A$  equal to 35.6, and Curve IV

$\Delta K$  Joule  
Mole

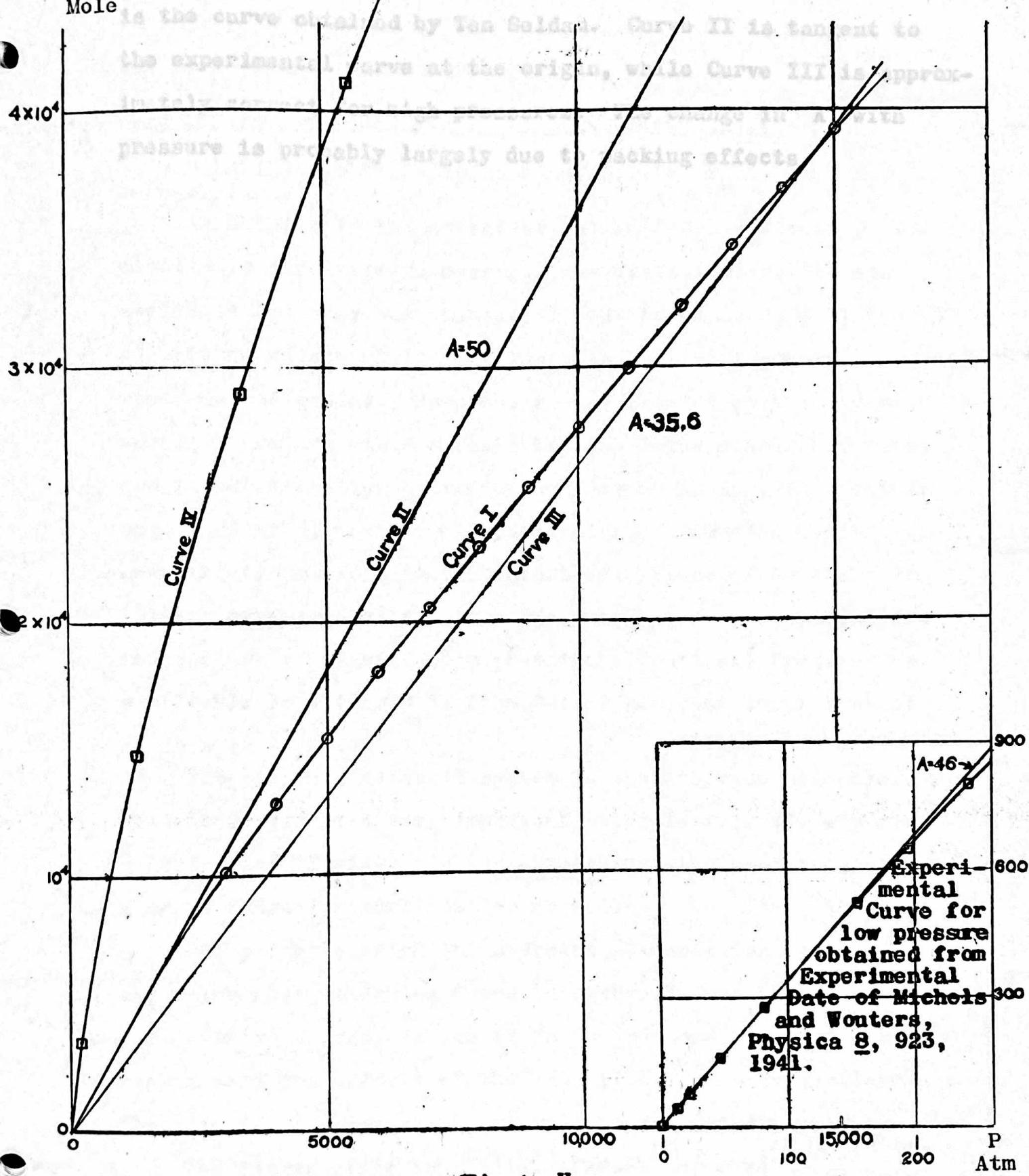


Figure V

is the curve obtained by Ten Seldam. Curve II is tangent to the experimental curve at the origin, while Curve III is approximately correct for high pressures. The change in A with pressure is probably largely due to packing effects.

In Chapter IV the effect of intermolecular forces on the electronic structure of hydrogen was investigated. As was stated in the previous chapter, it can be expected that the effects found are similar to those that exist for more complex atoms and molecules. However, in the case of polyatomic molecules, there are other effects besides those electronic ones, and calculations for hydrogen can give no indication of their magnitude or direction. In particular, the nuclear separation and vibrational frequency are changed. These effects are small, but are experimentally detectable. Measurements of the infrared spectra of liquids show that the vibrational frequency of a molecule in a liquid is from 0 to 5 per cent lower than it is in a gas (20).

The simplest diatomic system is the hydrogen molecule ion. While this is not a very important molecule from the experimental point of view, one may expect that the results are similar to those for more complex molecules.

One property which the hydrogen molecule ion possesses and which most molecules found in nature do not have is its net positive charge. Since it is the purpose here to investigate only the effects of the so-called Van der Waals forces, the effects of this net charge will be neglected.

The ground state for  $\text{H}_2^+$ . Before the effects of Van

der Waals forces on  $H_2^+$  can be determined.

## CHAPTER V

### INTERNUCLEAR SEPARATION. THE RESULTS

#### THE EFFECT OF INTERMOLECULAR FORCES ON THE INTERNUCLEAR

#### SEPARATION AND VIBRATIONAL FREQUENCY OF $H_2^+$

In Chapter IV the effect of intermolecular forces on the electronic structure of hydrogen was investigated. As was stated in the previous chapter, it can be expected that the effects found are similar to those that exist for more complex atoms and molecules. However, in the case of polyatomic molecules, there are other effects besides these electronic ones, and calculations for hydrogen can give no indication of their magnitude or direction. In particular, the nuclear separation and vibrational frequency are changed. These effects are small, but are experimentally detectable. Measurements of the infrared spectra of liquids show that the vibrational frequency of a molecule in a liquid is from 0 to 5 per cent lower than it is in a gas<sup>(20)</sup>.

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One property which the hydrogen molecule ion possesses and which most molecules found in nature do not have is its net positive charge. Since it is the purpose here to investigate only the effects of the so-called Van der Waals forces, the effects of this net charge will be neglected.

The ground state for  $H_2^+$ . Before the effects of Van

der Waals forces on  $H_2^+$  can be determined, it is necessary to determine the electronic ground state as a function of the internuclear separation. The Hamiltonian for this problem is given by

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \quad (69)$$

Table II

if the two protons are held fixed. Here  $r_1$  is the distance of the electron from one of the protons;  $r_2$  is its distance from the other, and  $R$  is the internuclear separation. While this problem cannot be solved exactly, many excellent approximate solutions have been given<sup>(21,22,23,24)</sup>. The function that will be used here was first tried by James<sup>(23)</sup>. This function is given by

$$\Psi = e^{-b\xi} \left[ 1 + c\eta^2 \right] \quad (70)$$

$$\xi = \frac{r_1 + r_2}{R}$$

$$\eta = \frac{r_1 - r_2}{R}$$

Taking the derivative with respect to  $R$  and setting it equal

to zero gives an equilibrium separation of 2.0156 Å. The where  $b$  and  $c$  are variation parameters. The quantities

$\xi$  and  $\eta$  are the coordinates of the electron in a confocal elliptic coordinate system with the foci at the two protons.

When the variational principle is applied to this function,  $b$  and  $c$  are obtained as a function of  $R$ . Table II

gives the values of  $b$ ,  $c$  and the expectation value of the energy for three values of  $R$  near the equilibrium separation.

nuclear distance and spring constant. Here two problems will be

$$R \quad b \quad c \quad -\frac{2a_0}{e^2} \langle E \rangle$$

and another molecule, and the effect of embedding an  $H_2^+$  molecule in a dielectric medium.

$$2.2 a_0 \quad 1.453 \quad 0.537 \quad 1.201178$$

$$2.0 a_0 \quad 1.354 \quad 0.452 \quad 1.20477$$

$$1.8 a_0 \quad 1.252 \quad 0.370 \quad 1.20002$$

The effect of the dispersion force between  $H_2^+$  and another molecule. As a model for this problem, the interacting molecule will be assumed **Table II** to be like a polarizable sphere.

Two cases will be considered. For the first case the interacting molecule will be taken to lie on the line joining the two

One may fit  $\langle \Delta E \rangle$  to a function of the form on a perpendicular bisector of this line. These two cases are illus-

$$\langle \Delta E \rangle = E_0 + A \frac{R}{a_0} + B \frac{R^2}{a_0^2} \quad (71)$$

The quantities  $E_0$ , A and B are found to be

$$E_0 = -0.69322 \frac{e^2}{2a_0}, \quad A = -0.46215 \frac{e^2}{2a_0}, \quad B = 0.104375 \frac{e^2}{2a_0}$$

Taking the derivative with respect to R and setting it equal to zero gives an equilibrium separation of  $2.0136 a_0$ . The second derivative of E gives a spring constant for the molecule of  $4.541 \times 10^{-12} \frac{\text{ergs}}{A^2}$ .

A. The effect of attractive forces on the internuclear separation and spring constant of  $H_2^+$ . Once the ground state

of  $H_2^+$  is known, the techniques used in Chapter V may be applied to determine the effect of attractive forces on its internuclear distance and spring constant. Here two problems will be

considered; the effect of the dispersion force between  $H_2^+$  and another molecule, and the effect of embedding an  $H_2^+$  molecule in a dielectric medium.

The effect of the dispersion force between  $H_2^+$  and another molecule. As a model for this problem, the interacting molecule will be assumed to behave like a polarizable sphere. Two cases will be considered. For the first case the interacting molecule will be taken to lie on the line joining the two protons; while in the second it will be taken to lie on a perpendicular bisector of this line. These two cases are illustrated in Figures VI and VII

Figure VII

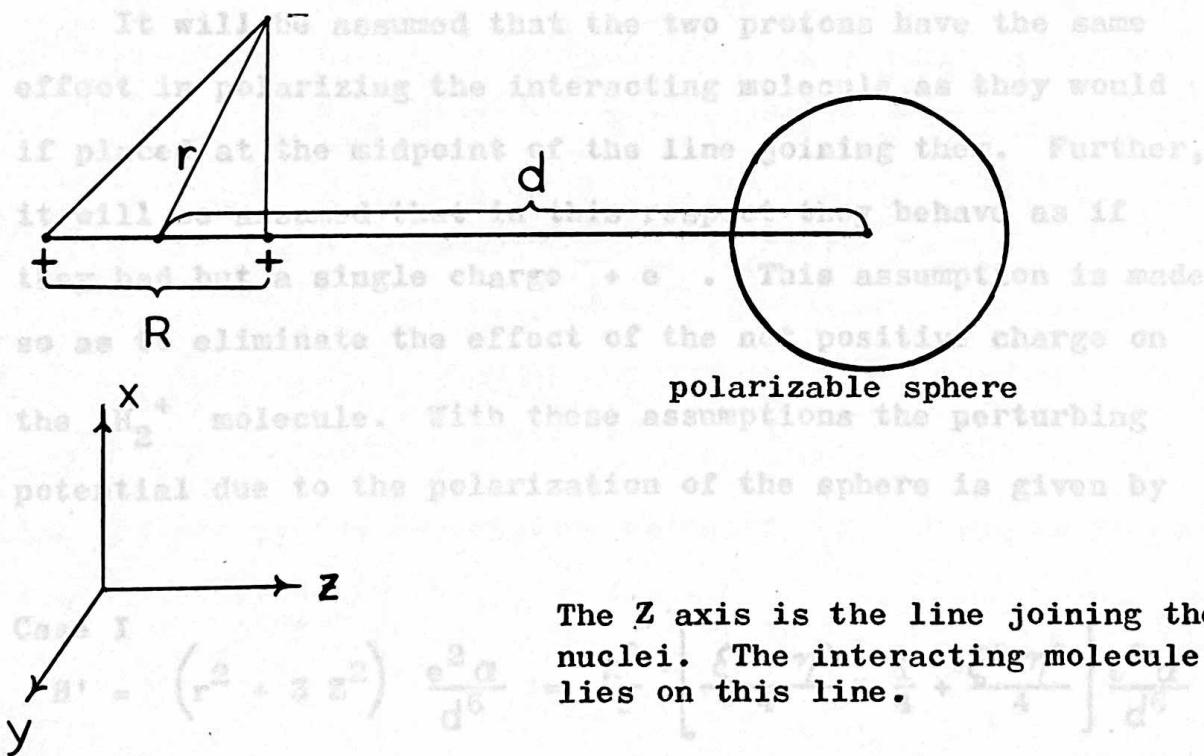
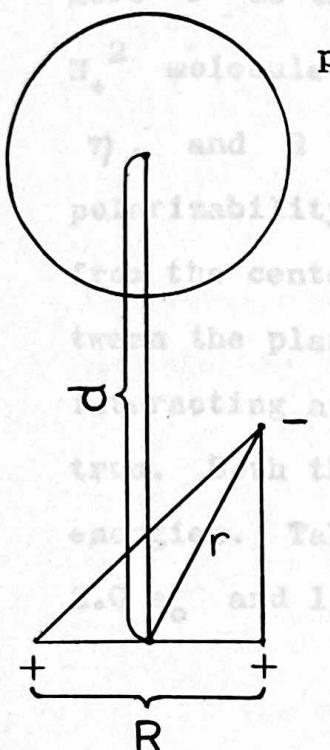
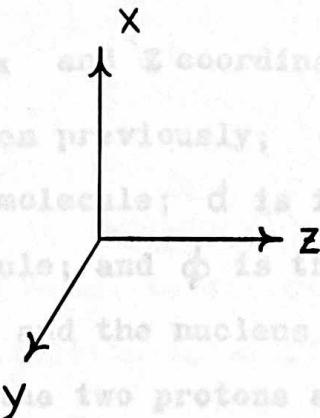


Figure VI



polarizable sphere



The Z axis is taken as the line joining the nuclei and the x axis is the line joining the center of the  $H_2^+$  molecule with the interacting molecule

Figure VII

It will be assumed that the two protons have the same effect in polarizing the interacting molecule as they would if placed at the midpoint of the line joining them. Further, it will be assumed that in this respect they behave as if they had but a single charge  $+e$ . This assumption is made so as to eliminate the effect of the net positive charge on the  $H_2^+$  molecule. With these assumptions the perturbing potential due to the polarization of the sphere is given by

Like the energy the expectation value of  $\langle H' \rangle$  can be fitted

to a power series in  $R$ . One finds

Case I

$$H' = \left( r^2 + 3z^2 \right) \frac{e^2 a}{d^6} = \frac{R^2}{2} \left[ \frac{\xi^2 + \eta^2}{4} - \frac{1}{4} + \frac{\xi^2 \eta^2}{4} \right] \frac{e^2 a}{d^6} \quad (72)$$

Case II

$$H' = \left( r^2 + 3x^2 \right) \frac{e^2 a}{d^6} = \frac{R^2}{2} \left[ \frac{\xi^2 + \eta^2}{4} - \frac{1}{4} + \frac{3}{4} (\xi^2 \eta^2 - \xi^2 \eta^2 - 1) \cos^2 \phi \right] x \frac{e^2 a}{d^6} \quad (73)$$

Here  $r$  is the electron's distance from the center of the  $H_2^+$  molecule  $x$  and  $z$  are its  $x$  and  $z$  coordinates;  $\xi$ ,  $\eta$ , and  $R$  have the meaning given previously;  $\alpha$  is the polarizability of the interacting molecule;  $d$  is its distance from the center of the  $H_2^+$  molecule; and  $\phi$  is the angle between the plane of the two protons and the nucleus of the interacting atom and the plane of the two protons and the electron. Both these perturbations give first order perturbation energies. Table III gives the value of this energy for  $R=2.2a_0$ ,  $2.0 a_0$  and  $1.8 a_0$ .

	Case I	Case II
$R$	$-\langle H' \rangle$	$-\langle H' \rangle$
$2.2 a_0$	$13.350 \frac{e^2 a_0^2}{2^6}$	$9.5914 \frac{e^2 a_0^2}{2^6}$
$2.0 a_0$	$11.785 \frac{e^2 a_0^2}{2^6}$	$8.863 \frac{e^2 a_0^2}{2^6}$
$1.8 a_0$	$10.380 \frac{e^2 a_0^2}{2^6}$	$8.141 \frac{e^2 a_0^2}{2^6}$

Table III

Like the energy the expectation value of  $\langle H' \rangle$  can be fitted to a power series in  $R$ . One finds

$$-\langle H' \rangle = \frac{e^2 a_0^2}{2 d^6} \left\{ 11.785 + 5.8220 \left( \frac{R}{a_0} - 2 \right) + 4.02 \left( \frac{R}{a_0} - 2 \right)^2 \right\} \quad (74)$$

$$\langle H' \rangle = \frac{e^2 a_0 \alpha}{2d^6} \left\{ 8.8628 + 3.425 \left( \frac{R}{a_0} - 2 \right) + 0.170 \left( \frac{R}{a_0} - 2 \right)^2 \right\} \quad (75)$$

$$k = 0.2088 \frac{e^2}{2d^6} + 8.04 \frac{a_0^2 \alpha^2}{2d^6} \quad (79)$$

## Case II

The total energy for the system is equal to the energy of the undisturbed molecule plus the expectation value of  $H'$

$$E = E_0 + \langle H' \rangle \quad (80)$$

$$E = E_0 + \langle H' \rangle \quad (76)$$

To find the new equilibrium distance one must take the derivative of  $E$  with respect to  $R$  and set it equal to zero. When this is done, the following results are found.

$$R = 2.0136 a_0 + 56.0 \frac{a_0^4 \alpha}{R^6} \quad (77)$$

$$\Delta R = 56 \frac{a_0^4 \alpha}{R^6} \quad (81)$$

## Case I Case I

$$R = 2.0136 a_0 + 33.0 \frac{a_0^4 \alpha}{R^6} \quad (78)$$

$$\Delta R = 33 \frac{a_0^4 \alpha}{R^6} \quad (82)$$

If  $\alpha$  is taken to be  $\frac{1}{2} a_0^3$ , the polarizability of hydrogen,

## Case II

The new spring constant is given by the second derivative of  $E$  with respect to  $R$ . The following values are found for the

spring constant

$$k = 0.2088 \frac{e^2}{2 a_0} + 8.04 \frac{e^2 a_0^2 \alpha}{2 d^6} \quad (79)$$

Case I

$$k = 0.2088 \frac{e^2}{2 a_0^3} + 0.340 \frac{e^2 a_0^2 \alpha}{2 d^6} \quad (80)$$

Case II

Since the vibrational frequency  $\nu$  is proportional to the square root of  $k$ , the change in vibrational frequency  $\Delta \nu$  divided by the frequency is equal to  $\frac{1}{2}$  the change in  $k$  divided by  $k$ . Hence one gets for  $\frac{\Delta \nu}{\nu}$

$$\text{for } \frac{\Delta \nu}{\nu} = 40 \frac{a_0^3 \alpha}{ad^6} \quad (81)$$

Case I

$$\frac{\Delta \nu}{\nu} = 1.7 \frac{a_0^3}{2d^6} \quad (82)$$

Case II

If  $\alpha$  is taken to be  $\frac{9}{2} a_0^3$ , the polarizability of hydrogen, one finds for  $\Delta R$  and  $\frac{\Delta \nu}{\nu}$

The effect of embedding an  $\text{H}_2^+$  molecule in a dielectric. When a molecule in a dense gas or liquid, it is acted on by forces from many neighboring molecules. As was

stated in Chapter IV, the average effect of the dispersion forces may be approximated by placing the molecule in a cavity in a dielectric. A model similar to this has been used by

Kirkwood according to Ref. (25) to explain the shifts in vibrational frequencies of polar molecules in liquids. Here the model will be applied to  $\text{H}_2^+$ .

for  $d = 4 a_0$  the  $\text{H}_2^+$  molecule is placed in the center of a spherical cavity in a dielectric as is illustrated in Figure VII.

$$\frac{\Delta \nu}{\nu} = \frac{90}{4096} = 0.022 \quad (86)$$

### Case I

$$\Delta R = \frac{33 \times 9}{2} \frac{a_0^7}{d^6} = 148.5 \frac{a_0^7}{d^6} \quad (87)$$

for  $d = 4 a_0$

~~$$\Delta R = \frac{148.5}{4096} a_0 = 0.036 a_0$$~~ 
$$\Delta R = \frac{148.5}{4096} a_0 = 0.036 a_0 \quad (88)$$

~~$$\frac{\Delta \nu}{\nu} = \frac{1.7 \times 9}{4} R \frac{a_0^6}{d^6}$$~~ 
$$\frac{\Delta \nu}{\nu} = \frac{1.7 \times 9}{4} R \frac{a_0^6}{d^6} \quad (89)$$

for  $d = 4 a_0$

Figure VII

$$\frac{\Delta \nu}{\nu} = \frac{3.85}{4096} = 0.00094 \quad (90)$$

As was shown in Chapter IV, the electron produces an image charge in the dielectric which attracts it. The potential due to this attraction is given by

### Case II

The effect of embedding an  $H_2^+$  molecule in a dielectric.

