

Positronium Negative Ion: Molecule or Atom?

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A highly accurate calculation is supplemented by an adiabatic approximation to explore the resonance spectrum of the positronium negative ion (Ps^-). Surprisingly, the spectrum can be understood and classified with H_2^+ quantum numbers by treating the interelectronic axis of Ps^- as an adiabatic parameter. We report and interpret the existence of 1S shape resonances, a phenomenon so far unknown in three-body Coulomb systems. The new results on Ps^- combined with previous results for H^- suggest the existence of a resonance spectrum and its similarity for all ABA Coulomb systems with charges $|Z_A/Z_B|=1$ and masses $m_A/m_B \geq 1$.

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Early calculations showed that the positronium negative ion (Ps^-) system composed of two electrons and their antiparticle, a positron, has a bound state [1]. The experimental proof [2] in 1981 together with an increasing interest in matter-antimatter interactions have stimulated continuing theoretical investigations of Ps^- . Recently, selected resonances [3,4], photoabsorption into low-energy resonances [5], and the ground-state annihilation rate [6] have been studied. However, a systematic and concise picture of the dynamics of this three-body system is still lacking. The attempt to achieve such a picture is challenging and the existence of a systematic pattern questionable at first glance: Three particles of equal mass and absolute charge tumble in space with their motion restricted only by the total angular momentum and parity of the system. Unlike other three-body systems with the same form of the potential, there is neither an obvious point of reference as the heavy nucleus in H^- nor a line of reference as the internuclear axis in H_2^+ . These properties contribute to the specific atomic or molecular structure of H^- or H_2^+ . Nevertheless, we will show that the resonance spectrum of Ps^- is dominated by the same type of quasiseparable motion as in the molecular case of H_2^+ ; i.e., the three charged particles behave very much like a molecule where the line joining the two electrons takes the role of the "internuclear" axis. However, we will also identify some exotic features unique to Ps^- , such as shape resonances for angular momentum S states. The occurrence of this type of resonance can be attributed to the delicate balance in the long-ranged dipole forces.

We have approached the dynamics of Ps^- in two different ways which supplement each other. First, we have solved the nonrelativistic Schrödinger equation of Ps^- in perimetric coordinates [7] with complex scaled basis-set techniques [8]. This calculation has provided us with well-converged data on resonance positions and widths even close to all two-body (positronium) thresholds and the three-body breakup threshold. To prove that the calculated data essentially reflect molecular-type behavior we have performed an independent calculation,

where we treat Ps^- as a molecule within an adiabatic approximation. Resonances appear then as bound states in excited molecular potential curves and decay is formally described by nonadiabatic coupling to lower potential curves. The specific form of the potential curves also demonstrates another possible mechanism for resonance formation, namely, the occurrence of shape resonances. The molecular set of quantum numbers as for H_2^+ provides a systematic classification of the resonance spectrum. The remarkable correspondence between the results of the exact calculation and the molecular approximation shows that Ps^- is essentially a molecule-type system. In this Letter we concentrate on the S spectrum of Ps^- (angular momentum $L=0$) since it features all important aspects and simplifies the notation, which will be given in atomic units.

The adiabatic molecular approximation (MA) represents the spatial wave function of an ABA system for S states by the product

$$\Psi(\mathbf{r}, \mathbf{R}) = f(R) \frac{\Phi(\mathbf{r}; R)}{R}, \quad (1)$$

where the interelectronic axis $\mathbf{R} = R\hat{z}$ is chosen to lie along the z axis of the coordinate system, and \mathbf{r} points from the middle of \mathbf{R} to the positron (see Fig. 1). The ansatz (1) separates vibrational motion $f(R)$ of the electrons from internal motion $\Phi(\mathbf{r}; R)$ and leads to the one-dimensional vibrational equation

$$\left[-\frac{1}{2m_{AA}} \frac{d^2}{dR^2} + U(R) - E_v \right] f_v(R) = 0 \quad (2)$$

with the adiabatic molecular potential

$$U(R) = \langle \Phi | H | \Phi \rangle_{\mathbf{r}} \equiv \mathcal{E}(R) + D(R). \quad (3)$$

