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Positronium hydride formation in collisions of positrons with molecular hydrogen*

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Summary. The feasibility of observing the threshold for the formation of positronium hydride, PsH, in collisions of low-energy positrons with hydrogen molecules in a mass spectrometric application is considered. The expected count rate of the signature ion H^+ using existing positron beams depends upon the cross section for a dissociative attachment reaction. The estimation of this cross section relies on knowledge of certain potential energy curves and leptonic wave functions. This knowledge does not yet exist. The curves are roughly estimated by considering the binding of a positron to the ionic B state of H_2. Methods of calculating the wave functions are briefly considered.

Key words: Positronium hydride – Exotic compounds – Positrons – Hydrogen molecule

1. Introduction

Exotic compounds, by which we mean compounds containing less common particles (i.e., particles other than electrons and nuclei), are intrinsically interesting. Muon and muonium binding energies to ordinary atoms and molecules are reasonably well given by simple reduced mass corrections to the vibrational levels of the proton-containing systems [2]. Binding energies of compounds containing kaons and pions are given more accurately in this way because these particles are more massive than muons.

Positronic compounds are quite a different matter; the calculation of their binding energies and other properties is not a simple task. Only two exotic compounds have been the subject of accurate calculations, PsH [3] and Ps_2 [4, 5], although some useful approximate calculations have been performed on other systems. (For recent reviews, see Refs. [2, 6].) Experimental work has established the stability of several positronic compounds, but has not yet yielded binding

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energies for any of these. The feasibility of an experimental determination of such binding energies is the subject of this paper.

Many practical applications of positron annihilation techniques, such as to the characterization of polymers and surfaces, are interpreted partly in terms of positronic compounds [7]. A recent observation of annihilation radiation from the region of the galactic center [8] was interpreted without consideration of PsH formation [9]. It is important to examine the influence of this process.

It is obvious that bound states of positronic compounds annihilate. Typical lifetimes are known to be 0.4–0.5 ns [10]. Thus, all positronic compounds are unstable with respect to annihilation. We are concerned here with chemical stability, which relates to cleavage or bond-breaking, or equally with positron and positronium affinities.

2. Mass spectrometry with positrons

A straightforward way to measure $BE(\mathrm{PsA})$, the Ps–A bond energy of the compound PsA, is to measure the lowest positron energy for which the reaction:

$$\mathrm{e}^+ + \mathrm{AB} \rightarrow \mathrm{PsA} + \mathrm{B}^+ \tag{1}$$

is thermodynamically possible. In favorable cases this critical energy is the appearance potential of B^+, $AP(\mathrm{B}^+)$, but actually only a bound on the desired quantity is provided by the experiment:

$$BE(\mathrm{PsA}) \geqslant BE(\mathrm{AB}) + IP(\mathrm{B}) - 6.8\ \mathrm{eV} - AP(\mathrm{B}^+). \tag{2}$$

$IP(\mathrm{B})$ is the ionization potential of B and 6.8 eV is the binding energy of positronium, Ps. The inequality results if the dissociation to products proceeds along a repulsive potential energy curve of the combined system $\mathrm{e}^+\mathrm{AB}$, because in that case $AP(\mathrm{B}^+)$ is larger than the thermodynamic threshold of Eq. (1). The chemical stability of PsA is established if an experiment yields a positive value of the right hand side of Eq. (2). If a series of experiments on AB, AC, AD, . . . , yields a common positive value of the right hand side, then one might argue that this value is $BE(\mathrm{PsA})$.

The idea of using positrons in mass spectrometry is original with McLuckey [11] and was first mentioned in the literature in 1982 [12]. The application to the measurement of binding energies of positronic compounds was first discussed in 1985 [13].

The count rate $i(\mathrm{B}^+)$ of ions B^+ in a mass spectrometer using positrons as the ionization agent is the product of several factors: the positron current $i(\mathrm{e}^+)$, the cross section σ for the process of Eq. (1) above, the effective path length L of the positrons in the ionization chamber of the mass spectrometer, the number density N of the target molecules, and the efficiency ϵ with which the B^+ ions are delivered to the detector:

