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Possible high-lying resonances in the positronium-hydrogen system

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We were previously successful in representing a series of low-lying Ps+H scattering resonances as due to quasibound Coulomb states in the closed-channel $e^+ + \mathrm{H}^-$ system. Here we investigate the analogous Coulomb states of $\mathrm{Ps}^- + \mathrm{H}^+$, which are also accessible from the Ps+H scattering system, but at considerably higher collision energies. We locate several such states and suggest that they may be scattering resonances, but because there are many open-channel thresholds lying below they may have large widths and shifts.

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I. INTRODUCTION

After the first Ps+H singlet-state resonance was found by the stabilization method [1] and later by complex-rotation calculations [2] it was of interest to characterize the mechanism producing the resonance. It was suggested [3] that the resonance (and presumably an infinite set of additional resonances) was generated by the Rydberg quasibound states in the closed, rearranged $e^+ + \mathrm{H}^-$ channel. This conjecture was supported by the absence of resonances in the triplet spin state; this would be expected since the hydrogen ion exists only in the singlet state (but see some recent work that seems to find one triplet resonance [4]). In addition, Blackwood, McAlinden, and Walters [5] showed that adding a term representing the hydrogen ion to their scattering trial function (containing an expansion in eigenstates and pseudostates) gave rise to the series of resonances predicted in Ref. [3]. In Ref. [12], Walters discusses the possibility that the other negative ion, Ps^-, might also have some effect on the scattering problem. In this paper we will compute energies of the quasibound states of $\mathrm{Ps}^- + \mathrm{H}^+$ and will suggest that they may produce analogous resonances at higher scattering energies. Again, such resonances would occur only in the electronic singlet spin state, since the positronium ion ground state is a spin singlet.

In the earlier work [3] simple wave functions were used to represent the negative hydrogen ion, and in the present calculations the same sort of approximation is employed for the positronium ion. Here, however, we do not employ a simple variational function but construct a physically reasonable expression, choosing its two parameters to fit the results of accurate calculations. This is, of course, just a first approximation. Definitive work on locating and verifying these possible resonances requires real scattering calculations, including as many of the open channels as practical, or perhaps an extensive complex rotation study.

II. FORMULATION

A. Basic ideas

The Hamiltonian describing the system of two electrons $(\vec{r}_1, \vec{r}_2)$ and a positron $(\vec{x})$, with distances measured from a proton fixed at the origin, in Rydberg atomic units, is the following:

$$H = -\nabla_1^2 - \nabla_2^2 - \nabla_x^2 + 2\left[\frac{1}{x} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} - \frac{1}{|\vec{r}_1 - \vec{x}|} - \frac{1}{|\vec{r}_2 - \vec{x}|}\right]. \tag{1}$$

We wish to describe the Ps^- ion approximately as a Ps atom plus a relatively distant second electron, so it is useful to convert to a system of Jacobi coordinates as follows:

$$\vec{P} = \frac{1}{3}(\vec{x} + \vec{r}_1 + \vec{r}_2), \quad \vec{\rho}_1 = \vec{r}_1 - \vec{x}, \quad \vec{R}_2 = \vec{r}_2 - \frac{1}{2}(\vec{r}_1 + \vec{x}). \tag{2}$$

The first of these coordinates is the center of mass of the Ps ion, the second is the internal coordinate of the Ps atom with electron 1, and the last is the position of electron 2 relative to the center of mass of the Ps atom containing electron 1. (A second equivalent set results from the interchange of 1 and 2.) We propose a wave function for the quasibound states that takes the following form in these Jacobi coordinates:

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{x}) = F(\vec{P})[\Phi(\rho_1, R_2) + \Phi(\rho_2, R_1)]. \tag{3}$$

The expression in the bracket is the exact wave function of the Ps ion where the two terms are needed to account correctly for the symmetry between the two electrons; we have suppressed the singlet spin function. The function F describes the motion of the Ps ion in the field of the proton and will include an infinite number of states of all possible orbital angular momenta.

