THE SYSTEM OF THE HELIUM ATOM AND A POSITRON

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ABSTRACT

The possibility of the formation of a bound state for the system of the Hydrogen atom and a positron and also for the system of a Helium atom and a positron is investigated theoretically. The theory of the Variational method for determining upper bounds for the energy of a physical system is developed. The Variational method is applied to several trial wave functions for the system of a Hydrogen atom and a positron. An equivalent one dimensional problem is formulated for the system of a Hydrogen atom and a positron. The solution of this problem determines the best form of wave function for the system, such that the energy of the system is a minimum. The results of the calculations do not indicate the binding of the system of a Hydrogen atom and a positron. The element of volume for the four particle system of a Helium atom and a positron is derived. The Variational method is applied to a three parameter and a four parameter trial wave function for the system of a Helium atom and a positron. The results do not show that the system forms a bound state, but are inconclusive since the Variational method provides only an upper bound for the energy of a system. Several improvements in the wave function for the system of a Helium atom and a positron are suggested.

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CHAPTER I

INTRODUCTION

The experimental discovery of the positive electron or positron and subsequent annihilation experiments verified the earlier prediction of the existence of the positron by Dirac. These experiments lent agreement to the view that the positron and electron are anti-particles in the sense of the Dirac theory, and thus can annihilate each other.

However before annihilation, the electron and positron may form a quasi-stable bound system, similar to the Hydrogen atom. The possible existence of this system was suggested by Mohorovicic[1]. Ruark[2] introduced the name of positronium atom for the system. Wheeler[3] investigated other systems theoretically, and found that the negative Chlorine ion and positron form a bound system. Hylleraas[4] found that two electrons and a positron form a bound state with a binding energy of .203 ev. Hylleraas and Ore[5] investigated the system consisting of two electrons and two positrons, and found this system to have a binding energy of .llev. Ore[6] investigated the system of the negative Hydrogen ion and positron, and obtained a value of .07 ev for the binding energy.

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1 S.Mohorovicic, Astron. Nacht. 253, 94, (1934).
2 A.E.Ruark, Phys.Rev. 68, 278, (1945).
3 J.A.Wheeler, Ann. N.Y.Acad. Sci. 48, 219, (1946) .
4 E.Hylleraas, Phys.Rev. 71, 491, (1947).
5 E.Hylleraas and A.Ore, Phys. Rev. 71, 493, (1947).
6 A.Ore , Phys. Rev. 83, 665, (1951) .

If this upper bound for the energy is very close to the energy of the system, it is doubtful whether this system could exist in nature, since the value obtained by Ore is very near thermal energies. Darewych[7] has found the binding energy of the system of the negative Hydrogen ion and positron to be .21 ev ,and has calculated the annihilation rate for positrons forming such a compound.

In the ground state of the positronium atom, the spins of the electron and positron may be parallel or anti-parallel. Positronium with the spins antiparallel is called singlet or parapositronium, and positronium with the spins parallel is called triplet or orthopositronium. It can be shown[8] that for lowest order, annihilation from the singlet state results in the emission of two photons, and annihilation from the triplet state is accompanied by the emission of three photons. The mean life of singlet positronium is $\sim 1.25 \times 10^{-10}$ sec. and the mean life of triplet positronium is $\sim 1.4 \times 10^{-7}$ sec.[8]

Two physical systems, the Hydrogen atom and positron and the Helium atom and positron, will be investigated in this thesis in order to determine if either forms a bound state. The three particle system ,consisting of a Hydrogen atom and a positron, is of interest because only one electron serves as a screen for the repulsive force between the nucleus and the positron.

7 G.Darewych, Thesis:The Interaction between a Positron and H^-. University of Manitoba, 1961.

8 S.DeBenedetti and H.C.Corben, Ann.Rev.of Nuclear Sci. 4, 196, (1954).

Thus if it can be shown that the Hydrogen atom and positron form a bound state, one could then have some measure of confidence that the system consisting of the Helium atom and the positron would form a bound state. This three particle system will also serve to familiarize the investigator with the techniques involved in the solution of this type of problem before passing on to the more complicated four particle problem, that is, the system of the Helium atom and the positron.

Recent experiments have been performed by Paul and Graham[9] and by Wackerle and Stump[10] on the annihilation of positrons in Helium. Certain discrepancies exist between the experimental results and their current interpretation. Paul and Graham suggested that the time spectrum for positron decay in Helium could be interpreted as the result of three components. These three components were due to the annihilation of singlet and of triplet positronium formed in the Helium, and the annihilation of positrons in flight. They found that the long -lived component had a mean life of 9.1×10^{-8} sec. They interpreted this as due to triplet positronium. However the mean life of triplet positronium is $\sim 1.5 \times 10^{-7}$ sec. The intermediate component was found to have a mean life of $\sim 1.83 \times 10^{-9}$ sec. This, they interpreted as due to the annihilation of free positrons. However, Dirac theory predicts a mean life of $\sim 3 \times 10^{-9}$ sec. The short lived component was found to have

9 D.A.L.Paul and R.L.Graham, Phys. Rev. 106, 16, (1957)
10 J.Wackerle and R.Stump, Phys. Rev. 106, 18, (1957)

a mean life of $\sim 2 \times 10^{-10}$ sec. They interpreted this as due to the annihilation of singlet positronium. The mean life of singlet positronium is 1.25×10^{-10} sec.

Ferrell[11] attempted to explain the existence of the long lived component in Helium by means of his "Bubble Theory". He showed that it was energetically favourable for positronium to be in a region of lower than average Helium density. He postulated that once in this region, the positronium atom would push away other Helium atoms and create a "bubble" in the liquid. The pick-off of electrons from the nearby Helium atoms would then be reduced, and thus the mean life would be increased. Ferrell also proposed an experimental verification of the theory by the measurement of the mean life of triplet positronium in liquid Helium near the critical point. At this point, the calculated mean life is $\frac{1}{3}$ the mean life at 4.2°K. Daniel and Stump[12] performed this experimental test of the theory and found that the results did not agree with the predictions of Ferrell's theory.

The suggestion is put forward in this thesis that the experimental results of Paul and Graham, and of Wackerle and Stump could be explained if it could be shown that the Helium atom and positron form a bound system. If the Helium atom and positron do indeed form a bound system, then the mean electron density near the position of the positron would be different from that found in positronium. This would

11 R.Ferrell , Phys. Rev. 108 , 167 , (1957).
12 T.B.Daniel and R.Stump, Phys.Rev. 115 , 1599 , (1959).

lead to different annihilation rates and mean lives, which might correspond to the experimental results. Darewych[7] has shown that the mean life for two photon annihilation of positrons in the ground state of the system of the negative Hydrogen ion and positron differs from the mean life of singlet positronium.

In chapter II, the Variational method for determining upper bounds for the energy of a system will be discussed. The system consisting of a Hydrogen atom and a positron will be investigated in chapter III. Chapter IV will deal with the possible binding of the system consisting of the Helium atom and the positron. The conclusions reached will be reported in chapter V.

CHAPTER II

THE VARIATIONAL METHOD

The applicability of the Variational method to the problem of determining whether the systems, consisting of the Helium atom and positron and of the Hydrogen atom and positron, respectively, form a bound state, shall be discussed. The theory of the Variational method for determining an upper bound for the energy of the ground state of a system shall be developed. It shall be shown how the method may be extended to determine upper bounds for the energy for excited states of a physical system. Using a trial wave function whose initial form is unspecified, the Variational method shall be applied and a form for the function shall be obtained such that the upper bound for the energy shall be a minimum.

The Variational method[1] provides a powerful means for determining an upper bound for the energy of a system in a given state. Kinoshita[2], using a trial wave function containing 39 parameters, obtained the ground state energy of the Helium atom which was within .0003% of the value obtained experimentally. The effectiveness of the method depends upon choosing a trial wave function which is a close approximation to the wave function describing the state of the physical system.

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1 L.I.Schiff, Quantum Mechanics, 2nd Ed. p.171 .
2 T.Kinoshita, Phys.Rev. 105, 1490, (1957).

The form of wave function for the ground state is known exactly for the Hydrogen atom and to a reasonable degree of approximation for the Helium atom. Trial wave functions may be chosen for the system of Hydrogen atom and positron and for the system of Helium atom and positron of similar form to the Hydrogen atom wave function and Helium atom wave function, respectively, assuming that the states of the systems under consideration are not greatly changed by the presence of the positron.

The theory of the Variational method for the ground state of a physical system shall now be developed. The physical system is assumed to have a lowest energy state.

In Quantum Mechanics, it is postulated that a correspondence between the states of a physical system and the elements of a Hilbert space exists. A correspondence between the dynamical variables for a physical system and linear operators in the Hilbert space is also postulated.

If φ, ψ are elements of the Hilbert space and if α is a linear operator in the Hilbert space, then the inner product of φ with $\alpha\psi$ is defined as,

$$(\varphi, \alpha\psi) = (\alpha\psi, \varphi)^* \qquad (2\text{-}1)$$

If the Hilbert space is a function space, the inner product of φ with $\alpha\psi$ is defined to be

$$(\varphi, \alpha\psi) = \int \varphi^* \alpha \psi \, d\tau \qquad (2\text{-}2)$$

Now α^* is defined to be the Hermitian adjoint of α if,

$$(\alpha^*\varphi, \psi) = (\varphi, \alpha\psi) \tag{2-3}$$

If $\alpha = \alpha^*$, α is said to be an Hermitian operator.

Let H be the quantum mechanical Hamiltonian operator. H is assumed to be an Hermitian operator. Let ψ_n be a state function for the system.

Consider the eigenvalue equation

$$H\psi_n = E_n\psi_n \tag{2-4}$$

ψ_n is said to be an eigenfunction of the Hamiltonian operator H ,belonging to the eigenvalue E_n ,the energy of the nth state.

Since H is Hermitian, the set of eigenfunctions of H , $\{\psi_n\}$, form a complete set. Hence any state ψ of the system may be expanded as a linear combination of the eigenfunctions of H .

Then,

$$\psi = \sum_n c_n\psi_n \tag{2-5}$$

where c_n are constants.

It can be shown that the eigenvalues of an Hermitian operator are real, and that the eigenfunctions of an Hermitian operator belonging to different eigenvalues are orthogonal, in the sense of the inner product of the two eigenfunctions being equal to zero.

That is, from equation (2-4) we have

$$H\psi_n = E_n \psi_n$$
$$H\psi_s = E_s \psi_n \qquad (2\text{-}6)$$

then $$(\psi_n, \psi_s) = \delta_{ns} \qquad (2\text{-}7)$$

assuming $\{\psi_i\}$ normalized to unity.

Define the expected average of the Hamiltonian operator H for a state ψ to be,

$$\langle H \rangle \equiv \frac{(\psi, H\psi)}{(\psi, \psi)} \qquad (2\text{-}8)$$

if ψ not normalized.

From (2-5), (2-8) becomes,

$$\langle H \rangle = \frac{\left(\sum_n c_n \psi_n, \sum_s c_s H\psi_s\right)}{\left(\sum_n c_n \psi_n, \sum_s c_s \psi_s\right)}$$
$$= \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \qquad (2\text{-}9)$$

Let E_0 be the lowest energy level or the ground state energy of the system, and E_1, E_2, etc., be the energies of successive excited states,

i.e.,
$$E_0 \leq E_1 \leq E_2 \cdots \qquad (2\text{-}10)$$

Therefore, from (2-9) and (2-10),

$$\langle H \rangle = \frac{E_0|c_0|^2 + E_1|c_1|^2 + \cdots}{|c_0|^2 + |c_1|^2 + \cdots}$$

$$\therefore \quad \langle H \rangle \geq \frac{E_0|c_0|^2 + E_0|c_1|^2 + \cdots}{|c_0|^2 + |c_1|^2 + \cdots} \qquad (2\text{-}11a)$$

Hence,

$$\langle H \rangle = \frac{(\psi, H\psi)}{(\psi, \psi)} \geq E_0 \qquad (2\text{-}11b)$$

This inequality, (2-11b), forms the basis for the Variational method and enables one to find an upper bound for the ground state energy by calculating the expected average of H.

The expression for $\langle H \rangle$ is calculated, using a trial wave function $\psi(a, b, \ldots, x, y, \ldots)$ where a, b, etc. are parameters and x, y, etc. are coordinates. The $\langle H \rangle$ is a function of these parameters. The values of these parameters are then varied so as to obtain a minimum value for $\langle H \rangle$. Hence the best value for an upper bound for the ground state energy is obtained, for the particular form of trial wave function selected.

If the ground state wave function ψ_0 is known precisely, then from (2-4),

$$H\psi_0 = E_0\psi_0 \tag{2-12}$$

and from (2-11b),

$$\frac{(\psi_0, H\psi_0)}{(\psi_0, \psi_0)} = E_0 \tag{2-13}$$

If the trial wave function ψ represents a linear combination of ground state and excited states of the system, then from (2-11b),

$$\frac{(\psi, H\psi)}{(\psi, \psi)} \geq E_0$$

Hence the effectiveness of the method depends upon choosing the trial wave function ψ to represent the ground state of the system as nearly as possible.

It will now be shown how the Variational method may be extended to obtain an upper bound for the energy of an excited state of the physical system.

Let E_1 be the energy of the first excited state of the system. If ψ_0 represents the ground state of the system, a wave function φ is chosen such that,

$$(\psi_0, \varphi) = 0 \tag{2-14}$$

Then from (2-11a) and (2-5),

$$\frac{(\varphi, H\varphi)}{(\varphi,\varphi)} = \frac{E_1|b_1|^2 + E_2|b_2|^2 + \cdots}{|b_1|^2 + |b_2|^2 + \cdots}$$

Hence from (2-10),

$$\frac{(\varphi, H\varphi)}{(\varphi,\varphi)} \geqslant E_1 \qquad (2\text{-}15)$$

Hence an upper bound is found for the energy of the first excited state by calculating the expected average of H, for the state φ. Clearly the method may be extended to higher excited states of the system.

It will now be shown how the Variational method may be applied to trial wave functions whose form is not initially specified, and the solution will determine the form of the wave function such that the upper bound for the energy will be a minimum.

Consider a trial wave function ψ for the system with Hamiltonian H, where $\psi = f(x,y,..,a,b,..)g(z)$ and $x, y,..$ are coordinates and $a, b,...$ are parameters for variation.[3] The form of the function $f(x,y,..a,b,..)$ is specified, while that of $g(z)$ is unspecified.

The method shall be illustrated for a one particle system. The extension to a many particle system will be clear. The Hamiltonian operator H for the system may be written,

$$H = -\frac{1}{k}\nabla^2 + V \qquad (2\text{-}16)$$

where $k = \frac{2m}{\hbar^2}$, m is the mass of the particle, ∇^2 is the Laplacian operator, and V is the potential energy.

3 Note that $x, y, ..., z$ need not be Cartesian coordinates.

Now consider the inner product $(\psi, H\psi)$, then from (2-16)

$$(\psi, H\psi) = \int \left[-\tfrac{1}{K}\psi\nabla^2\psi + V\psi^2 \right] d\tau \qquad (2\text{-}17)$$

But
$$\nabla\cdot\psi\nabla\psi = (\nabla\psi)^2 + \psi\nabla^2\psi \qquad (2\text{-}18)$$

Then by the Divergence Theorem,

$$\int_{\text{SPHERE}} \nabla\cdot\psi\nabla\psi \, d\tau = \int_{\text{SPHERE}} \psi\nabla\psi\cdot\underline{n}\, dS = 0 \qquad (2\text{-}19)$$

The right hand side of (2-19) equals zero for quadratically integrable functions as the radius of the sphere $\rightarrow \infty$.

Then from (2-18) and (2-19),

$$\int -\psi\nabla^2\psi \, d\tau = \int (\nabla\psi)^2 \, d\tau \qquad (2\text{-}20)$$

Hence the inner product $(\psi, H\psi)$ may be written, from (2-20),

$$(\psi, H\psi) = \int \left[\tfrac{1}{K}(\nabla\psi)^2 + V\psi^2 \right] d\tau \qquad (2\text{-}21)$$

where ∇ is the gradient operator.

Consider the expected average of the Hamiltonian H for the state $\psi = \mathcal{L}(x, y, .. a, b..)\, q(z)$, with ψ real.

$$\langle H \rangle = \frac{\int \psi H \psi \, d\tau_1 d\tau_2}{\int \psi^2 d\tau_1 d\tau_2} \qquad (2\text{-}22)$$

where $d\tau_1 \sim dx\,dy..$ and $d\tau_2 \sim dz$. Integrating over $d\tau_1$, (2-22) becomes[4]

$$\langle H \rangle = \frac{\int \mathcal{L}(q', q, z)\, d\tau_2}{\int F(z)\, q^2 \, d\tau_2} = \frac{I_1}{I_2} \qquad (2\text{-}23)$$

Since $\psi H \psi$ contains $(\nabla\psi)^2$, only first derivatives of $q(z)$ occur.

We wish to minimize the numerator of (2-23), subject to the condition that the denominator be a constant. Hence (2-23) is a conditioned integral.

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4 See footnote on page 12a.

In the simple case considered here, F , in the denominator of (2-23), is a constant. It is clear however, that in a more general case, the limits of integration for $d\tau_1$ would involve z and the element of volume would contain a function of $(x, y, \ldots, z)$. This would yield, on integration over $d\tau_1$, a function $F(z)$ in the denominator of (2-23).

For an extremum of the numerator of (2-23), the first variation of I_1 must vanish.

Hence, from (2-23),

$$\delta I_1 = 0 \qquad (2\text{-}24a)$$

But $$I_2 = \text{CONSTANT}$$

Therefore, $$\delta I_2 = 0 \qquad (2\text{-}24b)$$

since the variation of a constant vanishes.

Then, from (2-24a) and (2-24b),

$$\delta I = \delta I_1 - \lambda\,\delta I_2 = 0 \qquad (2\text{-}25a)$$

where λ is an undetermined multiplier. The first variation of I vanishing, subject to the condition that the first variation of I_2 vanish, implies that the first variation of I_1 will vanish.

Hence, $$0 = \delta \int \left[\mathcal{L} - \lambda F q^2 \right] d\tau_2 \qquad (2\text{-}25b)$$

This is achieved if the Euler-Lagrange equation is satisfied. The Euler-Lagrange equation for (2-25b) yields,

$$0 = \frac{d}{dz}\left(\frac{\partial \mathcal{L}}{\partial q'}\right) - \frac{\partial \mathcal{L}}{\partial q} + 2\lambda F q \qquad (2\text{-}26)$$

Equation (2-26) may be written as,

$$q'' + A q' + (\lambda - B) q = 0 \qquad (2\text{-}27a)$$

Let $$q(z) = f(z)\,\varphi(z) \qquad (2\text{-}27b)$$

and $$\frac{2 f'(z)}{f(z)} + A = 0 \qquad (2\text{-}27c)$$

Then equation (2-27a) becomes,

$$\varphi'' + (\lambda - \tilde{V})\varphi = 0 \qquad (2\text{-}28a)$$

and $$\tilde{V} = \frac{1}{2}\frac{dA}{dz} + \frac{A^2}{4} + B \qquad (2\text{-}28b)$$

As can be seen from the forms of (2-28a) and (2-28b), the problem has now been reduced to an equivalent one dimensional problem.

Equation (2-28a) represents the Schroedinger equation for the problem, and (2-28b) represents an effective potential for the problem.

It will now be shown that λ in (2-28a) corresponds to the energy for the original problem.