$$i(\mathrm{B}^+) = \epsilon N L \sigma i(\mathrm{e}^+). \tag{3}$$

Collection efficiencies of modern mass spectrometers approach unity, the effective path length can be taken to be 1 cm, and a common operating pressure for mass spectrometers is 10^{-4} torr for which N at room temperature is $3 \times 10^{12}\ \mathrm{cm}^{-3}$. The value of $10^5\ \mathrm{s}^{-1}$ for the positron current is achievable in relatively inexpensive table top positron beams [14]. With these values, Eq. (3) gives:

$$i(\mathrm{B}^+) \sim 10^{17}\sigma \ \mathrm{s}^{-1} \tag{4}$$

for σ in cm^2. A count rate of B^+ of $10 \ \mathrm{s}^{-1}$ is adequate for a straightforward experiment; by incorporating a coincidence test for the arrival of a positron and the detection of a B^+ ion, one drastically reduces the noise level, with the result that a B^+ count rate as low as $0.1 \ \mathrm{s}^{-1}$ is adequate [15]. With this lower figure, we see from Eq. (4) that a cross section of 10^{-18} cm^2 for Eq. (1) is sufficient for an experiment.

The threshold for the reaction of interest:

$$\mathrm{e}^+ + \mathrm{H}_2 \rightarrow \mathrm{PsH} + \mathrm{H}^+, \tag{5}$$

is known from Ho's calculation on PsH [3] to be 10.22 eV. Its cross section σ is not known (nor for any other compound), but an upper bound may be gotten from the measured total ionization cross section. Another process which produces an ion is positronium formation:

$$\mathrm{e}^+ + \mathrm{H}_2 \rightarrow \mathrm{Ps} + \mathrm{H}_2^+, \tag{6}$$

which has a threshold of 8.63 eV. These thresholds are illustrated in Fig. 1.

There is one ion-producing process which is possible at all energies, but its cross section at the 10.22 eV, the energy of interest, is very small. It is in-flight annihilation:

$$\mathrm{e}^+ + \mathrm{H}_2 \rightarrow 2\gamma + \mathrm{H}_2^+. \tag{7}$$

Its cross section is [16]:

$$\pi r_0^2 \frac{c}{v} Z_{\mathrm{eff}} \sim \frac{1.25 \times 10^{-22} Z_{\mathrm{eff}}}{\sqrt{E}} \ \mathrm{cm}^2, \tag{8}$$

where r_0 is the classical radius of the electron, c is the velocity of light, v is the velocity of the positron, Z_{eff} is the effective number of electrons available to the

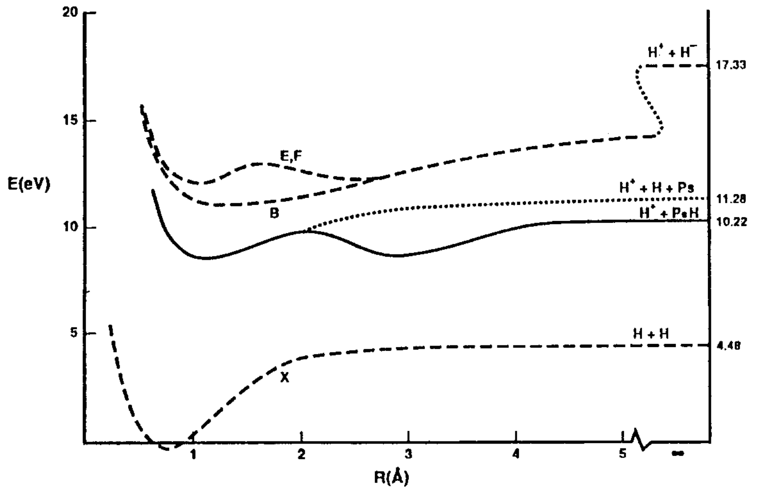

Fig. 1. Potential energy curves relevant to the discussion

positron for annihilation in one hydrogen molecule, and E is the energy of the positron in electron volts. Z_{eff} is no more than 4 [17], so Eq. (7) has a cross section of only about $1.5 \times 10^{-22}\,\text{cm}^2$ at the energy of interest and hence will produce a negligible count rate.

The total ionic cross section rises sharply from zero at the threshold of Eq. (6) to $\sim 10^{-16}\,\text{cm}^2$ within two volts higher. Equation (7) contributes negligibly. If the cross section for Eq. (5) accounts as little as one per-cent of the total, then the experiment is feasible.

