

ANNIHILATION OF POSITRONS IN ALKALI METAL HYDRIDES

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A new interpretation of the time distribution of annihilation radiation in alkali-metal hydrides is presented. It is shown that the presence of two components in the positron lifetime spectrum in the hydrides is due to annihilation at different excited levels of the e^+H^- system. The possible existence of a third component corresponding to annihilation at the ground level is predicted. The self-consistent field technique is used to calculate the stationary states of the e^+H^- bound system and the main annihilation characteristics.

1. INTRODUCTION

IT is well known that in the condensed phase (aqueous solutions, organic liquids, molecular crystals) the positron lifetime spectrum has two components. The short-lived component ($\tau_1 \approx 10^{-10}$ sec) is regarded as characteristic of annihilation of free positrons and parapositronium, and the long-lived component ($\tau_2 \approx 10^{-9}$ sec) is usually attributed to annihilation of orthopositronium.

Until recently it was assumed that metals and ionic crystals are exceptions in which only the short-lived component is observed. Quite recently, however, Bisi et al^[1] were able to measure both components in ionic crystals, too (in chlorides of alkali metals and in lithium hydride). Since the formation of the positronium atom is energy-forbidden in ionic crystals^[2], the usual interpretation of the positron lifetime spectrum is not suitable for these crystals. In this connection, the long-lived component is explained in^[1] by considering the annihilation of the positrons connected with many-electron negative ions.

However, attempts at interpreting τ_2 in lithium hydride with the aid of the previously performed calculations of the ground state of the e^+H^- system^[3] have led to serious difficulties. The theoretical value of τ_2 turned out to be one-third as small as the experimental value. Furthermore, other known calculations of e^+H^- ^[4], in which, as in^[3], only the ground state was considered, are likewise unable to provide a satisfactory explanation of τ_2 .

It must further be noted that the experimental data on the angular correlation of the annihilation γ quanta in hydrides of alkaline metals^[5] have so far not been reliably explained. The theoretical

curve obtained by Neamtan et al^[3] has only one-quarter the width of the experimental one, while that calculated with the aid of the functions of Ore^[6] is much wider. The reason for such discrepancies must be sought not so much in the inaccuracy of the wave functions used in these calculations, as primarily in the incorrect understanding of the mechanism of positron annihilation in ionic crystals.

In the present paper we apply the self-consistent field method to the problem of annihilation of positrons in the field of negative ions of hydrogen. A general analysis of the annihilation of positrons connected with many-electron negative ions was carried out, on the basis of the self-consistent field method, by Ivanova and Prokop'ev^[7].

The results of the calculations lead to the following conclusions: the e^+H^- system has a series of rather deep bound levels; annihilation from the first two excited levels gives the more intense short-lived component in the positron lifetime spectrum, while transitions from the higher levels give the less intense long-lived component. Annihilation from the ground level should correspond to a third component τ_0 of low relative intensity and of the order of 10^{-11} sec, i.e., even shorter than τ_1 . The calculated curves of the angular correlation of the γ quanta in two-photon annihilation for the ground and first-excited states of e^+H^- are quite close to the experimental ones. This is also evidence in favor of the proposed mechanism of annihilation in alkali-metal hydrides. Consequently, the annihilation of positrons in a bound system of the e^+ -anion type can explain not only the long-lived component, but the entire lifetime spectrum of positrons in ionic crystals. To this end it is necessary to consider, along with

the ground state, also the excited states of the e^+H^- system, which, as can be seen from the e^+H^- example, not only exist but also play a major role in the annihilation of positrons in ionic crystals.

2. SELF-CONSISTENT FIELD EQUATION FOR THE e^+H^- SYSTEM. POSITRON BINDING ENERGY

A negative hydrogen ion bound to a positron should be naturally regarded as a one-center system (with the center in the nucleus), i.e., not a molecule, as was done by Shmelev^[8], but as a unique atom whose outer shell belongs to the positron. The role of the latter in this system reduces to some deformation of the electron shell of H^- . The stationary e^+H^- states corresponding to such an approach can be calculated by the Hartree-Fock method.

