Resonant Photodetachment of the Positronium Negative Ion

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An adiabatic treatment in hyperspherical coordinates is used to predict the existence of resonant structures in Ps^- (Ps denotes positronium) photodetachment. This highly correlated system displays a weak series of narrow Feshbach resonances lying just below the $Ps(n=2)$ threshold, while a single strong shape resonance dominates the photodetachment spectrum above this threshold as in H^-. Use of a "prediagonalized" representation of hyperspherical harmonics dramatically improves the convergence of the adiabatic calculation.

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Ever since Mills observed[1] the ground state of the positronium negative ion ($e^-e^-e^+$), there has been much interest in the theoretical study of its autodetaching states.[2-5] On the basis of the simple ratio[4] of the binding energies of the ground state and the lowest $^1S^e$ doubly excited state of Ps^- to those of H^- (approximately a factor of $\frac{1}{2}$), one might expect a correspondence between these two systems to hold throughout the whole spectrum. Intuitively, however, this is not a foregone conclusion, since Ps^- consists of three particles tumbling about their center of mass, while H^- consists of two light particles undergoing correlated motion in the central field of an "infinitely massive" proton. In fact, this relationship is apparently not maintained in the case of a $^3P^e$ metastable state below the $n=2$ threshold that exists in H^- but has not shown up in two previous investigations of Ps^-.[5,6] In this Letter we predict the existence of a series of Feshbach resonances and of a single shape resonance in the $^1P^o$ Ps^- system, closely analogous to those first predicted by Burke and co-workers[7] and later by Lin[8] in H^-. Our conclusions are based on an adiabatic treatment in hyperspherical coordinates. An essential element of this treatment is a new method which selects a small subset of physically relevant hyperspherical harmonics that dominate the expansion of the few-particle adiabatic wave function.

As in our previous study of the Ps^- ground state,[4] we describe the three-particle configuration space in terms of symmetric Jacobi coordinates $\mathbf{r}_1$ (the interelectron separation) and $\mathbf{x}$ (the separation of the positron from the center of mass of the electron pair). These are in turn used to define hyperspherical coordinates: a hyperradius $R \equiv (r_1^2 + r_2^2)^{1/2}$ and a hyperangle $\alpha = \tan^{-1}(r_2/r_1)$, where $\mathbf{r}_2 = (\mu_{--,+}/\mu_{--})^{1/2}\mathbf{x} = (\frac{4}{3})^{1/2}\mathbf{x}$.[4]

The adiabatic treatment in hyperspherical coordinates begins by finding potential energy curves $U_\mu(R)$ which govern the motion of the system in R. These are eigenvalues of the fixed-R Hamiltonian,

$$\hat{U} - \hat{\Lambda}^2(\Omega)/R^2 + C(\Omega)/R, \tag{1}$$

in which Ω denotes all five angular coordinates $\Omega \equiv (\alpha, \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$, C/R denotes the total potential energy of the three particles, and $\hat{\Lambda}^2(\Omega)$ denotes the angular contribution to the kinetic energy operator. In this coordinate system the eigenfunctions of $\hat{\Lambda}^2(\Omega)$ [corresponding to eigenvalues $(\lambda+2)^2 - \frac{1}{4} = (2m + l_1 + l_2 + 2)^2 - \frac{1}{4}$] are hyperspherical harmonics,[9]

$$y_{ml_1l_2}(\Omega) = N_{ml_1l_2}(\cos\alpha)^{l_1+1}(\sin\alpha)^{l_2+1}F(-m, m+l_1+l_2+2; l_2+\tfrac{3}{2}; \sin^2\alpha)\, Y_{l_1l_2LM_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)\chi_{SM_S}. \tag{2}$$