Before we consider an approximate form for the function Φ let us re-write the Hamiltonian $H = H_0 + H_1$ in terms of our Jacobi coordinates. We have

$$H_0 = -2\nabla^2_{\rho_1} - \frac{3}{2}\nabla^2_{R_2} + 2\left[\frac{1}{\left|\vec{R}_2 - \frac{1}{2}\vec{\rho}_1\right|} - \frac{1}{\left|\vec{R}_2 + \frac{1}{2}\vec{\rho}_1\right|} - \frac{1}{\rho_1}\right],$$

$$H_1 = -\frac{1}{3}\nabla^2_P + 2\left[\frac{1}{\left|\vec{P} - \frac{1}{3}\vec{R}_2 - \frac{1}{2}\vec{\rho}_1\right|} - \frac{1}{\left|\vec{P} - \frac{1}{3}\vec{R}_2 + \frac{1}{2}\vec{\rho}_1\right|} - \frac{1}{\left|\vec{P} + \frac{2}{3}\vec{R}_2\right|}\right] \equiv T_P + V_1. \tag{4}$$

Notice that H_0 does not contain any mention of the center-of-mass coordinate P; it is the Hamiltonian for the free Ps ion. (Again, it could be rewritten with 1 and 2 interchanged.) The motion of the Ps ion relative to the fixed proton is determined by the second term, H_1, through the function $F(\vec{P})$. The total energy is given variationally in the usual way:

$$E = \frac{\int\int\int d\tau \Psi^*[H_0 + H_1]\Psi}{\int\int\int d\tau |\Psi|^2}, \tag{5}$$

and the unknown function is determined from $\frac{\delta E}{\delta F}=0$. Since we have included the exact wave function of the Ps ion in our trial function Ψ, the effect of H_0 is just to produce the exact energy of the ion, $E(\mathrm{Ps}^-)=-0.524\,01$ Ry. The variational equation for F is the following:

$$\left[-\frac{1}{3}\nabla^2_P + \bar{V} - \varepsilon\right]F(\vec{P}) = 0, \tag{6}$$

where $\varepsilon=E-E(\mathrm{Ps}^-)$. Before we define $\bar{V}$ it will be convenient to write the general form for the expectation value of any operator Q:

$$\langle Q\rangle = \frac{I[Q]}{I[1]},$$

where

$$I[Q] = \int\int d\vec{\rho}_1 d\vec{R}_2 Q[\Phi^2(\rho_1,R_2) + \Phi^2(\rho_2,R_1) + 2\Phi(\rho_1,R_2)\Phi(\rho_2,R_1)]. \tag{7}$$

Then the effective potential is just $\bar{V}=\langle V_1\rangle$, where V_1 was defined in Eq. (4), and once we have chosen a reasonable, approximate form for the function Φ we can proceed to evaluate $\bar{V}$ and solve Eq. (6) to obtain the eigenvalues ε.

B. The positronium ion wave function

We have previously used the following wave function [6]

$$f(R) = \frac{(e^{-\gamma R} - e^{-\beta R})}{R} \tag{8}$$

(with $\beta > \gamma$) to describe the motion of the center of mass of a positronium atom relative to a helium positive ion, with the two parameters adjusted to give some known results. It has the virtue of approaching the correct asymptotic form at large R, being finite for vanishing R, and possessing one additional parameter to adjust. In the present case we choose the approximate wave function for the positronium ion to have the form

$$\Phi(\rho,R) = \phi(\rho)f(R), \tag{9}$$

where the normalized Ps wave function $\phi(\rho) = \frac{1}{\sqrt{8\pi}}\exp(-\rho/2)$. The normalization integral [equivalent to I [1] of Eq. (7)] is

$$D = \int\int d\vec{\rho}_1 d\vec{R}_2[\phi^2(\rho_1)f^2(R_2) + \phi^2(\rho_2)f^2(R_1) + 2\phi(\rho_1)f(R_2)\phi(\rho_2)f(R_1)]. \tag{10}$$

The first two terms in this integral give the same result, since we are free to rewrite the volume element in the second term by interchanging subscripts 1 and 2. These two terms are separable, so the result can be obtained very easily and analytically:

$$D_I + D_{II} = \frac{4\pi(\beta-\gamma)^2}{\beta\gamma(\beta+\gamma)}. \tag{11}$$

To evaluate the third term in the normalization integral it is necessary to rewrite the second set of Jacobi coordinates in terms of the first set:

$$\vec{\rho}_2 = \vec{R}_2 + \frac{1}{2}\vec{\rho}_1; \quad \vec{R}_1 = -\frac{1}{2}\vec{R}_2 + \frac{3}{4}\vec{\rho}_1. \tag{12}$$

Then the third term in D takes the form

$$D_{III} = 16\pi^2\int_0^\infty dR R^2 f(R)\int_0^\infty d\rho\rho^2\phi(\rho)\int_{-1}^1 \times d\mu f\left(\sqrt{\frac{1}{4}R^2 + \frac{9}{16}\rho^2 - \frac{3}{4}R\rho\mu}\right) \times\phi\left(\sqrt{R^2 + \frac{1}{4}\rho^2 + R\rho\mu}\right). \tag{13}$$

Here $\mu=\hat{\rho}\cdot\hat{R}$, and this multiple integral must be performed numerically.