3. Term symbols and wave functions

Every mixed electron-positron system is a resonance in a continuum of states of a system with fewer particles and more photons. It is easy to show that the coupling is weak: Lifetimes of mixed systems are 0.4–0.5 ns [10], which gives rise to an uncertainty in the energies of about 10^{-6} eV. In other words, the system lives long enough to establish its energy and to map out its wave function to a high degree of precision. The shift due to the coupling has been calculated for positronium and was found to be only 5×10^{-4} eV [20–23]. It follows that we may use nonrelativistic wave mechanics, familiar to chemists everywhere, to calculate wave functions and energies, and that the application of the simplest first-order perturbation theory will yield reasonably accurate annihilation rates and other annihilation properties [10]. The only novelty is that we now have two kinds of electrons: Positrons and electrons are distinguishable, and wave function structure must reflect that. We also must be very careful about correlation between oppositely charged leptons, because the wave function is large at those parts of configuration space where an electron and a positron are close.

The set of operators which commute with the Hamiltonian and each other include all the spatial symmetry operators irrespective of the presence of the positron, as well as the total spin operators $\hat{S}$ and $\hat{S}_z$. In the absence of spin-dependent terms in the Hamiltonian, the total electron spin $\hat{S}_e$ and total positron spin $\hat{S}_p$ are also included in the commuting set. If we consider systems with only one positron, its spin quantum number S_p is always $\frac{1}{2}$ and need not be specified. In the past, [24] we have used term symbols of atomic states of the form:

$$^{2S+1,2S_e+1}L \tag{9}$$

to indicate the value of the additional quantum number which must be specified owing to the presence of a positron. For example, the ground state of the atom positronium hydride has the term symbol $^{2,1}S^e$; i.e., the electron spins are paired in a singlet, and the system overall is a doublet.

For the diatomic system which dissociates to PsH + H$^+$, the Wigner–Witmer rules [25, 26] give two term symbols: $^{2,1}\Sigma_g^+$ and $^{2,1}\Sigma_u^+$. The spatial wave functions in the asymptotic region are:

$$\begin{aligned}
\psi(^{2,1}\Sigma_g^+) &\equiv \psi_g \xrightarrow{R\to\infty} \frac{1}{\sqrt{2}}(\underbrace{aaa}+\underbrace{bbb}), \\
\psi(^{2,1}\Sigma_u^+) &\equiv \psi_u \xrightarrow{R\to\infty} \frac{1}{\sqrt{2}}(\underbrace{aaa}-\underbrace{bbb}).
\end{aligned} \tag{10}$$

The atomic orbital symbols are compressed from $1s_a$ and $1s_b$, and the underbrace means that the term is not a simple product of one-particle functions but rather contains correlating terms. The order of arguments in any string of one-particle functions is understood to be: electron 1, electron 2, and the positron. The spin function is unstated because, in the absence of spin-dependent terms in the Hamiltonian, it is exactly factorable from the spatial part of the wave function, and remains unchanged in the scattering event. It is, in familiar notation:

$$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\alpha \quad \text{or} \quad \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\beta. \tag{11}$$

We need to express ψ_g and ψ_u in terms appropriate to the scattering event; i.e., in the Franck–Condon region. We use molecular orbitals σ_g and σ_u which we denote simply g and u, respectively. In the simplest approximation these are:

$$\begin{aligned} g &= \frac{a+b}{\sqrt{2(1+\langle a|b\rangle)}}, \\ u &= \frac{a-b}{\sqrt{2(1-\langle a|b\rangle)}}. \end{aligned} \tag{12}$$

One can make six configurations from these orbitals for our system, and these are shown in Fig. 2. In these terms, the (spatial) wave functions are:

$$\begin{array}{llll} \psi_I = \underbrace{ggg} & \psi_{IV} = \underbrace{ggu} & \sigma_g^2 & X\,{}^1\Sigma_g^+ \\ \psi_{II} = \frac{1}{\sqrt{2}}(\underbrace{guu} + \underbrace{ugu}) & \psi_V = \frac{1}{\sqrt{2}}(\underbrace{gug} + \underbrace{ugg}) & \sigma_g\sigma_u & B\,{}^1\Sigma_u^+ \\ \psi_{III} = \underbrace{uug} & \psi_{VI} = \underbrace{uuu} & \sigma_u^2 & E,F\,{}^1\Sigma_g^+ \end{array} \tag{13}$$

