

Validity of the isolated resonance picture for H<sub>2</sub> autoionizing statesFelipe Morales,<sup>1,\*</sup> C. William McCurdy,<sup>2,3</sup> and Fernando Martín<sup>1</sup><sup>1</sup>*Departamento de Química C-IX, Universidad Autónoma de Madrid, 28049-Madrid, Spain*<sup>2</sup>*Departments of Applied Science and Chemistry, University of California, Davis, California 95616, USA*<sup>3</sup>*Lawrence Berkeley National Laboratory, Chemical Sciences, Berkeley, California 94720, USA*

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The isolated resonance picture (IRP) is tested by comparing calculations on doubly excited autoionizing states of H<sub>2</sub> by using two different theoretical approaches: a recent implementation of the exterior complex scaling method and the standard Feshbach method with *B*-spline basis sets. These calculations demonstrate that the IRP can yield poor approximations to autoionization widths when doubly excited states approach the ionization threshold at large internuclear distances, *R*. In contrast, at small *R* where avoided crossings appear, the IRP produces accurate resonance parameters.

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Many resonance phenomena observed in H<sub>2</sub> photoionization or in the scattering of electrons by H<sub>2</sub><sup>+</sup> ions can be explained by the existence of doubly excited autoionizing states [1–11]. These states are commonly viewed as bound states embedded in a nonresonant continuum to which they decay after a short time (typically a few femtoseconds) due to the electron-electron interaction [12]. The use of this simple image requires the knowledge of the resonance parameters: the energy position *E<sub>s</sub>* and the autoionization width  $\Gamma_s$  (i.e., the inverse of the autoionization lifetime  $\tau_s = 1/\Gamma_s$ ). In the framework of the Born-Oppenheimer approximation, the values of these parameters depend on internuclear distance, as is the case for all molecular electronic properties (apart from symmetry). Therefore, a complete description of resonance phenomena in H<sub>2</sub> requires the knowledge of energy positions and autoionization widths in a wide range of internuclear distances. This area has been the subject of extensive theoretical investigations for more than three decades [13–21].

The extraction of autoionization parameters depends very much on the particular method used to describe autoionizing states, e.g., time-delay [22–24], *R*-matrix [16,18,25], Feshbach [26], or complex scaling [27,28] methods. This paper focuses on the latter two methods. In the Feshbach method, one defines two orthogonal subspaces *P* and *Q*. The wave functions of the doubly excited states (DESs) and the corresponding energies result from diagonalizing the Schrödinger equation in the *Q* subspace; the autoionization widths are obtained from a simple golden rule equation that describes the coupling between the DES and a nonresonant continuum that mostly belongs to the *P* subspace. This method has been and still is widely used because it provides a simple physical image in agreement with our intuition. Complex scaling methods directly provide energy positions and widths through the poles of the *S* matrix by assuming that the effect of the autoionization decay can be described by a non-Hermitian Hamiltonian that results from rotating the Schrödinger equation into the complex plane. Although

both methods are, in principle, exact (i.e., capable of producing exact results when numerically converged), many applications of the Feshbach method make use of a simplifying approximation: the isolated resonance picture (IRP), in which one neglects the effects of neighboring DESs on the state of interest.

In this paper we compare the results of the Feshbach theory [26], implemented both exactly [19] and in the IRP, with the results of exterior complex scaling (ECS) calculations that locate the poles of the *S* matrix directly [29–31]. The two methods should agree in the case of narrow, isolated resonances. As described by Feshbach himself in [26], in the case where the resonances are narrow but nearly overlapping there is reason to suspect that the IRP might not be a good approximation. We demonstrate that, in H<sub>2</sub>, the regions of avoided crossings between resonance states are still well described within the IRP. However, we have found that there is another context in which the IRP is unsuccessful: when polarization of the residual electron cloud by the outgoing electron is important. Such polarization occurs, e.g., when a DES is close to the ionization threshold and, therefore, it is important for the description of resonance phenomena near the threshold (e.g., the dissociative recombination of a slow electron with a H<sub>2</sub><sup>+</sup> ion or the radiative decay of the excited hydrogen atoms produced in the dissociation of H<sub>2</sub> by xuv photons [2,8,11,32,33]).