When a molecule is embedded in a dense gas or liquid, it is acted on by forces from many neighboring molecules. As was stated in Chapter IV, the average effect of the dispersion forces may be approximated by placing the molecule in a cavity in a dielectric. A model similar to this has been used by Kirkwood according to West<sup>(25)</sup> to explain the shifts in vibrational frequencies of polar molecules in liquids. Here this model will be applied to  $H_2^+$ .

The  $H_2^+$  molecule is placed in the center of a spherical cavity in a dielectric as is illustrated in Figure VII.

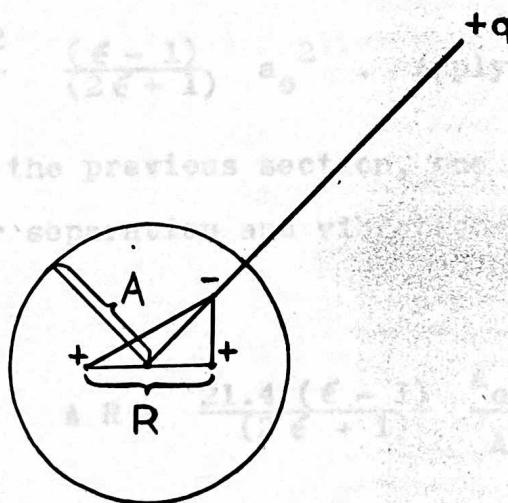


Figure VII

As was shown in Chapter IV, the electron produces an image charge in the dielectric which attracts it. The potential due to this attraction is given by

$$V = - \frac{e^2 r^2}{A^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)} \quad (91)$$

For this case the two protons also produce image charges in the dielectric since they are not at the center of the sphere. However, for reasonable-sized cavities these images are so far away that they have little effect. Also the two images are diametrically opposite so that their effects almost cancel. If the radius of the sphere is  $3 A$ , it turns out that these images give a contribution of about one-tenth that of the electrons' image. Hence the effect of the proton images may be neglected.

The expectation values of  $V$  for  $R = 1.8 a_0$ ,  $2.0 a_0$  and  $2.2 a_0$  are  $- \frac{4.444 e^2}{A^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)} a_0^2$ ,  $\frac{-4.918 e^2}{A^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)} a_0^2$

and  $- \frac{5.422 e^2}{A^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)} a_0^2$ . Applying the same procedure

as was used in the previous section, one finds for the change in internuclear separation and vibrational frequency the following values

$$\Delta R = \frac{21.4 (\epsilon - 1)}{(2\epsilon + 1)} \frac{a_0^4}{A^3} \quad (92)$$

$$\frac{\Delta \nu}{\nu} = - 7.2 \frac{a_0^3}{A^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)} \quad (93)$$

For  $\epsilon = 1.6$  and  $A = 6 a_0$  the values of  $\Delta R$  and  $\frac{\Delta \nu}{\nu}$  are

$$\Delta R = + 0.033 a_0 \quad (94)$$

If  $A$  is taken to be .50 as was found necessary in the case of helium, then one obtains for  $\Delta R$  and  $\frac{\Delta \nu}{\nu}$

$$(95)$$

B. The effect of pressure on the internuclear distance and vibrational frequency of  $H_2^+$ . Here, as in the case of the electronic structure of hydrogen, one can approximate the effect by assuming the average pressure effect is the same as that produced by a perturbing potential of the form

From these equations it can be seen that pressures of the order of 100,000 atmospheres would be required to produce appreciable changes in the internuclear spacing or vibrational frequencies

The expectation value of this potential for the three internuclear separations of  $1.8 a_0$ ,  $2.0 a_0$ , and  $2.2 a_0$  are

$4.231 A P a_0^3$ ,  $4.906 A P a_0^3$ , and  $5.635 A P a_0^3$ . Again applying the methods of the earlier sections, one finds for  $\Delta R$  and  $\frac{\Delta \nu}{\nu}$ .

$$\Delta R = -60 \frac{A P a_0^5}{e^2} \quad (97)$$

$$\frac{\Delta \nu}{\nu} = 14 \frac{A P a_0^4}{e^2} \quad (98)$$

Substituting in the values of  $e^2$  and  $a_0$  gives

$$\Delta R = -1.5 \times 10^{-7} A P a_0 \quad (99)$$

$$\frac{\Delta \nu}{\nu} = 3.5 \times 10^{-8} A P \quad (100)$$

If  $A$  is taken to be .50 as was found necessary in the case of helium, then one obtains for  $\Delta R$  and  $\frac{\Delta \nu}{\nu}$

CHAPTER VI  
THE CAGED DIATOMIC MOLECULE

$$\Delta R = - \frac{72 \times 10^{-7}}{\text{atm}} P a_0 \quad (101)$$

As has been stated earlier, some authors have attempted to determine the effect of pressure on the electronic structure of an atom or molecule by assuming that at high pressures

the neighboring molecules form a cage in which the given molecule and its electrons are confined. In the last chapter the effect of caging the electron of  $H^+$  on the vibrational motion was estimated by using a perturbing potential of the form of molecules.

$A P r^2$ . It might be expected that this caging would also have a direct effect on the vibrational motion. The motion of an atom within the molecule would be affected. This is equivalent to assuming that the average perturbing potential due to the neighbors depends on the instantaneous position of the nuclei. It is reasonable to assume that this is the case since the average force which a molecule exerts on a medium is probably higher when the atoms are far away from the molecular center than when they are near it. Since the mass of an atom is comparable to the mass of a molecule while the mass of an electron is not, it cannot be expected that a rigid cage gives as accurate results for vibrational caging as for electronic caging. Nevertheless, it is interesting to calculate this effect. Here only the case of a one-dimensional diatomic molecule contained in a rigid box will be considered. This problem is illustrated in Figure VIII.

## CHAPTER VI

### THE CAGED DIATOMIC MOLECULE

As has been stated earlier, some authors have attempted to determine the effect of pressure on the electronic structure of an atom or molecule by assuming that at high pressures the neighboring molecules form a cage in which the given molecule and its electrons are confined. In the last chapter the effect of caging the electron of  $\text{H}_2^+$  on its vibrational motion was estimated by using a perturbing potential of the form

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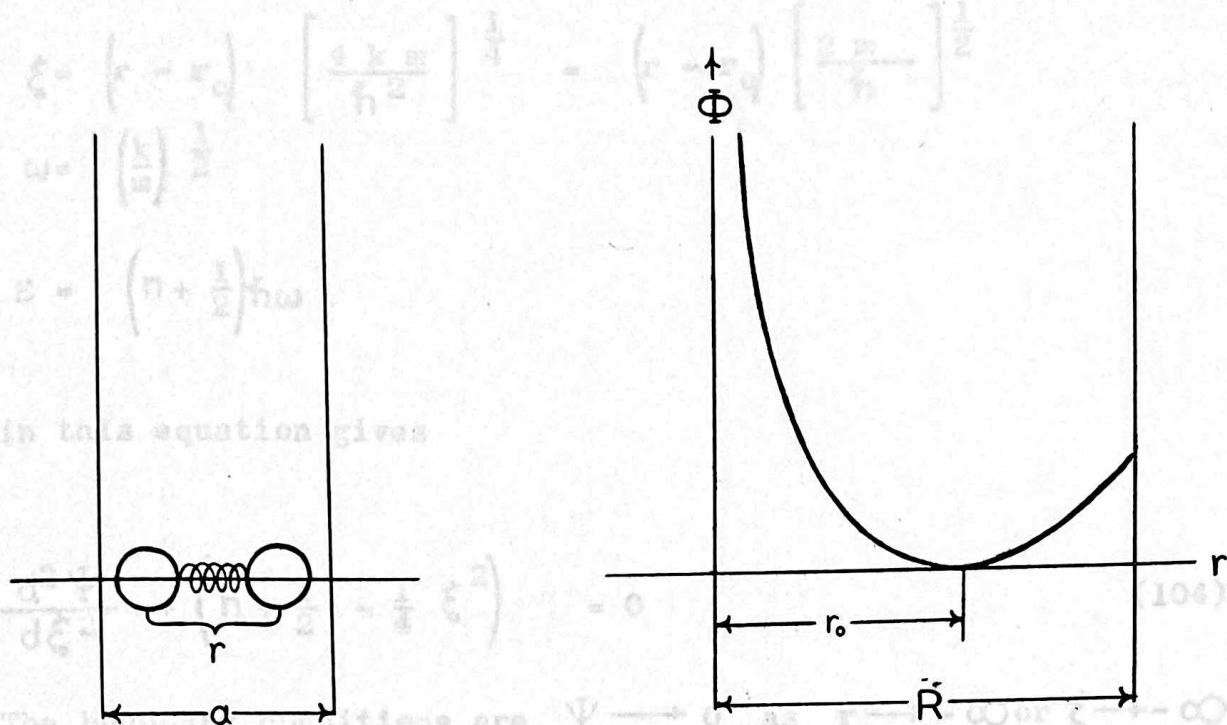


Figure VIII

In the figure  $r$  is the distance of separation between the two atoms and  $\Phi$  is the interatomic potential. A somewhat similar problem concerning the motion of an atom in a crystal has been solved by Auluck<sup>(26)</sup>. He considered the problem of the harmonic oscillator bounded on both sides where as here the problem is that of a harmonic oscillator bounded on only one side.

The Schrödinger equation for this system is

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dr^2} + \left( \frac{k}{2} [r - r_0]^2 - E \right) \Psi = 0 \quad (103)$$

where  $m$  is the reduced mass of the two atoms and  $\frac{k}{2} (r - r_0)^2$  is the potential energy of position. Substituting

$$\xi = \left( r - r_0 \right) \left[ \frac{4 k m}{\hbar^2} \right]^{\frac{1}{4}} = \left( r - r_0 \right) \left[ \frac{2 m}{\hbar} \right]^{\frac{1}{2}}$$

$$\omega = \left( \frac{k}{m} \right)^{\frac{1}{2}}$$

$$E = \left( n + \frac{1}{2} \right) \hbar \omega$$

in this equation gives

$$\frac{d^2 \Psi}{d\xi^2} + \left( n + \frac{1}{2} - \frac{1}{4} \xi^2 \right) = 0 \quad (104)$$

The boundary conditions are  $\Psi \rightarrow 0$  as  $r \rightarrow -\infty$  or  $\xi \rightarrow -\infty$

and  $\Psi = 0$  at  $r = R$  or  $\xi = \xi_0 = \left( R - r_0 \right) \left( \frac{2 m \omega}{\hbar} \right)^{\frac{1}{2}}$ .

The functions  $D_n(-\xi)$  converge properly for large negative values of  $\xi$  and are solutions of this equation. Whitaker and Watson<sup>(27)</sup> give the following expression for the asymptotic expansion of  $D_n(-\xi)$  for large positive values of  $\xi$ .

$$D_n(-\xi) = \left[ \exp \left( -\frac{1}{4} \xi^2 \right) \right] (-\xi)^n \left\{ 1 - \frac{n(n-1)}{2 \xi^2} \right.$$

$$+ \left. \frac{n(n-1)(n-2)(n-3)}{2 \cdot 4 \xi^4} + \dots \right\}$$

$$- \frac{\sqrt{2\pi}}{\Gamma(-m)} \exp \left( -i \left[ \exp \left( \frac{1}{4} \xi^2 \right) \right] (-\xi)^{-n-1} \right)$$

$$\left\{ 1 + \frac{(n+1)(n+2)}{2 \xi^2} + \frac{(n+1)(n+2)(n+3)(n+4)}{2 \cdot 4 \xi^4} + \dots \right\}$$

If the cell is large, the boundary conditions can be satisfied by setting this asymptotic expression equal to 0 at  $\xi = \xi_0$ .

Hence

$$D_n(\xi_0) = \left[ \exp -\frac{1}{4} \xi_0^2 \right] (-\xi_0)^n - \frac{\sqrt{2\pi}}{\Gamma(-n)} \quad \text{exp} = \pm i \quad (106)$$

$$\left[ \exp -\frac{1}{4} \xi_0^2 \right] (-\xi_0)^{-n-1} = 0$$

$$\left[ \exp -\frac{\xi_0^2}{2} \right] (-\xi_0)^{2n+1} - \frac{2\pi}{\Gamma(-n)} \quad \text{exp} = \pm i = 0 \quad (112)$$

For a large cell  $n$  will be almost an integer. Therefore one may write

$$n = n_0 + \delta \quad (107)$$

From the equations

where  $n_0$  is an integer and  $\delta$  is small. Now the  $\Gamma$  function of small arguments is approximately equal to the reciprocal of the argument. That is,

$$\Gamma(\delta) = \frac{1}{\delta} \quad 1 \gg \delta \quad (108)$$

Furthermore, the  $\Gamma$  function obeys the recursion rule

$$\Gamma(n+1) = n\Gamma(n) \quad (109)$$

$$\text{Hence} \quad (110)$$

$$\Gamma(-\delta) = -\frac{1}{\delta} \quad (110)$$

$$\text{and } \Gamma(-[1+\delta]) = \frac{1}{\delta(\delta+1)}$$

$$\Gamma(-[2+\delta]) = \frac{1}{\delta(1+\delta)(2+\delta)} \quad (110)$$

$$\Gamma(-[n_0+\delta]) = \frac{(-1)^{n+1}}{\delta(\delta+1)(\delta+2)\dots(\delta+n_0)} \quad (110)$$

The boundary condition is therefore given by

$$\left[ \exp - \frac{\xi_0^2}{2} \right] \left( + \xi_0 \right)^{2n_0+1} - \sqrt{2\pi} \delta (\delta+1) \dots - (\delta+n_0) = 0 \quad (111)$$

to terms of order  $\delta^{n_0}$

For  $n_0 = 0$  and  $n_0 = 1$ ,  $\delta$  is found to be

$$\delta = \frac{\xi_0 \left[ \exp - \frac{\xi_0^2}{2} \right]}{\sqrt{2\pi}} \quad n=0 \quad (112)$$

$$\delta = \frac{\xi_0 \frac{3}{4} \left[ \exp - \frac{\xi_0^2}{2} \right]}{\sqrt{2\pi}} \quad (113)$$

From the equations

$$E = \left( n + \frac{1}{2} \right) h\nu$$

$$\text{and } n = n_0 + \delta$$

The change in energy of the ground state and first excited state is

$$\frac{\Delta E_0}{h\nu} = \frac{\xi_0}{\sqrt{2\pi}} \left[ \exp - \frac{\xi_0^2}{2} \right] \quad \text{for the ground state} \quad (114)$$

and

$$\frac{\Delta E_1}{h\nu} = \frac{\xi_0^3}{\sqrt{2\pi}} \left[ \exp - \frac{\xi_0^2}{2} \right] \quad \text{for the first excited state} \quad (115)$$

It is interesting to compare these values with those that Auluck obtained for the harmonic oscillator bounded on both sides. He found

$$\frac{\Delta E_0}{h\nu} = \left(\frac{8}{\pi}\right)^{\frac{1}{2}} \left[ \exp - \frac{\xi_0^2}{2} \right] \text{ for the ground state} \quad (116)$$

and

$$\frac{\Delta E_1}{h\nu} = 1.2 \quad (121)$$

$$\frac{\Delta E_1}{h\nu} = \left(\frac{8}{\pi}\right)^{\frac{1}{2}} \xi_0^3 \left[ \exp - \frac{\xi_0^2}{2} \right] \text{ for the first excited state.} \quad (117)$$

These are exactly four times the values that were obtained here. These are exactly four times the values that were obtained here.

If the values of  $\omega$ ,  $m$ ,  $r_0$  are taken to be the values for  $\omega_0$  then they are equal to

determination of a reasonable cell size is a difficult problem since molecules do not have sharp boundaries. Because of the extreme sensitivity of the results on the size of the cell, it is hard to judge whether this effect is important.

$r_0 = 1.2 \times 10^{-8}$  cm

It seems probable that it is very small since a cell with a

diameter of only  $1.7 \times 10^{-3}$  cm is small. However, such a volume of a dense gas or liquid is taken up by the molecular size and it may be that this is not an unreasonable value.

$$\frac{\Delta E_0}{h\nu} = \frac{1.055 \times 10^9 x}{\sqrt{2\pi}} \left[ \exp - \frac{1.11 x^2 \times 10^{18}}{2} \right] \quad (118)$$

A further point which is likely to be important is the range of  $x$  in molecular sizes. These are of the order of several

tenths of an angstrom. Hence it does not seem likely that a

$$\frac{\Delta E_1}{h\nu} = \frac{1.18 \times 10^{27} x^3}{2} \left[ \exp - \frac{1.11 \times 10^{18} x^2}{2} \right] \quad (119)$$

For the case of the electron, the cell size is determined

if  $x$  is set equal to  $0.5 \times 10^{-8}$  cm  $\frac{\Delta E_0}{h\nu}$  and  $\frac{\Delta E_1}{h\nu}$  are equal to  $2 \times 10^{-6}$  and  $59 \times 10^{-6}$ . For  $x$  equal  $0.2 \times 10^{-8}$  they are given by

used since it is not known how much of this pressure is supported by the electrons and how much by the vibrations.

$$\frac{\Delta E_0}{h\nu} = 0.28 \quad (120)$$

Strictly speaking,  $h\nu$  must, of course, all be supported by the electrons. However, the pressure supported by a non-vibrating molecule and that supported by a vibrating molecule is different. This difference may be ascribed to the internal vibration.

This shows that the effect of caging is a very steep function of the cage size. For this last value of  $x$  the approximations that were used in deriving the formula are probably not correct. However, they do indicate that for such a small cage there would be a large effect.

The determination of a reasonable cell size is a difficult problem since molecules do not have sharp boundaries. Because of the extreme sensitivity of the results on the size of the cell, it is hard to judge whether this effect is important. It seems probable that it is very small since a cell with a diameter of only  $1.7 \times 10^{-8}$  cm is small. However, much of the volume of a dense gas or liquid is taken up by the molecular size and it may be that this is not an unreasonable value. A further point which is likely to be important is the range of intermolecular forces. These are of the order of several tenths of an angstrom. Hence it does not seem likely that a cell size can be given more accurately than this.

For the case of the electron, the cell size is determined

by requiring that the pressure which the electron exerts on the wall be equal to the pressure in the gas. For the diatomic molecule, this method of determining the cell size cannot be used since it is not known how much of this pressure is supported by the electrons and how much by the vibrations. Strictly speaking, it must, of course, all be supported by the electrons. However, the pressure supported by a non-vibrating molecule and that supported by a vibrating molecule is different. This difference may be ascribed to the internal vibration.

