I. INTRODUCTION

Shortly after the discovery of the positron ($e^+$) in 1932, it was recognized that $e^+$ may form an ‘atom’ ($e^+e^-$) which, from the point of view of spectroscopy, may be looked upon as an ultralight isotope of hydrogen. With the same right, ($e^+e^-$) may be considered as an ultralight isotope of antihydrogen. Together with the photon, the Majorana neutrino, and the electrically neutral $\pi$-meson ($\pi^0$), ($e^+e^-$) thus belongs to those ‘particles’ that are their own ‘antiparticles’. In 1945 ($e^+e^-$), at that time still hypothetical, was named positronium, later to be equipped with the ‘chemical’ symbol Ps. At about the same time its main properties were established. Among these are that Ps is rather short-lived due to the particle–antiparticle annihilation and that its ground state splits into two substates, a singlet state $1^3S_0$ and a triplet state $1^3P_1$.

In the $1^3S_0$ state, Ps is called parapositronium (p-Ps), and in the $1^3P_1$ state, orthopositronium (o-Ps). Under most circumstances, the energy excess of o-Ps over p-Ps, $\Delta E_{o-p} = 0.8412 \times 10^{-4} \text{ eV}$, is negligibly small, hence the ratio of the production rates of o-Ps and p-Ps is usually equal to that of the statistical weights of the substates, namely 3:1. The most important differences between o-Ps and p-Ps result from the different annihilation modes of these two substates, which, in turn, are consequences of the conservation of energy and angular momentum. The self-annihilation of p-Ps results in the generation of two $\gamma$-quanta of equal energies $E_\gamma = m_e c^2 = 0.511 \text{ MeV}$, where $m_e$ is the electron mass and $c$ the speed of light in vacuum, whereas the self-annihilation of o-Ps requires the generation of, at least, three $\gamma$-quanta. Owing to the smallness of the coupling constant of quantum electrodynamics ($\alpha \approx 1/137$) and to various statistical factors, the ratio between the 2$\gamma$ annihilation rate, $\Gamma_{2\gamma} = 7.99 \times 10^9 \text{ s}^{-1}$, and the 3$\gamma$ annihilation rate, $\Gamma_{3\gamma} = 7.04 \times 10^9 \text{ s}^{-1}$, exceeds $10^3$ and is therefore highly significant.

The preceding statements refer to Ps in vacuum or in extremely dilute gases. In dense gases and in condensed matter the fate of o-Ps is radically changed, since now the $e^+-e^-$ annihilation may involve electrons other than the 1s electrons of the Ps atoms. This leads to 2$\gamma$ annihilation by the ‘pick-off’ mechanism. This mechanism may be visualized as follows. An electron in the neighbourhood with spin direction opposite to that of the $e^+$ ‘picks off’ the positron from a Ps atom and annihilates it by a 2$\gamma$ reaction. The pick-off reaction rate $\Gamma_{po}$ is determined by the probability density of the electrons with opposite spin at the $e^+$ location. This density is clearly less than that of electrons in the 1s orbit of Ps, in condensed matter typically by about a factor of ten. Hence $\Gamma_{po}$ is smaller than the self-annihilation rate $\Gamma_{3\gamma}$ but still large compared to $\Gamma_{3\gamma}$. This has several important consequences:

(i) Positron annihilation in condensed matter takes place virtually exclusively by the generation of two $\gamma$ quanta.

(ii) The annihilation rate of o-Ps depends significantly on the environment in which the positronium atom is located.

(iii) Because of (ii), the o-Ps annihilation rate may be used as indicator of the preferred sites of Ps in condensed matter.

(iv) In Ps-forming solids containing imperfections that attract Ps, the site-sensitivity of $\Gamma_{po}$ may be used to detect and monitor such imperfections.