Consider the expected average of H ; then from (2-21),

$$(\psi, H\psi) = \int \left[\frac{1}{k}(\nabla\psi)^2 + V\psi^2 \right] d\tau$$

For a minimum of the energy, it is required that,

$$\delta \int \psi H \psi \, d\tau = 0$$

subject to the condition that,

$$\int \psi^2 d\tau = \text{CONSTANT}$$

Hence we have a conditioned integral, and as in (2-25b),

$$0 = \delta \int \left[\frac{1}{k}(\nabla\psi)^2 + V\psi^2 - \lambda\psi^2 \right] d\tau = \delta \int \mathcal{L} \, d\tau \qquad (2\text{-}29)$$

This condition is achieved if the Euler-Lagrange equation is satisfied. The Euler-Lagrange equation for the problem is,

$$0 = \frac{\partial}{\partial x}\left(\frac{\partial \mathcal{L}}{\partial(\frac{\partial\psi}{\partial x})} \right) + \frac{\partial}{\partial y}\left(\frac{\partial \mathcal{L}}{\partial(\frac{\partial\psi}{\partial y})} \right) + \frac{\partial}{\partial z}\left(\frac{\partial \mathcal{L}}{\partial(\frac{\partial\psi}{\partial z})} \right) - \frac{\partial \mathcal{L}}{\partial \psi} \qquad (2\text{-}30)$$

Then (2-30) yields

$$\frac{1}{k} \nabla^2\psi + (\lambda - V)\psi = 0 \qquad (2\text{-}31)$$

It is seen that (2-31) has the form of the Schroedinger equation and λ corresponds to the energy. Hence λ in (2-28a) corresponds to the energy. Equation (2-28a) may then be solved for the equivalent one dimensional problem, using a numerical integration procedure.

The dependence of the nodes of the integral curve of (2-28a) upon the energy will now be investigated. $\varphi(\zeta)$ the solution of (2-28a), must be quadratically integrable, so that an eigenfunction of the energy vanishes at $\zeta = +\infty$. Equation (2-28a) may be solved explicitly for small ζ to obtain the behavior of $\varphi(\zeta)$ for small ζ .

Consider now (2-28a),

$$\frac{1}{\varphi}\varphi'' = -(\lambda - \tilde{V})$$

Suppose λ is less than the lowest eigenvalue. Then the $\varphi(\zeta)$ curve will not cross the ζ axis as in Figure 1.

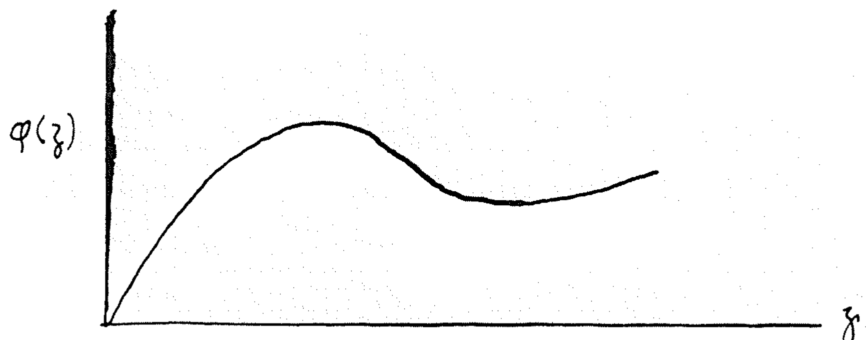

Figure 1

$\varphi(\zeta)$ for λ less than the eigenvalue.

As the energy λ is increased, the ratio $\frac{1}{\varphi}\varphi''$ becomes more negative, from (2-28a), and when λ equals the lowest eigenvalue, the $\varphi(\zeta)$ curve will approach the ζ axis asymptotically. As the energy λ is further increased, the ratio $\frac{1}{\varphi}\varphi''$ becomes more negative, and the $\varphi(\zeta)$ curve will cross the axis. The $\varphi(\zeta)$ curve will have a node which will move towards the left with increasing λ , as in Figure 2.

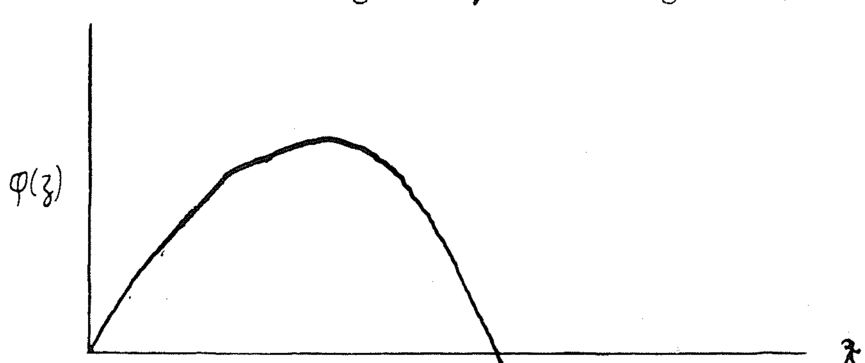

Figure 2

When λ equals the energy of the first excited level, the $\varphi(\zeta)$ curve will have a node in the finite region of the ζ axis, and will approach the axis asyptotically for large ζ .

An upper bound for the ground state energy may be obtained by choosing an energy greater than the eigenvalue for this particular problem. Then the $\varphi(\zeta)$ curve will cross the ζ axis in the finite region. The parameters are then varied until the distance of the node of the integral curve $\varphi(\zeta)$ from the origin is a minimum. Since decreasing the energy λ has the effect of moving the node away from the origin, the closeness of the node to the origin, for a given value of the energy, is taken as a qualitative measure of the amount by which the chosen energy lies above the lowest eigenvalue. Thus by varying the parameters to move the node closer to the origin, one would in effect be improving the effective potential in the sense of depressing the corresponding lowest eigenvalue. The energy is decreased until the integral curve has the proper asymptotic behavior. This energy is the eigenvalue for the new problem whose effective potential contains the varied values of the parameters. This gives an upper bound for the energy, but it is possible to improve upon this result by choosing better values for the parameters with this lower value for the enorgy. The parameters are varied again to improve the effective potential and thus depress the corresponding lowest eigenvalue. With this improved effective potential, the energy, obtained from the previous calculation, is greater than the eigenvalue which is required to insure the proper asymptotic behavior of the integral curve. Hence the $\varphi(\zeta)$ curve will cross the ζ axis in the finite region. The parameters are then varied so that the node is at a minimum distance from the origin. Using the best values of the parameters obtained by this procedure, the energy is decreased until the eigenvalue is reached and the $\varphi(\zeta)$ curve has the proper asymptotic behavior. This procedure may be repeated until a lowest upper bound for the energy for the type of trial wave function used is obtained. In this way, an upper bound for the energy of the ground state of the physical system is obtained from the equivalent one dimensional problem.

CHAPTER III

THE SYSTEM OF HYDROGEN ATOM AND POSITRON

In this chapter the Variational method will be applied to the problem of the possible binding of the positron to the Hydrogen atom, a three particle problem. The geometry of the three particle problem will first be examined. An element of volume for this configuration space, which will allow the necessary integrations to be performed, will be derived. The expression for $\langle H \rangle$ for several trial wave functions for the system of Hydrogen atom and positron will be determined. The Variational method will be applied to a trial wave function whose initial form is unspecified. This procedure will provide a form for the wave function which will correspond to a lowest upper bound for the energy of the ground state of the system of Hydrogen atom and positron.

Consider the configuration space for the three particle system. Let the origin for the coordinate system be at the position of the nucleus. Let r_1, θ_2, φ_1 be the polar coordinates of the electron with respect to some arbitrary initial direction and plane. Let r_2 , θ_1 , φ_2 be the polar coordinates of the positron with respect to the vector $\underline{r}_1$ as polar axis and some arbitrary initial plane, as in Fig.3 .

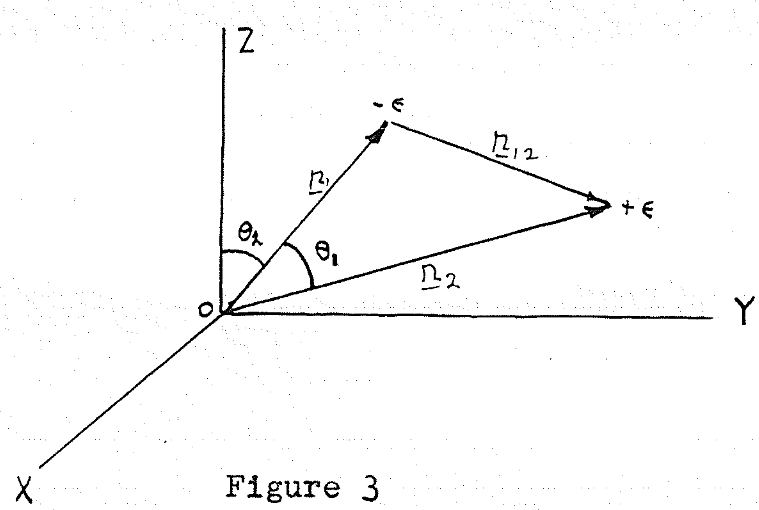

Figure 3

Coordinate system for Hydrogen atom and positron.

It is desirable to have a configuration space for the system with the three inter-particle distances as coordinates. Define a vector $\underline{r}_{12}$, as the electron-positron distance.

$$\underline{r}_{12} = \underline{r}_2 - \underline{r}_1 \tag{3-1}$$

Then,

$$r_{12}^2 = |\underline{r}_2 - \underline{r}_1|^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \mu_1 \tag{3-2}$$

where,

$$\mu_1 = \cos\theta_1 \qquad \mu_2 = \cos\theta_2$$

The element of volume $d\tau$ may be written as,

$$d\tau = r_1^2 \, dr_1 \, d\mu_1 \, d\varphi_1 \, r_2^2 \, dr_2 \, d\mu_2 \, d\varphi_2 \tag{3-3}$$

Equation (3-3) may be transformed to give an element of volume in the desired coordinates.

Then,

$$d\tau = r_1^2 r_2^2 \, J\left(\frac{r_1\, r_2\, \mu_1\, \mu_2\, \varphi_1\, \varphi_2}{r_1\, r_2\, r_{12}\, \mu_2\, \varphi_1\, \varphi_2}\right) dr_1 \, dr_2 \, dr_{12} \, d\mu_2 \, d\varphi_1 \, d\varphi_2 \tag{3-4}$$

where $J\left(\frac{r_1\, r_2\, \mu_1\, \mu_2\, \varphi_1\, \varphi_2}{r_1\, r_2\, r_{12}\, \mu_2\, \varphi_1\, \varphi_2}\right)$ is the Jacobian of the transformation.

Hence from (3-2) and (3-4),

$$d\tau = r_1 r_2 r_{12} \, dr_1 \, dr_2 \, dr_{12} \, d\mu_2 \, d\varphi_1 \, d\varphi_2 \tag{3-5a}$$

with the limits,

$$\begin{array}{ccc} 0 \le r_1 \le \infty & & 0 \le r_1 \le \infty \\ 0 \le r_{12} \le \infty & & 0 \le r_2 \le \infty \\ |r_1 - r_{12}| \le r_2 \le r_1 + r_{12} & \text{or} & |r_1 - r_2| \le r_{12} \le r_1 + r_2 \\ -1 \le \mu_2 \le 1 & & -1 \le \mu_2 \le 1 \\ 0 \le \varphi_1 \le 2\pi & & 0 \le \varphi_1 \le 2\pi \\ 0 \le \varphi_2 \le 2\pi & & 0 \le \varphi_2 \le 2\pi \end{array} \qquad (3\text{-}5b)$$

The expression given by (3-5a) is the desired element of volume in the configuration space.

The Laplacian operating on the coordinates of particle 1 is, for $\psi = f(r_1, r_2, r_{12})$,

$$\nabla_1^2 = \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \left(\frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\right)\frac{\partial^2}{\partial r_1 \partial r_{12}} \qquad (3\text{-}6)$$

and for particle 2 is,

$$\nabla_2^2 = \frac{\partial^2}{\partial r_2^2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}}\right)\frac{\partial^2}{\partial r_2 \partial r_{12}} \qquad (3\text{-}7)$$

and the expression for the square of the gradient operating on the coordinates of particle 1 is,

$$(\nabla_1 f)^2 = \left(\frac{\partial f}{\partial r_1}\right)^2 + \left(\frac{\partial f}{\partial r_{12}}\right)^2 + \left(\frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\right)\left(\frac{\partial f}{\partial r_1}\right)\left(\frac{\partial f}{\partial r_{12}}\right) \qquad (3\text{-}8)$$

and for particle 2, the expression is,

$$(\nabla_2 f)^2 = \left(\frac{\partial f}{\partial r_2}\right)^2 + \left(\frac{\partial f}{\partial r_{12}}\right)^2 + \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}}\right)\left(\frac{\partial f}{\partial r_2}\right)\left(\frac{\partial f}{\partial r_{12}}\right) \qquad (3\text{-}9)$$

An outline of the derivations of (3-6), (3-7),(3-8),(3-9) is given in Appendix A.

Consider the Hamiltonian operator for the system of Hydrogen atom and positron. This is a three particle system. Since the mass of the nucleus is $\sim$ 1800 electron masses, the motion of the nucleus is neglected and is considered at rest.

Let $\underline{r}_1$ be the position vector of the orbital electron with charge $-\epsilon$, and let $\underline{r}_2$ be the position vector of the positron with charge $+\epsilon$, as in Fig.3. The potential energy terms of the Hamiltonian are due to the Coulomb interaction between pairs of particles.

Then, by (2-16), the Hamiltonian operator for the ground state of the system becomes,

$$H = -\frac{1}{K}\nabla_1^2 - \frac{1}{K}\nabla_2^2 - \frac{\epsilon^2}{r_1} + \frac{\epsilon^2}{r_2} - \frac{\epsilon^2}{r_{12}} \qquad (3\text{-}10)$$

where $K = \frac{2m}{\hbar^2}$; m is the mass of the electron or positron

$\hbar = \frac{\text{PLANCK'S CONSTANT}}{2\pi}$.

Then from (2-17), (2-21) and (3-10), the inner product $(\psi, H\psi)$ for the system may be written as,

$$(\psi, H\psi) = \int\left[-\frac{1}{K}\psi\nabla_1^2\psi - \frac{1}{K}\psi\nabla_2^2\psi - \frac{\epsilon^2\psi^2}{r_1} + \frac{\epsilon^2\psi^2}{r_2} - \frac{\epsilon^2\psi^2}{r_{12}}\right]d\tau \qquad (3\text{-}11)$$

or $$(\psi, H\psi) = \int\left[\frac{1}{K}(\nabla_1\psi)^2 + \frac{1}{K}(\nabla_2\psi)^2 - \frac{\epsilon^2\psi^2}{r_1} + \frac{\epsilon^2\psi^2}{r_2} - \frac{\epsilon^2\psi^2}{r_{12}}\right]d\tau \qquad (3\text{-}12).$$

Consider trial wave functions for the system of Hydrogen atom and positron. It is assumed that the ground state is a state of zero angular momentum. A function of the inter-particle distances only will now be shown to be an eigenfunction of the orbital angular momentum belonging to the eigenvalue zero.

Let $\underline{L}_1 + \underline{L}_2$ be the orbital angular momentum operator for the two particles, where

$$\underline{L}_1 + \underline{L}_2 = -i\hbar(\underline{r}_1 \times \nabla_1 + \underline{r}_2 \times \nabla_2) \qquad (3\text{-}13a)$$

Let $f(r_1, r_2, r_{12})$ be a function of the inter-particle distances only.

Let $f_1 = \frac{\partial f}{\partial r_1}$ $\quad f_2 = \frac{\partial f}{\partial r_2}$ $\quad f_{12} = \frac{\partial f}{\partial r_{12}}$

$$\mathcal{L}_1 f = -i\hbar\left\{ \underline{r}_1 \times \left[f_1 \nabla_1 r_1 + f_2 \nabla_1 r_2 + f_{12} \nabla_1 r_{12} \right]\right\} = i\hbar\, \underline{r}_1 \times \frac{(\underline{r}_2 - \underline{r}_1)}{r_{12}} f_{12}$$

$$\mathcal{L}_2 f = -i\hbar\left\{ \underline{r}_2 \times \left[f_1 \nabla_2 r_1 + f_2 \nabla_2 r_2 + f_{12} \nabla_2 r_{12} \right]\right\} = -i\hbar\, \underline{r}_2 \times \frac{(\underline{r}_2 - \underline{r}_1)}{r_{12}} f_{12}$$

$$\therefore (\mathcal{L}_1 + \mathcal{L}_2) f = -i\hbar\left[(\underline{r}_2 - \underline{r}_1) \times \frac{(\underline{r}_2 - \underline{r}_1)}{r_{12}}\right] f_{12} = 0$$

The extension to many particles is clear.

A function of the inter-particle distances only is chosen for the ground state trial wave function, since this function will be an eigenfunction for a state with zero orbital angular momentum.

The state of the Hydrogen atom is assumed to be not greatly disturbed by the presence of the positron. This is a reasonable assumption, since, if the system is bound, it is expected that on the average the positron will be at a large distance from the nucleus. Hence a Hydrogen or exponential type wave function for the nuclear-electron coordinate r_1 is chosen. If the positron and Hydrogen atom form a bound system, the electron and positron will form a system which does not differ greatly from the positronium atom. Hence a positronium type wave function is chosen for the electron-positron distance. This also is an exponential type function.

Semi-classically, if the Hydrogen atom and positron do indeed form a bound system, it may be expected that on the average the positron will be at a large distance from the nucleus, since it is repelled by it. Hence a wave function, which will satisfy this condition, must be chosen.

Quantum mechanically, the probability that the positron is at the position of the nucleus must be zero. This is achieved if a power of the positron-nuclear distance or an exponential type function is chosen. Hence trial wave functions for the system are chosen to be,

$$\psi = r_2 e^{-k(r_1 + \alpha r_{12})} \tag{3-14}$$

$$\psi = r_2^2 e^{-k(r_1 + \alpha r_{12})} \tag{3-15}$$

$$\psi = e^{-k(r_1 + \alpha r_{12} - \beta r_2)} \tag{3-16}$$

The Variational method is now applied to the trial wave function (3-14), $\psi = r_2 e^{-k(r_1+\alpha r_{12})}$.

By (2-8), the expected average of H is,

$$\langle H \rangle = \frac{(\psi, H\psi)}{(\psi, \psi)} \tag{3-17}$$

Then by (2-22), (3-11) and (3-14),

$$\langle H \rangle = \frac{\int \frac{1}{K}\left[(-k^2 - 2k^2\alpha^2)\psi^2 + \frac{2k}{r_1}\psi^2 - \frac{2\psi^2}{r_2^2} + \frac{5k\alpha}{r_{12}}\psi^2 - \frac{k^2\alpha r_1}{r_{12}}\psi^2\right] d\tau}{\int \psi^2 d\tau}$$
$$+ \frac{\int \frac{1}{K}\left[\frac{k^2\alpha r_2^2}{r_1 r_{12}}\psi^2 - \frac{k^2\alpha r_{12}}{r_1}\psi^2 - \frac{k\alpha r_1^2}{r_2^2 r_{12}}\psi^2 + \frac{k\alpha r_{12}}{r_2^2}\psi^2\right] d\tau}{\int \psi^2 d\tau} + \frac{\int \epsilon^2\left[-\frac{\psi^2}{r_1} - \frac{\psi^2}{r_{12}} + \frac{\psi^2}{r_2}\right] d\tau}{\int \psi^2 d\tau} \tag{3-18}$$

where $d\tau$ is given by (3-5a).

An outline for the method for performing the integrations is found in Appendix B, and the integrals of (3-18) explicitly evaluated are listed in Appendix C.