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the total energy of the system,  $m_i$  is the mass of the  $i^{\text{th}}$  particle and  $\nabla_i^2$  is the Laplacian with respect to the coordinates of the  $i^{\text{th}}$  particle. If one operates on equation (I.1)

with  $\vec{r}_j \cdot \Psi^* \vec{\nabla}_j$ , one obtains

$$\sum_i -\frac{\hbar^2}{2m_i} \vec{r}_j \cdot \Psi^* \vec{\nabla}_j \nabla_i^2 \Psi + \vec{r}_j \cdot \Psi^* (\vec{\nabla}_j \cdot \vec{v}) \Psi \\ + \vec{r}_j \cdot \Psi^* (v - E) \vec{\nabla}_j \Psi = 0 \quad (I.2)$$

Equation (I.1) also holds for  $\Psi^*$ , the complex conjugate of  $\Psi$ . Hence one also has the equation

$$\sum_i -\frac{\hbar^2}{2m_i} \nabla_i^2 \Psi^* + (v - E) \Psi = 0 \quad (I.3)$$

If equation (I.3) is multiplied by  $\vec{r}_j \cdot \vec{\nabla}_j \Psi$

$$\sum_i -\frac{\hbar^2}{2m_i} \vec{r}_j \cdot \vec{\nabla}_j \Psi \vec{\nabla}_j^2 \Psi^* + (v - E) \vec{r}_j \cdot \vec{\nabla}_j \Psi \Psi^* = 0 \quad (I.4)$$

is obtained.

Subtracting (I.4) from APPENDIX I summing over  $j$  gives equation (I.5)

### A QUANTUM MECHANICAL DERIVATION

#### OF THE VIRIAL THEOREM

The Schrödinger equation for a system of interacting particles may be written in the following form

$$\sum_i - \frac{\hbar^2}{2m_i} \nabla_i^2 \Psi + (V - E) \Psi = 0 \quad (I.1)$$

Integrating (I.5) over all space,

Here  $V$  is the total potential energy of the system,  $E$  is the total energy of the system,  $m_i$  is the mass of the  $i^{\text{th}}$  particle and  $\nabla_i^2$  is the Laplacian with respect to the coordinates of the  $i^{\text{th}}$  particle. If one operates on equation (I.1)

with  $\vec{r}_j \cdot \Psi^* \vec{\nabla}_j$ , one obtains

$$\sum_i - \frac{\hbar^2}{2m_i} \vec{r}_j \cdot \Psi^* \vec{\nabla}_j \nabla_i^2 \Psi + \vec{r}_j \cdot \Psi^* (\vec{\nabla}_j V) \Psi + \vec{r}_j \cdot \Psi^* (\nabla - E) \vec{\nabla}_j \Psi = 0 \quad (I.2)$$

Equation (I.1) also holds for  $\Psi^*$ , the complex conjugate of  $\Psi$ . Hence one also has the equation

$$\sum_i - \frac{\hbar^2}{2m_i} \nabla_i^2 \Psi^* + (V - E) \Psi = 0 \quad (I.3)$$

If equation (I.3) is multiplied by  $\vec{r}_j \cdot \vec{\nabla}_j \Psi$

$$\sum_i - \frac{\hbar^2}{2m_i} \vec{r}_j \cdot \vec{\nabla}_j \Psi \vec{\nabla}_j^2 \Psi^* + (V - E) \vec{r}_j \cdot \vec{\nabla}_j \Psi \Psi^* = 0 \quad (I.4)$$

is obtained.

Equation (I.7) reduces to equation (I.6)

Subtracting (I.4) from (I.2) and summing over  $j$  gives equation (I.5)

$$\sum_j \sum_i -\frac{\hbar^2}{2m_i} \vec{r}_j \cdot \left[ \Psi^* \vec{\nabla}_j \vec{\nabla}_i^2 \Psi - \vec{\nabla}_j \Psi \vec{\nabla}_i^2 \Psi^* \right] + \sum_j \vec{r}_j \cdot \Psi^* \left( \vec{\nabla}_j v \right) \Psi = 0 \quad (I.5)$$

One may convert equation (I.5) into

Integrating (I.5) over all space,

$$\sum_i \int \sum_j -\frac{\hbar^2}{2m_i} \vec{r}_j \cdot \left[ \Psi^* \vec{\nabla}_j \vec{\nabla}_i^2 \Psi - \vec{\nabla}_j \Psi \vec{\nabla}_i^2 \Psi^* \right] d\tau \quad (I.6)$$

$$+ \sum_j \int \vec{r}_j \cdot \Psi^* \vec{\nabla}_j v \Psi d\tau = 0$$

Integration of (I.6) into (I.6) gives

Since  $\vec{\nabla}_i^2$  is a Hermitian operator the first term in (I.6) may be written as follows:

$$\sum_i \int - \sum_j \frac{\hbar^2}{2m_i} \left[ \vec{\nabla}_i^2 \vec{r}_j \Psi^* \vec{\nabla}_j \Psi - \vec{r}_j \vec{\nabla}_j \Psi^* \vec{\nabla}_i^2 \Psi^* \right] d\tau \quad (I.7)$$

$$= \sum_i \int - \sum_j \frac{\hbar^2}{2m_i} \left[ \delta_{ij} \vec{\nabla}_i \Psi^* \cdot \vec{\nabla}_j \Psi + \vec{r}_j \cdot \vec{\nabla}_i^2 \Psi^* \vec{\nabla}_j \Psi - \vec{r}_j \cdot \vec{\nabla}_j \Psi \vec{\nabla}_i^2 \Psi^* \right] d\tau$$

$$= \sum_i \int - \sum_j \frac{\hbar^2}{2m_i} \left[ 2 \vec{\nabla}_i \Psi^* \cdot \vec{\nabla}_j \right] d\tau$$

Here use has been made of the fact that

$$\vec{\nabla}_i^2 \vec{r}_j = 0 \quad \text{and} \quad \vec{\nabla}_i \vec{r}_j = \delta_{ij} \cdot$$

Thus equation (I.7) reduces to equation (I.8)

APPENDIX II

$$\sum_i \int \sum_j -\frac{\hbar^2}{2m_i} \left[ 2 \vec{\nabla}_i \Psi^* \cdot \vec{\nabla}_j \Psi \right] d\tau \quad (I.8)$$

The results of Appendix I can be applied to a system of two interacting atoms. Consider such a system where the internuclear separation is  $R$  and the nuclear charges  $Z_1$  and  $Z_2$ . One may convert equation (I.8) into

$$- \sum_i \int -\frac{\hbar^2}{2m_i} 2 \Psi^* \nabla_i^2 \Psi d\tau \quad (I.9)$$

by making use of the Hermitian property of  $i \vec{\nabla}_i$ . Substitution of (I.9) into (I.6) gives

$$-2 \sum_i \int -\frac{\hbar^2}{2m_i} \Psi^* \nabla_i^2 \Psi d\tau + \sum_j \int \vec{r}_j \cdot \vec{\nabla}_j \Psi^* \Psi d\tau = 0 \quad (I.10)$$

The first term is the negative of twice the expectation value of the kinetic energy for the total system while the second term is the expectation value of  $- \sum_j \vec{r}_j \cdot \vec{F}_j$ . Hence (I.10) may be written as follows

$$2 \langle K \rangle = - \left\langle \sum_j \vec{r}_j \cdot \vec{F}_j \right\rangle \quad (I.11)$$

Here the origin of coordinates was taken at nucleus 1. From This is equation (16).

equation (I.10) twice the kinetic energy of the electrons is given by

## APPENDIX II

### APPLICATION OF THE VIRIAL THEOREM TO A SYSTEM OF TWO INTERACTING ATOMS

The results of Appendix I may be applied to a system of two interacting atoms. Consider such a system where the internuclear separation is  $R$  and the nuclear charges  $Z_1$  and  $Z_2$ .

Substituting this expression in (I.10) gives the following

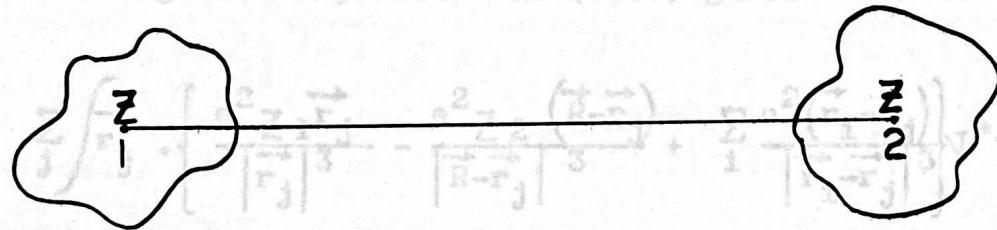


Figure IX

The two nuclei are to be considered held fixed. The potential for the electronic motion for this system is given by the following expression

$$V = \frac{Z_1 Z_2 e^2}{R} - \sum_i \frac{e_i^2 Z_1}{|\vec{r}_i|} = \sum_i \frac{e^2 Z_2}{|R - \vec{r}_i|} + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (\text{II.1})$$

Here the origin of coordinates was taken at nucleus 1. From

equation (I.10) twice the kinetic energy of the electrons is given by

$$2K = \sum_j \int \vec{r}_j \cdot \vec{\nabla}_j v \Psi^* \Psi d\tau \quad (\text{I.10})$$

The quantity  $\vec{\nabla}_j v$  may be obtained from (II.1) and is found to be

$$\vec{\nabla}_j v = \frac{e^2 Z_1 \vec{r}_j}{|\vec{r}_j|^3} - \frac{e^2 Z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} - \sum_i \frac{e^2 (\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|^3} \quad (\text{II.2})$$

Substituting this expression in (I.10) gives the following

$$2K = \sum_j \int \vec{r}_j \cdot \left\{ \frac{e^2 Z_1 \vec{r}_j}{|\vec{r}_j|^3} - \frac{e^2 Z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} + \sum_i \frac{e^2 (\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|^3} \right\} \Psi^* \Psi d\tau \quad (\text{II.3})$$

relation for  $2K$ .

$$= \sum_j \left[ - \frac{e^2 Z_1}{|\vec{r}_j|^3} - \frac{e^2 Z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \cdot \vec{r}_j + \sum_i \frac{e^2 (\vec{r}_i - \vec{r}_j) \cdot \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^3} \right] \Psi^* \Psi d\tau$$

The term  $\sum_j \sum_i \frac{e^2 (\vec{r}_i - \vec{r}_j) \cdot \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^3}$  may be written as

$$\sum_j \sum_i \frac{e^2 (\vec{r}_j - \vec{r}_i) \cdot \vec{r}_j}{|\vec{r}_j - \vec{r}_i|^3} \quad \text{by simply interchanging } i \text{ and } j.$$

j. Adding these two expressions and dividing by 2 gives

$$\frac{1}{2} \sum_{ij} \frac{e^2 (\vec{r}_i - \vec{r}_j) \cdot (\vec{r}_i - \vec{r}_j)}{|\vec{r}_j - \vec{r}_i|^3} = \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|^3} \quad (\text{II.4})$$

for  $\sum_{ij} \frac{e^2 (\vec{r}_i - \vec{r}_j) \cdot \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^3}$

This is the potential due to the interaction of the electrons with each other and will be called  $V_{elc}$  from now on.

The term  $-\sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j) \cdot \vec{r}_j}{|\vec{R} - \vec{r}_j|^3}$  may also be written in

another form. If  $\sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j) \cdot \vec{R}}{|\vec{R} - \vec{r}_j|}$  is added and sub-

tracted from this expression then the system. Subtracting equation

$$-\sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j) \cdot \vec{r}_j}{|\vec{R} - \vec{r}_j|^3} = \sum_j \frac{e^2 z_2}{|\vec{R} - \vec{r}_j|} - \sum_j \frac{e^2 z_2 \vec{R} \cdot (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \quad (II.5)$$

Substituting (II.4) and (II.5) in (II.3) gives the following relation for  $2K$ .

$$2k = - \int \left[ V_{elc} - \sum_j \frac{e^2 z_1}{|\vec{r}_j|} - \sum_j \frac{e^2 z_2}{|\vec{R} - \vec{r}_j|} + \sum_j \frac{e^2 z_2 \vec{R} \cdot (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \right] \Psi^* \Psi d\tau \quad (II.6)$$

$$= - \frac{z_1 z_2 e^2}{R} + \frac{z_1 z_2 e^2 \vec{R} \cdot \vec{R}}{|R|^3} - \int \left[ V_{elc} - \sum_j \frac{e^2 z_1}{|\vec{r}_j|} - \sum_j \frac{e^2 z_2}{|\vec{R} - \vec{r}_j|} \right] \Psi^* \Psi d\tau$$

$$= - \int \left[ \sum_j \frac{e^2 z_2 \vec{R} \cdot (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \right] \Psi^* \Psi d\tau$$

$$= - \langle V \rangle + \vec{R} \cdot \left[ \frac{z_1 z_2 e^2 \vec{R}}{|R|^3} - \int \sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \Psi^* \Psi d\tau \right]$$

The first term on the right hand side of (II.6),  $-\langle V \rangle$ , is the expectation value of the total potential energy, both electronic

and nuclear, while the second term is the scalar product of  $\vec{R}$  and the force acting on nucleus 2. If  $K$  is subtracted from both sides of (II.6), equation (II.7) is obtained.

$$K = \langle v \rangle - K + \vec{R} \cdot \left[ \frac{z_1 z_2 e^2 \vec{R}}{|R|^3} - \int \sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \Psi^* \Psi d\tau \right] \quad (II.7)$$

$$= U + \vec{R} \cdot \left[ \frac{z_1 z_2 e^2 \vec{R}}{|R|^3} - \int \sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \Psi^* \Psi d\tau \right]$$

Here  $U$  is the total energy of the system. Subtracting equation (II.7) for infinite separation from (II.7) for separation  $R$  gives a relation between the change in kinetic energy of the electrons, the change in potential energy of the electrons, and the force acting on nucleus 2

$$\Delta K = -\Phi + \vec{R} \cdot \left[ \frac{z_1 z_2 e^2 \vec{R}}{|R|^3} - \int \sum_j \frac{e^2 z_2 (\vec{R} - \vec{r}_j)}{|\vec{R} - \vec{r}_j|^3} \Psi^* \Psi d\tau \right] \quad (II.8)$$

$$\Delta K = K_{R=R} - K_{R=\infty} \Phi = U_{R=R} - U_{R=\infty}$$

The quantity  $\Phi$  is the internuclear potential that is obtained in the Born-Oppenheimer approximation. To see the significance of the last term on the right hand side, one may proceed as follows.

Consider the Schrödinger equation for the two atoms

$$\sum_j -\frac{\hbar^2}{2m_i} \nabla^2 \Psi + (V - E) \Psi = 0 \quad (II.9)$$

Let  $E_0(R)$  be the ground state energy of the system when the nuclei are held fixed at a separation  $R$ . Also, let  $\Psi_0(R)$  be the corresponding wave function. Then these quantities satisfy the equation

$$\sum_i -\frac{\hbar^2}{2m_i} \nabla_i^2 \Psi_0(R) + [V(R) - E_0(R)] \Psi_0(R) = 0 \quad (\text{II.10})$$

Here  $V(R)$  is the total potential energy. It depends on the nuclear separation. Suppose now the separation between the nuclei is changed by a small amount  $\Delta R$ . Whereas the potential energy  $V(R)$  is changed directly  $\Psi_0(R)$  and  $E_0(R)$  are changed only because a different Schrödinger equation must be satisfied. The slightly different Schrödinger equation may be solved by perturbation methods. To first orders in  $\Delta R$  the perturbing potential is given by

$$\left(\frac{\partial V}{\partial R}\right) \cdot \Delta R$$

And to first orders in  $\Delta R$  the perturbed energy is given by

$$\Delta E_0(R) = \frac{dE_0}{dR} \Delta R = \Delta R \int \Psi_0^*(R) \left(\frac{\partial V}{\partial R}\right) \Psi_0(R) dT \quad (\text{II.11})$$

Here  $\frac{dE_0}{dR} \Delta R$  expresses the change in  $E_0(R)$  with the change  $\Delta R$  in  $R$ . It may be written in this form since  $E_0(R)$  is a function of the nuclear separation alone. Dividing both sides of (II.11) by  $\Delta R$  and taking the limit as  $\Delta R$  goes to 0, one finds

$$\frac{dE_0}{dR} = \int \Psi_0^*(R) \left(\frac{\partial V}{\partial R}\right) \Psi_0(R) dT \quad (\text{II.12})$$

Now  $\int \Psi_0^* (\mathbf{R}) \left( \frac{\partial \mathbf{v}}{\partial \mathbf{R}} \right) \Psi_0 (\mathbf{R}) d\tau$  is given by

## APPENDIX III

$$- \frac{Z_1 Z_2 e^2 \vec{r}}{|\mathbf{R}|^3} + \int \sum_j \frac{e^2 Z_2 (\vec{r} - \vec{r}_j)}{|\vec{r} - \vec{r}_j|^3} \Psi_0^* \Psi_0 d\tau$$

The variation perturbation method given in Chapter II was based on the assumption that one could approximate

One sees from this and (II.8) that  $\Delta K$  is given by

$$\Delta K = -\vec{\Phi} - \vec{R} \cdot \frac{dE_0(\mathbf{R})}{d\mathbf{R}} \quad (\text{III.1})$$

by an expression of the form

$$\text{However } E_0(\mathbf{R}) \text{ is equal to } E_0, R=\infty + \vec{\Phi}_{\infty}. \text{ Hence } \frac{dE_0(\mathbf{R})}{d\mathbf{R}}$$

is equal to  $-\frac{d\vec{\Phi}}{d\mathbf{R}}$ , and equation (II.13) can be written

as follows

equation for the function given in IV. This eliminates the difficulties,  $\Delta K = -\vec{\Phi} - \vec{R} \cdot \frac{d\vec{\Phi}}{d\mathbf{R}}$ . The problem of solving this equation instead of with a definite answer.

In order to obtain this differential equation, one may proceed as follows. Let  $f$  be a function such that

$$\sum_{k=0}^{\infty} \frac{H_k^+ U_k}{E_0 - E_k} = f U_0 \quad (\text{III.3})$$

Multiply both sides of this equation by  $U_0^*$  and integrate over all space. This gives

$$\frac{H_0^+}{E_0 - E_0} = \int U_0^* f U_0 d\tau \quad (\text{III.4})$$

Multiplying each side of this by  $E_0 - E_e$  one obtains

### APPENDIX III

#### A MODIFICATION OF THE VARIATION PERTURBATION METHOD

(III.5)

The variation perturbation method given in Chapter II was based on the assumption that one could approximate

$$\sum_{k \neq 0} \frac{H'_{ko} U_k}{E_0 - E_k} = \int [U_e^* f H_0 U_0 - H_0 (f U_0)] d\tau \quad (\text{III.1})$$

Here use has been made of the fact that  $E_0$  and  $E_e$  are just by an expression of the form

numbers and commute with  $U_e^*$  and  $f$  and that  $H_0 U_0 = E_0 U_0$   
and  $H_0 U_e = E_e U_e$

$$\frac{1}{\epsilon} \sum_{k \neq 0} \frac{H'_{ko} U_k}{E_0 - E_k} = \frac{1}{\epsilon} U_0 \left( H' - H'_{oo} \right) \quad (\text{III.2})$$

Now  $H'$  is equal to  
As was pointed out in Chapter IV, one sometimes runs into difficulty by doing this. It is possible to write a differential equation for the function given in IV. This eliminates the difficulties, but leaves one with the problem of solving this equation instead of with a definite answer.

In order to obtain this differential equation, one may proceed as follows. Let  $f$  be a function such that

$$\sum_{k \neq 0} \frac{H'_{ko} U_k}{E_0 - E_k} = f U_0 \quad (\text{III.3})$$

since  $H_0$  is Hermitian.

Multiply both sides of this equation by  $U_e^*$  and integrate over-all space. This gives

$$\frac{H'_{eo}}{E_{eo} - E_e} = \int U_e^* f U_0 d\tau \quad (\text{III.4})$$

Multiplying each side of this by  $E_o - E_e$  one obtains

$$H'_{eo} = (E_o - E_e) \int U_e^* f U_o d\tau \quad (\text{III.5})$$

A perhaps simpler and more straightforward derivation of (III.5) can also be given. The function  $U_o$  is the ground state wave function for a Hamiltonian  $H_o$ . One desires the wave function for the Hamiltonian  $H_o + f U_o$ , a function of the form

$$= \int [U_e^* f H_o U_o - (H_o U_e^*) f U_o] d\tau$$

Here use has been made of the fact that  $E_o$  and  $E_e$  are just numbers and commute with  $U_e^*$  and  $f$  and that  $H_o U_o = E_o U_o$  may be tried.

$$\text{and } H_o U_e^* = E_e U_e^*.$$

The Schrödinger equation then requires that

$$\text{Now } H'_{eo} \text{ is equal to } (E_o + H') \Psi = E \Psi = (E_o + \epsilon) \Psi \quad (\text{III.10})$$

$$\text{or } (E_o + H') U_o (1 + \int U_e^* H' U_o d\tau) \Psi \quad (\text{III.6})$$

Hence

$$\int U_e^* H' U_o d\tau = \int [U_e^* f H_o U_o - (H_o U_e^*) f U_o] d\tau \quad (\text{III.7})$$

$$= \int U_e^* \left\{ f H_o U_o - H_o (f U_o) \right\} d\tau$$

since  $H_o$  is Hermitian.