The pick-off annihilation rates of o-Ps fall into a range that allows accurate measurements of their inverses, the o-Ps lifetimes. Often it is possible to perform $e^+$ lifetime spectroscopy, i.e., to distinguish different positron annihilation sites by the different $e^+$ lifetimes associated with them. In order to gain a theoretical understanding of the site dependence of the $e^+$ lifetimes, one has to calculate the wavefunctions of Ps atoms that are confined to the various imperfections that are capable of trapping Ps. This has turned out to be a very formidable task.

The electrostatic forces experienced by electrons and positrons are equal and opposite. In most situations the variation of the electrostatic potentials over the diameter of a Ps atom (about two Bohr radii, see below) is negligibly small compared with the positronium binding energy $E_{\text{binding}}$ (in vacuum about 6.8 eV). Unless a Ps atoms enters a kind of hydrogen bond, the electrostatic forces
on its constituents cancel to an excellent approximation. Then the interaction of Ps with its condensed-matter environment is entirely due to the exchange interaction between the Ps-electrons and the host electrons since for \( e^+ \) implanted into matter the Pauli principle is irrelevant. The fact that the ensuing repulsion of Ps by the host atoms is short-ranged suggests that the confinement of Ps to interstices or locations where atoms are missing may be represented by a rectangular potential well at these sites.

Since even this model is still a nontrivial quantum mechanical problem, Tao and Eldrup initiated a further simplified model in which the positronium is considered as a point particle in a spherical infinite potential well, being in the ground state,\(^{12}\) extending the ideas of Ferrell\(^{13}\) and Brandt et al.\(^{14}\) In this model, pick-off annihilation happens in a layer \( r_0 \leq r \leq R_0 \) near the surface of the spherical volume of radius \( R_0 \), the layer representing the medium outside the hole. The width of this layer is a parameter fitted experimentally. Later, this model was refined by considering a potential wall of finite height\(^{12}\) and of unsharped shape.\(^{15}\) In these modifications, the pick-off annihilation of the positron occurs in the region \( R_0 \leq r < \infty \), which seems to be a better approximation from the physical point of view and provides a better fit to the experimental data. Nevertheless, as stressed by Mukherjee et al.\(^{16}\), this approach is still an oversimplification since it treats the positronium as a single point particle.

In this paper, we provide an approach that avoids this simplification. We determine the quantum mechanical ground state of the positron-electron two-particle system with an infinite potential well that acts only on the electron, in addition to the Coulomb attraction between the positron and the electron. Hence, we give account of the arising nontrivial internal structure of a confined positronium.

Due to the complicated nature of the problem at hand, we calculate the ground state numerically, in terms of an expansion with respect to an appropriate set of basis functions (truncated to contain the first 216 basis functions) and via a variational method, for various pore sizes. The probability of finding the positron outside the void and the overlap of the positron and the electron inside the hole are also determined. We analyse and interpret the results, and discuss how further refinements of the model and the explanation of the observed temperature dependence of the pick-off rate can be implemented.

It is to be noted that a related investigation was done by Sommerfeld and Welker\(^{17}\), where the ground-state energy and wave function of a hydrogen atom in a hole is calculated. In that study, the proton is considered to be infinitely heavy and to reside in the center of the spherical hole, and the electron is confined to the cavity by an infinite potential well. We make a comparison between those results and our ones, and provide a simple common explanation of the behavior of both systems.

II. THE MODEL

Using the nonrelativistic framework and observing that, under the present conditions, spatial and spin degrees of freedom are decoupled, we formulate our model expounded above with a normalized electron–positron two-particle scalar wave function \( \Psi(r_e, r_p) \), the Hamiltonian

\[
H = -\frac{\hbar^2}{2m_e}(\nabla^2_{r_e} + \nabla^2_{r_p}) - \frac{\epsilon^2}{4\pi\epsilon_0} \frac{1}{|r_e - r_p|},
\]

and the boundary condition

\[
\Psi(r_e, r_p)|_{r_e = R_0} = 0, \quad \forall r_p.
\]

Here, \( r_e \) denotes the electron co-ordinates and \( r_p \) the positron co-ordinates, \( R_0 \) is the radius of the potential well to which the electron is confined, \( \epsilon \) is the elementary charge, \( \epsilon_0 = 8.854187 \times 10^{-12} \text{ As/Vm} \) is the dielectric constant of the vacuum, and \( 2\pi\hbar = h \) is Planck’s constant.