We start by briefly describing the ECS and Feshbach methods. In the ECS method, complex scaling is applied to the electronic coordinates *r* outside a fixed radius *R*<sub>0</sub> (which encloses the singular nuclear attraction potentials):

$$r \rightarrow \begin{cases} r, & \text{for } r \leq R_0 \\ R_0 + (r - R_0)e^{i\theta}, & \text{for } r > R_0 \end{cases} \quad (1)$$

In this method, the eigenvalues associated with the bound states of the scaled Hamiltonian *H*<sub>θ</sub> are the same as those of the original Hamiltonian *H*. Segments of the continuum spectrum of *H*<sub>θ</sub> beginning at each scattering threshold are rotated an angle 2θ. Isolated complex eigenvalues revealed by the rotated continua correspond to resonances. Their parameters are directly extracted from the ECS complex spec-

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trum:  $E_s = \text{Re}(E)$  and  $\Gamma = -2 \text{Im}(E)$ . These parameters are independent of  $\theta$ , as long as they are not covered by branches of the continuum spectrum of  $H_\theta$  and the basis set is practically complete. In an accurate calculation using the ECS approach, the isolated complex eigenvalues of the scaled Hamiltonian are the locations of the poles of the  $S$  matrix, and the interaction between different DESs is automatically included.

In the Feshbach method, the resonance energy is given by

$$E_s = \mathcal{E}_s + \text{Re}\langle \phi_s | Q \mathcal{H} P G_p^{(s)-}(E = \mathcal{E}_s) P \mathcal{H} Q | \phi_s \rangle \quad (2)$$

and the autoionization width by

$$\Gamma_s \equiv \sum_{\mu} \Gamma_{s,\mu} = 2\pi \sum_{\mu} |\langle P \psi_{\mu E = \mathcal{E}_s}^{0-} | P \mathcal{H} Q | \phi_s \rangle|^2, \quad (3)$$

where  $\phi_s$  is the resonant wave function of energy  $\mathcal{E}_s$ ; the solution of the projected Schrödinger equation

$$(Q \mathcal{H} Q - \mathcal{E}_s) \phi_s = 0, \quad (4)$$

$\psi_{\mu E}^{0-}$  is the nonresonant wave function in the  $\mu$  open channel that satisfies the equation

$$[P \mathcal{H} P + P \mathcal{H} Q G_Q^{(s)}(E) Q \mathcal{H} P - E] \psi_{\mu}^{0-} = 0, \quad (5)$$

where  $\Gamma_{s,\mu}$  is the  $\mu$  partial width, and  $G_p^{(s)-}$  and  $G_Q^{(s)}$  are Green's functions defined in the  $P$  and  $Q=1-P$  subspaces [34,35]. The index  $\mu$  represents a particular state of the remaining ion and the asymptotic angular momentum  $l$  of the outgoing electron. For two-electron systems,  $P = P_1 + P_2 - P_1 P_2$ , where  $P_i$  is a one-electron projection operator that includes all the  $H_2^+$  orbitals associated with the ionization thresholds lying below the DES of interest [36]. In an exact derivation of Feshbach theory, the integrals on the right-hand side of Eqs. (2) and (3) depend on energy [35]. They are just mathematical objects that allow one to express the exact scattering wave function in a convenient way for computations. The interpretation of these integrals as energy position  $E_s$  and autoionization width  $\Gamma_s$  comes from the fact that, for sufficiently narrow resonances, they are practically independent of energy and, therefore, can be assigned to the  $\phi_s$  resonance by fixing the energy,  $E = \mathcal{E}_s$ .

The Green function  $G_Q^{(s)}$  includes the effect of all DESs in the calculated wave functions but the  $\phi_s$  one. The IRP consists in neglecting  $G_Q^{(s)}$  wherever it appears. In other words, it consists in neglecting the coupling between resonance states in the  $Q$  space through the  $P$  space. In this approximation, the above equation reads:

$$[P \mathcal{H} P - E] \psi_{\mu E}^{0-} = 0, \quad (6)$$

where the potential  $V_p = P \mathcal{H} Q G_Q^{(s)}(E) Q \mathcal{H} P$  has been removed from Eq. (5). The IRP also affects the second term of Eq. (2) since the Green function  $G_p^{(s)-}$  contains information from the  $\psi_{\mu E}^{0-}$  wave functions for all  $E \neq \mathcal{E}_s$ . Neglecting  $G_Q^{(s)}$  is equivalent to using a restricted  $Q$  subspace containing a single adiabatic state,  $Q = |\phi_s\rangle\langle\phi_s|$ , instead of the exact  $Q$  subspace containing the whole spectrum that arises from Eq. (4).

All equations in this work have been solved in a basis of two-electron configurations built from  $H_2^+$  orbitals expanded in a basis of  $B$  splines (details about  $B$ -spline bases can be found in [37]). In the Feshbach calculations, we have used the same methods as in Ref. [19], namely a standard configuration interaction approach to solve Eq. (4) and the  $L^2$  close-coupling method to solve Eqs. (5) and (6). The configuration bases in both  $P$  and  $Q$  subspaces are the same as in Ref. [19], where it has been shown that they are accurate enough to describe the lowest DESs of each symmetry. In the ECS calculations, the configuration basis is the sum of the  $P$  and  $Q$  bases used in the Feshbach calculations, but scaled according to Eq. (1).

