

THE INTERACTION OF A POSITRON
AND A HYDROGEN MOLECULE

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A B S T R A C T

The possibility of the existence of a bound state of a hydrogen molecule and a positron is investigated using two approaches.

First, a variational calculation of the energy is performed using a wave function which represents a positronium atom bound to a hydrogen molecular ion.

Second, a wave equation describing a positron moving in the field of a hydrogen molecule is studied.

Neither line of investigation indicates that the positron will form a bound state with a hydrogen molecule. These results are inconclusive, however, due to the nature of the variational method used. This method can, under favourable circumstances, conclusively demonstrate the occurrence of binding. However, failure to demonstrate binding, as occurs in the present case, does not mean that the system studied is necessarily not bound.

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CHAPTER I

INTRODUCTION

The existence of the positively charged electron, or positron, was predicted by Dirac in 1928, and experimentally verified soon after. The experimental verification was accomplished by studying the electron-positron pairs created by γ -radiation from radioactive sources. In the study of the reverse process, γ -ray creation from an electron-positron pair, it was found that the two particles could form a quasi-stable two-particle atom similar to the hydrogen atom.

The existence of this electron-positron bound state was demonstrated by measuring the lifetimes of positrons in different gases. It was found that, in addition to the component due to the annihilation of free positrons, the decay curves had a component which was easily explained in terms of this electron-positron pair. This system was named "positronium" by Wheeler in 1946.

The main difference between positronium and the hydrogen atom is that the reduced mass of positronium is about one-half that of the hydrogen atom. This results in an increase in the linear dimensions of the positronium atom by a factor of two, and a reduction by a factor of one-half in the energies of the ground and excited states, as compared to the states of the hydrogen atom.

Two types of annihilation of the positron-electron pair are possible from the ground state of positronium. It can be shown¹ that the singlet state of positronium results in two-photon annihilation, while the triplet state results in three-photon annihilation.

1. S. De Benedetti and H. Corben, Ann. Rev. of Nuclear Sci. 4, 196, (1954).

The mean lifetimes of these two states are $\sim 1.25 \times 10^{-10}$ sec. for singlet positronium, and $\sim 1.4 \times 10^{-7}$ sec. for triplet positronium.¹

Positronium is not the only bound system of which a positron can be a member. Theoretical investigations have shown that systems consisting of two positrons and an electron² and two electrons and a positron² both have positive binding energies against dissociation into their constituent parts, while a system of a negative hydrogen ion and a positron has a positive binding energy against dissociation into a hydrogen atom and positronium.^{3,4}

On the other hand, positrons will not bind with all atoms or molecules. In particular, investigations by Oczkowski⁵ indicate that a positron will not bind with atomic hydrogen, or with helium.

The object of this thesis is to investigate the system of a hydrogen molecule and a positron. The approaches employed will be twofold. First, the behaviour of positronium in the vicinity of a hydrogen molecule ion (H_2^+) will be investigated, and second the behaviour of a positron near a hydrogen molecule (H_2) will be considered.

2. J. A. Wheeler, Ann. N.Y. Acad. Sci. 48: 219 (1946)

3. A. Ore, University of Bergen Yearbook, No. 5, Bergen, Norway (1952).

4. G. Darewych, Thesis: The Interaction of a Positron with Negative Hydrogen Ion, University of Manitoba, (1961).

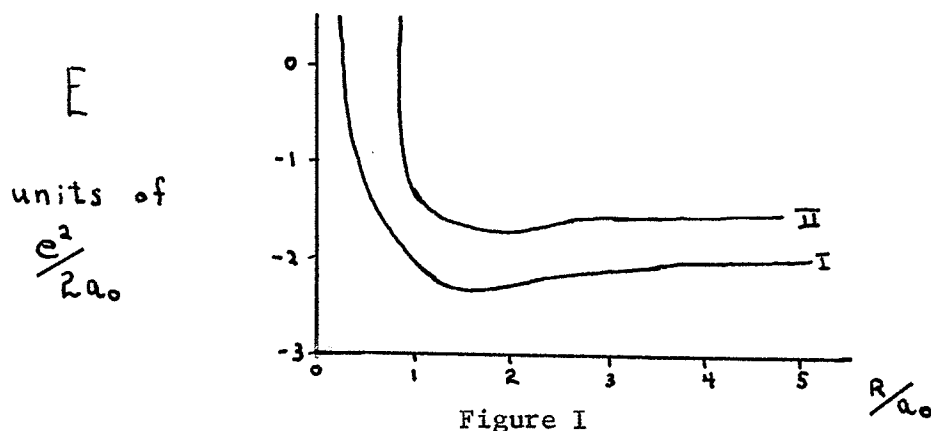
5. G. Oczkowski, Thesis: The System of a Helium Atom and a Positron, University of Manitoba, (1961).

CHAPTER II

REASONS FOR CHOOSING THE TWO LINES OF INVESTIGATION

The Schrodinger equation for a system of two protons and one electron, the hydrogen molecular ion, has been solved numerically by Burrau.¹ The system shows a minimum energy of - 16.39 e.v. against infinite separation of all components, and this value occurs at an inter-proton separation of $1.06\text{\AA}$, or $2 a_0$, where a_0 is the first Bohr Radius.

The hydrogen molecule itself has a minimum energy of - 31.78 e.v. against infinite separation of all constituent parts, and this value occurs at an internuclear separation of $.751\text{\AA}$ or $1.40 a_0$. Graphs of the energies of a hydrogen molecular ion and a positronium atom (Curve II), and of a hydrogen molecule plus a positron (Curve I), plotted as a function of R , the separation of the protons is made in Figure I. In Curve II, the molecular ion and the positronium atom are assumed to be separated - the energy of interaction between the two systems is neglected. In Curve I the positron is assumed to be not bound to the molecule.



1. O. Burrau, Kgl. Danske Vidensk. Selskab: Math-fys. Meddelelser, vii, 14 (1927).

The presence of a positron completely separated from the molecule (Curve I) does not affect the energy curve, and this curve is actually just the energy of the molecule plotted as a function of the internuclear separation. The presence of the positronium atom completely separated from the hydrogen molecular ion (Curve II) has the effect of adding to the energy of the molecular ion a constant amount - the energy of the positronium atom. This constant amount has a value of .50 in units of $e^2/2a_0$. Therefore Curve II is merely the graph of the energy of the molecular ion plotted as a function of R , but shifted downward by one-half a unit.

We shall now discuss qualitatively the two approaches we shall employ in investigating the interactions of these five particles.

We shall first assume that the positron is bound to the molecule, and qualitatively examine the resulting configuration. Since the electronic wave function for the hydrogen molecule is greatest in the region between the nuclei, this would be the region which attracts the positron. Coulomb repulsion will then cause the two protons to re-adjust themselves further apart than the equilibrium distance for the molecule itself. At the same time the net charge, neglecting the protons, is $-e$. This configuration (i.e. two protons further apart than in the hydrogen molecule, and a net charge of $-e$ distributed principally in the region between the nuclei) is the same sort of qualitative description which could be applied to the hydrogen molecular ion. It would, therefore, be not unreasonable to expect a graph of E vs R for the molecule-plus-positron system to have a shape similar to that of the molecular ion plot, with the minimum occurring at a

value of R larger than R_{H_2} , and perhaps approaching the value of $R_{H_2}^+$.

It will be noted that the "potential well" for H_2^+ is wider than the well for the molecule. This means that the curvature of the H_2^+ well, near the minimum, is less than the corresponding quantity for the molecule. If we consider the lowest vibrational level, of energy $\frac{1}{2} \hbar \omega$, in such a well, and use the semi-classical argument that the average potential energy is one-half the total energy, we have

$$\frac{1}{2} E = \frac{1}{4} \hbar \omega = \frac{1}{2} m \omega^2 \overline{x^2}$$

2-1

where $\sqrt{\overline{x^2}}$ represents the position which the particle in the well would occupy in order to have the kinetic energy at this position equal to the average kinetic energy.

We could write $\sqrt{\overline{x^2}} = \left(\frac{\hbar}{2m\omega} \right)^{1/2}$

In considering these two potential wells, the one with the greater curvature is the one with the greater angular frequency ω , and thus is the one with the least value of $\sqrt{\overline{x^2}}$.

In this case this would be the well for the molecule. This means that the wave function for the molecule, plotted as a function of R , would occupy a narrower region than the wave function for the molecular ion plus separated positronium system, these regions being centred about the minimum of the well in each case.

Assuming that the positron is bound to the hydrogen molecule, we now consider the relative transition probabilities between this system and the system of a molecule and a separated positron on one hand, and between the former system and the system of a molecule ion

and a separated positronium atom on the other.

The probability of a transition between any two states, denoted by ϕ_1 and ϕ_2 , will depend, to a large extent, on the amount of overlap of the two functions. This can be described in terms of the overlap integral for the two states, which is denoted (ϕ_1, ϕ_2) . When this overlap is small, there is a small probability of transition between the two states. In other words, a large overlap of wave functions is a necessary, but not sufficient, condition for large transition probabilities between the states defined by the functions. An exact calculation of the transition probabilities would have to take into account the mechanism by which these transitions take place, but the principle stated above holds true in most cases.

This procedure, when applied to radiative transitions between vibrational levels of molecules, is well-known as the Franck-Condon principle.²

Let us consider a graph of E vs. R for the system of a hydrogen molecule plus a bound positron, assuming for the moment that the positron is indeed bound. If, as was reasoned previously, this graph resembled more the graph of E vs. R for the molecular ion plus free positronium than the corresponding graph for the molecule plus free positron, then the overlap between ground state wave functions for the bound system and the molecular ion plus free positronium would be greater than the overlap between the ground state wave function for the bound system and the system of molecule plus free positron. This, in turn, would mean that the transition probability in the former case would be greater than

2. W. Kauzmann, Quantum Chemistry, Academic Press, (1957); pp. 664, ff.

the transition probability in the latter case.

A hydrogen molecule has an energy of -31.95 e.v., while the energy of a molecular ion is -16.39 e.v. Since the energy of a free positronium atom is -6.80 e.v., a positronium atom would have to be bound to a molecular ion with a binding energy of 8.76 e.v. in order that the system be stable against dissociation into a molecule plus free positron.

Such a binding energy, greater than the energy of the positronium atom, is not likely to occur, and the bound system would likely be unstable against dissociation into a hydrogen molecule plus free positron. However, if, as was discussed above, the overlap of the wave functions of the molecule plus positron and molecular ion plus bound positronium configurations is small, such a bound system might be sufficiently long-lived such that the lifetime of the positron in the bound positronium atom could be calculated. An investigation into molecular ion plus bound positronium configuration is justified for this reason.

If we consider a positron in an atmosphere of molecular hydrogen, the most favoured mode of binding, from a viewpoint of the energies of various configurations, is a configuration representing a positron bound to the molecule. Therefore, an investigation of the motion of a positron in the field of a hydrogen molecule will also be made, to see if such a direct mode of binding can be found.

CHAPTER III

THE CONFIGURATION OF A HYDROGEN MOLECULAR ION AND POSITRONIUM

Before discussing the details of the investigation of the configuration of a hydrogen molecular ion and a bound positronium atom, it will be necessary to discuss the calculation of upper bounds of energies by the variational method.

The mathematical basis for the variational method is outlined in most elementary quantum mechanics texts.¹ A brief summary of basic ideas of the variational method follows.

The postulates of quantum mechanics state that the states of a physical system are in one-to-one correspondence with the elements in a Hilbert space. Dynamical variables of the system can be represented as hermitian operators in the Hilbert space, such that a measurement of the variable corresponding to the operator A gives a value A' , where A' is an eigenvalue of A . Furthermore, after the measurement, the system will be in the state ψ_A , where ψ_A is an eigenfunction of A such that

$$A \psi_A = A' \psi_A$$

3-1

On the other hand, if the state of the system corresponds to the element ϕ in the Hilbert Space, the expectation value of A , the weighted average of all possible values of the variable corresponding to the operation A , is

$$\langle A \rangle = \frac{(\phi, A\phi)}{(\phi, \phi)}$$

3-2

1. See, for example, L. I. Schiff, Quantum Mechanics, McGraw-Hill, second edition, (1955); pp.171 ff.

where (ϕ, ψ) is the inner product defined for the Hilbert space.

If the Hilbert space is a function space, the inner product is defined such that

$$(\phi, \psi) = \int \phi^* \psi d\tau \quad 3-3$$

where the integration is over all the variables needed to specify the states.

The basis for the variational principle is that the energy expectation value for any state ψ must equal or exceed the least eigenvalue of the Hamiltonian, the Hamiltonian being the operator in the space corresponding to the energy. This can be written

$$\langle E_\psi \rangle = \frac{(\psi, H\psi)}{(\psi, \psi)} \geq E_0 \quad 3-4$$

where E_0 is the ground state energy of the system we are trying to describe. Furthermore, the exact equality holds true if and only if the state function ψ is an eigenfunction of H belonging to the eigenvalue E_0 .

This is the basis of the variational method. It is applied in the following manner:

A trial wave function ψ is assumed, where ψ is a function of several parameters, and the average energy corresponding to this state calculated. This energy will be a function of the parameters. The parameters are then varied so that the minimum energy is found. Since any state function serves as an upper bound to the least energy eigenvalue-the ground state energy-this minimum energy, found by varying the parameters, will be the least upper bound to the ground state

energy of the system for all wave functions of the type assumed. The degree to which this minimum energy is a measure of the actual ground state energy depends on how closely the type of trial function assumed approximates the true state function of the system.

Let us now turn our attention to the configuration of two protons, two electrons and a positron. We shall label the two protons "a" and "b", and the positron as "1". The two electrons will be denoted by "2" and "3". This configuration is illustrated in figure 2.

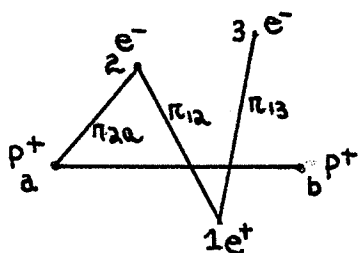


Figure 2
Configuration of two protons, two electrons and a positron.

We shall denote as π_{12} the distance between particles 1 and 2. The distance π_{2a} will be denoted by R .

We shall denote the spin coordinate of the j^{th} particle by σ_j .

The hydrogen molecular ion is a bound system of two protons and one electron. We shall neglect the motion of the protons, and regard them as fixed in space. This is a reasonable assumption, since the ratio of proton mass to electron mass is 1836:1. The velocity of the protons will therefore be much smaller than that of the electrons. Our configuration will therefore consist of two fixed particles and three particles whose positions are variable. Relative to the positions

of the two protons, nine coordinates will be required to completely specify the spatial orientation of the electrons and positron.

We now consider the type of wave function we shall choose for variation.

We shall assume a spin-independent Hamiltonian.

In order to satisfy the Pauli exclusion principle, the total wave function must be antisymmetric with respect to interchange of the two electrons. Therefore, if Ψ denotes the total wave function, we can write

$$\Psi(\underline{r}_1, \sigma_1; \underline{r}_2, \sigma_2; \underline{r}_3, \sigma_3) = -\Psi(\underline{r}_1, \sigma_1; \underline{r}_3, \sigma_3; \underline{r}_2, \sigma_2) \quad 3-5$$

Since we have assumed a spin-independent Hamiltonian, and since there are only two identical particles in the wave function, namely the electrons, we can write the wave function as

$$\Psi(\underline{r}_1, \sigma_1; \underline{r}_2, \sigma_2; \underline{r}_3, \sigma_3) = \psi(\underline{r}_1, \underline{r}_2, \underline{r}_3) u(\sigma_1) v(\sigma_2, \sigma_3) \quad 3-6$$

where either u is antisymmetric and ψ is symmetric, or u is symmetric and ψ is antisymmetric on interchange of the two electrons.

Since there is no apriori reason for choosing either type of wave function, both types will be considered.

With this spin-free Hamiltonian, the functions $u(\sigma_1)$ and $v(\sigma_2, \sigma_3)$ do not affect the expectation value of the energy, and we need not be concerned with the spin functions any further.

Let us now consider the details of the type of wave function which we shall choose. We wish to have a function which describes a positron bound to a hydrogen molecule. One choice of function could

be of the type

$$\psi(r_1, r_2, r_3) = f(r_{2a}, r_{2b}) g(r_{13}) h(r_{12}) \quad 3-7$$

where $f(r_{2a}, r_{2b})$ represents electron 2 bound to the two protons in a molecular ion configuration, $g(r_{13})$ represents the positron bound to electron 3 in a positronium configuration, and $h(r_{12})$ represents the binding of the two systems through the attraction between the positron and the electron bound to the protons.

This is not an acceptable wave function from the point of view that it implies we can tell which electron is bound to the molecular ion, and which one to the positron. In order that ψ have the required symmetry properties on interchange of the two electrons, we choose

$$\psi = f(r_{2a}, r_{2b}) g(r_{13}) h(r_{12}) \pm f(r_{2b}, r_{2a}) g(r_{12}) h(r_{13}) \quad 3-8$$

where choice of + or - sign depends on whether we wish to refer to the symmetric or to the antisymmetric spatial function.

We shall choose

$$\left. \begin{aligned} g(r) &= e^{-\gamma r} \\ h(r) &= e^{-\delta r} \end{aligned} \right\} \quad 3-9$$

These represent positronium-like wave functions. For the positronium ground state, the coefficient of r would be $(2a_0)^{-1}$. A value of $\delta = 0$ in equation (3-9) means that equation (3-9) would correspond to systems of a molecular ion and a positronium atom with no binding between them.

Our wave function will then have the form

$$\psi = f(r_{2a}, r_{2b}) e^{-\gamma r_{13} - \delta r_{12}} \pm f(r_{2b}, r_{2a}) e^{-\gamma r_{12} - \delta r_{13}} \quad 3-10$$

We now must choose $f(r_a, r_b)$, a function which describes the hydrogen molecular ion configuration. A good discussion of various variational functions for the ground state of H_2^+ is given by Pauling and Wilson.²

The greatest problem in dealing with this configuration (two protons, two electrons and a positron) is that most of the integrals involved have two fixed points - the positions of the protons. This greatly adds to the complexity of the resulting expressions for the kinetic and potential energies. The problem is to choose a wave function for the H_2^+ configuration which is simple enough so that the integrals involved can be calculated, and yet is a reasonably accurate description of the molecular ion.