Next we determine the two constants appearing in the function f. The constant γ is related to the binding energy B as $\gamma=\sqrt{\frac{2}{3}B}$, and from the variational binding energy [7] of 0.024 01 Ry we get the value $\gamma=0.126\,52$. There are several ways to determine the value of β. We calculate the expectation value of some operator using our approximate wave function and compare the result with the corresponding value obtained with an accurate wave function. We have chosen to use the expectation value of r_{12}^2. In our Jacobi form

$$r_{12}^2 = \left(\vec{R}_1 - \frac{1}{2}\vec{\rho}_2\right)^2 = R_1^2 + \frac{1}{4}\rho_2^2 - R_1\rho_2\mu_{12}. \tag{14}$$

Again, the first two terms in Eq. (7) give identical analytic results:

$$I_1[r_{12}^2]+I_2[r_{12}^2]=4\pi\left[\frac{3(\beta-\gamma)^2}{\beta\gamma(\beta+\gamma)}+\frac{1}{2\gamma^3}+\frac{1}{2\beta^3}-\frac{8}{(\beta+\gamma)^3}\right]. \tag{15}$$

[Notice that here only two terms of Eq. (14) remain in the integrand, since the part involving μ vanishes.] The third term $I_3(r_{12}^2)$ resembles D_{III} of Eq. (13) with the additional factor from Eq. (14) inserted. (In this case all three terms are nonzero.) According to the accurate calculations of Ref. [7] $\langle r_{12}^2\rangle=93.1714$, and we can reproduce this value to better than four figure accuracy if we take $\beta=0.2241$. (With these values of the parameters the normalization $D=16.5879$.) As a check on the consistency of this model wave function we calculate another expectation value, $\langle\rho_1^2\rangle$, which should be 48.4152 according to Ref. [7]. Our model gives 52.6265, in error by only 8.7%. This seems like a sufficiently good fit for us to proceed.

One more known quantity can be used as a test of the quality of our model wave function. The asymptotic normalization of the wave function is defined in our notation as $1/\sqrt{D}=0.2455$. This is to be compared with an accurate value [7] of 0.1856. The error of 32% is only marginally acceptable.

C. The effective potential

We have seen above that the effective potential $\bar{V}$ also involves an expectation value, but this time there is an additional vector, $\vec{P}$, which is the position of the center of mass of the Ps ion relative to the (fixed) proton. As usual, the direct part of Eq. (7) can be done analytically. Notice that the first two terms vanish by symmetry (as often happens when Ps wave functions are involved [8]). So the direct part of the effective potential is

$$\bar{V}_d(P)=-\frac{4}{D}\int d\vec{\rho}\,\phi^2(\rho)\int d\vec{R}\frac{f^2(R)}{|\vec{P}+(2/3)\vec{R}|}= -\frac{16\pi}{D}\left[\frac{1}{P}\int_0^{(3/2)P}dR(e^{-\gamma R}-e^{-\beta R})^2 +\frac{3}{2}\int_{(3/2)P}^{\infty}\frac{dR}{R}(e^{-\gamma R}-e^{-\beta R})^2\right]. \tag{16}$$

The normalization of the Ps function has been invoked, and the angular integral was trivial. The final result for this part of the potential is

$$\bar{V}_d(P)=\frac{-16\pi}{D}\left\{\frac{1}{P}\left[\frac{1}{2\gamma}(1-e^{-3\gamma P})+\frac{1}{2\beta}(1-e^{-3\beta P}) -\frac{2}{(\beta+\gamma)}(1-e^{-(3/2)(\beta+\gamma)P})\right] +\frac{3}{2}\left[E_1(3\gamma P)+E_1(3\beta P)-2E_1\left(\frac{3}{2}(\beta+\gamma)P\right)\right]\right\}, \tag{17}$$

