

LETTER TO THE EDITOR

Non-Hermitian diabatic formulation of antiproton collision: protonium formation

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Abstract

We present a non-Hermitian coupled-channel resonant diabatic approach to Rydberg protonium formation in the ultraslow rearrangement collision $\bar{p} + \text{H} \rightarrow \text{Pn} + e^-$, where the kinetic coupling between the electronic and the nuclear motions is strong. We calculate complex diabatic potential energy curves and associated coupling matrix elements that vary smoothly with $p\bar{p}$ distance. The $[\text{Pn} - e]^-$ resonances split into two groups converging to the first and second hydrogen thresholds.

Resonances are some of the most striking phenomena in quantum scattering [1, 2] whose lifetimes are normally associated with the imaginary part of the Hamiltonian eigenvalues. Resonant states are not therefore in the Hermitian domain of the Hamiltonian. Upon complex scaling, i.e., scaling the internal coordinates of the Hamiltonian by $\exp(i\theta)$, resonance wavefunctions become square integrable (for a recent review on the complex scaling (CS) formalism and its applications see [3]).

The complex-scaling method has been used successfully for the calculation of resonance properties in molecular systems within the framework of the fixed nuclei approximation. However, more often than not, the nuclear motion dramatically affects the electronic motion, and non-adiabatic coupling terms cannot be ignored, requiring that a closed coupled set of equations be solved. This is computationally resource-intensive and the judicious selection of basis set gains in importance. It has been shown that resonances, formed during $e^- - \text{H}_2$ scattering experiments, can be calculated in the adiabatic approximation when the *resonance* adiabatic eigenstates of the complex-scaled Hamiltonian are used as a basis set. In such a case, the non-adiabatic coupling between the electronic and nuclear coordinates is introduced by solving the nuclear equation of motion within a *complex* adiabatic potential energy surface [4, 5]. This approach is limited to cases where the molecular system has finite lifetimes within the adiabatic approximation. There are cases, however, as in the scattering of an antiproton from a hydrogen atom, where even upon CS, the adiabatic states do not describe the resonance phenomena.

In this work, we introduce a method that enables calculation of resonance energies, widths and cross sections for such cases. The key point is to use a *resonant diabatic representation* instead of the adiabatic representation. The ‘frozen’ diabatic states in the Hermitian approach, $\{\Phi_{\text{diab}}\}$, are defined as states for which the matrix elements $\langle \Phi_{\text{diab}}^{(j')} | d/dR | \Phi_{\text{diab}}^{(j)} \rangle = 0$, where the indices j and j' refer to diabatic channel quantum numbers. This strict definition of diabatic states provides in our case bound states in the continuum (i.e., zero widths). The question then is, how can diabatic resonance states be calculated in the non-Hermitian quantum mechanics? Here, we introduce a method for the calculation of resonant diabatic states which serve as an effective basis set in the solution of the full problem, where the coupling between the electron and the nuclear motions is taken into consideration.

We calculate the autodetachment rates of the protonium negative ion, $\text{Pn}^-(n)$ resonances that form in the collision between a slow antiproton, \bar{p} , and a hydrogen atom—for purposes of illustration and experimental interest, we deal with collision energies less than 10 eV, where only H(1s) is an open channel. We have chosen this exotic example since slow antiproton collision physics is currently the subject of intense theoretical [6, 9–13] and experimental [14–16] investigations. A slow antiproton can replace a bound atomic or molecular electron and form an exotic $p\bar{p}$ complex, i.e. a protonium atom. The intermediate resonant complex, the negative or positive Pn ion, depending on whether $\bar{p}\text{-H}$ or $p\text{-}\bar{\text{H}}$ collision occurs, represents an important step in the formation of highly excited $\text{Pn}(n, l)$ Rydberg states. The spectroscopic measurements of protonium excitation and de-excitation may help in testing fundamental symmetries, such as the CPT invariance [17]. Highly excited Rydberg states are desirable for stability against annihilation which could allow for high-precision spectroscopy of such exotic atoms.