Here, $\mathcal{E}(R)$ is the eigenvalue of the two-center Hamiltonian for fixed R ,

$$h(R) = -\frac{1}{2m_{AB}} \nabla_{\mathbf{r}}^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}, \quad (4)$$

with eigenfunction $\Phi(\mathbf{r}; R)$. The adiabatic correction

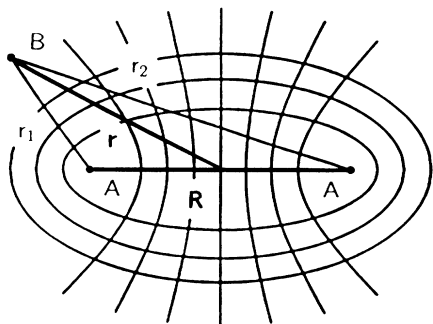


FIG. 1. Molecular Jacobi coordinates for ABA systems. The cylindrical components (ρ, z) of the vector \mathbf{r} are defined as $\rho = R/2[(\lambda^2 - 1)(1 - \mu^2)]^{1/2}$ and $z = R/2\lambda\mu$ in prolate spheroidal coordinates. Lines of constant λ (ellipses) and μ (hyperbolae) are also shown.

term

$$D(R) = \frac{1}{2m_{AA}} \langle \Phi | -\nabla_R^2 + \frac{1}{4} \nabla_r^2 | \Phi \rangle \quad (5)$$

is the expectation value of $H - h(R)$. Note that (4) contains the reduced mass $m_{AB} = m_A m_B / (m_A + m_B)$ rather than $m_{AA,B} = 2m_A m_B / (2m_A + m_B)$ as in the standard adiabatic treatment [where $h(R)$ is given by H at fixed R]. Consequently, the part $(1/2m_{AB} - 1/2m_{AA,B})\nabla_r^2$ of the kinetic-energy operator appears in (5). The choice of $h(R)$ and hence Φ in the MA is crucial for a successful adiabatic description of Ps^- . In contrast to the standard adiabatic approximation the MA guarantees the correct dissociation limit $U(R \rightarrow \infty)$ with $D(R \rightarrow \infty) = 0$ and small $D(R)$ for finite R due to the cancellation effect between the kinetic energies of R and r in (5).

Apart from a mass scaling factor (the reduced mass $m_{AB} = \frac{1}{2}$ for Ps^-), Eq. (4) is identical to the H_2^+ Born-Oppenheimer problem and thus the eigenfunctions Φ are *separable* in prolate spheroidal coordinates $\lambda = (r_1 + r_2)/R$, $\mu = (r_1 - r_2)/R$ and the azimuthal angle ϕ where $r_{1,2} = |\mathbf{r} \pm \mathbf{R}/2|$ are the two electron-positron distances (see Fig. 1). The nodal surfaces of Φ along the coordinates λ , μ , and ϕ constitute the quantum numbers n_λ, n_μ, m which specify a molecular channel according to Eqs. (3)-(5). In the dissociation limit $R \rightarrow \infty$ the nodal surfaces become parabolic with nodes $n_1 = n_\lambda$, $n_2 = [n_\mu/2]$, where $[x]$ is the integer value of x . The parabolic set of quantum numbers offers an alternative description with the convenience that the positronium threshold N to which a molecular channel converges in the dissociation limit (Fig. 2) can be directly seen from $N = n_1 + n_2 + m + 1$. Together with the total energy E [described by the vibrational quantum number ν in Eq. (2)] and the angular momentum quantum numbers LM the spheroidal quantum numbers classify the Ps^- dynamics so that the quanta actually count nodes along a well-defined coordinate system. Note that for S states $L = M = m = 0$.

As an example Fig. 2 shows for 1S symmetry all poten-

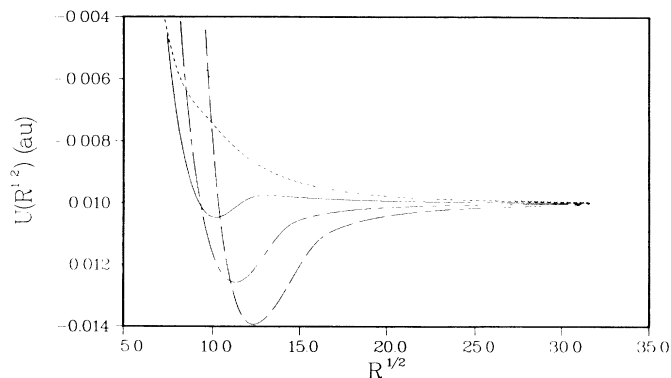


FIG. 2. Adiabatic molecular potential curves [Eq. (3)] for 1S states of Ps^- converging to the $N=5$ positronium threshold. The channel quantum numbers $(n_1 n_2 m)$ are from the bottom (040), (130), (220), (310), and (400).

tial curves converging to the $N=5$ positronium threshold. Each of the two lower curves supports a series of Feshbach resonances with $(n_1, n_2, m) = (0, 4, 0)$ and $(1, 3, 0)$. Grouped according to the molecular classification scheme, Table I compares resonance energies calculated in the molecular approximation with previous results [3] of full diagonalizations and with our highly accurate values. Good agreement is achieved for the lower vibrational states in the potential curves. In these states ($\nu \approx 0$) the electrons are on average roughly at equal distance from the positron whose probability density $\Phi^* \Phi$ is concentrated between the electrons, a characteristic molecular binding effect. For higher ν the adiabatic energies become more inaccurate since the MA fails to reproduce precisely the spacing between subsequent energies E_ν and $E_{\nu+1}$, which can be checked analytically with the Gailitis-Damburg theory [9] in the limit $\nu \rightarrow \infty$.