We wish to determine the ground-state wave function — from now on, \( \Psi(r_e, r_p) \) will refer to the ground state — together with the ground-state energy, and to calculate the following two ground-state related quantities. First, the probability

\[
p_{\text{out}} = \int_{r_p \geq R_0} \int_{r_e \leq R_0} d^3r_e |\Psi(r_e, r_p)|^2
\]

does that the positron will be found outside the hole. This quantity is a global measure of the pick-off annihilation rate of o-Ps. Second, the electron–positron contact parameter

\[
\kappa = \frac{\int_{r_e \leq R_0} d^3r_e |\Psi(r_e, r_p = r_e)|^2}{\int d^3r_e |\Psi_{\text{free–PS}}(r_e, r_p = r_e)|^2},
\]

where \( \Psi_{\text{free–PS}} \) is the ground-state wave function of the free positronium, having the form

\[
\frac{1}{\sqrt{8\pi\alpha_B^3}} \exp \left( -\frac{|r_p - r_e|}{2\alpha_B} \right)
\]

after separating the centre-of-mass motion, with \( \alpha_B = 4\pi\epsilon_0 \hbar^2/(m_e^2) = 0.529 \times 10^{-10} \text{ m} \) denoting the Bohr radius. This quantity measures the overlap of the electron and the positron, and is equal to the ratio of the self-annihilation rate of confined Ps to that of free Ps.

Because of the spherical symmetry of the system, the ground-state wave function depends on three independent scalar variables only. For these we choose the distance of the electron from the hole centre, \( r_e = |r_e| \), the electron–positron separation \( R = |r_p - r_e| \), and the angle \( \chi \) between \( r_e \) and \( r_p - r_e \), satisfying \( \cos \chi = r_e \cdot (r_p - r_e)/(r_e R) \).

A lengthy yet straightforward calculation shows that, in terms of these variables, the Hamiltonian reads...
The Hamiltonian is not separable and does not contain a small parameter on which a perturbation expansion might be based, therefore, we perform the subsequent calculations numerically.

### III. THE METHOD OF COMPUTATION

We use a variational method to compute the approximate ground-state wave function, minimizing the energy \( \langle \Phi, H \Phi \rangle \) in the function space

\[
\Psi = \sum_{n=1}^{N} C_n \Psi_n ,
\]

where the functions \( \Psi_n (n = 1, \ldots, N) \) form a set of appropriately chosen orthonormal base functions. The minimization is carried out by finding the eigenvector of the matrix of the elements \( H_{mn} = \langle \Psi_m , H \Psi_n \rangle \) with the lowest eigenvalue. The components of this eigenvector are then identified with the coefficients \( C_n \) of the approximate ground state wave function. The base functions are chosen in such a way that

(i) the \( r_e \)-dependence of the wave function is similar to the ground state of a single electron in an infinitely deep potential well,

\[
\psi_e (r_e) = \text{const.} \sin \left( \frac{\pi r_e R_0}{r_e} \right)
\]

(see, e.g., the work of Galindo and Pascual),

(ii) the \( R \)-dependence resembles that of the free positronium (cf. Eq. 5), and

(iii) that the matrix elements can be computed relatively fast.