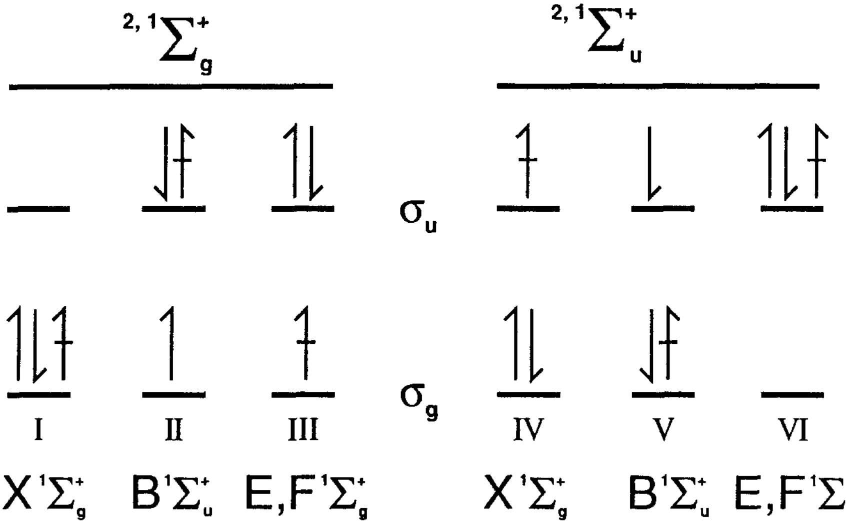

Fig. 2. Configurations relevant to the discussion. The arrows with a crossbar represent the positron spin. Each of these configurations can be associated with a state of H_2, and the term symbols of these states are shown at the bottom

The last two columns above give information about the electronic parent of the two e^+H_2 configurations in each line. From these six configurations one can make six orthogonal linear combinations which are correct in the asymptotic region. The two combinations which are equal to those given in Eqs. (10) are:

$$\left.\begin{aligned}\psi_g &\xrightarrow{R\to\infty} \frac{1}{2}\psi_I + \frac{1}{\sqrt{2}}\psi_{II} + \frac{1}{2}\psi_{III}\\ \psi_u &\xrightarrow{R\to\infty} \frac{1}{2}\psi_{IV} + \frac{1}{\sqrt{2}}\psi_V + \frac{1}{2}\psi_{VI}\end{aligned}\right\} \sim \mathrm{PsH} + \mathrm{H}^+ \qquad (14)$$

which has a threshold of 10.22 eV, as we have already noted.

For completeness we give the other linear combinations. Two describe dissociation, which has a threshold of 4.48 eV:

$$\left.\begin{aligned}\psi(^{2,1}\Sigma_g^+) &\xrightarrow{R\to\infty} \frac{1}{\sqrt{2}}(\psi_I - \psi_{III}) = \frac{1}{2}(ab+ba)(\tilde{a}+\tilde{b})\\ \psi(^{2,1}\Sigma_u^+) &\xrightarrow{R\to\infty} \frac{1}{\sqrt{2}}(\psi_{IV} - \psi_{VI}) = \frac{1}{2}(ab+ba)(\tilde{a}-\tilde{b})\end{aligned}\right\} \sim (\mathrm{e}^+, \mathrm{H}) + \mathrm{H}. \qquad (15)$$

Since e^+ and H do not form a bound state, [27] the symbol (e^+, H) is meant to denote a positron and a hydrogen atom far from each other. The tildes denote scattering functions. Two more linear combinations describe ion pair formation, the threshold for which is 17.33 eV:

$$\left.\begin{aligned}\psi(^{2,1}\Sigma_g^+) &\xrightarrow{R\to\infty} \frac{1}{2}\psi_I - \frac{1}{\sqrt{2}}\psi_{II} + \frac{1}{2}\psi_{III} = \frac{1}{\sqrt{2}}(\underbrace{aa\,\tilde{b}} + \underbrace{bb\,\tilde{a}})\\ \psi(^{2,1}\Sigma_u^+) &\xrightarrow{R\to\infty} \frac{1}{2}\psi_{IV} - \frac{1}{\sqrt{2}}\psi V + \frac{1}{2}\psi_{VI} = \frac{1}{\sqrt{2}}(\underbrace{aa\,\tilde{b}} - \underbrace{bb\,\tilde{a}})\end{aligned}\right\} \sim (\mathrm{e}^+, \mathrm{H}^+) + \mathrm{H}^-. \qquad (16)$$