The function which we shall choose is

$$f(r_a, r_b) = e^{-\alpha r_a} + e^{-\alpha r_b}$$

3-11

This function was first discussed by Finklestein and Horowitz.³ Due to changes in the accepted values of the physical constants, and the corresponding changes in the results, it will be necessary to redo the work of these authors. This is done in Appendix III. The values which give a minimum of energy were found to be $\alpha = 1.238a_0^{-1}$, $R = 2a_0$. The minimum energy is -15.96 e.v. giving a binding energy against dissociation into a hydrogen atom and a hydrogen ion of 2.36 e.v. This compares with the experimental value of 2.791 e.v. The error in the binding energy for this function is about 16%. The error in energy is due to the fact that the wave

2. L. Pauling and E.B. Wilson, Jr., Introduction to Quantum Mechanics, McGraw-Hill, (1935); pp. 327, f.f.

3. B. N. Finklestein and G. E. Horowitz, Z.f. Phys. 48, 118 (1928)

function does not sufficiently localize the electron charge density in the region between the two protons.

The total wave function for the two fixed protons, two electrons and a positron is therefore

$$\psi = (e^{-\alpha r_{2a}} + e^{-\alpha r_{2b}}) e^{-\gamma r_{13} - \delta r_{12}} \pm (e^{-\alpha r_{3a}} + e^{-\alpha r_{3b}}) e^{-\gamma r_{12} - \delta r_{13}} \quad 3-12$$

We now proceed to calculate the average energy, the expectation value of the Hamiltonian, as a function of the parameters α, γ, δ and R .

We write the wave function as

$$\psi = (\psi_1 + \psi_2) \pm (\psi_3 + \psi_4), \text{ where}$$

$$\begin{aligned} \psi_1 &= e^{-\alpha r_{2a} - \gamma r_{13} - \delta r_{12}} & \psi_3 &= e^{-\alpha r_{3a} - \gamma r_{12} - \delta r_{13}} \\ \psi_2 &= e^{-\alpha r_{2b} - \gamma r_{13} - \delta r_{12}} & \psi_4 &= e^{-\alpha r_{3b} - \gamma r_{12} - \delta r_{13}} \end{aligned} \quad 3-13$$

The Hamiltonian can be written, using Gaussian units, as

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + e^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} - \frac{1}{r_{3a}} - \frac{1}{r_{3b}} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right) \quad 3-14$$

We shall denote the Hamiltonian, as it appears in equation 3-14, as

$$H = T + V \quad 3-15$$

In order to perform the integrations involved in the calculation of the average value of H , the following volume elements for two-fixed point integrals will be used.

For the 3 dimensional coordinate system illustrated in figure 3, (r_a, r_b, ϕ) where ϕ is the angle between the

The contribution to the inner product $(\psi, H\psi)$ from the potential energy terms will be considered first.

Since our wave function is real, this contribution can be written

$$(\psi, V\psi) = \iiint \psi^2 V d\tau_1 d\tau_2 d\tau_3$$

3-19

where

$$\psi^2 = \psi_1^2 + \psi_2^2 + \psi_3^2 + \psi_4^2 + 2(\psi_1\psi_2 \pm \psi_1\psi_3 \pm \psi_1\psi_4 \pm \psi_2\psi_3 \pm \psi_2\psi_4 + \psi_3\psi_4)$$

3-20

Since there are ten terms in V , and ten distinct terms in ψ^2 , there would seem to be one hundred integrals to be calculated to find the contribution to $(\psi, H\psi)$ from $(\psi, V\psi)$. Due to the symmetries of the wave function and the Hamiltonian, however, this number can be reduced to twenty-six distinct nine-dimensional integrals.

These terms can all be expressed as functions of the parameters using the functions

$$f_{mn}(a, b, r) = \int_0^\infty \int_{|r-r_1|}^{r+r_1} e^{-ar_1 - br_2} \frac{r_1^m}{r_1} \frac{r_2^n}{r_2} dr_2 dr_1 \quad 3-21a$$

and

$$g_{mn}(a, b, r) = \int_0^\infty \int_{|r-r_1|}^{r+r_1} e^{-ar_1 - br_2} \frac{r_2^n}{r_1^m} dr_2 dr_1 \quad 3-21b$$

A discussion and table of these functions is found in Appendix I, and the explicit expression for $(\psi, V\psi)$ is found in Appendix II.

We now turn our attention to the evaluation of $(\psi, T\psi)$, the contribution of the kinetic energy part of the Hamiltonian to $(\psi, H\psi)$.

Using the divergence theorem, we write

$$(\psi, T\psi) = -\frac{\hbar^2}{2m} \int \psi \nabla^2 \psi d\tau = +\frac{\hbar^2}{2m} \int (\nabla \psi)^2 d\tau \quad 3-22$$

where ∇^2 is the Laplacian operator in a nine-dimensional space, and the integration is over the whole of the nine-dimensional space.

Within the nine-dimensional space, we can find a set of nine mutually orthogonal unit vectors $\{\underline{e}_k\}$, $k=1, \dots, 9$, such that the set $(\underline{e}_1, \underline{e}_2, \underline{e}_3)$ is a basis for the subspace defining the position of particle 1, $(\underline{e}_4, \underline{e}_5, \underline{e}_6)$ is a basis for the subspace defining the position of particle 2, and $(\underline{e}_7, \underline{e}_8, \underline{e}_9)$ is a basis for the subspace defining the position of particle 3. Associated with this set $\{\underline{e}_k\}$, $k=1, \dots, 9$, there will be 9 independent coordinates $\{x_k\}$, $k=1, \dots, 9$.

We can then write

$$\nabla \psi = \sum_{k=1}^9 \underline{e}_k \frac{\partial \psi}{\partial x_k} = \nabla_1 \psi + \nabla_2 \psi + \nabla_3 \psi \quad 3-23$$

where $\nabla_1 = \underline{e}_1 \frac{\partial}{\partial x_1} + \underline{e}_2 \frac{\partial}{\partial x_2} + \underline{e}_3 \frac{\partial}{\partial x_3}$, and ∇_2 and ∇_3 are similarly defined. In this case

$$(\nabla \psi)^2 = (\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 + (\nabla_3 \psi)^2 + 2(\nabla_1 \psi \cdot \nabla_2 \psi + \nabla_1 \psi \cdot \nabla_3 \psi + \nabla_2 \psi \cdot \nabla_3 \psi) \quad 3-24$$

However $\nabla_i \psi \cdot \nabla_j \psi = 0$ if $i \neq j$; $i, j = 1, 2, 3$ and therefore

$$(\nabla \psi)^2 = (\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 + (\nabla_3 \psi)^2$$

We can then write

$$(\psi, T\psi) = + \frac{\hbar^2}{2m} \int \{ (\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 + (\nabla_3 \psi)^2 \} d\tau \quad 3-25$$

Let us define an origin for our coordinate systems at the midpoint of the internuclear axis, and let $\underline{r}_i$ be the position of the i 'th particle. Furthermore, we shall define $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$ where i and j can have the values 1, 2, 3, and a or b.

We can then write

$$\nabla_i \psi = \frac{\partial \psi}{\partial \underline{r}_i} \nabla_i \underline{r}_i + \sum_{\substack{j=a,b,1,2,3 \\ j \neq i}} \frac{\partial \psi}{\partial \underline{r}_{ij}} \nabla_i \underline{r}_{ij}, \quad i=1,2,3 \quad 3-26$$

If we consider the points $\underline{r}_i$ and $\underline{r}_j$ to be defined by Cartesian coordinates $\underline{r}_i = (x_i, y_i, z_i)$, $\underline{r}_j = (x_j, y_j, z_j)$, then

$$\underline{r}_{ij} = [(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2]^{1/2}$$

and

$$\nabla_i \underline{r}_{ij} = -\frac{1}{\underline{r}_{ij}} \underline{r}_{ij}$$

Also

$$\nabla_j \underline{r}_{ij} = +\frac{1}{\underline{r}_{ij}} \underline{r}_{ij}$$

$$\text{Since } \psi = \psi(\underline{r}_{2a}, \underline{r}_{2b}, \underline{r}_{3a}, \underline{r}_{3b}, \underline{r}_{12}, \underline{r}_{13})$$

we can write

$$\begin{aligned} \nabla_1 \psi &= -\frac{\partial \psi}{\partial \underline{r}_{12}} \frac{\underline{r}_{12}}{\underline{r}_{12}} - \frac{\partial \psi}{\partial \underline{r}_{13}} \frac{\underline{r}_{13}}{\underline{r}_{13}} \\ \nabla_2 \psi &= -\frac{\partial \psi}{\partial \underline{r}_{2a}} \frac{\underline{r}_{2a}}{\underline{r}_{2a}} - \frac{\partial \psi}{\partial \underline{r}_{2b}} \frac{\underline{r}_{2b}}{\underline{r}_{2b}} + \frac{\partial \psi}{\partial \underline{r}_{12}} \frac{\underline{r}_{12}}{\underline{r}_{12}} \\ \nabla_3 \psi &= -\frac{\partial \psi}{\partial \underline{r}_{3a}} \frac{\underline{r}_{3a}}{\underline{r}_{3a}} - \frac{\partial \psi}{\partial \underline{r}_{3b}} \frac{\underline{r}_{3b}}{\underline{r}_{3b}} + \frac{\partial \psi}{\partial \underline{r}_{13}} \frac{\underline{r}_{13}}{\underline{r}_{13}} \end{aligned} \quad 3-27$$

We define the angle $\theta_{ij,ik}$ by

$$\theta_{ij,ik} = \cos^{-1} \left[\frac{\underline{r}_{ij} \cdot \underline{r}_{ik}}{\underline{r}_{ij} \underline{r}_{ik}} \right] = \cos^{-1} \left[\frac{\underline{r}_{ij}^2 + \underline{r}_{ik}^2 - \underline{r}_{jk}^2}{2 \underline{r}_{ij} \underline{r}_{ik}} \right] \quad 3-28$$

This is illustrated in figure 4.

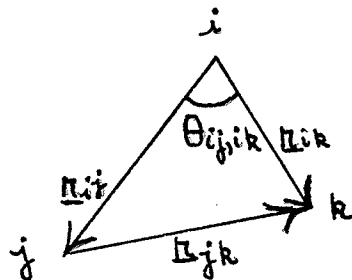


Figure 4.

We can then write

$$(\nabla_1 \psi)^2 = \left(\frac{\partial \psi}{\partial r_{12}} \right)^2 + \left(\frac{\partial \psi}{\partial r_{13}} \right)^2 + 2 \frac{\partial \psi}{\partial r_{12}} \frac{\partial \psi}{\partial r_{13}} \cos \theta_{12,13}$$

$$(\nabla_2 \psi)^2 = \left(\frac{\partial \psi}{\partial r_{2a}} \right)^2 + \left(\frac{\partial \psi}{\partial r_{2b}} \right)^2 + \left(\frac{\partial \psi}{\partial r_{2c}} \right)^2 + 2 \left(\frac{\partial \psi}{\partial r_{2a}} \right) \left(\frac{\partial \psi}{\partial r_{2b}} \right) \cos \theta_{2a,2b} \\ + 2 \left(\frac{\partial \psi}{\partial r_{2a}} \right) \left(\frac{\partial \psi}{\partial r_{2c}} \right) \cos \theta_{2a,2c} + 2 \left(\frac{\partial \psi}{\partial r_{2b}} \right) \left(\frac{\partial \psi}{\partial r_{2c}} \right) \cos \theta_{2b,2c}$$

3-29

$$(\nabla_3 \psi)^2 = \left(\frac{\partial \psi}{\partial r_{3a}} \right)^2 + \left(\frac{\partial \psi}{\partial r_{3b}} \right)^2 + \left(\frac{\partial \psi}{\partial r_{3c}} \right)^2 + 2 \left(\frac{\partial \psi}{\partial r_{3a}} \right) \left(\frac{\partial \psi}{\partial r_{3b}} \right) \cos \theta_{3a,3b} \\ + 2 \left(\frac{\partial \psi}{\partial r_{3a}} \right) \left(\frac{\partial \psi}{\partial r_{3c}} \right) \cos \theta_{3a,3c} + 2 \left(\frac{\partial \psi}{\partial r_{3b}} \right) \left(\frac{\partial \psi}{\partial r_{3c}} \right) \cos \theta_{3b,3c}$$

Since ψ is either symmetric or antisymmetric, we

can write

$$\int (\nabla_2 \psi)^2 d\tau_1 d\tau_2 d\tau_3 = \int (\nabla_3 \psi)^2 d\tau_1 d\tau_2 d\tau_3$$

Therefore

$$(\psi, T\psi) = \frac{\hbar^2}{2m} \int \{ (\nabla_1 \psi)^2 + 2 (\nabla_2 \psi)^2 \} d\tau_1 d\tau_2 d\tau_3$$

3-30

The explicit form of $(\psi, T\psi)$ is given in Appendix IV.

The only quantity remaining to be evaluated is the integral of the square of the wave function.

We can write, since ψ is real,

$$(\psi, \psi) = \int (\psi_1 + \psi_2 \pm \psi_3 \mp \psi_4)^2 d\tau \quad 3-31$$

Due to the symmetry of the wave function with respect to the two electrons, this can be simplified to

$$(\psi, \psi) = 4 \left\{ \int \psi_1^2 d\tau + \int \psi_1 \psi_2 d\tau \pm \int \psi_1 \psi_3 d\tau \pm \int \psi_1 \psi_4 d\tau \right\} \quad 3-32$$

Each of these four integrals also appears in the evaluation of

$\int (\nabla \psi)^2 d\tau$. Explicit expressions for them will therefore be found in Appendix IV.

The explicit value of the average energy for this trial wave function was programmed for the Bendix G-15D digital computer at the University of Manitoba, and values of the average energy, as a function of the four parameters were obtained. This was done for both the symmetric and antisymmetric functions. The results were as follows.

For both the symmetric and antisymmetric functions, the minimum value of the average energy was found to be at the values of the parameters corresponding to the separated systems. These values are

$$\begin{aligned}\alpha &= 1.238 a_0^{-1} \\ \gamma &= .500 a_0^{-1} \\ \delta &= 0 \\ R &= 2.00 a_0\end{aligned}$$

The values of $\langle E \rangle$ for the symmetric and antisymmetric functions are equal when $\delta = 0$.

This is to be expected, since the effect of the exchange terms becomes negligible. For $\delta \neq 0$, it was found that the energy for the symmetric function is lower than that for the antisymmetric function for the same values of the parameters.

Some of the results of the computations are illustrated in figures 5 to 9. These illustrations give contours of constant energy as two of the four parameters are varied. The illustrations shown vary γ and δ for the value of $\alpha = 1.23890^{-1}$ and two values of R ; $2.00a_0$ (the value giving the minimum energy) and $1.51 a_0$, and α and δ are varied for $R = 2.00a_0$ and $\gamma = .550a_0^{-1}$.