where E_1 is the exponential integral. The remaining part of the potential is considerably more complicated, and we have not been able to reduce the inherently six-dimensional integral to three dimensions as we did previously, using spherical coordinates. The trouble is that there are more angles in the calculation of the potential than in the simple integrals discussed above. Once we concluded that a six-dimensional numerical integral must be evaluated for each value of P, it proved to be easier to work in rectangular coordinates. We take $\vec{P}$ to lie along the z axis, and we write the complicated vectors that appear in the following way:

$$|\vec{A}+\vec{B}|=\sqrt{\sum_1^3(A_i+B_i)^2}, \tag{18}$$

where the subscripts refer to the three rectangular components of each vector. The volume element is just the product of the six differentials $d\rho_1 d\rho_2 d\rho_3 dR_1 dR_2 dR_3$, and the limits on each integral are ±∞. We were able to evaluate these multiple integrals to at least three significant figures.

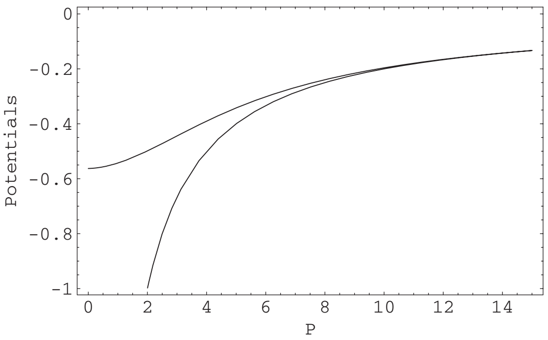

FIG. 1. Potential $V(P)$ (upper curve) and, for comparison, Coulomb potential $-2/P$ (lower curve) in Rydberg units, as functions of P in units of Bohr radii.

TABLE I. Energies of the high-lying states, arranged in order of increasing energy.

State	Eigenenergy ϵ (Ry)	Total energy E (Ry)	Ps energy (eV)
1s	−0.375	−0.899	8.18
2p	−0.281	−0.805	9.46
2s	−0.227	−0.751	10.19
3d	−0.207	−0.731	10.46
3p	−0.175	−0.699	10.90
4f	−0.151	−0.675	11.22
3s	−0.146	−0.670	11.29
4d	−0.134	−0.658	11.46
4p	−0.116	−0.640	11.70
5g	−0.110	−0.634	11.78
5f	−0.102	−0.626	11.89
4s	−0.100	−0.624	11.92
5d	−0.092	−0.616	12.03
5p	−0.082	−0.606	12.16
5s	−0.072	−0.596	12.30

We carried out the numerical integrations for a range of values of P from 0 to 15 at intervals $\Delta=1$, followed by interpolation to construct a smooth representation of the effective potential. Beyond $P=15$ the effective potential is not significantly different from the asymptotic Coulomb form $-2/P$. In Fig. 1 we have plotted the effective potential and the Coulomb potential for comparison.

We solved Eq. (6) numerically for all the states of principal quantum number $N\leqslant 5$ and give their energies in Table I. The table shows the eigenenergies ε, the total energies $E=-0.52401+\varepsilon$ in Ry, and the kinetic energy in eV of the Ps atom forming each resonance, $KE=(E-E_{Ps}-E_H)\text{Ry}=(E+1.5)$ 13.6058 eV.

III. CONCLUSIONS AND DISCUSSION

We have investigated the consequences of a model describing certain hypothetical quasibound or resonant states of the PsH system constructed from perturbed Coulomb bound states of the system Ps^-+H^+. We have used a very simple approximation for the negative ion and have properly symmetrized the wave function with respect to the two electrons. As expected, there is a series of such resonances that converge to the Ps^-+H^+ threshold. We have noted that the many channels that are open in the region of these states are likely to broaden them and shift their positions. The most practical way to look for such resonances might be the complex-rotation technique [9], which requires quite large expansions but does not need one to describe the open channels explicitly. We expect that some of the lower resonances predicted here, especially low-lying s states, will prove to be spurious [9,10], since our trial functions are not orthogonalized to the open-channel wave functions.

This calculation, in addition to its intrinsic interest, may lead to an analogous calculation of resonances in the Ps_2 system. (Some earlier work on resonances in this system has been carried out by Adhikari [11] using a scattering technique.) The quasibound states in question would then be Ps^-+e^+ (and its charge conjugate) and the direct potential is the same as that derived here. Additional complication arises due to the need to antisymmetrize the wave function with respect to the two positrons as well as the two electrons.

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