Annihilation of Positrons from the H^-e^+ Ground State*†

S. M. NEAMTAN, G. DAREWYCH, AND G. OCZKOWSKI
Department of Mathematical Physics, The University of Manitoba, Winnipeg, Canada

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The problem of the binding of a positron to a negative hydrogen ion has been treated by the variational method with a four-parameter trial function. The best values of the parameters yield a binding energy of 0.228 ev against the most favored mode of dissociation into hydrogen plus positronium. Pair annihilation from the ground state of similar bound H^-e^+ systems might be expected to contribute a principal component to the radiation from the annihilation of positrons in the alkali hydrides. The theory of positron annihilation has been suitably extended for application to the present problem. The above wave function yields a mean life against two-photon annihilation of about four times that for singlet positronium, the difference arising mainly out of spin considerations. The calculation of the angular correlation of the annihilation radiation indicates a narrower peak than has been obtained experimentally by others in LiH and NaH.

I. INTRODUCTION

THAT a positron can form a bound state with a negative hydrogen ion was first shown by Ore.[1] Applying the variational method to a simple three-parameter trial function, he obtained a binding energy of 0.07 ev against dissociation into hydrogen plus positronium, a result which has now been considerably improved upon. The introduction of positrons into a medium containing a high concentration of H^- ions would presumably lead to the formation of the compound H^-e^+ in appreciable amounts. Such a medium is provided by the alkali hydrides, and the binding of positrons to H^- ions in these substances and their subsequent annihilation from these bound states might be expected to contribute a principal component to the annihilation radiation in these solids.

Results of recent measurements[2] of the angular correlation of the radiation from the annihilation of positrons in LiH and NaH appear to indicate that models which are adequate for the calculation of such processes in the alkali halides are inadequate for the hydrides. It would appear necessary in the case of the hydrides to allow for a correlation in the motion of the positron and the electrons and to calculate the nature of the annihilation from H^-e^+ with the aid of a wave function which is an adequate approximation to the ground state of this bound system.

The purpose of the present investigation has been, first, to obtain an improved estimate of the binding energy of H^-e^+ and an improved wave function for the system, and, second, to calculate the corresponding annihilation rate and the angular correlation of the annihilation radiation for comparison with experiment.

II. THE WAVE FUNCTION AND THE BINDING ENERGY

For the system H^-+e^+, the hydrogen nucleus is taken to be fixed at the origin. Then, labeling the coordinates of the positron and of the two electrons, respectively, with subscripts 1, 2, and 3, a state of zero angular momentum will be specified by a function of the six interparticle distances r_1, r_2, r_3, r_{12}, r_{13}, and r_{23}. The choice of these six distances as coordinates, however, leads to a quite complicated element of volume. A simplification is achieved by choosing instead five of these distances and a suitable angle. For example, one may take as coordinates r_1, r_2, r_3, r_{12}, r_{13}, and ϕ_{23}, where ϕ_{23} is the angle between the planes (012) and (013). The element of volume then takes the form

$$d\tau = 8\pi^2 r_2 r_3 r_{12} r_{13} dr_1 dr_2 dr_3 dr_{12} dr_{13} d\phi_{23}.$$

The factor $8\pi^2$ results from prior integration over Euler angles which define the orientation of the tetrahedron formed by the four particles. The angle ϕ_{23} ranges from 0 to 2π and the ranges of the other variables are subject to triangle inequalities.

The complexity of the geometry of the four-particle system imposes severe practical restrictions on the choice of a trial wave function for variation. The following symmetrized four-parameter function was chosen:

$$\psi(1,2,3) = \exp[-\alpha r_2 - \beta r_{12} - \gamma r_3 - \delta r_{13}] + \exp[-\alpha r_3 - \beta r_{13} - \gamma r_2 - \delta r_{12}]. \quad (1)$$

With this choice it was possible to obtain an explicit expression for the average of the Hamiltonian as a function of the four parameters. In minimizing this function, one of the parameters could be immediately eliminated, and the remainder of the computation was performed on a Bendix G15 computer.[3]

For the above wave function the minimum energy is -1.5168 a. u. This gives for the binding energy against dissociation into hydrogen plus positronium the value 0.0168 a. u. $=0.228$ ev. The corresponding values of the

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[1] A. Ore, *University of Bergen Yearbook No. 5* (Bergen, Norway, 1952).

