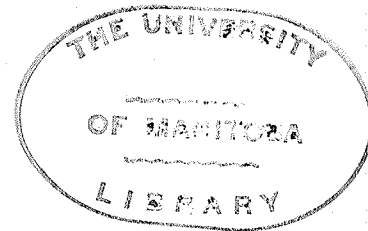THE INTERACTION OF A POSITRON WITH A

NEGATIVE HYDROGEN ION

———————————

A Thesis

Presented to

The Faculty of Graduate Studies and Research

University of Manitoba

———————————

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

———————————

by

George Darewych

September 1961

ABSTRACT

In this thesis, the variational method is used to determine
an upper bound to the ground state energy of a system of a positron
and a negative hydrogen ion. Two trial wave functions are used and
the better one of the two is employed in obtaining the lifetime
of the system against two photon pair annihilation of the positron
with an electron from the ground state of the system. The thesis
also includes short discussions of the variational method and the
geometry of the system under consideration.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. S. M. Neamtan for the suggestion of the problem. His constant interest, help and guidance greatly contributed to the development of the problem to its successful conclusion, and to the investigator's general knowledge of mathematical physics as well as computational and research techniques. The investigator also wishes to thank G. Oczkowski for his assistance in checking the lenghty computations, and the Faculty of Graduate Studies and Research of the University of Manitoba for providing financial support in the form of a Graduate Assistantship.

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

The object of this investigation is to determine, theoretically, the nature of the interaction of a positron with a negative hydrogen ion, in the absence of an external field. More specifically, it is the purpose of this study (1) to calculate an upper bound to the energy and the wave function of a positron - negative hydrogen ion system in the ground state; (2) to determine the mean lifetime of this system against two photon annihilation of a positron - electron pair from the ground state.

The interaction of positrons with matter has been the subject of previous investigations by a number of workers, such as Wheeler, Hylleraas, Ore, De Benedetti and others. The discovery of positive electrons, which were predicted by Dirac's theory, was immediately followed by a series of investigations in order to prove that these particles exhibited the properties predicted by Dirac's theory. This was accomplished by observing experimentally the creation of a positron - electron pair by γ - rays from radioactive sources. The reverse process, where an electron - positron pair annihilate with the emission of γ - rays, was also investigated.[1] In the latter process, just before annihilation occurs, an electron - positron pair may form a stable, hydrogen-like two particle system or atom. The existence of this quasi-stable system was first suggested by S. Mohorovičić.[2] This system was given the name

---

[1] L. J. Thibaud, <u>Physical</u> <u>Reviev</u>, 58:861, 1940.

[2] S. Mohorovicic, <u>Astron.</u> <u>Nacht.</u>, 253:94, 1934.

"positronium" by Ruark. When positronium is formed, its quantum states are similar to those of hydrogen, the main difference being that the reduced mass of positronium is about one half that of the hydrogen atom. The effect of this is that the energies of the positronium states are about one half the energies of the corresponding hydrogen states, while the linear dimensions of the wave functions are about twice as large.

It is possible that positronium is formed in an excited $n \neq 0$ state. In such a state it survives long enough to emit a line of the characteristic optical spectrum in its transition or transitions to one of the ground states: the spins parallel 1^3S triplet or orthopositronium or the spins antiparallel 1^1S singlet or parapositronium, from which it annihilates. These two states differ substantially in their annihilation properties, because of the existence of selection rules which prevent the annihilation of the ^3S state with the emission of two γ - rays. The annihilation of an electron - positron pair from the singlet spin state occurs mainly as two photon annihilation, while that from the triplet spin state as three photon annihilation.[3] From the point of view of perturbation theory, the two photon annihilation is a second order process while three photon annihilation is a third order process. Thus, pair annihilation through the higher order, three photon process is less likely to occur than through two photon annihilation. Also, the lower order process has a shorter lifetime; that is, the lifetime of singlet

---

[3] De Benedetti and Corben, <u>Annual Rev. of Nuc. Sci.</u>, 4:191, 1954.

positronium is $'\tau_{2\gamma} = 1.25 \times 10^{-10}$ secs., while for triplet positronium it is $^{3}\tau_{3\gamma} = 1115 \ '\tau_{2\gamma}$, for annihilation from the ground state.[4] The annihilation rates of both singlet and triplet positronium have also been obtained experimentally.[5]

The system of one positron and one electron is not the only possible bound system involving the positron. It has been shown theoretically that systems consisting of two positrons and an electron or two electrons and a positron also have small positive binding energies against dissociation into any of their constituent parts.[6] The binding of the positron to certain atoms, ions or molecules has also been considered. The investigation of these latter systems is particularly interesting in that it sheds new light upon the interaction of positrons with gases and solids. The annihilation rates of an electon-positron pair in such atomic systems are substantially different from the annihilation rates of free positronium.[7]

The dynamical stability of the system of a positron and a negative hydrogen ion has been theoretically established by A. Ore.[8] Ore shows that such a system posesses a positive binding energy of at least .07 eV

---

[4] A. Ore and J. L. Powell, Physical Review, 75:1696, 1949.
[5] M. Deutch, Progress in Nuclear Physics, 3:141, 1953.
[6] J. A. Wheeler, Ann. N. Y. Acad. Sci.,48:219, 1946.
[7] De Benedetti and Corben, Ann. Rev. of Nuc. Sci., 4:191, 1954.
[8] A. Ore, University of Bergen Yearbook No. 5, Bergen, Norway, 1952.
   E. Hylleraas, Physical Review, 71:491, 1947.
   E. Hylleraas and A. Ore, Physical Review, 71:493, 1947.

against dissociation into a positronium atom and a hydrogen atom. The availability of alkali hydrides commercially has led, recently, to some experimental investigation of the interaction of the positron with the negative hydrogen ion.[9] In this thesis, the binding of the positron to the negative hydrogen ion is established with a higher binding energy than that obtained by Ore, and also the two photon annihilation rate of an electron-positron pair out of the ground state of such a system is calculated. The natural extention of this work is the computation of the angular correlation of the photons from positron annihilation in the system of a positron and a negative hydrogen ion. This work is at present being carried out, under the direction of Dr. S. M. Neamtan, by G. Oczkowski and the investigator. The corresponding experimental measurments of the angular correlation of the photons from pair annihilation in the system of a positron and a negative hydrogen ion have already been obtained.[10] The parallel problem of the interaction of a positron with a helium atom was investigated by G. Oczkowski and is reported in his thesis.[11]

[9] A. T. Stewart and R. H. March, Physical Review, 122:75, 1961.

[10] Ibid.

[11] G. Oczkowski, The system of a positron and a helium atom, a thesis submitted to the Department of Mathematical Physics of the University of Manitoba in partial fullfilment of the requirements for the degree of Master of Science.

CHAPTER II

THE VARIATIONAL METHOD

There are relatively few physical systems, which obey the laws
of quantum mechanics, for which Schrodinger's equation is capable of
exact solution. In the majority of physical cases approximation methods
have to be used to solve Schrodinger's equation. If for a given problem
there exists a related problem capable of exact solution one may use
perturbation methods for obtaining an approximate solution. Another
useful approximation method is the so called WKB approximation method
which requires that Schrodinger's equation for the problem be separable.
A very useful method, which does not require a solvable related problem
or a separable Schrodinger equation, is the variational method.[1] Let $\mathcal{H}$
be the Hamiltonian operator of a physical system and φ_i the orthonormal
eigenfunctions of this operator. Consider any function Ψ in the Hilbert
space associated with the physical system; we have:

$$\Psi = \sum_i c_i \varphi_i$$

$$H \varphi_i = \varepsilon_i \varphi_i \qquad (\varphi_i, \varphi_i) = \delta_{ii}$$

$$\mathcal{H} \Psi = \sum_i c_i \mathcal{H} \varphi_i$$

Thus the expected average of the Hamiltonian for the system in the state Ψ
is:

$$\langle H \rangle = \frac{(\Psi, H \Psi)}{(\Psi, \Psi)} = \frac{(\Psi, \sum_i c_i H \varphi_i)}{(\Psi, \Psi)}$$

---

[1] The variational method was first used by Lord Rayleigh in
1873: Theory of Sound, Vol. 1, Sec. 88.

where as usually, $(\phi, \chi) = \int_\tau \phi^* \chi \, d\tau$

where τ represents all the configuration space of the physical system.

That is,

$$(\Psi, \Psi)\langle H \rangle = \left(\sum_j c_j \varphi_j, \sum_i c_i H \varphi_i \right)$$

$$= \sum_j \sum_i c_j^* c_i (\varphi_j, H \varphi_i)$$

$$= \sum_j \sum_i c_j^* c_i (\varphi_j, E_i \varphi_i)$$

$$= \sum_j \sum_i c_j^* c_i E_i (\varphi_j, \varphi_i)$$

$$= \sum_j \sum_i c_j^* c_i E_i \, \delta_{ji}$$

$$= \sum_i |c_i|^2 E_i \qquad ①$$

Let E_0 be the smallest eigenvalue, then:

$$\langle H \rangle (\Psi, \Psi) \geq \sum_i |c_i|^2 E_0$$

$$\langle H \rangle \geq \frac{\sum_i |c_i|^2}{(\Psi, \Psi)} E_0$$

But

$$(\Psi, \Psi) = \left(\sum_i c_i \varphi_i, \sum_j c_j \varphi_j \right)$$

$$= \sum_i \sum_j c_i^* c_j (\varphi_i, \varphi_j)$$

$$= \sum_i |c_i|^2 \qquad \text{i} \qquad \frac{(\Psi, H\Psi)}{(\Psi, \Psi)} \geq E_0$$

Hence $\frac{(\Psi, H\Psi)}{(\Psi, \Psi)}$ is an upper bound to the ground state energy of the physical system, and Ψ is an approximation to the wave function of the ground state. $\frac{(\Psi, H\Psi)}{(\Psi, \Psi)} = E_0$ when $\Psi = \varphi_0$, the ground state wave function of the system. The better Ψ approximates the ground state wave function of the physical system, the closer the upper bound approximates the actual value of the ground state energy of the physical system.