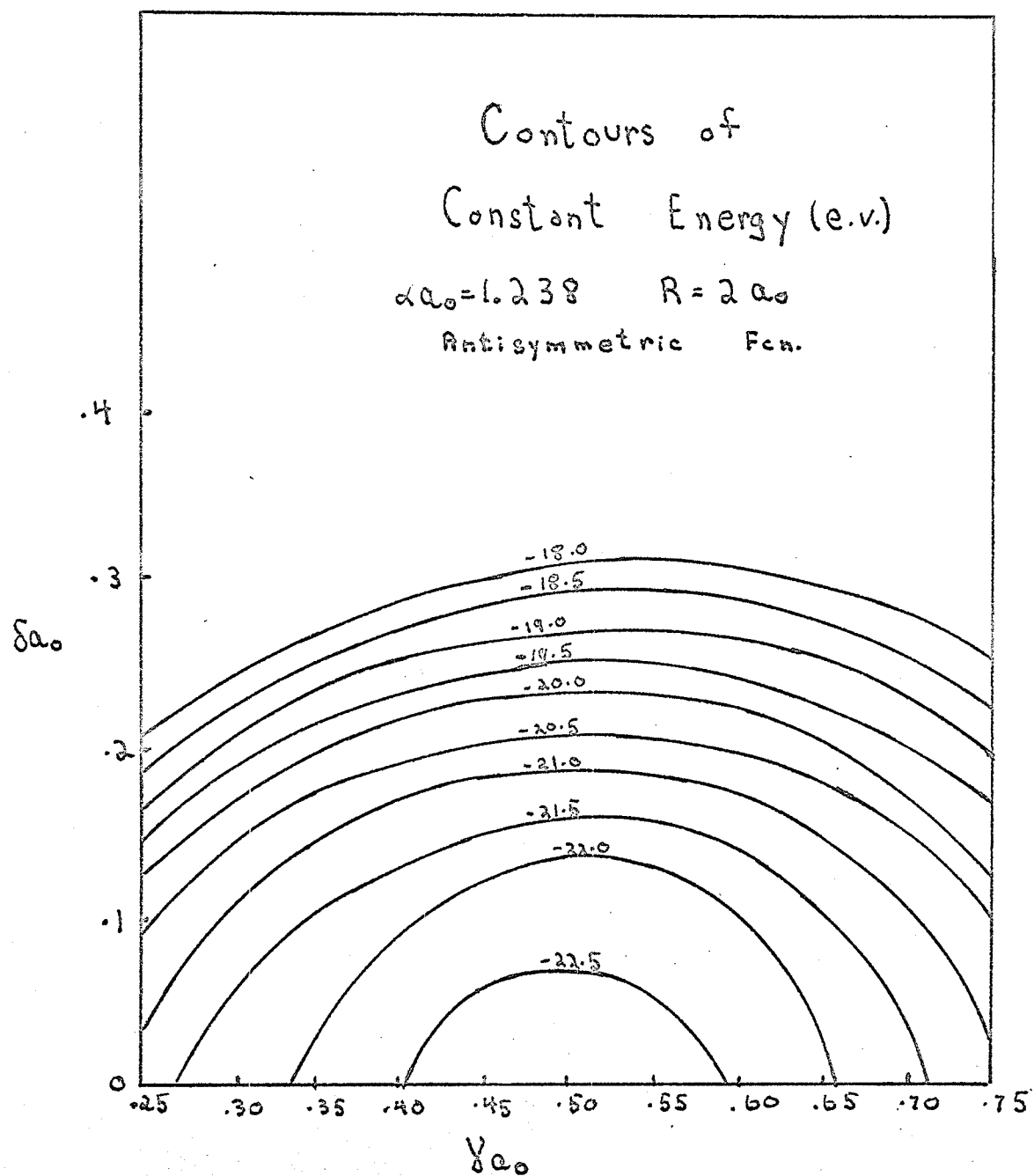


Fig. 5

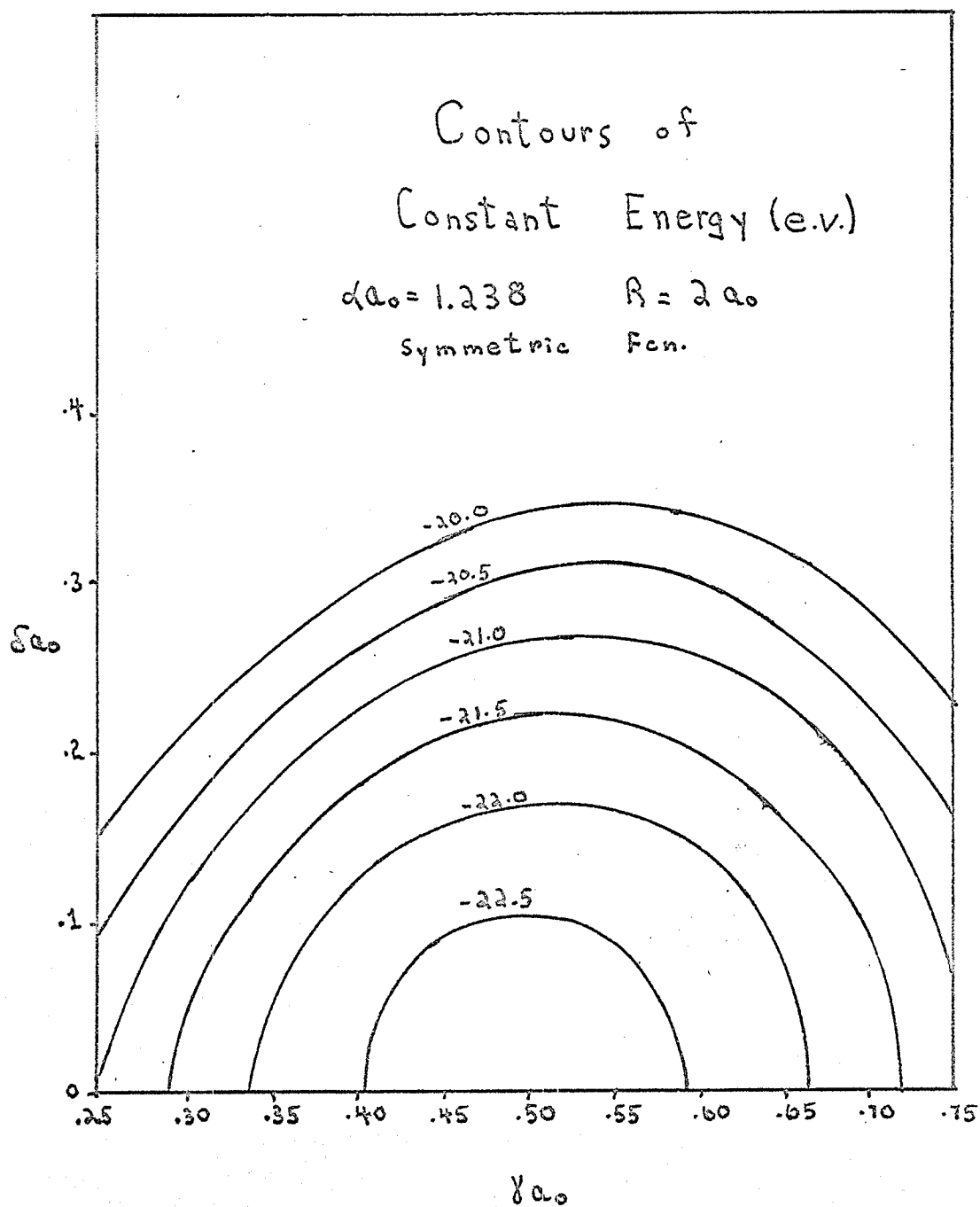


Fig. 6

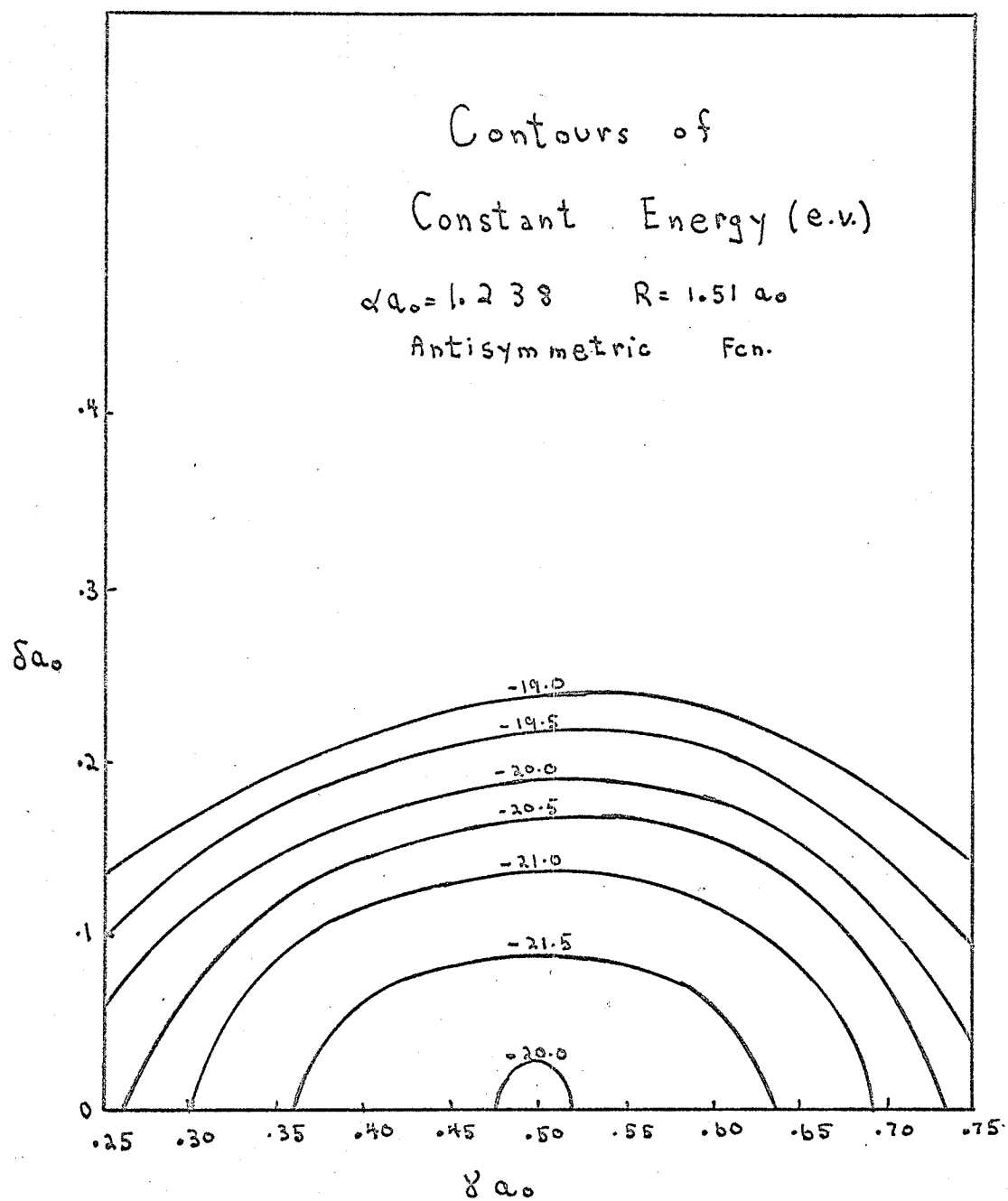


Fig. 7

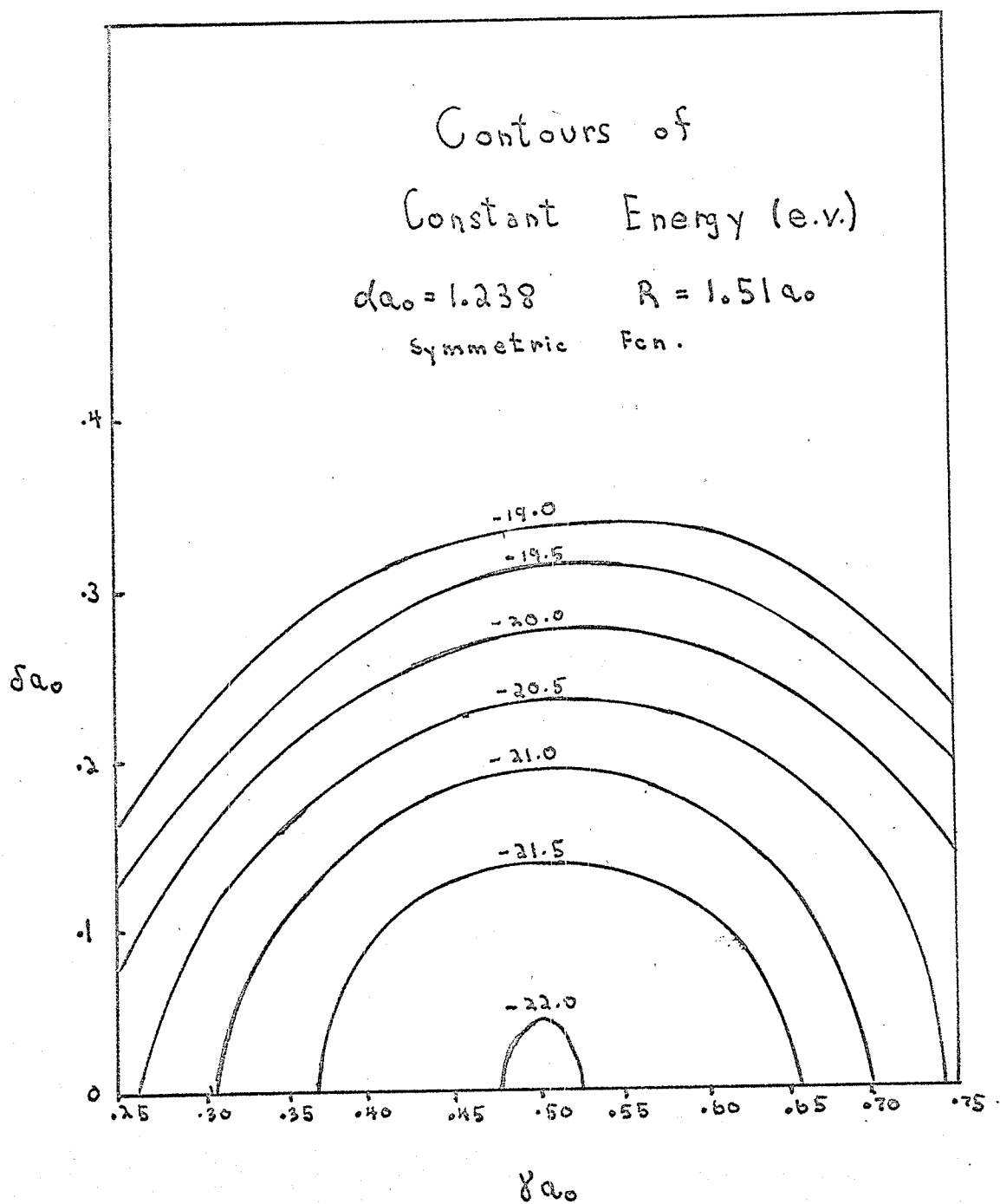


Fig. 8

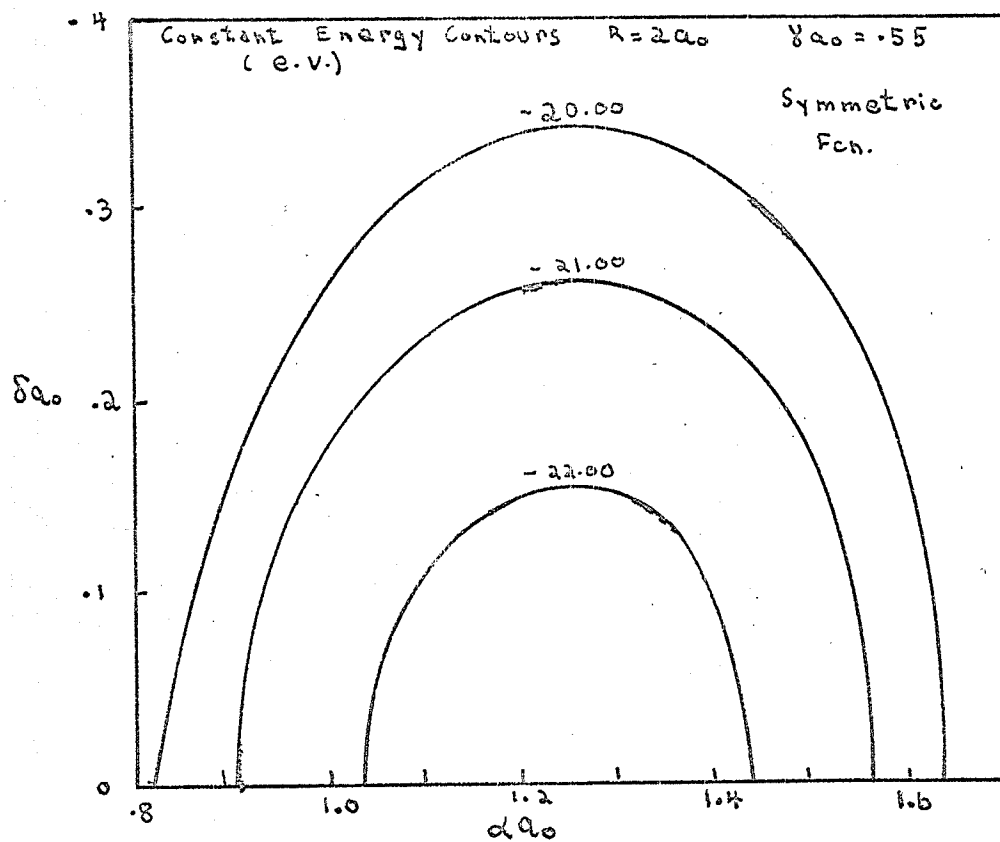


Fig. 9a

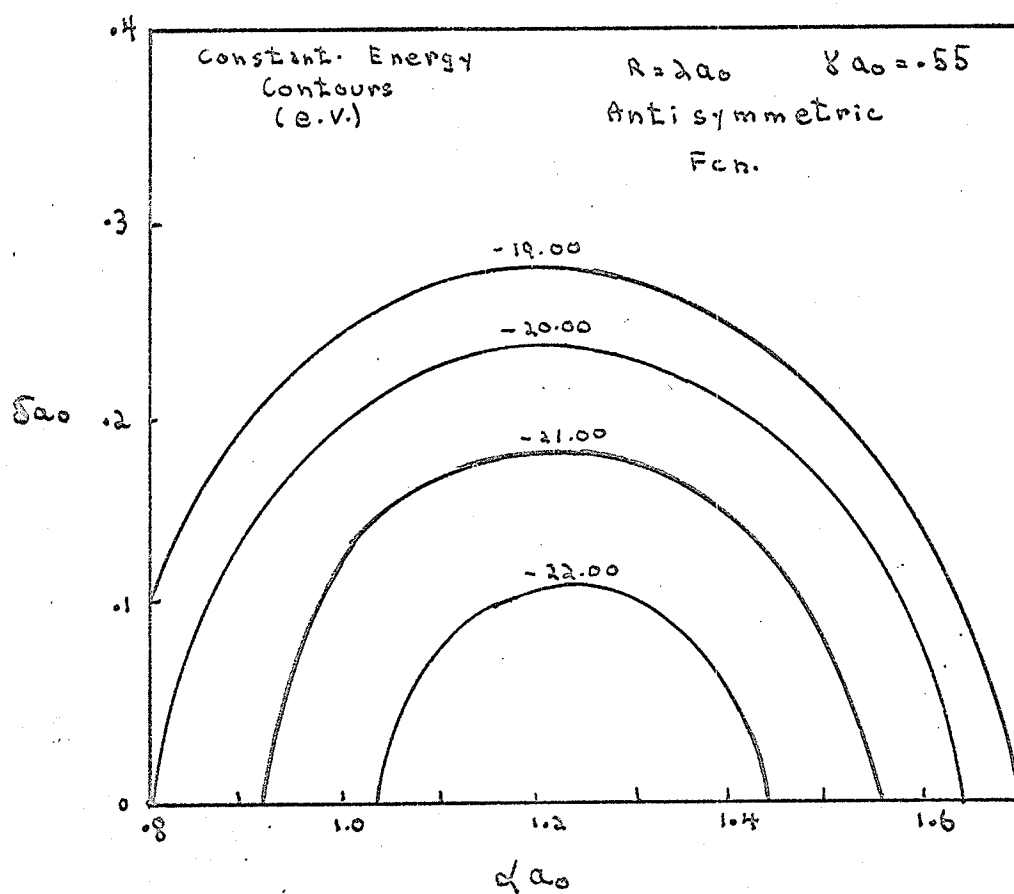


Fig. 9b

CHAPTER IV

THE CONFIGURATION OF A HYDROGEN MOLECULE AND A POSITRON

The previous chapter considered the interaction of two protons, two electrons and a positron from the viewpoint of a configuration of a positronium atom bound to a hydrogen molecular ion. In this chapter we shall consider the interaction of the same five particles from the point of view of a positron moving in the field arising from interaction with a hydrogen molecule. This is accomplished by applying the variational method to a wave function which is a product of two wave functions - one which depends only on the coordinates of the constituents of the hydrogen molecule, and the other which is a function of the positron coordinates only. Since we regard the two protons as fixed, this type of function can be written

$$\psi = \phi(\underline{r}_1) \chi(\underline{r}_2, \underline{r}_3) \quad 4-1$$

where $\chi(\underline{r}_2, \underline{r}_3)$ is a function which describes the electron distribution.