Before introducing the method, we need to motivate the problem with the complex adiabatic approach for the rearrangement collision $\bar{p} + \text{H} \rightarrow \text{Pn} + e^-$. Using the well-known result for the electron–dipole interaction [18, 19], it is expected that for $\bar{p}\text{-p}$ distances larger than $R \geq R_c = 0.338 \text{ \AA}$, the electron will be bound to the protonium. However, this Born–Oppenheimer (BO) value for R_c is smaller than the exact value by more than a factor of 2 [20, 21]. Therefore, one must go beyond the BO approximation and use the adiabatic states as a basis set. However, the high density of states involved in the rearrangement collision makes a direct approach prohibitive (for an idea of the density of states see figures 2 and 3 of [11]).

For the sake of simplicity and without loss of generality, we set the total angular momentum, $J = 0$, such that the rotational angular momentum of Pn is equal to the electron angular momentum in $[\text{H}\text{-}\bar{p}]$, $l = 0, 1, 2, \dots$. The adiabatic Hamiltonian is

$$\hat{H}_{\text{ad}} = \hat{H}_0 + \frac{1}{|\vec{r} - \vec{e}_z R|} - \frac{1}{R} + \frac{\hbar^2 \hat{l}^2}{m_p R^2} \quad (1)$$

where \hat{H}_0 is the hydrogen atom Hamiltonian, m_p is the proton mass, r is the electron–proton distance, $\vec{e}_z R$ implies that R is along the fixed-frame z -direction and \hat{l}^2 is the square of the electronic angular momentum. No restriction is placed on the orbital or rotational angular momenta.

We analytically continue the Hamiltonian matrix elements, calculated with even-tempered Gaussian basis functions, $|n, m, l, \alpha\rangle = x^n y^m z^l \exp(-\alpha r^2)$ —it is the Gaussian exponent that is complex-scaled, i.e. $\alpha \rightarrow \alpha \exp(i\theta)$, where θ is the rotation angle [3]. In doing so, we overcome the non-analytic nature of the ‘molecular’ potential $|\vec{r} - \vec{e}_z R|^{-1}$ [23]. This scaling enables us to calculate the molecular resonance curves, $E_{\text{ad}}(R) - \frac{i}{2}\Gamma_{\text{ad}}(R)$, identified with the stationary solutions in the complex variational space [3]. $\Gamma_{\text{ad}}(R)$ provides the adiabatic detachment rate for the decay of $\text{Pn}^-(R) \rightarrow \text{Pn}(R) + e^-$. Our result shows that the electron is bound to Pn for $R > R_c$, and nearly bound for $R < R_c$, where for the ground state $R_c \sim 0.5 \text{ \AA}$

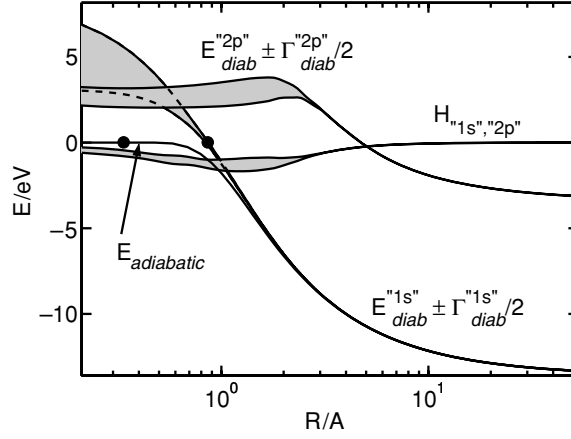


Figure 1. The adiabatic and diabatic complex potential energy curves, and the diabatic complex energy coupling between them, as a function of R . The full circles denote the critical dipoles at $R = R_c$, where the bound to resonance transitions occur.

(figure 1). The figure resembles the Born–Oppenheimer result. The resonances are extremely narrow for $R < R_c$ due to the adiabatic transition of the electron orbital from a localized hydrogen orbital to a diffuse Rydberg orbital. The transition regions are characterized by strong non-adiabatic coupling between resonances and/or bound states.

Following the above discussion, it is clear that the resonances in the rearrangement collision of an electron with Pn, or of an antiproton with H, result from strong non-adiabatic coupling. In such a case, one may use the diabatic representation rather than the adiabatic one. A diabatic approach was developed by Cohen *et al* [20] to calculate the 1s diabatic potential state, Φ_{diab}^{1s} . They calculated the frozen 1s diabatic energy curve using the 1s hydrogen orbital, $\Phi_{diab}^{1s} = \phi_{1s}^H$. The resonance width of this diabatic state was estimated, using the Fermi golden rule. Using the CS method, we confirm that $\Gamma_{diab}^{1s}(R) = -2 \text{Im}(\langle \phi_{1s}^H | \hat{H}_{ad} | \phi_{1s}^H \rangle)$ vanishes for all values of R , due to the absence of resonance continuum in the 1s hydrogen wavefunction; see figure 1.