To this end, we introduce the functions

\[
\varphi_i (r_e) = (r_e-B_0)^i \quad (i = 1, \ldots, N_1),
\]

\[
\varphi_j (R) = B_j^{-1} e^{-R/\xi} \quad (j = 1, \ldots, N_2),
\]

\[
\varphi_k (\chi) = \cos^{k-1} \chi \quad (k = 1, \ldots, N_3),
\]

from which, by means of the Gram–Schmidt orthonormalization procedure, we obtain the orthonormalized functions \( \psi_i (r_e) \), \( \psi_j (R) \) and \( \psi_k (\chi) \), respectively. The products

\[
\Psi_{ijk} (r_e, R, \chi) = \psi_i (r_e) \cdot \psi_j (R) \cdot \psi_k (\chi)
\]

serve as the base functions \( \Psi_n \), i.e., the expansion is implemented as

\[
\Psi = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \sum_{k=1}^{N_3} C_{ijk} \Psi_{ijk} .
\]

The variational method is improved by considering \( \xi \) as an additional, nonlinear adjustable parameter, with respect to which the energy is also minimized (for a free positronium, \( \xi = 2a_B = 1.058 \times 10^{-10} \) m).

For the first functions \( \psi_1 (r_e) \), \( \psi_2 (R) \) and \( \psi_3 (\chi) \), the orthonormalization procedure means only a normalization. It is plausible to expect that the product

\[
\Psi_{111} = \text{const.} \cdot \varphi_1 (r_e) \cdot \varphi_2 (R) \cdot \varphi_3 (\chi)
\]

proves to be the dominant basis function in the ground state.

The matrix components \( H_{mn} (R_0, \xi) \) were calculated analytically by the software Maple V \[12\] and subsequently exported to the format of programming language C, and the numerical solution of the eigenproblem, as a function of \( R_0 \) and \( \xi \), was performed by a C program using routines from Numerical Recipes \[18\]. For a fixed \( R_0 \), the lowest eigenvalue was minimized as a function of \( \xi \), and the eigenvector corresponding to this eigenvalue was determined. The lowest eigenvalue gave the approximate energy of the ground state, while the components of the eigenvector provided the coefficients \( C_{ijk} \) of the approximate ground-state function (cf. Eq. 13). Finally, using the resulting \( C_{ijk} \) values, \( \rho_{out} \) and \( \kappa \) were calculated again by Maple V. The computations took approximately two months on a workstation.

### IV. RESULTS

It was found that a base-function set with \( N_1 = N_2 = N_3 = 2 \) sufficed for determining the energy, \( N_1 = N_2 = N_3 = 3 \) for \( \rho_{out} \), and \( N_1 = N_2 = N_3 = 4 \) for \( \kappa \) — in the sense that any further increase of the number of base functions produced only a negligible change in the values of \( E \), \( \rho_{out} \), or \( \kappa \). The results presented below were calculated using the base-function set \( N_1 = N_2 = N_3 = 6 \). The calculations were performed for 33 different values of the hole size in the range \( a_B \leq R_0 \leq 98a_B \).

The resulting ground-state energy \( E \) is shown in Fig. 11 as the function of the hole radius. For large \( R_0 \) values, \( E \) approaches the ground-state energy \( E_{\text{free–PS}} = -6.80\text{eV} \).
of the free positronium. The dependence of the energy on $R_0$ is well described by the function

$$E = |E_{\text{free-PS}}| \left[ 8.75 \left( \frac{R_0}{a_B} \right)^{-2} + 11.78 \left( \frac{R_0}{a_B} \right)^{-2.53} - 1 \right].$$

(15)

The error of the numerical parameters in this fitted function is less than 3.7%. For comparison, Fig. 1 displays the ground-state energy of a single electron confined to a hole, $E_e = \pi^2 \hbar^2 / (2m_e R_0^2)$, and the dashed line denotes the ground-state energy of a hydrogen atom in a hole. The ground-state energy of the free positronium, $E_{\text{free-PS}}$, and the ground-state energy of the free hydrogen atom, $2E_{\text{free-PS}}$, are also indicated. Inset: the difference between the ground-state energies of the confined and free positronium on a log-log scale, together with the fit [15].