An upper bound to the first excited state energy of the system

is obtained by choosing a trial wave function Ψ which is orthogonal to φ_0 in the sense that $(\Psi, \varphi_0) = 0$, so that $\Psi = \sum_i c_i \psi_i$, with $c_0 = 0$. Thus in equation ① :

$$\langle H \rangle = \frac{\sum_{i=1}^{\infty} |c_i|^2 E_i}{(\Psi, \Psi)}$$

Replacing all the E_i by E_1 we get:

$$\langle H \rangle \geqslant \frac{\sum_{i=1}^{\infty} |c_i|^2}{(\Psi, \Psi)} E_1$$

since $c_0 = 0$ and E_0 does not enter into the sum. If Ψ is orthogonal to the ground state wave function then $\frac{(\Psi, H\Psi)}{(\Psi, \Psi)}$ is an upper bound to the energy of the first excited state and Ψ is then an approximation to the first excited state wave function.

In certain cases it is possible to choose a trial wave function Ψ, to be orthogonal to the ground state wave function φ_0 of the system, without the explicit knowledge of the ground state wave function φ_0. Thus, for example, if the ground state of a two electron system is a singlet spin state so that φ_0 is a spatially symmetric function of the electron coordinates, then if the first excited state is a triplet spin state, Ψ may be choosen orthogonal to φ_0 simply by taking it to be a spatially antisymmetric function. To be able to determine an upper bound to a first excited state in other cases, the explicit knowledge of the form of the ground state wave function would be required, so that the trial function could be chosen orthogonal to it.

In the majority of problems, one is not merely interested in

obtaining just any upper bound to the eigenvalue of Schrodinger's equation for the system, but usually the goal is to obtain an upper bound which is not far removed from the actual value of the energy level. By choosing the trial wave function to be a function of a set of variable scalar parameters, $\Psi = \Psi(\alpha, \beta, \gamma, \dots)$, the upper bound to the energy level is obtained as a function of these parameters:

$$\langle H \rangle = f(\alpha, \beta, \gamma, \dots)$$

The minimization of $\langle H \rangle$ with respect to these variable parameters yields the least upper bound to the energy level, for the particular type of trial function chosen . If the upper bound turns out to be very close to the actual energy level, then the corresponding trial wave function may be a good approximation to the actual wave function of the state under consideration.

The choice of the trial function is usually severely restricted by the fact that the integrations, which enter into the evaluation of $(\Psi, H\Psi)$, cannot be worked out explicitly, or for that matter carried far enough to facilitate numerical computation. In certain cases it may be possible to choose the trial function of the form $\Psi = f(\alpha, \beta, \gamma, \dots) h(q)$, where part of it, $f(\alpha, \beta, \gamma, \dots)$ is an explicit function of variable scalar parameters and all the coordinates of the system except q , while the functional dependence on the coordinate q is not specified. The problem is then reduced to one of lower order , that is, the variational problem is replaced by an equivalent differential equation, which is then solved numerically.[2] Finally, the

---

[2] For a discussion and application of this method see: G. Oczkowski, *op. cit.*

nature of the physical problem may guide one to a choice of functional dependence on certain coordinates.

As an example, let us consider a trial function for a system of two electrons and one positron:(Geometry and coordinates defined in the diagram.)
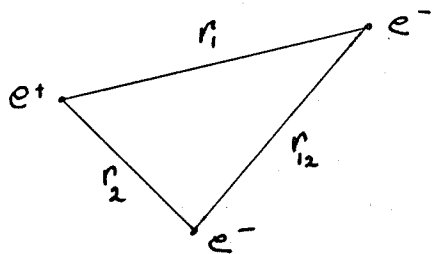
The fact that for an electron-positron system the ground state wave function is $\sim e^{-\frac{r}{2a_o}}$, where r is the interparticle distance and a_o the first Bohr radius of the hydrogen atom, suggests for our trial function a dependence on the coordinates r_1 and r_2 of the form:

$$\psi \sim e^{-(\alpha r_1 + \beta r_2)}$$

where α and β are variable scalar parameters. Furthermore, the fact that the probability of the two electrons being at the same point in space is zero, (that is, $r_{12} = 0$ is impossible) might lead one to choose a dependence on r_{12} such that $\psi(r_{12}=0)=0$.

CHAPTER III

THE SYSTEM OF FOUR CHARGED PARTICLES IN THE ABSENCE OF AN EXTERNAL FIELD

The computation of an upper bound to the energy of the ground state

of a system of a positron and a negative hydrogen ion requires a thorough

knowledge of the geometry of the system. Consider a system of four

particles — a nucleus of charge Ze, two electrons and a positron, in the

absence of any external field:
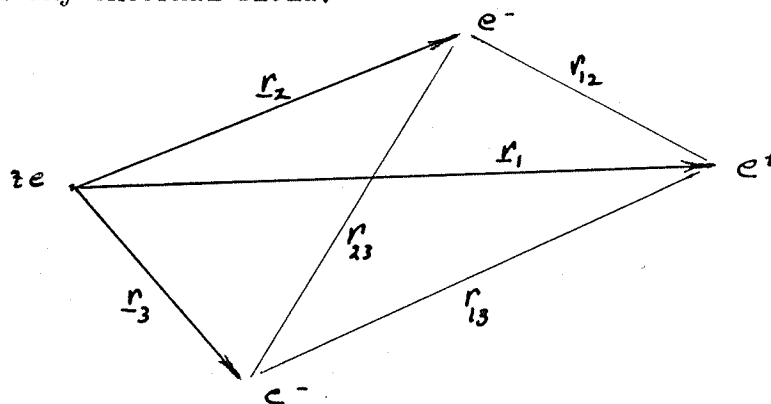
Choose an origin of coordinates at the position of the nucleus. We are

concerned with only the relative motion of the four particles, as it is

only the internal motion and structure of the system which determines

the state of the system. Since the mass of the nucleus is much larger

than the masses of the electrons and the positron, we shall neglect its

motion and treat it as fixed.

The first thing one must decide upon is the choice of a coordinate

system. This is in part dictated by the choice of trial wave function,

which will be introduced in the next chapter. The configuration of the

system is completely specified by the specification of the six interpar-

ticle distances, which specify the relative positions of the particles,

and a set of three angles, which specify the orientation of the system as a whole in space. Let r_1, r_2, r_3 be the position vectors of the positron and the electrons respectively and let $r_{12} = |r_1 - r_2|$, $r_{13} = |r_1 - r_3|$ and $r_{23} = |r_2 - r_3|$. The set r_1, r_2, r_3 , r_{12} , r_{13} and r_{23} of interparticle distances will be the generalized coordinates of the system, if the irrelevent orientation of the system in space is suppressed. This choice of generalized coordinates is by no means the only method of specifying the relative configuration of the system, but it is the one which best satisfies the three conditions: (1) The Hamiltonian of the system may be expressed as a reasonable function of these coordinates, so that it does not complicate excessively the integrations involved in $(\Psi, H \Psi)$. (2) The element of volume of configuration space may be written as a simple expression involving as many of these lenghts as possible (and any other generalized coordinates to make a total of six). (3) The trial function for the system may be reasonably chosen in terms of the interparticle distances. The first of these three conditions, especially, imposes a severe restriction on the type of coordinate system which may be used. For example, in the configuration of the system, the coordinate lenght r_{23} may be replaced by an angle φ_{23} , which is the angle between $r_1 \times r_2$ and $r_1 \times r_3$. Though in terms of this set of coordinates it was found possible to write down the element of volume of configuration space, it was not possible to write down the Hamiltonian of the system and still do the integrations entering into $\langle H \rangle$.

As mentioned above, the configuration of the system is completely

specified by the set of six coordinates, q , which specify the relative positions of the particles, and the set of three angles, Ω , which specify the orientation of the system in space (with respect to some fixed axis in space). The wave function of the system in its ground state (that is, with zero angular momentum) will not depend upon the orientation of the system in space; that is, $\Psi = \Psi(q)$. The Hamiltonian of the system in the absence of an external field is also independent of the orientation of the system in space: $H = H(q)$. Hence, after the integration over the set of angle coordinates Ω , the problem reduces to the form:

$$\langle H \rangle = \frac{\int_q \Psi^*(q)\, H(q)\, \Psi(q)\, dq}{\int_q \Psi^*(q)\, \Psi(q)\, dq}$$

where dq represents the effective element of volume of configuration space. Thus, as far as the computation of $\langle H \rangle$ is concerned, the set of three angles Ω , which specify the orientation of the system in space, may be neglected.

Consider again the system of four particles, with origin at the position of the fixed nucleus. Let $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, be the position vectors of the positron and the two electrons, where $\mathbf{r}_1 \equiv (x_1, y_1, z_1)$ and $\mathbf{r}_2 \equiv (x_2, y_2, z_2)$ with respect to a cartesian coordinate system fixed in space. Let $\mathbf{r}_3 \equiv (r_3, \theta_3, \varphi_3)$, in spherical polar coordinates, where the vector $\mathbf{r}_1$ has been chosen as the polar axis, and the azimuthal angle is

measured from the plane of $\mathbf{r}_1$ and $\mathbf{r}_2$.
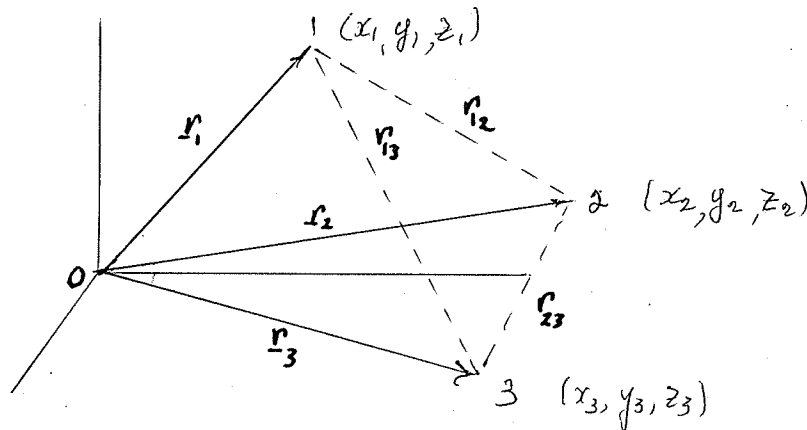
The element of volume of configuration space is $d\tau = d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, d^3\mathbf{r}_3$.
Let (ψ, θ, φ) be the Euler angles which specify the orientation of the "triangle" defined by the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, with respect to the fixed Cartesian coordinate system. Then,

$$d^3\mathbf{r}_1\, d^3\mathbf{r}_2 = dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2$$