We have carried out calculations of energy positions and autoionization widths for the lowest  $Q_1$  DESs of  $H_2$  with  $^1\Sigma_g^+$  and  $^1\Pi_u$  symmetries. These symmetries have been chosen because they contain DESs that are relevant in  $e^- + H_2^+$  scattering and  $H_2$  photoionization (see, e.g., [2,7–9,11,32,33]). The calculated energies and widths are shown in Figs. 1 and 2 as functions of internuclear distance. The results from the exact Feshbach method have been taken from Ref. [19]. A detailed comparison with previous works can also be found in that reference [19].

Figures 1(a) and 2(a) show that the IRP does an excellent job in describing resonance energies since the results are practically identical to those obtained from exact theories for all internuclear distances. As discussed in previous works [15,19], the energy curves exhibit avoided crossings in the region of small internuclear distances,  $R < 2$  a.u. It is worth noting that the agreement is excellent even in this region. As can be seen, the energy curves cross the ionization threshold at larger internuclear distances, where the DESs become truly bound states. For the lowest  $^1\Sigma_g^+$  state, this occurs at around 2.8 a.u.

Figures 1(b) and 1(c) show that total widths obtained with exact Feshbach and ECS approaches are practically indistinguishable for all internuclear distances (irrespective of the fact that extraction of resonance parameters is based on quite different assumptions). The total widths obtained within the IRP agree with the exact ones at small internuclear distances but differ significantly from them when the DES approaches the ionization threshold at large internuclear distances. The same holds for the  $s$  and  $d$  partial widths. It is worth noting that the IRP widths are accurate in the vicinity of the avoided crossings, where the IRP is expected to fail. This is because the energy separation between DESs in this region is still larger than the corresponding widths. The failure of the IRP near the ionization threshold is due to the impossibility of describing the polarization of the remaining electronic cloud by the outgoing electron [by construction of the  $P$  operator, the ionic core is frozen unless  $G_Q^{(s)}$  is included in Eq. (5)]. Such an effect is more important when the outgoing electron is slow (as in the vicinity of the threshold) and it is included in the exact Feshbach approach through the polarization potential  $V_p$ .

Inclusion of polarization effects is relevant for an accurate description of the dissociative recombination process  $e^- + H_2^+ \rightarrow H + H$ , in which a slow electron is resonantly captured in a low lying DES that further dissociates into two neutral H atoms. All theoretical models developed so far to

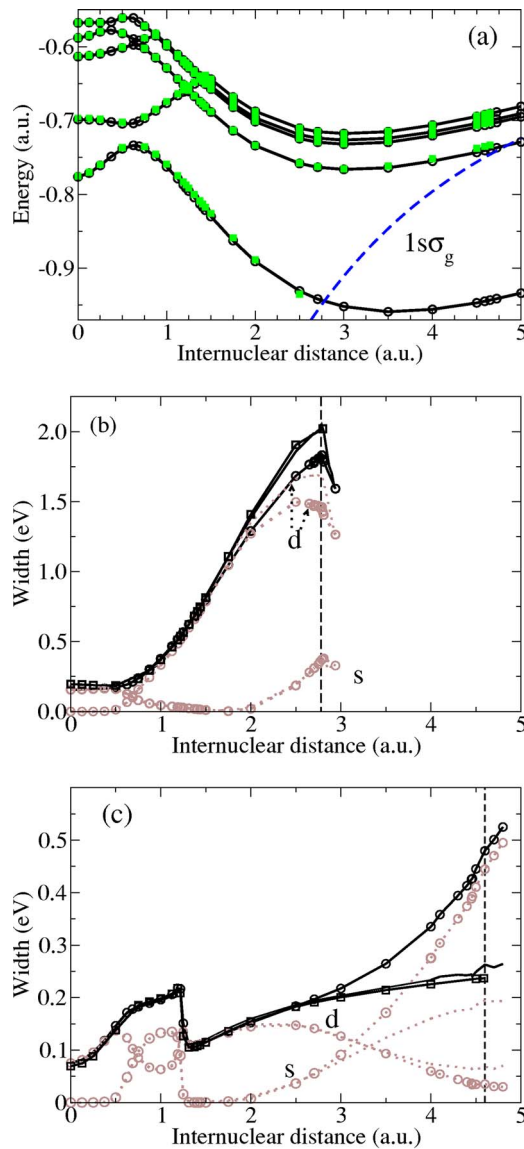


FIG. 1. (Color online) Resonance parameters as functions of internuclear distance for the  $1\Sigma_g^+$  symmetry. (a) Resonance positions. Full line, exact Feshbach results from [19]; squares, ECS results; circles, IRP Feshbach results. The dashed line shows the position of the  $1s\sigma_g$  ionization threshold. (b) Autoionization widths of the lowest DES. Full lines: total widths. Dotted lines: partial widths. Lines without symbols: exact Feshbach results from [19]; lines with squares, ECS results; lines with circles, IRP Feshbach results. The vertical dashed line indicates the internuclear distance where the DES crosses the ionization threshold. (c) The same as in (b) but for the second lowest DES.

