

## Resonance Coalescence in Molecular Photodissociation

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We study theoretically the photodissociation dynamics of the  $H_2^+$  molecular ion exposed to a linearly polarized laser light. It is shown that it is possible to choose a laser wavelength and intensity so as to produce a coalescence of two photodissociation vibronic resonance states. At such a coalescence point, also called an exceptional point, the photodissociative resonance wave function is self-orthogonal. This unique phenomenon which is presented here for light induced molecular dynamics enables us to transfer completely the nondissociated molecules from one vibronic state to another by varying adiabatically the laser frequency and intensity along a closed contour which encircles the exceptional point.

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When molecules are exposed to laser fields, their bound states become metastable (the so-called resonances) which have a finite lifetime due to ionization and/or dissociation. In the present Letter, we consider the photodissociation of  $H_2^+$ . The corresponding rates of decay  $\Gamma$  or lifetimes  $\hbar/\Gamma$  depend on the initial vibrational state and are associated with the imaginary part of the complex energy eigenvalues  $E - i\Gamma/2$  of the molecular Hamiltonian dressed by light. These eigenvalues represent the poles of the scattering matrix [1–3]. The value of  $\Gamma$  depends on the laser parameters (wavelength  $\lambda$  and intensity  $I$ ). It might happen that for very specific laser parameters two different resonances (each of them being issued from a different field-free vibrational state of  $H_2^+$ ) coalesce. This special situation cannot be adequately treated within the framework of the conventional Hermitian quantum mechanics (QM) where all of the state vectors possess a real positive definite norm and even the concept of a resonance is not well defined. The coalescence of two different mutually orthogonal resonance states into a *single* self-orthogonal state can be mathematically defined only within the framework of the non-Hermitian formalism of QM, where complex energy eigenvalues appear and where one deals with complex valued norms defined on the basis of the so-called  $c$  product [4]. The points  $(\lambda, I)$  in parameter space where self-orthogonality occurs are usually called exceptional points (EPs) [5,6]. In the present Letter, we will show that self-orthogonal resonance states do exist in the context of molecular photodissociation and have important experimentally observable consequences. Namely, we shall exploit the self-orthogonality phenomenon to build a chirped laser pulse which operates a selective transfer from one vibronic state of  $H_2^+$  into another for those molecules which have not dissociated during the process of interaction with the pulse.

Self-orthogonality phenomena in atomic physics have been analyzed theoretically a long time ago [7] for the case of the complex rotated Hamiltonian of the helium atom.

More recently, different manifestations of the EP phenomenon have been described in optics [8], in atomic physics [9,10], in electron-molecule collisions [11], superconductors [12], quantum phase transitions in a system of interacting bosons [13], and electric field oscillations in microwave cavities [14], and in  $\mathcal{PT}$ -symmetric waveguides [15]. Varying the Hamiltonian parameters in an adiabatic way along a closed path which encircles the EP has been examined in a study of Hernández, Jáuregui, and Mondragón [16], who have shown that there is an interchange between the two distinct resonance solutions which merge at the EP. This is a characteristic feature of an EP, interpreted mathematically as an effect of the multivaluedness of a function of a complex variable detected whenever going around a branch point. To the best of our knowledge, no theoretical or experimental work regarding EPs has so far been pursued in the context of laser driven photodissociation dynamics of molecules. It is the purpose of the present work to demonstrate numerically the existence and physical implications of EPs for the case of laser induced photodissociation dynamics of  $H_2^+$ . The Hamiltonian parameters to be varied here are the intensity and frequency of a linearly polarized laser light.

Let us briefly outline the theoretical formulation of the molecular photodissociation problem. We assume that the laser field couples only the two electronic states  $X^2\Sigma_g^+$  and  $A^2\Sigma_u^+$  of  $H_2^+$ , denoted hereafter as  $|g\rangle$  and  $|u\rangle$ , respectively. The associated Hamiltonian is expressed as a 2-by-2 matrix

$$\mathbf{H}(t) = \begin{pmatrix} T_R + V_g(R) & d(R)\mathcal{E}_0 \cos(\omega_L t) \\ d(R)\mathcal{E}_0 \cos(\omega_L t) & T_R + V_u(R) \end{pmatrix}. \quad (1)$$