Here $N_{ml_1l_2}$ is a normalization constant, F is a hypergeometric (Jacobi) polynomial, Y is a standard coupled spherical harmonic function, and χ is a two-electron spinor. Antisymmetry of the wave function under electron exchange is enforced by requiring $(-1)^{S+l_1+1} = -1$. The eigenvalue of the parity operator is $\pi = (-1)^{l_1+l_2}$. For $^1P^o$ then, $l_1 + l_2$ is l_1 is even, and $\lambda = 1, 3, 5, 7, \ldots$ since the number of nodes in α is $m = 0, 1, 2, \ldots$, etc. Solution of the eigenvalue equation $\hat{U}\phi_\mu(R;\Omega) = U_\mu(R)\phi_\mu(R;\Omega)$ is the most difficult step in our calculation. Here we extend an approach introduced by Lin,[10] which diagonalizes the matrix $U_{ml_1l_2,m'l_1'l_2'}$ calculated in a hyperspherical-harmonic basis set. This basis set possesses two advantageous properties: (i) It is ideal in the limit $R \to 0$, where C/R is negligible; and (ii) the basis functions $y_{ml_1l_2}(\Omega)$ are independent of R whereby the matrix C can be calculated once and for all and used to diagonalize U at all R values. A well-known disadvantage of the hyperspherical-harmonic expansion of an adiabatic eigenfunction ϕ_μ is its extremely slow convergence at $R \to \infty$. This convergence is slow because the ϕ_μ becomes confined into a smaller and smaller portion of the (α, θ_{12}) plane as R increases, where it describes a positronium bound-state wave function. (Reference 4 used an asymptotic basis set in its study of $^1S^e$ symmetry. That is less practical here because the angular wave functions are

substantially more complicated in the case of $^1P^o$ and most other symmetries.) In order to speed up this slow convergence at large R, we introduce the following method for selecting the most important basis states.

In general each eigenvalue of $\hat{\Lambda}^2$ has a large degeneracy. For $^1P^\circ$ symmetry each successive eigenvalue of $\hat{\Lambda}^2$ contains one additional degenerate state (ml_1l_2), the actual degeneracy being $(\lambda+1)/2$. The linear increase of degeneracy with increasing λ introduces two questions: What is the significance of this high multiplicity of states, and is there a meaningful way to distinguish among them? In Lin's analysis of H^-, l_1 and l_2 are the orbital angular momenta of electrons 1 and 2 about the proton.[8] A natural truncation of the basis set could therefore be obtained by restricting the number of (l_1l_2) pairs to only one or two (e.g., *sp* and *pd* for $^1P^\circ$ H^- states associated with $n<3$). The same truncation would make no sense in our Jacobi coordinate system for Ps^-, where l_1 is the orbital angular momentum of the electrons about each other (i.e., conjugate to $\hat{\mathbf{r}}_1$), while l_2 is the orbital angular momentum associated with rotation of the positron and the electron pair about their center of mass (i.e., conjugate to $\hat{\mathbf{r}}_2$). That is, as $R\rightarrow\infty$ the basis set must include infinitely high (l_1l_2) (at large radii $l_1^{\max}$ must increase in direct proportion to R/n^2) in order to represent the localized $Ps(n)$ wave function, making it far more difficult to obtain converged potential curves for Ps^- than for H^-.