The Hamiltonian can be written

$$H = T + V \quad 4-2$$

where

$$T = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2)$$

$$V = e^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} - \frac{1}{r_{3a}} - \frac{1}{r_{3b}} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}} \right) \quad 4-3$$

Then

$$(\psi, T\psi) = -\frac{\hbar^2}{2m} \left\{ \int |\chi|^2 d\tau_2 d\tau_3 \int \phi^* \nabla_1^2 \phi d\tau_1 + \int |\phi|^2 d\tau_1 \int \chi^* (\nabla_2^2 + \nabla_3^2) \chi d\tau_2 d\tau_3 \right\} \quad 4-4$$

and

$$\begin{aligned} (\psi, V\psi) &= e^2 \int |\phi|^2 d\tau_1 \int |\chi|^2 \left(\frac{1}{R} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} - \frac{1}{r_{3a}} - \frac{1}{r_{3b}} + \frac{1}{r_{23}} \right) d\tau_2 d\tau_3 \\ &+ e^2 \int |\chi|^2 d\tau_2 d\tau_3 \int |\phi|^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} \right) d\tau_1 + e^2 \int |\phi|^2 \left\{ \int |\chi|^2 \left(-\frac{1}{r_{12}} - \frac{1}{r_{13}} \right) d\tau_2 d\tau_3 \right\} d\tau_1 \end{aligned} \quad 4-5$$

while

$$(\psi, \psi) = \int |\phi|^2 d\tau_1 \int |\chi|^2 d\tau_2 d\tau_3 \quad 4-6$$

We denote

$$\langle E \rangle = \frac{-\frac{\hbar^2}{2m} \int \chi^* (\nabla_2^2 + \nabla_3^2) \chi d\tau_2 d\tau_3 + e^2 \int |\chi|^2 \left(\frac{1}{R} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} - \frac{1}{r_{3a}} - \frac{1}{r_{3b}} + \frac{1}{r_{23}} \right) d\tau_2 d\tau_3}{\int |\chi|^2 d\tau_2 d\tau_3}$$

Then the average value of the energy can be written

$$\begin{aligned} \langle E \rangle &= \frac{(\psi, H\psi)}{(\psi, \psi)} = \frac{1}{\int |\phi|^2 d\tau_1} \left\{ -\frac{\hbar^2}{2m} \int \phi^* \nabla_1^2 \phi d\tau_1 \right. \\ &+ e^2 \int |\phi|^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} \right) d\tau_1 \\ &+ \frac{e^2}{\int |\chi|^2 d\tau_2 d\tau_3} \int |\phi|^2 \left[\int |\chi|^2 \left(-\frac{1}{r_{12}} - \frac{1}{r_{13}} \right) d\tau_2 d\tau_3 \right] d\tau_1 \left. \right\} + \langle E \rangle \end{aligned} \quad 4-7$$

This could be regarded as the average value of energy for one-particle Hamiltonian, $H^{(1)}$

$$\langle E \rangle = \frac{(\phi, H^{(1)} \phi)}{(\phi, \phi)}$$

where $H^{(1)}$ is given

by $H^{(1)} =$

$$-\frac{\hbar^2}{2m} \nabla_1^2 + e^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} + \frac{1}{(r_1, r)} \right) \int |\chi|^2 \left(\frac{-1}{r_{1a}} - \frac{1}{r_{1b}} \right) d\tau_2 d\tau_3 + \langle E_\alpha \rangle \quad 4-8$$

We can interpret $H^{(1)}$ as being the one-particle operator whose average value is the average energy of the system. $\langle E_\alpha \rangle$ is the energy of the two protons and two electrons when they are in the state χ . The function $\chi(r_2, r_3)$ will therefore be a function describing the ground state of the hydrogen molecule. The remainder of $\frac{(\phi, H^{(1)} \phi)}{(\phi, \phi)}$ will be the average energy of the system due to the presence of the positron. This energy consists of the kinetic energy of the positron and the potential energy arising from Coulomb interactions between the positron and the other constituents. We shall denote this remainder as

$$H^{(2)} = H^{(1)} - \langle E_\chi \rangle = -\frac{\hbar^2}{2m} \nabla^2 + e^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} + \frac{1}{(r_1, \chi)} \int |\chi|^2 \left(\frac{-1}{r_{12}} - \frac{1}{r_{13}} \right) d\tau_2 d\tau_3 \right) \quad 4-9$$

The assumption of a state function of the form $\psi = \phi(r_1) \chi(r_2, r_3)$ in a calculation of the expectation value of H is equivalent to assuming a state function $\phi(r_1)$ for a Hamiltonian given by $H^{(1)}$. If it can be shown that $H^{(1)}$ has no eigenvalues less than $\langle E_\chi \rangle$ or equivalently, $H^{(2)}$ has no negative eigenvalues, for a given function χ , then it can be concluded that the positron will not be bound to the hydrogen molecule if the latter is assumed to be in the state χ . In other words, showing that $H^{(2)}$ has no negative eigenvalues for a given function χ is equivalent to showing that the original assumption of a function of the form

$\psi = \phi(r_1) \chi(r_2, r_3)$ in the calculation of the average value of the total Hamiltonian H leads to no bound states for the positron, regardless of the choice of $\phi(r_1)$, for this choice of $\chi(r_2, r_3)$.

We now proceed to choose the function $\chi(r_2, r_3)$ and calculate the potential for the positron.

There have been many suggested wave functions for the ground state of the hydrogen molecule.¹ The choice of function for use here is limited to some extent, however, by the presence of integrals of the form $\int |\chi|^2 \frac{1}{r_{12}} d\tau_2 d\tau_3$. Since the two protons are regarded as fixed, and since, in these integrals, the position of the positron is also fixed, we have integrations involving three non-collinear fixed points.

In order to make the potential energy calculations feasible a not-too-complicated form for χ must be chosen.

1. A bibliography of hydrogen molecule calculations is given by McLean, Weiss, and Yoshimine, Rev. Mod. Phys., 32, 211, (1960).

The form of χ which we shall choose is

$$\chi = c \left(e^{\frac{-\alpha(r_{2a} + r_{3b})}{r_{12}}} + e^{\frac{-\alpha(r_{3a} + r_{2b})}{r_{12}}} \right) + \left(e^{\frac{-\alpha(r_{1a} + r_{3b})}{r_{12}}} + e^{\frac{-\alpha(r_{2b} + r_{3a})}{r_{12}}} \right) \quad 4-10$$

This was first discussed by Weinbaum,² who found the best values of the parameters were $R=1.40a_0$, $\alpha = 1.193/a_0$, $C=3.9$. The value of the binding energy of the hydrogen molecule against dissociation into two hydrogen atoms, as calculated by using this function, is 4.024 e.v., while the experimental value is 4.746 e.v. The equilibrium internuclear distance has an experimental value of 1.4008 a_0 .

We now proceed to calculate the Hamiltonian $H^{(2)}$, which can be considered as the operator describing the energy of the system due to the presence of the positron.

Since the function $\chi(r_1, r_2)$ is symmetric in the positions of the two electrons, we can write

$$H^{(2)} = \frac{-\hbar^2}{2m} \nabla_1^2 + e^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{2}{(r_1, r_2)} \int \frac{\chi^2}{r_{12}} d\tau_2 d\tau_3 \right) \quad 4-11$$

The explicit calculation of the integrals arising in equation 4-11 is given in Appendix VI. Only one particular point need be discussed at present.

In the calculation of $\int \chi^2 / r_{12} d\tau_2 d\tau_3$, integrals of the form $\int \frac{e^{\frac{-\alpha(r_{2a} + r_{3b})}{r_{12}}}}{r_{12}} d\tau_2$ arise. These are integrals which, in general, are functions of three non-collinear points defined by the positions of the two protons and the positron. This integral can be evaluated, however, by noting that evaluating this integral

$$I = \int \frac{e^{\frac{-\alpha(r_{2a} + r_{3b})}{r_{12}}}}{r_{12}} d\tau_2$$

2. S. Weinbaum, J. Chem. Phys. 1, 593, (1933).

is equivalent to solving the Poisson equation

$$\nabla^2 \mathcal{I} = -4\pi e^{-\alpha(r_a + r_b)}$$

This is simplified further by changing to the (ξ, η, ϕ) coordinate system discussed in Appendix I, in which this equation becomes

$$\nabla^2 \mathcal{I} = -4\pi e^{-\alpha R \xi}$$

4-12

The solution of this equation is discussed in Appendix V.

Numerical calculations of the potential show that the potential has two peaks at the positions of the nuclei. The potential is independent of the angle of rotation about the internuclear axis. A calculation of the potential along a curve $\xi = \text{constant}$, that is, along an ellipse with foci at the positions of the protons, indicate that the potential is a minimum at the point $\eta=0$. The locus of these points is the right bisector of the internuclear axis. A cross section of the potential, taken along the right bisection of the internuclear axis, indicates a potential barrier at the axis. This barrier has a height of 24.891 e.v. The potential decreases along the bisector until there is a shallow well, of depth .079 e.v. at a distance of $1.6\text{\AA}^0$ from the axis. Then it begins to increase asymptotically towards zero, approaching a form of $-A/\eta^3$, where η is the distance along the bisector from the internuclear axis.

We now proceed to show that there are no bound states for the positron for this potential function. We can accomplish this by showing that $H^{(2)}$ has no negative eigenvalues.

Let us consider bound energy states for the one-particle Schrodinger equations corresponding to two potentials $V_1(\eta)$ and $V_2(\eta)$, where $V_1(\eta) \leq V_2(\eta)$. Specifically we show

that, if $V_2(r)$ has a bound state with energy E_2 , then there exists a bound energy state for V_1 with the energy less than or equal to that of E_2 .

The proof is quite simple. Let $\bar{\Psi}(r)$ be the wave function which is an eigenfunction of the Hamiltonian with $V_2(r)$, belonging to the eigenvalue E_2 . Then

$$-\frac{\hbar^2}{2m} \nabla^2 \bar{\Psi} + V_2(r) \bar{\Psi} = E_2 \bar{\Psi} \quad 4-13$$

We assume, for simplicity, that $\bar{\Psi}$ is normalized.

Let us now apply the variational method to the Hamiltonian with $V_1(r)$, using $\bar{\Psi}$ as our trial function. The average value of the energy is

$$\begin{aligned} \langle E \rangle &= (\bar{\Psi}, H \bar{\Psi}) = (\bar{\Psi}, \{-\frac{\hbar^2}{2m} \nabla^2 + V_1\} \bar{\Psi}) \\ &= (\bar{\Psi}, \{-\frac{\hbar^2}{2m} \nabla^2 + V_2\} \bar{\Psi}) + (\bar{\Psi}, \{V_1 - V_2\} \bar{\Psi}) \end{aligned} \quad 4-14$$

or $\langle E \rangle = E_2 + (\bar{\Psi}, \{V_1 - V_2\} \bar{\Psi})$

Since $V_1(r) \leq V_2(r)$ and since $\bar{\Psi}^* \bar{\Psi} \geq 0$ we have that $(\bar{\Psi}, [V_1 - V_2] \bar{\Psi}) \leq 0$.

Therefore $\langle E \rangle \leq E_2$

Since the average energy for any trial function is an upper bound to the ground state energy, which we shall denote by E_1 , it follows that

$$E_1 \leq \langle E \rangle \leq E_2 \quad 4-15$$

This is what we had set out to show.

Our next step will be to replace the actual potential in the Hamiltonian $H^{(2)}$ by one which is of lesser value at every point. We shall then investigate to find whether or not this lesser potential

gives rise to any bound states. If it does not, then the greater potential gives rise to no bound states also. If there is a bound state for the lesser potential, there is, of course, nothing which can be said with certainty about the bound states for the greater one.

The lesser potential we shall employ is spherically symmetric in a spherical polar coordinate system which has its origin at the midpoint of the internuclear axis, and has its polar axis along the internuclear axis. We then define our potential $V_1(r)$ to be equal to the value of the actual potential V_2 at a distance along the right bisector of the internuclear axis. If we denote the internuclear axis as the line defined by $\theta = 0$, then

$$V_1(r, \theta, \phi) = V_2(r, \pi/2, \phi) = V_2(r, \pi/2, 0)$$

4-16

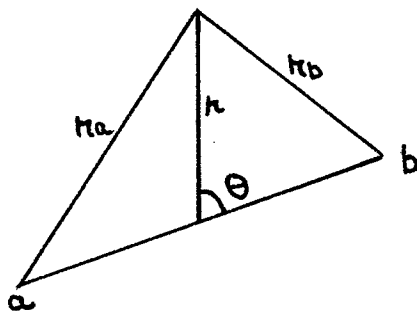


Figure 10.

Configuration In a Spherical Polar Coordinate System

Since V_2 is independent of ϕ , V_1 is also independent of ϕ .

We now study the ground state energy eigenfunction for the potential V_1 . This ground state eigenfunction will itself be spherically symmetric, and therefore be a function of r only.

The Schrodinger equation then becomes

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\bar{\Psi}}{dr} \right) + V_1(r) \bar{\Psi}(r) = E \bar{\Psi}(r) \quad 4-17$$

If we write $\bar{\Psi}(r) = \frac{1}{r} u(r)$, then we have

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) + V_1(r) u(r) = E u(r) \quad 4-18$$

This is a one-dimensional Schrodinger equation with the same eigenvalue (E) as the three-dimensional one.

We now consider the properties of the solution of this equation as a function of E .

We require that the function $\bar{\Psi}(r)$ be finite everywhere, which, in turn, implies $u(r) \rightarrow 0$ as $r \rightarrow 0$. This is to be true for every value of E .

If E is less than the least eigenvalue E_0 , the function will not cross the axis, and will approach a non-zero value as $r \rightarrow \infty$. This is illustrated in figure 11.

If E is equal to the least eigenvalue E_0 the function will, as before, not cross the axis but will approach zero asymptotically as $r \rightarrow \infty$. This is illustrated in figure 12.

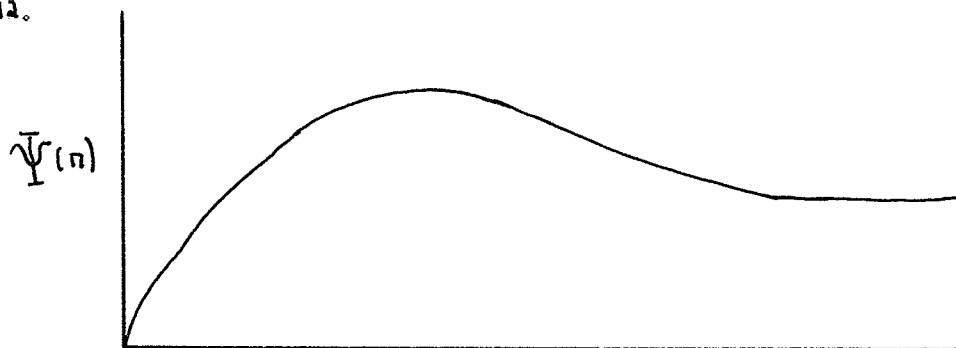


Figure 11.

$$E < E_0$$

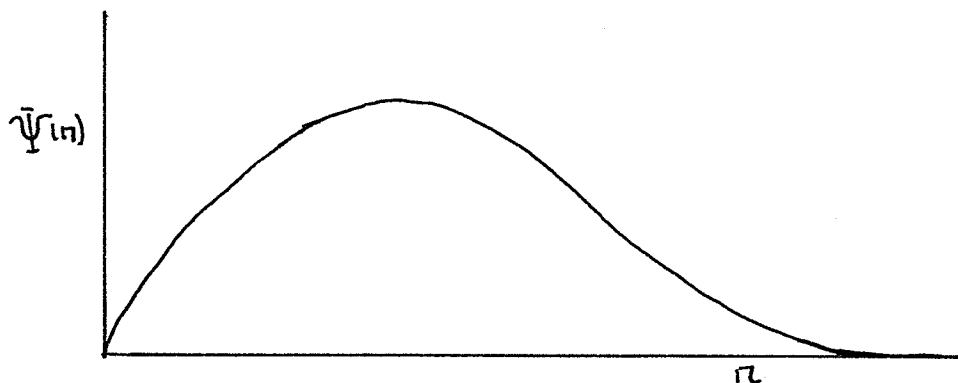


Figure 12
E=E₀

We now attempt to show that this potential, $V_1(r)$, gives rise to no bound states.

Let us initially consider this potential for large values of r , ($r \gg R$). This potential can be written

$$V_1(r) = e^2 \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{2}{(r, r)} \int \frac{\chi^2 d\tau_2 d\tau_3}{r_{12}} \right)_{r_{1a} = r_{1b}}$$

where r is the distance from the origin to the positron when the latter is on the right bisector of the internuclear axis. If we considered $\frac{1}{r_{1a}}$ and $\frac{1}{r_{1b}}$ expanded in powers of $\frac{1}{r}$ (multipole expansions), the following results could easily be obtained. First, the net charge that the positron "sees", when $r \gg R$, is zero. Therefore the monopole term in the expansion of V_2 does not appear. The contribution to the dipole terms from $\frac{1}{r_{1a}}$ and $\frac{1}{r_{1b}}$ is easily seen to be zero from the fact that, along the right bisector of the internuclear axis, the line joining the midpoint of the axis to one of the protons (this line is the internuclear axis) is normal to the line joining the midpoint to the positron position (on the right bisector). We can also easily see that the dipole term arising from $\int \frac{\chi^2 d\tau_2 d\tau_3}{r_{12}}$ is zero in the following manner.

Define a spherical polar coordinate system with origin at the midpoint of the internuclear axis, and polar axis passing through the positron position (along the right bisector of the internuclear axis). Then, in the integration over the azimuthal angle Θ , $\int \chi^2(r_2, r_3) d\tau_3$ is symmetric about $\Theta_2 = \pi/2$, and the coefficient of $\frac{1}{r_2}$ in the expansion of $\frac{1}{r_{12}}$ will be proportional to $\cos \Theta$. The coefficient of $\frac{1}{r_2}$ in $\int \frac{\chi^2(r_2, r_3)}{r_{12}} d\tau_3 d\tau_2$ will then be of the form

$$\int_0^\pi (\text{symmetric function}) \sin \Theta \cos \Theta d\Theta$$

This will give a value of zero when the integration is performed.

Therefore the leading term in the potential, for $r \gg R$ is at least a quadrupole term. Numerical calculations verify this, for the value of

$$\lim_{r \rightarrow \infty} r^3 V_1 = -.599 \text{ e.v. } -A^0^3$$

Defining $2m/\hbar^2 = K$, we can write the one-dimensional Schrodinger equation, for large values of r , as

$$-\frac{1}{K} \frac{d^2 u}{dr^2} - \frac{A}{r^3} u = E u$$

We set $KA = \alpha_0$, and note that

$$-\frac{\alpha_0}{r^3} \geq -\frac{2\alpha_0}{r^3} + \frac{\alpha_0^2}{r^4} \quad \text{for } r \geq \alpha_0 \geq 0. \quad 4-19$$

The reason for introducing a potential of the form

$$\frac{1}{K} \left(-\frac{2\alpha_0}{r^3} + \frac{\alpha_0^2}{r^4} \right), \text{ as we shall soon see, is that the}$$

solution of the Schrodinger equation for this potential can be easily expressed.

It was noted from the numerical calculations that V_1 approaches this limit $-A/r^3$ from above. If we define r_0 as the value for which $r^3 V_1$ is within 2% of its limiting value, r_0 can be calculated numerically. Such a calculation indicates that $r_0 \approx 6.4 A^0$. On the other hand, α_0 has a value of $.157A^0$.

We now define a potential $V_3(r)$ in such a manner that $V_3(r) \leq V_1(r)$ at every value of r . Then showing that $V_3(r)$ has no bound states will show that $V_1(r)$ has no bound states also.

We define $V_3(r)$ by the relations

$$V_3(r) = V_1(r) \quad , \quad 0 \leq r < r_0$$

$$V_3(r) = \frac{1}{K} \left(-\frac{2\alpha_0}{r^3} + \frac{\alpha_0^2}{r^4} \right) \quad , \quad r_0 \leq r \leq \infty \quad 4-20$$

Consider the solution of the one-dimensional Schrodinger equation for V_3 ,

$$-\frac{1}{K^2} \frac{d^2 w}{dr^2} + V_3(r) w = 0 \quad 4-21$$

for zero energy.

