Partial widths with interchannel coupling to all orders for the H^- two-electron ionization ladder of ^1D symmetry

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We present correlated-wave-function characteristics, energies, and partial widths with interchannel coupling to all orders, for the H^- two-electron ionization ladder resonances of ^1D symmetry for $n=3$, 4, and 5. Our computations took into account the interaction of up to 19 open channels. The resulting energies and total widths are compared to earlier computations and with the experimental energy for $n=3$.

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Over the past few years, publications from this institute have dealt with the theory and *ab initio* computation of a number of properties of special classes of doubly and triply excited states whose wave functions exhibit localization at specific geometries [1–7]. Among these properties are the autoionization partial widths, which are calculated by a method incorporating the effect of interchannel coupling to all orders [3,6,7].

In this Brief Report we present our predictions for the partial widths of the H^- two-electron ionization ladder (TEIL) of ^1D symmetry. Previous such calculations dealt with the ^1S and $^1P^o$ TEIL's [3,6]. The ^1D TEIL states could be reached by one-photon absorption from the $^1P^o$ TEIL states, which already have been detected experimentally [8,9], or in one-photon transitions from the ^1S ground state in the presence of a static electric field.

We have studied the ^1D TEIL resonances with $n=3$, 4, and 5. The numbers of the open channels are 4, 10, and 19, respectively, while interelectronic correlations are strong. Following the published theory [1–7] we write, for the zeroth-order multiconfigurational representation for each hydrogenic manifold n,

$$\Phi_0^n(^1D)=\sum_{l=0}^{n-3} a_l\varphi(nl,nl+2;^1D)+\sum_{l=1}^{n-1} b_l\varphi(nl^2;^1D)\ . \tag{1}$$

TABLE I. Mixing coefficients of the Φ_0^n of the H^- ^1D TEIL resonances, corresponding energies (ε_0^n), and total energies (E_0^n), in a.u., obtained by including additional localized correlation. Note that for $n=5$, the a_l coefficients are larger than the b_l ones [Eq. (1)]. In particular, the main configuration is *sd* rather than p^2.

$n=3$	$n=4$	$n=5$
0.574 $3s3d$	0.646 $4s4d$	0.623 $5s5d$
0.797 $3p^2$	0.659 $4p^2$	0.590 $5p^2$
0.188 $3d^2$	0.262 $4p4f$	0.380 $5p5f$
	0.277 $4d^2$	0.306 $5d^2$
	0.056 $4f^2$	0.114 $5d5g$
		0.109 $5f^2$
		0.019 $5g^2$
$\varepsilon_0^n=-0.064\,618$	$\varepsilon_0^n=-0.038\,819$	$\varepsilon_0^n=-0.025\,566\,6$
$E_0^n=-0.065\,949$	$E_0^n=-0.039\,044$	$E_0^n=-0.025\,631$

The radial parts of the orbitals were optimized self-consistently while they were kept orthogonal to the hydrogenic radials of the lower-lying open channels. The mixing coefficients a_l and b_l and the energies ε_0^n are given in Table I. Whereas for low energies ($n=3,4$) the dominant configuration is p^2, for $n=5$ the *sd* configuration takes over. This dependence of the principal configurational description of the TEIL states on excitation energy has also been seen in our earlier work [3,6,7]. This is why more basic criteria for computing *a priori* a Wannier TEIL state have been proposed [1], these being the self-consistent optimization within each manifold and the choice of the lowest-energy state, and the emergence of equal average radii and strong localization toward $\theta=180°$ as revealed by conditional probability plots.

The remaining localized single and pair electron correlations, $X_{\rm loc}^n$, are added in terms of Slater-type occupied and core orthogonalized virtual orbitals, whose nonlinear parameters are optimized variationally. Two sets of virtual orbitals [two Slater-type orbitals (STO's) per orbital angular momentum l] were used for the state with $n=3$ and one set for the states $n=4,5$. The corresponding energies are in Table I.

Having thus obtained the localized part of the TEIL resonances, $\Psi_0^n=\Phi_0^n+X_{\rm loc}^n$, the open-channel asymptotic part $X_{\rm as}^n$ is added in the form

$$X_{\rm as}^n=\sum_{\substack{n'\\ n'<n}} c^{n'l'l}u(n'l',\varepsilon l;^1D)\ . \tag{2}$$

The continuum orbitals were represented by complex STO's, which were kept orthogonal to each other but not

TABLE II. Number of configurations used to describe the function spaces Φ_0^n, $X_{\rm loc}^n$, $X_{\rm as}^n$, number of complexified STO's used per open channel, and optimum values of the nonlinear parameters α and θ.

n	Φ_0^n	$X_{\rm loc}^n$	$X_{\rm as}^n$	Number of STO's per open channel	$\alpha_{\rm opt}$	$\theta_{\rm opt}$ (rad)
3	3	31	36	9	0.55	0.48
4	5	15	80	8	0.25	0.43
5	7	20	114	6	0.20	0.40

TABLE III. Energies from threshold (including the shift due to the mixing with the continuum), and total widths (in a.u.) for the $n=3,4,5$ ^1D TEIL states of H^-. Comparison is made with other theoretical results and experimental data.