[2] A. T. Stewart and R. H. March, Phys. Rev. **122**, 75 (1961).

[3] Details of the calculations are included in G. Darewych, M.Sc. thesis, University of Manitoba (unpublished).

parameters in atomic units are $\alpha=0.221$, $\beta=0.472$, $\gamma=1.024$, and $\delta=0.0844$.

III. POSITRON ANNIHILATION IN A TWO-ELECTRON BOUND SYSTEM

The problem of the annihilation of a positron with an electron in a bound atomic system has been treated by Ferrell[4] for the situation in which one can take as a wave function for the system a simple product of a function of the electron coordinates into a function of the positron coordinates. For the present problem the theory must be modified to be applicable to an initial-state wave function which is not of a simple product form and which involves the coordinates of two electrons with either one of which the positron may annihilate.

We consider the process of two-photon pair annihilation from a state of a system of two electrons and one positron which has a wave function of the form

$$\psi=[f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+f(\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_2)]\times[\alpha(2)\beta(3)-\beta(2)\alpha(3)]\alpha(1)N2^{-\frac{1}{2}}, \quad (2)$$

where

$$N^{-2}=\int|f(1,2,3)+f(1,3,2)|^2 d^3r_1 d^3r_2 d^3r_3. \quad (3)$$

In the above, α and β represent "spin up" and "spin down" spin functions, respectively.

On introducing the Fourier transform of f, viz.,

$$\varphi(\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3)=(2\pi)^{-9/2}\int f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\times\exp[(-i/\hbar)(\mathbf{p}_1\cdot\mathbf{r}_1+\mathbf{p}_2\cdot\mathbf{r}_2+\mathbf{p}_3\cdot\mathbf{r}_3)]d^3r_1 d^3r_2 d^3r_3, \quad (4)$$

we can take for the initial state of the electron-positron and photon fields the expression

$$\omega_i=N\int d^3p_1 d^3p_2 d^3p_3\ \varphi(\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3)b^\dagger(\mathbf{p}_1,\uparrow)\times[a^\dagger(\mathbf{p}_2,\downarrow)a^\dagger(\mathbf{p}_3,\uparrow)+a^\dagger(\mathbf{p}_3,\downarrow)a^\dagger(\mathbf{p}_2,\uparrow)]\omega_0, \quad (5)$$

where ω_0 is the vacuum state and $a^\dagger$ and $b^\dagger$ are electron and positron creation operators, respectively. Since we shall be dealing essentially with low-energy particles, the spins need not be related to the momentum directions and can be designated as above by $\uparrow$ and $\downarrow$, that is, as spin up and spin down. It is clear on inspection that ω_i changes sign under exchange of the electron spins, and it is a simple matter to verify that N is the correct normalization factor.

For the final state of the system we wish to set up a state vector which represents the existence in the field of the two annihilation photons together with a system of one electron with normalized wave function $u(\mathbf{r})$ which we take to be one of a complete orthogonal and normalized set of functions over which summation is ultimately to be performed. We introduce the Fourier transform,

$$\chi(\mathbf{p})=(2\pi)^{-\frac{3}{2}}\int u(\mathbf{r})\exp[(-i/\hbar)\mathbf{p}\cdot\mathbf{r}]d^3r. \quad (6)$$

The final state can now be taken to be

$$\omega_f=\int d^3p'\,\chi(\mathbf{p}')a^\dagger(\mathbf{p}',\uparrow)c^\dagger(\mathbf{k},\mathbf{e}_1)c^\dagger(\mathbf{p}-\mathbf{k},\mathbf{e}_2)\omega_0. \quad (7)$$

In the above, $c^\dagger$ is a photon creation operator, $\mathbf{k}$ and $\mathbf{p}-\mathbf{k}$ are the momenta of the two photons created, and $\mathbf{e}_1$ and $\mathbf{e}_2$ their respective polarization vectors. The spin assignment to the electron is determined by the fact that the pair annihilation from the initial state (5) will leave the surviving electron with spin up $\uparrow$.