The e^+H^- system so regarded is an analog of a lithium atom with the valence electron replaced by a positron. However, from the point of view of applying the method, the two systems are essentially different. Whereas allowance for exchange in the calculation of the lithium atom greatly improves the results of Fock and Petrashen'^[9], the exchange interaction between the positron and the electron is of relativistic order of smallness,^[10] so that the exchange terms vanish from the equations for e^+H^- . In the latter case, as for the ground state of the helium atom, the Hartree and Hartree-Fock equations coincide. On the other hand, the reaction of the optical electron on the core in the lithium atom is negligibly small^[11]. This causes the Hartree-Fock system of equations to break up into two systems, the first of which is solved independently of the second. To the contrary, it can be stated beforehand that the presence of the second positive charge (positron) in the e^+H^- system greatly changes the electronic structure of H^- . Consequently, in order to take into account the polarization of the ion by the positron within the framework of the single-electron approximation, it is necessary to apply to the e^+H^- the Hartree-Fock system in a rigorous formulation, i.e., by consecutive analysis of the interactions of all the particles in the system. The latter greatly complicates the procedure for the numerical integration of the corresponding system of equations.

Taking all the foregoing into consideration, we obtain for e^+H^- a system of self-consistent field equations (in atomic units) in the form

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r} + F_0^{10,10} - F_0^{nl,nl}\right)f_{10} = \lambda_{10,0}f_{10}, \quad (1a)$$

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r} + \frac{l(l+1)}{2r^2} - 2F_0^{10,10}\right)\chi_{nl} = \mu_{nl,nl}\chi_{nl}, \quad (1b)$$

where

$$f_{10}(r) = rR_{10}(r), \quad \chi_{nl}(r) = rR_{nl}(r),$$

R_{10} and R_{nl} —radial parts of the single-electron and single-positron wave functions, respectively;

$$F_0^{10,10}(r) = \int_0^\infty f_{10}^2(r')K_0(r,r')dr',$$

$$F_0^{nl,nl}(r) = \int_0^\infty \chi_{nl}^2(r')K_0(r,r')dr', \quad (2)$$

$$K_0(r,r') = \begin{cases} 1/r & r' < r \\ 1/r' & r' > r \end{cases}, \quad (3)$$

$\lambda_{10,10}$ and $\mu_{nl,nl}$ —Lagrangian multipliers corresponding to the conditions for the normalization of the wave functions f_{10} and χ_{nl} to unity. It is easy to see that the presence in (1a) of a term $F_0^{nl,nl}$ that takes into account the influence of the positron on the electron shell of the H^- ion makes it necessary to solve both equations simultaneously.

The system (1a-b), with boundary conditions

$$f_{10}(0) = f_{10}(\infty) = 0, \quad \chi_{nl}(0) = \chi_{nl}(\infty) = 0 \quad (4)$$

was solved for the ground and the two first excited states of e^+H^- . The calculation was made on an electronic computer, using programs based on a procedure described in detail in^[12].

It is well known^[13] that the self-consistent field method does not give bound states for the negative hydrogen ion, so that we used the potential obtained by Lowdin^[14] for H^- in the initial approximation for (1a). The single-electron and single-positron wave functions of the e^+H^- system, normalized to unity, for the configurations $1s^2(1s)$, $1s^2(2p)$, and $1s^2(2s)$ (the parentheses contain the positron states) are shown in Fig. 1. A comparison of the functions f_{10} corresponding to the ground state of the H^- ion with the different states of the e^+H^- system shows the appreciable role played by the reaction of the positron on the K shell. Indeed, as the positron goes over to higher levels, the K shell "swells up"; the maximum of the corresponding wave function, while remaining at the same place, drops somewhat, and the region in which the main part of the electron charge is concentrated increases.