The third potential curve of Fig. 2 with parabolic quantum numbers (2,2,0) is most interesting since it shows the possible occurrence of a shape resonance which is indeed predicted in the MA and confirmed by our exact result (see Table I). In the MA shape resonances can occur for

TABLE I. Energies of the 1S resonances in Ps^- converging to the $N=5$ positronium threshold. The italic numbers are taken from the work of Ho [3].

$(n_1 n_2 m)$	ν	$-E$ (a.u.)	
		Exact	MA
(040)	0	0.01303093	0.013034
		<i>0.01290</i>	
	1	0.01151961	0.011521
	2	0.01069913	0.010596
(130)	3	0.01033401	0.010255
	0	0.01172282	0.011685
		<i>0.01170</i>	
(220)	1	0.01049793	0.010398
	2	0.01016116	0.010092
	0	0.00994014	0.00991

channels with $n_1 = n_2$. Then the major contribution to the long-range tail of the molecular potential from $\mathcal{E}(R)$, proportional to $(n_1 - n_2)/R^2$, vanishes, leaving only the small adiabatic correction $D(R)$. The correction is positive for large R and thus forms a slightly repulsive barrier (see Fig. 2). Whether the potential actually supports a shape resonance cannot be predicted *a priori* and depends on subtle features of the dynamics which in the MA are related to the depth and width of the potential curve. However, we have identified the corresponding shape resonance for $n_1 = n_2 = 1$ in the $N=3$ manifold with $E = -0.02745$ (exact $E = -0.0277436$).

Additional light on the subtle nature of shape resonances is shed by the fact that they do not exist in H^- where the 1S resonances with $n_1 = n_2$ lie below threshold [10]. The MA also shows that in general 3S potentials with the same quantum numbers $n_1 = n_2$ and hence a long-range behavior dominated by the same dipole potential do not support (shape) resonances. Apart from this feature (and from substantial differences in the decay widths which, however, are beyond the scope of this Letter), 1S and 3S spectra for Ps^- are very similar. Hence, for the overall structure it is sufficient to concentrate on the 1S spectrum.

So far we have discussed resonant states whose energies converge to a fixed *two-body* (positronium) breakup threshold N as a function of increasing vibrational quantum number ν (Table I and Fig. 2). A section through the resonance structure converging to the three-body breakup threshold ($E=0$) as a function of N with $n_2 = N-1$, but n_1 , m , and ν fixed, yields more information on the accuracy of the MA over a wide energy range. Figure 3 shows that the MA energies do not converge to the exact values in either limit of N ; however, the devia-

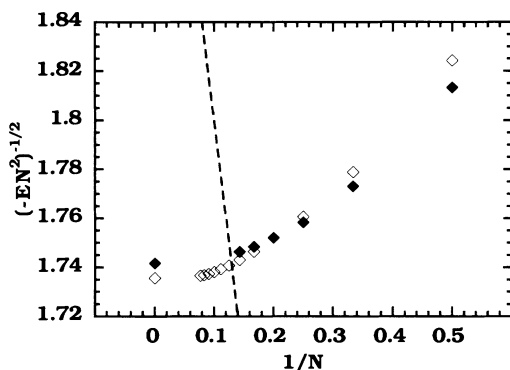


FIG. 3. Energies, parametrized as $(-EN^2)^{-1/2}$, of the lowest 1S resonance in each manifold N as a function of $1/N$. Solid symbols are from the exact calculation; open symbols from the MA. At $1/N=0$ the solid symbol indicates the inverse actions $1/S$ from the fundamental (asymmetric stretch) periodic orbit of the classical Ps^- motion analogous to [12]. The open symbol is the extrapolated value from the MA data for $1/N > 0$. The dashed line gives the positronium threshold energy $E_{N-1} = -1/4(N-1)^2$; see text.