Here  $R$  stands for the vibrational coordinate, and  $T_R = [-\hbar^2/(2\mu_{H_2^+})](d^2/dR^2)$  is the usual vibrational kinetic energy operator, with  $\mu_{H_2^+}$  the reduced mass. The functions  $V_{g,u}(R)$  represent the potential energy curves of the two electronic states. The dipole matrix element between these two electronic states is denoted as  $d(R)$ . The standard

length gauge with dipole approximation is used, with symbols  $\mathcal{E}_0$  and  $\omega_L$  defining, respectively, the amplitude and frequency of the monochromatic laser light. The wavelength is  $\lambda = 2\pi c/\omega_L$ . Since the Hamiltonian is time periodic with period  $T = 2\pi/\omega_L$ , the light induced molecular dynamics can be most conveniently studied using the formalism of the Floquet theory [17]. This essentially means the use of an ansatz  $|\Psi(R, t)\rangle = e^{-iE_F t/\hbar}|\Phi_F(R, t)\rangle$ , where  $E_F$  is the so-called quasienergy. In our case  $|\Phi_F(R, t)\rangle = \phi_g(R, t)|g\rangle + \phi_u(R, t)|u\rangle$ . The Schrödinger equation becomes now equivalent to a Floquet eigenvalue problem

$$\left[ \mathbf{H}(t) - i\hbar \frac{\partial}{\partial t} \right] \begin{pmatrix} \phi_g(R, t) \\ \phi_u(R, t) \end{pmatrix} = E_F \begin{pmatrix} \phi_g(R, t) \\ \phi_u(R, t) \end{pmatrix}, \quad (2)$$

where the time variable  $t$  is treated as an additional dynamical coordinate running through an interval  $[0, T]$ . Note that the quasienergy  $E_F$  plays to some extent the same role as an eigenenergy of a time-independent Hamiltonian. By applying the Fourier expansion

$$\phi_{g,u}(R, t) = \sum_{n=-\infty}^{n=+\infty} e^{in\omega_L t} \varphi_{g,u}^n(R), \quad (3)$$

one obtains from problem (2) an equivalent set of coupled equations

$$\begin{aligned} [T_R + V_g(R) + n\hbar\omega_L - E_F] \varphi_g^n(R) \\ + d(R)(\mathcal{E}_0/2)[\varphi_u^{n+1}(R) + \varphi_u^{n-1}(R)] = 0 \end{aligned} \quad (4)$$

accompanied by similar equations constructed via an interchange of subscripts  $g \leftrightarrow u$ . The above representation of the solutions of the time-dependent Schrödinger equation as a Floquet eigenvalue problem is physically insightful since it enables one to interpret different coupled channels (labeled by index  $n$ ) in terms of the number of photons that the molecule has absorbed or emitted [17]. The excited state electronic potential  $V_u(R)$  is purely repulsive, leading thus to photodissociation in the presence of the laser. For this reason, the system of coupled eigenvalue equations (4) does not possess any bound state solutions as soon as  $\mathcal{E}_0 \neq 0$ . Resonances are characterized by outgoing boundary conditions [1–3,18]. This is compatible only with quantized complex eigenenergies identifiable as poles of the scattering matrix. The real part  $\text{Re}(E_F)$  of a given complex Floquet eigenvalue  $E_F$  is interpreted physically as the energy of the resonance state, whereas  $\Gamma_F = -2\text{Im}(E_F)$  determines the corresponding decay rate. Outgoing boundary conditions imply that the resonance wave functions are not square integrable. To overcome this difficulty, we shall follow the well established approach of complex scaling transformations [2,3] which forces the resonance wave functions to decay exponentially as  $R \rightarrow \infty$ . After the complex scaling transformation is implemented, the so-called self-overlap  $\sigma$  of a given resonance solution  $\Phi_F(R, t)$  is evaluated as

$$\sigma = \sum_{n=-\infty}^{n=+\infty} \int_0^\infty dR \{ [\varphi_g^n(R)]^2 + [\varphi_u^n(R)]^2 \}. \quad (5)$$

Expression (5) is used to study the self-orthogonality phenomenon that occurs whenever two photodissociation resonances coalesce. Importantly, no complex conjugates of the Fourier components  $\varphi_{g,u}^n(R)$  are taken here, in consistency with the definition of the non-Hermitian  $c$  product (see Refs. [2,4]). The self-orthogonality phenomenon cannot be properly described using the standard Hermitian definition of  $\sigma$  where the usual complex conjugates of  $\varphi_{g,u}^n(R)$  would appear. The photodissociation resonances of  $H_2^+$  were calculated previously [19,20]. We use the  $H_2^+$  potential energy curves and the transition dipole element taken from the work of Bunkin and Tugov [21]. The coupled eigenvalue equations (4) are solved on a grid using a matching technique based on the Fox-Goodwin propagator, with exterior complex scaling [19].