The eigenvalues $\lambda_{10,10}$ and $\lambda_{nl,nl}$ are shown in Table I, which lists also the total energy E of the e^+H^- system compared with the results by others^[3,6,8], and the binding energy of the positron to the H^- ($\epsilon_{e^+} = E_{H^-} - E$).

We note an interesting feature of the energy spectrum of the e^+H^- system: in this spectrum the

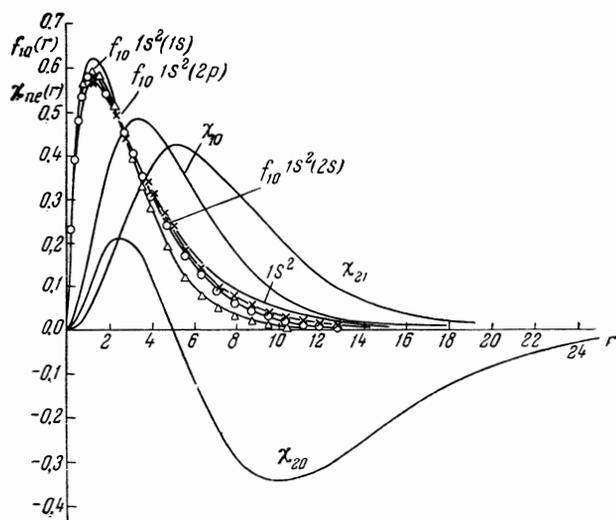


FIG. 1. Single-electron and single-positron wave functions of the e^+H^- system for the following configurations: Δ — $1s^2(1s)$, \times — $1s^2(2p)$, \circ — $1s^2(2s)$, solid curves—single-electron wave function of negative hydrogen ion (ground state).

sequence of the s and p levels is inverted compared with the sequence of the corresponding atomic levels. This is a natural consequence of the opposite sign of the interaction between the positron and the other particles of the system.

As already indicated, the self-consistent field method does not confirm the stability of the negative hydrogen ion. The total energy calculated by this method, $E_{H^-} = -0.4885$ a.u. [13], yields a negative ionization potential, i.e., no binding whatever. Such a result is explained by the fact that the Hartree-Fock method is apparently insufficiently accurate for the calculation of such a weakly bound system as is H^- (with a binding energy amounting to merely 0.75 eV). Nonetheless, the same method turns out to be suitable for the calculation of the e^+H^- system, since the presence of a positron in a many-electron system makes the latter more bound. This is confirmed by the calculations: the binding energy of the positron with H^- is equal to several eV for both the ground state and the first two excited states. We note that in calculating ϵ_{e^+} we set the total energy of the negative hydrogen ion equal to the energy of the hydrogen atom ($E_{H^-} = -0.5$ a.u.), without introducing a large error in the result, in view of the small difference between these two quantities.

The results obtained show therefore that the e^+H^- system is stable against decay into a positron and H^- in both the ground and the excited states. The energetically more favored decay into positronium and a hydrogen atom in hydrides of alkali metal is not realized, by virtue of the Ferrell-forbiddenness. [2]

Table I

State	$-\lambda_{10,10}$	$-\mu_{nl,nl}$	$-E(\text{Ry})$	ϵ_{e^+} , eV
$1s^2(1s)$	0.2988	0.1910	1.335 1.506 [6] 1.517 [3] 1.6 [8]	4.57
$1s^2(2p)$	0.2144	0.1033	1.179	2.72
$1s^2(2s)$	0.1592	0.0705	1.1122	1.52
$1s^2$	0.0927 [13]		0.977 [10]	