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

$$= r_1\, r_2\, r_{12} \sin\theta\, dr_1\, dr_2\, dr_{12}\, d\psi\, d\theta\, d\varphi$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Now, $d^3\mathbf{r}_3 = r_3^2\, d\mu_3\, d\varphi_3$ where $\mu_3 = -\cos\theta_3$; that is $d^3\mathbf{r}_3 = r_3 \frac{\partial\mu_3}{\partial r_{13}} dr_{13}\, d\varphi_3$, where $r_{13} = |\mathbf{r}_1 - \mathbf{r}_3|$. But $r_{13}^2 = r_1^2 + r_3^2 + 2r_1 r_3 \mu_3$, therefore $2r_{13} = 2r_1 r_3 \frac{\partial\mu_3}{\partial r_{13}}$ and $\frac{\partial\mu_3}{\partial r_{13}} = \frac{r_{13}}{r_1 r_3}$, so that

$$d^3\mathbf{r}_3 = \frac{r_3\, r_{13}}{r_1} dr_3\, dr_{13}\, d\varphi_3$$

$$d\tau = r_2\, r_3\, r_{12}\, r_{13}\, dr_1\, dr_2\, dr_3\, dr_{12}\, dr_{13}\, d\varphi_3 \sin\theta\, d\psi\, d\theta\, d\varphi$$

$$= dq\, d\Omega$$

$$dq = r_2\, r_3\, r_{12}\, r_{13}\, dr_1\, dr_2\, dr_3\, dr_{12}\, dr_{13}\, d\varphi_3$$

---

[1] See Appendix I: Element of Volume of Configuration Space for the system of a Positron and a Negative Hydrogen Ion.

and where φ_3 is defined as the angle between $\underline{\ell}_1 \times \underline{\ell}_2$ and $\underline{\ell}_1 \times \underline{\ell}_3$.

The Hamiltonian of the system is

$$H = -\frac{1}{K}\left(\nabla_1^2 + \nabla_2^2 + \nabla_3^2\right) + \varepsilon^2 \left(\frac{z}{r_1} - \frac{z}{r_2} - \frac{z}{r_3} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

$$= -\frac{1}{K}\nabla^2 + \varepsilon^2 V$$

where $K = \frac{2m}{\hbar^2}$, m : mass of the electron, ε : charge of the electron, $\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ for $i = 1, 2, 3$

and where $\underline{r}_i = (x_i, y_i, z_i)$ for $i = 1, 2, 3$. . For a well behaved function Ψ, using the divergence theorem, we obtain

$$\int_{\tau_\infty} \Psi \nabla^2 \Psi \, d\tau = - \int_{\tau_\infty} (\nabla \Psi)^2 \, d\tau$$

where τ_∞ stands for all configuration space. Hence, as far as the computation of $\langle H \rangle$ for the system is concerned

$$(\Psi, H\Psi) = -\frac{1}{K} \int_\tau \Psi \nabla^2 \Psi \, d\tau + \varepsilon^2 \int_\tau V \Psi^2 \, d\tau$$

$$= \frac{1}{K} \int_\tau (\nabla \Psi)^2 \, d\tau + \varepsilon^2 \int_\tau V \Psi^2 \, d\tau$$

For $\Psi = \Psi(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})$, since

$$r_1 = (x_1^2 + y_1^2 + z_1^2)^{\frac{1}{2}}$$
$$r_2 = (x_2^2 + y_2^2 + z_2^2)^{\frac{1}{2}}$$
$$r_3 = (x_3^2 + y_3^2 + z_3^2)^{\frac{1}{2}}$$
$$r_{12} = \left[(x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2\right]^{\frac{1}{2}}$$
$$r_{13} = \left[(x_3-x_1)^2 + (y_3-y_1)^2 + (z_3-z_1)^2\right]^{\frac{1}{2}}$$
$$r_{23} = \left[(x_3-x_2)^2 + (y_3-y_2)^2 + (z_3-z_2)^2\right]^{\frac{1}{2}}$$

we obtain:[2]

---

[2] See Appendix II: The Square of the Gradient of the Configuration Space.

$$H\psi \simeq \frac{1}{k}\left\{ \left(\frac{\partial \psi}{\partial r_1}\right)^2 + \left(\frac{\partial \psi}{\partial r_2}\right)^2 + \left(\frac{\partial \psi}{\partial r_3}\right)^2 + 2\left(\frac{\partial \psi}{\partial r_{12}}\right)^2 + 2\left(\frac{\partial \psi}{\partial r_{13}}\right)^2 + 2\left(\frac{\partial \psi}{\partial r_{23}}\right)^2 \right.$$

$$+ \frac{\partial \psi}{\partial r_1}\frac{\partial \psi}{\partial r_{12}}\frac{r_1^2+r_{12}^2-r_2^2}{r_1 \, r_{12}} + \frac{\partial \psi}{\partial r_1}\frac{\partial \psi}{\partial r_{13}}\frac{r_1^2+r_{13}^2-r_3^2}{r_1 \, r_{13}} + \frac{\partial \psi}{\partial r_{12}}\frac{\partial \psi}{\partial r_{13}}\frac{r_{12}^2+r_{13}^2-r_{23}^2}{r_{12} \, r_{13}}$$

$$+ \frac{\partial \psi}{\partial r_2}\frac{\partial \psi}{\partial r_{12}}\frac{r_2^2+r_{12}^2-r_1^2}{r_2 \, r_{12}} + \frac{\partial \psi}{\partial r_2}\frac{\partial \psi}{\partial r_{23}}\frac{r_2^2+r_{23}^2-r_3^2}{r_2 \, r_{23}} + \frac{\partial \psi}{\partial r_{23}}\frac{\partial \psi}{\partial r_{12}}\frac{r_{23}^2+r_{12}^2-r_{13}^2}{r_{23} \, r_{12}}$$

$$+ \frac{\partial \psi}{\partial r_3}\frac{\partial \psi}{\partial r_{13}}\frac{r_3^2+r_{13}^2-r_1^2}{r_3 \, r_{13}} + \frac{\partial \psi}{\partial r_3}\frac{\partial \psi}{\partial r_{23}}\frac{r_3^2+r_{23}^2-r_2^2}{r_3 \, r_{23}} + \frac{\partial \psi}{\partial r_{13}}\frac{\partial \psi}{\partial r_{23}}\frac{r_{13}^2+r_{23}^2-r_{12}^2}{r_{13} \, r_{23}}$$

$$+ \varepsilon^2\left(\frac{z}{r_1} - \frac{z}{r_2} - \frac{z}{r_3} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}}\right)\psi$$

Thus, in the computation of $\langle H \rangle$, $H\psi$ is equivalent to the above form.

CHAPTER IV

## THE GROUND STATE ENERGY OF THE SYSTEM OF A POSITRON AND A NEGATIVE HYDROGEN ION

The system of a positron and a negative hydrogen ion is stable if there exists a state of the system with an energy which is lower than the sum of the energies of the constituent parts into which the system might dissociate. The system of a positron and a negative hydrogen ion can dissociate in a number of different ways: It can dissociate into its four constituent particles, into a positron and a negative hydrogen ion, into a positronium atom and a hydrogen atom, etc. The total energy of a free positron and a free negative hydrogen ion in the ground state is simply the energy of the negative hydrogen ion, which is $-1.05512 \frac{\varepsilon^2}{2a_0}$. The sum of the energies of the free positronium and hydrogen atoms is $-1.5 \frac{\varepsilon^2}{2a_0}$, if both are in their ground states. Clearly, the most favourable mode of dissociation of the system of a positron and a negative hydrogen ion is into a positronium atom and a hydrogen atom. If the energy of the system $E(H + e^+) < -1.5 \frac{\varepsilon^2}{2a_0}$ then the system is stable against any mode of dissociation, and if $E(H + e^+) > -1.5 \frac{\varepsilon^2}{2a_0}$ then the system is unstable and dissociates spontaneously into a positronium atom and a hydrogen atom.

The fact that the most favourable mode of dissociation of the system is into a positronium atom and a hydrogen atom suggests that if the system is bound at all, then it probably resembles most closely a positronium atom loosely bound to a hydrogen atom. With this in mind

and assuming that the system in its ground state is singlet with regard to the two electrons, we take as our first trial wave function for the system the space symmetric function of the electron coordinates

$$\phi = e^{-(\alpha r_2 + \beta r_{12} + \tau r_3)} + e^{-(\tau r_2 + \beta r_{13} + \alpha r_3)} = \phi_2 + \phi_3$$

where the coordinate system used is defined in the diagram:[1]
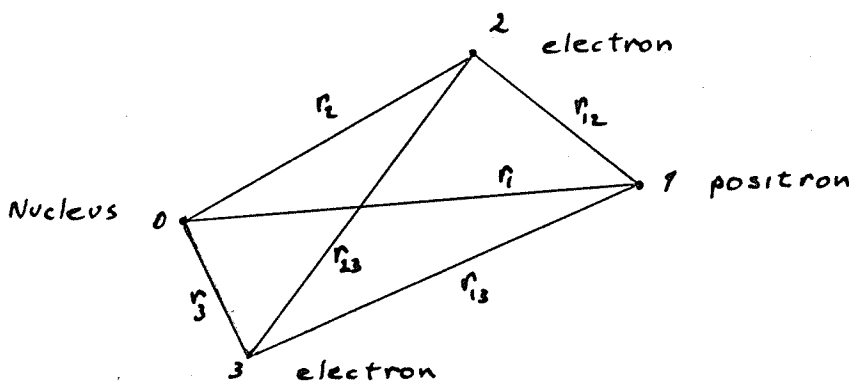
Since the element of volume $d\tau$ does not contain the coordinate r_{23} explicitly while the Hamiltonian does, it is necessary to choose $\frac{\partial \phi}{\partial r_{23}} = 0$ so as to be able to compute $\langle H \rangle$. To facilitate the computation of the term $\left(\phi, \frac{1}{r_{23}} \phi \right)$ we have to take $\frac{\partial \phi}{\partial r_1} = 0$ since $\frac{1}{r_{23}}$, when expressed as a function of the other lenghts and an angle, is not explicitly integrable.