In the united atom limit, the target states are those which correlate with the *X*, *B*, and *E,F* states of H_2. They are, in order of increasing energy, the $1s^2\,{}^1S$, $1s2p\,{}^1P$, and $2p^2\,{}^1S$ states of He. Evidently the $^{2,1}\Sigma_g^+$ and $^{2,1}\Sigma_u^+$ states in (15) correlate with *s*- and *p*-wave positron scattering, resp., from the ^1S united atom state; the $^{2,1}\Sigma_g^+$ and $^{2,1}\Sigma_u^+$ states in (14) correlate with *p*- and *s*-wave scattering from the ^1P united atom state; and the $^{2,1}\Sigma_g^+$ and $^{2,1}\Sigma_u^+$ states in Eq. (16) correlate with *s*- and *p*-wave scattering from the $2p^2\,{}^1S$ united atom state:

$$\left.\begin{aligned}\psi_g &\xrightarrow{R\to 0} \psi_{II} = (\underbrace{1s2p} + \underbrace{2p1s}) \otimes \tilde{p}\\ \psi_u &\xrightarrow{R\to 0} \psi_V = (\underbrace{1s2p} + \underbrace{2p1s})\tilde{s}\end{aligned}\right\} \sim (\mathrm{e}^+, \mathrm{He}^*) \qquad (14')$$

$$\left.\begin{aligned}\psi(^{2,1}\Sigma_g^+) &\xrightarrow{R\to 0} \psi_I = \underbrace{1s1s}\,\tilde{s}\\ \psi(^{2,1}\Sigma_u^+) &\xrightarrow{R\to 0} \psi_{IV} = \underbrace{1s1s}\,\tilde{p}\end{aligned}\right\} \sim (\mathrm{e}^+, \mathrm{He}) \qquad (15')$$

$$\left.\begin{array}{l}\psi({}^{2,1}\Sigma_g^+)\xrightarrow{R\to 0}\psi_{III}=\underbrace{2p\otimes 2p}\,\tilde{s}\\ \psi({}^{2,1}\Sigma_u^+)\xrightarrow{R\to 0}\psi_{VI}=\underbrace{2p\otimes 2p}\,\tilde{p}\end{array}\right\}\sim(\mathrm{e}^+,\mathrm{H}^{**}) \qquad (16')$$

where $\otimes$ means the angular momentum is coupled into an *S* state.

We are interested in the Franck–Condon region. There the mixing coefficients for the six configurations in Eq. (13) will be different than shown above for either of the two limits. Attempting to assign values to the coefficients in the Franck–Condon region from plausibility arguments alone is difficult. Perhaps it is safe to say that the coefficients will have values betwen those indicated above for the two limits. Thus the electronic part of the wave function for the combined system which dissociates to PsH will be between 50% and 100% *B* state, as indicated in Eqs. (14) and (14′), resp., and smaller amounts of the *X* and *E,F* states. The lowest state (Eqs. (15) and (15′)) will be mostly *X* in electronic character, and the highest (Eqs. (16) and (16′)), *E,F*.

Thus we have identified the *B* state as the electronic component of the combined e^+-H_2 scattering system which can dissociate to the product of interest, PsH, and we have identified the broad characteristics of the wave function of the combined system. These are the principal results of this section.

4. Potential energy curves

In order to demonstrate that an appreciable cross section (i.e., $\geqslant 10^{-18}\,\mathrm{cm}^2$) for Eq. (5) is feasible, we need to show that the combined system e^+H_2 has a resonant state which dissociates to PsH and which is accessible in the Franck–Condon region at about 10.22 eV. The *X* state cannot bind a positron [28], and our analysis above shows that, although the *E,F* state is ionic, the combined system has the positron on the repulsive end of the molecule. Only that part of the target wave function which has *B* character (configurations ψ_{II} and ψ_V) contributes to the formation of a quasi-bound or resonant state.

In Fig. 1 we show the three states of H_2 involved in our considerations as dashed lines. These states are also the zero energy scattering states for the combined system. The dotted line is the potential curve for the ground state of H_2^+ drawn 6.8 eV below its normal energy; at each internuclear distance it represents H_2^+ and a positronium atom far away and at rest. The dissociation products and threshold energies are shown on the right. The threshold for Ps formation (Eq. (6)) is 8.63 eV, and the lowest excitation threshold, to the *B* state, is about 11.1 eV. Excitation to the triplet *b* state (not shown) is forbidden in the approximation of a spinless Hamiltonian. Thus the only processes possible from 10.22 to 11.1 eV are interactions with the *X* state (which include elastic scattering, vibrational and rotational excitation, and dissociation), positronium formation (with possible vibrational and rotational excitation of H_2^+), and positronium hydride formation. We have already established that annihilation in flight is negligible (discussion follows Eq. (8)).