The only way that this equation can hold for all  $U_e^*$  is for the following equation to hold.

$$H' U_o = f H_o U_o - H_o (f U_o) + H'_{oo} U_o \quad (\text{III.8})$$

If now it is assumed that  $H'$  is small and hence  $\epsilon$  and  $f$  are also small, then  $H' U_o f$  and  $\epsilon U_o f$  can be neglected.

$$H'_{oo} = \int U_o^* H' U_o d\tau$$

Equation (III.11) then becomes

The term  $H'_{00} U_0$  must be added to make equation (III.7) hold

for  $\epsilon = 0$ . It adds nothing to the integral for the other terms since  $U_0$  is orthogonal to all  $U_e$  for  $e \neq 0$ .

A perhaps simpler and more straight forward derivation of (III.8) can also be given. The function  $U_0$  is the ground state wave function for a Hamiltonian  $H_0$ . One desires the wave function for the Hamiltonian  $H_0 + H'$ . A function of the form

$$\Psi = U_0 (1 + f) \quad (\text{III.9})$$

may be tried.

The Schrödinger equation then requires that

$$(H_0 + H') \Psi = E \quad \Psi = (E_0 + \epsilon) \Psi \quad (\text{III.10})$$

$$\text{or } (H_0 + H') U_0 (1 + f) = (E_0 + \epsilon) \Psi$$

$$H_0 U_0 = E_0 U_0$$

Carrying out the operations one gets

$$E_0 U_0 + H_0 (U_0 f) + H' U_0 + H' U_0 f = E_0 U_0 + f E_0 U_0 + \epsilon U_0 + \epsilon U_0 f$$

$$= E_0 U_0 + f H_0 U_0 + \epsilon U_0 + \epsilon U_0 f$$

$$H_0 (U_0 f) - f H_0 U_0 + H' U_0 + H' U_0 f = \epsilon U_0 + \epsilon U_0 f$$

If now it is assumed that  $H'$  is small and hence  $\epsilon$  and  $f$  are also small, then  $H' U_0 f$  and  $\epsilon U_0 f$  can be neglected.

Equation (III.11) then becomes

$$H_0 (U_0 f) - f(H_0 U_0) + H' U_0 = \epsilon U_0 \quad (\text{III.12})$$

Now for  $f U_0$  may be expanded in terms of the functions  $U_e$ .

If this equation can be solved for  $f$  then the perturbed wave function  $\Psi$

$$f U_0 = \sum_{e \neq 0} a_e U_e \quad (\text{III.13})$$

No  $U_0$  term appears since when  $\Psi$  is expanded in such a series the  $U_0$  term takes care of this. The function  $\Psi$  is not normalized. From (III.3) it follows that

if certain boundary conditions. One condition is that  $U_0 f$

be normalizable. Hence the relations

$$\int U_0^* [H_0 (U_0 f) - f(H_0 U_0) + H' U_0] d\tau = \int U_0^* H' U_0 d\tau \quad (\text{III.14})$$

$$= H'_{00} = \int_{r \rightarrow 0} \epsilon U_0^* U_0 d\tau = \epsilon$$

Since  $f H_0 U_0 = E_0 f U_0 = E_0 \sum_{e \neq 0} a_e U_e$  and  $H_0 U_0 f = \sum_{e \neq 0} E_e a_e U_e$  parameters. These can be found by applying the variational both of which are orthogonal to  $U_0$ . Hence (III.2) becomes

The variation perturbation procedure may now be modified

$$H_0 (U_0 f) - f(H_0 U_0) + H' U_0 = H'_{00} e_0 \quad (\text{III.15})$$

This is identical to equation (III.8). This equation can be written in the form of a differential equation if  $H_0$  is set equal to

function will satisfy the Hamiltonian  $H_0$  given by

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V \quad (\text{III.16})$$

Substituting this in equation (III.8) gives

$$\frac{\hbar^2}{2m} \left[ 2 \vec{\nabla} f \cdot \vec{\nabla} U_0 + U_0 (\nabla^2 f) \right] + H_{00}^0 U_0 = H' U_0 \quad (\text{III.17})$$

The quantity  $\frac{H'}{H}$  may be treated like a perturbation. If this equation can be solved for  $f$  then the perturbed wave function  $\Psi$  proved wave function may be obtained by solving the equation.

$$\Psi = U_0 (1 + f)$$

can be found. Of course since  $f$  is a solution to a second order partial differential equation, it must be chosen so as to satisfy certain boundary conditions. One condition is that  $U_0 f$  be normalizable. Hence the relations

$$\lim_{r \rightarrow \infty} r^3 U_0 f \rightarrow 0$$

$$\lim_{r \rightarrow 0} r^3 U_0 f \rightarrow 0$$

must hold. The function  $f$  may also contain several arbitrary parameters. These can be found by applying the variational principle to  $\Psi$ .

The variation perturbation procedure may now be modified as follows. As before, one is given a Hamiltonian  $H$  for which one desires the ground state wave function. An approximate solution may be obtained by applying the variational principle to a function  $\Psi_0$  containing some adjustable parameters. This function will satisfy the Hamiltonian  $H_0$  given by

$$H_0 = E - \frac{H \Psi_0}{\Psi_0} + H$$

The actual Hamiltonian  $H$  is equal to

$$H_0 - \left( \bar{E} - \frac{H\Psi_0}{\Psi_0} \right)$$

The quantity  $\bar{E} - \frac{H\Psi_0}{\Psi_0}$  may be treated like a perturbation.

Hence an improved wave function may be obtained by solving the equation.

$$\frac{\hbar^2}{2m} \left[ 2\vec{\nabla} f \cdot \vec{\nabla} \Psi + \Psi_0 \nabla^2 f \right] = \left[ \bar{E} - \frac{H\Psi_0}{\Psi_0} \right] \Psi_0 \quad (\text{III.18})$$

Here  $H'_{00} = \frac{\int \Psi^* \left[ \bar{E} - \frac{H\Psi_0}{\Psi_0} \right] \Psi_0 d\tau}{\int \Psi^* \Psi_0 d\tau} = 0$

since  $\bar{E} = \frac{\int \Psi_0^* H \Psi_0 d\tau}{\int \Psi_0^* \Psi_0 d\tau}$

A better wave function is therefore

$$\Psi_1 = \Psi_0 (1 + f) \quad (\text{III.19})$$

As with the variation perturbation procedure, the method may be repeated as many times as desired.

#### APPLICATION TO A PARTICULAR CASE

In Chapter IV it was stated that

$$\sum_{k \neq 0} \frac{H'_{ko} U_k}{E_0 - E_k}$$

was equal to  $c r U_0$  if the  $U_k$  and  $E_k$  are eigenfunctions and eigenenergies for the hydrogen atom and  $H'$  has the form

$\frac{\epsilon}{r}$ . With the results just obtained, this is quite easily proved. One has

is of the form

$$\sum_{k \neq 0} \frac{H_{ko} U_k}{E_0 - U_k} = f U_0 \stackrel{?}{=} c r U_0 \quad (III.20)$$

This or just the  $f \stackrel{?}{=} c r$  term of

Substituting  $c r$  in equation (III.17) with  $U_0 = \left[ \exp - \frac{r}{a_0} \right]$  one finds

when  $\exp - \frac{r}{a_0}$  is expanded. In this case the actual potential, (III.21)

original plus perturbing, is coulombic in nature. Its actual wave function is a hydrogenic wave function and has the form

$$= \frac{\epsilon}{r} \left[ \exp - \frac{r}{a_0} \right]$$

Now  $H'_{oo} = \frac{\epsilon}{a_0}$  and  $\frac{\hbar^2}{2m} = \frac{e^2 a_0}{2}$

Hence (III.21) becomes

$$- e^2 c + \frac{a_0 c e^2}{r} + \frac{\epsilon}{a_0} - \frac{\epsilon}{r} = 0$$

$$c = \frac{\epsilon}{e^2 a_0}$$

Therefore the function

$$\frac{e}{e^2 a_0} r$$

satisfies equation (III.17) and the perturbed wave function is of the form

$$\Psi = \exp - \frac{r}{a_0} \left( 1 + \frac{er}{e^2 a_0} \right)$$

This is just the first terms of

$$\Psi = \left[ \exp - \frac{r}{a_0} \right] \left[ \exp \frac{er}{e^2 a_0} \right]$$

when  $\left[ \exp \frac{er}{e^2 a_0} \right]$  is expanded. In this case the actual perturbed wave function may be found since the total potential, original plus perturbing, is coulombic in nature. The actual wave function is a hydrogenic wave function and has the form

$$\Psi = \left[ \exp - \frac{r}{a_0} \frac{1 + \frac{er}{e^2}}{1 + \frac{er}{e^2}} \right] \approx \left[ \exp - \frac{r}{a_0} \left( 1 - \frac{er}{e^2} \right) \right]$$

$$\frac{P^2}{2} \left[ \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{2}{(2b)^2} + \frac{10}{(2b)^3} + \frac{24}{(2b)^4} + \frac{24}{(2b)^5} \right) + \left( \frac{2}{15} + \frac{4c}{35} + \frac{2c^2}{63} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} \right) \right] \div \left[ \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - \left( \frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7} \right) \frac{1}{2b} \right] = < \text{Ans} >$$

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
$\frac{1+2c+c^2}{3}$	$\frac{2}{(2b)^2}$	$\frac{10}{(2b)^3}$	$\frac{24}{(2b)^4}$	$\frac{24}{(2b)^5}$	$\frac{2}{15}$	$\frac{4c}{35}$	$\frac{2+4c+2c^2}{63}$	$\frac{1}{2b}$	$\frac{1}{(2b)^2}$	$(8)(9)$	$\frac{P^2}{2}(11)$

$P = 2$  1.335807867 2.72729851 5.83543298 9.46289438 16.4824673 1.397386894 1.857304793 1.90904889 5.05641143 0.96529364 1.953834159 4.91838017

1.92 mm

$P = 2.2$  2.42

1.415473800 2.36831123 4.07486498 3.34533887 1.15806562 1.896458026 1.552510035 2.03859333 4.42531183 0.94291298 1.646801333 5.422144854

1.61 mm

$P = 1.8$  1.62

1.279056667 3.18978452 6.36937814 6.10483518 2.43803222 1.810243094 2.346283221 1.799450279 5.59850248 1.00573529 2.404854750 4.44363854

2.35 mm

$$2P^2 \left\{ \left[ \frac{1}{26} + \frac{4}{(26)^2} + \frac{12}{(26)^3} + \frac{24}{(26)^4} + \frac{24}{(26)^5} \right] \left[ \frac{1+2c+c^2}{3} - \frac{1+2}{5} - \frac{2}{7} \right] - \left[ \frac{1}{26} + \frac{2}{(26)^2} + \frac{2}{(26)^3} \right] \left( \frac{1+2c}{5} - \frac{2}{7} \right) \right\} \div \left[ \left( \frac{1+2c+c^2}{3} \right) \left( \frac{1+2}{5} + \frac{2}{(26)^3} \right) - \left( \frac{1+2c+c^2}{5} \right) \frac{1}{26} \right] = \frac{k^2 \langle \xi^2 \eta^2 \rangle}{a_5}$$

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
$\frac{1}{26}$	$\frac{4}{(26)^2}$	$\frac{12}{(26)^3}$	$\frac{24}{(26)^4}$	$\frac{24}{(26)^5}$	(1) thru (5)	$\frac{1+2c+c^2}{3}$	(4) (7)	$\frac{1+2+c}{5}$	$\frac{1+2c}{7}$	(9) (10)	(8) - (11)	$\frac{1}{(26)}$

9. 155031464

.369276218 .545459702 .604275889 .446289430 .164804073 .2130105312 .541205333 1.152824355 .742718717 .328 .243611739 .909212614 1.144378933

9.15503144

$$\frac{1}{a_5} \langle \xi^2 \rangle = 2.28875786$$

2.2 10. 570788177 .344115622 473662247 488983737 .336533887 .1158065681.759102061 .589367476 1.034757542 .662444035 .353428571 .234126449 .802630893 1.092023572

10.57078816

$$\frac{1}{a_5} \langle \xi^2 \rangle = 2.64269704$$

1.8 7. 9150422994 .399341022 .637956904 764325345 .610483518 .243803323 .2.655930131 .500890476 1.330330108 .845727035 .305714286 .258550837 1.07177921 1.221457145

7.91504233

$$\frac{1}{a_5} \langle \xi^2 \rangle = 1.97876058$$

① Case I

$$\begin{array}{r} \frac{2^2}{3^2} \\ \frac{3^2}{4^2} \\ \frac{4^2}{5^2} \\ \frac{5^2}{6^2} \\ \frac{6^2}{7^2} \end{array}$$
$$\begin{array}{r} 18 \\ 18 \\ 144 \\ 18 \\ 324 \end{array}$$

648

$$\frac{6 e^2 a_0^3}{R^6}$$

If  $R = 6a_0$  then we get

$$\frac{6 e^2 a_0^3}{6^6 a_0^6} = \frac{e^2}{6^5 a_0^3}$$

perturbing molecule  
○

$\rightarrow z$

$$H' = \pi^2 + 3z^2 = R^2 \left\langle \frac{\pi^2 + \pi^2}{4} - \frac{1}{4} + \frac{3\pi^2 \pi^2}{4} \right\rangle$$

for  $\rho = 2$

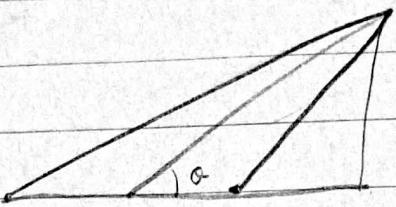
$$\langle H' \rangle = 11.78465375 \frac{e^2 a_0^5}{R^6}$$

for  $\rho = 2.2$

$$\langle H' \rangle = 13.35025597 \frac{e^2 a_0^5}{R^6}$$

for  $\rho = 1.8$

$$\langle H' \rangle = 10.37991428 \frac{e^2 a_0^5}{R^6}$$



$$\nu^2 = \nu^2 \sin^2 \theta = \nu^2 (1 - \cos^2 \theta)$$

$$\nu^2 = \frac{\nu_A^2 + R^2 - 2\nu_A R \cos \theta}{4}$$

$$\nu^2 = \frac{\nu_A^2 + R^2}{4} - \nu_B$$

$$\nu_B^2 = \nu^2 + \frac{R^2}{4} - \nu R \cos \theta$$

$$\nu_B^2 = \nu^2 + \frac{R^2}{4} + \nu R \cos \theta$$

$$\cancel{\nu^2 = \frac{\nu_A^2 + \nu_B^2}{2} \neq \frac{R^2}{4}}$$

$$\frac{\nu^2 + \nu_B^2}{4} - \frac{R^2}{4}$$

$$2\nu R \cos \theta = \nu_A^2 - \nu_B^2 = \underline{\underline{s \nu R^2}}$$

$$\nu^2 \cos^2 \theta = \frac{s^2 \nu^2 R^2}{4}$$

$$\psi = e^{+(-\xi + \frac{\eta^2}{\xi})}$$

$$\frac{d\psi}{d\xi} = -\left(1 + \frac{\eta^2}{\xi^2}\right) e^{+(-\xi + \frac{\eta^2}{\xi})}$$

$$\frac{d^2\psi}{d\xi^2} = \left[ +\frac{2\eta^2}{\xi^3} + \left(1 + \frac{\eta^2}{\xi^2}\right)^2 \right] e^{+(-\xi + \frac{\eta^2}{\xi})}$$

$$\frac{d\psi}{d\eta} = \frac{2\eta}{\xi} e^{(-\xi + \frac{\eta^2}{\xi})}$$

$$\frac{d^2\psi}{d\eta^2} = \left(\frac{2}{\xi} + \frac{4\eta^2}{\xi^2}\right) e^{(-\xi + \frac{\eta^2}{\xi})}$$

$$(\xi^2 - 1) \left[ \frac{2\eta^2 \xi + \xi^4 + 2\xi^2\eta^2 + 2\xi^4}{\xi^4} \right] - \frac{(2\xi^5 + 2\eta^2\xi^3)}{\xi^4}$$

$$+ \frac{(1 - \eta^2)(2\xi^2 + 4\eta^2)}{\xi^2} - \frac{4\eta^2}{\xi}$$



$$\psi_1 = e^{-\xi/a}$$

$$\frac{d\psi}{d\xi} = -\frac{1}{a} e^{-\xi/a}$$

$$\frac{d\psi}{d\eta} = 0$$

$$\frac{d^2\psi}{d\xi^2} = \frac{1}{a^2} e^{-\xi/a}$$

$$\frac{d^2\psi}{d\eta^2} = 0$$

$$\nabla^2\psi = \frac{4}{R^2(\xi^2-\eta^2)} \left\{ \frac{(\xi^2-1)}{a^2} + \frac{2\xi}{a} \right\}$$

$$\text{try } H' = \frac{4(\xi^2-1)}{R^2a^2(\xi^2-\eta^2)}$$

$$\text{try } \psi = e^{-\xi/a} \left( 1 + \frac{b(\xi^2-1)}{(\xi^2-\eta^2)} \right)$$

$$\frac{d\psi}{d\xi} = e^{-\xi/a} \left[ \left( 1 + \frac{b(\xi^2-1)}{(\xi^2-\eta^2)} \right) \right.$$

$$+ \frac{2b\xi}{(\xi^2-\eta^2)} - \frac{2b\xi(\xi^2-1)}{(\xi^2-\eta^2)} \Big]$$

$$\frac{d\psi}{d\xi} = e^{-\xi/a} \left[ -\frac{1}{a} \left( 1 + \frac{b(\xi^2-1)}{(\xi^2-\eta^2)} \right) + \frac{2b\xi(1-\eta^2)}{(\xi^2-\eta^2)^2} \right]$$

$$\frac{d^2\psi}{d\xi^2} = e^{-\xi/a} \left[ \frac{1}{a^2} \left( 1 + \frac{b(\xi^2-1)}{(\xi^2-\eta^2)} \right) - \frac{4b\xi(1-\eta^2)}{a(\xi^2-\eta^2)^2} \right]$$

$$+ \frac{2b(1-\eta^2)}{(\xi^2-\eta^2)^2} - \frac{8b\xi^2(1-\eta^2)}{(\xi^2-\eta^2)^3} \Big] = e^{-\xi/a} \left[ \frac{1}{a^2} \left( 1 + \frac{b(\xi^2-1)}{(\xi^2-\eta^2)} \right) \right.$$

$$- \frac{4b\xi}{a} \frac{(1-\eta^2)}{(\xi^2-\eta^2)^2} + \frac{2b(1-\eta^2)}{(\xi^2-\eta^2)^2} - \frac{8b\xi^2(1-\eta^2)}{(\xi^2-\eta^2)^3} \Big]$$

$$\frac{\partial \langle E \rangle}{\partial R} = -\frac{2 \langle E \rangle}{R} - \frac{\frac{4e^2 a_0}{2R^2} \frac{1}{a_0} \left(1 + \frac{2c}{3} + \frac{c^2}{5}\right) \left(\frac{1}{2b} + \frac{1}{(2b)^2}\right)}{\left[\left(1 + \frac{2c}{3} + \frac{c^2}{5}\right) \left(\frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3}\right) - \left(\frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7}\right) \frac{1}{2b}\right]}$$

