Zero-width Resonances and Exceptional Points in Laser-induced Molecular Photodissociation

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Zero-Width Resonances (Oximorons!)

Zero-Width Resonances (ZWR) occur in different contexts

As early as 1929 von Neumann and Wigner (Phys. Z. **30**, 465) have devised a potential leading to an integrable wave function with a positive energy. Another example: two closed channels interacting with an open channel, with near degeneracy of two resonances (H. Friedrich and D. Wintgen, Phys. Rev. A **32**, 3231(1985)). In the molecular context: Predissociation in the intermediate coupling regime. First described by Bandrauk and Child, Mol. Phys. **19**, 95(1970). This is related to a coincidence or near-coincidence between "diabatic" and "adiabatic" energies. It is also possible to view this phenomenon as implying the destructive interference of two paths contributing to the outgoing scattering amplitude in the open channel. The resonances of the present study belong to this category.

Zero-Width Resonances (ZWRs) in intense-field molecular photodissociation

OUTLINE

- ZWRs in C_+ predissociation from interfering paths: a review
- Intense-field photodissociation: the Floquet
- The Floquet formalism can be used even for a pulsed laser
- Examples of critical intensities giving ZWRs for H_2^+
- Filtering of a particular vibrational state

Potential arrangement in C_+ predissociation

Crossing to the right of equilibrium distance. The condition for the occurrence of a zero-width resonance can be derived from a short-range study in the dash-dotted rectangle. In a semiclassical approach all quantities are expressed in terms of the wave numbers associated with the adiabatic potentials.
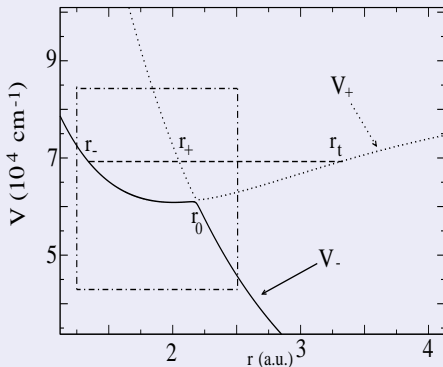
Interfering paths of the semiclassical picture

The boxes symbolize the avoided crossing region. The avoided crossing acts as a beam splitter. An incoming wave of amplitude C''_+ on the upper adiabatic potential meets the lower box. The interfering paths which can produce a vanishing of the total outgoing amplitude C'_- in the open lowest adiabatic channel are shown in red and green.
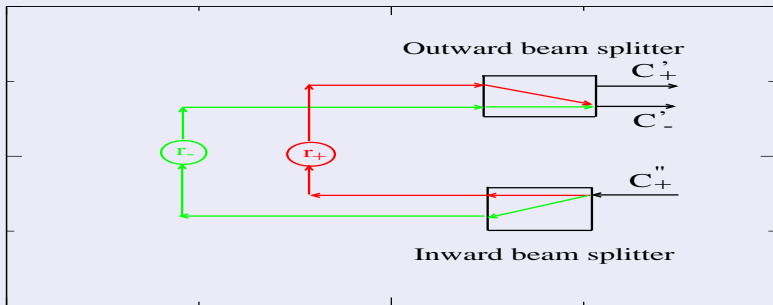
Outgoing scattering amplitude

The outgoing scattering amplitude C'_{-} can be written

$$C'_{-} \propto e^{2i\Phi_1} - e^{2i\Phi_2}$$

with

$$\Phi_1 = \int_{r_+}^{r_0} dr \; k_+(r) + \int_{r_0}^{r_t} dr \; k_+(r) + \chi$$

$$\Phi_2 = \int_{r_-}^{r_0} dr \; k_-(r) + \int_{r_0}^{r_t} dr \; k_+(r)$$

These combinations of integrals are similar to those found in the Bohr-Sommerfeld quantization rule. However in Φ_1 with integrals over the wave numbers of the upper adiabatic potential, there is a phase correction χ equal to $-\pi/4$ in weak coupling and zero in strong coupling. The phase Φ_2 implies in part the lower adiabatic potential and in part the upper adiabatic potential. There is a discontinuity at the crossing point.

Quenching of Predissociation

The condition for the vanishing of $C_{-}^{'}$ can now be formulated. Let us assume that the energy E is such that the two following conditions can be simultaneously satisfied

$$\Phi_1 = (v_+ + \frac{1}{2})\pi \quad \rightarrow \quad e^{2i\Phi_1} = -1 \qquad \Phi_2 = (v_d + \frac{1}{2})\pi \quad \rightarrow \quad e^{2i\Phi_2} = -1$$

where v_+ and v_d are two integers. It means that there is a coincidence between a corrected adiabatic energy and a corrected diabatic energy. This is a sufficient condition for the vanishing of the outgoing amplitude in the lower (open) adiabatic channel. Such a coincidence can only be accidental in the predissociation problem, since the potentials and the couplings cannot be modified at will. One possibility, however, is to look at a series of levels differing by the rotational quantum number. This was the case in the *IBr* spectrum analyzed by Child.