The determined ground state $\Psi$ of the positronium in a pore is characterized by the coefficients $C_{ijk}$ and $\xi$, Fig. 2 presents the most dominant coefficients and $\xi$, as the function of the hole radius. The coefficients are displayed in their squared form, $|C_{ijk}|^2$, which give the physical weights of the corresponding base functions $\psi_{ijk}$ in the ground state $\Psi$. All coefficients $C_{ijk}$ were found real, as was to be expected.

The calculated $R_0$-dependence of the probability $p_{\text{out}}$ that the positron can be found outside the void is shown in Fig. 3. The data may be fitted by the function

$$p_{\text{out}} = \frac{1 + 0.018 \left( \frac{R_0}{a_B} \right)^2}{1 + 0.34 \left( \frac{R_0}{a_B} \right)^2 + 0.004 \left( \frac{R_0}{a_B} \right)^5}$$

(16)

with an uncertainty of the coefficients of less than 4%.

Similarly, the results for the density parameter $\kappa$ (cf. Fig. 4) may be described by the function

$$\kappa = 1 + \frac{1}{0.41 \frac{R_0}{a_B} + 0.024 \left( \frac{R_0}{a_B} \right)^{3.22}}$$

(17)

with uncertainties of the fit parameters of less than 2%. 
V. ANALYSIS OF THE RESULTS

The first observation to make is that, as expected, for large hole radii, the system tends to the free positronium. This can be seen on each the quantities $\chi_{017}$ and $\chi_{170}$ as functions of the hole radius. The data points are fitted with the equation $E_0 = \pi^2 \hbar^2 / (2m_e R_0^2)$, similarly as it does with a single electron. Fig. 4 shows that this interpretation is fairly good. In Appendix A, we show that, with an only somewhat more involved physical argument, it is possible to give an even more precise approximation to the energy as the function of $R_0$.

Turning to the ground-state energy, a simple interpretation of its found $R_0$-dependence can be that the presence of the finite hole increases the energy of the electron by the amount of $E_0 = \pi^2 \hbar^2 / (2m_e R_0^2)$, similarly as it does with a single electron. Fig. 5 shows that this interpretation is fairly good. In Appendix A, we show that, with an only somewhat more involved physical argument, it is possible to give an even more precise approximation to the energy as the function of $R_0$.

The probability that the positron can be found outside the hole, $p_{\text{out}}$, is one for holes much smaller than $a_B$, since the characteristic space region needed for the positron is of the order of $a_B$, like in the free positronium (see Appendix A as well on this subject). On the other side, for large hole sizes, $p_{\text{out}}$ falls down to zero as $R_0 \rightarrow a_B$ (cf. Eq. 10). This latter can also be understood, an explanation for this is presented in Appendix B.

The density parameter $\kappa$ also behaves as expected. For $R_0$ large, it is 1 since the positronium is almost free. By gradually squeezing the hole, the allowed space for the electron becomes smaller, it can no more go so far away from the positron as in a free positronium. This results in some increasing in the overlap-measuring $\kappa$. We can guess what happens when $R_0$ becomes much smaller than...
converge to the value 8 reached at the Bohr radius: The electron is practically confined at
the origin, the wave function of the positron becomes similar to what it is like in the antihydrogen atom, and,
therefore, the \( R \)-dependent part of \( \Psi \) becomes

\[
\frac{1}{\sqrt{\pi a_B}} \exp\left(-\frac{R}{a_B}\right).
\]

The \( \kappa \) value corresponding to this wave function is 8 [cf. Eqs. (14) and (16)] so the increase that can be observed in Fig. 4 is expected to slow down for \( R_0 < a_B \) and to converge to the value 8 reached at \( R_0 = 0 \).

We mention that a similar behavior of \( \kappa \) is expected if one replaces the infinite potential well by some other confining potential. Limiting the electron to a region is plausible to cause a kind of squeezing the two particles onto each other, irrespective of the concrete form of the confining mechanism.