$$\frac{\partial^2 \langle E \rangle}{\partial c \partial R} = -\frac{4e^2 a_0}{2R^2 a_0} \left( \frac{2}{3} + \frac{2c}{5} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} \right)$$

$$- \left[ \left(1 + \frac{2c}{3} + \frac{c^2}{5}\right) \left(\frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3}\right) - \left(\frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7}\right) \frac{1}{2b} \right]$$

$$\frac{+4e^2 a_0}{2R^2 a_0} \left\{ \left(1 + \frac{2c}{3} + \frac{c^2}{5}\right) \left(\frac{1}{2b} + \frac{1}{(2b)^2}\right) \right\} \left[ \left(\frac{2}{3} + \frac{2c}{5}\right) \left(\frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3}\right) \right.$$

$$- \left. \left(\frac{2}{3} + \frac{2c}{5}\right) \frac{1}{2b} \right] \div \left[ \left(1 + \frac{2c}{3} + \frac{c^2}{5}\right) \left(\frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3}\right) \right.$$

$$- \left. \left(\frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7}\right) \frac{1}{2b} \right]^2$$

$$\frac{\partial^2 \langle E \rangle}{\partial c \partial R} = \frac{4e^2}{2R^2} \left\{ \left(\frac{1}{3} + \frac{2c}{3} + \frac{c^2}{7}\right) \frac{1}{2b} \left(\frac{2}{3} + \frac{2c}{5}\right) \left(\frac{1}{2b} + \frac{1}{(2b)^2}\right) \right.$$

$$- \left. \left(\frac{2}{3} + \frac{2c}{5}\right) \frac{1}{2b} \right\} \div \left[ \left(1 + \frac{2c}{3} + \frac{c^2}{5}\right) \left(\frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3}\right) \right.$$

$$- \left. \left(\frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7}\right) \frac{1}{2b} \right]^2$$

$$\frac{\partial^2 \langle E \rangle}{\partial C \partial R} = \frac{4e^2}{2R^2} \left\{ \frac{(.333 + .2 + .0357)}{2.7} \right\} (.667 + .2) \left( \frac{1}{2.7} + \frac{1}{(2.7)^2} \right)$$

$$-\frac{(4 + .1429)}{2.7}$$

.50755

.54

$$.04 \times .569 \times .867 = .0197$$

$$\begin{array}{r} .533 \\ .036 \\ \hline .569 \end{array}$$

.867

$$.569 \times .867 \times .507544 = .5429$$

$$\begin{array}{r} -.5429 \\ .2500 \\ \hline .2929 \end{array}$$

$$\text{let } K = 1.6 \quad R = 6a_0$$

$$\frac{36}{216}$$

$$\phi = -\frac{1}{2} \frac{e^2}{216a_0^3} \pi^2 \frac{(1.6)(6.8)}{3.6} = -\frac{1.1333}{164} \frac{e^2}{2a_0} \frac{\pi^2}{a_0^2}$$

$$\langle \phi \rangle = -\frac{1.1333}{216} \frac{e^2}{2a_0} \left[ \frac{.015}{.04} \left( \frac{R}{a_0} - z \right)^2 + \frac{.63}{.2} \left( \frac{R}{a_0} - z \right) \right. \\ \left. + 4.44a_0^2 \right] .00524$$

$$\langle E \rangle \approx \frac{e^2 \cdot 0.04}{2a_0} \left( \frac{R}{a_0} - z \right)^2$$

$$\langle E_T \rangle = \frac{e^2}{2a_0} \left[ (.1 + .001) \left( \frac{R}{a_0} - z \right)^2 - .0165 \left( \frac{R}{a_0} - z \right) \right]$$

$$\left( \frac{R}{a_0} - z \right) = .165$$

$$\Delta R = .165 a_0$$

(1)

$$\psi = e^{-bs} (1 + c\eta^2)$$

$$\psi^* \psi = e^{-2bs} (1 + 2c\eta^2 + c^2\eta^4)$$

$$\int \psi^* \psi d\sigma = \frac{R^3}{8} \int_0^\infty \int_0^1 (s^2 - \eta^2) e^{-2bs} (1 + 2c\eta^2 + c^2\eta^4) ds d\eta$$

$$= \frac{R^3}{8} \int_0^\infty s^2 e^{-2bs} \left( 1 + \frac{2c}{3} + \frac{c^2}{s^2} \right) ds - \frac{R^3}{8} \int_0^\infty e^{-2bs} \left( \frac{1}{3} + \frac{2c}{s^2} + \frac{c^2}{s^4} \right) ds$$

$$= 2 \left[ \left( 1 + \frac{2c}{3} + \frac{c^2}{s^2} \right) \left( \frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - \left( \frac{1}{3} + \frac{2c}{s^2} + \frac{c^2}{s^4} \right) \left( \frac{1}{2b} \right) \right] \frac{R^3}{8} e^{-2b}$$

$$\frac{d\psi}{ds} = -b e^{-bs} (1 + c\eta^2)$$

$$\frac{\partial^2 \psi}{\partial s^2} = b^2 e^{-bs} (1 + c\eta^2)$$

$$\frac{d\psi}{d\eta} = +2c\eta e^{-bs}$$

$$\frac{\partial^2 \psi}{\partial \eta^2} = -2c e^{-bs}$$

$$\nabla^2 \psi = \frac{4}{R^2(s^2 - \eta^2)} \left\{ (s^2 - 1) \frac{\partial^2 \psi}{\partial s^2} + 2s \frac{\partial \psi}{\partial s} + (1 - \eta^2) \frac{\partial^2 \psi}{\partial \eta^2} - 2\eta \frac{\partial \psi}{\partial \eta} \right\}$$

$$+ \frac{4}{R^2} \frac{1}{(s^2 - 1)(1 - \eta^2)} \frac{\partial^2 \psi}{\partial \phi^2}$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{4e^2 \zeta^2 \xi}{R(\xi^2 - \eta^2)} = -\frac{e^2 a_0}{2} \nabla^2 - \frac{4e^2 \xi}{R(\xi^2 - \eta^2)}$$

$$H\psi = \frac{-4e^2 a_0}{2R^2(\xi^2 - \eta^2)} \left\{ +(\xi^2 - 1)b^2 e^{-b\xi}(1 + c\eta^2) - 2b\xi e^{-b\xi}(1 + c\eta^2) \right.$$

$$\left. + (1 - \eta^2) zce^{-b\xi} - 3\eta^2 c e^{-b\xi} \right\} - \frac{4e^2}{R} \frac{\xi}{\xi^2 - \eta^2} e^{-b\xi}(1 + c\eta^2)$$

$$= \frac{4e^2 a_0}{R^2(\xi^2 - \eta^2)} \left\{ (\xi^2 - 1)b^2 e^{-b\xi}(1 + c\eta^2) + \left( 2b - \frac{2R}{a_0} \right) \xi e^{-b\xi}(1 + c\eta^2) \right\}$$

$$H\psi = \frac{-4e^2 a_0}{2R^2(\xi^2 - \eta^2)} \left\{ (\xi^2 - 1)b^2 e^{-b\xi}(1 + c\eta^2) - \left( 2b - \frac{2R}{a_0} \right) \xi e^{-b\xi}(1 + c\eta^2) \right.$$

$$\left. + 2c(1 - 3\eta^2) e^{-b\xi} \right\}$$

$$\psi^* H \psi d\xi = -\frac{4e^2 a_0}{R^2} \left\{ b^2 e^{-2b\xi} (\xi^2 - 1)(1 + 2c\eta^2 + c^2\eta^4) \right.$$

$$\left. - \left( 2b - \frac{2R}{a_0} \right) \xi e^{-2b\xi} (1 + 2c\eta^2 + c^2\eta^4) + 2c(1 - 3\eta^2)(1 + c\eta^2) e^{-2b\xi} \right\}$$

~~$+ (1 - 3\eta^2)(1 + c\eta^2) e^{-2b\xi}$~~   
 $1 + (c - 3)\eta^2 - 3\eta^4$

$$\int_1^\infty \int_0^1 \psi^* H \psi d\xi = \frac{R^3}{8} - \frac{4e^2 a_0 e^{-2b}}{2R^2} \left\{ b^2 \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} + \frac{1}{(2b)^3} - \frac{1}{2b} \right) \right.$$

$$\left. - \left( 2b - \frac{R}{a_0} \right) \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} \right) + \frac{2c}{2b} \left( 1 + \frac{(1-3c)}{3} + \frac{c^2}{5} \right) \right\}$$

$$\langle E_e \rangle = -\frac{R^3}{8} \times \frac{4e^2 a_0 e^{-2b}}{2R^2} \left\{ b^2 \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) \right.$$

$$-\left( 2b - \frac{2R}{a_0} \right) \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} \right) + \frac{c}{b} \left( 1 + \frac{(c-2a_0)}{b} - \frac{3c}{5} \right) \left. \right\} \div$$

$$\frac{R^3}{8} \times e^{-2b} \left[ \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - \left( \frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7} \right) \frac{1}{2b} \right]$$

$$R = 2a_0$$

$$b = 1.35$$

$$c = .448$$

$$b^2 = 1.8225$$

$$b^3 = 2.4604$$

$$c^2 = .2007$$

$$\frac{2}{(2b)^2} + \frac{2}{(2b)^3} = .37596$$

$$\frac{1}{2b} + \frac{1}{(2b)^2} = .50754$$

$$\left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) = 1.3388$$

$$2b - \frac{R}{a_0} = .70$$

$$\left( 1 + \frac{(1-3c)}{3} + \frac{3c}{5} \right) = 1.154133$$

$$\left( \frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7} \right) = .54121$$

$$\left( \frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) = .74633$$

$$\langle E_e \rangle = -\frac{e^2}{2a_0} \left\{ .91733 \right.$$

$$+ .88334$$

$$- .6395 \left. \right\} \div$$

$$\left\{ .99919 - .2004 \right\}$$

$$.7988$$

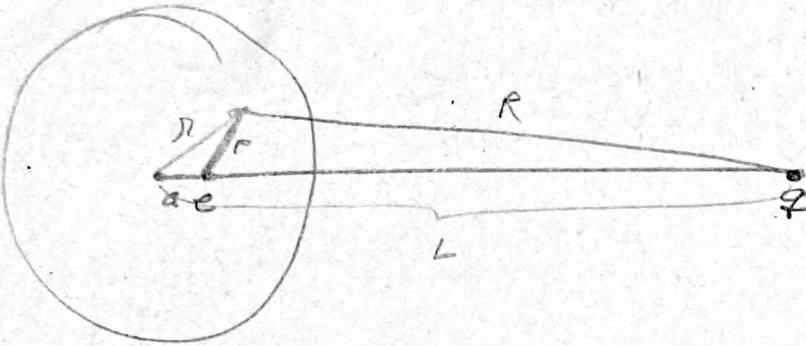
$$\langle E_e \rangle = -\frac{e^2}{2a_0} \frac{1.76117}{.7988}$$

$$= -\frac{e^2 (2.20477)}{2a_0}$$

$$\langle E_T \rangle = -\frac{e^2 (1.20477)}{2a_0}$$

$$E_{\text{binding}} = -\frac{e^2}{2a_0} \times .20477$$

$$= 2.784 \text{ eV}$$



$$\phi_I = -\frac{e}{\rho} + \frac{q}{R}$$

$$\rho^2 = r^2 + a^2 - 2ra \cos \theta$$

$$\phi_0 = -\frac{e'}{\rho} \quad \text{for } r > a$$

$$\rho \approx r \left(1 - \frac{a}{r} \cos \theta\right)$$

$$R^2 = L^2 + r^2 - 2rl \cos \theta$$

$$R \approx l \left(1 - \frac{r}{l} \cos \theta\right)$$

$$\phi_I = -\frac{e}{r} \left(1 + \frac{a}{r} \cos \theta\right) + \frac{q}{L} \left(1 + \frac{r}{L} \cos \theta\right)$$

$$\phi_0 = -\frac{e'}{r} \left(1 + \frac{a}{r} \cos \theta\right)$$

$$\frac{\partial \phi_I}{\partial \theta} = \frac{\partial \phi_0}{\partial \theta}$$

$$\text{or } + \frac{ea}{d^2} \sin \theta - \frac{qd}{L^2} \sin \theta = \frac{e'a}{d^2} \sin \theta$$

$$\text{or } \boxed{(ea - e'a)' = \frac{qd^3}{L^2}}$$

$$\frac{\partial \phi_I}{\partial r} = D \frac{\partial \phi_0}{\partial r}$$

$$\frac{e}{d^2} + 2 \frac{e^2}{d^3} \cos\theta + \frac{q}{L^2} \cos\theta = D \frac{e'}{d^2} + 2 D \frac{e' a'}{d^3} \cos\theta$$

$$e = De'$$

$$2(ea - De'a) = - q \frac{d^3}{L^2} = -(ea - e'a')$$

$$-\frac{e}{d} + \frac{q}{L} = -\frac{e'}{d}$$

$$3ea - (ea' + e'a') = 0$$

$$ea = a'(ze - \frac{e}{D})$$

$$a' = \frac{3aD}{(2D+1)}$$

$$q = (e - e') \frac{L}{d} = \frac{(D-1)}{D} \frac{eL}{d}$$

$$\cancel{qa} \left(1 - \frac{3}{2D+1}\right) = \frac{(D-1)}{D} \cancel{\frac{qL}{d}} \frac{d^2}{L^2}$$

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

$$L = \frac{d^2(2D+1)}{2D a}$$

$$L = \frac{d^2(2D+1)}{2D \cdot a}$$

$$a = \frac{1}{2} \quad D = 1.5$$

$$L = \frac{8 \times 9}{3} = 24$$

$\Phi$  due to the nuclear image charges is

$$\frac{2 \frac{q}{R^2}}{27^3} = \frac{2}{27^3} \cdot \frac{.5}{2.25} 4 \times 3 e \text{ is } \frac{6 \frac{e^2 x^2}{R^2}}{27^3}$$

$$\frac{e^2 x^2}{27^3} \cdot \frac{.5}{4}$$

$$\frac{q}{R_1^2} - \frac{q}{R_2^2}$$

$$\frac{q}{(R+E)^2} - \frac{q}{(R-E)^2}$$

$$\frac{q}{R^3}$$

$$\frac{q}{R^2} \left(1 - \frac{E}{R}\right) - \frac{q}{R^2} \left(1 + \frac{E}{R}\right)$$

Table 5 (Table 1)

To check method and calculations

		1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0				
N	S																
0	0	0	0.017067466	0.021665741	0.020483939	0.017112870	0.013334670	0.006025394	0.002370729	0.000860814	0.000296355	0.000098202	0.000031613	1			
1	1	0.000672741	0.017613518	0.022089771	0.020802029	0.017345003	0.013500332	0.006091553	0.002395198	0.000869386	0.000299241	0.000099143	0.000031912	2			
2	2	0.002764104	0.019298405	0.02339193	0.021775728	0.018053998	0.014005493	0.0064292825	0.002469510	0.000895395	0.000307988	0.000101990	0.000032822	3			
3	3	0.006498417	0.022265205	0.025064100	0.023464287	0.019278140	0.014874629	0.006637460	0.002596413	0.000939733	0.000322884	0.000106852	0.000034364	4			
4	4	0.012265901	0.024761872	0.029064930	0.025969661	0.021083112	0.016150386	0.007139577	0.002780553	0.001003902	0.000344405	0.000113857	0.000036593	5			
5	5	0.020647190	0.033155514	0.033828139	0.029441351	0.023514837	0.017895118	0.007819515	0.003028559	0.001090247	0.000373235	0.000123228	0.000039569	6			
6	6	0.032447664	0.041952389	0.040274164	0.034083206	0.026285334	0.020190143	0.008704420	0.003349250	0.001200991	0.000409470	0.000135542	0.000043378	7			
7	7	0.048741559	0.053823518	0.048825096	0.040162022	0.0311117805	0.023145087	0.009829061	0.003753803	0.001340287	0.000454611	0.000150247	0.000048130	8			
8	8	0.070905929	0.069436132	0.060022880	0.048018212	0.034657309	0.026894109	0.011236648	0.004255978	0.001512284	0.000513633	0.000168661	0.000053949	9			
9	9	0.100789412	0.090490725	0.074550966	0.058078438	0.043486293	0.031605556	0.012980035	0.004872423	0.001722193	0.000582951	0.000190983	0.000040990	10			
10	10	0.140560490	0.177638777	0.093259191	0.070849939	0.052185870	0.037424720	0.015123063	0.005622993	0.001976182	0.000666462	0.000217793	0.000069428	11			
11	11	0	0.024577151	0.042464852	Tabel 5 (Table 1)		X Tabel 4 = Z								12		
12	12	0	0.00466014	0.025187331	0.043075053	0.053045174	0.056024340	0.0593338680	0.037658713	0.021336552	0.010544972	0.004741680	0.001988591	0.000790325	13		
13	13	0	0.002653540	0.027017767	0.044912506	0.054874835	0.057772794	0.055401752	0.039078443	0.022126810	0.010932773	0.004915488	0.002001337	0.000819737	14		
14	14	0	0.005913559	0.030058027	0.047991867	0.057956789	0.060726141	0.058160816	0.040884754	0.023134040	0.011427153	0.005137084	0.002154136	0.000856007	15		
15	15	0	0.010303357	0.034255196	0.052316874	0.062327186	0.064935985	0.062019402	0.043480024	0.024580089	0.012137175	0.005455375	0.002287387	0.000908970	16		
16	16	0	0.015486393	0.039455062	0.057846118	0.068009521	0.070458863	0.067106493	0.044917090	0.026499891	0.013080514	0.005878451	0.002464560	0.000979333	17		
17	17	0	0.020766505	0.045308575	0.064438662	0.074983053	0.077337636	0.073493941	0.051269034	0.028937520	0.014279783	0.004404111	0.002489963	0.001068834	18		
18	18	0	0.024858195	0.051132342	0.071772891	0.083135386	0.085574239	0.081239255	0.056615391	0.031944864	0.015761775	0.007082037	0.002968881	0.001179664	19		
19	19	0	0.025533338	0.055708906	0.079230203	0.092194967	0.095090037	0.090364189	0.063037595	0.035579976	0.017557617	0.007889403	0.003307442	0.001314198	20		
20	20	0	0.019149038	0.057009157	0.085733611	0.101637267	0.105471685	0.100821705	0.0704111390	0.039905144	0.019701888	0.008855026	0.003712710	0.001475348	21		
21	21	0	0.051816106	0.089528823	0.110557105	0.116894039		1/3 [1.0 + 1.8 + 2(1.4)] + 4(1.8 + 1.6) + 2/3 [1.8 + 2.0] + 5/3 [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)]	1/12454160	0.079396081	0.044983944	0.022232048	0.009991931	0.004192515	0.001666272	1.92	22
22	22	0												1.28139055	23		