To overcome this problem, a unique set of diabatic states is constructed as resonance states, in the spirit of Fano interaction formalism [7], as bound hydrogen orbitals augmented by states in the continuum. This diabatic transformation leads to smoothly varying potential curves and coupling matrix elements (see figure 1).

For instance, the diabatic $\bar{1}s$ resonant state is constructed as

$$\Phi_{diab}^{\bar{1}s} = c_{1s, \bar{1}s} \phi_{1s}^H + \int dk c_{k, \bar{1}s} \phi_k^H \quad (2)$$

where ϕ_{1s}^H and ϕ_k^H are, respectively, the bound and continuum hydrogenic orbitals. The $\bar{2}p$ diabatic resonance state is similarly described as a linear combination of the 2p hydrogen bound state, ϕ_{2p}^H , and the continuum hydrogen orbitals, ϕ_k^H —likewise, the $\bar{2}s$ diabatic state can be formed whose contribution is smaller than the two diabatic states considered here. The diabatic states form a non-orthogonal basis whose expansion coefficients, as the eigenvectors of a generalized eigenvalue equation, are variationally calculated. The issue of numerical dependence is addressed in the usual fashion by transforming into the representation in which the overlap matrix is diagonal [8]. The d/dR coupling matrix elements between the bound and continuum diabatic states will not be strictly zero, but are made small—at times by nearly an order of magnitude over similar adiabatic d/dR couplings. We also find that CS greatly

reduces the d/dR coupling between the diabatic $\overline{1s}$ and $\overline{2p}$ bound states and the continuum states.

The corresponding eigenvalues, $V_{\text{diab}}^{\overline{1s}}(R) = E_{\text{diab}}^{\overline{1s}}(R) - \frac{i}{2}\Gamma_{\text{diab}}^{\overline{1s}}(R)$ in one case and $V_{\text{diab}}^{\overline{2p}}(R) = E_{\text{diab}}^{\overline{2p}}(R) - \frac{i}{2}\Gamma_{\text{diab}}^{\overline{2p}}(R)$ in the second case, provide the resonant diabatic energies and widths (autodetachment decay rates) presented in figure 1. As one can see from the results presented in figure 1, $\Gamma_{\text{diab}}^{\overline{1s}} = 0$, when $R > R_c = 0.857 \text{ \AA}$. This compares well with the value of 0.845 \AA obtained in [20] for ‘polarized’ diabatic states. In our case, we obtain the polarization effects due to the inclusion of the coupling to the continuum. $\Gamma_{\text{diab}}^{\overline{1s}}(R)$ increases substantially as $R < R_c$, however, it is three to four times smaller than the approximate values which have been obtained from frozen diabatic bound states using the Fermi golden rule [20]. In agreement with the results presented in [9, 20], our calculations show a sudden transition from a bound electron–protonium state to an autodetaching state (Pn formation) at a distance R_c which is more than twice as *large* than the adiabatic critical dipole, $R_c^{\text{ad}} = 0.338 \text{ \AA}$ —the adiabatic and diabatic critical dipole values are marked in figure 1. Our result is in agreement with the conclusion of Sakimoto [9] who has shown that the probability for the protonium formation remains nonzero for $0.338 < R < 1 \text{ \AA}$, when non-adiabatic couplings are incorporated in the calculation.