VI. DISCUSSION

In the framework of our model, the lifetime of an orthopositronium is determined by the pick-off annihilation rate, proportional to \( p_{\text{out}} \), and the intrinsic \( 3\gamma \) decay rate of the orthopositronium, which is considered to be its vacuum value multiplied by \( \kappa \). The angular correlation of the two emitted photons of the pick-off process can be obtained by generalizing the Fourier approach of Mukherjee and coworkers to the total momentum of the present two-particle system.

The infinite potential well, chosen in our calculations presented here, can be a good approximation for the confining mechanism for the electron in the pore for some materials and less good for others. The same variational method can be applied for other potential shapes, modifying only the electronic base functions, in the appropriate way. Naturally, finding and using the corresponding electronic base functions for various potential shapes may make the calculations hard to carry out in practice. In this respect, it is worth mentioning a feasible alternative approach for this purpose. It is known from quantum mechanics that the boundary condition of requiring the vanishing of the wave function \( \Psi \), Eq. (4), is not the only possibility for confining a particle to a finite region. There exists actually a one-parameter family of quantum mechanically allowed boundary conditions, of the form \( \Psi + L \partial \Psi / \partial r_c = 0 \), that is, the vanishing of a combination of the wave function and its derivative, where \( L \) is an arbitrary (real) length scale parameter. The well-known and most frequently used case, the vanishing of the wave function itself is simply the special case \( L = 0 \). Instead of choosing different potential shapes it is simpler to choose only a different value of \( L \) in the boundary condition. The corresponding electronic base functions can still be chosen as polynomials, fulfilling now the new boundary condition. One can expect that the precise shape of the confining potential is not so important in practice. Bearing in mind that these boundary conditions express nothing but that the quantum probability cannot flow outside from the hole, and that any confining potential shape wishes to ensure the same — although not completely strictly —, we can guess that all confining potentials will, in their effect, resemble one or another boundary condition (potential well) with an appropriate \( L \). Therefore, the possibilities provided by the general potential shapes may be fairly well represented with the one-parameter family of sharp potential wells.

In this paper, we have calculated the ground state only. To give account of the observed temperature dependence of the pick-off decay rate, it would be useful to determine the excited states, too. Indeed, as demonstrated by Goworek and coworkers and Gidley and coworkers for some variants of the Tao-Eldrup model, this temperature dependence can be attributed to the fact that it is also possible for the positronium to be in one of its excited states, approximately with the thermal equilibrium probability \( e^{-E/\kappa T} \). Explaining the effect in our framework, the excited states possess different \( p_{\text{out}} \) and, consequently, a different annihilation rate. Calculating the excited states is also possible in the variational method, after suitable modifications.

In the end we mention that it would be interesting to perform a calculation similar to the one presented here for systems when the two particles are of different mass, e.g., when the positron is replaced with a proton or a \( \mu^+ \) particle, as an interpolation between the positron and the infinitely heavy limit discussed by Sommerfeld and Welker. Unfortunately, our results cannot be simply ‘renormalized’ to be applicable to such situations. The reason for this is that, for different masses, the Hamiltonian has a more general form than Eq. (4) has, and these differences are not only some easily rescalable numerical

\[
\begin{align*}
E_{\text{free-PS}} + E_c & \quad \text{[cf. Eq. (A1)]} \\
E_{\text{approx}} & \\
E_{\text{free-PS}} + E_c & \quad \text{[cf. Eq. (A8)]}
\end{align*}
\]
factors but mean a more general and complicated structure of the Hamiltonian. However, the considerations of Section 4 and the Appendices may more easily be adjusted to the case of different masses, and in this way at least some approximate information could be obtained for those systems.

Acknowledgments

We wish to thank Nikolay Djourellov for useful references.

APPENDIX A: ESTIMATING THE GROUND STATE ENERGY

A closer, yet not involved interpretation of the found \( R_0 \)-dependence of the energy of the positronium in a hole is motivated by the simple derivation of the ground-state energy of the free hydrogen atom. There, based on the uncertainty relation, one approximates the average momentum of the electron by \( p = \hbar / r \), where \( r \) is the size of the average space region “run” by the electron. Thus the energy of the electron is

\[
E = \frac{\hbar^2}{2m_e} \frac{1}{r^2} = \frac{\hbar^2}{2m_e} \frac{1}{r^2} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r^2}.
\]  

(A1)

Minimizing this expression in \( r \) one reaches just the correct ground-state energy, and the corresponding \( r \) is also nothing else than the Bohr radius \( a_B \).