Equation (3-18) may be written as,

$$\langle H \rangle = \frac{1}{K} k^2 A(\alpha) + \epsilon^2 B(\alpha) \tag{3-19}$$

The $\langle H \rangle$ is minimized with respect to k by setting $\frac{\partial \langle H \rangle}{\partial k} = 0$.

Then,

$$\langle H \rangle = -\frac{B^2}{4A} K\epsilon^4 \tag{3-20a}$$

or
$$\langle H \rangle = -\frac{(6\alpha^6 + 18\alpha^5 + 21\alpha^4 + 19\alpha^3 + 21\alpha^2 + 18\alpha + 6)^2}{48(1+\alpha^2)(1+\alpha)^6(6\alpha^4 + 4\alpha^2 + 3)} \tag{3-20b}$$

The $\langle H \rangle$, (3-20b) is a minimum for $\alpha = 0$.

Then,

$$\langle H \rangle = -\frac{1}{4} \kappa \epsilon^4$$

where $\kappa\epsilon^4$ is a unit of energy, and $\frac{\kappa\epsilon^4}{4}$ is the atomic unit of energy.

Similarly for $\psi = r_2^2 e^{-k(r_1+\alpha r_{12})}$ and $\psi = e^{-k(r_1+\alpha r_{12}-\beta r_2)}$ the minimum for $\langle H \rangle$ is found to be $-\frac{1}{4} \kappa\epsilon^4$.

The energy of the Hydrogen atom in the ground state is $-\frac{1}{4} \kappa\epsilon^4$. Since the binding energy of the Hydrogen atom is twice that of the positronium atom, the favourable mode of dissociation of the system is into Hydrogen atom and positron. Clearly the energy of the system of Hydrogen atom and positron must be less than that of the Hydrogen atom if the system is to form a bound state. Hence, with trial wave functions (3-14), (3-15) and (3-16), binding is not indicated for the system of Hydrogen atom and positron. This result is in agreement with that of Inokuti, Katsuura and Mimura[1], who have shown that binding is not indicated for the system, using a trial wave function of the form $\psi = r_2^m e^{-k(r_1+\alpha r_{12}+\beta r_2)}$.

The Variational method is now applied to a wave function whose form is not initially specified. A wave function of the form,

$$\psi = e^{-k_1 r_1 - k_2 r_{12}} \, g(r_2) \qquad (3\text{-}21)$$

is chosen.

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1 Inokuti, Katsuura, and Mimura, Prog. Theor. Phys. 23, 186, (1960).

Then from (3-13b) and (2-22), using the element of volume given by (3-5a), the $\langle H\rangle$ is, $\kappa_1 = 2k_1$, $\kappa_2 = 2k_2$

$$\langle H\rangle = \frac{\frac{1}{K}\int\left[\left(r_2 R + r_2^3 W - r_2 P + \kappa\epsilon^2 U\right)q^2 + r_2 U\left(\frac{dq}{dr_2}\right)^2 + \left(r_2^2 S + T\right)q\frac{dq}{dr_2}\right]dr_2}{\int r_2 U q^2\, dr_2} \qquad (3\text{-}22)$$

where,
$$R = 8\pi^2\int\frac{(\kappa_1^2+2\kappa_2^2)}{4}\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,r_1 r_{12}\,dr_1\,dr_{12} + 8\pi^2\int\frac{\kappa_1\kappa_2}{4}\,(r_1^2+r_{12}^2)\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,dr_1\,dr_{12}$$

$$W = 8\pi^2\int\frac{\kappa_1\kappa_2}{4}\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,dr_1\,dr_{12}$$

$$U = 8\pi^2\int r_1 r_{12}\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,dr_1\,dr_{12}$$

$$P = 8\pi^2\kappa\epsilon^2\int(r_1+r_{12})\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,dr_1\,dr_{12}$$

$$S = -8\pi^2\int\frac{\kappa_2}{2}\,r_1\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,dr_1\,dr_{12}$$

$$T = 8\pi^2\int\frac{\kappa_2}{2}\,(r_1 r_{12}^2 - r_1^3)\,e^{-\kappa_1 r_1-\kappa_2 r_{12}}\,dr_1\,dr_{12}$$

These are evaluated in Appendix D.

It is required that the numerator of (3-22) be a minimum subject to the condition that the denominator be a constant. This is a conditioned integral. Then, from the theory of chapter II, the Euler-Lagrange equation must be satisfied, and hence from (2-26) and (2-27a),

$$\frac{d^2q}{dr_2^2} + A\frac{dq}{dr_2} + (\lambda - B)q = 0 \qquad (3\text{-}23a)$$

where
$$A = \frac{1}{r_2} + \frac{1}{U}\frac{dU}{dr_2} \qquad (3\text{-}23b)$$

and
$$B = \frac{2r_2 R + \frac{dT}{dr_2} - 2r_2 S - r_2^2\frac{dS}{dr_2} - 2r_2^3 W - 2r_2 P + 2\kappa\epsilon^2 U}{2r_2 U} \qquad (3\text{-}23c)$$

Equation (3-23a) is transformed by (2-27b) and the condition (2-27c) is imposed. The result is an equivalent one dimensional problem with Schroedinger equation,

$$\frac{d^2\varphi}{dr_2^2} + (\lambda - \tilde{V})\varphi = 0 \qquad (3\text{-}24a)$$

and effective potential,

$$\tilde{V} = \frac{1}{2}\frac{dA}{dr_2} + \frac{1}{4}A^2 + B \tag{3-24b}$$

The effective potential is given by,

$$\tilde{V} = \frac{(K_1^2+2K_2^2)}{4} + \frac{1}{r_2} - \frac{1}{4r_2^2} - \frac{1}{4}\left[\frac{\left\{\frac{K_1(K_1^2+3K_2^2)}{I} - K_1K_2r_2\right\} + e^{-(K_1-K_2)r_2}\left\{-\frac{K_2(3K_1^2+K_2^2)}{I} - K_1K_2r_2\right\}}{\left\{K_1r_2^2 - \frac{4K_1K_2}{I}\right\} + e^{-(K_1-K_2)r_2}\left\{\frac{4K_1K_2}{I} + K_2r_2\right\}}\right]^2$$

$$+\frac{\frac{K_1(K_1^2+3K_2^2)}{I^2} + \left[-\frac{K_1K_2(3K_1^2+5K_2^2)}{I^2} - \frac{2(K_1-K_2)}{I}\right]r_2 + \left[\frac{K_1(K_1^2+K_2^2)}{I} - 1\right]r_2^2 + e^{-(K_1-K_2)r_2}\left[-\frac{K_2(3K_1^2+K_2^2)}{I^2} + \left\{\frac{K_1K_2(K_1^2+7K_2^2)}{I^2} + \frac{2(K_1-K_2)}{I}\right\}r_2 + \left(\frac{2K_2^3}{I}+1\right)r_2^2\right]}{2\left[\left(\frac{K_1r_2^2}{I} - \frac{4K_1K_2r_2}{I^2}\right) + e^{-(K_1-K_2)r_2}\left(\frac{K_2r_2^2}{I} + \frac{4K_1K_2r}{I^2}\right)\right]} \tag{3-25}$$

The differential equation (3-24a) cannot be solved explicitly, but may be solved by means of a numerical procedure. A difference equation is formed from the differential equation.

Let,

$$\varphi = \varphi_n$$

$$\varphi' = \frac{\varphi_n - \varphi_{n-1}}{\delta} \tag{3-26}$$

$$\varphi'' = \frac{\varphi_n' - \varphi_{n-1}'}{\delta}$$

From (3-24a) and (3-26), the difference equation becomes,

$$\varphi_{n+1} = \left[2 - (\lambda - \tilde{V})\delta^2\right]\varphi_n - \varphi_{n-1} \tag{3-27}$$

where δ is a small interval of r_2 .

Thus if two initial values of φ are known, successive values on the integral curve may be computed from (3-27). The two initial values of φ are obtained by solving (3-24a) in a series solution for small r_2 . The approximation of the effective potential $\tilde{V}$, given by (3-25) for small values of r_2 ,is found to be,

$$\tilde{V} \sim \frac{1}{r_2} \tag{3-28}$$

A series solution must be found for,

$$\varphi'' + (\lambda - \frac{1}{r_2})\varphi = 0 \tag{3-29}$$

for small r_2 .

Let a solution of (3-29) be,

$$\varphi = r_2^{\tau} \sum_0^{\infty} a_s r_2^{s} \qquad (3\text{-}30)$$

From (3-30), (3-29) becomes,

$$\sum_{s=0}^{\infty} (\tau+s)(\tau+s-1)\, a_s r_2^{\tau+s-2} + \lambda a_s r_2^{\tau+s} - a_s r_2^{\tau+s-1} = 0 \qquad (3\text{-}31)$$

Equating the coefficient of the lowest power of r_2 to zero, we get,

$$\tau(\tau-1)\, a_0 = 0$$

Hence $\tau = 1$, since φ is required to be zero at $r_2 = 0$.

Equation (3-31) becomes,

$$\sum_{s=0}^{\infty} \left[s(s+1)\, a_s r_2^{s-1} + \lambda a_s r_2^{s+1} - a_s r_2^{s} \right] = 0 \qquad (3\text{-}32)$$

Equating the coefficient of r_2^m to zero in (3-32), we get,

$$a_{m+1} = \frac{a_m - \lambda a_{m-1}}{(m+1)(m+2)} \quad , \quad \therefore\ a_1 = \frac{a_0}{2}$$

Hence a series solution to two terms is,

$$\varphi \sim r_2 + \frac{r_2^2}{2} \qquad (3\text{-}33)$$

A numerical integration of the differential equation (3-24a) is performed using the difference equation (3-27), and the two initial values of φ from the asymptotic solution (3-33). The parameters are varied until the energy is a minimum and the integral curve has the proper asymptotic behavior. The energy λ is found to approach a limiting value of $-\frac{1}{4} K\epsilon^4$. Hence binding of the system whose state is described by the wave function $\psi = e^{-K_1 r_1 - K_2 r_{12}} \varphi(r_2)$ is not indicated.

Thus the results of the computations, using trial wave functions (3-14), (3-15), (3-16) and (3-21), do not show that the Hydrogen atom and positron form a bound system. However we are unable to conclude that the physical system does not form a bound state, since the Variational method yields only an upper bound for the ground state energy.

CHAPTER IV

THE SYSTEM OF HELIUM ATOM AND POSITRON

This chapter will deal with the problem of whether the Helium atom and positron form a bound system. A configuration space for the four particle problem will be investigated and an element of volume in this space will be derived. The Variational method for obtaining upper bounds for the energy of a system will be applied to two trial wave functions, containing three and four parameters respectively.The procedure for obtaining a minimum value for $\langle H \rangle$ of a system,whose state is described by the four parameter wave function, will be discussed.

Consider the configuration space for the four particle system. Since the nucleus of the Helium atom has a mass equal to 7200 electron masses, the motion of the nucleus is neglected. Since the nucleus is considered at rest, it is taken to be the origin of the coordinate system. Since each moving particle has three degrees of freedom, the configuration space for the system will have nine dimensions.

Let $\underline{r}_1$ be the position vector of the positron, $\underline{r}_2$ be the position vector of one elctron and $\underline{r}_3$ be the position vector of the other electron.[1]

1 In the problem of the Hydrogen atom and positron, chapterIII the position vector of the positron was $\underline{r}_2$, and the position vector of the electron was $\underline{r}_1$.

The inter-particle distances are defined as,

$$r_1 = |\underline{r}_1| \qquad r_2 = |\underline{r}_2| \qquad r_3 = |\underline{r}_3|$$
$$r_{12} = |\underline{r}_2 - \underline{r}_1| \qquad r_{13} = |\underline{r}_3 - \underline{r}_1| \qquad r_{23} = |\underline{r}_3 - \underline{r}_2| \qquad (4-1)$$

Since the six inter-particle distances (4-1) arise in the Hamiltonian operator for the system from the Coulomb interaction between pairs of particles, it is desirable that these six distances occur as coordinates in the configuration space of the system.In the following the positron will be referred to as particle 1, and the two electrons will be referred to as particles 2 and 3 respectively.

The six dimensional configuration space for particles 1 and 2 will first be considered. Then the space will be extended to include particle 3.In terms of Cartesian coordinates, the coordinates of particles 1 and 2 are (x_1, y_1, z_1) and (x_2, y_2, z_2) respectively.The three inter-particle distances r_1, r_2, r_{12} are chosen to be three coordinates in this two particle configuration space. These three distances form a triangle in the space.The orientation of this triangle in the space may be completely specified by the Eulerian angles (θ, φ, ψ) .[2] Any configuration of particles 1 and 2 is completely specified by the three inter-particle distances r_1, r_2, r_{12}, and the three Eulerian angles(θ, φ, ψ).Hence $r_1, r_2, r_{12}, \theta, \varphi, \psi$ are chosen to be the coordinates of the two particle configuration space.

The element of volume for particles 1 and 2, in terms of Cartesian coordinates is,

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2 H.Goldstein, Classical Mechanics, ADD.-Wes. p.107.

$$d\tau = d\tau_1\, d\tau_2 = dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2 \qquad (4\text{-}2)$$

In order to obtain the element of volume in terms of the coordinates of the configuration space, the transformation equations between the coordinates $(x_1, y_1, z_1, x_2, y_2, z_2)$ and the coordinates $(r_1, r_2, r_{12}, \theta, \varphi, \psi)$ are needed. These may be obtained by considering two orientations of the triangle whose sides are r_1, r_2 and r_{12}. The final orientation is produced from the initial orientation by three successive rotations through the angles φ, θ and ψ in the sense of Euler.

This corresponds to the transformation matrix T [3], where,

$$T = \begin{pmatrix} \cos\psi\cos\varphi - \cos\theta\sin\varphi\sin\psi & \cos\psi\sin\varphi + \cos\theta\cos\varphi\sin\psi & \sin\psi\cos\theta \\ -\sin\psi\cos\varphi - \cos\theta\sin\varphi\cos\psi & -\sin\psi\sin\varphi + \cos\theta\cos\varphi\cos\psi & \cos\psi\sin\theta \\ \sin\theta\sin\varphi & -\sin\theta\cos\varphi & \cos\theta \end{pmatrix} \qquad (4\text{-}3)$$

The initial coordinates of particle 1 are $(0, 0, r_1)$ and the final coordinates are (x_1, y_1, z_1). Let η be the angle between r_1 and r_2. Then

$$r_{12}^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \cos\eta \qquad (4\text{-}4)$$

Thus the initial coordinates of particle 2 are $(r_2 \sin\eta, 0, r_2\cos\eta)$, and the final coordinates are (x_2, y_2, z_2).

Thus the relations between initial and final coordinates are,

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = T \begin{pmatrix} 0 \\ 0 \\ r_1 \end{pmatrix} \qquad (4\text{-}5)$$

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = T \begin{pmatrix} r_2 \sin\eta \\ 0 \\ r_2\cos\eta \end{pmatrix} \qquad (4\text{-}6)$$

3 H.Goldstein p.109

Then from (4-3), (4-5) and (4-6), we get,

$$\begin{aligned} x_1 &= r_1 \sin\psi \sin\theta \\ y_1 &= r_1 \cos\psi \sin\theta \\ z_1 &= r_1 \cos\theta \end{aligned} \qquad (4\text{-}7)$$

and

$$\begin{aligned} x_2 &= r_2 \sin\eta \cos\psi \cos\varphi - r_2 \sin\eta \sin\psi \sin\varphi \cos\theta + r_2 \cos\eta \sin\psi \sin\theta \\ y_2 &= -r_2 \sin\eta \sin\psi \cos\varphi - r_2 \sin\eta \cos\psi \sin\varphi \cos\theta + r_2 \cos\eta \cos\psi \sin\theta \\ z_2 &= r_2 \sin\eta \sin\varphi \sin\theta + r_2 \cos\eta \cos\theta \end{aligned} \qquad (4\text{-}8)$$

Hence the element of volume $d\tau$ for the configuration space in terms of $(r_1, r_2, r_{12}, \theta, \varphi, \psi)$ is,

$$d\tau = J\left(\frac{x_1, y_1, z_1, x_2, y_2, z_2}{r_1, r_2, r_{12}, \theta, \varphi, \psi}\right) dr_1\, dr_2\, dr_{12}\, d\theta\, d\varphi\, d\psi \qquad (4\text{-}9)$$

where $J\left(\frac{x_1 y_1 z_1 x_2 y_2 z_2}{r_1 r_2 r_{12}\, \theta, \varphi\, \psi}\right)$ is the Jacobian of the transformation.
Then from (4-4), (4-7) and (4-8), the Jacobian is,

$$J\left(\frac{x_1 y_1 z_1 x_2 y_2 z_2}{r_1 r_2 r_{12}\, \theta\, \varphi\, \psi}\right) = r_1 r_2 r_{12} \sin\theta \qquad (4\text{-}10)$$

Hence an element of volume in the two particle configuration space is given by,

$$d\tau = d\tau_1\, d\tau_2 = r_1 r_2 r_{12} \sin\theta\, dr_1\, dr_2\, dr_{12}\, d\theta\, d\varphi\, d\psi \qquad (4\text{-}11)$$

The configuration space will now be extended to particle 3. The orientation of the triangle formed by r_1, r_2, r_{12} is specified by the three Eulerian angles θ, φ, ψ. Particle 3, whose distance from the origin is r_3, is introduced by choosing $\underline{r_1}$ as the polar axis for r_3, and defining ω to be the angle between the plane formed by r_1 and r_2, and the plane formed by r_1 and r_3. Let ξ be the angle between r_1 and r_3 with

$$\mu = \cos\xi \qquad (4\text{-}12)$$

as in Fig.4.

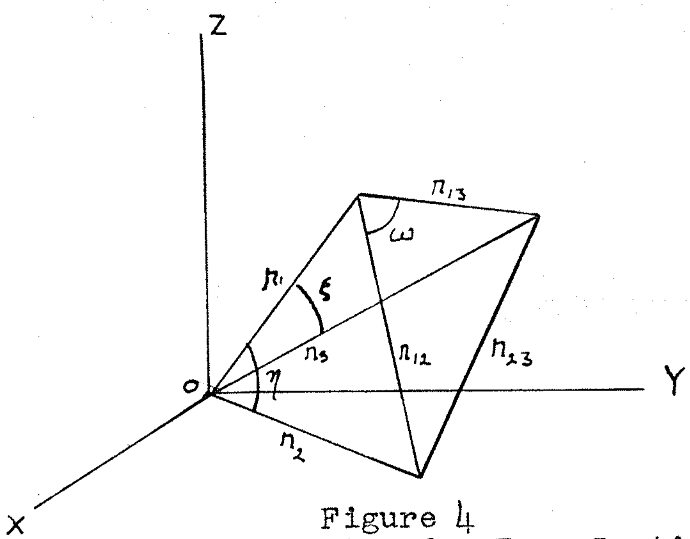

Figure 4
Coordinate System for Four Particles.