In figure 2, we represent the complex eigenvalues obtained by solving the following nuclear Schrödinger equations,

$$\left(-\frac{\hbar^2}{m_p} \frac{d^2}{dR^2} + V_{\text{diab}}^{(j)}\right) \chi_{\alpha}^{(j)} = \lambda_{\alpha}^{(j)} \chi_{\alpha}^{(j)} \quad (j) = \overline{1s}, \overline{2p} \quad (3)$$

where α is the ‘vibrational’ quantum number of Pn, and $\chi_{\alpha}^{(j)}$ is the corresponding ‘vibrational’ autodetaching wavefunction. $V_{\text{diab}}^{(j)}(R)$; $(j) = \overline{1s}, \overline{2p}$ are the potential energy curves, for the $\overline{1s}$ and $\overline{2p}$ diabatic states, and the eigenenergies are $\lambda_{\alpha}^{(j)} = E_{\alpha}^{(j)} - \frac{i}{2}\Gamma_{\alpha}^{(j)}$. The results presented in figure 2 show that the two diabatic resonances cross in the complex energy plane at an energy $E_{\alpha}^{(j)} = -18 \text{ eV}$ and width $\Gamma_{\alpha}^{(j)} = 1.2 \text{ eV}$ —the states lying in the vicinity of the crossing are poorly described in the single-channel diabatic approximation. To obtain the avoided crossing correctly, a set of coupled channel equations is solved:

$$\sum_{j'} \left[\left(-\frac{\hbar^2}{m_p} \frac{d^2}{dR^2} + V_{\text{diab}}^{(j)}\right) \delta_{jj'} + V_{\text{diab}}^{(jj')} \right] \chi_{\alpha}^{(j')} = \lambda_{\alpha}^{(j)} \chi_{\alpha}^{(j)} \quad (4)$$

where the complex-diabatic coupling term is given by

$$V_{\text{diab}}^{\overline{1s}, \overline{2p}} = V_{\text{diab}}^{\overline{2p}, \overline{1s}} = \langle \Phi_{\text{diab}}^{\overline{1s}} | \hat{H}_{\text{ad}} | \Phi_{\text{diab}}^{\overline{2p}} \rangle.$$

Here the complex-inner product rather than the usual scalar product has been used due to non-Hermiticity of the Hamiltonian [3, 24]. The real and the imaginary parts of the diabatic energy coupling as a function of R are shown in figure 1. The diabatic coupling has its maximum value at $R \simeq 1 \text{ \AA}$, where the two complex diabatic potential energy curves do not overlap. The diabatic coupling curve penetrates, however, into the small- R region where the two diabatic curves do overlap. The resonance energies and widths of the $[\text{Pn-e}]^-$ complex calculated in the coupled-diabatic representation are presented in figure 2. The results (open triangles) clearly show the avoided crossing of the two coupled diabatic resonances.

The resonances, presented in figure 2, split into two groups converging to the first and second hydrogen thresholds. Those which converge to the second energy threshold (with energies above -13.6 eV) have an open ‘dissociation’ channel. Therefore, these resonances can be populated during the ultra-slow \bar{p} -H(1s) scattering experiment. The resonances, that converge to the first energy threshold, were accurately obtained within the framework of the

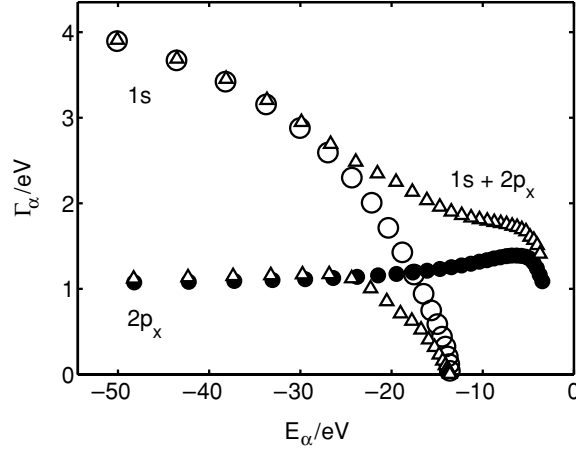


Figure 2. The vibrational autodetaching resonances of $[\text{Pn-e}]^-$: the open and full circles obtained from the uncoupled calculations for the $1s$ and $2p_x$ diabatic electronic states respectively (equation (3)). The avoided crossing behaviour obtained when the coupled problem is solved.

current diabatic approximation. These resonances decay via ionization only. Since for these resonances the ‘dissociation’ of Pn is a closed channel, they are not directly observable in $\bar{\text{p}}\text{-H}(1s)$ scattering. However, they would play an important role in the scattering of electrons from protonium. Hereafter, we denote the resonance energies, widths and wavefunctions, obtained from the solutions of diabatic equations, E_α , Γ_α and $\Psi_\alpha(r, R)$, respectively.