In order to obtain an expression for the transition matrix element between initial and final state we consider the contribution of individual terms in (5). The term $b^\dagger(\mathbf{p}_1,\uparrow)a^\dagger(\mathbf{p}_2,\downarrow)a^\dagger(\mathbf{p}_3,\uparrow)\omega_0$ can be interpreted as contributing (in lowest order) to the two-photon annihilation process through the mutual annihilation of the positron and electron 2 from a spin state which may be written as a linear combination of singlet and triplet, viz.,

$$\uparrow\downarrow=2^{-\frac{1}{2}}[2^{-\frac{1}{2}}(\uparrow\downarrow-\downarrow\uparrow)+2^{-\frac{1}{2}}(\uparrow\downarrow+\downarrow\uparrow)]. \quad (8)$$

For this state the positron-electron system is singlet only half of the time. Then, since two-photon annihilation from the triplet state is forbidden, a factor of $2^{-\frac{1}{2}}$ will appear in the transition matrix element to multiply the corresponding matrix element for transition from a pure singlet state. Similar considerations apply to the term $b^\dagger(\mathbf{p}_1,\uparrow)a^\dagger(\mathbf{p}_3,\downarrow)a^\dagger(\mathbf{p}_2,\uparrow)\omega_0$. A simplification results from the fact that the particle momenta involved are predominantly small, so that a matrix element which would ordinarily be a function of the momenta of the annihilating pair can be replaced by its value for zero momenta.

In view of the above considerations, the transition matrix element between ω_i and ω_f can now be written

$$M=N\int d^3p'd^3p_1d^3p_2d^3p_3\,\chi^*(\mathbf{p}')\varphi(\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3)\times[\delta^3(\mathbf{p}'-\mathbf{p}_3)\delta^3(\mathbf{p}-\mathbf{p}_1-\mathbf{p}_2)+\delta^3(\mathbf{p}'-\mathbf{p}_2)\delta^3(\mathbf{p}-\mathbf{p}_1-\mathbf{p}_3)]2^{-\frac{1}{2}}M(0,0), \quad (9)$$

where $M(0,0)$ is the matrix element for two-photon annihilation from the singlet state of electron and positron with zero momenta. This expression reduces to

$$\begin{aligned}M&=2^{-\frac{1}{2}}NM(0,0)\int d^3p_2d^3p_3[\chi^*(\mathbf{p}_3)\varphi(\mathbf{p}-\mathbf{p}_2,\mathbf{p}_2,\mathbf{p}_3)+\chi^*(\mathbf{p}_2)\varphi(\mathbf{p}-\mathbf{p}_3,\mathbf{p}_2,\mathbf{p}_3)]\\&=2^{-\frac{1}{2}}NM(0,0)\int d^3p_2d^3p_3\,\chi^*(\mathbf{p}_2)[\varphi(\mathbf{p}-\mathbf{p}_3,\mathbf{p}_2,\mathbf{p}_3)+\varphi(\mathbf{p}-\mathbf{p}_3,\mathbf{p}_3,\mathbf{p}_2)]. \quad (10)\end{aligned}$$

[4] R. A. Ferrell, Revs. Modern Phys. 28, 308 (1956).

On the reintroduction of the configuration space functions, the above expression becomes

$$M=2^{-\frac{1}{2}}NM(0,0)\int d^3r_2d^3r_3\{u^*(\mathbf{r}_2)\exp[(-i/\hbar)\mathbf{p}\cdot\mathbf{r}_3]\times f(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_3)+u^*(\mathbf{r}_3)\exp[(-i/\hbar)\mathbf{p}\cdot\mathbf{r}_2]f(\mathbf{r}_2,\mathbf{r}_2,\mathbf{r}_3)\}$$
$$=2^{-\frac{1}{2}}NM(0,0)\int d^3r_2d^3r_3\,u^*(\mathbf{r}_2)\exp[(-i/\hbar)\mathbf{p}\cdot\mathbf{r}_3]\times[f(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_2)]. \quad (11)$$