Then for particle 3, the element of volume is,

$$d\tau_3 = r_3^2\, dr_3\, d\mu\, d\omega \tag{4-13}$$

But
$$r_{13}^2 = r_1^2 + r_3^2 - 2 r_1 r_3 \mu \tag{4-14}$$

The coordinate r_{13} may be introduced into the element of volume.

$$d\tau_3 = r_3^2\, J\left(\frac{r_3\, \mu\, \omega}{r_3\, r_{13}\, \omega}\right) dr_3\, dr_{13}\, d\omega \tag{4-15}$$

$$d\tau_3 = \frac{r_3 r_{13}}{r_1}\, dr_3\, dr_{13}\, d\omega$$

Then for the three particles, the element of volume in the configuration space becomes,

$$d\tau = r_2 r_{12} r_3 r_{13} \sin\theta\, dr_1\, dr_2\, dr_{12}\, dr_3\, dr_{13}\, d\omega\, d\theta\, d\varphi\, d\psi \tag{4-16}$$

with

$$\begin{array}{lll} 0 \le r_1 \le \infty & 0 \le r_2 \le \infty & |r_1 - r_2| \le r_{12} \le r_1 + r_2 \\ 0 \le r_3 \le \infty & |r_1 - r_3| \le r_{13} \le r_1 + r_3 & 0 \le \omega \le 2\pi \\ 0 \le \theta \le \pi & 0 \le \varphi \le 2\pi & 0 \le \psi \le 2\pi \end{array} \tag{4-17}$$

In the above, ω in Fig. 4 is the angle between the planes intersecting in $\underline{r_1}$. If instead ω is taken as being the angle between the planes that intersect in $\underline{r_{23}}$, then the element of volume is,

$$d\tau = r_2 r_{12} r_3 r_{13} \sin\theta\, dr_{23}\, dr_2\, dr_{12}\, dr_3\, dr_{13}\, d\omega\, d\theta\, d\varphi\, d\psi \tag{4-18}$$

with

$$\begin{array}{lll} 0 \le r_{23} \le \infty & 0 \le r_3 \le \infty & |r_3 - r_{23}| \le r_2 \le r_3 + r_{23} \\ 0 \le r_{13} \le \infty & |r_{13} - r_{23}| \le r_{12} \le r_{13} + r_{23} & 0 \le \omega \le 2\pi \\ 0 \le \theta \le \pi & 0 \le \varphi \le 2\pi & 0 \le \psi \le 2\pi \end{array} \tag{4-19}$$

The inter-electron distance r_{23} may be introduced into the element of volume (4-16), where,

$$r_{23}^2 = r_2^2 + r_3^2 - 2 r_2 r_3 \left[\cos\eta \cos\zeta + \sin\eta \sin\zeta \cos\omega\right] \qquad (4\text{-}20)$$

Then the element of volume is given by,

$$d\tau = r_2 r_{12} r_3 r_{13} \sin\theta \, J\left(\frac{r_1 r_2 r_{12} r_3 r_{12} r_{23} \theta \varphi \psi}{r_1 r_2 r_{12} r_3 r_{13} \omega \theta \varphi \psi}\right) dr_1 dr_2 dr_{12} dr_3 dr_{13} dr_{23} d\theta d\varphi d\psi \qquad (4\text{-}21)$$

However the Jacobian in (4-21) is a complicated expression due to (4-20) and hence the element of volume (4-21) is not suitable for the integrations to be performed.

Hence the elements of volume (4-16) and (4-18) in the configuration space of the system will be employed for the evaluation of integrals arising in this problem.

The system under consideration consists of a Helium atom with a nucleus of charge $+2\epsilon$ fixed at the origin, and with two electrons, each of charge $-\epsilon$, at $\underline{r}_2$ and $\underline{r}_3$ respectively, and a positron of charge $+\epsilon$ at $\underline{r}_1$. Hence the Hamiltonian operator H for the system may be written as,

$$H = -\frac{1}{K}\nabla_1^2 - \frac{1}{K}\nabla_2^2 - \frac{1}{K}\nabla_3^2 + \frac{2\epsilon^2}{r_1} - \frac{2\epsilon^2}{r_2} - \frac{2\epsilon^2}{r_3} - \frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_{13}} + \frac{\epsilon^2}{r_{23}} \qquad (4\text{-}22)$$

where $K = \frac{2m}{\hbar^2}$; m is the mass of the electron or positron; and $\nabla_1^2, \nabla_2^2, \nabla_3^2$ are Laplacians operating on the coordinates of particles 1, 2, and 3 respectively. From (2-21) and (4-22), the inner product $(\psi, H\psi)$ for the physical system may be written as,

$$(\psi, H\psi) = \int\left[\frac{1}{K}(\nabla_1\psi)^2 + \frac{1}{K}(\nabla_2\psi)^2 + \frac{1}{K}(\nabla_3\psi)^2 + \frac{2\epsilon^2\psi^2}{r_1} - \frac{2\epsilon^2\psi^2}{r_2} - \frac{2\epsilon^2\psi^2}{r_3} - \frac{\epsilon^2\psi^2}{r_{12}} - \frac{\epsilon^2\psi^2}{r_{13}} + \frac{\epsilon^2\psi^2}{r_{23}}\right] d\tau \qquad (4\text{-}23)$$

where, for a function of the interparticle distances,

$$
\begin{aligned}
(\nabla_1\psi)^2 &= \left(\frac{\partial\psi}{\partial r_1}\right)^2 + \left(\frac{\partial\psi}{\partial r_{12}}\right)^2 + \left(\frac{\partial\psi}{\partial r_{13}}\right)^2 + \left(\frac{r_{12}^2+r_1^2-r_2^2}{r_1 r_{12}}\right)\left(\frac{\partial\psi}{\partial r_1}\right)\left(\frac{\partial\psi}{\partial r_{12}}\right) \\
&\quad + \left(\frac{r_{13}^2+r_1^2-r_3^2}{r_1 r_{13}}\right)\left(\frac{\partial\psi}{\partial r_1}\right)\left(\frac{\partial\psi}{\partial r_{13}}\right) + \left(\frac{r_{12}^2+r_{13}^2-r_{23}^2}{r_{12} r_{13}}\right)\left(\frac{\partial\psi}{\partial r_{12}}\right)\left(\frac{\partial\psi}{\partial r_{13}}\right) \\
(\nabla_2\psi)^2 &= \left(\frac{\partial\psi}{\partial r_2}\right)^2 + \left(\frac{\partial\psi}{\partial r_{12}}\right)^2 + \left(\frac{\partial\psi}{\partial r_{23}}\right)^2 + \left(\frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\right)\left(\frac{\partial\psi}{\partial r_2}\right)\left(\frac{\partial\psi}{\partial r_{12}}\right) \\
&\quad + \left(\frac{r_{23}^2+r_2^2-r_3^2}{r_2 r_{23}}\right)\left(\frac{\partial\psi}{\partial r_2}\right)\left(\frac{\partial\psi}{\partial r_{23}}\right) + \left(\frac{r_{23}^2+r_{12}^2-r_{13}^2}{r_{12} r_{23}}\right)\left(\frac{\partial\psi}{\partial r_{12}}\right)\left(\frac{\partial\psi}{\partial r_{23}}\right) \qquad (4\text{-}24) \\
(\nabla_3\psi)^2 &= \left(\frac{\partial\psi}{\partial r_3}\right)^2 + \left(\frac{\partial\psi}{\partial r_{13}}\right)^2 + \left(\frac{\partial\psi}{\partial r_{23}}\right)^2 + \left(\frac{r_{23}^2+r_3^2-r_2^2}{r_3 r_{23}}\right)\left(\frac{\partial\psi}{\partial r_3}\right)\left(\frac{\partial\psi}{\partial r_{23}}\right) \\
&\quad + \left(\frac{r_{13}^2+r_3^2-r_1^2}{r_3 r_{13}}\right)\left(\frac{\partial\psi}{\partial r_3}\right)\left(\frac{\partial\psi}{\partial r_{13}}\right) + \left(\frac{r_{23}^2+r_{13}^2-r_{12}^2}{r_{13} r_{23}}\right)\left(\frac{\partial\psi}{\partial r_{13}}\right)\left(\frac{\partial\psi}{\partial r_{23}}\right)
\end{aligned}
$$

The expressions (4-24) are derived in Appendix E.

The ground state of the system of the Helium atom and positron is assumed to be a state of zero angular momentum. Hence by an extension of the result of the previous chapter , functions of the inter-particle distances only are eigenfunctions of the angular momentum operator belonging to the eigenvalue zero. Hence functions of the inter-particle distances only will be considered as trial wave functions for the system.

It is further assumed that the state of the Helium atom is not greatly disturbed by the presence of the positron. The total wave function for a system of Fermions is postulated to be antisymmetric. In the ground state of the Helium atom, the two electrons have a total spin of zero. Hence the spin function for the system is antisymmetric. Thus the spacial part of the wave function must be symmetric with respect to the interchange of the two electrons.

Since the state of the Helium atom is not greatly disturbed by the presence of the positron, trial wave functions, symmetric with respect to the interchange of the coordinates of the two electrons, are chosen.

If the Coulomb interaction between the two electrons was not present, the wave function for the Helium atom alone would be a product of two Hydrogen-like wave functions. Hence, as an approximation, a product of two Hydrogen-like wave functions is taken as part of the wave function for the system of Helium atom and positron. Since the nucleus repells the positron, on the average, the nuclear-positron distance will be relatively large. Also the electron will tend to be farther away from the nucleus, on the average, due to the attraction of the positron. Then if the system forms a bound state, the positron and electron will form a nearly positronium like system. Thus a positronium-like wave function is chosen for the electron-positron coordinate.

The function must be symmetric with respect to the interchange of the two electrons, particles 2 and 3. Hence a symmetrized trial wave function for the system is chosen to be,

$$\psi = \psi_2 + \psi_3 = e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3)} + e^{-(\alpha r_3 + \beta r_{13} + \gamma r_2)} \qquad (4\text{-}25)$$

where α, β, γ are parameters for variation.

The motion of the positron is also correlated to the other electron. Hence a trial wave function which accounts for this correlation may be written as,

$$\psi = \psi_2 + \psi_3 = e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3 + \delta r_{13})} + e^{-(\alpha r_3 + \beta r_{13} + \gamma r_2 + \delta r_{12})} \qquad (4\text{-}26)$$

where $\alpha, \beta, \gamma, \delta$ are parameters for variation.

The Variational method will now be applied to the three parameter wave function (4-25). Then, from (4-23) and (4-24), the $\langle H \rangle$ for the state (4-25) may be written as,

$$\langle H \rangle = \frac{\int \frac{1}{K}\left[(\alpha^2+2\beta^2+\gamma^2)\psi_2^2 + (\alpha^2+2\beta^2+\gamma^2)\psi_3^2 + 4\alpha\gamma\psi_2\psi_3 + \left(\frac{r_{12}^2+r_{13}^2-r_{23}^2}{r_{12}r_{13}}\right)\beta^2\psi_2\psi_3\right]d\tau}{\int(\psi_2^2+\psi_3^2+2\psi_2\psi_3)\,d\tau}$$

$$+ \frac{\int \frac{1}{K}\left[\left(\frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\right)(\alpha\beta\psi_2^2+\beta\gamma\psi_2\psi_3) + \left(\frac{r_{13}^2+r_3^2-r_1^2}{r_3 r_{13}}\right)(\alpha\beta\psi_3^2+\beta\gamma\psi_2\psi_3)\right]d\tau}{\int(\psi_2^2+\psi_3^2+2\psi_2\psi_3)\,d\tau} \qquad (4\text{-}27)$$

$$+ \frac{\int\left[(\psi_2^2+\psi_3^2+2\psi_2\psi_3)\left(\frac{2\epsilon^2}{r_1} - \frac{2\epsilon^2}{r_2} - \frac{2\epsilon^2}{r_3} - \frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_{13}} + \frac{\epsilon^2}{r_{23}}\right)\right]d\tau}{\int(\psi_2^2+\psi_3^2+2\psi_2\psi_3)\,d\tau}$$

Since there is symmetry between particles 2 and 3 in the wave function and in the element of volume, it is clear that,

$$\int \psi_2^2\,d\tau = \int \psi_3^2\,d\tau \qquad \int \psi_2\psi_3\frac{r_{12}}{r_{13}}\,d\tau = \int \psi_2\psi_3\frac{r_{13}}{r_{12}}\,d\tau$$

$$\int \psi_3^2\left(\frac{r_{13}^2+r_3^2-r_1^2}{r_3 r_{13}}\right)d\tau = \int \psi_2^2\left(\frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\right)d\tau$$

$$\int \frac{\psi_2^2}{r_1}\,d\tau = \int \frac{\psi_3^2}{r_1}\,d\tau \qquad \int \frac{\psi_2\psi_3}{r_2}\,d\tau = \int \frac{\psi_2\psi_3}{r_3}\,d\tau \qquad \text{etc.}$$

Hence $\langle H \rangle$ may be written as,

$$\langle H \rangle = \frac{\int \frac{1}{K}\left[2(\alpha^2+2\beta^2+\gamma^2)\psi_2^2 + 4\alpha\gamma\psi_2\psi_3 + \beta^2\left(\frac{r_{12}^2+r_{13}^2-r_{23}^2}{r_{12}r_{13}}\right)\psi_2\psi_3 + 2\alpha\beta\left(\frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\right)\psi_2^2 + 2\beta\gamma\left(\frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\right)\psi_2\psi_3\right]d\tau}{\int(2\psi_2^2+2\psi_2\psi_3)\,d\tau} \qquad (4\text{-}28)$$

$$+ \epsilon^2\frac{\int\left[\frac{4\psi_2^2}{r_1} + \frac{4\psi_2\psi_3}{r_1} - \frac{4\psi_2^2}{r_2} - \frac{8\psi_2\psi_3}{r_2} - \frac{4\psi_2^2}{r_3} - \frac{2\psi_2^2}{r_{12}} - \frac{2\psi_2^2}{r_{13}} - \frac{4\psi_2\psi_3}{r_{12}} + \frac{2\psi_2^2}{r_{23}} + \frac{2\psi_2\psi_3}{r_{23}}\right]d\tau}{\int(2\psi_2^2+2\psi_2\psi_3)\,d\tau}$$

The expression for $\langle H \rangle$ and the integrals are evaluated and listed in Appendix F.

The minimum value for $\langle H \rangle$ must now be found. The $\langle H \rangle$ may be written as,

$$\langle H \rangle = \frac{\frac{1}{K}A(\alpha,\beta,\gamma) + \epsilon^2 B(\alpha,\beta,\gamma)}{C(\alpha,\beta,\gamma)} \qquad (4\text{-}29)$$

where $A(\alpha,\beta,\gamma)$ is due to the kinetic energy terms, and $B(\alpha,\beta,\gamma)$ is due to the potential energy terms, and $C(\alpha,\beta,\gamma)$ is due to the normalization.

Let $a = \frac{\alpha}{\beta}$ $\quad c = \frac{\gamma}{\beta}$

Since A, B and C are homogeneous of degree $-7, -8, -9$, respectively, in the parameters, (4-29) may be written,

$$\langle H \rangle = \frac{\frac{1}{K}\beta^2 A(a,1,c) + \beta\epsilon^2 B(a,1,c)}{C(a,1,c)} \tag{4-30}$$

The $\langle H \rangle$ may be minimized with respect to β by setting,

$$\frac{\partial \langle H \rangle}{\partial \beta} = 0 = \frac{2\beta}{K}\frac{A}{C} + \epsilon \frac{B}{C}$$

Then (4-30) becomes,

$$\langle H \rangle = -\frac{B^2(a,1,c)}{4A(a,1,c)C(a,1,c)} K\epsilon^4 \tag{4-31}$$

The value of (4-31) was computed for various values of a and c. The $\langle H \rangle$ was plotted on a plane with a and c as coordinate axes. Contours were drawn through points of equal energy. In this way the best values of the parameters and the minimum value for $\langle H \rangle$ were quickly obtained.

It was found that,

$$\langle H \rangle \rightarrow -1.4378 \; K\epsilon^4$$

for $\quad a \rightarrow \infty \quad c \rightarrow \infty \quad$ or $\beta \rightarrow 0$

Since $\beta \rightarrow 0$ the wave function tends to the form $\psi = e^{-(\alpha r_2 + \gamma r_3)} + e^{-(\alpha r_3 + \gamma r_2)}$.

This wave function corresponds to the system of the Helium atom, and thus the $\langle H \rangle$ actually represents an upper bound for the energy of the Helium atom.

The Variational method will now be applied to the four parameter wave function, (4-26),

$$\psi = \psi_2 + \psi_3 = e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3 + \delta r_{13})} + e^{-(\alpha r_3 + \beta r_{13} + \gamma r_2 + \delta r_{12})}$$

Then from (4-23) and (4-24), the $\langle H \rangle$ for the state given by (4-26) is,

$$\langle H\rangle = \frac{\int \frac{1}{K}\left[(4\beta^2+4\delta^2+2\alpha^2+2\gamma^2)\psi_2^2+(4\alpha\gamma+8\beta\delta)\psi_2\psi_3+\left(\frac{r_{12}^2+r_{13}^2-r_{23}^2}{r_{12}r_{13}}\right)\left(\{\beta^2+\delta^2\}\psi_2\psi_3+\beta\delta\psi_2^2+\beta\delta\psi_3^2\right)\right]d\tau}{\int[2\psi_2^2+2\psi_2\psi_3]\,d\tau}$$

$$+\frac{\int \frac{1}{K}\left[\left(\frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\right)\left(2\{\beta\gamma+\alpha\delta\}\psi_2\psi_3+2\gamma\delta\psi_3^2+2\alpha\beta\psi_2^2\right)\right]d\tau}{\int[2\psi_2^2+2\psi_2\psi_3]\,d\tau} \tag{4-32}$$

$$+\epsilon^2\frac{\int\left[\frac{2Z\psi_2^2}{r_1}+\frac{2Z\psi_2\psi_3}{r_1}-\frac{2Z\psi_2^2}{r_2}-\frac{4Z\psi_2\psi_3}{r_2}-\frac{2Z\psi_2^2}{r_3}-\frac{2\psi_2^2}{r_{12}}-\frac{4\psi_2\psi_3}{r_{12}}-\frac{2\psi_2^2}{r_{13}}+\frac{2\psi_2^2}{r_{23}}+\frac{2\psi_2\psi_3}{r_{23}}\right]d\tau}{\int[2\psi_2^2+2\psi_2\psi_3]\,d\tau}$$

The symmetry between particles 2 and 3 has been taken into account. Z is the charge of the nucleus. The expression for $\langle H\rangle$ and the evaluated integrals are listed in Appendix G.

We wish to minimize $\langle H\rangle$ in order to obtain the lowest upper bound for the energy of the system. The $\langle H\rangle$ may be written as,

$$\langle H\rangle = \frac{k\,A(\alpha,\beta,\gamma,\delta)+\epsilon^2 B(\alpha,\beta,\gamma,\delta)}{C(\alpha,\beta,\gamma,\delta)} \tag{4-33}$$

Let $\quad b=\frac{\beta}{\alpha} \quad c=\frac{\gamma}{\alpha} \quad d=\frac{\delta}{\alpha}$

Then because of the homogeneity of A , B and C , (4-33) may be written as,

$$\langle H\rangle = \frac{k\,\alpha^2 A(1,b,c,d)+\alpha\epsilon^2 B(1,b,c,d)}{C(1,b,c,d)}$$

Then , by the procedure used with (4-30) and (4-31),

$$\langle H\rangle = -\frac{B^2(1,b,c,d)}{4A(1,b,c,d)\,C(1,b,c,d)}\,k\epsilon^4 \tag{4-34}$$

Hence the expression for $\langle H\rangle$, (4-34) has been minimized with respect to the variable α . The $\langle H\rangle$, (4-34) must now be minimized with respect to the variables b, c and d .

The four particle system consisting of the negative Hydrogen ion and positron was investigated by Darewych[4]. He found that a minimum for $\langle H\rangle$ for the three parameter existed. Thus the best values of the parameters from the three parameter wave function could be used with the four parameter

[4] G. Darewych, Thesis, University of Manitoba, 1961.

wave function and then varied slightly until the minimum for $\langle H \rangle$ was obtained.