For $r > r_0$, the solution of this equation is

$$w = e^{-\alpha_0/r} \left(B + C_0 \int_{r_0}^r e^{+\alpha_0/\eta} d\eta \right) \quad 4-22$$

We shall assume, for the moment, that w does not cross the axis in the range $0 \leq r < r_0$. This can be verified by numerical calculation.

Since we further require w and $\frac{dw}{dr}$ to be continuous at $r = r_0$, we have $B > 0$. In order that V_3 show no bound states at all, we would then have to show $C_0 \geq 0$

From the relations

$$w(r_0) = B e^{-\alpha_0/r_0}$$

$$\left(\frac{dw}{dr}\right)_{r=r_0} = \frac{\alpha_0}{r_0^2} w(r_0) + C_0 e^{\alpha_0/r_0}$$

we find

$$C_0 = e^{-\alpha_0/r_0} \left[\left(\frac{dw}{dr}\right)_{r_0} - \frac{\alpha_0}{r_0^2} w(r_0) \right]$$

4-23

The condition $C_0 \geq 0$ becomes

$$\left(\frac{r^2}{w} \frac{dw}{dr}\right)_{r=r_0} \geq \alpha_0$$

4-24

In order to verify that this is so, equation 4-20 must be solved for the region $0 \leq r < r_0$.

As we saw previously, $u(r)$, and therefore $w(r)$, must be zero at $r=0$. In order to numerically integrate equation 4-20 in the region $0 \leq r < r_0$ one other point near $r=0$ is required. This is found by noticing that $\frac{dV_3}{dr} = 0$ at $r=0$. We can then approximate $V_3(r)$ near the origin, by

$$V_3(r) = F - Gr^2 + \dots$$

4-25

Substituting a series expansion of $u(r)$, valid near $r=0$, into equation 4-20 enables us to obtain the first few coefficients of powers of r in the expansion of u in terms of F and G , which can, in turn, be found from the explicit values of $V_3(r)$ at $r=0$ and one neighbouring point.

This procedure was carried out, and the numerical integration performed on the Bendix G-15D digital computer at the University of Manitoba. The result was that

$$\left(\frac{r^2}{\omega} \frac{d\omega}{dr} \right)_{r=6.4A^0} = 6.3800 A^0,$$

while $\alpha_0 = .157A^0$.

This means that $E=0$ is lower than the least eigenvalue for the Hamiltonian with V_3 as a potential. There are no bound states for V_3 and therefore no bound states are indicated for the hydrogen molecule-positron configuration when the molecule is in the state defined by $\chi(r_2, r_3)$.

CHAPTER V

CONCLUSIONS

We have considered the interaction of two protons, two electrons and a positron from two points of view.

The first investigation, a variational calculation of the average energy for a configuration which represented a positronium atom bound to a hydrogen molecular ion did not indicate any binding. Since the variational method gives only an upper limit to the actual energy of the system, however, we are unable to conclude definitely whether or not a positronium atom will attach itself to a hydrogen molecular ion.

It is not unlikely that a better choice of wave function for variation could indicate a binding between the two systems. Such a wave function should describe the H_2^+ ion better from the viewpoint of concentrating the electron more in the region between the two nuclei. Also, mutual repulsion of the electrons, and the repulsion of the positron from the nuclei should be incorporated into the trial wave function. Such refinements would, however, greatly increase the complexity of the integrals to be evaluated.

The second investigation considered the Coulomb potential which a positron experiences in the region of a hydrogen molecule. This was accomplished by assuming that the molecule can be described by a function $\chi(\underline{r}_2, \underline{r}_3)$, where 2 and 3 denote the electrons, and the total wave function is of the form $\phi(\underline{r}_1) \chi(\underline{r}_2, \underline{r}_3)$ where the subscript 1 denotes the positron. A wave function of this type gives the electrostatic potential for the positron averaged over the positions of the electrons.

With the function $\chi(\underline{r}_2, \underline{r}_3)$ chosen, a potential well for the positron was found, but it was insufficiently deep to cause binding of the positron. However, the result of this investigation is also inconclusive, since we have been able to show only that the positron does not bind to the molecule in the manner suggested.

APPENDIX I

DERIVATION OF THE VOLUME ELEMENTS AND EVALUATION OF CERTAIN INTEGRALS.

We consider first the element of volume in the coordinate system (π_a, π_b, ϕ) . Let us define a spherical polar coordinate system with origin at a , and polar axis along the line ab .

This configuration is illustrated in figure A1-1

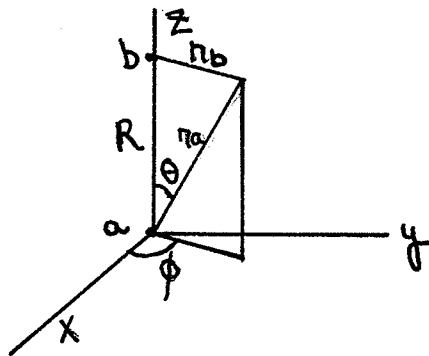


Fig. A1-1

The relations between the spherical polar and prolate spheroidal coordinate systems are

$$\begin{aligned} R &= \pi_a \\ \theta &= \cos^{-1} \left\{ \frac{R^2 + \pi_a^2 - \pi_b^2}{2 R \pi_a} \right\} \end{aligned}$$

$$\phi = \phi$$

If we imagine a cartesian coordinate system (x, y, z) as illustrated in figure A1-1 as well, then the volume element is

$$d\tau = dx dy dz = J \begin{pmatrix} x & y & z \\ \pi_a & \pi_b & \phi \end{pmatrix} d\pi_a d\pi_b d\phi \quad \text{A1-1}$$

where $J \begin{pmatrix} x & y & z \\ \pi_a & \pi_b & \phi \end{pmatrix}$ is the Jacobian of the transformation between the (x, y, z) coordinate system and the (π_a, π_b, ϕ) coordinate system.

Using the spherical polar coordinate system as an intermediate transformation gives

$$dV = J \begin{pmatrix} x & y & z \\ r & \theta & \phi \end{pmatrix} J \begin{pmatrix} r & \theta & \phi \\ r_a & r_b & \phi \end{pmatrix} dr d\theta d\phi \quad A1-2$$

where $J \begin{pmatrix} x & y & z \\ r & \theta & \phi \end{pmatrix} = r^2 \sin \theta$, and

$$J \begin{pmatrix} r & \theta & \phi \\ r_a & r_b & \phi \end{pmatrix} = \det \begin{pmatrix} 1 & 0 & 0 \\ \frac{\partial \theta}{\partial r_a} & \frac{\partial \theta}{\partial r_b} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad A1-3$$

$$= \frac{\partial \theta}{\partial r_b} = \frac{-1}{\sqrt{1-r^2}} \frac{\partial r}{\partial r_b}$$

where $\Gamma^2 = \frac{R^2 + r_a^2 - r_b^2}{2 R r_a}$ A1-4

Writing everything in terms of (r_a, r_b, ϕ) , gives

$$J \begin{pmatrix} x & y & z \\ r_a & r_b & \phi \end{pmatrix} = r_a^2 \sqrt{1-\Gamma^2} \begin{pmatrix} -1 \\ \frac{1}{\sqrt{1-\Gamma^2}} \\ \frac{-2r_b}{2Rr_a} \end{pmatrix}$$

$$= \frac{r_a r_b}{R}$$

Then $dV = \frac{r_a r_b}{R} dr_a dr_b d\phi$ A1-5

where

$$\begin{aligned} |r_a - R| &\leq r_b \leq R + r_a \\ 0 &\leq r_a < \infty \\ 0 &\leq \phi \leq 2\pi \end{aligned}$$

We also wish to obtain the volume element for the

(ξ, η, ϕ) coordinate system, where

$$\xi = \frac{r_a + r_b}{R}$$

$$\eta = \frac{r_a - r_b}{R}$$

$$\phi = \phi$$

A1-6

The volume element for this coordinate system is

$$dV = J \begin{pmatrix} x & y & z \\ r_a & r_b & \phi \end{pmatrix} J \begin{pmatrix} r_a & r_b & \phi \\ \xi & \eta & \phi \end{pmatrix} d\xi d\eta d\phi$$

$$= \frac{R}{4} (\xi^2 - \eta^2) J \begin{pmatrix} r_a & r_b & \phi \\ \xi & \eta & \phi \end{pmatrix} d\xi d\eta d\phi$$

$$\text{or } dV = \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\phi$$

A1-7

$$\begin{aligned} \text{where } & 1 \leq \xi \leq \infty \\ & -1 \leq \eta \leq 1 \\ & 0 \leq \phi \leq 2\pi \end{aligned}$$

A1-8

In the evaluation of the potential and kinetic energy terms, integrals of the type

$$f_{mn}(a, b, r) = \int_0^\infty \int_{|R-r_1|}^{R+r_1} e^{-a r_1 - b r_2} r_1^m r_2^n dr_2 dr_1$$

and

$$g_{mn}(a, b, r) = \int_0^{\infty} \int_{|r-r_1|}^{r+r_1} e^{-ar_1 - br_2} \frac{r_2^m}{r_1^m} dr_2 dr_1$$

often occur. The first type, for the case $a \neq b$, has been extensively tabulated by Darewych¹, and the particular integrals required for this problem are listed in the following pages.

For the case $a=b$, it is simpler to make the transformation to (ξ, η) coordinates, to obtain

$$f_{mn}(a, a, r) = \int_{-1}^{+1} \int_0^{\infty} e^{-ar\xi} \left[\frac{r}{2}(\xi + \eta) \right]^{m-1} \left[\frac{r}{2}(\xi - \eta) \right]^{n-1} \frac{r^4}{8} (\xi^2 - \eta^2) d\xi d\eta$$

These can also be integrated explicitly, and the ones required are listed in the following tables.

The integrals $g_{mn}(a, b, r)$ which arise cannot be evaluated in terms of well known functions, but are best expressed as convergent infinite series.

1. G. Darewych, Thesis, The Interaction of a Positron with a Negative Hydrogen Ion, University of Manitoba, 1961.

Table of Integrals Used:

I. $\underline{f_{mn}(a, b, n)}, \quad a \neq b$

$$f_{00}(a, b, n) = \frac{2}{(x)} \left(e^{-bn} - e^{-an} \right)$$

$$f_{10}(a, b, n) = \frac{4a}{(x)^2} e^{-bn} - \frac{2}{(x)} e^{-an} \left(-n - \frac{2a}{(x)} \right) \quad \text{where } (x) = a^2 - b^2$$

$$f_{11}(a, b, n) = \frac{2}{(x)} e^{-bn} \left(\frac{2an}{(x)} - \frac{8ab}{(x)^2} \right) + \frac{2}{(x)} e^{-an} \left(\frac{2bn}{(x)} + \frac{8ab}{(x)^2} \right)$$

$$f_{12}(a, b, n) = \frac{2}{(x)} e^{-bn} \left(\frac{2an^2}{(x)} - \frac{16abn^2}{(x)^2} + \frac{48ab^2}{(x)^3} + \frac{8a}{(x)^2} \right) +$$

$$\frac{2}{(x)} e^{-an} \left(-\frac{8b^2n}{(x)^2} - \frac{2n}{(x)} - \frac{4ab^2}{(x)^3} - \frac{8a}{(x)^2} \right)$$

$$f_{13}(a, b, n) = \frac{12}{(x)} e^{-bn} \left(-\frac{24ab}{(x)^3} - \frac{64ab^3}{(x)^4} + \frac{4an}{(x)^2} + \frac{24ab^2n}{(x)^3} - \frac{4abn^2}{(x)^2} + \frac{an^3}{3(x)} \right)$$

$$+ \frac{12}{(x)} e^{-an} \left(\frac{24ab}{(x)^3} + \frac{64ab^3}{(x)^4} + \frac{4bn}{(x)^2} + \frac{8b^3n}{(x)^3} \right)$$

$$f_{30}(a, b, n) = \frac{2}{(x)} e^{-bn} \left(\frac{48a^3}{(x)^3} - \frac{24a}{(x)^2} \right) +$$

$$\frac{2}{(x)} e^{-an} \left(-n^3 - \frac{6an^2}{(x)} - \frac{24a^2n}{(x)^2} + \frac{6n}{(x)} - \frac{48a^3}{(x)^3} + \frac{24a}{(x)^2} \right)$$

$$f_{20}(a, b, n) = \frac{2}{(x)} e^{-bn} \left(\frac{8a^2}{(x)^2} - \frac{2}{(x)} \right) + \frac{2}{(x)} e^{-an} \left(-\frac{n^2}{(x)} - \frac{4an}{(x)} - \frac{8a^2}{(x)^2} + \frac{2}{(x)} \right)$$

II $\underline{f_{mn}(a, a, n)}$

$$f_{00}(a, a, n) = \frac{n}{a} e^{-an}$$

$$f_{10}(a, a, n) = \frac{n}{2a^2} e^{-an} (1 + an)$$

$$f_{11}(a, a, n) = \frac{n}{2a^3} e^{-an} \left(\frac{a^2n^2}{3} + an + 1 \right)$$

III $\underline{f_{mn}(a, b, \pi)}$, $a \neq b, b \neq 0$

$$f_{10}(a, b, \pi) = \frac{e^{-b\pi}}{b} \left[\sum_{n=1}^{\infty} \frac{[-(a-b)\pi]^n}{n n!} - \sum_{n=1}^{\infty} \frac{[-(a+b)\pi]^n}{n n!} \right] \\ + \frac{M}{b} \left[-\gamma_0 - \ln(a+b)\pi - \sum_{n=1}^{\infty} \frac{[-(a+b)\pi]^n}{n n!} \right]$$

where $M = e^{b\pi} - e^{-b\pi}$, and γ_0 the Euler constant,
 $\gamma_0 = .5772157\dots$

$$f_{11}(a, b, \pi) = \frac{e^{-b\pi}}{b^2} (1+b\pi) \left[\sum_{n=1}^{\infty} \frac{[-(a-b)\pi]^n}{n n!} - \sum_{n=1}^{\infty} \frac{[-(a+b)\pi]^n}{n n!} \right] \\ - \frac{e^{-b\pi}}{b} \left[\frac{1 - e^{-(a-b)\pi}}{a-b} + \frac{1 - e^{-(a+b)\pi}}{a+b} \right] + \frac{M}{b} \frac{e^{-(a+b)\pi}}{(a+b)} \\ + \frac{1}{b^2} \left[e^{b\pi} (1-b\pi) - e^{-b\pi} (1+b\pi) \right] \left[-\gamma_0 - \ln(a+b)\pi - \sum_{n=1}^{\infty} \frac{[-(a+b)\pi]^n}{n n!} \right]$$

IV $\underline{f_{mn}(a, a, \pi)}$

$$f_{10}(a, a, \pi) = -\frac{e^{-a\pi}}{a} \sum_{n=1}^{\infty} \frac{(-2a\pi)^n}{n n!} + \frac{(e^{a\pi} - e^{-a\pi})}{a} \left[-\gamma_0 - \ln 2a\pi - \sum_{n=1}^{\infty} \frac{(-2a\pi)^n}{n n!} \right]$$

$$f_{11}(a, a, \pi) = -\frac{e^{-a\pi}}{a^2} (1+a\pi) \sum_{n=1}^{\infty} \frac{(-2a\pi)^n}{n n!} - \frac{\pi}{a} e^{-a\pi} \\ + \frac{1}{a^2} \left[e^{a\pi} (1-a\pi) - e^{-a\pi} (1+a\pi) \right] \left[-\gamma_0 - \ln(2a\pi) - \sum_{n=1}^{\infty} \frac{(-2a\pi)^n}{n n!} \right]$$

V $\underline{f_{mn}(a, 0, \pi)}$

$$f_{10}(a, 0, \pi) = \frac{2}{a} (1 - e^{-a\pi}) + 2\pi \left[-\gamma_0 - \ln a\pi - \sum_{n=1}^{\infty} \frac{(-a\pi)^n}{n n!} \right]$$

EVALUATION OF $(\Psi, V\Psi)$ FOR THE HYDROGEN MOLECULAR ION-POSITRONIUM CONFIGURATION

Due to the symmetries of the Hamiltonian and the wave function, the quantity $(\Psi, V\Psi)$ can be written as

$$\begin{aligned}
 (\Psi, V\Psi) = e^2 \bigg\{ & \frac{1}{R} (\Psi_1, \Psi) + 4 \left(\Psi_1, \frac{1}{r_{23}} \Psi_1 \right) + 4 \left(\Psi_1, \frac{1}{r_{23}} \Psi_2 \right) \pm 4 \left(\Psi_1, \frac{1}{r_{23}} \Psi_3 \right) \pm 4 \left(\Psi_1, \frac{1}{r_{23}} \Psi_4 \right) \\
 & + 4 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_1 \right) + 8 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_2 \right) \pm 4 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_3 \right) \pm 8 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_4 \right) + 4 \left(\Psi_1, \frac{1}{r_{1b}} \Psi_1 \right) \\
 & \pm 4 \left(\Psi_1, \frac{1}{r_{1b}} \Psi_3 \right) - 4 \left(\Psi_1, \frac{1}{r_{2a}} \Psi_1 \right) - 8 \left(\Psi_1, \frac{1}{r_{2a}} \Psi_2 \right) - 4 \left(\Psi_2, \frac{1}{r_{2a}} \Psi_2 \right) - 8 \left(\Psi_1, \frac{1}{r_{2a}} \Psi_3 \right) \\
 & \mp 8 \left(\Psi_1, \frac{1}{r_{2a}} \Psi_4 \right) \mp 8 \left(\Psi_2, \frac{1}{r_{2a}} \Psi_3 \right) - 4 \left(\Psi_3, \frac{1}{r_{2a}} \Psi_3 \right) \mp 8 \left(\Psi_1, \frac{1}{r_{2b}} \Psi_3 \right) \\
 & - 4 \left(\Psi_3, \frac{1}{r_{2b}} \Psi_3 \right) - 8 \left(\Psi_1, \frac{1}{r_{3b}} \Psi_2 \right) - 4 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_1 \right) - 4 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_2 \right) \\
 & \mp 8 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_3 \right) \mp 8 \left(\Psi_1, \frac{1}{r_{1a}} \Psi_4 \right) - 4 \left(\Psi_3, \frac{1}{r_{1a}} \Psi_4 \right) - 4 \left(\Psi_1, \frac{1}{r_{1b}} \Psi_1 \right) \bigg\}
 \end{aligned}$$

A2-1

where the quantities Ψ_i , $(i=1,2,3,4)$ are defined by equation 3-13, and in the expressions $\pm$ and $\mp$, the upper sign refers to the symmetric function, and the lower one to the antisymmetric.

The first term, $\frac{e^2}{R} (\Psi_1, \Psi)$, does not have to be evaluated explicitly, since we are seeking to evaluate $\langle E \rangle = \frac{(\Psi, H\Psi)}{(\Psi, \Psi)}$, and this term merely contributes e^2/R to the final result.