Since

$$\frac{\partial \phi}{\partial r_1} = 0 \qquad \frac{\partial \phi}{\partial r_{23}} = 0$$

$$\frac{\partial \phi}{\partial r_2} = -\alpha \phi_2 - \tau \phi_3 \qquad \frac{\partial \phi}{\partial r_3} = -\tau \phi_2 - \alpha \phi_3$$

$$\frac{\partial \phi}{\partial r_{12}} = -\beta \phi_2 \qquad \frac{\partial \phi}{\partial r_{13}} = -\beta \phi_3$$

making use of the above stated symmetry of ϕ, the average of the

---

[1] See also Chapter II.

Hamiltonian may be written: $\dfrac{(\phi, H\phi)}{(\phi, \phi)}$ where

$$(\phi, H\phi) = \frac{1}{K}\Big[2(\alpha^2 + 2\beta^2 + \gamma^2)(\phi_2, \phi_2) + 4\alpha\gamma(\phi_2, \phi_3)$$

$$+ \beta^2\Big(\phi_2, \Big\{\frac{2 r_{12}}{r_{13}} - \frac{r_{23}^2}{r_{12} r_{13}}\Big\}\phi_3\Big) + 2\alpha\beta\Big(\phi_2, \Big\{\frac{r_{12}}{r_2} + \frac{r_2}{r_{12}} - \frac{r_1^2}{r_2 r_{12}}\Big]\phi_2\Big)$$

$$+ 2\beta\gamma\Big(\phi_2, \Big\{\frac{r_2}{r_{12}} + \frac{r_{12}}{r_2} - \frac{r_1^2}{r_2 r_{12}}\Big\}\phi_3\Big)\Big] - \varepsilon^2\Big[2z\Big(\phi_2, \frac{1}{r_2}\phi_2\Big) + 2z\Big(\phi_2, \frac{1}{r_3}\phi_2\Big)$$

$$+ 2\Big(\phi_2, \frac{1}{r_{12}}\phi_2\Big) + 2\Big(\phi_2, \frac{1}{r_{13}}\phi_2\Big) - 2z\Big(\phi_2, \frac{1}{r_1}\phi_3\Big) + 4z\Big(\phi_2, \frac{1}{r_2}\phi_3\Big)$$

$$+ 4\Big(\phi_2, \frac{1}{r_{12}}\phi_3\Big) - 2\Big(\phi_2, \frac{1}{r_1}\phi_3\Big) - 2\Big(\phi_2, \frac{1}{r_{23}}\phi_3\Big) - 2\Big(\phi_2, \frac{1}{r_{23}}\phi_3\Big)\Big]$$

$$(\phi, \phi) = 2(\phi_2, \phi_2) + 2(\phi_2, \phi_3)$$

All these inner products are integrals of the type

$$\int_0^\infty f_{ab}(A, B)\, f_{cd}(C, D)\, r^n\, dr$$

where A, B, C, D are parameters and a, b, c, d, n are integers,

and where

$$\frac{1}{2} f_{ab}(A, B) = \int_0^\infty \int_{|r-x|}^{r+x} e^{-(Ax + By)}\, x^a\, y^b\, dy\, dx \quad [2]$$

Hence

$$\langle H \rangle = \frac{\frac{1}{K}\mathscr{A}(\alpha, \beta, \gamma) + \varepsilon^2 \mathscr{B}(\alpha, \beta, \gamma)}{\mathscr{L}(\alpha, \beta, \gamma)} \quad [3]$$

where $\mathscr{A}(\alpha, \beta, \gamma)$, $\mathscr{B}(\alpha, \beta, \gamma)$, $\mathscr{L}(\alpha, \beta, \gamma)$ are homogeneous functions of

degree of homogeneity of −7, −8, and −9 respectively. Thus

$$\langle H \rangle = \frac{\alpha^2}{K}\frac{\mathscr{A}(1, b, c)}{\mathscr{L}(1, b, c)} + \varepsilon^2\alpha\,\frac{\mathscr{B}(1, b, c)}{\mathscr{L}(1, b, c)}$$

where $b = \dfrac{\beta}{\alpha}$, $c = \dfrac{\gamma}{\alpha}$. Thus the minimization of $\langle H \rangle$ with respect to

---

[2] See Appendix III: Table of Integrals.
[3] See Appendix IV: Evaluation of $\langle H \rangle$ using the trial function

$$e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3)} + e^{-(\gamma r_2 + \beta r_{13} + \alpha r_3)}.$$

one of the parameters, α, may be carried out directly:

$$\frac{\partial \langle H \rangle}{\partial \alpha} = \frac{2\alpha}{K} \frac{\mathcal{A}}{\mathcal{C}} + \frac{\varepsilon^2 \mathcal{B}}{\mathcal{C}} = 0$$

$$\alpha = -\frac{\mathcal{B}}{2\mathcal{A}} K \varepsilon^2$$

$$\langle H \rangle_{\min \alpha} = -\frac{\mathcal{B}^2}{4 \mathcal{A} \mathcal{C}} K \varepsilon^4$$

The minimization with respect to the other two parameters was carried out numerically[4] with the following results:

$$\langle H \rangle_{\min} = -.37636 \ K \varepsilon^4 \doteq -1.50504 \ \frac{\varepsilon^2}{2a_0}$$

for

$$\alpha = .1298 \quad K \varepsilon^2 = .2596 \ \frac{1}{a_0}$$

$$\beta = .2529 \quad K \varepsilon^2 = .5058 \ \frac{1}{a_0}$$

$$\gamma = .5086 \quad K \varepsilon^2 = 1.0172 \ \frac{1}{a_0}$$

where $\frac{\varepsilon^2}{2a_0}$ is the ionization energy of the hydrogen atom and is the most commonly used unit of atomic energy, while a_0 is the radius of the first Bohr orbit of the hydrogen atom and which is the most commonly used unit of atomic length. The sum of the energies of the hydrogen atom and the positronium atom is $E_0 = -1.5 \ \frac{\varepsilon^2}{2a_0}$, where the mass of the nucleus of the hydrogen atom is taken to be infinitely large. Thus

$$E_0 - \frac{(\phi, H\phi)}{(\phi, \phi)} = (-1.50000 + 1.50504) \ \frac{\varepsilon^2}{2a_0}$$

$$= .00504 \ \frac{\varepsilon^2}{2a_0} = .06827 \quad \text{eV.}[5]$$

This shows that a system consisting of a positron and a negative hydrogen ion can exist in a bound state with a binding energy of at least .07 eV.

---

[4] The numerical computations were carried out on the Bendix G-15D computer of the University of Manitoba Computation Centre.

[5] This agrees with the result obtained by A. Ore: Physical Review, 83:665, 1951.

If $\Psi = e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3 + \delta r_{13})} + e^{-(\alpha r_3 + \beta r_{13} + \gamma r_2 + \delta r_{12})}$ is chosen as the

trial wave function, it is still possible to perform all the necessary integrations. As with the previous function, $\Psi(r_1, r_2, r_3) = \Psi(r_1, r_3, r_2)$ and

$$\frac{\partial \Psi}{\partial r_1} = 0 \quad , \quad \frac{\partial \Psi}{\partial r_{23}} = 0 \quad , \quad \frac{\partial \Psi}{\partial r_2} = -\alpha \Psi_2 - \gamma \Psi_3$$

$$\frac{\partial \Psi}{\partial r_3} = -\gamma \Psi_2 - \alpha \Psi_3 \quad , \quad \frac{\partial \Psi}{\partial r_{12}} = -\beta \Psi_2 - \delta \Psi_3 \quad , \quad \frac{\partial \Psi}{\partial r_{13}} = -\delta \Psi_2 - \beta \Psi_3$$

Thus $\langle H \rangle = \dfrac{(\Psi, H\Psi)}{(\Psi, \Psi)}$ where

$$(\Psi, H\Psi) = \frac{1}{K}\left[2(\alpha^2 + \gamma^2 + 2\beta^2 + 2\delta^2)(\Psi_2, \Psi_2) \right.$$

$$+ 4(\alpha\gamma + 2\beta\delta)(\Psi_2, \Psi_3) + 2\beta\delta\left(\Psi_2, \left\{\frac{r_{12}}{r_{13}} + \frac{r_{13}}{r_{12}} - \frac{r_{23}^2}{r_{12} r_{13}}\right\}\Psi_2\right)$$

$$+ (\beta^2 + \delta^2)\left(\Psi_2, \left\{\frac{2r_{12}}{r_{13}} - \frac{r_{13}^2}{r_{12} r_{13}}\right\}\Psi_3\right) + 2\alpha\beta\left(\Psi_2, \left\{\frac{r_{12}}{r_2} + \frac{r_2}{r_{12}} - \frac{r_1^2}{r_2 r_{12}}\right\}\Psi_2\right)$$

$$+ 2\gamma\delta\left(\Psi_3, \left\{\frac{r_{12}}{r_2} + \frac{r_2}{r_{12}} - \frac{r_1^2}{r_2 r_{12}}\right\}\Psi_3\right) + 2(\beta\gamma + \alpha\delta)\left(\Psi_2, \left\{\frac{r_{12}}{r_2} + \frac{r_2}{r_{12}} - \frac{r_1^2}{r_2 r_{12}}\right\}\Psi_3\right)\right]$$

$$- \varepsilon^2\left[-2z\left(\Psi_2, \frac{1}{r_1}\Psi_2\right) + 2z\left(\Psi_2, \left\{\frac{1}{r_2} + \frac{1}{r_3}\right\}\Psi_2\right) + 2\left(\Psi_2, \left\{\frac{1}{r_{12}} + \frac{1}{r_{13}}\right\}\Psi_2\right)\right.$$

$$\left. -2\left(\Psi_2, \frac{1}{r_{23}}\Psi_2\right) - 2z\left(\Psi_2, \frac{1}{r_1}\Psi_3\right) + 2z\left(\Psi_2, \left\{\frac{1}{r_2} + \frac{1}{r_3}\right\}\Psi_3\right) + 2\left(\Psi_2, \left\{\frac{1}{r_{12}} + \frac{1}{r_{13}}\right\}\Psi_3\right) - 2\left(\Psi_2, \frac{1}{r_{23}}\Psi_3\right)\right]$$

and $(\Psi, \Psi) = 2(\Psi_2, \Psi_2) + 2(\Psi_2, \Psi_3)$

Following the same procedure as with the previous function, we obtain:[6]

$$\langle H \rangle_{min.} = -1.516832 \quad \frac{\varepsilon^2}{2a_0}$$

for
$$\alpha = .220 \quad \frac{1}{a_0}$$
$$\beta = .472 \quad \frac{1}{a_0}$$
$$\gamma = 1.024 \quad \frac{1}{a_0}$$
$$\delta = .0844 \quad \frac{1}{a_0}$$