However this procedure could not be adopted for the Helium atom and positron problem, since a minimum for the energy was not indicated with the use of the three parameter wave function. Thus no knowledge of the approximate values of the parameters for the four parameter wave function was available. The best values of the parameters b, c and d, and the corresponding minimum value of $\langle H \rangle$ could be obtained by calculating $\langle H \rangle$ for a three dimensional network of points (b, c, d). This procedure would be difficult, since the region in which a minimum for $\langle H \rangle$ might exist, was not known.

Another procedure was followed. This involved the tracing of the location of the minimum of $\langle H \rangle$, in the sense of the best values of b, c and d, for values of Z from $Z=1$ to $Z=2$. Z is the charge of the nucleus. For $Z=1$ the system would consist of the negative Hydrogen ion and positron, and for $Z=2$ the system would consist of the Helium atom and positron. The best values for the parameters for $Z=1$ were determined by Darewych.

If a Z value, differing by a small amount from $Z=1$ is chosen, the values of the parameters which will yield a minimum for $\langle H \rangle$, will also differ slightly from the best values obtained for $Z=1$.

A value of $Z=1.2$ was chosen, and a value of b differing slightly from the best value for $Z=1$, was fixed. The $\langle H \rangle$ was calculated for c and d near the best values obtained for $Z=1$. A contour graph was plotted and the best values of c and d, and the minimum value of $\langle H \rangle$ were determined. This was repeated for several b values, until the best values of b, c and d, and the minimum for $\langle H \rangle$ were obtained for $Z=1.2$. The process was repeated for $Z=1.4, 1.6, 1.8, 1.9, 2$. In this way, the minimum for $\langle H \rangle$ was obtained.

The results obtained for $\langle H \rangle$ were,

$$\langle H \rangle = -1.438 \ K\epsilon^4$$

$$\text{at} \quad b = \frac{\beta}{\alpha} \doteq 0 \qquad c = \frac{\gamma}{\alpha} = 1.8 \qquad d = \frac{\delta}{\alpha} \doteq 0$$

The ground state energy of the Helium atom is $-1.45188 \ K\epsilon^4$. This is equal to -78.4 ev, The energy of the positive Helium ion and positronium is -60.25 ev. Thus it is energetically favourable for the system to dissociate into the Helium atom and positron. Hence binding of the system will be indicated if the value of $\langle H \rangle$ is less than $-1.45188 \ K\epsilon^4$. Thus, in both cases, binding of the system of Helium atom and positron is not indicated. However, we are unable to conclude that the Helium atom and positron do not form a bound system, since the Variational method yields only an upper bound for the energy of a physical system.

CHAPTER V

CONCLUSIONS

The possible binding of the system consisting of the Hydrogen atom and positron was investigated in chapterIII. The Variational method was applied to several trial wave functions for the system. An equivalent one dimensional problem was formulated, which would determine the best form of wave function in order that the energy be a minimum.

The results which were obtained did not indicate binding of the system. However, as was shown in chapter II, the Variational method yields only an upper bound for the energy of a system. Hence it could not be concluded that the Hydrogen atom and positron do not form a bound state.

The problem might be resolved if a trial wave function, which more closely approximates the state of the system, were chosen and were to indicate binding. However another more promising approach might lead to the resolution of the problem. Bazley [1] has devised a method for determining lower bounds for eigenvalues, and has applied this method to the system of the Helium atom. The application of this method to the system of Hydrogen atom and positron would yield a lower bound for the energy of the system. Thus from a knowledge of an upper and lower bound for the energy, the question, as to whether the Hydrogen atom and positron form a bound system, might be resolved.

1 N.W. Bazley, Phys. Rev. 120, 144, (1960).

The system of Helium atom and positron was investigated in chapter IV. The Variational method was applied to a three parameter and a four parameter trial wave function for the system, in order to determine whether the Helium atom and positron form a bound state.

The results obtained did not indicate binding of the system. For each trial wave function, certain parameters vanished for a minimum value for $\langle H \rangle$. The trial wave functions reduced to the form of Helium-type wave functions for two electrons. Thus the value of $\langle H \rangle$ which was obtained, represented an upper bound for the energy of the Helium atom. It is clear that an improved trial wave function might indicate binding of the system. The two trial wave functions did not contain terms which would correlate the motion of the two electrons. The use of this type of wave function for the Helium atom does not yield a value for the energy which is in close agreement with experiment. Thus a term involving the inter-electron coordinate must be included in the wave function.

An equivalent one dimensional problem for the Helium atom was formulated. It was found that a linear function of the inter-electron coordinate would yield a minimum energy. This is in agreement with the result of Green et al.[2]

2 Green et al., Jour.Chem.Phys. 30, 1061, (1959).

However the four particle element of volume involves five inter-particle distances. Hence any term of $\langle H \rangle$ which contains all six distances cannot be evaluated. The sixth inter-particle distance must be expressed in terms of the other five distances and a angle. Such a term occurs in $\langle H \rangle$ if a linear function of the inter-electron distance r_{23}, is added to the four parameter wave function, and the integrations cannot be performed. The difficulty is overcome if a quadratic function of r_{23} is chosen with an adjustable parameter to approximate the linear function over a suitable region. Thus a function of the form,

$$\psi = (1+\omega r_{23}^2)\left[e^{-(\alpha r_2+\beta r_{12}+\gamma r_3+\delta r_{13})}+e^{-(\alpha r_3+\beta r_{13}+\gamma r_2+\delta r_{12})}\right]$$

was chosen. The expression for $\langle H \rangle$ has been evaluated and is in the process of being programmed for a computer. However the calculation is beyond the scope of this thesis.

A further improvement of the wave function may be envisaged. One would expect that, on the average, the positron would be at a large distance from the nucleus if the Helium atom and positron form a bound system. Hence a term, involving the nuclear-positron distance r_1, which would assure this, should be included in the trial wave function. A function of the form, $\psi = [1+\Omega r_{23}^2+\xi r_1^2]\left(e^{-(\alpha r_2+\beta r_{12}+\gamma r_3+\delta r_{13})}+e^{-(\alpha r_3+\beta r_{13}+\gamma r_2+\delta r_{12})}\right)$ has the desired features and the integrals which arise may be explicitly evaluated.

APPENDIX A

LAPLACIAN AND SQUARE OF GRADIENT FOR TWO PARTICLE PROBLEM

Let $\underline{r}_{12} = \underline{r}_2 - \underline{r}_1$, $r_{12}^2 = r_1^2 + r_2^2 - 2\,\underline{r}_1\cdot\underline{r}_2$

$r_1^2 = x_1^2 + y_1^2 + z_1^2$ $\quad r_2^2 = x_2^2 + y_2^2 + z_2^2$

$r_{12}^2 = (x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2$

The gradient operating on the coordinates of particle 1 is,

$$\nabla_1 = \underline{i}\frac{\partial}{\partial x_1} + \underline{j}\frac{\partial}{\partial y_1} + \underline{k}\frac{\partial}{\partial z_1}$$

$$= \underline{i}\left(\frac{\partial r_1}{\partial x_1}\frac{\partial}{\partial r_1} + \frac{\partial r_{12}}{\partial x_1}\frac{\partial}{\partial r_{12}}\right) + \underline{j}\left(\frac{\partial r_1}{\partial y_1}\frac{\partial}{\partial r_1} + \frac{\partial r_{12}}{\partial y_1}\frac{\partial}{\partial r_{12}}\right) + \underline{k}\left(\frac{\partial r_1}{\partial z_1}\frac{\partial}{\partial r_1} + \frac{\partial r_{12}}{\partial z_1}\frac{\partial}{\partial r_{12}}\right)$$

$$= \underline{i}\left(\frac{x_1}{r_1}\frac{\partial}{\partial r_1} - \frac{(x_2-x_1)}{r_{12}}\frac{\partial}{\partial r_{12}}\right) + \underline{j}\left(\frac{y_1}{r_1}\frac{\partial}{\partial r_1} - \frac{(y_2-y_1)}{r_{12}}\frac{\partial}{\partial r_{12}}\right) + \underline{k}\left(\frac{z_1}{r_1}\frac{\partial}{\partial r_1} - \frac{(z_2-z_1)}{r_{12}}\frac{\partial}{\partial r_{12}}\right)$$

Hence,

$$\nabla_1 = \frac{\underline{r}_1}{r_1}\frac{\partial}{\partial r_1} - \frac{\underline{r}_{12}}{r_{12}}\frac{\partial}{\partial r_{12}}$$

Similarly,

$$\nabla_2 = \frac{\underline{r}_2}{r_2}\frac{\partial}{\partial r_2} + \frac{\underline{r}_{12}}{r_{12}}\frac{\partial}{\partial r_{12}}$$

Hence,

$$(\nabla_1 f)^2 = (\nabla_1 f)\cdot(\nabla_1 f) = \left(\frac{\partial f}{\partial r_1}\right)^2 + \left(\frac{\partial f}{\partial r_{12}}\right)^2 + \left(\frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\right)\left(\frac{\partial f}{\partial r_1}\right)\left(\frac{\partial f}{\partial r_{12}}\right)$$

and

$$(\nabla_2 f)^2 = \left(\frac{\partial f}{\partial r_2}\right)^2 + \left(\frac{\partial f}{\partial r_{12}}\right)^2 + \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}}\right)\left(\frac{\partial f}{\partial r_2}\right)\left(\frac{\partial f}{\partial r_{12}}\right)$$

The Laplacian operating on the coordinates of particle 1 is,

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

Now

$$\frac{\partial f}{\partial x_1} = \frac{\partial r_1}{\partial x_1}\frac{\partial f}{\partial r_1} + \frac{\partial r_{12}}{\partial x_1}\frac{\partial f}{\partial r_{12}}$$

Then

$$\frac{\partial^2 f}{\partial x_1^2} = \frac{\partial}{\partial x_1}\left(\frac{\partial r_1}{\partial x_1}\frac{\partial f}{\partial r_1}\right) + \frac{\partial}{\partial x_1}\left(\frac{\partial r_{12}}{\partial x_1}\frac{\partial f}{\partial r_{12}}\right)$$

$$= \frac{\partial r_1}{\partial x_1}\frac{\partial}{\partial x_1}\left(\frac{\partial f}{\partial r_1}\right) + \frac{\partial f}{\partial r_1}\frac{\partial^2 r_1}{\partial x_1^2} + \frac{\partial r_{12}}{\partial x_1}\frac{\partial}{\partial x_1}\left(\frac{\partial f}{\partial r_{12}}\right) + \frac{\partial f}{\partial r_{12}}\frac{\partial^2 r_{12}}{\partial x_1^2}$$

$$= \left(\frac{\partial r_1}{\partial x_1}\right)^2\frac{\partial^2 f}{\partial r_1^2} + 2\frac{\partial r_1}{\partial x_1}\frac{\partial r_{12}}{\partial x_1}\frac{\partial^2 f}{\partial r_1\partial r_{12}} + \frac{\partial^2 r_1}{\partial x_1^2}\frac{\partial f}{\partial r_1} + \frac{\partial^2 r_{12}}{\partial x_1^2}\frac{\partial f}{\partial r_{12}} + \left(\frac{\partial r_{12}}{\partial x_1}\right)^2\frac{\partial^2 f}{\partial r_{12}^2}$$

$$= \frac{\partial^2 f}{\partial r_1^2}\left(\frac{x_1}{r_1}\right)^2 - 2\frac{\partial^2 f}{\partial r_1\partial r_{12}}\left(\frac{x_1}{r_1}\right)\left(\frac{x_2-x_1}{r_{12}}\right) + \frac{\partial f}{\partial r_1}\left(\frac{1}{r_1} - \frac{x_1^2}{r_1^3}\right)$$

$$+ \frac{\partial^2 f}{\partial r_{12}^2}\left(\frac{x_2-x_1}{r_{12}}\right)^2 + \frac{\partial f}{\partial r_{12}}\left(\frac{1}{r_{12}} - \frac{(x_2-x_1)^2}{r_{12}^3}\right)$$

with similar terms for y_1 and z_1 .

Therefore the Laplacian for particle 1 is,

$$\nabla_1^2 = \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_{12}^2} + \left(\frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\right)\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}$$

Similarly, the Laplacian for particle 2 is,

$$\nabla_2^2 = \frac{\partial^2}{\partial r_2^2} + \frac{\partial^2}{\partial r_{12}^2} + \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}}\right)\frac{\partial^2}{\partial r_2 \partial r_{12}} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} .$$

APPENDIX B

METHOD FOR EVALUATING INTEGRALS

In evaluating $(\psi, H\psi)$ and (ψ,ψ), integrals of the form

$$\int_0^\infty \int_{|z-x|}^{z+x} x^a y^b e^{-K_1 x - K_2 y}\, dx\, dy \qquad \text{occur.}$$

Let

$$F_{K_1,K_2}(a,b) = \int_0^\infty \int_{|z-x|}^{z+x} x^a y^b e^{-K_1 x - K_2 y}\, dx\, dy$$

where K_1, K_2 are parameters and x, y, z are any coordinates.

Differentiating with respect to one parameter under the integral sign, we get

$$\frac{\partial F_{K_1,K_2}(a,b)}{\partial K_1} = - F_{K_1,K_2}(a+1, b)$$

Then

$$F_{K_1,K_2}(a,b) = (-1)^{a+b} \left(\frac{\partial}{\partial K_1}\right)^a \left(\frac{\partial}{\partial K_2}\right)^b F_{K_1,K_2}(0,0)$$

Thus $F_{K_1,K_2}(a,b)$ may be obtained from $F_{K_1,K_2}(0,0)$ by differentiation.

Consider Taylor's expansion of $F_{K_1-\xi, K_2-\eta}(0,0)$ about $\xi = \eta = 0$.

$$F_{K_1-\xi, K_2-\eta}(0,0) = \sum \xi^a \eta^{b-a} \frac{(-1)^{a+b}}{\underline{|a}\,\underline{|b}} \left(\frac{\partial}{\partial K_1}\right)^a \left(\frac{\partial}{\partial K_2}\right)^b F_{K_1,K_2}(0,0)$$

$F_{K_1,K_2}(a,b) = \underline{|a}\,\underline{|b} \times$ the coefficient of $\xi^a \eta^b$ in the expansion of $F_{K_1-\xi, K_2-\eta}(0,0)$ with

$$F_{K_1,K_2}(0,0) = \frac{2\left(e^{-K_2 z} - e^{-K_1 z}\right)}{(K_1^2 - K_2^2)}$$

Similarly $F_{K,K}(a,b)$ may be obtained from the expansion of $F_{K-\xi, K-\eta}(0,0)$.

Thus we get, $\qquad I = (K_1^2 - K_2^2)$

$$F_{K_1,K_2}(0,0) = e^{-K_2 z}\left(\frac{2}{I}\right) + e^{-K_1 z}\left(-\frac{2}{I}\right)$$

$$F_{K_1,K_2}(1,0) = e^{-K_2 z}\left(\frac{4K_1}{I^2}\right) + e^{-K_1 z}\left(-\frac{4K_1}{I^2} - \frac{2z}{I}\right)$$

$$F_{K_1K_2}(0,1) = e^{-K_2 z}\left(-\frac{4K_2}{I^2} + \frac{2z}{I}\right) + e^{-K_1 z}\left(\frac{4K_2}{I^2}\right)$$

$$F_{K_1,K_2}(1,1) = e^{-K_2 z}\left(\frac{4K_1 z}{I^2} - \frac{16K_1K_2}{I^3}\right) + e^{-K_1 z}\left(\frac{4K_2 z}{I^2} + \frac{16K_1K_2}{I^3}\right)$$

$$F_{K_1,K_2}(2,1) = e^{-K_2 z}\left(-\frac{96K_1^2K_2}{I^4} + \frac{16K_2}{I^3} + \frac{16K_1^2 z}{I^3} - \frac{4z}{I^2}\right) + e^{-K_1 z}\left(\frac{96K_1^2K_2}{I^4} - \frac{16K_2}{I^3} + \frac{32K_1K_2 z}{I^3} + \frac{4K_2 z^2}{I^2}\right)$$

$$F_{K_1,K_2}(1,2) = e^{-K_2 z}\left(\frac{96K_1K_2^2}{I^4} + \frac{16K_1}{I^3} + \frac{4K_1 z^2}{I^2} - \frac{32K_1K_2 z}{I^3}\right) + e^{-K_1 z}\left(-\frac{96K_1K_2^2}{I^4} - \frac{16K_1}{I^3} - \frac{16K_2^2 z}{I^3} - \frac{4z}{I^2}\right)$$

$$F_{K_1,K_2}(2,0) = e^{-K_2 z}\left(\frac{16K_1^2}{I^3} - \frac{4}{I^2}\right) + e^{-K_1 z}\left(\frac{4}{I^2} - \frac{16K_1^2}{I^3} - \frac{8K_1 z}{I^2} - \frac{2z^2}{I}\right)$$

$$F_{K_1,K_2}(0,2) = e^{-K_2 z}\left(\frac{4}{I^2} + \frac{16K_2^2}{I^3} - \frac{8K_2 z}{I^2} + \frac{2z^2}{I}\right) + e^{-K_1 z}\left(-\frac{4}{I^2} - \frac{16K_2^2}{I^3}\right)$$

$$F_{K_1,K_2}(3,0) = e^{-K_2 z}\left(-\frac{48K_1}{I^3} + \frac{96K_1^3}{I^4}\right) + e^{-K_1 z}\left(\frac{48K_1}{I^3} - \frac{96K_1^3}{I^4} + \frac{12z}{I^2} - \frac{48K_1^2 z}{I^3} - \frac{12K_1 z^2}{I^2} - \frac{2z^3}{I}\right)$$

$$F_{K_1,K_2}(0,3) = e^{-K_2 z}\left(-\frac{96K_2^3}{I^4} - \frac{48K_2}{I^3} + \frac{48K_2^2 z}{I^3} + \frac{12z}{I^2} - \frac{12K_2 z^2}{I^2} + \frac{2z^3}{I}\right) + e^{-K_1 z}\left(\frac{48K_2}{I^3} + \frac{96K_2^3}{I^4}\right)$$

$$F_{K,K}(0,0) = e^{-Kz}\left(\frac{z}{K}\right)$$

$$F_{K,K}(1,0) = e^{-Kz}\left(\frac{z^2}{2K} + \frac{z}{2K^2}\right)$$

$$F_{K,K}(1,1) = e^{-Kz}\left(\frac{z}{2K^3} + \frac{z^3}{6K} + \frac{z^2}{2K^2}\right)$$

$$F_{K,K}(2,0) = e^{-Kz}\left(\frac{z^3}{3K} + \frac{z^2}{2K^2} + \frac{z}{2K^3}\right)$$

$$F_{K,K}(2,1) = e^{-Kz}\left(\frac{z^4}{12K} + \frac{z^3}{3K^2} + \frac{3z^2}{4K^3} + \frac{3z}{4K^4}\right)$$

$$F_{K,K}(3,0) = e^{-Kz}\left(\frac{z^4}{4K} + \frac{z^3}{2K^2} + \frac{3z^2}{4K^3} + \frac{3z}{4K^4}\right)$$