(Table a)  $\times \chi = Z_2$ 

	$N$	$S$	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0	
1	0	0	0	.031394437	.056502096	.072678688	.080046320	.080211120	.062712759	.039347064	.021534306	.010722960	.004977933	.002191740	1
2	1	.1	-.000815398	.032120946	.057220478	.073399008	.080749701	.080872385	.063196741	.039644181	.021695589	.010802845	.005017014	.002208036	2
3	2	.2	-.003233198	.034259580	.059374426	.075515561	.080869354	.082807169	.0644658357	.040541987	.022182069	.011044575	.005128956	.002257224	3
4	1	.3	.007149300	.037852490	.062953658	.079191081	.080430813	.084226581	.067126089	.042058996	.023006026	.011452987	.005318273	.002340439	4
5	2	.4	.012327698	.042492860	.067917810	.084282450	.091467851	.090997029	.070645890	.044226033	.024183057	.012036977	.005588853	.002459471	5
6	1	.5	.018796121	.048559131	.074158613	.090818844	.098008041	.097232314	.075278940	.047085335	.025737414	.012808627	.005946720	.002116757	6
7	2	.6	.024189247	.054974186	.081441233	.098714824	.100054142	.104980066	.081097586	.050688911	.027699412	.013783123	.006398771	.002815561	7
8	1	.7	.028511061	.061088424	.089318824	.107767332	.115548383	.114263147	.088180264	.055098207	.030105059	.014979245	.006953837	.003059774	8
9	2	.8	.022814306	.065495428	.097013052	.117598662	.121331845	.125052599	.096103694	.060380786	.032995566	.016418499	.007622218	.003353917	9
10	1	.9	.021254535	.065912448	.103251084	.127501474	.138083064	.136871672	.106432517	.066107863	.036416921	.018125183	.008415553	.003703250	10
11	f	1.0	0	.058923463	.106048782	.136410641	.150238852	.150548160	.117705591	.073850473	.040417089	.020126664	.009346885	.004113660	11
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$$0 + f + 4(1's) + 2(2's) \text{ of } Z_2 \\ \text{perp}$$

$$\cdot \frac{2}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.6)] \text{ of } \sum Z_2 = 1.705153650$$

$$\cdot \frac{2}{3} [1.8 + 2.0] = .621942709$$

$$\cdot \frac{2}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)] = 3.450758432$$

$$\sum 5.777854719 = 2.35 \\ .033 \dots (\Sigma) = 1.92595160$$

(Table 3)  $\times \chi = Z_3$ 

		$N$	$\xi$	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0
1	0	0	0	-0.19379525	0.32184883	0.38200189	0.38832466	0.35897380	0.22955625	0.11780708	0.05273258	0.02147760	0.00815878	0.00293440	1
2	1	1	0.00547302	0.19894887	0.32702432	0.38707580	0.39294268	0.36319794	0.23209835	0.11908709	0.05330419	0.02170809	0.00824474	0.00296825	2
3	2	2	0.02191448	0.21446527	0.34247110	0.402424269	0.40725733	0.37575955	0.23980434	0.12298252	0.05503497	0.02241239	0.00851434	0.00306440	3
4	3	3	0.04922889	0.24051027	0.36909950	0.42843139	0.43147423	0.39720213	0.25291123	0.12961119	0.05798735	0.02361205	0.00896757	0.00322784	4
5	4	4	0.08648323	0.27700323	0.40663311	0.46512862	0.46622837	0.42804970	0.27180665	0.13917395	0.062224440	0.02534138	0.00962389	0.00346398	5
6	5	5	0.13193418	0.32310341	0.45531882	0.51453210	0.51234120	0.41904288	0.29701716	0.15194913	0.06179344	0.02715279	0.01049880	0.00377938	6
7	6	6	0.17944707	0.37631849	0.51442763	0.57536325	0.57039916	0.52099657	0.32918359	0.16828816	0.07521682	0.03061256	0.011162328	0.00418361	7
8	7	7	0.21807397	0.43111521	0.58169852	0.64762455	0.64074290	0.58406751	0.36904615	0.18860547	0.08428710	0.03430288	0.01302418	0.00468735	8
9	8	8	0.22751724	0.47712437	0.65223204	0.72949105	0.72318580	0.66056060	0.41736884	0.21336932	0.09536694	0.03881403	0.01473972	0.00530434	9
10	9	9	0.17332627	0.49598001	0.71492425	0.81691408	0.81636442	0.74668987	0.47490539	0.24308938	0.10870511	0.04425316	0.01680315	0.00604935	10
11	10	1.0	0	0.45781590	0.76031155	0.90243647	0.91713464	0.84802632	0.54229547	0.27829224	0.12457423	0.05073600	0.01927233	0.0069320	11
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$$0 + f + 4(1') + 2(2') \text{ of } Z_3 = -334874168 \quad 1.010019315 \quad 1.471432782 \quad 1.480857626 \quad 1.481509634 \quad 1.542069128 \quad 1.979209768 \quad 5.01309326 \quad .224191063 \quad .91249020 \quad .034058933 \quad .012475074$$

$$\frac{1}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.4)] \text{ of } \sum Z_3 = 1.048183897$$

$$\frac{1}{2} [1.8 + 2.0] = .322357876$$

$$\frac{1}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)] = 1.281989992$$

$$\sum \dots (\Sigma) = .088417722$$

( $S^2 + N^2 - 1$ )<sup>1/2</sup>

$N$	5	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0
1	0	0	.85184	.884736	3.796416	11.237424	27.0	144.703125	512.0	1423.828125	3375.0	7133.328125	13824.0
2	.1	.000001	.091125	.912473	3.849893	11.390625	27.270901	145.531574	513.922401	1427.628376	3381.754501	7144.450776	13841.28720
3	.2	.000064	.110592	1.0	4.096000	11.852352	28.094444	148.035889	519.718404	1439.069089	3402.072064	7177.888089	13893.23526
4	.3	.000729	.148877	1.157625	4.492125	12.449337	29.503629	152.273304	529.475129	1458.274104	3436.115229	7233.848504	13980.10393
5	.4	.004094	.216000	1.404928	5.088448	13.824000	31.554496	158.340421	543.338494	1485.446221	3484.154096	7312.480421	14102.32730
6	.5	.015625	.328509	1.771561	5.929741	15.438249	34.328125	166.375000	541.515625	1580.875000	3546.578125	7414.875000	14260.51563
7	.6	.040654	.512000	2.299948	7.077888	17.576000	37.933056	176.558481	584.277056	1564.936281	3623.878656	7541.066081	14455.45786
8	.7	.117447	.804357	3.048625	8.615125	20.346417	42.508549	189.119224	611.960049	1618.096024	3716.672157	7692.038424	14688.12485
9	.8	.242144	1.259712	4.096000	10.648	23.887872	48.228544	204.336469	644.972544	1680.914269	3325.694144	7868.724669	14959.67334
10	.9	.531441	1.953125	5.545233	13.312053	28.372625	55.301341	222.545016	683.797841	1754.049816	3951.805941	8072.216216	15271.45064
11	1.0	1.0	2.985984	7.529536	16.777216	34.012024	64.0	244.140625	729.0	1838.215625	4091.0	8303.715625	15125.1
12	$\sqrt{\text{Table 6}} = \text{Table 7}$												
13	0	291862981	.940604061	1.948439375	3.35455010	5.196152430	12.02926119	22.6271169	37.73364712	58.09475019	84.45903222	117.5755076	
14	.001	.301869176	.955339206	1.947204361	3.375000	5.202154830	12.06364687	22.66985666	37.78396983	58.15285462	84.52485300	117.649	
15	.2	.008	.332553755	1.0	2.023857700	3.442724500	5.300421110	12.167	22.79733458	37.93507202	58.32728404	84.72241786	117.8695688
16	.3	.027	.385845824	1.075929830	2.119463375	3.556590640	5.431724310	12.33790696	23.01032457	38.18735529	58.61838644	85.05203407	118.2374895
17	.4	.044	.464758000	1.185294587	2.255758852	3.718064010	5.61733870	12.58333902	23.30962239	38.54148701	59.02674051	85.51421297	118.7532201
18	.5	.125	.573157046	1.331	2.435105952	3.727915320	5.859020820	12.89864333	23.69632091	38.99839740	59.55315377	86.10966844	119.4174008
19	.6	.214	.715541752	1.514564538	2.660430040	4.192374020	6.158981730	13.28753103	24.17182359	39.55927553	60.19865991	86.83931529	120.2308523
20	.7	.343	.896859520	1.746031213	2.935153317	4.510700070	6.519858050	13.75306253	24.73782627	40.22556430	60.96451549	87.70426685	121.1945743
21	.8	.512	1.122368923	2.023857700	3.263127334	4.887522070	6.944677380	14.29463077	25.39630965	40.99895448	61.85219595	88.70533221	122.3097434
22	.9	.729	1.397542485	2.354831841	3.648568420	5.326594000	7.434823310	14.917942750	26.14952850	41.88137791	62.86339110	89.84551305	123.5777109
23	1.0	1.0	1.728	2.744	4.096	5.832	8.0	15.625	27.0	42.875	64.0	91.125	125.0

( $S^2 + N^2 - 1$ )<sup>1/2</sup>

Table  
 $\xi^2 + N^2 - 1$

5

$H_2$  plus - Pressure Effects

$N$	$\xi$	1.0	1.2	1.4	1.5	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0	
1	0	0	.44	.96	1.25	1.56	2.24	3.00	5.25	8.00	11.25	15.00	19.25	24.00	1
2	.1	.01	.45	.97	1.57		2.01	3.01	5.01	8.01	11.26	15.01	19.26	24.01	2
3	.2	.04	.48	1.00	1.29	1.60	2.28	3.04	5.09	8.04	11.29	15.04	19.29	24.04	3
4	.3	.09	.53	1.05	1.45		2.33	3.09	5.34	8.09	11.34	15.09	19.34	24.09	4
5	.4	.14	.60	1.12	1.41	1.72	2.40	3.16	5.41	8.16	11.41	15.16	19.41	24.16	5
6	.5	.25	.69	1.21	1.81		2.49	3.25	5.50	8.25	11.50	15.25	19.50	24.25	6
7	.6	.36	.80	1.32	1.41	1.92	2.60	3.36	5.61	8.36	11.61	15.36	19.61	24.36	7
8	.7	.49	.93	1.45	2.05		2.73	3.49	5.74	8.49	11.74	15.49	19.74	24.49	8
9	.8	.64	1.08	1.60	1.89	2.20	2.88	3.64	5.89	8.64	11.89	15.64	19.89	24.64	9
10	.9	.81	1.25	1.77	2.37		3.05	3.81	6.04	8.81	12.06	15.81	20.06	24.81	10
11	1.0	1.0	1.44	1.90	2.25	2.56	3.24	4.0	6.25	9.0	12.25	16.0	20.25	25.0	11
12	0	0	6336	1.8816	3.9936	7.2576	12.0	32.8125	72.0	137.8125	240.0	389.8125	600.0		12
13	.1	.0099	6435	1.8915	4.0035	7.2675	12.0099	32.8224	72.0099	137.8224	240.0099	389.8224	600.0099		13
14	.2	.0384	.672	1.92	4.0320	7.2940	12.0384	32.8509	72.0384	137.8509	240.0384	389.8509	600.0384		14
15	.3	.0819	7155	1.9635	4.0755	7.3395	12.0819	32.8944	72.0819	137.8944	240.0819	389.8944	600.0819		15
16	.4	.1344	.7680	2.0160	4.128	7.3920	12.1344	32.9469	72.1344	137.9469	240.1344	389.9469	600.1344		16
17	.5	.1875	.8211	2.0691	4.1811	7.4451	12.1875	33.0000	72.1875	138.0	240.1875	390.0	600.1875		17
18	.6	.2304	.8640	2.1120	4.2240	7.4880	12.2304	33.0429	72.2304	138.0429	240.2304	390.0429	600.2304		18
19	.7	.2499	.8835	2.1315	4.2435	7.5075	12.2499	33.0624	72.2499	138.0624	240.2499	390.0624	600.2499		19
20	.8	.2304	.8640	2.1120	4.2240	7.4880	12.2304	33.0429	72.2304	138.0429	240.2304	390.0429	600.2304		20
21	.9	.1539	.7875	2.0355	4.1475	7.4115	12.1220	32.9664	72.1539	137.9664	240.1539	389.9664	600.1539		21
22	1.0	0	6336	1.8816	3.9936	7.2576	12.0	32.8125	72.0	137.8125	240.0	389.8125	600.0		22

$R = 2a_0$ 

Table 1

H<sub>2</sub> plus - Pressure Effects

Sheet A, (6) x Sheet B, (2)

		1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0		
	N														
0		.2582054	.194951	.1502281	.1145894	.08740523	.066670	.03387764	.01721455	.00874739	.00444489	.00225862	.001147694		
1		.25937249	.19784122	.15090713	.11510734	.08780030	.06697135	.03403077	.01729234	.008781928	.004464981	.002268829	.001152882		
2		.26287375	.20051187	.15294422	.11646118	.08898552	.06787539	.03449015	.01752579	.008905543	.004525254	.002299456	.001168444		
3		.26870920	.20496297	.15633938	.11925090	.09096087	.06938214	.03525578	.01791484	.009103234	.004625708	.002350501	.001194382		
4		.27687381	.21119450	.16109240	.122876505	.09372438	.07149157	.03632767	.01845951	.009380101	.004766344	.002421963	.001230695		
5		.28738761	.21920446	.117203815	.12753800	.09708222	.07420371	.03770581	.01915979	.009735845	.004947163	.002513844	.001277383		
6		.30020058	.22899887	.17467322	.13323539	.10102781	.07751854	.03939021	.02001570	.010170765	.005168163	.002626143	.001334497		
7		.31539273	.24057171	.18350062	.13994866	.10670374	.08143607	.04138086	.02102723	.010684762	.005429344	.002758859	.001401885		
8		.33289906	.25392499	.19368608	.14773782	.11268981	.08595630	.04367774	.022194375	.011277835	.005730708	.002911994	.001479699		
9		.35273954	.26905870	.20522961	.15654287	.11940603	.09107922	.04628092	.02351714	.011949984	.004072253	.003085546	.001567888		
10		.37491424	.28597285	.21813120	.16638381	.12691239	.09680424	.04919033	.02499553	.012701210	.006453780	.003279516	.001661457		
11		.06667003	.03878964	.02256848	.01313073	.00763964	(Tab 1c 1) 0.00444489 0.001147694 0.0015809	(Tab 1c 1) 0.000499341 0.0000765168 0.0000772101	0.0000765168	0.000019757	0.0000051014	0.0000013172			
12		.06727409	.03914115	.02277294	.01324970	.00770289	.00448516								
13		.06910261	.04020501	.02339193	.01360983	.00791842	.00460707	.00118957	.000307153	.0000793087	.0000204779	.0000052875	.0000013453		
14		.07220463	.04200982	.02444200	.01422078	.00827388	.00481388	.00124297	.000320941	.0000838689	.0000213972	.0000055249	.0000014265		
15		.07666188	.04460312	.02595083	.01509864	.00878463	.00511104	.00131970	.000340754	.000087984	.0000229180	.0000058659	.0000015146		
16		.08258876	.04805147	.02795714	.01626594	.00946379	.00550619	.00142173	.000367098	.0000947867	.0000244744	.0000016394	.0000016317		
17		.09013240	.05244048	.03051073	.01775167	.01032821	.00600912	.00155159	.000400628	.0001034445	.0000266582	.0000068966	.0000017807		
18		.09947257	.05787475	.03367248	.01959123	.01139850	.00643183	.00171238	.000442144	.0001141641	.0000294778	.0000074113	.0000019653		
19		.11082178	.06447790	.03751430	.02183646	.01269899	.00738849	.00190775	.000492590	.0001271896	.0000328410	.00000847977	.0000021895		
20		.12442520	.07239258	.04211919	.02450567	.01485780	.00829542	.00214192	.000553056	.0001428021	.0000368723	.0000095206	.0000024583		
21		.14056049	.08178047	.04758122	.02718357	.01610675	.00937118	.00241919	.000624777	.000161321	.0100414539	.0000107557	.0000027771		

## H<sub>2</sub> plus - Pressure Effects

## Sheet A

$N$	$N^2$	$1 + .452N^2$	$1 + .370N^2$	$1 + .537N^2$
0	0	1	1	1
.1	.01	1.00452	1.0037	1.00537
.2	.04	1.01808	1.01480	1.02148
.3	.09	1.04068	1.03330	1.04833
.4	.16	1.07232	1.05920	1.08592
.5	.25	1.11300	1.09250	1.13425
.6	.36	1.16272	1.13320	1.19332
.7	.49	1.22148	1.18130	1.24313
.8	.64	1.28928	1.23480	1.34368
.9	.81	1.36612	1.29970	1.43497
1.0	1.0	1.452	1.370	1.537

R = 1.80

Table 2

H<sub>2</sub> plus - Pressure Effects

Sheet A, (5) x Sheet B, (3)

	N	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0
1	0	.2959324	.2225953	.17328806	.1349029	.1050205	.0817573	.0437178	.02337706	.01250033	.00648424	.00357425	.00191125
2	.1	.28499035	.22341890	.173929226	.13540204	.105407074	.08205980	.043879556	.023463555	.01254658	.00670899	.003587475	.001918322
3	.2	.290164920	.22588971	.17585272	.13689946	.10657480	.08294731	.04434482	.02372304	.01268533	.00678319	.003627149	.001939537
4	.3	.29545395	.23000772	.17905855	.13939517	.10851768	.08447982	.04517360	.02415552	.01291659	.006906846	.003693273	.001974895
5	.4	.30285940	.23577294	.18354671	.14288915	.11123771	.08659733	.04630589	.02474098	.01324035	.00707997	.003785846	.002024394
6	.5	.31238115	.243185365	.189317205	.14738142	.11473490	.08931985	.04776170	.02553944	.01315611	.00730255	.003904868	.002088041
7	.6	.32401860	.25224499	.19637003	.15287197	.11900923	.09244737	.04954101	.026449088	.01416537	.00757460	.004050340	.0021165829
8	.7	.33777194	.21295183	.204705185	.159360796	.12406072	.09657990	.05164384	.02761532	.01476664	.007894116	.004222215	.002257160
9	.8	.35364119	.27530587	.21432267	.16684791	.12988935	.101111743	.054070175	.02891275	.01546041	.00826709	.004420632	.002343834
10	.9	.37162034	.28930711	.22522249	.17533330	.13649514	.10625994	.05482002	.03038316	.01624668	.00848753	.004645453	.002484052
11	1.0	.39172239	.30495556	.23740464	.18481697	.143879085	.11200750	.05989339	.03202657	.01712545	.009157436	.004891629	.002618413
12	.0	.08175734	.04954867	.03002875	.01819879	Table 2 <sup>1</sup>	(Table 2) <sup>2</sup>						
13	.1	.08236346	.04991600	.030251376	.01833371	.01111107	.00668426	.001911746	.000546487	.000156258	.000044679	.0000127752	.0000036597
14	.2	.08419526	.05102616	.03092418	.01874146	.01135819	.00688357	.001968237	.000562783	.000160918	.0000460117	.0000131562	.0000037618
15	.3	.08729304	.05290355	.03206194	.01943101	.01177609	.00713684	.002040654	.000583489	.000166838	.0000477045	.0000136403	.0000037002
16	.4	.09172394	.05558888	.03308939	.02041731	.01237383	.00749910	.002144235	.000613104	.000175307	.0000501260	.0000143326	.0000040982
17	.5	.09758198	.05913912	.03584100	.02172128	.01314410	.007978036	.002281180	.000165203	.000186503	.0000533272	.0000152480	.0000043599
18	.6	.10498805	.06342753	.03856119	.02334984	.01416320	.008583535	.002454312	.000701747	.000200658	.0000573744	.0000164053	.0000046908
19	.7	.11408988	.06914364	.04190421	.02539586	.01539104	.00932768	.002667086	.000762606	.000218054	.0000423484	.0000178275	.0000050975
20	.8	.12506209	.07579332	.04593421	.027838225	.01687124	.010224735	.002923584	.000835947	.000239034	.0000683448	.0000195420	.0000055877
21	.9	.13810614	.08349860	.05072517	.030741766	.01813092	.011291179	.003228516	.000923136	.000243955	.0000754733	.0000215902	.0000066705
22	1.0	.15345035	.09299789	.05634096	.034157312	.02070090	.01254568	.003587218	.001025701	.000293281	.0000838586	.0000239779	.0000068561

R = 2.2 60

Table 3

H<sub>2</sub> plus - Pressure Effects

Sheet A,(7) x Sheet B,(4)