---

[6] See Appendix V: Evaluation of $\langle H \rangle$ for the trial wave function

$$e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3 + \delta r_{13})} + e^{-(\gamma r_2 + \delta r_{12} + \alpha r_3 + \beta r_{13})}.$$

Hence $\quad E_0 - \dfrac{(\psi, H\psi)}{(\psi, \psi)} \quad = \quad (-1.500000 + 1.516832) \dfrac{\varepsilon^2}{2a_0}$

$$= \quad .016832 \ \dfrac{\varepsilon^2}{2a_0}$$

$$= \quad .22799 \text{ eV.}$$

Thus, the binding energy of the system of a positron and a negative

hydrogen ion against dissociation into a positronium atom and a

hydrogen atom is at least .228 eV.

CHAPTER V

THE MEAN LIFETIME OF A SYSTEM OF A POSITRON AND A NEGATIVE HYDROGEN ION

AGAINST TWO PHOTON ANNIHILATION FROM THE GROUND STATE OF THE SYSTEM

The lifetime, τ , of a positron against two photon annihilation
in a medium for which the density of electrons at the position of the po-
sitron is ρ , is given by[1]

$$\frac{1}{\tau} = \pi r_0^2 \rho c$$

where $r_0 = \frac{e^2}{mc^2}$ is the classical radius of the electron. This result
represents an average over the initial spin states of an electron
positron pair. If the initial state of the pair is definitely known to
be singlet then the annihilation rate becomes

$$\frac{1}{\tau} = 4\pi r_0^2 \rho c ,$$

since in the above case the pair is in a triplet spin state for three
quarters of the time, from which two photon annihilation cannot occur.[2]
For the case of two photon annihilation of an electron-positron pair
from a system of a positron and a negative hydrogen ion in its ground
state, the wave function of the initial state is given by

$$X(2,3) = \psi(2,3)\,f(2,3)$$

where $\psi(2,3)$ is the symmetric space function of the system, symmetric with
respect to the electrons 2 and 3. Since the total wave function must be
antisymmetric with respect to the interchange of the two like fermions
2 and 3, then the spin function $f(2,3)$ must be antisymmetric: $f(2,3) = -f(3,2)$.

---

[1] Jauch and Rohrlich, _Theory of Photons and Electrons_, p. 269.
[2] Chapter I, page 2.

If α, β are the normalized single electron spin functions, then an antisymmetric spin function of the system is

$$f(2,3) = \frac{1}{\sqrt{2}}\left[\alpha(2)\,\beta(3) - \beta(2)\,\alpha(3)\right]\alpha(1)$$

For definitness let us assume that the positron annihilates with electron 2, then to determine the contribution to the annihilation rate, we write

$$f(2,3) = \frac{1}{\sqrt{2}}\alpha(2)\,\beta(3)\,\alpha(1) - \frac{1}{2}\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\,\alpha(2)\right]\alpha(3) - \frac{1}{2}\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\alpha(3)$$

$$= f_1(2,3) - \frac{1}{2}f_2(2,3) - \frac{1}{2}f_3(2,3)$$

We note that of these three spin states only $f_3(2,3) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\alpha(3)$ is a normalized, singlet spin function and the probability of the electron-positron pair being in this singlet state is the square of the coeficient of $f_3(2,3)$ in the above equation. Thus the pair will be in the singlet state one quarter of the time. Hence, since two photon annihilation occurs only out of the singlet state, the lifetime for two photon pair annihilation out of the ground state of a system of a positron and a negative hydrogen ion is given by

$$\frac{1}{\tau} = \frac{1}{4}\left(4\pi\,r_0^2\,\rho\,c\right)$$

Furthermore, this annihilation process, of a positron annihilating with an electron bound to a nucleus, in the lowest order is a second order process, with a net conservation of energy and momentum, for which a typical Feynman diagram is:
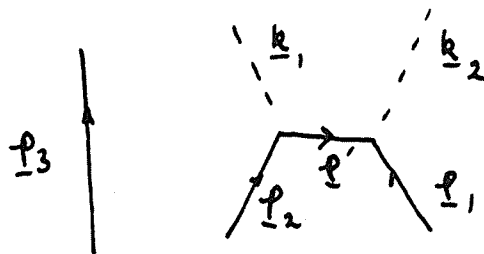
The annihilation with either of the electrons is not affected by the other, and since there are two electrons, with equal electron densities at the position of the positron, the annihilation rate finally becomes:

$$\frac{1}{\tau} = 2 \cdot \frac{1}{4}\left(4\pi r_0^2 \rho c\right) = 2\pi r_0^2 \rho c$$

Using the same notation as in Chapter IV, the density of electrons at the position of the positron, in the system of a positron and a negative hydrogen ion , is given by:

$$\rho = \left(\frac{2}{a_0}\right)^3 \frac{8\pi^2 \int |\psi(r_1, r_2, r_1)|^2 d\tau}{16\pi^3 \int |\psi(r_1, r_2, r_2)|^2 dq}$$

where dq is the element of volume of configuration space of the four particle system, introduced in chapter III as $d T_4 = dq\, d\Omega_4$ and $\int_\Omega dT_4 = 16\pi^3 dq$. The symbol $d\tau$, is an element of volume for a three particle configuration:
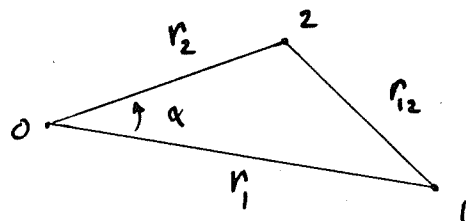
In this case $dT_3 = d^3 r_1\, d^3 r_2$. Let $\underline{r}_1 \equiv (r_1, \theta, \varphi)$ (in spherical polar coordinates) relative to a polar axis fixed in space, and let $\underline{r}_2 \equiv (r_2, \alpha, \beta)$ relative to $\underline{r}_1$ as the polar axis. Therefore

$$dT_3 = r_1^2 \sin\theta\, dr_1\, d\theta\, d\varphi\, r_2^2 \sin\alpha\, d\alpha\, d\beta$$
$$= r_1^2 r_2^2 \sin\alpha\, dr_1\, dr_2\, d\alpha\, d\Omega_3$$

where $d\Omega_3 = \sin\theta\, d\theta\, d\varphi\, d\beta$.

Hence $\int d\tau_3 = 8\pi^2 d\tau$ where $d\tau = r_1^2 r_2^2 \sin\alpha \, dr_1 \, dr_2 \, d\alpha$.

But $r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\alpha$; therefore $2r_{12} dr_{12} = 2 r_1 r_2 \sin\alpha \, d\alpha$,

that is $\sin\alpha \, d\alpha = \dfrac{r_{12} dr_{12}}{r_1 r_2}$ and $d\tau = r_1 r_2 r_3 \, dr_1 \, dr_2 \, dr_{12}$.

Using $\Psi = e^{-(\alpha r_2 + \beta r_{12} + \tau r_3 + \delta r_{13})} + e^{-(\tau r_2 + \delta r_{12} + \alpha r_3 + \beta r_{13})}$

as the unnormalized state function of the system in the ground state (with values of the parameters as determined in Chapter IV), we obtain[3]

$$\rho(\alpha, \beta, \tau, \delta) = \frac{.062952}{\pi a_o^3}$$

hence $\tau = 4.941 \ 10^{-10}$ sec. Thus the mean lifetime of the system of a positron and a negative hydrogen ion against two photon annihilation from the ground state is about four times as long as that of free singlet positronium in the 1^1S state, for which the lifetime is about $1.25 \ 10^{-10}$ sec.[4]

---

[3] Appendix V, The Density of Electrons at the Position of the Positron in a System of a Positron and a Negative Hydrogen Ion in its Ground State.

[4] De Benedetti and Corben, op. cit., p. 196.