APPENDIX C

INTEGRALS EVALUATED FOR THE TWO PARTICLE PROBLEM

The element of volume is $d\tau = 8\pi^2\, r_1 r_2 r_{12}\, dr_1\, dr_2\, dr_{12}$

$$\psi = r_2\, e^{-k(r_1 + \alpha r_{12})}$$

$$\int \psi^2\, d\tau = 8\pi^2 \int_0^\infty r_2^3\, \underset{2k,2k\alpha}{F(1,1)}\, dr_2 = \frac{3\pi^2(1+\alpha^2)}{k^8\alpha^5}$$

$$\int \frac{\psi^2}{r_1}\, d\tau = 8\pi^2 \int_0^\infty r_2^3\, \underset{2k,2k\alpha}{F(0,1)}\, dr_2 = \frac{3\pi^2(2+\alpha^2)}{2k^7\alpha^5}$$

$$\int \frac{\psi^2}{r_2}\, d\tau = 8\pi^2 \int_0^\infty r_2^2\, \underset{2k,2k\alpha}{F(1,1)}\, dr_2 = \frac{8\pi^2}{3}\left[\frac{3(3\alpha^2+2)}{16k^7\alpha^5} - \frac{3}{16k^7\alpha^4(1+\alpha)^3} - \frac{3}{8k^7\alpha^5(1+\alpha)^2}\right]$$

$$\int \frac{\psi^2}{r_{12}}\, d\tau = 8\pi^2 \int_0^\infty r_2^3\, \underset{2k,2k\alpha}{F(1,0)}\, dr_2 = \frac{3\pi^2}{2k^7\alpha^4}(1+2\alpha^2)$$

$$\int \frac{\psi^2 r_1}{r_{12}}\, d\tau = 8\pi^2 \int_0^\infty r_2^3\, \underset{2k,2k\alpha}{F(2,0)}\, dr_2 = \pi^2\left[\frac{9}{4k^8\alpha^4} + \frac{15}{2k^8\alpha^2}\right]$$

$$\int \frac{\psi^2 r_2^2}{r_1 r_{12}}\, d\tau = 8\pi^2 \int_0^\infty r_2^5\, \underset{2k,2k\alpha}{F(0,0)}\, dr_2 = \frac{15\pi^2}{2}\left[\frac{1}{k^8\alpha^6} + \frac{1}{k^8\alpha^4} + \frac{1}{k^8\alpha^2}\right]$$

$$\int \frac{\psi^2 r_{12}}{r_1}\, d\tau = 8\pi^2 \int_0^\infty r_2^3\, \underset{2k,2k\alpha}{F(0,2)}\, dr_2 = \pi^2\left[\frac{15}{2k^8\alpha^6} + \frac{9}{4k^8\alpha^4}\right]$$

$$\int \frac{\psi^2 r_1^2}{r_2^2 r_{12}}\, d\tau = 8\pi^2 \int_0^\infty r_2\, \underset{2k,2k\alpha}{F(3,0)}\, dr_2 = \frac{3\pi^2}{k^7\alpha^2}$$

$$\int \frac{\psi^2 r_{12}}{r_2^2}\, d\tau = 8\pi^2 \int_0^\infty r_2\, \underset{2k,2k\alpha}{F(1,2)}\, dr_2 = \frac{3\pi^2}{2k^7\alpha^4}$$

$$\int \frac{\psi^2}{r_2^2}\, d\tau = 8\pi^2 \int_0^\infty r_2\, \underset{2k,2k\alpha}{F(1,1)}\, dr_2 = \frac{\pi^2}{k^6\alpha^3}$$

APPENDIX D

INTEGRALS EVALUATED FOR THE EQUIVALENT ONE DIMENSIONAL PROBLEM

$$R = 8\pi^2 \frac{(K_1^2+2K_2^2)}{4} \underset{K_1,K_2}{F}(1,1) + 8\pi^2 \frac{K_1 K_2}{4}\left[\underset{K_1,K_2}{F}(2,0) + \underset{K_1,K_2}{F}(0,2)\right]$$

$$= 8\pi^2 (K_1^2+2K_2^2)\left[e^{-K_2 n_2}\left(\frac{K_1 n_2}{I^2} - \frac{4K_1K_2}{I^3}\right) + e^{-K_1 n_2}\left(\frac{K_2 n_2}{I^2} + \frac{4K_1K_2}{I^3}\right)\right]$$

$$+ 8\pi^2 K_1K_2\left[e^{-K_2 n_2}\left(\frac{4K_1^2}{I^3}+\frac{4K_2^2}{I^3}-\frac{2K_2 n_2}{I^2}+\frac{n_2^2}{2I}\right)+e^{-K_1 n_2}\left(-\frac{4K_1^2}{I^3}-\frac{4K_2^2}{I^3}-\frac{2K_1 n_2}{I^2}-\frac{n_2^2}{2I}\right)\right]$$

$$W = 8\pi^2 \frac{K_1K_2}{4} \underset{K_1,K_2}{F}(0,0) = 4\pi^2 K_1K_2\left[\frac{e^{-K_2 n_2} - e^{-K_1 n_2}}{I}\right]$$

$$U = 8\pi^2 \underset{K_1,K_2}{F}(1,1) = 8\pi^2\left[e^{-K_2 n_2}\left(\frac{4K_1 n_2}{I^2} - \frac{16K_1K_2}{I^3}\right) + e^{-K_1 n_2}\left(\frac{4K_2 n_2}{I^2} + \frac{16K_1K_2}{I^3}\right)\right]$$

$$P = 8\pi^2 K\epsilon^2\left[\underset{K_1,K_2}{F}(1,0) + \underset{K_1,K_2}{F}(0,1)\right] = 8\pi^2 K\epsilon^2\left[e^{-K_2 n_2}\left(\frac{4K_1}{I^2} - \frac{4K_2}{I^2} + \frac{2n_2}{I}\right) + e^{-K_1 n_2}\left(-\frac{4K_1}{I^2} + \frac{4K_2}{I^2} - \frac{2n_2}{I}\right)\right]$$

$$S = -4\pi^2 K_2 \underset{K_1,K_2}{F}(1,0) = -4\pi^2 K_2\left[e^{-K_2 n_2}\left(\frac{4K_1}{I^2}\right) + e^{-K_1 n_2}\left(-\frac{4K_1}{I^2} - \frac{2n_2}{I}\right)\right]$$

$$T = 4\pi^2 K_2\left[\underset{K_1,K_2}{F}(1,2) - \underset{K_1,K_2}{F}(3,0)\right]$$

$$= 4\pi^2 K_2\left[e^{-K_2 n_2}\left(\frac{-32K_1}{I^3} + \frac{4K_1 n_2^2}{I^2} - \frac{32K_1K_2 n_2}{I^3}\right) + e^{-K_1 n_2}\left(\frac{32K_1}{I^3} + \frac{32K_1^3 n_2}{I^3} + \frac{12K_1 n_2^2}{I^2} + \frac{2n_2^3}{I}\right)\right]$$

APPENDIX E

SQUARE OF GRADIENT OPERATORS FOR THE FOUR PARTICLE PROBLEM

Let $$f = f(r_1, r_2, r_{12}, r_3, r_{13}, r_{23})$$

and $$\underline{r}_{12} = \underline{r}_2 - \underline{r}_1 \qquad \underline{r}_{13} = \underline{r}_3 - \underline{r}_1 \qquad \underline{r}_{23} = \underline{r}_3 - \underline{r}_2$$

Then

$$\nabla_1 f = \underline{i}\left(\frac{\partial r_1}{\partial x_1}\frac{\partial f}{\partial r_1} + \frac{\partial r_{12}}{\partial x_1}\frac{\partial f}{\partial r_{12}} + \frac{\partial r_{13}}{\partial x_1}\frac{\partial f}{\partial r_{13}}\right) + \underline{j}\left(\frac{\partial r_1}{\partial y_1}\frac{\partial f}{\partial r_1} + \frac{\partial r_{12}}{\partial y_1}\frac{\partial f}{\partial r_{12}} + \frac{\partial r_{13}}{\partial y_1}\frac{\partial f}{\partial r_{13}}\right) + \underline{k}\left(\frac{\partial r_1}{\partial z_1}\frac{\partial f}{\partial r_1} + \frac{\partial r_{12}}{\partial z_1}\frac{\partial f}{\partial r_{12}} + \frac{\partial r_{13}}{\partial z_1}\frac{\partial f}{\partial r_{13}}\right)$$

$$= \underline{i}\left(\frac{x_1}{r_1}\frac{\partial f}{\partial r_1} - \frac{(x_2 - x_1)}{r_{12}}\frac{\partial f}{\partial r_{12}} - \frac{(x_3 - x_1)}{r_{13}}\frac{\partial f}{\partial r_{13}}\right) + \underline{j}\left(\frac{y_1}{r_1}\frac{\partial f}{\partial r_1} - \frac{(y_2 - y_1)}{r_{12}}\frac{\partial f}{\partial r_{12}} - \frac{(y_3 - y_1)}{r_{13}}\frac{\partial f}{\partial r_{13}}\right) + \underline{k}\left(\frac{z_1}{r_1}\frac{\partial f}{\partial r_1} - \frac{(z_2 - z_1)}{r_{12}}\frac{\partial f}{\partial r_{12}} - \frac{(z_3 - z_1)}{r_{13}}\frac{\partial f}{\partial r_{13}}\right)$$

Thus

$$\nabla_1 f = \frac{\underline{r}_1}{r_1}\frac{\partial f}{\partial r_1} - \frac{\underline{r}_{12}}{r_{12}}\frac{\partial f}{\partial r_{12}} - \frac{\underline{r}_{13}}{r_{13}}\frac{\partial f}{\partial r_{13}}$$

Similarly,

$$\nabla_2 f = \frac{\underline{r}_2}{r_2}\frac{\partial f}{\partial r_2} + \frac{\underline{r}_{12}}{r_{12}}\frac{\partial f}{\partial r_{12}} - \frac{\underline{r}_{23}}{r_{23}}\frac{\partial f}{\partial r_{23}}$$

$$\nabla_3 f = \frac{\underline{r}_3}{r_3}\frac{\partial f}{\partial r_3} + \frac{\underline{r}_{13}}{r_{13}}\frac{\partial f}{\partial r_{13}} + \frac{\underline{r}_{23}}{r_{23}}\frac{\partial f}{\partial r_{23}}$$

Hence

$$(\nabla_1 f)^2 = (\nabla_1 f)\cdot(\nabla_1 f) = \left(\frac{\partial f}{\partial r_1}\right)^2 + \left(\frac{\partial f}{\partial r_{12}}\right)^2 + \left(\frac{\partial f}{\partial r_{13}}\right)^2 + \left(\frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\right)\left(\frac{\partial f}{\partial r_1}\right)\left(\frac{\partial f}{\partial r_{12}}\right)$$
$$+ \left(\frac{r_{13}^2 + r_1^2 - r_3^2}{r_1 r_{13}}\right)\left(\frac{\partial f}{\partial r_1}\right)\left(\frac{\partial f}{\partial r_{13}}\right) + \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}}\right)\left(\frac{\partial f}{\partial r_{12}}\right)\left(\frac{\partial f}{\partial r_{13}}\right)$$

Similarly,

$$(\nabla_2 f)^2 = \left(\frac{\partial f}{\partial r_2}\right)^2 + \left(\frac{\partial f}{\partial r_{12}}\right)^2 + \left(\frac{\partial f}{\partial r_{23}}\right)^2 + \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}}\right)\left(\frac{\partial f}{\partial r_2}\right)\left(\frac{\partial f}{\partial r_{12}}\right)$$
$$+ \left(\frac{r_{23}^2 + r_2^2 - r_3^2}{r_2 r_{23}}\right)\left(\frac{\partial f}{\partial r_2}\right)\left(\frac{\partial f}{\partial r_{23}}\right) + \left(\frac{r_{23}^2 + r_{12}^2 - r_{13}^2}{r_{12} r_{23}}\right)\left(\frac{\partial f}{\partial r_{12}}\right)\left(\frac{\partial f}{\partial r_{23}}\right)$$

$$(\nabla_3 f)^2 = \left(\frac{\partial f}{\partial r_3}\right)^2 + \left(\frac{\partial f}{\partial r_{13}}\right)^2 + \left(\frac{\partial f}{\partial r_{23}}\right)^2 + \left(\frac{r_{13}^2 + r_3^2 - r_1^2}{r_3 r_{13}}\right)\left(\frac{\partial f}{\partial r_3}\right)\left(\frac{\partial f}{\partial r_{13}}\right)$$
$$+ \left(\frac{r_{23}^2 + r_3^2 - r_2^2}{r_3 r_{23}}\right)\left(\frac{\partial f}{\partial r_3}\right)\left(\frac{\partial f}{\partial r_{23}}\right) + \left(\frac{r_{23}^2 + r_{13}^2 - r_{12}^2}{r_{13} r_{23}}\right)\left(\frac{\partial f}{\partial r_{13}}\right)\left(\frac{\partial f}{\partial r_{23}}\right)$$

APPENDIX F

INTEGRALS EVALUATED AND THE EXPRESSION FOR $\langle H \rangle$ FOR THE THREE PARAMETER TRIAL WAVE FUNCTION

The element of volume, after integrating over the angular coordinates is,

$$d\tau = 16\pi^3 \, r_2 r_{12} r_3 r_{13} \, dr_1 \, dr_2 \, dr_{12} \, dr_3 \, dr_{13}$$

or

$$d\tau = 16\pi^3 \, r_2 r_3 r_{12} r_{13} \, dr_{23} \, dr_2 \, dr_3 \, dr_{12} \, dr_{13}$$

, since the wave function is independent of angle.

$$\psi_2 = e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3)} \qquad \psi_3 = e^{-(\alpha r_3 + \beta r_{13} + \gamma r_2)}$$

Then,

$$\int \psi_2^2 \, d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,1)} \; \underset{2\gamma,0}{F(1,1)} \, dr_1 = \frac{\pi^3}{\alpha^3 \beta^3 \gamma^3}$$

$$\int \psi_2 \psi_3 \, d\tau = 16\pi^3 \int_0^\infty \underset{\alpha+\gamma,\beta}{F(1,1)} \; \underset{\alpha+\gamma,\beta}{F(1,1)} \, dr_1$$

$$= 16\pi^3 \left[\frac{4(\alpha+\gamma)^2}{\beta^3 I^4} + \frac{4\beta^2}{(\alpha+\gamma)^3 I^4} - \frac{32(\alpha+\gamma)^2}{\beta I^5} + \frac{32\beta^2}{(\alpha+\gamma) I^5} + \frac{320\beta(\alpha+\gamma)}{(\alpha+\beta+\gamma)^3 I^4} \right]$$

$$I = [(\alpha+\gamma)^2 - \beta^2]$$

$$\int \psi_2 \psi_3 \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)} \; \underset{\beta,\beta}{F(2,0)} + \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)} \; \underset{\beta,\beta}{F(0,2)} - r_{23}^2 \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)} \; \underset{\beta,\beta}{F(0,0)} \right] dr_{23}$$

$$= 16\pi^3 \left[\frac{80}{\beta(\alpha+\gamma)(\alpha+\beta+\gamma)^7} + \frac{8}{\beta^3(\alpha+\gamma)^3(\alpha+\beta+\gamma)^3} + \frac{4}{\beta^2(\alpha+\gamma)^3(\alpha+\beta+\gamma)^4} \right.$$

$$+ \frac{20}{\beta(\alpha+\gamma)^2(\alpha+\beta+\gamma)^6} + \frac{20}{\beta^2(\alpha+\gamma)^2(\alpha+\beta+\gamma)^5} - \frac{12}{\beta(\alpha+\gamma)^3(\alpha+\beta+\gamma)^5} - \frac{120}{\beta(\alpha+\gamma)(\alpha+\beta+\gamma)^7}$$

$$\left. - \frac{60}{\beta(\alpha+\gamma)^2(\alpha+\beta+\gamma)^6} \right]$$

$$\int \psi_2^2 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{2\alpha,2\beta}{F(2,0)} \; \underset{2\gamma,0}{F(1,1)} + \underset{2\alpha,2\beta}{F(0,2)} \; \underset{2\gamma,0}{F(1,1)} - r_1^2 \underset{2\alpha,2\beta}{F(0,0)} \; \underset{2\gamma,0}{F(1,1)} \right] dr_1$$

$$= 16\pi^3 \left[\frac{3}{32\alpha^2\beta^4\gamma^3} + \frac{3}{32\alpha^4\beta^2\gamma^3} - \frac{3(\alpha^2+\beta^2)}{32\alpha^4\beta^4\gamma^3} \right]$$

$$\int \psi_2 \psi_3 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{\alpha+\gamma,\beta}{F}(0,2) \underset{\alpha+\gamma,\beta}{F}(1,1) + \underset{\alpha+\gamma,\beta}{F}(2,0) \underset{\alpha+\gamma,\beta}{F}(1,1) - r_1^2 \underset{\alpha+\gamma,\beta}{F}(0,0) \underset{\alpha+\gamma,\beta}{F}(1,1) \right] dr_1$$

$$= 16\pi^3 \left[-\frac{8(\alpha+\gamma)}{\beta^2 I^4} + \frac{48(\alpha+\gamma)}{I^5} - \frac{128(\alpha+\gamma)\beta^2}{I^6} - \frac{128\beta^3}{I^6} \right.$$

$$+ \frac{64\beta^3}{(\alpha+\beta+\gamma)^2 I^5} - \frac{192(\alpha+\gamma)\beta^2}{(\alpha+\beta+\gamma)^2 I^5} + \frac{32\times 16(\alpha+\gamma)\beta^3}{(\alpha+\beta+\gamma) I^6} + \frac{112\beta}{(\alpha+\beta+\gamma)^4 I^3} - \frac{8\beta}{(\alpha+\gamma)^2 I^4} - \frac{16\beta^3}{(\alpha+\gamma)^2 I^5}$$

$$- \frac{48\beta}{I^5} + \frac{16(\alpha+\gamma)^3}{\beta^2 I^5} - \frac{128(\alpha+\gamma)^3}{I^6} - \frac{128(\alpha+\gamma)^2\beta}{I^6} - \frac{192(\alpha+\gamma)^2}{(\alpha+\beta+\gamma)^3 I^4} + \frac{128(\alpha+\gamma)^2\beta}{(\alpha+\beta+\gamma)^2 I^5}$$

$$\left. + \frac{32\times 16(\alpha+\gamma)^3\beta}{(\alpha+\beta+\gamma) I^6} - \frac{112(\alpha+\gamma)}{(\alpha+\beta+\gamma)^4 I^3} + \frac{48}{(\alpha+\beta+\gamma)^5 I^2} \right]$$

$$\int \frac{\psi_2^2}{r_1} d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_1} \underset{2\alpha,2\beta}{F}(1,1) \underset{2\gamma,0}{F}(1,1)\, dr_1 = 16\pi^3 \left[\frac{\alpha}{16\beta^2\gamma^3(\alpha^2-\beta^2)^2} + \frac{\beta}{16\alpha^2\gamma^3(\alpha^2-\beta^2)^2} \right.$$

$$\left. - \frac{\alpha}{4\gamma^3(\alpha^2-\beta^2)^3} + \frac{\beta}{4\gamma^3(\alpha^2-\beta^2)^3} \right]$$

$$\int \frac{\psi_2\psi_3}{r_1} d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_1} \underset{\alpha+\gamma,\beta}{F}(1,1) \underset{\alpha+\gamma,\beta}{F}(1,1)\, dr_1$$

$$= 16\pi^3 \left[\frac{4(\alpha+\gamma)^2}{\beta^2 I^4} - \frac{64(\alpha+\gamma)^2}{I^5} + \frac{4\beta^2}{(\alpha+\gamma)^2 I^4} + \frac{64\beta^2}{I^5} + \frac{32(\alpha+\gamma)\beta}{(\alpha+\beta+\gamma)^2 I^4} \right.$$

$$\left. + \frac{128(\alpha+\gamma)^2\beta}{(\alpha+\beta+\gamma) I^5} - \frac{128(\alpha+\gamma)\beta^2}{(\alpha+\beta+\gamma) I^5} + \frac{16\times 16(\alpha+\gamma)^2\beta^2}{I^6} \ln\left\{ \frac{(\alpha+\beta+\gamma)^2}{4(\alpha+\gamma)\beta} \right\} \right]$$