3. PROBABILITIES OF ANNIHILATION IN RADIATIVE PROCESSES. ANGULAR CORRELATION OF GAMMA QUANTA IN TWO-PHOTON ANNIHILATION

We have established in the preceding section that the e^+H^- system has a series of discrete levels, so that the bound positrons can participate in two competing processes: either be annihilated by the electrons of the system, or experience radiative transitions to lower levels. The probability of two-photon annihilation of a bound positron in a state (nl) by the electrons of the H^- ion, averaged over the initial spin states of the positron and of the electrons, is ¹⁾

$$W = 0.2 \cdot 10^{10} K \bar{\rho} / \bar{\rho}_0 \text{ (sec}^{-1}\text{)}, \quad (5)$$

$$\bar{\rho} = 2 \int f_{10}^2(r) \chi_{nl}^2(r) dr, \quad (6)$$

where $\bar{\rho}_0 = 1/8\pi a_0^3$ —electron density in the positronium atom, averaged over the initial spin states, a_0 —radius of the first Bohr orbit,

$$K = \left| \int_0^\infty f_{10}^H(r) f_{10}(r) dr \right|^2 \quad (7)$$

—a factor that accounts for the change in wave function of the electron that does not participate in the annihilation process, and f_{10}^H —radial eigenfunction of the hydrogen atom (ground state). For the calculated configurations $1s^2(1s)$, $1s^2(2p)$, and $1s^2(2s)$ of the e^+H^- system, the factor K is equal to 0.91, 0.88, and 0.88, respectively. The quantity reciprocal to W gives the lifetime of the positron in the state (nl) .

The probability of radiative transition of the positron from the state (nl) to the state $(n'l')$ can be calculated from the formula

$$A_{nn'} = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} |\mathbf{r}_{n'n}|^2 \text{ (sec}^{-1}\text{)}, \quad (8)$$

where $\omega = (E_n - E_{n'})/\hbar$, $|\mathbf{r}_{n'n}|$ —matrix element of the electric dipole moment. The calculated rates

¹⁾This formula, like (11), was derived by Chang Li [15] in connection with the problem of annihilation of positrons by helium atoms (para-state).

Table II

State	$W, 10^{10}\text{sec}^{-1}$	$A_{nn'}, 10^8\text{sec}^{-1}$	$W_{\text{capt}}, 10^8\text{sec}^{-1}$
$1s^2(1s)$	1.25 0.20 ^[3] 0.1 ^[4]		0.24
$1s^2(2p)$	0.43	0.565 ($2p \rightarrow 1s$) 0.067 ($2s \rightarrow 2p$)	49.6
$1s^2(2s)$	0.24		3.30

of two-photon annihilation from the ground and the first two excited levels, and the calculated probabilities of the radiative transitions $1s^2(2p) - 1s^2(2s)$ and $1s^2(2s) - 1s^2(2p)$ are listed in Table II.

The competition between the annihilation and radiative transitions brings about a situation wherein not all the levels are of importance to the annihilation, but only those for which the annihilation probability exceeds the radiative-transition probability, or for which both processes are equally probable. Moreover, on going from the ground state to the excited levels, the lifetime τ increases [$\bar{\rho}$ in (5) decreases], and consequently the short-lived component is due to annihilation from the first few excited levels, while the long lived component comes from the series of higher levels, for which the indicated probability ratio of the two processes is satisfied. Indeed, a comparison of the obtained of annihilation and radiative-transition probabilities shows that at the three levels in question only value $\tau = 2.84 \times 10^{-10}$ sec, which is in good agreement with the experimental value of the short-lived component $\tau_1 = (2.1 \pm 0.3) \times 10^{-10}$ sec, observed in the lifetime spectrum of the positrons in LiH^[1].

It also follows from the results that the lifetime spectrum of the positrons in the alkali-metals hydrides should contain, in addition to the two known

components, also a third component $\tau_0 \approx 10^{-11}$ sec, corresponding to annihilation from the ground state of the e^+H^- system.

The absence of the component τ_0 from the experimental lifetime spectrum, as well as the fact that the component τ_1 has a higher intensity than τ_2 , indicates that the annihilation occurs predominantly at the first excited levels. The probability of capture of thermalized positrons, as follows from our preliminary estimates²⁾ (see last column of Table II), is much larger for these levels than for the ground state. The low relative intensity of τ_2 (6.4%^[1]) is apparently connected with the fact that at the levels responsible for the existence of this component annihilation is not a dominating process. Some of the positrons can experience radiative transitions from these levels to lower levels, causing the intensity of the component τ_2 to decrease and that of τ_1 to increase.