We now estimate the binding energy of a positron to the *B* state of H_2, and take that result as a rough estimate of the potential energy curve of a resonant state which dissociates to PsH.

A fixed dipole greater than 0.338 e-Å bind an electron or a positron [29]. The binding energies for dipoles greater than this have been computed by several. The tables of Turner, Anderson, and Fox [30] are most convenient. To estimate the ionic character of the B state as a function of internuclear distance, we use the accurate calculation of Kołos and Wolniewicz [31]. These authors express their wave function as the sum of an ionic part, covalent parts with $1s2s$ and $1s2p$ character, and a small remainder:

$$\psi_B = c_i\varphi_i + c_s\varphi_s + c_p\varphi_p + c_r\varphi_r. \tag{17}$$

We take the fractional ionic character [32] of the B state to be given by

$$c_i^2 + c_i c_s S_{is} + c_i c_p S_{ip}, \tag{18}$$

where S_{is}, for example, is the overlap integral between φ_i and φ_s. These coefficients and overlap integrals are given in the paper of Kołos and Wolniewicz as functions of internuclear distance, so the fractional ionic character is easily worked out from $R = 1$ to 12 a.u. We take the product of this quantity and the internuclear distance as the effective dipole for binding the positron, and the tables of Turner et al., yield the binding energy of the positron.

The resulting curve was modified in two ways: For large R (4 to 5 Å) the resulting curve is ~1.5 eV below the 10.22 eV asymptote, which is a consequence of the B state's higher multipole moments. We therefore increased the curve by that amount. A crossing with the $H_2^+ + Ps$ curve then occurs at $R \approx 2$ Å, so for smaller internuclear distances we followed the latter curve. The result is the solid curve in Fig. 1.

There are two symmetries: $^{2,1}\Sigma_g^+$ and $^{2,1}\Sigma_u^+$. Perhaps the g state will be the lower in energy, and we offer the solid curve in Fig. 1 as an approximation to its energy. We see that a vertical transition from the ground state is favorable at the threshold energy of the desired dissociation products. Thus, we have established, within the crudity of the approximations described here, a necessary condition for the measurement of the binding energy of PsH, as stated in the first sentence of this section.

5. Estimating the cross section for PsH formation

The theory of O'Malley [33] gives the cross section for dissociative attachment of an electron. The theory is valid for dissociative attachment of a positron, Eq. (5). In simplest form, the cross section (σ in Eqs. (3) and (4)) is [34]:

$$\sigma(\varepsilon) = \sigma_0\, e^{-\tau_s/\tau_a}, \tag{19}$$

where ε is the positron incident energy, σ_0 is the cross section for the formation of the compound state $e^+H_2^*$, τ_s is the time require for separation to products, and τ_a^{-1} is the sum of the rates for emission of the positron, formation of Ps, and annihilation. τ_s can be estimated from $V(R)$, the potential energy curve of the compound system:

$$\tau_s \sim \sqrt{\frac{m}{4}} \int_{R_0}^{R_{asy}} \frac{dR}{\sqrt{\varepsilon - V(R)}}, \tag{20}$$

where m is the mass of the proton, R_0 is the equilibrium distance of the target X state, R_{asy} is the onset of the asymptotic region for the compound system (i.e., the value of R large enough so that the three-lepton oscillation frequency of the system $PsH + H^+$ prepared with the leptons on one nucleus is larger than the rate for emission of the positron accompanied by formation of the X state of the target).

The estimation of the quantities on the right side of Eq. (19) requires wave functions for the states involved. A calculation is beyond the scope of the present work. A minimal calculation would involve, for each symmetry, the mixing of three configurations. Two of the resulting three states will be unbound. The state of interest will be intermediate in energy between the two unbound states. It will be a resonance embedded in the continuum of the lower unbound state. One reasonable way to proceed is to project out the X target state and perform a quasi-bound state calculation on the combined system, taking care to deal with possible crossing with the $H_2^+ + Ps$ continuum onset. The variational principles of Prager [35] may be useful in such a calculation.

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