tion is small over the entire excitation range and of opposite sign in the N limits. The discrepancy in the limits is not surprising since adiabatic behavior in the interelectronic axis R is not expected for the ground state ($N=1$) and generally breaks down for extremely high excitation ($1/N=0$). It is much more surprising that a direct comparison with the exact results as presented here actually verifies that the global pattern of the Ps^- dynamics is well described by an adiabatic molecular picture. However, this simple picture presumably does not hold for arbitrary high excitations N . As soon as the lowest resonance in a potential converging to the threshold N drops below the energy of the $N-1$ threshold (shown as a dashed line in Fig. 3), the entire dipole series $\nu \rightarrow \infty$ converging to the $N-1$ threshold is perturbed and the resonances have to be interpreted as perturber states in a generalized multichannel-quantum-defect theory [11]. One sees from Fig. 3 that this begins to happen near $N=8$. Hence for $N \gg 7$ the resonance spectrum becomes very complicated and any description in terms of individual resonances classified by a full set of quantum numbers becomes questionable.

The MA has been shown to be applicable for H^- [13], leading to the same type of quasiseparable motion and resonance pattern. Since the entire three-body Hamiltonian changes smoothly as a function of the mass ratio $\delta = m_A/m_B$ from $\delta=1$ (Ps^-) to $\delta \rightarrow \infty$ (H^-), the new result for Ps^- allows us to predict that *all* ABA systems with identical absolute charge of the particles but $\delta \geq 1$ possess a resonance spectrum which has *qualitatively* the same pattern. Furthermore, the reduced mass m_{AB} of the AB subsystem determines a global energy scale and accounts for the major *quantitative* differences between spectra of different ABA species. Our prediction extends similar conclusions for the ground states of ABA Coulomb systems [14] and the empirically discovered similarities between low-lying H^- and Ps^- resonances [5].

The prediction for the entire resonance spectrum and all ABA systems with $\delta \geq 1$ is based on the following argument: The tail $\nu \rightarrow \infty$ of a series of resonances belongs to a single potential curve and converges to its positronium threshold energy which scales trivially with m_{AB} since it is hydrogenic. More surprisingly, the lower end, i.e., the energy of states with $\nu=0$, scales also with m_{AB} . This can be understood from the two-center energies $\mathcal{E}(R)$. They scale exactly with m_{AB} at the *minimum* of the potential curve and for $R \rightarrow \infty$, a consequence of the virial theorem [15]. While the dissociation limit reflects the scaling of the hydrogenic threshold energies, the minimum energy corresponds to the $\nu=0$ states. Deviations from the exact scaling behavior result in the MA from small contributions to the resonance energy which do not scale, such as vibrational excitation in R , the adiabatic correction $D(R)$ and, in the case of $L \neq 0$, a centrifugal barrier. These perturbations which are largest for moderate vibrations ν (in the limit $\nu \rightarrow \infty$ the threshold

energy dominates the resonant energies and restores scaling) prevent the global scaling from being exact for the actual spectra. It is also clear that subtle features such as the 1S shape resonances in Ps^- cannot be predicted by the global resonance pattern.

Our analysis relies on the general scaling properties of the homogeneous Coulomb potentials and in addition on the separability of the two-center Coulomb problem [Eq. (4)]. Hence the conclusions are restricted to *Coulomb* systems. However, there is some evidence that the existence of a resonance spectrum and its *qualitative* similarity among species with different mass ratio δ pertains to a far more general class of *ABA* systems characterized by their subsystem *AB* being bound by a central force. One example is the *nuclear* motion of triatomic molecules. Their dynamics exhibits "normal" (or hyperspherical) and "local" mode resonances [16], which play the same role as for Ps^- the class of resonances as a function of N converging to the three-body breakup threshold (Fig. 3) and the class of states with different ν belonging to a single potential curve.

In summary, the investigation of the Ps^- dynamics obtained by highly accurate full diagonalization methods and within the framework of an adiabatic molecular approximation has demonstrated the molecular nature of Ps^- . We have shown that over a wide energy range the three particles of equal mass are far away from tumbling about their center of mass but their motion is strongly structured and the resonance spectrum appropriately classified with H_2^+ quantum numbers. Our combined analysis has also uncovered the existence of 1S shape resonances, a new phenomenon in three-body Coulomb systems. The molecular structure allows the prediction that *ABA* Coulomb systems composed of particles with equal absolute charge but different mass ratios $m_B/m_A \geq 1$ follow a universal resonance pattern reflecting the Coulombic nature of the interparticle forces. The resonance spectra of individual species differ mainly by a scale factor for the energy, the reduced mass m_{AB} of the respec-

tive *AB* subsystem. This is a powerful result since it provides a rough picture of the resonance structure for many exotic particle combinations ($e^- \mu^+ e^-$, $\mu^- p \mu^-$, etc.) which may be realized experimentally in the near future.

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