A way to circumvent this difficulty, and in effect to put Lin's truncation of Hilbert space into a form applicable to *any* few-particle system, emerges upon consideration of Fig. 1, where we plot the absolute value of the eigenvector of U corresponding to the lowest eigenvalue U_1 at $R=20$. Figure 1(a) shows this eigenvector $|a_{ml_1l_2,\mu}|$ in the "primitive" representation of hyperspherical harmonics $y_{ml_1l_2}(\Omega)$ given in Eq. (2). Clearly, the eigenvector components are distributed comparably among most of the (ml_1l_2) values without any discernible pattern. Eigenvector components $|a_{\lambda\nu,\mu}|$ of this *same* adiabatic eigenstate $(\mu=1)$ are shown in Fig. 1(b), but they have been transformed into an alternative representation in which each degenerate block of the potential matrix C corresponding to a given λ has been made diagonal. In this representation the index $\nu=1,2,\ldots,(\lambda+1)/2$ labels successive eigenvalues $c_{\lambda\nu}$ of the fixed-λ C matrix, in increasing order. Figure 1(b) shows that only the two or three eigenstates in each fixed-λ manifold corresponding to the most attractive potential eigenvalues $c_{\lambda\nu}$ contribute appreciably to the adiabatic wave function. The reason why this prediagonalization sorts out the physically relevant hyperspherical harmonics is clear: The eigenstates associated with the lower eigenvalues $c_{\lambda\nu}$ of C within each degenerate-λ manifold must lie primarily in the attractive portions of the three-particle potential surface and hence are associated with configurations such as e^--e^+-e^-. Those eigenstates associated instead with the higher $c_{\lambda\nu}$ must correspond to repulsive, highly unstable configurations like (e^-e^-)-e^+ which cannot represent any quasibound or resonant state.

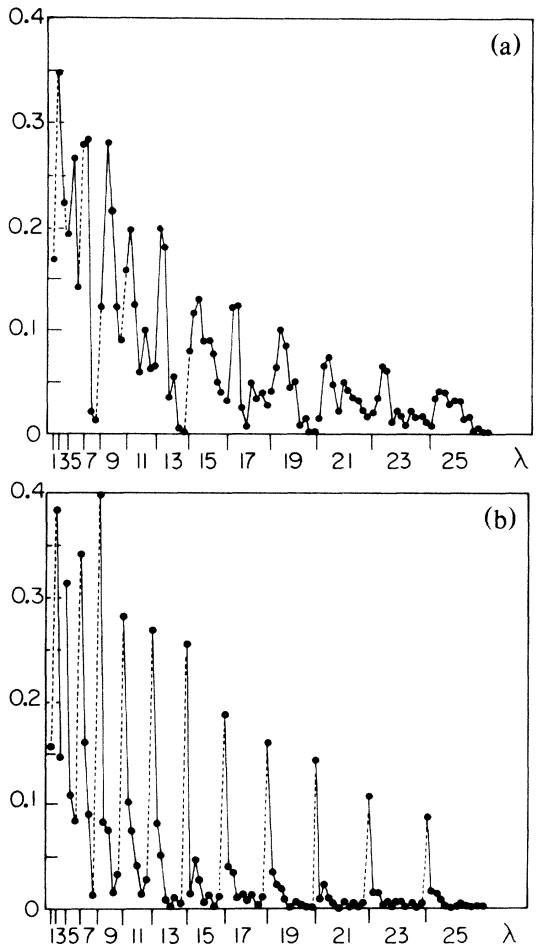

FIG. 1. Absolute values of the expansion coefficients of the lowest $^1P^\circ$ adiabatic eigenstate at $R=20$ plotted in two different representations. Below each plot is λ, the grand angular momentum corresponding to a set of degenerate hyperspherical harmonics. Each dot is the coefficient of a single such harmonic. Solid lines interconnect those states within the same fixed-λ manifold, while dashed lines connect adjacent states having different values of λ. In (a), the representation of harmonics used is that of Eq. (2). In (b) instead, the "prediagonalized" representation is adopted, as described in the text.

We truncate the basis set accordingly, retaining only the lower eigenstates within each λ manifold. This allows the inclusion of very high (l_1l_2), but in their physically relevant linear combinations only. Numerical tests of this procedure showed that only the lowest three such states in each λ manifold contribute appreciably. This enables us to improve convergence by in-

cluding far more λ values. For example, the final diagonalization at many R values involved 108 of these "prediagonalized" basis functions, but incorporated the effects of 666 "primitive" basis functions $y_{ml_1l_2}(\Omega)$. This method of identifying quantum numbers through the condensed-atom limit $R \to 0$ should prove to be generally applicable to other few-particle systems as well (see the work of Clark and Greene,[11] for example).