CHAPTER VI

CONCLUSIONS

The following facts about the interaction of the positron with the negative hydrogen ion have been established: The system can exist in a bound state for short periods of time, subject to pair annihilation of the positron with one of the electrons. The ground state energy of the bound system $\varepsilon_0 \leqslant -1.516832$ (atomic units of energy), that is a binding energy of at least .228 eV against its most favourable mode of dissociation into a hydrogen atom and a positronium atom. Thus the binding is strong enough to ensure stability against dissociation due to thermal collisions with other systems. The ground state function of the system can be approximated by the wave function

$$\Psi = \frac{1}{\sqrt{(\Psi,\Psi)}}\left[e^{-(\alpha r_1 + \beta r_{12} + \gamma r_3 + \delta r_{13})} + e^{-(\gamma r_1 + \delta r_{12} + \alpha r_3 + \beta r_{13})}\right]$$

where

$$\alpha = .220 \ \frac{1}{a_0}$$

$$\beta = .472 \ \frac{1}{a_0}$$

$$\gamma = 1.024 \ \frac{1}{a_0}$$

$$\delta = .0844 \ \frac{1}{a_0}$$

Using this approximation for the wave function of the ground state of the system, the lifetime of the system against two photon annihilation of the positron with either of the two electrons is found to be:

$$\tau = 4.941 \quad 10^{-10} \text{ sec.}$$

This is about four times the lifetime of free positronium against two photon annihilation out of the singlet ground state. In order to improve

these results further, the investigator, together with G. Oczkowski and under the direction of Dr. S. M. Neamtan, is investigating the problem using for a trial wave function

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

The r_{23}^2 term has been introduced to take account of the mutual repulsion of the two electrons in the system. Also, since r_{23}^2 can be expressed as a relatively simple function of the other coordinates, all the integrals involved in $(\psi H \psi)$ can be explicitly evaluated. Recent improvements in the methods of determining lower bounds to eigenvalues[1] may make it possible for one to calculate a lower bound to the ground state energy of the system of a positron and a negative hydrogen ion, and in conjunction with the upper bound to determine more closely the ground state energy of the system.

---

[1] N. Bazley, Lower Bounds for Eigenvalues, Phys. Rev., 120:144, 1960

APPENDIX I

ELEMENT OF VOLUME OF CONFIGURATION SPACE FOR THE SYSTEM OF A POSITRON

AND A NEGATIVE HYDROGEN ION

Consider the configuration of the system as defined in Chapter III, p. 13. We wish to evaluate

$$J\left(\frac{x_1 \; y_1 \; z_1 \; x_2 \; y_2 \; z_2}{r_1 \; r_2 \; r_{12} \; \psi \; \theta \; \varphi}\right)$$

where $\underline{r}_1 \equiv (x_1, y_1, z_1)$ and $\underline{r}_2 \equiv (x_2, y_2, z_2)$. To establish a relation between the set of coordinates x_1, y_1, z_1, x_2, y_2, z_2 and the set r_1, r_2, r_{12}, ψ, θ, φ, we write

$$J\left(\frac{x_1 \; y_1 \; z_1 \; x_2 \; y_2 \; z_2}{r_1 \; r_2 \; r_{12} \; \psi \; \theta \; \varphi}\right) = J\left(\frac{x_1 \; y_1 \; z_1 \; x_2 \; y_2 \; z_2}{r_1 \; r_2 \; \chi \; \psi \; \theta \; \varphi}\right) J\left(\frac{r_1 \; r_2 \; \chi \; \psi \; \theta \; \varphi}{r_1 \; r_2 \; r_{12} \; \psi \; \theta \; \varphi}\right)$$

where χ is the angle between $\underline{r}_1$ and $\underline{r}_2$, and where

$$x_1 = r_1 \sin \psi \sin \theta$$
$$y_1 = -r_1 \cos \psi \sin \theta$$
$$z_1 = r_1 \cos \theta$$

$$x_2 = r_2 \sin \theta \sin \psi \cos \chi + r_2 \sin \chi (\cos \psi \cos \varphi - \cos \theta \sin \varphi \sin \psi)$$

$$y_2 = r_2 \sin \theta \cos \psi \cos \chi + r_2 \sin \chi (-\sin \psi \cos \varphi - \cos \theta \sin \varphi \cos \psi)$$

$$z_2 = r_2 \sin \chi \sin \theta \sin \varphi + r_2 \cos \chi \cos \theta$$

Thus, working out the six by six determinant of partial derivatives and collecting terms, we obtain:

$$J\left(\frac{x_1 \; y_1 \; z_1 \; x_2 \; y_2 \; z_2}{r_1 \; r_2 \; \chi \; \psi \; \theta \; \varphi}\right) = r_1^2 r_2^2 \sin \chi \sin \theta$$

and

$$J\left(\frac{r_1\ r_2\ \chi\ \psi\ \theta\ \varphi}{r_1\ r_2\ r_{12}\ \psi\ \theta\ \varphi}\right) = \frac{\partial \chi}{\partial r_{12}} = \frac{r_{12}}{\sin \chi\ r_1\ r_2}$$

as $\quad r_{12}^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \cos \chi$

Therefore

$$J\left(\frac{x_1\ y_1\ z_1\ x_2\ y_2\ z_2}{r_1\ r_2\ r_{12}\ \psi\ \theta\ \varphi}\right) = r_1\ r_2\ r_{12}\ \sin \theta .$$

APPENDIX II

THE SQUARE OF THE GRADIENT OF THE CONFIGURATION SPACE

We have $\psi = \psi(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})$ and we wish to obtain

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

where $\nabla_i\psi = \dfrac{\partial\psi}{\partial x_i}\underline{i} + \dfrac{\partial\psi}{\partial y_i}\underline{j} + \dfrac{\partial\psi}{\partial z_i}\underline{k}$ for $i = 1, 2, 3$

and where $r_i = (x_i^2 + y_i^2 + z_i^2)^{\frac{1}{2}}$ for $i = 1, 2, 3$

$r_{ij} = \left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right]^{\frac{1}{2}}$ for $i, j = 1, 2, 3$ and $i \neq j$

where $r_{ij} = |\underline{r}_i - \underline{r}_j|$.

Now $\nabla_1\psi = \dfrac{\partial\psi}{\partial r_1}\nabla_1 r_1 + \dfrac{\partial\psi}{\partial r_{12}}\nabla_1 r_{12} + \dfrac{\partial\psi}{\partial r_{13}}\nabla_1 r_{13}$

and similarly for $\nabla_2\psi$ and $\nabla_3\psi$. Since $\nabla_1 r_1 = \dfrac{\underline{r}_1}{r_1}$,

$\nabla_1 r_{12} = \dfrac{\underline{r}_1 - \underline{r}_2}{r_{12}}$, and $\nabla_1 r_{13} = \dfrac{\underline{r}_1 - \underline{r}_3}{r_{13}}$, we obtain:

$$\nabla_1\psi = \frac{\partial\psi}{\partial r_1}\frac{\underline{r}_1}{r_1} + \frac{\partial\psi}{\partial r_{12}}\frac{\underline{r}_1 - \underline{r}_2}{r_{12}} + \frac{\partial\psi}{\partial r_{13}}\frac{\underline{r}_1 - \underline{r}_3}{r_{13}}$$

Similarly

$$\nabla_2\psi = \frac{\partial\psi}{\partial r_2}\frac{\underline{r}_2}{r_2} + \frac{\partial\psi}{\partial r_{23}}\frac{\underline{r}_2 - \underline{r}_3}{r_{23}} + \frac{\partial\psi}{\partial r_{12}}\frac{\underline{r}_2 - \underline{r}_1}{r_{12}}$$

$$\nabla_3\psi = \frac{\partial\psi}{\partial r_3}\frac{\underline{r}_3}{r_3} + \frac{\partial\psi}{\partial r_{13}}\frac{\underline{r}_3 - \underline{r}_1}{r_{13}} + \frac{\partial\psi}{\partial r_{23}}\frac{\underline{r}_3 - \underline{r}_2}{r_{23}}$$

Squaring these we obtain:

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

$$+ \frac{\partial\psi}{\partial r_1}\frac{\partial\psi}{\partial r_{13}}\frac{r_1^2 + r_{13}^2 - r_3^2}{r_1 r_{13}} + \frac{\partial\psi}{\partial r_{12}}\frac{\partial\psi}{\partial r_{13}}\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}}$$

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

$$+ \frac{\partial \psi}{\partial r_2}\frac{\partial \psi}{\partial r_{12}}\frac{r_2^2 + r_{12}^2 - r_1^2}{r_2\, r_{12}} + \frac{\partial \psi}{\partial r_{23}}\frac{\partial \psi}{\partial r_{12}}\frac{r_{23}^2 + r_{12}^2 - r_{13}^2}{r_{23}\, r_{12}}$$

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

$$+ \frac{\partial \psi}{\partial r_3}\frac{\partial \psi}{\partial r_{23}}\frac{r_3^2 + r_{23}^2 - r_2^2}{r_3\, r_{23}} + \frac{\partial \psi}{\partial r_{13}}\frac{\partial \psi}{\partial r_{23}}\frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{r_{13}\, r_{23}} .$$

APPENDIX III

TABLE OF INTEGRALS

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

$$f_{00}(a,b) = \frac{2}{I}\left(e^{-br} - e^{-ar}\right) \qquad I = a^2 - b^2$$

$$f_{10}(a,b) = \frac{2e^{-br}}{I}\left[\frac{2a}{I}\right] + \frac{2e^{-ar}}{I}\left[-r - \frac{2a}{I}\right]$$

$$f_{01}(a,b) = \frac{2e^{-br}}{I}\left[r - \frac{2b}{I}\right] + \frac{2e^{-ar}}{I}\left[\frac{2b}{I}\right]$$

$$f_{11}(a,b) = \frac{2e^{-br}}{I}\left[\frac{2ar}{I} - \frac{8ab}{I^2}\right] + \frac{2e^{-ar}}{I}\left[\frac{2br}{I} + \frac{8ab}{I^2}\right]$$

$$f_{20}(a,b) = \frac{2e^{-br}}{I}\left[\frac{8a^2}{I^2} - \frac{2}{I}\right] + \frac{2e^{-ar}}{I}\left[-r^2 - \frac{4ar}{I} - \frac{8a^2}{I^2} + \frac{2}{I}\right]$$

$$f_{02}(a,b) = \frac{2e^{-br}}{I}\left[r^2 - \frac{4br}{I} + \frac{8b^2}{I^2} + \frac{2}{I}\right] + \frac{2e^{-ar}}{I}\left[-\frac{8b^2}{I^2} - \frac{2}{I}\right]$$

$$f_{21}(a,b) = \frac{2e^{-br}}{I}\left[\frac{8a^2r}{I^2} - \frac{2r}{I} - \frac{48a^2b}{I^3} + \frac{8b}{I^2}\right]$$
$$+ \frac{2e^{-ar}}{I}\left[\frac{2br^2}{I} + \frac{16abr}{I^2} + \frac{48a^2b}{I^3} - \frac{8b}{I^2}\right]$$