It is now necessary to sum the square of the matrix element over all final states of the surviving electron, that is, over the complete set of functions $u(r)$. With the aid of the closure relation one obtains

$$\sum_u|M|^2=2^{-1}N^2|M(0,0)|^2\int d^3r_2'd^3r_3'd^3r_2d^3r_3\times\exp[(i/\hbar)\mathbf{p}\cdot(\mathbf{r}_3'-\mathbf{r}_3)]\times[f(\mathbf{r}_3',\mathbf{r}_2',\mathbf{r}_3')+f(\mathbf{r}_3',\mathbf{r}_3',\mathbf{r}_2')]^*\times[f(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_2)]\sum_u u(\mathbf{r}_2')u^*(\mathbf{r}_2)$$
$$=\tfrac{1}{2}N^2|M(0,0)|^2\int d^3r_2'd^3r_3'd^3r_2d^3r_3\times\exp[(i/\hbar)\mathbf{p}\cdot(\mathbf{r}_3'-\mathbf{r}_3)]\times[f(\mathbf{r}_3',\mathbf{r}_2',\mathbf{r}_3')+f(\mathbf{r}_3',\mathbf{r}_3',\mathbf{r}_2')]^*\times[f(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_2)]\delta^3(\mathbf{r}_2'-\mathbf{r}_2). \quad (12)$$

Integration over $\mathbf{r}_2'$ and replacement of $\mathbf{r}_3'$ by $\mathbf{r}_1$ yields

$$\sum_u|M|^2=\tfrac{1}{2}N^2|M(0,0)|^2\int d^3r_1d^3r_2d^3r_3\times\exp[(i/\hbar)\mathbf{p}\cdot(\mathbf{r}_3-\mathbf{r}_1)]\times[f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_1)+f(\mathbf{r}_1,\mathbf{r}_1,\mathbf{r}_2)]^*\times[f(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_2)]. \quad (13)$$

This is the basic result from which one can proceed to the calculation of either the angular distribution of the annihilation radiation or the annihilation rate. It may be remarked that the identical result is obtained if one assumes the surviving electron to be left in a free-particle momentum state.

IV. ANNIHILATION RATE

For calculation of the annihilation rate the expression (13) must be integrated over all values of $\mathbf{p}$. This yields

$$\int d^3p\sum_u|M|^2$$
$$=\tfrac{1}{2}N^2|M(0,0)|^2(2\pi)^3\int d^3r_1d^3r_2d^3r_3\,\delta^3(\mathbf{r}_3-\mathbf{r}_1)\times[f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_1)+f(\mathbf{r}_1,\mathbf{r}_1,\mathbf{r}_2)]^*[f(\mathbf{r}_3,\mathbf{r}_2,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_2)]$$
$$=\tfrac{1}{2}N^2(2\pi)^3|M(0,0)|^2\int d^3r_1d^3r_2|f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_1)+f(\mathbf{r}_1,\mathbf{r}_1,\mathbf{r}_2)|^2$$
$$=\tfrac{1}{2}(2\pi)^3|M(0,0)|^2\rho, \quad (14)$$

where

$$\rho=N^2\int d^3r_1d^3r_2|f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_1)+f(\mathbf{r}_1,\mathbf{r}_1,\mathbf{r}_2)|^2 \quad (15)$$

can be interpreted as the density of electron 3 at the location of the positron averaged over all positions of the positron and electron 2. At this point most of the remaining calculation can be circumvented by making use of known results for positronium. For singlet positronium one obtains at the same stage instead of (14) the expression

$$(2\pi)^3|M(0,0)|^2\rho_{\text{pos}},$$

where $\rho_{\text{pos}}=0.0398a_0^{-3}$ is the density of the electron at the location of the positron in the ground state of positronium. Thus one can write for the ratio of the desired annihilation rate γ to that of singlet positronium, γ_{pos},

$$\gamma/\gamma_{\text{pos}}=\tfrac{1}{4}(2\rho/\rho_{\text{pos}}). \quad (16)$$

As written, the factor 2 can be thought of as due to there being two equivalent electrons with either of which the positron may annihilate, while the factor $\frac{1}{4}$ arises out of the fact that the spin state of the annihilating pair is singlet only one quarter of the time.

On applying the above theory to the wave function (1) with best values of the parameters, one obtains

$$\gamma/\gamma_{\text{pos}}=\tfrac{1}{4}(0.989). \quad (17)$$

The average electron density (due to both electrons) at the position of the positron is seen to differ little from that found in the ground state of positronium.