As a next step, let us consider the free positronium. There, the average distance between the electron and the positron in \( 2a_B \) (cf. Eq. 5). Neglecting the motion of the center-of-mass, the average region run by the effective particle of reduced mass \( m_e/2 \) belonging to the relative motion is then \( 2a_B \). The energy is, therefore, considered as

\[
\frac{\hbar^2}{2(m_e/2)} \frac{1}{(2a_B)^2} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{2a_B}.
\]  

(A2)

which proves to be just the correct energy value \( E_{\text{free--PS}} \). If we return to the ‘two particles’-picture, the kinetic energy in Eq. (A2) is shared by the two particles so each possesses the half of it,

\[
\frac{1}{2} \frac{\hbar^2}{2(m_e/2)} \frac{1}{(2a_B)^2} = \frac{\hbar^2}{2m_e} \frac{1}{(2a_B)^2}.
\]  

(A3)

Using this in the reverse way, we find that the characteristic space region for both particles is \( 2a_B \).

Now, when we confine the electron in a hole, its characteristic region will be influenced by the hole as well. To this end, let us determine the characteristic space size of a single electron in a hole with the same logic as before, from its known energy:

\[
E_c = \frac{\pi^2\hbar^2}{2m_eR_0^2} = \frac{\hbar^2}{2m_e} \frac{1}{(R_0/\pi)^2}.
\]  

(A4)

“implies” that the corresponding characteristic distance is \( R_0/\pi \).

When the electron is both confined to a hole and attracted by a positron, its allowed space region will be determined by the smaller of the two corresponding length scales — except for some narrow intermediate region when the two length scales are equal or similar. A simple as well as reasonable formula for estimating such a joint length scale from two ones is

\[
\frac{1}{r^2_{\text{joint}}} = \frac{1}{r^2_1} + \frac{1}{r^2_2},
\]  

which in our case reads

\[
\frac{1}{r^2_c} = \frac{1}{(2a_B)^2} + \frac{1}{(R_0/\pi)^2}.
\]  

(A6)

Concerning the space region of the positron, we make the simplest choice to consider it unaltered with respect to the case of the free positronium, i.e., to be \( 2a_B \). The average distance between the electron and the positron, \( r_{ep} \), also has to be estimated: For this we can use the formula

\[
r = \sqrt{\frac{r^2_1 + r^2_2}{2}}
\]  

(A7)

as being a “half-way” between the minimal distance \( |r_1 - r_2| \) and the maximal one \( r_1 + r_2 \):

\[
|r_1 - r_2| = \sqrt{r^2_1 - 2r_1r_2 + r^2_2} \leq \sqrt{r^2_1 + r^2_2} \leq \sqrt{r^2_1 + 2r_1r_2 + r^2_2} = r_1 + r_2
\]

(A8)

\((r_1, r_2 \geq 0)\). Putting all these together, we estimate the energy as

\[
E^{\text{approx}} = K_e + K_p + V(r_{ep}) = \frac{\hbar^2}{2m_e} \frac{1}{r^2_c} + \frac{\hbar^2}{2m_e} \frac{1}{(2a_B)^2} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\sqrt{(r_c)^2 + (2a_B)^2}}.
\]  

(A9)

As can be seen on Fig. 8 this formula provides a pretty good approximation for the ground-state energy of the confined positronium.