The other quantities contained in equation A2-1 are nine dimensional integrals. Using the functions tabled in Appendix I, they can be evaluated. The results are as follows:

$$(\psi_1, \frac{1}{\pi_{23}} \psi_1) = \frac{\pi^3}{\alpha^3} \left[\frac{1}{\gamma^3 \delta^2} - \frac{1}{\gamma^3 (\gamma + \delta)^2} - \frac{1}{\gamma^2 (\gamma + \delta)^3} \right]$$

$$(\psi_1, \frac{1}{\pi_{23}} \psi_2) = \frac{4\pi^3}{(\gamma^2 - \delta^2)^2} \left[\frac{\gamma}{4\delta^2} + \frac{\delta}{4\gamma^2} + \frac{\delta}{(\gamma^2 - \delta^2)} - \frac{\gamma}{(\gamma^2 - \delta^2)} \right] e^{-\alpha R} \left(\frac{R^2}{3\alpha} + \frac{R}{\alpha^2} + \frac{1}{\alpha^3} \right)$$

$$\begin{aligned} (\psi_1, \frac{1}{\pi_{23}} \psi_3) &= 16\pi^3 \left[\frac{1}{(\alpha + \gamma + \delta)^2} \left(\frac{16\alpha(\gamma + \delta)}{(\gamma)^4} - \frac{16\alpha}{3(\gamma)^3(\gamma + \delta)} + \frac{2\alpha}{(\gamma)^2(\gamma + \delta)^3} \right) \right. \\ &\quad + \frac{4}{(\alpha + \gamma + \delta)^3} \left(\frac{\alpha}{(\gamma)^2(\gamma + \delta)^2} - \frac{8\alpha}{3(\gamma)^3} \right) + \frac{4\alpha}{(\gamma)^2(\gamma + \delta)(\alpha + \gamma + \delta)^4} \\ &\quad + \frac{1}{\alpha^2} \left(-\frac{16\alpha(\gamma + \delta)}{(\gamma)^4} + \frac{16\alpha}{3(\gamma)^3(\gamma + \delta)} - \frac{2\alpha}{(\gamma)^2(\gamma + \delta)^3} \right) \\ &\quad \left. + \frac{1}{4\alpha^3} \left(\frac{4}{3(\gamma)^2(\gamma + \delta)} - \frac{8(\gamma + \delta)}{3(\gamma)^3} - \frac{1}{(\gamma)(\gamma + \delta)^3} \right) \right] \end{aligned}$$

$$\text{where } (y) = \alpha^2 - (\gamma + \delta)^2$$

$$\begin{aligned} (\psi_1, \frac{1}{\pi_{23}} \psi_4) &= \frac{8\pi^3}{R} \left[\left(\frac{16\alpha(\gamma + \delta)}{(\gamma)^4} - \frac{16\alpha}{3(\gamma)^3(\gamma + \delta)} + \frac{2\alpha}{(\gamma)^2(\gamma + \delta)^3} \right) f_{10}(\alpha, \gamma + \delta, R) \right. \\ &\quad \left. + \left(\frac{2\alpha}{(\gamma)^2(\gamma + \delta)^2} - \frac{16\alpha}{3(\gamma)^3} \right) f_{11}(\alpha, \gamma + \delta, R) + \frac{2\alpha}{3(\gamma)^2(\gamma + \delta)} f_{12}(\alpha, \gamma + \delta, R) \right] \\ &\quad + 4\pi^3 e^{-\alpha R} \left[\frac{1}{\alpha^2} (1 + \alpha R) \left(-\frac{16\alpha(\gamma + \delta)}{(\gamma)^4} + \frac{16\alpha}{3(\gamma)^3(\gamma + \delta)} - \frac{2\alpha}{(\gamma)^2(\gamma + \delta)^3} \right) \right. \\ &\quad \left. + \frac{1}{\alpha^3} \left(\frac{\alpha^2 R^2}{3} + \alpha R + 1 \right) \left(\frac{4}{3(\gamma)^2(\gamma + \delta)} - \frac{8(\gamma + \delta)}{3(\gamma)^3} - \frac{1}{(\gamma)(\gamma + \delta)^3} \right) \right] \end{aligned}$$

$$\text{where } (y) = \alpha^2 - (\gamma + \delta)^2$$

$$(\psi_1, \frac{1}{\pi_{12}} \psi_1) = \frac{8\pi^3}{\gamma^3} \left[\frac{\alpha}{8\delta^2(\alpha^2 - \delta^2)^2} - \frac{\alpha}{2(\alpha^2 - \delta^2)^3} + \frac{\delta}{8\alpha^2(\alpha^2 - \delta^2)^2} + \frac{\delta}{2(\alpha^2 - \delta^2)^3} \right]$$

$$(\psi_1, \frac{1}{\pi_{1a}} \psi_2) = \frac{4\pi^3}{y^3 R} \left[\frac{1}{2\delta^3} (f_{01}(d, d, R) - f_{01}(d+2\delta, d, R)) - \frac{1}{2\delta^2} f_{11}(d+2\delta, d, R) \right]$$

$$(\psi_1, \frac{1}{\pi_{1a}} \psi_3) = \frac{256\pi^3}{(y)^4} \left[-4 + \frac{d^2}{4(\delta+\delta)^2} + \frac{10d(\delta+\delta)}{(d+\delta+\delta)^2} + \frac{(\delta+\delta)^2}{4d^2} + \frac{16d^2(\delta+\delta)^2}{(y)^2} \log_e \left(\frac{(d+\delta+\delta)^2}{4d(\delta+\delta)} \right) \right] \quad \text{where } (y) = d^2 - (\delta+\delta)^2$$

$$\begin{aligned} (\psi_1, \frac{1}{\pi_{1a}} \psi_4) = & \frac{128\pi^3}{(y)^4 R} \left[\left\{ d^2 f_{10} - \frac{4d^2(\delta+\delta)}{(y)} (f_{00} + g_{11}) + \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{\delta+\delta, \delta+\delta, R} \right. \\ & + \left\{ d(\delta+\delta) f_{01} - \frac{4d(\delta+\delta)^2}{(y)} g_{11} + \frac{4d^2(\delta+\delta)}{(y)} f_{00} + \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{\delta+\delta, d, R} \\ & + \left\{ d(\delta+\delta) f_{01} - \frac{4d(\delta+\delta)^2}{(y)} f_{00} + \frac{4d^2(\delta+\delta)}{(y)} g_{11} - \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{d, \delta+\delta, R} \\ & \left. + \left\{ (\delta+\delta)^2 f_{10} + \frac{4d(\delta+\delta)^2}{(y)} (f_{00} + g_{11}) + \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{d, d, R} \right] \end{aligned}$$

where $(y) = d^2 - (\delta+\delta)^2$, and the notation $\left\{ \right\}_{a,b,R}$

means that the functions inside the bracket are evaluated for the argument (a, b, R) .

$$(\psi_1, \frac{1}{\pi_{1b}} \psi_1) = \frac{2\pi^3}{R\delta^3\delta^3} \left[f_{10}(2d, 0, R) - \delta f_{11}(2d, 2\delta, R) - f_{10}(2d, 2\delta, R) \right]$$

$$\begin{aligned} (\psi_1, \frac{1}{\pi_{1b}} \psi_3) = & \frac{128\pi^3}{(y)^4 R} \left[\left\{ d^2 f_{10} - \frac{8d^2(\delta+\delta)}{(y)} f_{00} + \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{2d, \delta+\delta, 0, R} \right. \\ & + 2 \left\{ d(\delta+\delta) f_{10} + \frac{4d(\delta+\delta)(d-\delta-\delta)}{(y)} f_{00} - \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{d+\delta+\delta, 0, R} \\ & \left. + \left\{ (\delta+\delta)^2 f_{10} + \frac{8d(\delta+\delta)^2}{(y)} f_{00} + \frac{16d^2(\delta+\delta)^2}{(y)^2} g_{10} \right\}_{2d, 0, R} \right] \end{aligned}$$

$$(\psi_1, \frac{1}{\pi_{2a}} \psi_1) = \frac{\pi^3}{d^2 y^3 \delta^3}$$

53.

$$(\psi_1, \frac{1}{\pi_{2a}} \psi_2) = \frac{2\pi^3}{y^3 \delta^3 R} f_{10}(d, d, R)$$

$$(\psi_2, \frac{1}{\pi_{2a}} \psi_2) = \frac{2\pi^3}{y^3 \delta^3 R} f_{10}(2d, 0, R)$$

$$(\psi_1, \frac{1}{\pi_{2a}} \psi_3) = \frac{128\pi^3}{(y)^3} \left[\frac{4(\delta+\delta)^2}{(y)^2} + \frac{(\delta+\delta)^2}{2d^2(y)} - \frac{16d(\delta+\delta)^2}{(y)^2(d+\delta+\delta)} \right. \\ \left. - \frac{2(\delta+\delta)^2}{(y)(d+\delta+\delta)^2} + \frac{6d(\delta+\delta)}{(y)(d+\delta+\delta)^2} + \frac{2(\delta+\delta)}{(d+\delta+\delta)^3} \right. \\ \left. + \frac{4d(\delta+\delta)}{(y)^2} + \frac{d}{4(\delta+\delta)^3} - \frac{3d}{2(y)(\delta+\delta)} \right]$$

$$(\psi_1, \frac{1}{\pi_{2a}} \psi_4) = \frac{64\pi^3}{R(y)^3} \left[\left\{ d f_{11} - \frac{6d(\delta+\delta)}{(y)} f_{10} + \frac{8d(\delta+\delta)^2}{(y)^2} f_{00} \right\}_{\delta+\delta, \delta+\delta, R} \right. \\ \left. + \left\{ (\delta+\delta) f_{11} - \frac{2(\delta+\delta)^2}{(y)} f_{10} - \frac{16d(\delta+\delta)^2}{(y)^2} f_{00} \right\}_{d, \delta+\delta, R} \right. \\ \left. + \frac{6d(\delta+\delta)}{(y)} f_{10}(\delta+\delta, d, R) \right. \\ \left. + \left\{ \frac{2(\delta+\delta)^2}{(y)} f_{10} + \frac{8d(\delta+\delta)^2}{(y)^2} f_{00} \right\}_{d, d, R} \right]$$

$$(\psi_2, \frac{1}{\pi_{2a}} \psi_3) = \frac{32\pi^3}{(y)^2 R} \left[\frac{d}{6(\delta+\delta)} f_{12}(d, \delta+\delta, R) + \left(\frac{d}{d(\delta+\delta)^2} - \frac{2d}{(y)} \right) f_{11}(d, \delta+\delta, R) \right. \\ \left. + \left(\frac{d}{2(\delta+\delta)^3} - \frac{2d}{(y)(\delta+\delta)} + \frac{12d(\delta+\delta)}{(y)^2} \right) f_{10}(d, \delta+\delta, R) \right. \\ \left. + \frac{32d(\delta+\delta)^2}{(y)^3} \left(f_{11}(d, d, R) - f_{11}(\delta+\delta, d, R) \right) + \frac{4(\delta+\delta)^2}{(y)^2} f_{10}(d, d, R) \right]$$

$$(\psi_3, \frac{1}{\pi_{2a}} \psi_3) = \frac{2\pi^3}{y^2(y^2-\delta^2)^2} \left[\frac{1}{y} \left(\frac{\alpha}{2\delta^2} - \frac{2\alpha}{(d^2-\delta^2)} + \frac{\delta}{2d^2} + \frac{2\delta}{(d^2-\delta^2)} \right. \right. \\ \left. \left. - \frac{\alpha}{2(y+\delta)^2} + \frac{2\alpha\delta}{(d^2-\delta^2)(y+\delta)} - \frac{\delta}{2(d+y)^2} - \frac{2\alpha\delta}{(d^2-\delta^2)(d+y)} \right) \right. \\ \left. - \left(\frac{\alpha}{2(y+\delta)^3} - \frac{\alpha\delta}{(d^2-\delta^2)(y+\delta)^2} + \frac{\delta}{2(d+y)^3} + \frac{2\delta}{(d^2-\delta^2)(d+y)^2} \right) \right] \quad 54.$$

$$(\psi_1, \frac{1}{\pi_{2b}} \psi_3) = \frac{32\pi^3}{(y)^3 R} \left[\left\{ \frac{\alpha}{2(y+\delta)^3} \left(\frac{(y+\delta)^2}{3} f_{30} + (y+\delta) f_{20} + f_{10} \right) \right. \right. \\ \left. - \frac{2\alpha}{(y)(y+\delta)} \left(f_{10} + (y+\delta) f_{20} \right) + \frac{4(y+\delta)\alpha}{(y)^2} \left(f_{10} - \frac{4(y+\delta)}{(y)} f_{00} \right) \right. \\ \left. + \frac{8\alpha(y+\delta)}{(y)^2} \left(f_{10} - \frac{2(y+\delta)}{(y)} f_{00} \right) \right\}_{d+y+\delta, 0, R} + \left\{ \frac{16\alpha(y+\delta)^2}{(y)^3} f_{00} \right. \\ \left. + \frac{4(y+\delta)^2}{(y)^2} \left(f_{10} + \frac{4\alpha}{(y)} f_{00} \right) \right\}_{2d, 0, R} \right]$$

$$(\psi_1, \frac{1}{\pi_{12}} \psi_4) = \frac{64\pi^3}{(y)^3 R} \left[\frac{2\alpha(y+\delta)}{(y)} \left\{ \frac{-(y)}{2\alpha} f_{11} - \frac{4\alpha f_{00}}{(y)} - 3f_{10} \right\}_{d, d, R} \right. \\ \left. + \alpha \left\{ -f_{11} + \frac{6(y+\delta)}{(y)} f_{10} - \frac{2\alpha}{(y)} f_{01} + \frac{16\alpha(y+\delta)}{(y)^2} f_{00} \right\}_{d, y+\delta, R} \right. \\ \left. + \frac{2\alpha^2}{(y)} \left\{ f_{10} - \frac{4(y+\delta)}{(y)} f_{00} \right\}_{y+\delta, y+\delta, R} \right]$$

$$(\psi_3, \frac{1}{\pi_{12}} \psi_4) = \frac{2\pi^3}{R y^2 \delta^3} f_{11} (d, d, R)$$

$$(\psi_1, \frac{1}{\pi_{13}} \psi_1) = \frac{\pi^3}{\alpha^3 \delta^3 y^2}$$

$$\begin{aligned}
 (\psi_3, \frac{1}{\pi_{2b}} \psi_3) &= \frac{4\pi^3}{\gamma^2 R} \left[\left(-\frac{1}{2\gamma\delta^2} - \frac{\gamma}{2(\gamma^2 - \delta^2)^2} - \frac{1}{2\gamma(\gamma^2 - \delta^2)} \right) f_{11}(2d, 2\delta, R) \right. \\
 &\quad + \left(-\frac{1}{2\gamma\delta^3} + \frac{\gamma\delta}{(\gamma^2 - \delta^2)^3} + \frac{\delta}{2\gamma(\gamma^2 - \delta^2)^2} \right) f_{10}(2d, 2\delta, R) - \frac{\delta}{2(\gamma^2\delta^2)^2} f_{11}(2d, 2\gamma, R) \\
 &\quad \left. + \left(-\frac{\gamma\delta}{(\gamma^2 - \delta^2)^3} - \frac{\delta}{2\gamma(\gamma^2 - \delta^2)^2} \right) f_{10}(2d, 2\gamma, R) + \frac{1}{2\gamma\delta^3} f_{10}(2d, 0, R) \right]
 \end{aligned}$$

$$\begin{aligned}
 (\psi_1, \frac{1}{\pi_{3b}} \psi_2) &= \frac{2\pi^3}{R(\gamma^2 - \delta^2)^2} \left[-\frac{\delta}{\gamma^3} \left\{ \gamma f_{11} + \left(1 + \frac{2\gamma^2}{(\gamma^2 - \delta^2)} \right) f_{10} \right\}_{d, d+2\gamma, R} \right. \\
 &\quad - \frac{\gamma}{\delta^3} \left\{ \delta f_{11} + \left(1 - \frac{2\gamma^2}{(\gamma^2 - \delta^2)} \right) f_{10} \right\}_{d, d+2\delta, R} \\
 &\quad \left. + \frac{(\gamma^2 - \delta^2)^2}{\gamma^3\delta^3} f_{10}(d, d, R) \right]
 \end{aligned}$$

$$(\psi_1, \frac{1}{\pi_{12}} \psi_1) = \frac{\pi^3}{d^3 \gamma^3 \delta^2}$$

$$(\psi_1, \frac{1}{\pi_{12}} \psi_2) = \frac{2\pi^3}{\gamma^3 \delta^2 R} f_{11}(d, d, R)$$

$$\begin{aligned}
 (\psi_1, \frac{1}{\pi_{12}} \psi_3) &= \frac{128\pi^3}{(\gamma)^4} \left[\frac{(\gamma + \delta)}{d} \left(-\frac{3}{2} - \frac{1}{4d^2} \right) \right. \\
 &\quad + 2d \left(\frac{3(\gamma + \delta)}{(d + \gamma + \delta)^2} - \frac{1}{(d + \gamma + \delta)^3} - \frac{2(\gamma + \delta)}{(\gamma)} \right) \\
 &\quad \left. + 2d^2 \left(\frac{-1}{(d + \gamma + \delta)^2} + \frac{8(\gamma + \delta)}{\gamma(d + \gamma + \delta)} - \frac{2}{(\gamma)} + \frac{1}{4(\gamma + \delta)^2} \right) \right]
 \end{aligned}$$

EVALUATION OF $\langle E \rangle$ FOR THE HYDROGEN MOLECULAR ION:

We wish to calculate the average of the Hamiltonian for the hydrogen molecular ion function,

$$\psi = (e^{-\alpha r_a} + e^{-\alpha r_b})$$

A3-1

and minimize this with respect to the parameter α , and with respect to R , the internuclear distance.