$$\int \frac{\psi_2^2}{r_2} d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F}(0,1) \underset{2\gamma,0}{F}(1,1)\, dr_1 = 16\pi^3 \left[\frac{1}{16\alpha^2\beta^3\gamma^3} \right]$$

$$\int \frac{\psi_2\psi_3}{r_2} d\tau = 16\pi^3 \int_0^\infty \underset{\alpha+\gamma,\beta}{F}(0,1) \underset{\alpha+\gamma,\beta}{F}(1,1)\, dr_1$$

$$= 16\pi^3 \left[\frac{2(\alpha+\gamma)}{\beta^3 I^3} - \frac{12(\alpha+\gamma)}{\beta I^4} + \frac{32(\alpha+\beta+\gamma)\beta}{I^5} + \frac{32\beta}{(\alpha+\beta+\gamma)^3 I^3} \right.$$

$$\left. + \frac{32(\alpha+\gamma)\beta}{(\alpha+\beta+\gamma)^2 I^4} - \frac{128(\alpha+\gamma)\beta^2}{(\alpha+\beta+\gamma) I^5} + \frac{4\beta^2}{(\alpha+\gamma)^2 I^4} \right]$$

$$\int \frac{\psi_2^2}{r_3}\, d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,1)}\; \underset{2\gamma,0}{F(0,1)}\, dr_1 = 16\pi^3 \left[\frac{1}{16\alpha^3\beta^3\gamma^2} \right]$$

$$\int \frac{\psi_2^2}{r_{12}}\, d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,0)}\; \underset{2\gamma,0}{F(1,1)}\, dr_1 = 16\pi^3 \left[\frac{1}{16\alpha^3\beta^2\gamma^3} \right]$$

$$\int \frac{\psi_2^2}{r_{13}}\, d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,1)}\; \underset{2\gamma,0}{F(1,0)}\, dr_1 = 16\pi^3 \left[\frac{\alpha^3+\beta^3}{16\alpha^2\beta^2\gamma^3(\alpha^2-\beta^2)^2} - \frac{1}{4(\alpha+\beta)\gamma^3(\alpha^2-\beta^2)^2} \right.$$

$$- \frac{\alpha}{16(\beta+\gamma)^2\gamma^3(\alpha^2-\beta^2)^2} - \frac{\beta}{16(\alpha+\gamma)^2\gamma^3(\alpha^2-\beta^2)^2} + \frac{\alpha\beta}{4(\beta+\gamma)\gamma^3(\alpha^2-\beta^2)^3}$$

$$- \frac{\alpha\beta}{4(\alpha+\gamma)\gamma^3(\alpha^2-\beta^2)^3} - \frac{\alpha}{16(\beta+\gamma)^3\gamma^2(\alpha^2-\beta^2)^2} - \frac{\beta}{16(\alpha+\gamma)^3\gamma^2(\alpha^2-\beta^2)^2}$$

$$\left. + \frac{\alpha\beta}{8(\beta+\gamma)^2\gamma^2(\alpha^2-\beta^2)^3} - \frac{\alpha\beta}{8(\alpha+\gamma)^2\gamma^2(\alpha^2-\beta^2)^3} \right]$$

$$\int \frac{\psi_2\psi_3}{r_{12}}\, d\tau = 16\pi^3 \int_0^\infty \underset{\alpha+\gamma,\beta}{F(1,0)}\; \underset{\alpha+\gamma,\beta}{F(1,1)}\, dr_1 = 16\pi^3 \left[-\frac{32(\alpha+\gamma)(\alpha+\beta+\gamma)}{I^5} + \frac{4(\alpha+\gamma)^2}{\beta^2 I^4} \right.$$

$$\left. + \frac{32(\alpha+\gamma)\beta}{(\alpha+\beta+\gamma)^2 I^4} - \frac{32(\alpha+\gamma)}{(\alpha+\beta+\gamma)^3 I^3} + \frac{128(\alpha+\gamma)^2\beta}{(\alpha+\beta+\gamma) I^5} - \frac{2\beta}{(\alpha+\gamma)^2 I^3} - \frac{12\beta}{(\alpha+\gamma) I^4} \right]$$

$$\int \frac{\psi_2^2}{r_{23}}\, d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_{23}}\, \underset{2\gamma,2\alpha}{F(1,1)}\; \underset{0,2\beta}{F(1,1)}\, dr_{23} = 16\pi^3 \left[\frac{\gamma}{16\alpha^2\beta^3(\alpha^2-\gamma^2)^2} + \frac{\alpha}{16\beta^3\gamma^2(\alpha^2-\gamma^2)^2} \right.$$

$$\left. + \frac{\gamma}{4\beta^3(\alpha^2-\gamma^2)^3} - \frac{\alpha}{4\beta^3(\alpha^2-\gamma^2)^3} \right]$$

$$\int \frac{\psi_2\psi_3}{r_{23}}\, d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_{23}}\, \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)}\; \underset{\beta,\beta}{F(1,1)}\, dr_{23}$$

$$= 16\pi^3 \left[\frac{5}{4(\alpha+\gamma)^2\beta^3(\alpha+\beta+\gamma)^2} + \frac{5}{2(\alpha+\gamma)^2\beta^2(\alpha+\beta+\gamma)^4} + \frac{10}{3(\alpha+\gamma)\beta(\alpha+\beta+\gamma)^6} \right]$$

$$\langle H \rangle = \frac{\frac{1}{K} A(\alpha,\beta,\gamma) + \epsilon^2 B(\alpha,\beta,\gamma)}{C(\alpha,\beta,\gamma)},$$

$$A(\alpha,\beta,\gamma) = 16\pi^3 \left\{ \frac{\alpha^2+2\beta^2+\gamma^2}{8\alpha^3\beta^3\gamma^3} + \frac{8\left[(\alpha+\gamma)^2+7(\alpha+\gamma)\beta+\beta^2\right]}{(\alpha+\gamma)\beta(\alpha+\beta+\gamma)^7} \right.$$

$$\left. + \frac{16\gamma\left[(\alpha+\gamma)^2+7(\alpha+\gamma)\beta+\beta^2\right]}{(\alpha+\gamma)^2\beta(\alpha+\beta+\gamma)^7} + \frac{16\alpha\gamma\left[(\alpha+\gamma)^4+7(\alpha+\gamma)^3\beta+17(\alpha+\gamma)^2\beta^2+7(\alpha+\gamma)\beta^3+\beta^4\right]}{(\alpha+\gamma)^3\beta^3(\alpha+\beta+\gamma)^7} \right\}$$

$$B(\alpha,\beta,\gamma) = 16\pi^3 \left\{ \frac{32\times 32(\alpha+\gamma)^2\beta^2}{I^6} \ln\left[\frac{(\alpha+\beta+\gamma)^2}{4(\alpha+\gamma)\beta}\right] + \frac{16\times 16(\alpha-2\beta+\gamma)}{(\alpha+\beta+\gamma)^3\, I^3} \right.$$

$$+ \frac{(\alpha^2+3\alpha\beta+\beta^2)}{8\alpha^2\beta^2\gamma^3(\alpha+\beta)^3} + \frac{(\alpha^2+3\alpha\gamma+\gamma^2)}{8\alpha^2\beta^3\gamma^2(\alpha+\gamma)^3} - \frac{2(\alpha+\gamma)+\beta}{8\alpha^3\beta^3\gamma^3}$$

$$+ \frac{5}{(\alpha+\gamma)\beta(\alpha+\beta+\gamma)^2}\left[\frac{4}{3(\alpha+\beta+\gamma)^4} + \frac{1}{(\alpha+\gamma)\beta(\alpha+\beta+\gamma)^2} + \frac{1}{2\beta^2(\alpha+\gamma)^2}\right]$$

$$+ \frac{\alpha\beta(2\alpha+3\gamma)}{4(\alpha+\gamma)^2\gamma^3(\alpha^2-\beta^2)^3} - \frac{\alpha\beta(2\beta+3\gamma)}{4(\beta+\gamma)^2\gamma^3(\alpha^2-\beta^2)^3} + \frac{\alpha(\beta+2\gamma)}{8(\beta+\gamma)^3\gamma^3(\alpha^2-\beta^2)^2}$$

$$+ \frac{\beta(\alpha+2\gamma)}{8(\alpha+\gamma)^3\gamma^3(\alpha^2-\beta^2)^2} + \frac{16\times 16(\alpha+\gamma)\beta}{(\alpha+\beta+\gamma)^2\, I^4} - \frac{16(\alpha+\gamma)^2}{\beta^2\, I^4} + \frac{48\left[2(\alpha+\gamma)^2+\beta^2\right]}{(\alpha+\gamma)\beta\, I^4}$$

$$\left. - \frac{16\times 16}{I^4} + \frac{16\left[(\alpha+\gamma)^2+\beta^2\right]}{(\alpha+\gamma)^2\beta^2\, I^3} - \frac{16(\alpha+\gamma)}{\beta^3\, I^3} + \frac{8\beta}{(\alpha+\gamma)^2\, I^3} \right\}$$

$$C(\alpha,\beta,\gamma) = 16\pi^3 \left\{ \frac{1}{8\alpha^3\beta^3\gamma^3} + \frac{8\left[(\alpha+\gamma)^4+7(\alpha+\gamma)^3\beta+17(\alpha+\gamma)^2\beta^2+7(\alpha+\gamma)\beta^3+\beta^4\right]}{(\alpha+\gamma)^3\beta^3(\alpha+\beta+\gamma)^7} \right\}$$

APPENDIX G

INTEGRALS EVALUATED AND THE EXPRESSION FOR $\langle H \rangle$ FOR THE FOUR PARAMETER TRIAL WAVE FUNCTION

The element of volume is,

$$d\tau = 16\pi^3 r_2 r_{12} r_3 r_{13}\, dr_1\, dr_2\, dr_{12}\, dr_3\, dr_{13}$$

or

$$d\tau = 16\pi^3 r_2 r_3 r_{12} r_{13}\, dr_{23}\, dr_2\, dr_3\, dr_{12}\, dr_{13}$$

Then,
$$\psi_2 = e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3 + \delta r_{13})} \qquad \psi_3 = e^{-(\alpha r_3 + \beta r_{13} + \gamma r_2 + \delta r_{12})}$$

$$\mathrm{I} = (\alpha^2 - \beta^2) \qquad \mathrm{II} = (\gamma^2 - \delta^2) \qquad \mathrm{III} = (\alpha^2 - \gamma^2) \qquad \mathrm{IV} = (\beta^2 - \delta^2)$$

$$\int \psi_2^2\, d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,1)}\ \underset{2\gamma,2\delta}{F(1,1)}\, dr_1 = 16\pi^3 \Bigg\{ \frac{\alpha\beta\gamma\delta}{2\,\mathrm{I}^3\,\mathrm{II}^3} \left[\frac{1}{\beta+\delta} + \frac{1}{\alpha+\gamma} - \frac{1}{\alpha+\delta} - \frac{1}{\beta+\gamma} \right]$$

$$+ \frac{1}{16\,\mathrm{I}^2\,\mathrm{II}^2} \left[\frac{\alpha\gamma}{(\beta+\delta)^3} + \frac{\beta\gamma}{(\alpha+\delta)^3} + \frac{\alpha\delta}{(\beta+\gamma)^3} + \frac{\beta\delta}{(\alpha+\gamma)^3} \right] + \frac{1}{8\,\mathrm{I}^2\,\mathrm{II}^3} \left[\frac{\alpha\gamma\delta}{(\beta+\gamma)^2} + \frac{\beta\gamma\delta}{(\alpha+\gamma)^2} - \frac{\alpha\gamma\delta}{(\beta+\delta)^2} - \frac{\beta\gamma\delta}{(\alpha+\delta)^2} \right]$$

$$+ \frac{\alpha\beta}{8\,\mathrm{I}^3\,\mathrm{II}^2} \left[\frac{\gamma}{(\alpha+\delta)^2} - \frac{\gamma}{(\beta+\delta)^2} - \frac{\delta}{(\beta+\gamma)^2} + \frac{\delta}{(\alpha+\gamma)^2} \right] \Bigg\}$$

$$\int \psi_2 \psi_3\, d\tau = 16\pi^3 \int_0^\infty \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)}\ \underset{\beta+\delta,\beta+\delta}{F(1,1)}\, dr_{23} = 16\pi^3 \Bigg[\frac{20}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^7} + \frac{4}{(\alpha+\gamma)^3(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^3}$$

$$+ \frac{12}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^5} \Bigg]$$

$$\int \psi_2^2 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau = 16\pi^3 \int_0^\infty \Big[\underset{2\alpha,2\beta}{F(2,0)}\ \underset{2\gamma,2\delta}{F(1,1)} + \underset{2\alpha,2\beta}{F(0,2)}\ \underset{2\gamma,2\delta}{F(1,1)} - r_1^2\, \underset{2\alpha,2\beta}{F(0,0)}\ \underset{2\gamma,2\delta}{F(1,1)} \Big]\, dr_1$$

$$= 16\pi^3 \Bigg\{ \frac{(\alpha^2+\beta^2)}{8\,\mathrm{I}^3\,\mathrm{II}^2} \left[\frac{\gamma}{(\beta+\delta)^2} - \frac{\gamma}{(\alpha+\delta)^2} + \frac{\delta}{(\beta+\gamma)^2} - \frac{\delta}{(\alpha+\gamma)^2} \right]$$

$$+ \frac{(\alpha^2+\beta^2)\gamma\delta}{2\,\mathrm{I}^3\,\mathrm{II}^3} \left[\frac{1}{\alpha+\delta} - \frac{1}{\beta+\delta} + \frac{1}{\beta+\gamma} - \frac{1}{\alpha+\gamma} \right] + \frac{1}{8\,\mathrm{I}^2\,\mathrm{II}^2} \left[-\frac{\beta\delta}{(\beta+\gamma)^3} - \frac{\alpha\gamma}{(\alpha+\delta)^3} - \frac{\beta\gamma}{(\beta+\delta)^3} - \frac{\alpha\delta}{(\alpha+\gamma)^3} \right]$$

$$+ \frac{\gamma\delta}{4\,\mathrm{I}^2\,\mathrm{II}^3} \left[\frac{\alpha}{(\alpha+\delta)^2} - \frac{\beta}{(\beta+\gamma)^2} + \frac{\beta}{(\beta+\delta)^2} - \frac{\alpha}{(\alpha+\gamma)^2} \right] \Bigg\}$$

$$\int \psi_3^2 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{2\gamma,2\delta}{F(2,0)} \underset{2\alpha,2\beta}{F(1,1)} + \underset{2\gamma,2\delta}{F(0,2)} \underset{2\alpha,2\beta}{F(1,1)} - r_1^2 \underset{2\gamma,2\delta}{F(0,0)} \underset{2\alpha,2\beta}{F(1,1)} \right] dr_1$$

$$= \int \psi_2^2 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau \quad \text{WITH} \quad \alpha \leftrightarrow \gamma \quad \beta \leftrightarrow \delta$$

$$\int \psi_2 \psi_3 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{\alpha+\gamma,\alpha+\gamma}{F(1,2)} \underset{\beta+\delta,\beta+\delta}{F(1,0)} + \underset{\alpha+\gamma,\alpha+\gamma}{F(1,0)} \underset{\beta+\delta,\beta+\delta}{F(1,2)} \right] dr_{23} - r_1^2 \underset{\alpha+\gamma,\beta+\delta}{F(0,0)} \underset{\alpha+\gamma,\beta+\delta}{F(1,1)} dr_1$$

$$= 16\pi^3 \left[\frac{60}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^7} + \frac{15}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^5} \right.$$

$$+ \frac{3}{(\alpha+\gamma)^3(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^3} + \frac{3}{(\alpha+\gamma)^4(\beta+\delta)^4(\alpha+\beta+\gamma+\delta)} - \frac{\{3(\alpha+\gamma)^5 - 3(\beta+\delta)^5\}}{(\alpha+\gamma)^4(\beta+\delta)^4[(\alpha+\gamma)^2-(\beta+\delta)^2]^3}$$

$$\left. + \frac{8\{(\alpha+\gamma)^3+(\beta+\delta)^3\}}{(\alpha+\gamma)^2(\beta+\delta)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4} + \frac{48}{(\alpha+\beta+\gamma+\delta)^5[(\alpha+\gamma)^2-(\beta+\delta)^2]^2} - \frac{128(\alpha+\gamma)(\beta+\delta)}{(\alpha+\beta+\gamma+\delta)^3[(\alpha+\gamma)^2-(\beta+\delta)^2]^4} \right]$$

$$\int \psi_2 \psi_3 \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}} \right) d\tau = 16\pi^3 \int_0^\infty \left[2 \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)} \underset{\beta+\delta,\beta+\delta}{F(2,0)} - r_{23}^2 \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)} \underset{\beta+\delta,\beta+\delta}{F(0,0)} \right] dr_{23}$$

$$= 16\pi^3 \left[\frac{-40}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^7} + \frac{20(\alpha+\gamma) - 20(\beta+\delta)}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^6} \right.$$

$$\left. + \frac{12}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^5} + \frac{8}{(\alpha+\gamma)^2(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^4} \right]$$

$$\int \psi_2^2 \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{2\delta,2\beta}{F(2,0)} + \underset{2\delta,2\beta}{F(0,2)} - r_{23}^2 \underset{2\delta,2\beta}{F(0,0)} \right] \underset{2\gamma,2\alpha}{F(1,1)} \, dr_{23}$$

$$= \int \psi_2^2 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau \quad \text{WITH} \quad \alpha \leftrightarrow \delta \quad \beta \leftrightarrow \beta \quad \gamma \leftrightarrow \gamma$$

$$\int \psi_3^2 \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}} \right) d\tau = 16\pi^3 \int_0^\infty \left[\underset{2\beta,2\delta}{F(2,0)} \underset{2\alpha,2\gamma}{F(1,1)} + \underset{2\beta,2\delta}{F(0,2)} \underset{2\alpha,2\gamma}{F(1,1)} - r_{23}^2 \underset{2\beta,2\delta}{F(0,0)} \underset{2\alpha,2\gamma}{F(1,1)} \right] dr_{23}$$

$$= \int \psi_2^2 \left(\frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \right) d\tau \quad \text{WITH} \quad \begin{matrix} \alpha \to \beta & \beta \to \delta \\ \gamma \to \alpha & \delta \to \gamma \end{matrix}$$

$$\int \frac{\psi_2^2}{r_1} d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_1} \underset{2\alpha,2\beta}{F(1,1)} \underset{2\gamma,2\delta}{F(1,1)} dr_1 = 16\pi^3 \left\{ \frac{1}{16 I^2 II^2} \left[\frac{\alpha\gamma}{(\beta+\delta)^2} + \frac{\beta\gamma}{(\alpha+\delta)^2} + \frac{\alpha\delta}{(\beta+\gamma)^2} + \frac{\beta\delta}{(\alpha+\gamma)^2} \right] \right.$$

$$+ \frac{\alpha\beta}{4 I^3 II^2} \left[\frac{\gamma}{\alpha+\delta} - \frac{\delta}{\beta+\gamma} + \frac{\delta}{\alpha+\gamma} - \frac{\gamma}{\beta+\delta} \right] + \frac{\gamma\delta}{4 I^2 II^3} \left[\frac{\alpha}{\beta+\gamma} + \frac{\beta}{\alpha+\gamma} - \frac{\alpha}{\beta+\delta} - \frac{\beta}{\alpha+\delta} \right]$$

$$+ \frac{\alpha\beta\gamma\delta}{I^2 II^3} \ln\left[\frac{(\alpha+\gamma)(\beta+\delta)}{(\beta+\gamma)(\alpha+\delta)}\right]\Bigg\}$$