For comparison, Table II lists the annihilation rates calculated in the earlier investigation^[3,4]. As already indicated, these calculations took account of the ground state only, and therefore yield values obviously corresponding to the component τ_0 . In these cases the values of τ_0 , which are much higher than ours, were obviously due to the crudeness of the wave functions used in the calculations: Tkachenko^[4] used a simple analytic function with three varied parameters, while Neamtan et al^[3] used an antisymmetrized trial function with four parameters.

The angular correlation of the γ quanta in two-photon annihilation is determined by the relative probability

$$P(\mathbf{k}) = w(\mathbf{k}) / w(0), \quad (9)$$

where $w(\mathbf{k})$ —probability of annihilation per unit time, averaged over the spins of the initial states of the electrons and of the positron, and summed over the polarizations of the radiated photons, is determined from the formula:

$$w(\mathbf{k}) = 2\pi r_0^2 c \left| \int e^{-i\mathbf{k}\cdot\mathbf{r}} \chi(\mathbf{r}) d\mathbf{r} \right|^2, \quad (10)$$

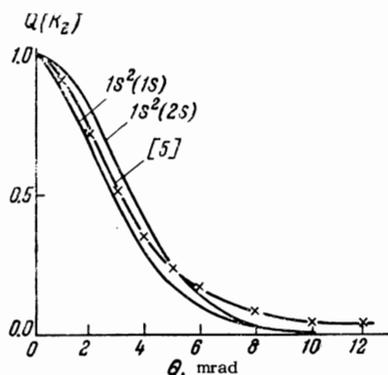


FIG. 2. Angular correlation of γ quanta in two-photon annihilation: continuous curves—calculated for the annihilation of (1s) and (2s) positrons, \times —experimental curve for LiH^[5].

²⁾The positron radiative-capture probabilities were calculated less accurately than W and $A_{nn'}$, since the single-positron wave functions of the continuous spectrum, unlike the functions of the bound states, were calculated without account of polarization of the H^- ion by the positron. However, we can take into account the deformation of the ion by the incoming positron, and still remain within the framework of the single-electron approximation, if we solve for the continuous-spectrum states Hartree-Fock equations analogous to those proposed in^[16].

where \mathbf{k} —summary vector of the radiated photons and r_0 —classical radius of the electron. It is possible to compare with the experimental curve the relative probability, which depends on the z component of the vector \mathbf{k} . In this case the sought probability for the annihilation of the bound positrons in the s -states takes the form

$$P(k_z) = \int_{\mathbf{k}_z} \int_0^\infty f_{10}\chi_{n0} \times \frac{\sin kr}{kr} dr \Big|_0^\infty k dk \Big/ \int_0^\infty \int_0^\infty f_{10}\chi_{n0} \frac{\sin kr}{kr} dr \Big|_0^\infty k dk. \quad (11)$$

The calculated angular-correlation curves corresponding to annihilation from the levels $1s^2(1s)$ and $1s^2(2s)$ are shown in Fig. 2 along with the experimental curve for $\text{LiH}^{[5]}$ which is seen to be close to both theoretical curves and to lie between them. The closeness of the curve corresponding to annihilation from the first excited level to the experimental curve confirms once more the appreciable role played by the lower excited states in the annihilation of positrons in bound systems.

In conclusion we note that the proposed interpretation of the positron lifetime spectrum is applicable not only to hydrides of alkali metals, but to other ionic crystals, such as alkali-halide ones. The latter should have, along with the two observed lifetime components, a third component $\tau_0 \approx 10^{-11}$ sec, corresponding to annihilation from the ground level. It would be interesting to undertake a search for this component, although its measurement is a difficult problem, since the expected relative intensity of τ_0 is quite small.

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