The adiabatic treatment approximates the total wave function by

$$\phi(R;\Omega) = F_\mu(R)\phi_\mu(R;\Omega). \quad (3)$$

When substituted into the Schrödinger equation, this gives a radial equation for $F_\mu(R)$,

$$[-\partial^2/\partial R^2 + W_{\mu\mu}(R) + U_\mu(R) - E]F_\mu(R) = 0, \quad (4)$$

where we neglect the coupling between different channels but retain the diagonal adiabatic correction term $W_{\mu\mu}(R)$.[4]

The potential curves $U_\mu(R) + W_{\mu\mu}(R)$ are shown in Fig. 2. (The ground state, a completely repulsive curve converging to the ground state of Ps, is not shown.) For $R < 50$ a.u., the diagonalization procedure described above suffices to generate reasonably well-converged potential curves. At larger radii this convergence gets increasingly worse. These three potential curves were accordingly connected smoothly to their known asymptotic form

$$U_\mu(R) + W_{\mu\mu}(R) \underset{R\to\infty}{\longrightarrow} -1/4n^2 + D_\mu/R^2. \quad (5)$$

The permanent dipole moments D_μ for these three channels were found to be $D_- = -5.544$, $D_+ = 2$, $D_{pd} = 11.544$, by use of the standard procedure[12] of Seaton and of Gailitis and Damburg.

The Ps^- potential curves of Fig. 2 bear a close qualitative resemblance to those calculated by Lin[8] and by Klar and Klar[13] for H^-, and we adopt the same classification ("+", "−", and "*pd*") introduced by Cooper, Fano, and Prats[14] and used in Ref. 8. In both systems the + curve is the most attractive at small R, while the − curve is the most attractive at large R. These adiabatic states do not strictly have different symmetry, and consequently cannot cross as shown in the figure. In fact they show an avoided crossing for Ps^- whose minimum separation is $\Delta U = 0.0012$ a.u. at $R = 35.5$, compared with Klar and Klar's[13] minimum separation of $\Delta U = 0.002$ at $R = 12.5$ for H^-. A Landau-Zener–type estimation[15] gives an 80% probability for a nonadiabatic transition between the adiabatic channels, for an energy which coincides with the top of the barrier of the + potential 8.3×10^{-4} a.u. above threshold. This justifies our *diabatic* interpolation of the + and − potentials in the range $28 < R < 42$, where we have allowed them to simply cross in Fig. 2 just as Lin[8] concluded was correct for H^-.

Despite the strong attraction at small distances, the + potential curve is not sufficiently deep to support a quasibound state below $Ps(n=2)$, but it does support a *shape resonance* at an energy that we estimate to be 4×10^{-4} a.u. above threshold. Figure 3 shows the elastic scattering phase shift for this + channel and its derivative with respect to energy, the time delay. The width of the shape resonance originates from tunneling through the barrier, and is thus estimated to be $\Gamma = 4\times10^{-4}$ a.u. The "accepted" position and width of this resonance in H^- appear to be 6×10^{-4} a.u. and 7×10^{-4} a.u., respectively.[16] The − channel also has resonances, but they are qualitatively different. Even though the − potential curve is far less attractive than

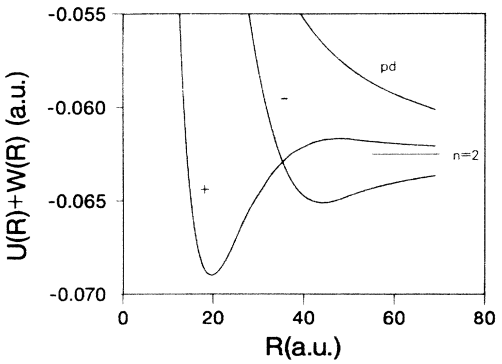

FIG. 2. Hyperspherical potential curves converging to the $Ps(n=2)$ threshold, including the diagonal adiabatic correction term $W_{\mu\mu}(R)$. These have been interpolated smoothly and diabatically through the avoided crossing at $R = 35.5$ a.u.