$$\int \frac{\psi_2^2}{r_2}\,d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(0,1)}\ \underset{2\gamma,2\delta}{F(1,1)}\,dr_1 = 16\pi^3 \Bigg\{ \frac{1}{16\, I\, II^2}\left[\frac{\gamma}{(\beta+\delta)^3} + \frac{\delta}{(\beta+\gamma)^3}\right]$$

$$+ \frac{\beta}{16\, I^2 II^2}\left[\frac{\gamma}{(\alpha+\delta)^2} - \frac{\gamma}{(\beta+\delta)^2} - \frac{\delta}{(\beta+\gamma)^2} + \frac{\delta}{(\alpha+\gamma)^2}\right] + \frac{\gamma\delta}{8\, I\, II^3}\left[\frac{1}{(\beta+\gamma)^2} - \frac{1}{(\beta+\delta)^2}\right]$$

$$+ \frac{\beta\gamma\delta}{4\, I^2 II^3}\left[\frac{1}{\alpha+\gamma} + \frac{1}{\beta+\delta} - \frac{1}{\alpha+\delta} - \frac{1}{\beta+\gamma}\right]\Bigg\}$$

$$\int \frac{\psi_2^2}{r_3}\,d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,1)}\ \underset{2\gamma,2\delta}{F(0,1)}\,dr_1 = \int \frac{\psi_2^2}{r_2}\,d\tau \quad \text{WITH } \alpha \leftrightarrow \gamma \quad \beta \leftrightarrow \delta$$

$$\int \frac{\psi_2^2}{r_{12}}\,d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,0)}\ \underset{2\gamma,2\delta}{F(1,1)}\,dr_1 = 16\pi^3 \Bigg\{ \frac{1}{16\, I\, II^2}\left[-\frac{\delta}{(\alpha+\gamma)^3} - \frac{\gamma}{(\alpha+\delta)^3}\right]$$

$$+ \frac{\alpha}{16\, I^2 II^2}\left[\frac{\gamma}{(\beta+\delta)^2} + \frac{\delta}{(\beta+\gamma)^2} - \frac{\delta}{(\alpha+\gamma)^2} - \frac{\gamma}{(\alpha+\delta)^2}\right] + \frac{\gamma\delta}{8\, I\, II^3}\left[\frac{1}{(\alpha+\delta)^2} - \frac{1}{(\alpha+\gamma)^2}\right]$$

$$+ \frac{\alpha\gamma\delta}{4\, I^2 II^3}\left[\frac{1}{\beta+\gamma} - \frac{1}{\beta+\delta} + \frac{1}{\alpha+\delta} - \frac{1}{\alpha+\gamma}\right]\Bigg\}$$

$$\int \frac{\psi_2^2}{r_{13}}\,d\tau = 16\pi^3 \int_0^\infty \underset{2\alpha,2\beta}{F(1,1)}\ \underset{2\gamma,2\delta}{F(1,0)}\,dr_1 = \int \frac{\psi_2^2}{r_{12}}\,d\tau \quad \text{WITH } \alpha \leftrightarrow \gamma \quad \beta \leftrightarrow \delta$$

$$\int \frac{\psi_2^2}{r_{23}}\,d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_{23}}\ \underset{2\gamma,2\alpha}{F(1,1)}\ \underset{2\delta,2\beta}{F(1,1)}\,dr_{23} = \int \frac{\psi_2^2}{r_1}\,d\tau \quad \text{WITH } \begin{array}{l} \alpha \to \gamma \\ \beta \to \alpha \\ \gamma \to \delta \\ \delta \to \beta \end{array}$$

$$\int \frac{\psi_2\psi_3}{r_1}\,d\tau = 16\pi^3 \int_0^\infty \frac{1}{r_1}\ \underset{\alpha+\gamma,\beta+\delta}{F(1,1)}\ \underset{\alpha+\gamma,\beta+\delta}{F(1,1)}\,dr_1 = 16\pi^3 \Bigg\{ \frac{4(\alpha+\gamma)^2}{(\beta+\delta)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4}$$

$$+ \frac{4(\beta+\delta)^2}{(\alpha+\gamma)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4} - \frac{64(\alpha+\gamma)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^5} + \frac{64(\beta+\delta)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^5}$$

$$+ \frac{160(\alpha+\gamma)(\beta+\delta)}{(\alpha+\beta+\gamma+\delta)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4} + \frac{1(\times 16(\alpha+\gamma)^2(\beta+\delta)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^6} \ln\left[\frac{(\alpha+\beta+\gamma+\delta)^2}{4(\alpha+\gamma)(\beta+\delta)}\right]\Bigg\}$$

$$\int \frac{\psi_2\psi_3}{r_2}\,d\tau = 16\pi^3 \int_0^\infty \underset{\alpha+\gamma,\alpha+\gamma}{F(1,0)}\ \underset{\beta+\delta,\beta+\delta}{F(1,1)}\,dr_{23} = 16\pi^3 \Bigg\{ \frac{10}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^6}$$

$$+\frac{4}{(\alpha+\gamma)(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^5}+\frac{2}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^4}+\frac{2}{(\alpha+\gamma)^2(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^3}\Bigg\}$$

$$\int\frac{\psi_2\psi_3}{r_{12}}\,d\tau = 16\pi^3\int_0^\infty \underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)}\ \underset{\beta+\delta,\beta+\delta}{F(1,0)}\,dr_{23} = \int\frac{\psi_2\psi_3}{r_2}\,d\tau \qquad \text{WITH } \alpha+\gamma\leftrightarrow\beta+\delta$$

$$\int\frac{\psi_2\psi_3}{r_{23}}\,d\tau = 16\pi^3\int\frac{1}{r_{23}}\underset{\alpha+\gamma,\alpha+\gamma}{F(1,1)}\ \underset{\beta+\delta,\beta+\delta}{F(1,1)}\,dr_{23} = 16\pi^3\Bigg\{\frac{10}{3(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^6}$$

$$+\frac{5}{2(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^4}+\frac{5}{4(\alpha+\gamma)^3(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^2}\Bigg\}$$

$$\langle H\rangle = \frac{\frac{1}{K}A(\alpha,\beta,\gamma,\delta)+\epsilon^2 B(\alpha,\beta,\gamma,\delta)}{C(\alpha,\beta,\gamma,\delta)}$$

$$\frac{A(\alpha,\beta,\gamma,\delta)}{16\pi^3} = (2\alpha^2+2\gamma^2+4\beta^2+4\delta^2)\Bigg\{\frac{\alpha\beta\gamma\delta}{2\,\mathrm{I}^3\,\mathrm{II}^3}\left[\frac{1}{\alpha+\gamma}+\frac{1}{\beta+\delta}-\frac{1}{\alpha+\delta}-\frac{1}{\beta+\gamma}\right]+\frac{1}{16\,\mathrm{I}^2\,\mathrm{II}^2}\left[\frac{\alpha\gamma}{(\beta+\delta)^3}+\frac{\beta\gamma}{(\alpha+\delta)^3}\right.$$

$$\left.+\frac{\alpha\delta}{(\beta+\gamma)^3}+\frac{\beta\delta}{(\alpha+\gamma)^3}\right]+\frac{\gamma\delta}{8\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{\alpha}{(\beta+\delta)^2}+\frac{\beta}{(\alpha+\delta)^2}-\frac{\alpha}{(\beta+\gamma)^2}-\frac{\beta}{(\alpha+\gamma)^2}\right]+\frac{\alpha\beta}{8\,\mathrm{I}^3\,\mathrm{II}^2}\left[\frac{\gamma}{(\alpha+\delta)^2}-\frac{\gamma}{(\beta+\delta)^2}-\frac{\delta}{(\beta+\gamma)^2}+\frac{\delta}{(\alpha+\gamma)^2}\right]\Bigg\}$$

$$+\frac{(16\alpha\gamma+32\beta\delta)\left[(\alpha+\gamma)^4+7(\alpha+\gamma)^3(\beta+\delta)+17(\alpha+\gamma)^2(\beta+\delta)^2+7(\alpha+\gamma)(\beta+\delta)^3+(\beta+\delta)^4\right]}{(\alpha+\gamma)^3(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^7}+\frac{8(\beta^2+\delta^2)\left[(\alpha+\gamma)^2+7(\alpha+\gamma)(\beta+\delta)+(\beta+\delta)^2\right]}{(\alpha+\gamma)(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^7}$$

$$+\frac{\beta\delta(\beta^2+\delta^2)}{4\,\mathrm{III}^2\,\mathrm{IV}^3}\left[\frac{\gamma}{(\alpha+\delta)^2}-\frac{\alpha}{(\beta+\gamma)^2}-\frac{\gamma}{(\alpha+\beta)^2}+\frac{\alpha}{(\gamma+\delta)^2}\right]+\frac{\alpha\beta\gamma\delta(\beta^2+\delta^2)}{\mathrm{III}^3\,\mathrm{IV}^3}\left[\frac{1}{\alpha+\delta}-\frac{1}{\alpha+\beta}+\frac{1}{\beta+\gamma}-\frac{1}{\gamma+\delta}\right]$$

$$+\frac{\beta\delta}{4\,\mathrm{III}^2\,\mathrm{IV}^2}\left[\frac{-\alpha\beta}{(\beta+\gamma)^3}-\frac{\gamma\delta}{(\alpha+\delta)^3}-\frac{\beta\gamma}{(\alpha+\beta)^3}-\frac{\alpha\delta}{(\gamma+\delta)^3}\right]+\frac{\alpha\beta\gamma\delta}{2\,\mathrm{III}^3\,\mathrm{IV}^2}\left[\frac{\beta}{(\beta+\gamma)^2}-\frac{\delta}{(\alpha+\delta)^2}-\frac{\beta}{(\alpha+\beta)^2}+\frac{\delta}{(\gamma+\delta)^2}\right]$$

$$+\frac{16(\beta\gamma+\alpha\delta)\left[(\alpha+\gamma)^2+7(\alpha+\gamma)(\beta+\delta)+(\beta+\delta)^2\right]}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^7}+\frac{\alpha\beta(\alpha^2+\beta^2)}{4\,\mathrm{I}^3\,\mathrm{II}^2}\left[\frac{\gamma}{(\beta+\delta)^2}-\frac{\gamma}{(\alpha+\delta)^2}+\frac{\delta}{(\beta+\gamma)^2}-\frac{\delta}{(\alpha+\gamma)^2}\right]$$

$$+\frac{\alpha\beta\gamma\delta(\alpha^2+\beta^2)}{\mathrm{I}^3\,\mathrm{II}^3}\left[\frac{1}{\alpha+\delta}-\frac{1}{\beta+\delta}-\frac{1}{\alpha+\gamma}+\frac{1}{\beta+\gamma}\right]+\frac{\alpha\beta}{4\,\mathrm{I}^3\,\mathrm{II}^2}\left[\frac{-\alpha\gamma}{(\alpha+\delta)^3}-\frac{\beta\delta}{(\beta+\gamma)^3}-\frac{\beta\gamma}{(\beta+\delta)^3}-\frac{\alpha\delta}{(\alpha+\gamma)^3}\right]$$

$$+\frac{\alpha\beta\gamma\delta}{2\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{\alpha}{(\alpha+\delta)^2}-\frac{\beta}{(\beta+\gamma)^2}+\frac{\beta}{(\beta+\delta)^2}-\frac{\alpha}{(\alpha+\gamma)^2}\right]+\frac{\gamma\delta(\gamma^2+\delta^2)}{4\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{\alpha}{(\beta+\delta)^2}-\frac{\alpha}{(\beta+\gamma)^2}+\frac{\beta}{(\alpha+\delta)^2}-\frac{\beta}{(\alpha+\gamma)^2}\right]$$

$$+\frac{\alpha\beta\gamma\delta(\gamma^2+\delta^2)}{\mathrm{I}^3\,\mathrm{II}^3}\left[\frac{1}{\beta+\gamma}-\frac{1}{\beta+\delta}+\frac{1}{\alpha+\delta}-\frac{1}{\alpha+\gamma}\right]+\frac{\gamma\delta}{4\,\mathrm{I}^2\,\mathrm{II}^2}\left[\frac{-\alpha\gamma}{(\beta+\gamma)^3}-\frac{\beta\delta}{(\alpha+\delta)^3}-\frac{\alpha\delta}{(\beta+\delta)^3}-\frac{\beta\gamma}{(\alpha+\gamma)^3}\right]$$

$$+\frac{\alpha\beta\gamma\delta}{2\,\mathrm{I}^3\,\mathrm{II}^2}\left[\frac{\delta}{(\beta+\delta)^2}-\frac{\gamma}{(\alpha+\gamma)^2}+\frac{\gamma}{(\beta+\gamma)^2}-\frac{\delta}{(\alpha+\delta)^2}\right]$$

$$\frac{B(\alpha,\beta,\gamma,\delta)}{16\pi^3} = Z\left\{\frac{1}{8\,\mathrm{I}^2\,\mathrm{II}^2}\left[\frac{\alpha\gamma}{(\beta+\delta)^2}+\frac{\beta\gamma}{(\alpha+\delta)^2}+\frac{\alpha\delta}{(\beta+\gamma)^2}+\frac{\beta\delta}{(\alpha+\gamma)^2}\right]+\frac{\alpha\beta}{2\,\mathrm{I}^3\,\mathrm{II}^2}\left[\frac{\gamma}{\alpha+\delta}-\frac{\delta}{\beta+\gamma}+\frac{\delta}{\alpha+\gamma}-\frac{\gamma}{\beta+\delta}\right]\right.$$

$$+\frac{\gamma\delta}{2\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{\alpha}{\beta+\gamma}+\frac{\beta}{\alpha+\gamma}-\frac{\alpha}{\beta+\delta}-\frac{\beta}{\alpha+\delta}\right]$$ [redacted] $$\left.\frac{2\alpha\beta\gamma\delta}{\mathrm{I}^3\,\mathrm{II}^3}\ln\left[\frac{(\alpha+\gamma)(\beta+\delta)}{(\beta+\gamma)(\alpha+\delta)}\right]\right\}_1+\Big\{\quad\Big\}_1 \text{ WITH } \begin{matrix}\alpha\to\gamma\\ \beta\to\alpha\\ \gamma\to\delta\\ \delta\to\beta\end{matrix}$$

$$+\left\{\frac{-Z}{8\,\mathrm{I}\,\mathrm{II}^2}\left[\frac{\gamma}{(\beta+\delta)^3}+\frac{\delta}{(\beta+\gamma)^2}\right]-\frac{Z\beta}{8\,\mathrm{I}^2\,\mathrm{II}^2}\left[\frac{\gamma}{(\alpha+\delta)^2}-\frac{\gamma}{(\beta+\delta)^2}-\frac{\delta}{(\beta+\gamma)^2}+\frac{\delta}{(\alpha+\gamma)^2}\right]\right.$$

$$\left.+\frac{Z\gamma\delta}{4\,\mathrm{I}\,\mathrm{II}^3}\left[\frac{1}{(\beta+\delta)^2}-\frac{1}{(\beta+\gamma)^2}\right]+\frac{Z\beta\gamma\delta}{2\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{1}{\alpha+\delta}+\frac{1}{\beta+\gamma}-\frac{1}{\alpha+\gamma}-\frac{1}{\beta+\delta}\right]\right\}_2+\Big\{\quad\Big\}_2 \text{ WITH } \begin{matrix}\alpha\leftrightarrow\gamma\\ \beta\leftrightarrow\delta\end{matrix}$$

$$+\frac{8Z(\alpha+\gamma)^2}{(\beta+\delta)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4}-\frac{128Z(\alpha+\gamma)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^5}+\frac{8Z(\beta+\delta)^2}{(\alpha+\gamma)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4}+\frac{128Z(\beta+\delta)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^5}$$

$$+\frac{320Z(\alpha+\gamma)(\beta+\delta)}{(\alpha+\beta+\gamma+\delta)^2[(\alpha+\gamma)^2-(\beta+\delta)^2]^4}+\frac{16\times 32Z(\alpha+\gamma)^2(\beta+\delta)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^6}\ln\left[\frac{(\alpha+\beta+\gamma+\delta)^2}{4(\alpha+\gamma)(\beta+\delta)}\right]$$

$$+\left\{\frac{-40Z}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^6}-\frac{16Z}{(\alpha+\gamma)(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^5}-\frac{8Z}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^4}\right.$$

[redacted] $$\left.\frac{8Z}{(\alpha+\gamma)^2(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^3}\right\}_3+\frac{1}{Z}\Big\{\quad\Big\}_3 \text{ WITH } \alpha+\gamma\leftrightarrow\beta+\delta+\left\{\frac{+1}{8\,\mathrm{I}\,\mathrm{II}^2}\left[\frac{\delta}{(\alpha+\gamma)^3}+\frac{\gamma}{(\alpha+\delta)^3}\right]\right.$$

$$-\frac{\alpha}{8\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{\gamma}{(\beta+\delta)^2}+\frac{\delta}{(\beta+\gamma)^2}-\frac{\delta}{(\alpha+\gamma)^2}-\frac{\gamma}{(\alpha+\delta)^2}\right]+\frac{\gamma\delta}{4\,\mathrm{I}\,\mathrm{II}^3}\left[\frac{1}{(\alpha+\gamma)^2}-\frac{1}{(\alpha+\delta)^2}\right]$$

$$\left.+\frac{\alpha\gamma\delta}{2\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{1}{\beta+\delta}-\frac{1}{\beta+\gamma}-\frac{1}{\alpha+\delta}+\frac{1}{\alpha+\gamma}\right]\right\}_4+\Big\{\quad\Big\}_4 \text{ WITH } \alpha\leftrightarrow\gamma \quad \beta\leftrightarrow\delta$$

$$+\frac{20}{3(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^6}+\frac{5}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^4}+\frac{5}{2(\alpha+\gamma)^3(\beta+\delta)^3(\alpha+\beta+\gamma+\delta)^2}$$

$$\frac{C(\alpha,\beta,\gamma,\delta)}{16\pi^3} = \frac{\alpha\beta\gamma\delta}{\mathrm{I}^3\,\mathrm{II}^3}\left[\frac{1}{\beta+\delta}+\frac{1}{\alpha+\gamma}-\frac{1}{\alpha+\delta}-\frac{1}{\beta+\gamma}\right]+\frac{1}{8\,\mathrm{I}^2\,\mathrm{II}^2}\left[\frac{\alpha\gamma}{(\beta+\delta)^3}+\frac{\beta\gamma}{(\alpha+\delta)^3}+\frac{\alpha\delta}{(\beta+\gamma)^3}+\frac{\beta\delta}{(\alpha+\gamma)^3}\right]$$

$$+\frac{\gamma\delta}{4\,\mathrm{I}^2\,\mathrm{II}^3}\left[\frac{\alpha}{(\beta+\gamma)^2}+\frac{\beta}{(\alpha+\gamma)^2}-\frac{\alpha}{(\beta+\delta)^2}-\frac{\beta}{(\alpha+\delta)^2}\right]+\frac{\alpha\beta}{4\,\mathrm{I}^3\,\mathrm{II}^2}\left[\frac{\gamma}{(\alpha+\delta)^2}-\frac{\gamma}{(\beta+\delta)^2}-\frac{\delta}{(\beta+\gamma)^2}+\frac{\delta}{(\alpha+\gamma)^2}\right]$$

$$+\frac{40}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^7}+\frac{8}{(\alpha+\gamma)^3(\beta+\delta)^3}+\frac{24}{(\alpha+\gamma)^2(\beta+\delta)^2(\alpha+\beta+\gamma+\delta)^5}$$