V. ANGULAR CORRELATION OF THE ANNIHILATION RADIATION

The correlation between the directions of emission of pairs of photons resulting from annihilations is contained in the dependence of (13) on $\mathbf{p}$, the momentum of the two photons. In this connection, multiplicative factors independent of $\mathbf{p}$ are of no consequence. For purposes of symmetry of appearance in respect to the electron coordinates, the integral in (13) is rewritten:

$$I=\int d^3r_1d^3r_2d^3r_3\exp[(i/\hbar)\mathbf{p}\cdot(\mathbf{r}_3-\mathbf{r}_2)]\times[f(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_2)+f(\mathbf{r}_2,\mathbf{r}_2,\mathbf{r}_1)]^*\times[f(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_1)]. \quad (18)$$

For a wave function which is invariant under rotation, as is the function in (1), I will be independent of the direction of $\mathbf{p}$ and can be simplified on replacement by its integral over solid angle in the $\mathbf{p}$ space divided by 4π. Thus we have

$$I=(4\pi)^{-1}\int I d\Omega_p$$

$$=\int d^3r_1 d^3r_2 d^3r_3 \frac{\sin pr_{23}}{pr_{23}}[f(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_2)+f(\mathbf{r}_2,\mathbf{r}_2,\mathbf{r}_1)]^* \times[f(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_3)+f(\mathbf{r}_3,\mathbf{r}_3,\mathbf{r}_1)]. \quad (19)$$

The above expression gives the shape of the curve for the angular correlation of the pairs of photons, the angle between the directions of emission of two such photons differing from π by p/mc for small p.

When applied to the wave function (1), the angular correlation function (19) takes the form

$$I=\int d^3r_1 d^3r_2 d^3r_3 \frac{\sin pr_{23}}{pr_{23}} \times[\exp(-\alpha r_1-\beta r_{12}-\gamma r_2)+\exp(-\alpha r_2-\gamma r_1-\delta r_{12})] \times[\exp(-\alpha r_1-\beta r_{13}-\gamma r_3) +\exp(-\alpha r_3-\gamma r_1-\delta r_{13})]. \quad (20)$$

If this is expanded as a power series in p^2 it is possible in principle to evaluate each expansion coefficient as an algebraic function of the parameters. The calculation, however, becomes increasingly arduous with each successive term in the series. For the present purpose only the first two terms were evaluated. This corresponds to fitting to the peak of the curve a parabola of the form

$$1-\tfrac{1}{2}b^2k^2, \quad (21)$$

where we have written $k=p/\hbar$. Evaluation of the ratio of the coefficients of the first two terms in the expansion of (20) yields the value $b=5.20$ A.

A comparison can now be made with the experimental results of Stewart and March.[2] The angular correlation curves obtained by them in LiH and NaH can be fitted by a function of the form $\exp(-k^2/2\alpha)$. The first two terms in the expansion of this function have the form (21) with a value of $b=1.20$. This corresponds to a width of the distribution which is 4.37 times as great as that calculated above. A qualitative estimate has been made which indicates that the above measure of the width of the calculated curve would not be seriously modified by consideration of higher terms in the expansion of (20).

VI. CONCLUSION

The disagreement found between the experimental and calculated angular correlation curves might be ascribed to a number of causes. The fact that the experimental curve is intermediate in width between that calculated in this paper and the width calculated in reference 1 might be due to a superposition of two or more different annihilation processes, one of them being annihilation from the bound state of H^-e^+. However, the validity of the wave function (1) can of course be questioned. A calculation of the average of r_1 (the positron distance from the origin) yields the result 2.73 A. Comparison of this with the distance of 2.04 A between adjacent Li^+ and H^- ions in the LiH crystal indicates that the H^-e^+ structure described by the function (1) could not exist as a (nearly) separate entity in the solid. Nonetheless, the possibility remains that similar bound systems might be formed in the solid, but they would be presumably described by wave functions arrived at by taking suitable account of the effect of the surrounding ions. Measurements of annihilation rates in the alkali hydrides could throw some light on this question. The presence of a significant component with an annihilation rate of approximately one-fourth of that of singlet positronium could be taken as partial evidence for the formation of bound H^-e^+ structures in the solid.