E^n	Γ^n	E^n	Γ^n	E^n	Γ^n
$n=3$		$n=4$		$n=5$	
		State-specific complex eigenvalue theory (this work)			
0.065 436	0.001 28	0.038 708	0.000 96	0.025 372	0.000 68
		Other theoretical methods			
0.065 95[a]	0.001 6				
0.065 955[b]	0.001 635				
		0.038 750[c]	0.000 95	0.025 375[c]	0.000 650
0.065 975[d]		0.038 936[d]			
0.065 951[e]	0.001 57	0.038 754[e]	0.001 26		
0.065 953[f]	0.001 658				
		0.038 70[g]	0.001 25		
		Experiment[h]			
0.065 807[i]					

[a]Reference [11].
[b]Reference [12].
[c]Reference [13].
[d]Reference [14].
[e]Reference [15].
[f]Reference [16].
[g]Reference [17].
[h]We used 1 a.u. = 27.211 396 eV.
[i]Reference [18].

to the radials present in the localized part of the wave function. By combining the two function spaces, a complex non-Hermitian, nonorthonormal Hamiltonian matrix is constructed (e.g., [3,6,7]). Its solution is carried out for different values of the rotation angle θ, and of the nonlinear parameter in the complex STO's, α, until the complex eigenvalue of the resonance state at each n is stabilized (see Table II). The corresponding root fixes the coefficients $c^{n'l'l}$ of the channels within $X^n_{\rm as}$. Then, the partial widths including the interactions to all orders are given by [3,6,7,10]

$$\gamma_{n'l'l} = -2\,\mathrm{Im}\left[\frac{c^{n'l'l}}{c_0}\langle \Psi_0^n | H | u(n'l',\varepsilon l)\rangle\right], \qquad (3)$$

a simple relationship between the observable partial width and the corresponding configuration-interaction (CI) coefficient of the open channel.

Our results for the energies and the total widths are presented in Table III, which also includes results obtained with other theoretical methods [11–17] which, however, are aimed at the calculation of resonances without identifying them as Wannier TEIL states. There is also an experimental energy for $n=3$ [18]. The previous calculations were performed by applying Feshbach's projection-operator formalism [14], the close-coupling theory [12,17], and R-matrix theory [15] and the conventional complex-coordinate rotation [11,13,16]. For

TABLE IV. Breakdown, percentagewise, of the total width of the $n=3,4,5$ ^1D TEIL states of H^- to partial widths calculated to all orders.

Channel \ n	3 (%)		4 (%)		5 (%)	
$1s\varepsilon d$	1.0		0.0		0.0	
$2s\varepsilon d$	14.7		0.1	4.1	0.4	
$2p\varepsilon p$	82.0	99.0	3.8		0.0	0.6
$2p\varepsilon f$	2.3		0.2		0.2	
$3s\varepsilon d$			16.5		1.0	
$3p\varepsilon p$			51.0		5.4	
$3p\varepsilon f$			2.5	95.9	0.5	8.5
$3d\varepsilon s$			21.2		1.2	
$3d\varepsilon d$			4.4		0.3	
$3d\varepsilon g$			0.3		0.1	
$4s\varepsilon d$					14.8	
$4p\varepsilon p$					45.8	
$4p\varepsilon f$					1.3	
$4d\varepsilon s$					15.6	
$4d\varepsilon d$					6.8	90.9
$4d\varepsilon g$					1.8	
$4f\varepsilon p$					4.7	
$4f\varepsilon f$					0.1	
$4f\varepsilon h$					0.0	

$n=4,5$ there is excellent agreement with the results produced by the large-scale computations of Ho, Callaway, and Bhatia [11,13,16]. For $n=3$, there is a small discrepancy. Scattering theories [12,15,17] have produced slightly different widths than the ones obtained by considering resonances as complex eigenvalues of a non-Hermitian Hamiltonian.

Our partial widths, the main goal of this work, are presented in Table IV. Here, there are no previous theoretical or experimental values.

From Tables III and IV, the following characteristics can be recognized immediately. As in the case of the ^1S and $^1P^o$ TEIL resonances [3,6], the lifetime of the ^1D resonances increases with increasing energy. This fact can be understood in terms of the reduction of bound-continuum wave-function overlap and of $\langle 1/r_{12} \rangle$ [19], as the electrons move apart with increasing principal quantum number n. Also as before, the closest threshold contributes the most to the decay probability. This fact, which was predicted in [3], is also seen in the experimental data of Halka *et al.* [20] for $^1P^o$ states. Finally, we note that the p-wave continua have the largest width.

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