$$f_{12}(a,b) = \frac{2e^{-br}}{I}\left[\frac{2ar^2}{I} - \frac{16abr}{I^2} + \frac{48ab^2}{I^3} + \frac{8a}{I^2}\right]$$

$$+ \frac{2e^{-ar}}{I}\left[-\frac{8b^2r}{I^2} - \frac{2r}{I} - \frac{48ab^2}{I^3} - \frac{8a}{I^2}\right]$$

$$f_{30}(a,b) = \frac{2e^{-br}}{I}\left[\frac{48a^3}{I^3} - \frac{24a}{I^2}\right]$$

$$+ \frac{2e^{-ar}}{I}\left[-r^3 - \frac{6ar^2}{I} - \frac{24a^2r}{I^2} + \frac{6r}{I} - \frac{48a^3}{I^3} + \frac{24a}{I^2}\right]$$

$$f_{03}(a,b) = \frac{2e^{-br}}{I}\left[r^3 - \frac{6br^2}{I} + \frac{24b^2r}{I^2} + \frac{6r}{I} - \frac{48b^3}{I^3} - \frac{24b}{I^2}\right]$$

$$+ \frac{2e^{-ar}}{I}\left[\frac{48b^3}{I^3} + \frac{24b}{I^2}\right]$$

APPENDIX IV

EVALUATION OF $\langle H \rangle$ USING THE TRIAL FUNCTION $e^{-(\alpha r_1 + \beta r_{12} + \gamma r_3)} + e^{-(\gamma r_2 + \beta r_{13} + \alpha r_2)}$

$$\langle H \rangle = \frac{\frac{1}{k}\mathcal{A}(\alpha,\beta,\gamma) + \mathcal{E}^2 \mathcal{B}(\alpha,\beta,\gamma)}{\mathcal{E}(\alpha,\beta,\gamma)}$$

$$\mathcal{A}(\alpha,\beta,\gamma) = 2(\alpha^2 + 2\beta^2 + \gamma^2)\int_0^\infty f_{11}(2\alpha,2\beta)\,f_{11}(2\gamma,0)\,dr_1$$

$$+ 4\alpha\gamma\int_0^\infty f_{11}^2(\alpha+\gamma,\beta)\,dr_1 + 2\beta^2\int_0^\infty f_{12}(\alpha+\gamma,\beta)\,f_{10}(\alpha+\gamma,\beta)\,dr_1$$

$$- \beta^2\int_0^\infty f_{10}(\alpha+\gamma,\beta)\left[f_{30}(\alpha+\gamma,\beta) + f_{12}(\alpha+\gamma,\beta)\right]dr_1 + \frac{\beta^2}{2}\int_0^\infty \left[f_{30}(\alpha+\gamma,\beta) - f_{12}(\alpha+\gamma,\beta)\right]^2 \frac{dr_1}{r_1^2}$$

$$+ \frac{\beta^2}{2}\int_0^\infty f_{10}^2(\alpha+\gamma,\beta)\,r_1^2\,dr_1 + 2\alpha\beta\int_0^\infty \left[f_{20}(2\alpha,2\beta) + f_{02}(2\alpha,2\beta) - r_1^2 f_{00}(2\gamma,2\beta)\right]f_{11}(2\gamma,0)\,dr_1$$

$$+ 2\beta\gamma\int_0^\infty \left[f_{20}(\alpha+\gamma,\beta) + f_{02}(\alpha+\gamma,\beta) - f_{00}(\alpha+\gamma,\beta)\right]f_{11}(\alpha+\gamma,\beta)\,dr_1$$

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

$$+ \frac{\rho\left[(\alpha+\gamma)^2 + 7(\alpha+\gamma)\beta + \beta^2\right]}{(\alpha+\gamma)\beta(\alpha+\beta+\gamma)^7}\left[1 + \frac{2\gamma}{\alpha+\gamma}\right]$$

$$B(\alpha, \beta, \gamma) = -2z \int_0^\infty f_{11}(2\gamma, 0) \, f_{01}(2\alpha, 2\beta) \, dr_1 - 2z \int_0^\infty f_{11}(2\alpha, 2\beta) f_{01}(2\gamma, 0) \, dr_1$$

$$-2 \int_0^\infty f_{10}(2\alpha, 2\beta) f_{11}(2\gamma, 0) \, dr_1 - 2 \int_0^\infty f_{11}(2\alpha, 2\beta) f_{10}(2\gamma, 0) \, dr_1$$

$$+2z \int_0^\infty f_{11}(2\alpha, 2\beta) f_{11}(2\gamma, 0) \frac{dr_1}{r_1} - 4z \int_0^\infty f_{11}(\alpha+\gamma, \beta) f_{01}(\alpha+\gamma, \beta) \, dr_1$$

$$-4 \int_0^\infty f_{11}(\alpha+\gamma, \beta) f_{10}(\alpha+\gamma, \beta) \, dr_1 + 2 \int_0^\infty f_{11}^2(\alpha+\gamma, \beta) \frac{dr_1}{r_1}$$

$$+2 \int_0^\infty f_{11}(2\alpha, 2\gamma) f_{11}(2\beta, 0) \frac{dr_{23}}{r_{23}} + 2 \int_0^\infty f_{11}(\alpha+\gamma, \alpha+\gamma) f_{11}(\beta, \beta) \frac{dr_{23}}{r_{23}}$$

$$= \frac{32(16) \, z \, (\alpha+\gamma)^2 \beta^2}{(\alpha^2-\gamma^2)^6} \log_e \frac{(\alpha+\beta+\gamma)^2}{4(\alpha+\gamma)\beta} + \frac{(16)^2(\alpha+\gamma-z\beta)}{(\alpha+\beta+\gamma)^3 (\alpha^2-\gamma^2)^3}$$

$$+ \frac{(z-1)(\alpha^2+3\alpha\beta+\beta^2)}{8(\alpha+\beta)^3 \gamma^3 \alpha^2 \beta^2} + \frac{\alpha^2+3\alpha\gamma+\gamma^2}{8(\alpha+\gamma)^3 \beta^3 \alpha^2 \gamma^2} - \frac{z(\alpha+\gamma)+\beta}{8(\alpha\beta\gamma)^3}$$

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

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

$$+ \frac{\beta(\alpha+2\gamma)}{8(\alpha+\gamma)^3\gamma^3(\alpha^2-\beta^2)^2} + \frac{4(16)(\alpha+\gamma)\beta(3z-2)}{(\alpha+\beta+\gamma)^2(\alpha^2-\gamma^2)^4} - \frac{16(\alpha+\gamma)^2}{\beta^2(\alpha^2-\gamma^2)^4}$$

$$+ \frac{48(z[\alpha+\gamma]^2+\beta^2)}{\beta(\alpha+\gamma)(\alpha^2-\gamma^2)^4} - \frac{128z}{(\alpha^2-\gamma^2)^4} - \frac{8z(\alpha+\gamma)}{\beta^3(\alpha^2-\gamma^2)^3} + \frac{8\beta}{(\alpha+\gamma)^3(\alpha^2-\gamma^2)^3} + \frac{8z[(\alpha+\gamma)^2+\beta^2]}{\beta^2(\alpha+\gamma)^2(\alpha^2-\gamma^2)^3}$$

$$\mathscr{E}(\alpha, \beta, \gamma) = 2 \int_0^\infty f_{11}(2\alpha, 2\beta) \, f_{11}(2\gamma, 0) \, dr_1$$

$$+ 2 \int_0^\infty f_{11}^2(\alpha+\gamma, \beta) \, dr_1$$

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

APPENDIX V

VALUE OF $\langle H \rangle$ FOR THE TRIAL FUNCTION $e^{-(\alpha r_2 + \beta r_{12} + \gamma r_3 + \delta r_{13})} + e^{-(\gamma r_2 + \delta r_{12} + \alpha r_3 + \beta r_{13})}$

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

$$
\mathcal{A}(\alpha,\beta,\gamma,\delta) = \frac{\alpha^2+\gamma^2+2\beta^2+2\delta^2}{8\,(\alpha^2-\beta^2)^2(\gamma^2-\delta^2)^2}\left[\frac{\alpha\gamma}{(\beta+\delta)^3} + \frac{\beta\gamma}{(\alpha+\delta)^3} + \frac{\beta\delta}{2(\alpha+\gamma)^3}\right.
$$

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

$$
+ \frac{2\alpha\beta}{\alpha^2-\beta^2}\left(\frac{\gamma}{(\alpha+\delta)^2} - \frac{\gamma}{(\beta+\delta)^2} + \frac{\delta}{(\alpha+\gamma)^2} - \frac{\delta}{(\beta+\gamma)^2}\right)
$$

$$
+ \frac{8\alpha\beta\gamma\delta}{(\alpha^2-\beta^2)(\gamma^2-\delta^2)}\left(-\frac{1}{\alpha+\delta} - \frac{1}{\beta+\gamma} + \frac{1}{\beta+\delta} + \frac{1}{\alpha+\gamma}\right)\Bigg]
$$

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

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

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

$$
+ \frac{4\alpha\gamma(\beta^2+\delta^2)}{(\alpha^2-\gamma^2)(\beta^2-\delta^2)}\left\{\frac{1}{\beta+\gamma} + \frac{1}{\alpha+\delta} - \frac{1}{\alpha+\beta} - \frac{1}{\gamma+\delta}\right\} + \left\{-\frac{\alpha\delta}{(\gamma+\delta)^3} - \frac{\beta\gamma}{(\alpha+\beta)^3}\right.
$$

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

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

$$+ \frac{4\gamma\delta(\alpha^2+\beta^2)}{(\gamma^2-\delta^2)(\alpha^2-\beta^2)}\left\{\frac{1}{\alpha+\delta} + \frac{1}{\beta+\gamma} - \frac{1}{\alpha+\gamma} - \frac{1}{\beta+\delta}\right\} - \frac{\gamma\beta}{(\beta+\delta)^3} - \frac{\alpha\delta}{(\alpha+\gamma)^3}$$