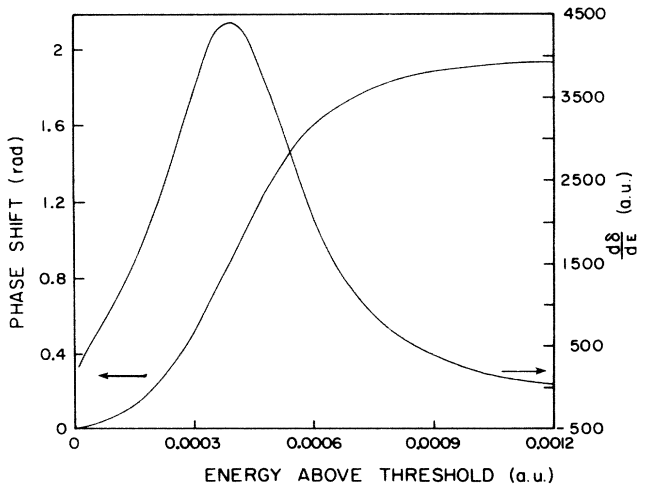

FIG. 3. The elastic scattering phase shift and its energy derivative as functions of energy just above the $Ps(n=2)$ threshold for the + channel. These indicate a shape resonance in this channel at an energy of 4×10^{-4} a.u. above threshold. (All coupling between different diabatic channels has been neglected.)

+ at small R, the long-range dipole attraction guarantees that an infinity of Feshbach resonances must lie just below the Ps($n=2$) threshold (ignoring relativistic effects and the Lamb shift). The lowest such resonance is obtained by solving Eq. (4) with the − potential, giving $E=8.7\times10^{-5}$ a.u. below the $n=2$ threshold. The next lies at 6×10^{-6} a.u., and the binding energy of successive levels converges exponentially to zero. They should be narrow and weak, as in H^-, as a result of the mock centrifugal barrier which keeps the particles much farther away from each other ($R\gtrsim30$ a.u.) than in the + configuration. Since we have not accounted for interchannel coupling, we cannot calculate the width of the − resonance. A crude estimate can be derived by comparison with H^-, nevertheless, if we make use of the fact that resonance widths and binding energies scale proportionately in a long-range dipole field. Since the predicted binding energy of the first Ps^- − resonance is roughly an order of magnitude smaller than the corresponding value for H^- ($E=0.001$ a.u.),[16] this suggests that the width in Ps^- should be around 10^{-7} a.u.

Previous studies[9] of few-electron systems using hyperspherical coordinates have been primarily qualitative, attempting to provide an *interpretation* of atomic properties which had been obtained previously from more sophisticated calculations or from experiment. In this study, however, we *predict* the main resonance features which should be seen in Ps^- photodetachment, relying only on the hyperspherical potential curves. They provide an immediate visual interpretation of the doubly-excited-state properties, showing in particular how the shape-resonance decay width comes primarily from tunneling whereas the Feshbach-resonance decay widths originate entirely in interchannel coupling, an entirely separate physical mechanism. There remains unsolved the mystery of why some symmetries of Ps^-, namely $^1S^e$ and $^1P^o$, parallel H^- so closely, while the $^3P^e$ metastable state of H^- did not show up in previous studies of Ps^-. A hyperspherical calculation[17] similar to the present one has confirmed these studies in failing to find any $^3P^e$ metastable level below Ps($n=2$), but a shape resonance just above threshold analogous to the $^1P^o$ shape resonance did emerge and will be discussed elsewhere. Clearly the e-Ps interaction is less attractive than the e-H interaction, but the implications of this lessened attraction must still be investigated on a case-by-case basis.

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