Figure 1 shows an outcome of our numerical calculations aimed at demonstrating the existence of coalescent photoinduced resonances for specifically chosen wavelengths  $\lambda_{\text{EP}}$  and intensities  $I_{\text{EP}}$  ( $\approx \mathcal{E}_0^2$ ). Energies and rates are evaluated as a function of intensity for various  $\lambda$ 's until a near coincidence of both energies and rates is obtained. We have found that the resonance associated with the field-free vibronic bound state  $v = 8$  coincides with that of  $v = 9$  at  $\lambda_{\text{EP}}^{8-9} = 442.26$  nm and  $I_{\text{EP}}^{8-9} = 0.3949 \times 10^{13}$  W/cm<sup>2</sup>. Another coalescence point corresponding to  $v = 9$  and  $v = 10$  is detected at  $\lambda_{\text{EP}}^{9-10} = 401.14$  nm and  $I_{\text{EP}}^{9-10} = 0.5130 \times 10^{13}$  W/cm<sup>2</sup>. In both cases the tangents to the curves of Fig. 1 at the exceptional points are vertical (i.e., showing a cusp behavior at the EP [16]). We have also checked the characteristic signature of the EP on the wave functions. More precisely, the resonance wave

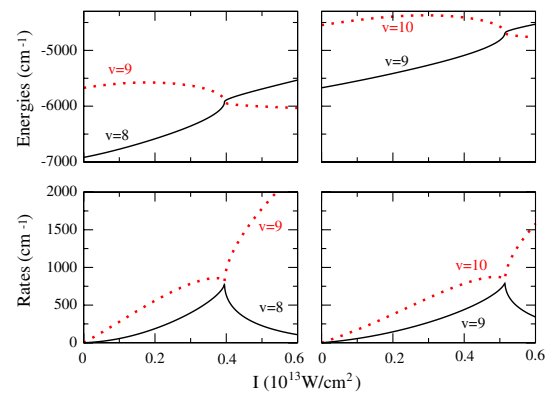


FIG. 1 (color online). Left column: Near coincidence of two resonance energies issued, respectively, from the field-free vibrational states  $v = 8$  and  $v = 9$  of the  $X^2\Sigma_g^+$  state of  $H_2^+$  for the laser parameters  $\lambda_{\text{EP}}^{8-9} = 442.26$  nm and  $I_{\text{EP}}^{8-9} = 0.3949 \times 10^{13}$  W/cm<sup>2</sup>. Right column: The same for the case of  $v = 9$  and  $v = 10$  and  $\lambda_{\text{EP}}^{9-10} = 401.14$  nm and  $I_{\text{EP}}^{9-10} = 0.5130 \times 10^{13}$  W/cm<sup>2</sup>.

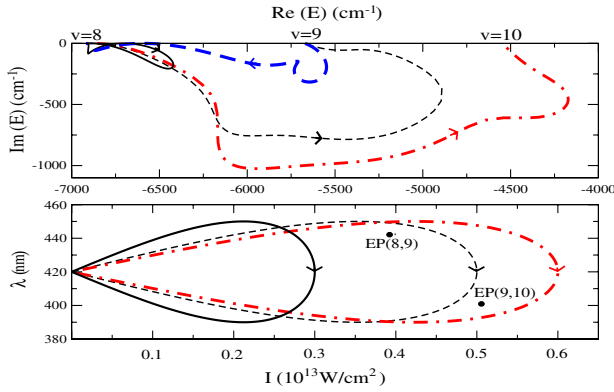


FIG. 2 (color online). Lower panel: Different contours in the parameter plane with no EPs encircled (solid black curve), with one EP  $\nu = 8, 9$  encircled (dashed black curve), and two successive EPs  $\nu = 8, 9$  and  $\nu = 9, 10$  encircled (dashed-dotted red curve). The corresponding trajectories in the energy plane are shown in the upper panel, in each case with the associated initial state and the final state. Note that for the pair 8–9 we have two trajectories, starting either from  $\nu = 8$  (dashed black curve) or from  $\nu = 9$  (long dashed blue curve).

functions become indistinguishable from one other (and thus self-orthogonal) when approaching the EP. Close to the EP a dramatic reduction of the self-overlap  $\sigma$  is observed numerically (at the EP  $\sigma = 0$ ).

As mentioned in the introductory part, the presence of an EP has also important consequences, which should become apparent when going adiabatically around the EP along a closed contour in the  $(I, \lambda)$  parameter space using an appropriate chirped pulse. Figure 2 demonstrates that this is indeed the case also in the present context of molecular photodissociation. The considered closed contour is defined by formulas

$$I = I_{\max} \sin(\phi/2), \quad \lambda = \lambda_0 + \delta\lambda \sin(\phi), \quad (6)$$