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

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

$$+ \frac{4\alpha\beta(\gamma^2+\delta^2)}{(\alpha^2-\beta^2)(\gamma^2-\delta^2)}\left\{\frac{1}{\beta+\gamma} + \frac{1}{\alpha+\delta} - \frac{1}{\alpha+\gamma} - \frac{1}{\beta+\delta}\right\} - \frac{\alpha\delta}{(\beta+\delta)^3} - \frac{\beta\gamma}{(\alpha+\gamma)^3}$$

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

$$B(\alpha,\beta,\gamma,\delta) = \frac{2z\,\alpha\beta\gamma\delta}{(\alpha^2-\beta^2)^3(\gamma^2-\delta^2)^3}\log_e\frac{(\beta+\delta)(\alpha+\gamma)}{(\beta+\gamma)(\alpha+\delta)}$$

$$+ \frac{z}{8(\alpha^2-\beta^2)^2(\gamma^2-\delta^2)^2}\left[\frac{\alpha\gamma}{(\beta+\delta)^2} + \frac{\beta\gamma}{(\alpha+\delta)^2} + \frac{\beta\delta}{(\alpha+\gamma)^2} + \frac{\alpha\delta}{(\beta+\gamma)^2}\right.$$

$$- \frac{4\gamma\delta}{\gamma^2-\delta^2}\left\{\frac{\alpha}{\beta+\delta} - \frac{\alpha}{\beta+\gamma} - \frac{\beta}{\alpha+\gamma} + \frac{\beta}{\alpha+\delta}\right\} + \frac{4\alpha\beta}{\alpha^2-\beta^2}\left\{\frac{\gamma}{\alpha+\delta} - \frac{\gamma}{\beta+\delta}\right.$$

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

$$- \frac{\beta}{(\alpha+\delta)^3} + \frac{2\beta\delta}{\beta^2-\delta^2}\left\{\frac{1}{(\beta+\gamma)^2} + \frac{1}{(\alpha+\delta)^2} - \frac{1}{(\gamma+\delta)^2} - \frac{1}{(\alpha+\beta)^2}\right\}$$

$$+ \frac{1}{\alpha+\gamma}\left\{\frac{\beta}{(\gamma+\delta)^2} - \frac{\delta}{(\alpha+\beta)^2} + \frac{\delta}{(\beta+\gamma)^2} - \frac{\beta}{(\alpha+\delta)^2}\right\} - \frac{4\beta\delta}{(\beta^2-\delta^2)(\alpha+\gamma)}\left\{\frac{1}{\gamma+\delta}\right.$$

$$+ \frac{1}{\alpha+\beta} - \frac{1}{\beta+\gamma} - \frac{1}{\alpha+\delta} \Big\} \Big] \; - \; \frac{1}{8(\alpha^2-\gamma^2)^2(\beta^2-\delta^2)} \left[\frac{\alpha}{(\gamma+\delta)^3} - \frac{\gamma}{(\alpha+\beta)^3} \right.$$

$$+ \frac{\gamma}{(\alpha+\delta)^3} - \frac{\alpha}{(\beta+\gamma)^3} - \frac{2\alpha\gamma}{\alpha^2-\gamma^2} \Big\{ \frac{1}{(\gamma+\delta)^2} + \frac{1}{(\alpha+\beta)^2} - \frac{1}{(\alpha+\delta)^2} - \frac{1}{(\beta+\gamma)^2} \Big\}$$

$$+ \frac{1}{\beta+\delta} \Big\{ \frac{\alpha}{(\gamma+\delta)^2} - \frac{\gamma}{(\alpha+\beta)^2} + \frac{\gamma}{(\alpha+\delta)^2} - \frac{\alpha}{(\beta+\gamma)^2} \Big\} - \frac{4\alpha\gamma}{(\beta+\delta)(\alpha^2-\gamma^2)} \Big\{ \frac{1}{\gamma+\delta}$$

$$+ \frac{1}{\alpha+\beta} - \frac{1}{\alpha+\delta} - \frac{1}{\beta+\delta} \Big\} \Big] + \frac{1}{8(\alpha^2-\gamma^2)^2(\beta^2-\delta^2)^2} \left[\frac{\alpha\beta}{(\gamma+\delta)^2} + \frac{\beta\gamma}{(\alpha+\delta)^2} \right.$$

$$+ \frac{\gamma\delta}{(\alpha+\beta)^2} + \frac{\alpha\delta}{(\beta+\gamma)^2} - \frac{4\beta\delta}{\beta^2-\delta^2} \Big\{ \frac{\alpha}{\gamma+\delta} - \frac{\alpha}{\beta+\gamma} - \frac{\gamma}{\alpha+\beta} + \frac{\gamma}{\alpha+\delta} \Big\}$$

$$+ \frac{4\alpha\gamma}{\alpha^2-\gamma^2} \Big\{ \frac{\beta}{\alpha+\delta} - \frac{\beta}{\gamma+\delta} + \frac{\delta}{\alpha+\beta} - \frac{\delta}{\beta+\gamma} \Big\} \Big] + \frac{z \, 8^3 (\alpha+\gamma)^2 (\beta+\delta)^2}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^6} \times$$

$$\log_e \frac{(\alpha+\beta+\gamma+\delta)^2}{4(\alpha+\gamma)(\beta+\delta)} \;+\; \frac{2\,\alpha\beta\gamma\delta}{(\alpha^2-\gamma^2)^3(\beta^2-\delta^2)^3} \; \log_e \frac{(\alpha+\delta)(\beta+\gamma)}{(\alpha+\beta)(\gamma+\delta)}$$

$$+ \frac{8z}{[(\alpha+\gamma)^2-(\beta+\delta)^2]^4} \left[\frac{(\alpha+\gamma)^2}{(\beta+\delta)^2} + \frac{(\beta+\delta)^2}{(\alpha+\gamma)^2} + \frac{40(\alpha+\gamma)(\beta+\delta)}{(\alpha+\beta+\gamma+\delta)^2} - 16 \right]$$

$$- \frac{8(z+1)}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^4} \left[\frac{5}{(\alpha+\beta+\gamma+\delta)^2} + \frac{1}{(\alpha+\gamma)(\beta+\delta)} \right]$$

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

$$+ \frac{10}{(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^2} \left[\frac{1}{4(\alpha+\gamma)^2(\beta+\delta)^2} + \frac{1}{2(\alpha+\gamma)(\beta+\delta)(\alpha+\beta+\gamma+\delta)^2} \right.$$

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

$$\varphi(\alpha, \beta, \gamma, \delta) = \frac{1}{16\,(\alpha^2-\beta^2)^2(\gamma^2-\delta^2)^2}\left[\frac{\alpha\gamma}{(\beta+\delta)^3} + \frac{\beta\gamma}{(\alpha+\delta)^3}\right.$$

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

$$\left.+ \frac{\beta}{(\alpha+\gamma)^2}\right) + \frac{2\,\alpha\beta}{\alpha^2-\beta^2}\left(\frac{\gamma}{(\alpha+\delta)^2} - \frac{\gamma}{(\beta+\delta)^2} + \frac{\delta}{(\alpha+\gamma)^2} - \frac{\delta}{(\beta+\gamma)^2}\right)$$

$$\left.- \frac{8\,\alpha\beta\gamma\delta}{(\alpha^2-\beta^2)(\gamma^2-\delta^2)}\left(\frac{1}{\alpha+\delta} + \frac{1}{\beta+\gamma} - \frac{1}{\beta+\delta} - \frac{1}{\alpha+\gamma}\right)\right]$$

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

APPENDIX VI

THE DENSITY OF ELECTRONS AT THE POSITION OF THE POSITRON IN A SYSTEM OF

A POSITRON AND A NEGATIVE HYDROGEN ION IN ITS GROUND STATE

As stated in Chapter V, p. 24, the density of electrons at the position of the positron is given by

$$\rho = \left(\frac{2}{a_0}\right)^3 \frac{8\pi^2 \int |\Psi(r_1, r_2, r_1)|^2 d\tau}{16\pi^3 \int |\Psi(r_1, r_2, r_3)|^2 dq}$$

where $\int |\Psi(r_1, r_2, r_3)|^2 dq = \mathcal{E}(\alpha, \beta, \tau, \delta)$, which is worked out in

Appendix V, and where

$$\int |\Psi(r_1, r_2, r_1)|^2 = \int_0^\infty e^{-2\alpha r_1} f_{11}(2\tau, 2\delta) r_1 dr_1 + \int_0^\infty e^{-2\tau r_1} f_{11}(2\alpha, 2\beta) r_1 dr_1$$

$$+ \int_0^\infty 2 e^{-(\alpha+\tau) r_1} f_{11}(\alpha+\tau, \beta+\delta) r_1 dr_1$$

$$= \frac{1}{8(\tau^2 - \delta^2)^2}\left[\frac{\tau}{(\alpha+\delta)^3} + \frac{\delta}{(\alpha+\tau)^3} - \frac{2\tau\delta}{(\tau^2-\delta^2)(\alpha+\delta)^2} + \frac{2\tau\delta}{(\tau^2-\delta^2)(\alpha+\tau)^2}\right]$$

$$+ \frac{1}{8(\alpha^2 - \beta^2)^2}\left[\frac{\alpha}{(\tau+\beta)^3} + \frac{\beta}{(\alpha+\tau)^3} - \frac{2\alpha\beta}{(\alpha^2-\beta^2)(\tau+\beta)^2} + \frac{2\alpha\beta}{(\alpha^2-\beta^2)(\alpha+\tau)^2}\right]$$

$$+ \frac{16}{[(\alpha+\tau)^2 - (\beta+\delta)^2]^2}\left[\frac{\alpha+\tau}{(\alpha+\beta+\tau+\delta)^3} + \frac{\beta+\delta}{8(\alpha+\tau)^3} - \frac{2(\alpha+\tau)(\beta+\delta)}{[(\alpha+\tau)^2-(\beta+\delta)^2](\alpha+\beta+\tau+\delta)^2}\right.$$

$$\left. + \frac{(\alpha+\tau)(\beta+\delta)}{2[(\alpha+\tau)^2-(\beta+\delta)^2](\alpha+\tau)^2}\right]$$