study this process need total and partial autoionization widths, but also the couplings of the corresponding DESs with the Rydberg states that lie below the ionization threshold [8]. Such couplings entirely determine the population of the different dissociation channels and are usually represented in the form of a pseudowidth that smoothly correlates to the physical autoionization width above the threshold. Evaluation of these pseudowidths in the context of the Feshbach method is very simple if one encloses the system in a finite box that transforms the infinite series of Rydberg states

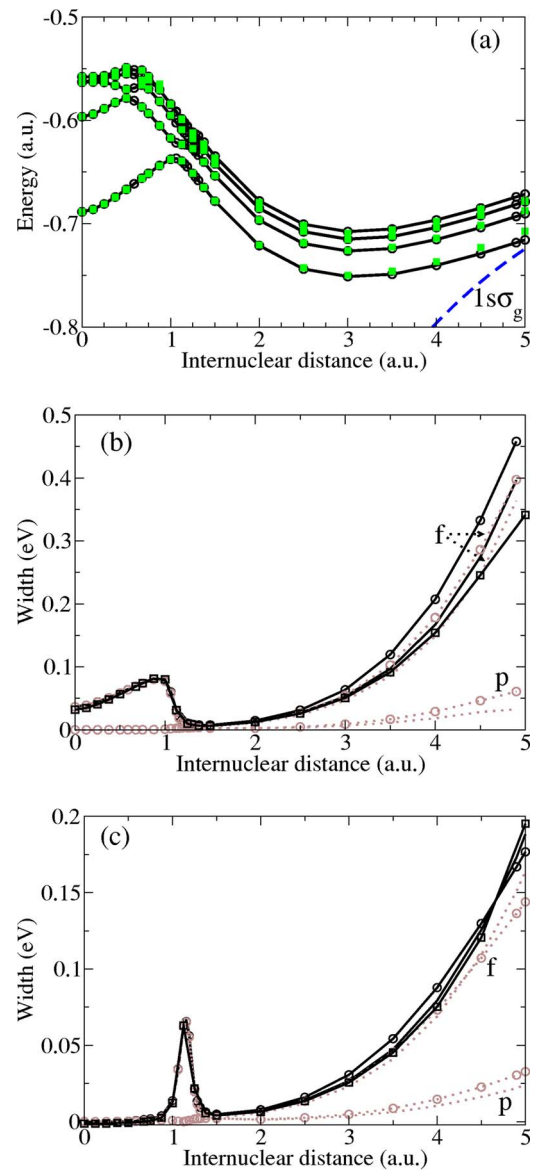


FIG. 2. (Color online) Resonance parameters as functions of the internuclear distance for the  $1\Pi_u$  symmetry. Notations as in Fig. 1.

in a fine set of discrete states similar to those used to represent true continuum states with an  $L^2$  integrable basis [38]. Figures 1(b) and 1(c) show that the pseudowidths obtained using the IRP beyond the crossing point between the DES and the ionization threshold significantly differ from the exact ones.

The results obtained for the DESs of  $1\Pi_u$  symmetry lead to similar conclusions. For this symmetry the main effect of the narrow avoided crossing is to produce abrupt variations of the widths with internuclear distances (see [15,19]). These variations are due to the sudden exchange of character in the region of the avoided crossing. However, the IRP still leads to an accurate description of both energies and widths. As it does for  $1\Sigma_g^+$  symmetry, the IRP fails for the states of this symmetry when the DES approaches the ionization threshold, although the errors are less pronounced than in the previous case. The same holds for the  $p$  and  $f$  partial widths.

In conclusion, we have shown that the isolated resonance picture is a reasonable approximation to describe (i) energy positions of DESs in the whole range of internuclear distances and (ii) the corresponding autoionization widths in the region of small and intermediate internuclear distances. At large internuclear distances, when the doubly excited state approaches the ionization threshold, the IRP fails in describing the autoionization widths due to the absence of polarization effects. This may have important consequences in the analysis of  $H_2$  dissociation into two neutral hydrogen atoms,

in particular, when extrapolations of autoionization widths (calculated at intermediate internuclear distances) are performed beyond the ionization threshold.

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