	N	5	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0
1	0		.2338676	.1748896	.1307851	.097803	.07313852	.05469406	.02644994	.01279117	.00618579	.00299144	.00144114	.000699601
2	.1		.23512347	.17582870	.131487416	.09832820	.07353127	.05498777	.02659200	.01285986	.006219008	.003007504	.001454429	.000703358
4	.2		.23889108	.17864623	.13359436	.09990381	.074709535	.05580882	.02701811	.01304592	.006318661	.003055694	.001477734	.000714629
5														
6	.3		.24517042	.18334201	.13710594	.10252982	.076473305	.05733742	.02772829	.01340937	.006484749	.003136014	.001516577	.000733413
7	.4		.25396150	.18991611	.142022154	.10620023	.07942258	.05939387	.02872254	.01389019	.006717273	.003248465	.001570957	.000759711
9	.5		.265214325	.19831853	.14834300	.11093305	.08295737	.06203174	.03000087	.014508385	.007014232	.003393041	.001640874	.000793523
10														
11	.6		.279078884	.20869926	.154068474	.116710276	.08727764	.065217516	.03156327	.01526394	.007381627	.003569745	.001726328	.000834848
12														
13	.7		.29540518	.22090830	.16519858	.12353790	.09238346	.06908571	.03340974	.01615491	.007813457	.003778578	.001827320	.000883687
14														
15	.8		.31424322	.23499566	.17573332	.131415935	.09827477	.073491315	.03554028	.01718724	.008311722	.004019538	.001943898	.000940090
16														
17	.9		.33559299	.25096133	.18767269	.14034437	.10495158	.078484335	.03795490	.018354945	.008874423	.004292657	.002075914	.001003907
18														
19	1.0		.35945450	.26880535	.20101670	.15032321	.112413905	.0840477	.04045359	.019660038	.009502559	.004597813	.002223514	.001075287
20														
21	.054694054	.030586372	.017104742	.009565427	Table 3 <sup>1</sup> = (7451e-3) / 0.05349283	.009211494								
22	.1		.055283046	.030915753	.017288941	.009668435	.005404848	.003023055	.000707134	.000165376	.000038670	.000009045	.000002115	.0000004947
23														
24	.2		.057068948	.031914475	.017847453	.009980771	.005581515	.003121333	.000729978	.000170718	.000039925	.000009337	.000002184	.0000005107
25														
26	.3		.060108535	.033614293	.018798039	.010512314	.005878796	.003287580	.000768858	.000179811	.000042053	.000009835	.000002300	.0000005379
27														
28	.4		.064494443	.034068129	.020170293	.011279763	.006307946	.003527572	.000824984	.000192937	.000045122	.000010553	.000002448	.0000005772
29														
30	.5		.070365112	.039350074	.022005460	.012306142	.006881925	.003848557	.000900052	.000210493	.000049228	.000011513	.000002692	.00000061297
31														
32	.6		.077885023	.043555381	.024357369	.013621289	.007617390	.004259849	.000996240	.000232988	.000054488	.000012743	.000002980	.0000006970
33														
34	.7		.087264220	.048800477	.027290571	.015261413	.008534704	.004772835	.001116211	.000261046	.000061050	.000014278	.000003339	.0000007809
35														
36	.8		.098748801	.055222290	.030882200	.017270148	.009657930	.005400973	.001263112	.000295401	.000069085	.000016157	.000003779	.0000008837
37														
38	.9		.112622655	.062981589	.035221039	.019694542	.011014834	.006159791	.001440574	.000336904	.000078791	.000018427	.000004309	.0000010078
39														
40	1.0		.129207538	.072256297	.040407714	.022597017	.012036884	.007064886	.00145271	.000380517	.000090394	.000021140	.000004744	.0000011512

$$\frac{d^2 E_p}{c^2/a_0} = \frac{-4}{\rho^2} \left\{ b^2 \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - (2b - 2\rho) \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} \right) - \frac{4c^2}{15} \right\} \div \left[ \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - \left( \frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7} \right) + \frac{1}{2b} \right]$$

$\rho = 2$

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	
$b$	$b^2$	$b^3$	$\frac{1+2c+c^2}{3}$	$\frac{2}{(2b)^2}$	$\frac{2}{(2b)^3}$	$2b - 2\rho$	$\frac{1}{2b}$	$\frac{1}{(2b)^2}$	$(7) + (8)$	$\frac{4c^2}{15b}$	$b^2(3)[(4)+(5)]$	$(6)(3)[(7)+(8)]$	$(3)[(7)+(4)+(5)]$	$\frac{1+2c+c^2}{3}$
1.354	1.833316	2.482309864												

$$1.338867467 \quad .272729851 \quad .100712498 \quad -1.292 \quad .369276218 \quad .134364925 \quad .505441143 \quad .0395281142 \quad .916598612 \quad -874627330 \quad .751697828 \quad .994357364 \quad .541205333$$

$$c = .448$$

$$(14) \\ (15) \quad (16) \\ (14)(7) \quad (13) - (15) \quad (4/\rho^2) \quad (12)' \quad (12)' \\ (11) \\ .1998542585 \quad .794503165 \quad -1 \quad -1(12) \quad -2.2047715$$

$$\rho = 2.2$$

$$b \quad b^2 \\ 1.453 \quad 2.111209$$

$$1.415673800 \quad .236831123 \quad .081497290 \quad -1.494 \quad .344115822 \quad .118415561 \quad .462531183 \quad .052923882 \quad .951414634 \quad -978261156 \quad 1.876752008 \quad .937804664 \quad .589307476$$

$$c = .537$$

$$(14) \quad \frac{4}{\rho^2} \\ .202810555 \quad .734994109 \quad -82644628 \quad -1.55103715 \quad -2.1102682$$

$$\rho = 1.8$$

$$b \quad b^2 \\ 1.252 \quad 1.567504$$

$$1.274046667 \quad .318978452 \quad .127387561 \quad -1.094 \quad .399361022 \quad .159489296 \quad .558850248 \quad .029158679 \quad .891425623 \quad -780353420 \quad 1.442620364 \quad 1.077495710 \quad .500890476$$

$$c = .370$$

$$(14) \quad \frac{4}{\rho^2} \\ .200036132 \quad .877459578 \quad -1.234567791 \quad -2.027926375 \quad -2.31113367$$

$P = 1.9$ 

(4)

(11)

(12)

(17)

26 - 2 $\rho$ 

$$(4)(3)[(7)+(8)](10)-(11)-(9)$$

(12)

(16)

$$\begin{matrix} b & b^2 & b^3 & c^2 & c \\ 1.2 & 1.44 & 1.728 & .09 & .3 \\ .14 & .4 & & & \\ .25 & .5 & & & \\ .34 & .6 & & & \end{matrix}$$

$$\frac{4}{10} = 1.10803324$$

$$1.3 \quad 1.69 \quad 2.197$$

$$-1.2$$

$$\begin{matrix} -1.006542094 & 1.849291786 \\ -1.073204108 & 1.957537400 \\ -1.143171727 & 2.067476751 \\ -1.216444902 & 2.179111255 \end{matrix}$$

MINUS

(16)

$$\begin{matrix} 2.245849 & \\ 2.248050 & \\ 2.246476 & \\ 2.241714 & \end{matrix}$$

$$1.234567901$$

$$\begin{matrix} -2.778366310 & 1.603135565 \\ -.829277517 & 1.695533954 \\ -.884023040 & 1.790433324 \\ -.940685722 & 1.885916521 \end{matrix}$$

$$\begin{matrix} 1.4 \quad 1.96 \quad 2.744 & \\ -1.0 & \\ -.590357118 & 1.399714160 \\ -.627455756 & 1.480217553 \\ -.670493169 & 1.561564481 \\ -.713469358 & 1.643754949 \end{matrix}$$

$$\begin{matrix} 1.5 \quad 2.25 \quad 3.375 & \\ -0.8 & \\ -.433066666 & 1.229466666 \\ -.461748148 & 1.299081481 \\ -.491851851 & 1.34929628 \\ -.523377777 & 1.440711109 \end{matrix}$$

$$\begin{matrix} & (12) \frac{4}{10} \\ & 2.049076769 \\ & 2.169016508 \\ & 2.290832963 \\ & 2.414527704 \end{matrix}$$

$$\begin{matrix} & 1.776327494 \\ & 1.878702981 \\ & 1.983859637 \\ & 2.089058193 \end{matrix}$$

$$\begin{matrix} & 1.550929816 \\ & 1.640130251 \\ & 1.730265351 \\ & 1.821335122 \end{matrix}$$

$$\begin{matrix} & 1.341846720 \\ & 1.439425462 \\ & 1.517595154 \\ & 1.594355798 \end{matrix}$$

 $P = 1.8$ 

(4)

(11)

(12)

(17)

(16)

(16)

$$\begin{matrix} -862750325 & 1.705500065 \\ -919889235 & 1.804222527 \\ -979861480 & 1.904166594 \\ -1.042667059 & 2.005333412 \end{matrix}$$

$$2.2985264$$

$$\begin{matrix} -1.48638592 & 1.473407847 \\ -1.691597142 & 1.557853579 \\ -.734685866 & 1.643094150 \\ -.783904708 & 1.729135567 \end{matrix}$$

$$\begin{matrix} -.472285494 & 1.281642734 \\ -.503564604 & 1.354326403 \\ -.536394535 & 1.427465847 \\ -.570775480 & 1.501061077 \end{matrix}$$

$$\begin{matrix} -.3248 & 1.1208 \\ -.346311111 & 1.183644444 \\ -.348888887 & 1.246666666 \\ -.392533333 & 1.309846665 \end{matrix}$$

$$\begin{matrix} 2.10555635 & \\ 2.227435218 & \\ 2.350822844 & \\ 2.475720261 & \end{matrix}$$

$$\begin{matrix} 1.819022033 & \\ 1.923276023 & \\ 2.022513765 & \\ 2.134735267 & \end{matrix}$$

$$\begin{matrix} 1.5822274982 & \\ 1.672007705 & \\ 1.762303514 & \\ 1.853161823 & \end{matrix}$$

$$\begin{matrix} 1.383703703 & \\ 1.441289437 & \\ 1.539094649 & \\ 1.617119339 & \end{matrix}$$

 $P = 2.1$ 

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$$2 \frac{E_c}{c^2 k_0} = - \frac{4}{\rho^2} \left\{ \frac{b^4}{3} \left( 1 + \frac{2c}{5} + \frac{c^2}{5} \right) \left( \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - (2b - 2\rho) \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{1}{(2b)^2} \right) - \frac{4c^2}{15} \right\} \div \left[ \left( 1 + \frac{2c}{3} + \frac{c^2}{5} \right) \left( \frac{1}{2b} + \frac{2}{(2b)^2} + \frac{2}{(2b)^3} \right) - \left( \frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7} \right) \frac{1}{2b} \right]$$

$P = 2$

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	
$c^2$	$b^2$	$b^3$	$\frac{1+2c}{3} + \frac{c^2}{5}$	$\frac{2}{(2b)^2}$	$\frac{2}{(2b)^3}$	$2b - 2\rho$	$\frac{1}{2b}$	$\frac{1}{(2b)^2}$	$\frac{4c^2}{15}$	$b^2 (3)(4) + b^3$	$(4)(3)(7) + b^3$	$(10) - (11) - (9)$	$(3)(7) + (4) + b^3$	
$b = 1.2$	.09	.3	1.44	1.729	1.218	.347222	.144676	-1.6	.410667	.173611	.02	.862149740	-1.150333766 1.993083506 1.10643217	
	.16	.4			1.298667	"		"	"	"	.035	.919888848	-1.226519295 2.110852587 1.179923080	
	.25	.5			1.383333	"		"	"	"	.055	.979860580	-1.306481659 2.230784683 1.256848250	
	.36	.6			1.472	"	"	"	"	"	.08	1.042666353	-1.390222740 2.352889099 1.337407680	
$b = 1.3$	.3	1.49	2.197		.295858	.113791534	-1.4	.384615	.147929	.018461538	.843230793	-908094029 1.732863284	.967414202	
	.4				"	"		"	"	.032820513	.899074650	-968235998	1.8344949435 1.031484875	
	.5				"	"		"	"	.051282051	.957692335	-1.031360213	1.937770497 1.098732605	
	.4				"	"		"	"	.073846154	1.019076953	-1.097466675	2.042697474 1.169157394	
$b = 1.4$	.3	1.96	2.744		.255102	.09110787	-1.2	.357142857	.127551	.017142857	.826499899	-708428541	1.517785583	.8566836215
	.4				"	"		"	"	.030476190	.881237987	-755346907	1.606108704	.9134202417
	.5				"	"		"	"	.047619048	.9384690360	-804591803	1.695663115	.972971272
	.4				"	"		"	"	.068571429	.998857020	-856163229	1.786448820	1.035335214
$b = 1.5$	.3	2.25	3.375		.222222	.074074074	-1	.333333	.111111	.016	.812	-541333333	1.337333333	.7646888988
	.4				"	"		"	"	.0284	.865777777	-577185185	1.414518518	.8176790117
	.5				"	"		"	"	.044	.922222221	-614814814	1.492592591	.8709876532
	.4				"	"		"	"	.064	.981333332	-6.542222221	1.571555554	.9268148139
										(14)	(14)(7)	(13) - (15)	(12) / (16)	
										$\frac{1}{3} + \frac{2c}{5} + \frac{c^2}{7}$				

$b$	$c$	minus
1.2	.3	.466190476
	.4	.516190471
	.5	.549047619
	.6	.6247619047

$b$	$c$	minus
1.3	.3	.179303850
	.4	.198534600
	.5	.218864250
	.6	.240297800

$b$	$c$	minus
1.4	.3	.1664945986
	.4	.1843537414
	.5	.203231294
	.6	.2231272516
1.5	.3	.155394825
	.4	.172063492
	.5	.1896825396
	.6	.208253968

Table 5

 $G^2 - N^2$ 

	$G$	$N$	0	.2	.4	.6	.8	1.0		0	.2	.4	.6	.8	1.0
1															
2	1.0		1.00	.96	.84	.64	.36	0		2.00	1.92	1.68	1.28	.72	0
3	1.5		2.25	2.21	2.09	1.89	1.61	1.25		4.50	4.42	4.18	3.78	3.22	2.50
4	2.0		4.00	3.96	3.84	3.64	3.34	3.00		8.00	7.92	7.68	7.28	6.72	6.00
5	2.5		6.25	6.21	6.09	5.89	5.61	5.25		12.50	12.42	12.18	11.78	11.22	10.50
6	3.0		9.0	8.96	8.84	8.64	8.34	8.00		18.0	17.92	17.68	17.28	16.72	16.0
7	3.5		12.25	12.21	12.09	11.89	11.61	11.25		24.50	24.42	24.18	23.78	23.22	22.50
8	4.0		16.0	15.96	15.84	15.64	15.34	15.00		32.0	31.92	31.68	31.28	30.72	30.00
9	4.5		20.25	20.21	20.09	19.89	19.61	19.25		40.50	40.42	40.18	39.78	39.22	38.50
10	5.0		25.00	24.96	24.84	24.64	24.34	24.00		50.0	49.92	49.68	49.28	48.72	48.00

Table 6 = Tables 2, 3 and 4.

	$G$	$N$	0	.2	.4	.6	.8	1.0		0	.2	.4	.6	.8	1.0
1															
2	1.0		.514953372	.543169265	.477816947	.368894415	.216407671	.020350715		.282476686	.282900459	.284414849	.288200324	.300566209	0
3	1.5		.672506408	.668343985	.655856714	.635044596	.605907631	.568445819		.149445968	.151209694	.154903520	.168001816	.188170072	.227378328
4	2.0		.598693133	.401182878	.608652124	.621100862	.638529993	.660936805		.074834442	.075904929	.079251579	.085316052	.095019310	.110150138
5	2.5		.465848880	.470009915	.482494500	.503302140	.532432844	.569884602		.037267871	.037842988	.039613670	.042725139	.047453908	.054274914
6	3.0		.334625105	.338494808	.350102348	.369448247	.390532605	.431355124		.018590311	.018889219	.019802149	.021380107	.023716059	.036959695
7	3.5		.227804520	.230807843	.239811812	.254818424	.275827683	.302839590		.009298225	.009451591	.009917776	.010715661	.011878834	.013459537
8	4.0		.149187159	.151311308	.157483763	.168304515	.183173570	.202290926		.004662099	.004740329	.004977392	.005380579	.005962681	.006743031
9	4.5		.094865168	.096286039	.100548655	.107653013	.117599112	.130386956		.002342350	.002382139	.002502455	.002706209	.002998448	.003384674
10	5.0		.058940532	.059854919	.062598080	.067170009	.073570713	.081800191		.001178811	.001199017	.001260026	.001363028	.001510072	.001704171

H<sub>2</sub> plus - Pressure Effects

Table 4

 $\zeta^2 - N^2$ 

	$N$	$\zeta$	1.0	1.2	1.4	1.5	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0	
1	0		1.00	1.44	1.96	2.25	2.56	3.24	4.0	4.25	9.0	12.25	16.0	20.25	25.00	1
2	.1		.99	1.43	1.95	2.25	2.55	3.23	3.99	4.24	8.99	12.24	15.99	20.24	24.99	2
3	.2		.96	1.40	1.92	2.21	2.52	3.20	3.96	4.21	8.96	12.21	15.96	20.21	24.96	3
4	.3		.91	1.35	1.87	2.17	2.47	3.15	3.91	4.16	8.91	12.16	15.91	20.16	24.91	4
5	.4		.84	1.28	1.80	2.09	2.40	3.08	3.84	4.09	8.84	12.09	15.84	20.09	24.84	5
6	.5		.75	1.19	1.71	2.31	2.99	3.75	4.00	8.75	12.00	15.75	20.00	24.75	6	
7	.6		.64	1.08	1.60	2.09	2.60	3.08	3.64	3.89	8.64	11.89	15.64	19.89	24.64	7
8	.7		.51	.95	1.47	2.07	2.75	3.51	5.76	8.51	11.76	15.51	19.76	24.51	8	
9	.8		.36	.80	1.32	1.61	1.92	2.60	3.34	5.61	8.36	11.61	15.36	19.61	24.36	9
10	.9		.19	.63	1.15	1.75	2.42	3.19	5.44	8.19	11.44	15.19	19.44	24.19	10	
11	1.0		0	.44	.96	1.25	1.56	2.24	3.00	5.25	8.00	11.25	15.00	19.25	24.00	11
12	.1		0	4.20282193	1.843533960	4.988044800	10.862181032	20.784629680	35.182882438	64.05175291	142.2371713	229.5140330	471.0295402	293.9387290	22	
13			0.00099	4.31672922	1.862911452	5.014371121	10.901258	20.83639773	35.27715147	60.38020114	120.4757907	292.8041454	471.0783025	294.049510	23	
14	.2		0.0142	4.65575257	1.92	51.00121404	11.01671840	20.98966740	75.557070	204.2641178	463.1872294	930.9034533	1712.240065	2942.004437	24	
15	.3		0.2457	5.20891862	2.011988782	5.235074534	11.20326052	21.23804205	76.01382687	205.0220097	464.3582403	932.6185283	1714.449007	2945.295843	25	
16	.4		0.5374	5.94890240	2.133533857	5.413821245	11.45163714	21.57058126	76.63253463	206.0570619	465.9665780	934.9835497	1717.980539	2949.829987	26	
17	.5		0.9375	1.82054885	2.274010	5.625094749	11.748169423	21.97132808	77.39191998	207.3428080	467.9807688	937.96217191722.193369	2955.580670	27		
18	.6		1.3824	7.72785092	2.424503261	5.852946088	12.07403718	22.41869350	78.24355777	208.845558	470.3597861	941.5070410	1727.233981	2962.488201	28	
19	.7		1.7493	8.52016544	2.564465883	6.075747366	12.40442574	22.88470176	79.21188017	210.5189016	473.0524362	945.5596352	1733.036313	2970.479016	29	
20	.8		1.8432	8.978951384	2.67149244	6.265204481	12.70755738	23.334114	80.19287862	212.3131487	475.99786151	950.0497298	1739.521370	2977.465349	30	
21	.9		1.3851	8.80451766	2.708056417	6.384995085	12.744362828	23.72346634	81.15360850	214.1444384	479.1229633	954.8949108	1744.594774	2989.344827	31	
22	1.0		0	76.0320000	2.634240	6.389760	13.063680	24.0	82.03125	216.0	482.34375	960.0	1754.156250	3000.0	32	

Table 4 X

Table 7 = Q

A

$$2(a) \times 4(a) \times 10(a)$$

$$\cancel{2(a) \times 4(a) \times 10(b)}$$

,, 10(c)

,, 10(d)

B

$$2(b) \times 4(b) \times 10(a)$$

,, 10(b)

,, 10(c)

,, 10(d)

C

$$2(c) \times 4(c) \times 10(a)$$

,, 10(b)

,, 10(c)

,, 10(d)