The Pn formation probability is obtained from a spectral decomposition of the reactive scattering Green function. The probability amplitude to populate an n, l state of protonium is approximated using the non-Hermitian equivalent of the Lippmann–Schwinger formula for the cross section [25, 26],

$$\sigma(n, l; E) = \left| \sum_{\alpha} \frac{a_{n,l,\alpha}}{E + E_{\text{H}(1s)} - E_{\alpha} + \frac{i}{2}\Gamma_{\alpha}} \right|^2 \quad (5)$$

where E is the relative kinetic energy of the ‘reactants’ $\bar{\text{p}}$ and $\text{H}(1s)$, and $a_{n,l,\alpha}$ is the transition probability amplitude for forming the ‘products’, Pn and e^- . The transition probability is obtained from the product of $W_{1s,\alpha}$ and $\gamma_{n,l,\alpha}$, where $W_{1s,\alpha}$ is the probability amplitude for populating the α th resonance state during the collision process, and $\gamma_{n,l,\alpha}$ is the partial width amplitude for the resonance state α to decay to the open product channel $\text{Pn}(nl)$. The probability amplitude $W_{1s,\alpha}$ is approximated here by the overlap between the $1s$ hydrogen atom orbital and Ψ_α as

$$W_{1s,\alpha} = \sqrt{\langle \Psi_\alpha^* | \phi_{1s}^{\text{H}} \rangle_{\vec{r}} \langle \phi_{1s}^{\text{H}} | \Psi_\alpha \rangle_{\vec{r}}}. \quad (6)$$

The partial width amplitude is approximated by $\gamma_{n,l,\alpha}^2 = \Gamma_\alpha P_{n,l,\alpha}$, where

$$P_{n,l,\alpha} = \lim_{r_e \rightarrow \infty} \frac{\langle \Psi_\alpha^* | \phi_n^{\text{Pn}} \rangle_R \delta(r - r_e) \langle \phi_n^{\text{Pn}} | \Psi_\alpha \rangle_{R,\vec{r}}}{\langle \Psi_\alpha^* | \delta(r - r_e) | \Psi_\alpha \rangle_{R,\vec{r}}}. \quad (7)$$

The Pn formation distribution in highly excited Rydberg states as a function of collision energy is shown in figure 3. The probability peaks move from $n = 28$ to $n = 33$ as the energy collision is increased from ~ 0 to 5 eV. This shows that the assumption of the energy-matching condition [27], which predicts Pn formation in quantum numbers from $n = 30$ to $n = 39$ in

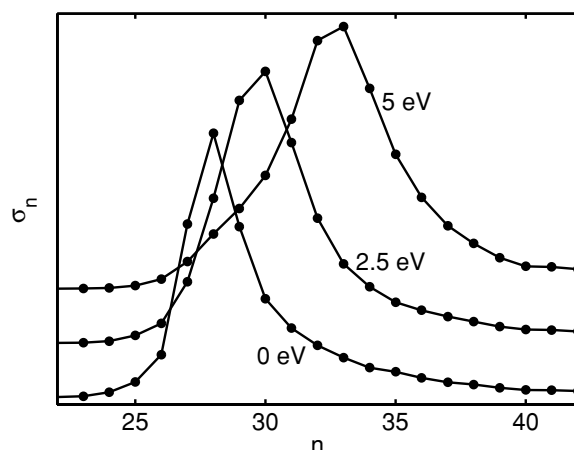


Figure 3. The P_n formation probability in the rearrangement collision $\bar{p} + H \rightarrow P_n + e^-$, where n is the n th Rydberg state of protonium. The collision energy is $E = 0, 2.5, 5$ eV. The distribution is peaked and broad.

this energy interval, is reasonably accurate. The calculations show that the n -distributions are peaked, but rather broad. The width of the distribution is expected to increase with increasing collision energy. We therefore expect that P_n in a single clearly dominating excited Rydberg state can be only formed in ultra-slow \bar{p} -H collision experiments, when the energy collision is likely to be less than 5 eV. Diabatic states converging to the second and higher hydrogen thresholds should also be included in the coupled-channel scheme, as the collision energy approaches the $H(n = 2)$ threshold.

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