where the parameter  $\phi$  runs from 0 to  $2\pi$ . Our calculations were done for three distinct closed contours. The first one is obtained by setting  $I_{\max} = 0.3 \times 10^{13}$  W/cm<sup>2</sup>,  $\lambda_0 = 430$  nm, and  $\delta\lambda = 30$  nm. This contour does not encircle any EP. Starting from the  $\nu = 8$  vibronic molecular state at  $I = 0$  and completing the closed loop which returns to  $I = 0$ , one finds that the molecule returns to its  $\nu = 8$  vibronic field-free state, provided of course that dissociation did not take place during the passage along the loop. In the next paragraph, we examine the corresponding dissociation probability and give numerical estimates showing that a considerable portion of molecules is indeed left undissociated. Before delving into these matters, let us look at the second contour which is constructed by increasing  $I_{\max}$  to  $0.5 \times 10^{13}$  W/cm<sup>2</sup>. This contour is much more interesting since it encircles the EP associated with  $\nu = 8$  and  $\nu = 9$ . Figure 2 clearly shows that, by starting from the  $\nu = 8$  (or reciprocally  $\nu = 9$ ) vibronic molecular state at  $I = 0$  and completing the closed loop which returns to  $I = 0$ , one

finds the molecule in its  $\nu = 9$  (or reciprocally  $\nu = 8$ ) vibronic field-free state. Of course, this applies again only if not all molecules have dissociated during an adiabatic passage along the loop. If a significant portion of undissociated molecules is left after completion of the contour, we have achieved a selective light induced transfer between two specific molecular vibronic states. The third contour drawn in Fig. 2 uses  $I_{\max} = 0.6 \times 10^{13}$  W/cm<sup>2</sup> and encircles two EPs corresponding to  $\nu = 8, 9$  and  $\nu = 9, 10$ . Here, starting from  $\nu = 8$  at  $I = 0$  leads to a transfer into the  $\nu = 10$  vibronic state after completion of the loop. This behavior can again be exploited in the context of coherent control.

In order to obtain a well defined estimate of the fraction of undissociated molecules left after completion of a loop, we shall employ the formalism of the adiabatic Floquet theory [20,22]. This assumes that the chirped laser pulse envelope and its frequency vary sufficiently slowly with time such that the overall fraction of nondissociated molecules  $P_{\text{ND}}$  is given as

$$P_{\text{ND}} = \exp\left[-\int_0^{t_f} \Gamma_F(t) dt\right]. \quad (7)$$

Here  $\Gamma_F(t)$  is associated with the relevant Floquet quasi-energy eigenvalue calculated using the instantaneous field parameters at time  $t$ , and the symbol  $t_f$  stands for the duration of the light pulse. Let us consider a chirped pulse built by choosing  $\phi = 2\pi t/t_f$  in Eq. (6). We have previously shown [20] that for the choice of  $t_f = 56$  fs (about 40 optical cycles) the light induced molecular dynamics of  $H_2^+$  follows indeed an adiabatic path, as demonstrated by comparison with time-dependent wave packet evolution. Now we are ready to estimate what fraction of molecules remains undissociated after they are exposed to different chirped pulses generating different loops shown in Fig. 2. Consider first the 8 to 8 process (first loop in the parameter plane of Fig. 2). Equation (7) yields  $P_{\text{ND}} \doteq 0.25$ . This means that at the end of the pulse there is a quarter of the molecules back in the initial state. More important of course is the case of the 8 to 9 or 9 to 8 transfers. We observe in Fig. 2 that the instantaneous rates  $\Gamma_F(t)$  differ considerably for the two  $8 \rightarrow 9$  and  $9 \rightarrow 8$  trajectories, with the  $9 \rightarrow 8$  process being better protected against dissociation. Correspondingly, Eq. (7) implies  $P_{\text{ND}}$  to be very close to zero ( $\sim 0.001$ ) for the  $8 \rightarrow 9$  transfer, while  $P_{\text{ND}} \sim 0.1$  for the  $9 \rightarrow 8$  transfer. The just discussed asymmetry between the two opposite processes arises due to the fact that the same point on the laser parameter loop corresponds to two different resonances, depending on the choice of the initial molecular vibronic state.

We can summarize by saying that for the laser parameters we have used in our calculations it turns out that the transition from the 9th vibrational level of  $H_2^+$  to the 8th one is feasible by our new mechanism which is based on the self-orthogonality phenomenon (10% of the molecules

do not dissociate during the application of the adiabatically chirped laser pulse), while the 8th to 9th transition is not feasible. Owing to the multichannel character of the formalism, the observed coherent control scheme is expected to persist for other molecular species and with the introduction of rotational degrees of freedom. Other possible signatures of exceptional points would be to examine, in the context of photodissociation, the zeros in absorption line shapes resulting from the interference between overlapping resonances, as done by Shapiro [23,24]. An EP is actually an extreme case of overlap. Such signatures have already been discussed in scattering processes for one-dimensional model systems by Vanroose *et al.* [25] and Hernández, Jáuregui, and Mondragón [26].

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