D

$$5(a) \times 10(a)$$

$$,, \times 10(b)$$

$$,, \times 10(c)$$

$$,, \times 10(d)$$

E

$$5(b) \times 10(a)$$

,, \times 10(b)

,, \times 10(c)

,, \times 10(d)

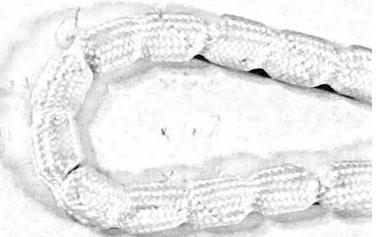
F

$$5(c) \times 10(a)$$

,, \times 10(b)

,, \times 10(c)

,, \times 10(d)



G

$$\text{col } D \times 1.4$$

$$\text{col } D \times 1.3$$

$$\text{col } D \times 1.2$$

J

$$\text{col } D \times 1.7$$

$$\text{col } D \times 1.0$$

$$\text{col } D \times 1.6$$

M

$$\text{col } D \times 1.5$$

Same for col E+F  
etc col E \times 1.4  
col E \times 1.3, col E \times 1.2  
etc

N

$$7(a) \times 11(a) \times 8(a)$$

,, 11(b) \times 8(b)

,, 11(c) \times 8(c)

,, 11(d) \times 8(d)

O

$$7(b) \times 11(a) \times 8(a)$$

,, \times 11(b) \times 8(b)

,, \times 11(c) \times 8(c)

,, \times 11(d) \times 8(d)

$$7(c) \times 11(a) \times 8(a)$$

,, \times 11(b) \times 8(b)

,, \times 11(c) \times 8(c)

,, \times 11(d) \times 8(d)

Q

$$6(a) \times 10(a)$$

,, 10(b)

,, 10(c)

,, 10(d)

R

$$6(b) \times 10(a)$$

,, \times 10(b)

,, \times 10(c)

,, \times 10(d)

S

$$6(c) \times 10(a)$$

,, \times 10(b)

,, \times 10(c)

,, \times 10(d)

$$5 \times 7(a) \times 16(a)$$

,, , \times 16(b)

,, , \times 16(c)

,, , \times 16(d)

U

$$5 \times 7(b) \times 16(a)$$

16(b)

16(c)

16(d)

V

$$5 \times 7(c) \times 16(a)$$

16(b)

16(c)

16(d)

$b/c$ 

.440 .445 .450 .455

1.30 2.202798 2.19683 2.20281 2.20283

$R = 2a$

1.35 2.218370 2.204754 2.20476 2.20477

1.40 2.203361 2.203366 2.203382 2.203394

 $b$  $b^2$  $b^3$  $\left(\frac{2}{(2b)^2} + \frac{2}{(2b)^3}\right)$  $\left(\frac{1}{2b} - \frac{1}{(2b)^2}\right)$  $\frac{1}{2b} + \frac{2}{(2b)^2}$  $+ \frac{3}{(2b)^3}$  $\frac{1}{b}$ 1.30 1.6900 .2.197 .40965 .53255<sup>44</sup> .794265 .76923 .11.35 1.8225 .2.4604 .37596 .50795<sup>44</sup> .74633 .74074 .2

1.40 1.9600 .2.7440 .39621 .48469 .70335 .714286 .3

1.40 .C . $\frac{1+2c+\frac{c^2}{5}}{15}$  C 1.30 1.35 1.40<sup>13</sup> .14 .4

1.40 .19360 .1.3321 .11733 .33846 .32593 .3142857 .6

1.45 .19803 .1.3363 .11867 .34231 .32963 .317851 .7

1.50 .20250 .1.3405 .12000 .34615 .33333 .32143 .8

1.55 .20703 .1.3447 .12133 .34500 .27.33704 .32500 .9

1.55 .C . $\frac{1+2c+\frac{c^2}{5}}{15}$  1.30 1.35 1.40<sup>13</sup> .14 .4

1.40 .53699 .53962 .54226 .54491 .15 .16 .17 .18 .19 .19 .20 .21 .21 .22 .22 .23 .23 .24 .24 .25 .25 .26 .26 .27 .27 .28 .28 .29 .29 .30 .30 .31 .31 .32 .32 .33 .33 .34 .34 .35 .35 .36 .36 .37 .37 .38 .38 .39 .39 .40 .40

2.25616

7.95284

$R = 1.9a$

1.35

1.40

1.30 2.25864

$R = 2.1a$

1.35

1.40



$$b^2 \left(1 + \frac{2c}{3} + \frac{c^2}{6}\right) \left(\frac{2}{(2b)^2} + \frac{2}{(2b)^2}\right)$$

$$\left(1 + \frac{2c}{3} + \frac{c^2}{6}\right) \left(\frac{1}{2b} + \frac{1}{(2b)^2}\right)$$

$$\left(2b - \frac{2R}{a_0}\right) \left(1 + \frac{2c}{3} + \frac{c^2}{6}\right) \left(\frac{1}{2b} + \frac{1}{(2b)^2}\right)$$

Page 1

$$(A) b = 1.3 \\ 2(a) \times 4(a) \times 10(n)$$

(B)

(C)

(D)

(E)

(F)

$10^{-5}$

$10^{-4}$

$10^{-3}$

$10^{-2}$

$10^{-1}$

$\times 10(n)$

$$\Delta F = -\frac{e^2}{2} \frac{1}{r_{\text{ao}}}$$

c/b

1.3

1.4

1.5

$$R = 1.9 \alpha_0$$

.3

.4

.5

.6

$$\begin{array}{l} ? \\ 2.2563364 \\ 2.2547282 \\ 2.24969089 \end{array}$$

$$\begin{array}{l} 2.2496292 \\ 2.24785678 \\ 2.2424548 \end{array}$$

$$\begin{array}{l} 2.2295397 \\ 2.2274820 \\ 2.22160136 \end{array}$$

$$R = 2 \alpha_0$$

.3

.4

.5

.6

$$\begin{array}{l} 2.2024033 \\ 2.20234142 \\ 2.19913380 \end{array}$$

$$\begin{array}{l} 2.2029647 \\ 2.2029036 \\ 2.1995023 \end{array}$$

$$\begin{array}{l} 2.19096111 \\ 2.19078502 \\ 2.18708760 \end{array}$$

$$R = .2 \alpha_0$$

.3

.4

.5

.6

$$\begin{array}{l} 2.1482658 \\ 2.1494740 \\ 2.14777468 \end{array}$$

$$\begin{array}{l} 2.15477459 \\ 2.15611470 \\ 2.1543665 \end{array}$$

$$\begin{array}{l} 2.14944452 \\ 2.15070767 \\ 2.14891604 \end{array}$$

The Nuclear  
Table I  
Separation is 2.0A  
 $b = 1.354$   
 $c = .448$

	0	.2	.4	.6	.8	1.0
1.	25820538	26283242	276713546	2998487437	3322580366	3738813962
2.	13120425	1335557302	1406089796	1523648714	1688231326	1899837540
3.	.066600000	067864726	0714487156	0774226316	085785622	085785621
4.	0.88877643	0344847306	0363057321	039344409	0435710408	04705482706
5.	.017214556	0176301084	0184484737	0199909196	0201503135	02419266771
6.	0.08747388	0089041119	0093744008	0101581667	011255439	012666278
7.	.0044448908	0045246352	0047635106	0051617628	0057193279	006413620188
8.	0.022586028	00829707732	0094205309	0098622879349	002871631513	0032710485814
9.	0.011476947	0016826389	00168297616	001332794701	00141767617	001661861936
10.	1.2928x281	Table II	Table III	Table IV	Table V	Table VI
11.	0	.2	.4	.6	.8	1.0

	0	.2	.4	.6	.8	1.0
1.	0	0	0	0	0	0
2.	1.5	30061735635	3060616338	3222258441	3491661957	3868826877
3.	2.	36668153316	37325346413	3929652651	4253199308	4718164601
4.	3.	326069231	3319123920	349441873	378657674	419553801
5.	4.	2524177765	257002169	2705715374	293197382	324868173
6.	5.	18441317176	1836461759	1933451885	2095102073	232141346
7.	6.	1322233443	1244237616	130995428	141947349	1579800852
8.	7.	0791709809	081138208	085428409	092565408	102564205
9.	8.	0504980894	0514030156	054117793	0586426116	0641716705
10.	9.	07312132265				
11.	10.	896 (1 - 3N^2) e^{-1.854} \$				
12.	11.	2313520205	203589778	180303051	-018508166	-212843859
13.	12.	117559008	103157927	0611306842	-009447302	-1081546874
14.	13.	057363200	0525679616	0310628744	-0047718256	054957444
15.	14.	0303526813	03671184395	01571842045	-0024283475	027360187
16.	15.	0154242176	0135783311	0080206853	-0012337937	0141703028
17.	16.	00783765765	006897114049	0040755302	-0062701275	0073106468
18.	17.	003982622157	0035047075	00807096352	-00031860777	0036640188
19.	18.	0133669517	0140739051	015349603	016896346	01701460444
20.	19.	00202372603	0017808789	00105232753	-001618938	0018218297
21.	20.	0010383345	00090493432	00053473391	-0008226676	0009462677
22.	21.	0020566689024				



$$(\xi^2 + N^2 - 1)$$

Table 14 = H'

Table 14 x Table 13 = Table 15

		Table 15 x Table 5 = Table 15'					
		(1)	(2)	(3)	(4)	(5)	(6)
1	1.0	1.0	0	-0.000069056	0.00767244	0.02935663	0.05028281
2	1.5	-0.0177482225	-0.01515185	-0.00786536	-0.00016855	-0.01059200	-0.09587441
3	2.0	-0.01072524	-0.00893633	-0.00422505	+0.00031675	-0.00472520	-0.04325508
4	2.5	0.00087119	0.00195398	0.00489884	0.00837540	0.00864518	0.00318019
5	3.0	0.00466993	0.00540214	0.00712181	0.00949545	0.01123325	0.00931480
6	3.5	0.004151425	0.00447045	0.00538549	0.00674684	0.00821907	0.00878774
7	4.0	0.002533680	0.00268841	0.00313141	0.00383884	0.004701235	0.00543840
8	4.5	0.001298025	0.00134458	0.00154762	0.00189552	0.00232849	0.00278721
9	5.0	0.00059400	0.00062400	0.00070819	0.00085730	0.00104431	0.00127200
		$\rightarrow -0.00868524 - 0.00497137 + 0.000606391 + 0.02081464 , 0.01802511 - 0.06336614$					
		$\frac{5}{3}[(1+9)+4(2+4+6+8)+2(3+5+7)]$					

(Table 10)<sup>2</sup> = Table 11

Table 11 x Table 5 = Table 12

	<i>S</i>	<i>N</i>	0	.2	.4	.6	.8	1.0	0	.2	.4	.6	.8	1.0
1														
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40														

*E*

Table 9 x Table 1 = Table 13

1.0	.000559678	.001798314	.005708660	.012698192	.021824137	1.54099521
1.5	- .000630853	- .00053176	- .000266703	- .000005539	- .000348087	- .003408868
2.0	- .000089377	- .000074222	- .000034819	+ .000002590	- .000038635	- .000360459
2.5	.000002655	.000005948	.000014869	.000025347	.000026115	- .000009692
3.0	.000006486	.000007499	.000009373	.000013146	.000015552	.000012940
3.5	.000003016	.000003243	.000003904	.000004902	.000005954	.0000046378
4.0	.000001057	.000001120	.000001304	.000001598	.000001957	.000002266
4.5	.000000333	.000000350	.000000402	.000000486	.000000597	.000000715
5.0	.000000099	.000000104	.000000118	.000000142	.000000174	.000000212

Table 8 = Table 1 x 2.2047715

(Table 8') - (Table 7) = Table 9

$\rho = 2$     $b = 1.354$  ,  $c = .448$

---

$\rho = 1.8$     $b = 1.252$  ,  $c = .370$

---

$\rho = 2.2$     $b = 1.453$  ,  $c = .537$

$$(Table 3)^2 \times Q = \gamma^r r^3 (\xi^2 - N^2)$$

$$R = 2.2 \text{ \AA}$$

	$N$	$S$	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0	
1	0	0	0	0.12854923	0.31534028	0.47712391	0.58104444	0.62175913	0.52597945	0.33385723	0.17687043	0.08318339	0.03579448	0.01438536	1
2	1	.1	.000054730	.013345493	.032207766	.048500458	.058941402	.063002078	.053231937	.033703961	.017886714	.008410621	.003618306	.001454442	2 1
3	2	.2	.000438290	.014858590	.034207110	.050903144	.061489979	.065515743	.055154999	.034871562	.018492750	.008691846	.003739530	.001502472	3 2
4	3	.3	.001476867	.017509412	.037821444	.055033009	.065861683	.069821762	.058443839	.036815913	.019527193	.009172303	.003943693	.001584275	4 3
5	4	.4	.003407329	.021456578	.043034003	.061066621	.072236309	.076091778	.063220615	.039756031	.021025344	.009866882	.004239976	.001702642	5 4
6	5	.5	.004596734	.026838989	.050085070	.069223215	.080850023	.084557905	.069651752	.043644810	.023037757	.010798758	.004636145	.001861129	6 5
7	6	.6	.010766826	.033658949	.059103235	.079724670	.091972450	.095500249	.077969287	.048658275	.025628944	.011997624	.005147157	.002004854	7 6
8	7	.7	.015265130	.041578814	.070045778	.092706010	.105868102	.109224906	.088417172	.054955117	.028879863	.013500700	.005786608	.002319447	8 7
9	8	.8	.018201379	.047584467	.082501555	.108201009	.122728700	.126024930	.101292587	.062717516	.032884312	.015349953	.006573651	.002432954	9 8
10	9	.9	.015599364	.055452251	.095380568	.125702324	.142571917	.146131595	.116907778	.072152923	.037750577	.017595849	.007526085	.003012662	10 9
11	10	1.0	0	.054937908	.106443617	.144389835	.165084735	.169105264	.135573867	.083487672	.043600981	.030294400	.008672549	.003418600	11 0
12															12 1
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$$0 + f + 4(1's) + 2(2's) =$$

$$.281718948 .925809755 1.717951955 2.356873183 2.736416461 2.847003571 2.330073100 1.454165859 765679180 358338173 153696177 .061641640$$

$$1.301651405$$

$$\frac{1}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.6)]$$

$$\frac{1}{2} [1.8 + 2.0]$$

$$.558542003$$

$$\frac{1}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)]$$

$$3.255574517$$

$$\sum 5.115767925$$

$$\frac{1}{3} \left[ \frac{1}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.6)] + \frac{1}{2} [1.8 + 2.0] + \frac{5}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)] \right]$$

$$170525597$$

$$(Table 1)^2 \times Q = 4\pi r^3 (\xi^2 - N^2)$$

$$R = 2.0 \text{ \AA}$$

$$\Psi = e^{-\xi^2} (1 + CN^2)$$

	N	$\xi$	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0
1	0	0	.0	.014302638	.041604888	.065496144	.082983582	.092385304	.086286943	.060448905	.035368906	.018364448	.008724901	.003871761
2	1	.1	.0000666013	.016896175	.042424008	.066445412	.084034537	.093454578	.087177722	.060942100	.035707802	.018537865	.008806427	.003907618
3	2	.2	.000530708	.018718458	.044912504	.069411785	.087235003	.096700868	.089880424	.062740337	.036734771	.019062948	.009053469	.004016746
4	3	.3	.001774068	.021882573	.049177030	.074446843	.092694433	.102237386	.094482906	.065799949	.038480857	.019955425	.009473264	.004201465
5	4	.4	.004121343	.026533961	.055366979	.081741339	.100598395	.110248104	.101131956	.070214708	.040997790	.021240957	.010077502	.004467812
6	5	.5	.007742191	.032773836	.043030730	.091497454	.111182210	.120978307	.110030414	.076115130	.044358353	.022954061	.010883229	.004822621
7	6	.6	.012455993	.040525221	.074034386	.103899567	.124703192	.134716619	.121432954	.083668922	.048656133	.025098883	.011912942	.005275303
8	7	.7	.017400737	.049310244	.086426006	.119031756	.141391847	.151767452	.135140839	.093079669	.054005628	.027873018	.013190659	.005837882
9	8	.8	.020400670	.057894393	.100219158	.136747235	.161373144	.172403883	.152987964	.104583334	.060541978	.031200583	.014750619	.006523539
10	9	.9	.017234134	.043738175	.114061151	.156468583	.184547463	.194796117	.173824537	.118445938	.068419765	.035209172	.016628649	.007348704
11	f	1.0	0	.012179327	.125340353	.176891368	.210413428	.224908320	.198490195	.134951832	.077812176	.039987744	.018866301	.008331300
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$$dN [\Psi^2 (\xi^2 - N^2)] = .251950193 / 1.104230043 / 1.388888989 / 3.057627554 / 3.696627178 / 4.006347932 / 3.420267906 / 2.495363189 / 1.450932062 / .749685098 / .355107378 / .157243029$$

$$\frac{1}{3} \left\{ \frac{2}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.6)] \right\}$$

$$1.658252383$$

$$\frac{2}{3} [1.8 + 2.0]$$

$$.770299524$$

$$\frac{5}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)] \}$$

$$5.393157154$$

$$\sum 7.821709061$$

$$.0333 (\Sigma) = .240723435$$

$$(Table 2) \times Q = 4\pi r^3 (S^2 - N^2) \quad R = 1.8 \text{ \AA}$$

	$N$	$S$	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	3.5	4.0	4.5	5.0	
1	0		0	.020824498	.055340522	.090775652	.119802362	.138929735	.143692983	.111511630	.072228257	.041529845	.021849306	.010737287	1
2	1		.000081540	.021547384	.050355635	.091908493	.121124552	.140308343	.144939766	.112200752	.072801552	.041853650	.022017778	.010819379	2
3	2		.000146620	.023754518	.059374406	.095583721	.125129981	.144483846	.148714221	.114956373	.074535163	.042832450	.022521573	.011047308	3
4	3		.002144790	.027557029	.064508304	.101722786	.131930604	.151572508	.155117920	.119628087	.077472600	.044490101	.023388327	.011487243	4
5	4		.004931079	.0330169282	.071877454	.110535617	.141700611	.161759946	.164318163	.126334821	.081687203	.046866986	.024623128	.012088993	5
6	5		.009148311	.0403316241	.081574474	.122184258	.154654080	.175228046	.170544900	.135242042	.087279817	.050018896	.026260004	.012884071	6
7	6		.014513548	.049170407	.0935168853	.136782414	.171100703	.192431640	.192083189	.146560217	.094381454	.054018590	.028335792	.013896440	7
8	7		.019957743	.058911542	.107554106	.154299337	.190917261	.213461175	.211264897	.160542977	.103151020	.058954319	.030895705	.015142017	8
9	8		.023051444	.0646490174	.122712882	.174412172	.214392250	.238585153	.234450617	.177482540	.113774913	.04493059	.033993727	.016448359	9
10	9		.019129981	.073692580	.137344632	.196286025	.241151703	.267865905	.262005643	.197703088	.126466902	.072068975	.037491908	.018445752	10
11	1.0	0	.070708150	.148468295	.218257026	.270429933	.301094320	.294243977	.221551416	.141462257	.080504256	.042060983	.020568300	11	
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$$0 + f + 4(1's) + 2(2's) = .288131242 \quad 1.325084490 \quad 2.688332651 \quad 4.009505022 \quad 5.053804785 \quad 5.708531133 \quad 5.716581844 \quad 4.344998732 \quad 2.811135544 \quad 1.608875835 \quad .843883677 \quad .413829497$$

$$\cdot \frac{2}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.6)]$$

2.137130425

$$\cdot \frac{2}{3} [1.8 + 2.0]$$

1.076233592

$$\cdot \frac{5}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)]$$

9.259419003

$$\cdot \frac{11}{3} \left\{ \cdot \frac{2}{3} [1.0 + 1.8 + 2(1.4) + 4(1.2 + 1.6)] + \cdot \frac{4}{3} [1.8 + 2.0] + \cdot \frac{5}{3} [2.0 + 5.0 + 2(3.0 + 4.0) + 4(2.5 + 3.5 + 4.5)] \right\}$$

.415759444