The Hamiltonian for H_2^+ is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + e^2 \left(-\frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \right)$$

A3-2

We can write the average value of the Hamiltonian,

as

$$\langle E \rangle = \frac{1}{(\psi, \psi)} \left[-\frac{\hbar^2}{2m} (\psi, \nabla^2 \psi) + e^2 \left\{ -(\psi, \frac{1}{r_a} \psi) - (\psi, \frac{1}{r_b} \psi) + \frac{1}{R} (\psi, \psi) \right\} \right]$$

A3-3

The quantities appearing in $\langle E \rangle$ are given below in terms of the functions

$$f_{mn}(a, b, r) = \int_0^\infty \int_{|r-r_1|}^{r+r_1} e^{-a r_1 - b r_2} \frac{r_1^m}{r_1} \frac{r_2^n}{r_2} dr_2 dr_1$$

A table of the functions is found in Appendix I.

$$(\psi, \psi) = 2\pi \left[\frac{1}{d^3} + \frac{2}{R} f_{11}(d, d, R) \right]$$

57.

$$(\psi, \nabla^2 \psi) = -2\pi \left[\frac{1}{d} + \frac{4d}{R} f_{10}(d, d, R) - \frac{2d^2}{R} f_{11}(d, d, R) \right]$$

$$\left(\psi, \left(\frac{1}{\pi a} + \frac{1}{\pi b} \right) \psi \right) = 2\pi \left[\frac{1}{d^2} + \frac{2}{R} f_{10}(2d, 0, R) + \frac{4}{R} f_{10}(d, d, R) \right]$$

The value of $\langle E \rangle$ as a function of d and R was calculated on an I.B.M. 1620 digital computer at the University of Manitoba.

The best values of the parameter were found to be

$$d = 1.2380 a_0^{-1}$$

$$R = 2a_0$$

$$\langle E \rangle = -15.959 \text{ e.v.}$$

These, as can be easily seen, differ slightly from the best values found by Finkelstein and Horowitz¹, which were

$$d = 1.228a_0^{-1}, R = 2a_0, \text{ and } \langle E \rangle = -15.85 \text{ e.v.}$$

1. B.N. Finkelstein & G. E. Horowitz, Z.phys, 48, 118 (1928)

APPENDIX IV

EVALUATION OF THE INTEGRALS OF SQUARE OF THE LAPLACIAN AND THE SQUARE OF THE WAVE FUNCTION FOR THE HYDROGEN MOLECULAR ION PLUS POSITRONIUM CONFIGURATION

The integrals of square of the Laplacian for the hydrogen molecular ion plus positronium configuration can be written

$$\int (\nabla^2 \Psi)^2 d\tau = \int \{ (\nabla_1^2 \Psi)^2 + 2 (\nabla_2^2 \Psi)^2 \} d\tau$$

A4-1

Using the symmetry of Ψ with respect to particles 2 and 3, we can express

$$\begin{aligned} \int (\nabla_1^2 \Psi)^2 d\tau = & 4(\gamma^2 + \delta^2) \left\{ \int \psi_1^2 d\tau + \int \psi_1 \psi_2 d\tau \right. \\ & \left. \pm \int \psi_1 \psi_3 \cos \Theta_{12,13} d\tau \pm \int \psi_1 \psi_4 \cos \Theta_{12,13} d\tau \right\} \\ & + 8\gamma\delta \left\{ \pm \int \psi_1 \psi_3 d\tau \pm \int \psi_1 \psi_4 d\tau \right. \\ & \left. + \int \psi_1^2 \cos \Theta_{12,13} d\tau + \int \psi_1 \psi_2 \cos \Theta_{12,13} d\tau \right\} \end{aligned}$$

where $\psi_{\bar{v}}, \bar{v} = 1, \dots, 4$ are defined by equation III-13, and the integrations are carried out over the nine-dimensional configuration space.

Similarly we can write

$$\begin{aligned} \int (\nabla_2^2 \Psi)^2 d\tau = & 2(\alpha^2 + \gamma^2 + \delta^2) \int \psi_1^2 d\tau + 2(\gamma^2 + \delta^2) \int \psi_1 \psi_2 d\tau \\ & \pm 4\gamma\delta \int (\psi_1 \psi_3 + \psi_1 \psi_4) d\tau + 2\alpha^2 \int \psi_1 \psi_2 \cos \Theta_{29,20} d\tau \\ & + 4 \int \left\{ \alpha\delta (\psi_1^2 + \psi_1 \psi_2) \pm \alpha\gamma (\psi_1 \psi_3 + \psi_1 \psi_4) \right\} \cos \Theta_{29,21} d\tau \end{aligned}$$

Then

59.

$$\begin{aligned}
 \int (\nabla \psi)^2 d\tau &= \int (\nabla_1 \psi)^2 d\tau + 2 \int (\nabla_2 \psi)^2 d\tau \\
 &= 4(\alpha^2 + 2\gamma^2 + 2\delta^2) \int \psi_1^2 d\tau + 8(\gamma^2 + \delta^2) \int \psi_1 \psi_2 d\tau \\
 &\quad \pm 16\gamma\delta \left[\int \psi_1 \psi_3 d\tau + \int \psi_1 \psi_4 d\tau \right] + 4\alpha^2 \int \psi_1 \psi_2 \cos \Theta_{2\alpha, 2\beta} d\tau \\
 &\quad + 8 \int \left\{ 2\delta(\psi_1^2 + \psi_1 \psi_2) \pm 2\gamma(\psi_1 \psi_3 + \psi_1 \psi_4) \right\} \cos \Theta_{2\alpha, 2\beta} d\tau \\
 &\quad \pm 4(\gamma^2 + \delta^2) \int (\psi_1 \psi_3 + \psi_1 \psi_4) \cos \Theta_{12, 13} d\tau \\
 &\quad + 8\gamma\delta \int (\psi_1^2 + \psi_1 \psi_2) \cos \Theta_{12, 13} d\tau
 \end{aligned}$$

As is shown in Chapter III, the integral of the square of the wave function can be written

$$\int \psi^2 d\tau = 4 \int \psi_1^2 d\tau + 4 \int \psi_1 \psi_2 d\tau \pm 4 \int \psi_1 \psi_3 d\tau \pm 4 \int \psi_1 \psi_4 d\tau$$

In all the above cases, the expression $\pm$ refers to + for the symmetric function and - for the antisymmetric function.

The specific values of the integrals arising in these nine-dimensional integrals are as follows.

$$\int \psi_1^2 d\tau = \frac{\pi^3}{\alpha^3 \gamma^3 \delta^3}$$

$$\int \psi_1 \psi_2 d\tau = \frac{2\pi^3}{\gamma^3 \delta^3 R} f_{11}(\alpha, \delta, R)$$

$$\begin{aligned}
 \int \psi_1 \psi_3 d\tau &= \frac{64\pi^3}{(\gamma)^2} \left\{ \frac{-32\alpha(\gamma+\delta)^2}{(\gamma)^3(\alpha+\gamma+\delta)^2} + \frac{24\alpha(\gamma+\delta)}{(\gamma)^2(\alpha+\gamma+\delta)^3} - \frac{12\alpha}{(\gamma)(\alpha+\gamma+\delta)^4} \right. \\
 &\quad + \frac{4\alpha}{(\gamma+\delta)(\alpha+\gamma+\delta)^5} + \frac{8(\gamma+\delta)^2}{(\gamma)^3\alpha} + \frac{(\gamma+\delta)^2}{(\gamma)^2\alpha^3} + \frac{3\alpha}{(\gamma+\delta)^2(\alpha+\gamma+\delta)^4} \\
 &\quad \left. - \frac{4\alpha}{(\gamma)(\gamma+\delta)(\alpha+\gamma+\delta)^3} + \frac{\alpha}{(\gamma+\delta)^3(\alpha+\gamma+\delta)^3} \right\}
 \end{aligned}$$

where $(y) = d^2 - (x+\delta)^2$.

$$\begin{aligned} \int \psi_1 \psi_4 d\tau = & \frac{4\pi^3}{R} \left[\frac{4d}{3(x+\delta)(y)^2} f_{13}(d, x+\delta, R) + \left(\frac{4d}{(y)^2(x+\delta)^2} - \frac{16d}{(y)^3} \right) f_{12}(d, x+\delta, R) \right. \\ & + \left(\frac{96d(x+\delta)}{(y)^4} + \frac{4d}{(x+\delta)^3(y)^2} - \frac{16d}{(x+\delta)(y)^3} \right) f_{11}(d, d, R) - \frac{256d(x+\delta)^2}{(y)^5} f_{10}(d, x+\delta, R) \Big] \\ & + \frac{\pi^3 R^3}{2} \left[\frac{256(x+\delta)^2}{(y)^5} \frac{4e^{-dR}}{dR^3} (1+dR) + \frac{128(x+\delta)^2}{(y)^4} e^{-dR} \left(\frac{1}{3dR} + \frac{1}{d^2 R^2} + \frac{1}{d^3 R^3} \right) \right] \end{aligned}$$

$$\int \psi_1 \psi_2 \cos \Theta_{20,20} d\tau = \frac{R^2 \pi^3 e^{-dR}}{d^2 8^3} \left[-\frac{1}{3} + \frac{1}{dR} + \frac{1}{d^2 R^2} \right]$$

$$\int \psi_1^2 \cos \Theta_{20,20} d\tau = 0$$

$$\int \psi_1 \psi_2 \cos \Theta_{20,21} d\tau = 0$$

$$\begin{aligned} \int \psi_1 \psi_3 \cos \Theta_{20,21} d\tau = & \frac{64\pi^3}{(y)^4} \left[-\frac{d}{(x+\delta)^2} + \frac{2d^3}{(x+\delta)^2(y)} + \frac{6d}{(y)} - \frac{16d^3}{(y)^2} \right. \\ & - \frac{16d(x+\delta)^2}{(y)^2} - \frac{(x+\delta)}{d^2} - \frac{6(x+\delta)}{(y)} - \frac{2(x+\delta)^3}{d^2(y)} - \frac{16d^2(x+\delta)}{(y)^2} \\ & - \frac{16(x+\delta)^3}{(y)^2} - \frac{8(d^2 + (x+\delta)^2)}{(d+x+\delta)^3} - \frac{8(d-x-\delta)^3}{(y)(d+x+\delta)^2} \\ & \left. + \frac{64d(x+\delta)(d^2 + (x+\delta)^2)}{(y)^2(d+x+\delta)} \right] \end{aligned}$$

$$\int \psi_1^2 \cos \Theta_{12,13} d\tau = 0$$

$$\int \psi_1 \psi_2 \cos \Theta_{12,13} d\tau = 0$$

$$\begin{aligned}
\int \psi_1 \psi_4 \cos \Theta_{22,21} d\tau &= \frac{16\pi^3}{R(y)^2} \left\{ \left[\frac{-8d(x+\delta)}{(y)^2} f_{11} + \frac{16d}{(y)^3} (d^2 + 3(x+\delta)^2) f_{10} \right. \right. \\
&\quad \left. \left. - \frac{64d(x+\delta)(d^2 + (x+\delta)^2)}{(y)^4} f_{00} \right]_{x+\delta, x+\delta, R} + \left[\frac{-8d(x+\delta)}{(y)^2} f_{11} \right. \right. \\
&\quad \left. \left. - \frac{16(x+\delta)}{(y)^3} ((x+\delta)^2 + 3d^2) f_{10} - \frac{64d(x+\delta)(d^2 + (x+\delta)^2)}{(y)^4} f_{00} \right]_{d, d, R} \right\} \\
&+ \left\{ \frac{-8(d^2 + (x+\delta)^2)}{(y)^2} f_{11} - \frac{16d}{(y)^3} [d^2 + 3(x+\delta)^2] f_{01} \right. \\
&\quad \left. + \frac{16(x+\delta)(3d^2 + (x+\delta)^2)}{(y)^3} f_{10} + \frac{128d(x+\delta)(d^2 + (x+\delta)^2)}{(y)^4} f_{00} \right\}_{d, x+\delta, R}
\end{aligned}$$

$$\begin{aligned}
\int \psi_1 \psi_3 \cos \Theta_{12,13} d\tau &= \frac{16\pi^3}{y(x+\delta)} \left[\frac{1}{y(x+\delta)^2} \left\{ \frac{4d}{(d+x+\delta)^3} - \frac{8d(x+\delta)}{(y)(d+x+\delta)^2} + \frac{(x+\delta)}{2d^3} \right. \right. \\
&\quad \left. \left. + \frac{2(x+\delta)}{d(y)} \right\} + \frac{1}{y(x+\delta)^4} \left\{ \frac{12d}{y(x+\delta)^4} - \frac{32d(x+\delta)}{y(d+x+\delta)^3} + \frac{48d(x+\delta)^2}{(y)^2(d+x+\delta)^2} + \frac{8d}{(y)(d+x+\delta)^2} \right. \right. \\
&\quad \left. \left. - \frac{2(x+\delta)^2}{(y)d^3} - \frac{1}{2d^3} - \frac{12(x+\delta)^2}{d(y)^2} - \frac{2}{(y)d} \right\} \right. \\
&\quad \left. + \left\{ \frac{48d(x+\delta)}{(y)^3(d+x+\delta)^2} + \frac{128d(x+\delta)^3}{(y)^4(d+x+\delta)^2} - \frac{16d}{(y)^2(d+x+\delta)^3} - \frac{96d(x+\delta)^2}{(y)^3(d+x+\delta)^3} \right. \right. \\
&\quad \left. \left. + \frac{48d(x+\delta)}{(y)^2(d+x+\delta)^4} - \frac{16d}{(y)(d+x+\delta)^5} - \frac{12(x+\delta)}{d(y)^3} - \frac{32d(x+\delta)^3}{d(y)^4} \right. \right. \\
&\quad \left. \left. - \frac{2(x+\delta)}{d^3(y)^2} - \frac{4(x+\delta)^3}{(y)^3 d^3} \right\} \right]
\end{aligned}$$

$$\begin{aligned}
 \int \psi_1 \psi_4 \cos \Theta_{12,13} d\tau &= \frac{8\pi^3}{R(\gamma+\delta)(\gamma)^2} \left\{ -\frac{2d}{3} f_{13} + \left(\frac{2d}{(\gamma+\delta)} + \frac{8d(\gamma+\delta)}{(\gamma)} \right) f_{12} \right. \\
 &\quad \left. + \left(\frac{2d}{(\gamma+\delta)^2} - \frac{24d}{(\gamma)} - \frac{48d(\gamma+\delta)^2}{(\gamma)^2} \right) f_{11} + \left(\frac{46d(\gamma+\delta)}{(\gamma)^2} + \frac{128d(\gamma+\delta)^3}{(\gamma)^3} \right) f_{10} \right\} \\
 &\quad + \frac{64\pi^3 R^3}{(\gamma)^3} e^{-dR} \left[\left(\frac{1}{dR^3} + \frac{1}{R^2} \right) \left(\frac{-6}{(\gamma)} - \frac{8(\gamma+\delta)^2}{(\gamma)^2} \right) \right. \\
 &\quad \left. - \left(1 + \frac{(\gamma+\delta)^2}{(\gamma)} \right) \left(\frac{1}{3dR} + \frac{1}{d^2 R^2} + \frac{1}{d^3 R^3} \right) \right]
 \end{aligned}$$

SOLUTION OF POISSON EQUATION IN PROLATE SPHEROIDAL COORDINATE SYSTEM

We wish to solve the Poisson equation

$$\nabla^2 V = -4\pi \rho(\xi) \quad \text{A5-1}$$

where ξ, η, ϕ are prolate spheroidal coordinates. In particular, we wish to find $V(\xi, \eta, \phi)$ for the density function

$$\rho(\xi) = e^{-\alpha R \xi}$$

If we first attempt to find an axially symmetric solution ($\frac{\partial V}{\partial \phi} = 0$), we can write¹

$$\nabla^2 V = \frac{4}{R^2(\xi^2 - \eta^2)} \left\{ \frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial V}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial V}{\partial \eta} \right] \right\} \quad \text{A5-2}$$

where

$$\begin{aligned} 1 &\leq \xi < \infty \\ -1 &\leq \eta < 1 \\ 0 &\leq \phi < 2\pi \end{aligned}$$

We seek a solution of the form

$$V(\xi, \eta) = u(\xi) + \eta^2 v(\xi) \quad \text{A5-3}$$

Substituting this form into A5-1, and equating coefficients of powers of η gives the equations

$$\begin{aligned} \frac{d}{d\xi} \left[(\xi^2 - 1) \frac{du}{d\xi} \right] + 2v &= -\xi^2 \pi R^2 \rho(\xi) \\ \frac{d}{d\xi} \left[(\xi^2 - 1) \frac{dv}{d\xi} \right] - 6v &= +\pi R^2 \rho(\xi) \end{aligned} \quad \text{A5-4}$$

1. P. Morse and H. Feshbach, Methods of Theoretical Physics, McGraw-Hill, (1953), p. 1284.

In the second of these, we make the substitution

$$v = (3\xi^2 - 1) w(\xi) \quad \text{A5-5}$$

and find

$$\frac{d^2 w}{d\xi^2} \left[(\xi^2 - 1)(3\xi^2 - 1) \right] + \frac{dw}{d\xi} \left[18\xi^3 - 14\xi \right] = \pi R^2 p(\xi) \quad \text{A5-6}$$

An integrating factor is $(3\xi^2 - 1)$. Multiplying through by $(3\xi^2 - 1)$ and integrating once gives rise to

$$\frac{dw}{d\xi} = \frac{\pi R^2}{(\xi^2 - 1)(3\xi^2 - 1)^2} \left\{ \int_{\infty}^{\xi} (3\xi^2 - 1) p(\xi) d\xi + C_1 \right\} \quad \text{A5-7}$$

where C_1 is an arbitrary constant.

This equation has the solution, when we set $p(\xi) = e^{-\alpha R \xi}$,

$$\begin{aligned} w(\xi) = & -\pi R^2 \left[\int_{\infty}^{\xi} \frac{e^{-\alpha R \xi}}{(\xi^2 - 1)} \left(\frac{1}{2\alpha R} + \frac{3\xi}{2(\alpha R)^2} + \frac{3}{2(\alpha R)^3} \right) d\xi \right. \\ & + \frac{e^{-\alpha R \xi}}{(\xi^2 - 1/3)} \left(\frac{1}{2(\alpha R)^2} + \frac{3\xi}{2(\alpha R)^3} \right) \\ & \left. - C_1 \left\{ \frac{1}{8} \ln \left(\frac{\xi - 1}{\xi + 1} \right) + \frac{3\xi}{4(3\xi^2 - 1)} \right\} \right] \quad \text{A5-8} \end{aligned}$$

This then provides us with a solution for $v(\xi)$.

In order to find a solution for $u(\xi)$, we multiply the first equation in (AIV-4) by three and add to the second.

This leads to

$$\begin{aligned} \frac{d}{d\xi} (3u + v) &= -\frac{\pi R^2}{(\xi^2 - 1)} \int (3\xi^2 - 1) p(\xi) d\xi \\ &= -\frac{\pi R^2}{(\xi^2 - 1)} \left[-\frac{e^{-\alpha R \xi}}{(\alpha R)} (3\xi^2 - 1) - \frac{6\xi e^{-\alpha R \xi}}{(\alpha R)^2} - \frac{6e^{-\alpha R \xi}}{(\alpha R)^3} + D_1 \right] \quad \text{A5-9} \end{aligned}$$

when the form of $P(\xi)$ is substituted in. D_1 is another arbitrary constant of integration.