We can apply the same style of approach for the case of the hydrogen atom in a hole as well. There, the joint length scale of the length scale \( a_B \) of the free hydrogen and the one of the hole, \( R_0/\pi \), is given by

\[
\frac{1}{r^2_H} = \frac{1}{a_B} + \frac{1}{(R_0/\pi)^2}.
\]  

(A10)

In the potential energy this same length scale will appear, since the proton stands in the center of the hole. Consequently, our estimate for the energy of a hydrogen atom in a hole is

\[
E^{\text{approx}}_H = \frac{\hbar^2}{2m_e} \frac{1}{r^2_H} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_H}.
\]  

(A11)

Fig. 8 shows that our reasoning gives a fairly good approximation for this system as well.
APPENDIX B: THE PROBABILITY $p_{\text{out}}$ FOR LARGE HOLES

An explanation for the found large-$R_0$ asymptotic behavior $p_{\text{out}} \sim R_0^{-3}$ can be given by the following argument: Let us rewrite Eq. (3) as

$$p_{\text{out}} = 8\pi^2 \int_0^\infty R^2 dR \int_0^{R_0} r^2 dr_e \int_0^{\chi_1} d\chi |\Psi(r_e, R, \chi)|^2,$$

where the integration boundaries $\chi_1 \geq 0$ and $\chi_2 \leq \pi$ for $\chi$ are determined from the condition $r_p = \sqrt{r_e^2 + R^2 + 2r_eR\cos\chi} \geq R_0$. Expanding $|\Psi(r_e, R, \chi)|^2$ corresponding to Eq. (13) and also expanding all $\psi$s in it in terms of $\varphi$s, let us examine the integral of one term,

$$\varphi_{i'}(r_e) \varphi_{j'}(r_e) \varphi_{j}(R) \varphi_{j'}(R) \varphi_{k}(\chi) \varphi_{k'}(\chi).$$

Concerning the variable $r_e$, the main contribution to the integral must come from $r_e \approx R_0$, within the range $|r_e - R_0| \sim \xi$, since otherwise $R$ has to be around $R_0$ to ensure $r_p \geq R_0$, but that is exponentially suppressed by $e^{-2R/\xi} \approx e^{-2R_0/\xi}$ in the integrand. Now, for $r_e \approx R_0$ and $R \ll R_0$, the condition $r_p \geq R_0$ is fulfilled by $\chi$ in the region $0 \leq \chi \leq \pi/2$. The integral of $\sin\chi \varphi_{k}(\chi) \varphi_{k'}(\chi)$ over this region gives an $R_0$-independent numerical factor. Turning to the $r_e$-integration, for $r_e \approx R_0$, the factor $r_e^2 \varphi_{i'}(r_e) \varphi_{i'}(r_e)$ behaves as

$$r_e^2 (r_e - R_0)^{i'+i'} = r_e^2 (r_e + R_0)^{i'+i'} (r_e - R_0)^{i'+i'} \approx R_0^2 (2R_0)^{i'+i'} (r_e - R_0)^{i'+i'}$$

so its integral within the range $0 \leq |r_e - R_0| \sim \xi$ is proportional to $R_0^{i+i' + 2}\xi ^{i'+i+1}$. The normalizing factors standing before $\varphi_{i'}(r_e)$ and $\varphi_{i'}(r_e)$ bring in a factor $R_0^{-(i+i'+1)}$, resulting in a behavior $R_0^{-(i+i'+1)}$. The last integration, with respect to $R$, is an independent one,

$$\int_0^\infty R^2 dR \varphi_{j}(R) \varphi_{j'}(R),$$

with a result depending only on $\xi$ so it does not modify the $R_0$-asymptotics (note that, for large $R_0$, $\xi$ is independent of the hole size, it tends to the constant $2a_0$). Hence, we can see that the strongest $R_0$-asymptotics among the terms in $p_{\text{out}}$ is caused by the $i = i' = 1$ term, and is found to be $R_0^{-3}$.

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22. It is reasonable that this distance is smaller than $R_0$ since, in a hole with an impenetrable wall around it, the particle is not allowed to extend beyond $R_0$ while, for a hydrogen atom, the electron can go further than the Bohr radius.