Performing the integration and substituting for v leads to the solution

$$\begin{aligned}
 u = \frac{1}{3} \left\{ -\pi R^2 \left[D_2 + \frac{3}{(4R)^2} e^{-4R\xi} + \int_{\infty}^{\xi} \frac{e^{-4R\xi}}{(\xi^2-1)} \left(-\frac{2}{4R} - \frac{6\xi}{(4R)^2} - \frac{6}{(4R)^3} \right) d\xi \right. \right. \\
 \left. \left. + \frac{D_1}{2} \ln \left(\frac{\xi-1}{\xi+1} \right) \right] \right. \\
 \left. + \pi R^2 \left[(3\xi^2-1) \int_{\infty}^{\xi} \frac{e^{-4R\xi}}{(\xi^2-1)} \left(\frac{1}{24R} + \frac{3\xi}{2(4R)^2} + \frac{3}{2(4R)^3} \right) d\xi \right. \right. \\
 \left. \left. + 3e^{-4R\xi} \left(\frac{1}{2(4R)^2} + \frac{3\xi}{2(4R)^3} \right) \right. \right. \\
 \left. \left. - (3\xi^2-1) C_1 \left(\frac{1}{8} \ln \left(\frac{\xi-1}{\xi+1} \right) + \frac{3\xi}{4(3\xi^2-1)} \right) \right] \right\}
 \end{aligned} \tag{A5-10}$$

We impose the boundary condition that $V(\xi, \eta) \rightarrow 0$ as $\xi \rightarrow \infty$ for every value of η . In particular, if $\eta=0$, $V(\xi, 0) = u(\xi)$ and therefore $u(\xi) \rightarrow 0$ as $\xi \rightarrow \infty$. This in turn implies $D_2=0$.

We can then write the solution of $\nabla^2 V = -4\pi e^{-4R\xi}$ as $V = u(\xi) + \eta^2 v(\xi)$ where

$$\begin{aligned}
 u(\xi) = -\pi R^2 \left[\frac{1}{2(4R)^2} e^{-4R\xi} - \frac{3\xi e^{-4R\xi}}{2(4R)^3} \right. \\
 \left. - (3\xi^2+1) \int_{\infty}^{\xi} \frac{e^{-4R\xi}}{(\xi^2-1)} \left(\frac{1}{24R} + \frac{3\xi}{2(4R)^2} + \frac{3}{2(4R)^3} \right) d\xi \right. \\
 \left. + \frac{D_1}{6} \ln \left(\frac{\xi-1}{\xi+1} \right) + C_1 \left(\xi^2 - \frac{1}{3} \right) \left(\frac{1}{8} \ln \left(\frac{\xi-1}{\xi+1} \right) + \frac{3\xi}{4(3\xi^2-1)} \right) \right]
 \end{aligned} \tag{A5-11}$$

and

$$\begin{aligned}
 v(\xi) = -\pi R^2 \left[(3\xi^2-1) \int_{\infty}^{\xi} \frac{e^{-4R\xi}}{(\xi^2-1)} \left(\frac{1}{24R} + \frac{3\xi}{2(4R)^2} + \frac{3}{2(4R)^3} \right) d\xi \right. \\
 \left. + e^{-4R\xi} \left(\frac{3}{2(4R)^2} + \frac{9\xi}{2(4R)^3} \right) \right. \\
 \left. - (3\xi^2-1) C_1 \left[\frac{1}{8} \ln \left(\frac{\xi-1}{\xi+1} \right) + \frac{3\xi}{4(3\xi^2-1)} \right] \right]
 \end{aligned} \tag{A5-12}$$

In order to evaluate the constants, we impose the condition that

$V(\xi, \eta)$ be finite as $\xi \rightarrow 1$. Requiring v to be finite as $\xi \rightarrow 1$ gives $C_1 = \frac{b}{(\alpha R)^3} e^{-\alpha R} \left(\frac{(\alpha R)^2}{3} + \alpha R + 1 \right)$

Requiring u to be finite implies that $C_1 = D_1$

If we write $\Delta = e^{-\alpha R} \left[\frac{(\alpha R)^2}{3} + \alpha R + 1 \right]$ we can then write

these expressions as

$$u(\xi) = -\pi R^2 \left[\frac{e^{-\alpha R \xi}}{2(\alpha R)^2} \left(1 - \frac{3\xi}{(\alpha R)} \right) + \frac{3\Delta \xi}{2(\alpha R)^3} + \frac{3\Delta(\xi^2+1)}{4(\alpha R)^3} \ln \left(\frac{\xi-1}{\xi+1} \right) - \frac{3(\xi^2+1)}{2(\alpha R)^3} \int_{-\infty}^{\xi} \frac{e^{-\alpha R \xi}}{(\xi^2-1)} \left(\frac{(\alpha R)^2}{3} + \alpha R \xi + 1 \right) d\xi \right] \quad A5-13$$

$$v(\xi) = -\pi R^2 \left[\frac{3(3\xi^2-1)}{2(\alpha R)^3} \int_{-\infty}^{\xi} \frac{e^{-\alpha R \xi}}{(\xi^2-1)} \left(\frac{(\alpha R)^2}{3} + \alpha R \xi + 1 \right) d\xi + \frac{3e^{-\alpha R \xi}}{2(\alpha R)^2} \left(1 + \frac{3\xi}{(\alpha R)} \right) - \frac{3(3\xi^2-1)\Delta}{4(\alpha R)^3} \ln \left(\frac{\xi-1}{\xi+1} \right) - \frac{9\Delta}{2(\alpha R)^3} \xi \right] \quad A5-14$$

This expression for $V(\xi, \eta)$ can be arrived at in another manner.

The solution of the Poisson equation A5-1 is equivalent to evaluation of the expression

$$V(\xi_0, \eta_0, \phi_0) = \int p(\underline{r}) G(\underline{r}, \underline{r}_0) d\tau_{\underline{r}} \quad A5-15$$

Where $G(\underline{r}, \underline{r}_0)$ is the Green's function for the Laplacian operator. The Green's function is given by Morse and

$$G(\underline{r}, \underline{r}_0) = \frac{2}{R} \sum_{n=0}^{\infty} (2n+1) \sum_{m=0}^n \epsilon_m i^m \left[\frac{(n-m)!}{(n+m)!} \right]^2 \cos[m(\phi - \phi_0)] P_n^m(\eta_0) P_n^m(\eta) h_n^m(\xi, \xi_0)$$

A5-16

where
$$h_n^m(\xi, \xi_0) = P_n^m(\xi_0) Q_n^m(\xi); \xi > \xi_0$$

$$= P_n^m(\xi) Q_n^m(\xi_0); \xi < \xi_0$$

where ϵ_m is the Neumann factor, $\epsilon_0 = 1$

$\epsilon_m = 2$ when $m > 0$

The functions $P_n^m(\beta)$ are the Associated Legendre functions, and the functions $Q_n^m(\beta)$ are the Legendre functions of the second kind. The Legendre functions of the second kind can be defined by

$$Q_n^0(z) = \frac{1}{2^n n!} \frac{d^n}{(dz)^n} \left[(z^2 - 1)^n \ln \left(\frac{z+1}{z-1} \right) \right] - \frac{1}{2} P_n^0(z) \ln \left(\frac{z+1}{z-1} \right)$$

A5-17

and
$$Q_n^m(z) = (-1)^m (z^2 - 1)^{\frac{m}{2}} \frac{d^m}{(dz)^m} Q_n^0(z)$$

In the expression which we are particularly concerned with,

$$V(\xi_0, \eta_0, \phi_0) = \int_1^{\infty} \int_{-1}^1 \int_0^{2\pi} G(\underline{r}, \underline{r}_0) e^{-4R\xi} \frac{R^3}{8} (\xi^2 - \eta^2) d\phi d\eta d\xi$$

the integration over the variable ϕ leaves zero in the double

summation for all terms corresponding to $m \neq 0$. Thus we have

$$V(\xi_0, \eta_0) = \int_{-1}^{+1} \int_{-1}^{+1} \frac{4\pi R^2}{8} e^{-4R\xi} \sum_{n=0}^{\infty} (2n+1) P_n^0(\eta_0) P_n^0(\eta) h_n^0(\xi, \xi_0) (\xi^2 - \eta^2) d\eta d\xi \quad A5-18$$

using the relations

$$1 = P_0^0(\eta)$$

$$\eta^2 = \frac{2}{3} P_2^0(\eta) + \frac{1}{3} P_0^0(\eta)$$

and the orthogonality

relation of the Legendre functions

$$\int_{-1}^{+1} P_m^0(z) P_n^0(z) dz = \frac{2}{(2n+1)} \delta_{mn} \quad A5-19$$

the integration over η gives

$$V(\xi_0, \eta_0) = \int_{-1}^{+1} \frac{\pi R^2}{2} e^{-4R\xi} \left[2\left(\xi^2 - \frac{1}{3}\right) h_0^0(\xi, \xi_0) - \frac{4}{3} P_2^0(\eta_0) h_2^0(\xi, \xi_0) \right] d\xi \quad A5-20$$

It is worthwhile to note that the solution of $V(\xi_0, \eta_0, \phi_0)$ can be carried to this point for any density function of the form $\rho(\xi)$, since we have not yet made use of the specific form of $\rho(\xi)$.

Substituting the specific form for $h_n^0(\xi, \xi_0)$ and the relation

$$P_2^0(\eta_0) = \frac{1}{2} (3\eta_0^2 - 1) \quad A5-21$$

we can now write

$$\begin{aligned}
 V(\xi_0, \eta_0) = & \int_1^{\xi_0} \pi R^2 e^{-\alpha R \xi} \left\{ (\xi^2 - \frac{1}{3}) P_0^0(\xi) Q_0^0(\xi_0) - \frac{1}{3} (3\eta_0^2 - 1) P_2^0(\xi) Q_2^0(\xi_0) \right\} d\xi \\
 & + \int_{\xi_0}^{\infty} \pi R^2 e^{-\alpha R \xi} \left\{ (\xi^2 - \frac{1}{3}) P_0^0(\xi_0) Q_0^0(\xi) - \frac{1}{3} (3\eta_0^2 - 1) P_2^0(\xi_0) Q_2^0(\xi) \right\} d\xi
 \end{aligned}$$

A5-22

If we write this as

$$V(\xi_0, \eta_0) = u(\xi_0) + \eta^2 v(\xi_0),$$

A5-23

$$\begin{aligned}
 u(\xi_0) = & \int_1^{\xi_0} \pi R^2 e^{-\alpha R \xi} \left\{ (\xi^2 - \frac{1}{3}) Q_0^0(\xi_0) + \frac{1}{6} Q_2^0(\xi_0) (3\xi^2 - 1) \right\} d\xi \\
 & + \int_{\xi_0}^{\infty} \pi R^2 e^{-\alpha R \xi} \left\{ \frac{1}{2} (\xi^2 - \frac{1}{3}) \ln \left(\frac{\xi+1}{\xi-1} \right) + \frac{1}{3} P_2^0(\xi_0) \left(\frac{1}{4} (3\xi^2 - 1) \ln \left(\frac{\xi+1}{\xi-1} \right) \right) \right\} d\xi
 \end{aligned}$$

A5-24

$$\begin{aligned}
 v(\xi_0) = & \int_1^{\xi_0} \pi R^2 e^{-\alpha R \xi} \left\{ -\frac{1}{2} (3\xi^2 - 1) Q_2^0(\xi_0) \right\} d\xi \\
 & + \int_{\xi_0}^{\infty} \pi R^2 e^{-\alpha R \xi} \left\{ -\frac{1}{4} (3\xi^2 - 1) \ln \left(\frac{\xi+1}{\xi-1} \right) + \frac{3}{2} \xi \right\} P_2^0(\xi_0) d\xi
 \end{aligned}$$

A5-25

where we have made use of the explicit forms

$$P_0^0(\xi) = 1 \qquad P_2^0(\xi) = \frac{1}{2} (3\xi^2 - 1)$$

A5-26

$$Q_0^0(\xi) = \frac{1}{2} \ln \left(\frac{\xi+1}{\xi-1} \right) \qquad Q_2^0(\xi) = \frac{1}{4} (3\xi^2 - 1) \ln \left(\frac{\xi+1}{\xi-1} \right) - \frac{3}{2} \xi$$

Using the relations

$$\int_{\xi_0}^{\infty} e^{-\beta \xi} \ln\left(\frac{\xi+1}{\xi-1}\right) d\xi = \frac{e^{-\beta \xi_0}}{\beta} \ln\left(\frac{\xi_0+1}{\xi_0-1}\right) - \frac{2}{\beta} \int_{\xi_0}^{\infty} \frac{e^{-\beta \xi}}{(\xi^2-1)} d\xi$$

and

$$\int_{\xi_0}^{\infty} e^{-\beta \xi} \xi^2 \ln\left(\frac{\xi+1}{\xi-1}\right) d\xi = \frac{d^2}{d\beta^2} \left\{ \int_{\xi_0}^{\infty} e^{-\beta \xi} \ln\left(\frac{\xi+1}{\xi-1}\right) d\xi \right\}$$

equation A5-24 can be integrated to yield

$$\begin{aligned} u(\xi_0) = \pi R^2 \left[-\frac{e^{-\alpha R \xi_0}}{2(\alpha R)^2} + \frac{3\xi_0 e^{-\alpha R \xi_0}}{2(\alpha R)^3} - \frac{3\Delta \xi_0}{2(\alpha R)^3} \right. \\ \left. + \frac{3\Delta(\xi_0^2+1)}{4(\alpha R)^3} \ln\left(\frac{\xi_0+1}{\xi_0-1}\right) \right. \\ \left. - \frac{3(\xi_0^2+1)}{2(\alpha R)^3} \int_{\xi_0}^{\infty} \frac{e^{-\alpha R \xi}}{(\xi^2-1)} \left(\frac{(\alpha R)^2}{3} + \alpha R \xi + 1 \right) d\xi \right] \quad \text{A5-27} \end{aligned}$$

Also, equation A5-25 gives

$$\begin{aligned} N(\xi_0) = -\pi R^2 \left[\frac{9\xi_0}{2(\alpha R)^3} e^{-\alpha R \xi_0} + \frac{3}{2(\alpha R)^2} e^{-\alpha R \xi_0} \right. \\ \left. + \frac{3(3\xi_0^2-1)\Delta}{4(\alpha R)^3} \ln\left(\frac{\xi_0+1}{\xi_0-1}\right) - \frac{9\Delta \xi_0}{2(\alpha R)^3} \right. \\ \left. - (3\xi_0^2-1) \int_{\xi_0}^{\infty} \frac{e^{-\alpha R \xi}}{(\xi^2-1)} \left(\frac{1}{2\alpha R} + \frac{3\xi}{2(\alpha R)^2} + \frac{3}{2(\alpha R)^3} \right) d\xi \right] \quad \text{A5-28} \end{aligned}$$

These expressions for $u(\xi)$ and $N(\xi)$ are in agreement with the expressions contained in equations A5-13 and A5-14.

CALCULATION OF TERMS IN THE CONFIGURATION OF HYDROGEN MOLECULE PLUS POSITRON:

We wish to express in explicit form the terms (χ, χ) and $\int \frac{\chi^2(\underline{r}_2, \underline{r}_3)}{\pi_{12}} d\tau_2 d\tau_3$, both of which arise in the definition of the operator $H^{(2)}$ given in equation 4-11.

First we consider (χ, χ) , where $\chi(\underline{r}_2, \underline{r}_3)$ is given by

$$\chi = c \left[e^{-\alpha(\pi_{2a} + \pi_{3b})} + e^{-\alpha(\pi_{3a} + \pi_{2b})} \right] + \left[e^{-\alpha(\pi_{2a} + \pi_{2b})} + e^{-\alpha(\pi_{3a} + \pi_{3b})} \right] \quad A6-1$$

Now

$$\begin{aligned} (\chi, \chi) = & \int \left\{ e^{-2\alpha\pi_{2a}} \left(c^2 e^{-2\alpha\pi_{3b}} + e^{-2\alpha\pi_{3a}} \right) \right. \\ & + e^{-2\alpha\pi_{2b}} \left(c^2 e^{-2\alpha\pi_{3a}} + e^{-2\alpha\pi_{3b}} \right) \\ & + 2c \left(e^{-\alpha(2\pi_{2a} + \pi_{3a} + \pi_{3b})} + e^{-\alpha(2\pi_{2b} + \pi_{3a} + \pi_{3b})} \right) \\ & + e^{-\alpha(2\pi_{3a} + \pi_{2a} + \pi_{2b})} + e^{-\alpha(2\pi_{3b} + \pi_{2a} + \pi_{2b})} \\ & \left. + 2(1+c^2) e^{-\alpha(\pi_{2a} + \pi_{2b} + \pi_{3a} + \pi_{3b})} \right\} d\tau_2 d\tau_3 \end{aligned}$$

Performing the integrations gives

$$(\chi, \chi) = \left(\frac{2\pi^2}{\alpha^6} + \frac{8\pi^2}{R^2} f_{11}(d, d, R) \right) (c^2 + 1) + \frac{16\pi^2 c}{R \alpha^3} f_{11}(d, d, R) \quad A6-2$$

We can also write

$$\begin{aligned} \int \frac{\chi^2}{\pi_{12}} d\tau_2 d\tau_3 = & \int \frac{d\tau_2}{\pi_{12}} \left\{ \int \chi^2(\underline{r}_2, \underline{r}_3) d\tau_3 \right\} \\ = & \int \frac{d\tau_2}{\pi_{12}} \left\{ \left(e^{-2\alpha\pi_{2a}} + e^{-2\alpha\pi_{2b}} \right) \left(\frac{\pi}{\alpha^3} (c^2 + 1) + \frac{4\pi c}{R} f_{11}(d, d, R) \right) \right. \\ & \left. + e^{-2\alpha(\pi_{2a} + \pi_{2b})} \left(\frac{4\pi}{R} (1+c^2) f_{11}(d, d, R) + \frac{4\pi c}{\alpha^3} \right) \right\} \quad A6-3 \end{aligned}$$

If we denote

$$V(\xi_1, \eta_1) = \int \frac{e^{-dR\xi_2}}{\pi_{12}} d\tau_2$$

where $V(\xi_1, \eta_1)$

was given explicitly in Appendix V, we

can write

$$\begin{aligned} \int \frac{x^2 d\tau_2 d\tau_3}{\pi_{12}} &= \left[\frac{\pi}{d^3} (c^2 + 1) + \frac{4\pi c}{R} f_{11}(d, d, R) \right] 2\pi \left(\frac{f_{10}(d, d, \pi_{12})}{\pi_{12}} + \frac{f_{10}(d, d, \pi_{13})}{\pi_{13}} \right) \\ &+ \left[\frac{4\pi}{R} (1 + c^2) f_{11}(d, d, R) + \frac{4\pi c}{d^3} \right] V(\xi_2, \eta_2). \end{aligned} \quad A6-4$$