Intense-field photodissociation of a diatomic species

When the rotational period is much longer than the laser pulse duration, only the interatomic distance R is needed in the quantum-mechanical description of the nuclear motion

$$|\Psi(R,t)\rangle = \chi_1(R,t)|1\rangle + \chi_2(R,t)|2\rangle$$

The nuclear wave functions are solutions of the time-dependent Schrödinger equation, written in the length-gauge as :

$$i\hbar\frac{\partial}{\partial t}\left[\begin{array}{c} \chi_1(R,t) \\ \chi_2(R,t) \end{array}\right] = \left\{T_N + \left[\begin{array}{cc} V_1 & 0 \\ 0 & V_2 \end{array}\right] - \mu_{12}E(t)\left[\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array}\right]\right\}\left[\begin{array}{c} \chi_1(R,t) \\ \chi_2(R,t) \end{array}\right]$$

where T_N is the nuclear kinetic energy operator and $E(t)$ the laser electric field amplitude. V_1 and V_2 are the two electronic potential energies of states $|1>$ and $|2>$. In the following V_1 is assumed to support a series of bound vibrational states while V_2 is purely repulsive. This is the situation in H_2^+. μ_{12} is the electronic transition moment, generally function of R.

Floquet Approach

The Floquet ansatz is applied by writing

$$\left[\begin{array}{c} \chi_1(R,t) \\ \chi_2(R,t) \end{array} \right] = e^{-iE_F t/\hbar} \left[\begin{array}{c} \phi_1(R,t) \\ \phi_2(R,t) \end{array} \right]$$

E_F is the quasi-energy. $\phi_k(R,t), (k=1,2)$ being time-periodic, they can be Fourier expanded as

$$\phi_k(R,t) = \sum_{n=-\infty}^{+\infty} e^{in\omega t} \Psi_{k,n}(R)$$

Floquet Coupled Equations

Introduction of these Fourier expansions in the wave equation and integration over an optical cycle produces, if the field is weak enough to allow only for a one-photon absorption the coupled equations

$$\left[T_N + V_1 + n\,\hbar\omega - E \right]\Psi_1(R) - \frac{E_0}{2}\mu_{12}(R)\Big[\Psi_2(R)\Big] = 0$$

$$\left[T_N + V_2 + (n-1)\,\hbar\omega - E \right]\Psi_2(R) - \frac{E_0}{2}\mu_{21}(R)\Big[\Psi_1(R)\Big] = 0$$

The analogy with Quantum Electrodynamics is striking. Of course in QED n has to be positive and the coupling is proportional to $\sqrt{n}$. This is of no importance if the n is large. The Floquet formalism is an energy-conserving description.

Dressed Molecular Picture

The coupled equations express the fact that the initial molecular state in the presence of a photon is coupled to the dissociative continuum. Note the similarity between the potential arrangement and that of predissociation. Solution of the coupled equations with the outgoing wave conditions appropriate for a decaying system yields a complex quasi-energy.
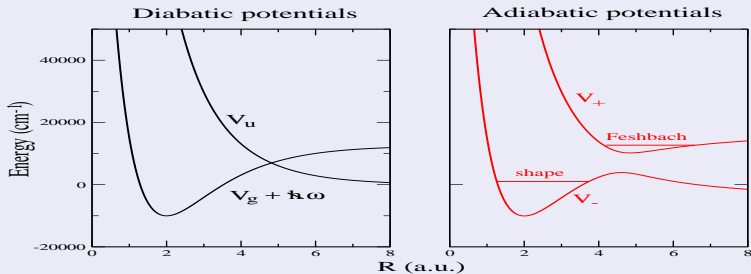
Adiabatic Floquet picture

The Floquet method assumes that the cw field is permanantly present. The adiabatic Floquet picture uses the Floquet results to describe the effect of a pulsed field. Let us assume that the initial wave function is that of a vibrational state of the field-free molecule, say $\chi_v(R)$. For a sufficiently smooth pulse we expect the Floquet wave function to behave as

$$\left[\begin{array}{c} \chi_1(R,t) \\ \chi_2(R,t) \end{array} \right] = e^{-\frac{i}{\hbar} \int_0^t E(t') dt'} \left[\begin{array}{c} \phi_1(R,t) \\ \phi_2(R,t) \end{array} \right]$$

with $\phi_1(R,0) = \chi_v(R)$ and $\phi_2(R,0) = 0$. The Floquet wave function is calculated at each instant $\bar{t}$ with the cw field $f(\bar{t}) E_0 \cos(\omega t)$. Since photodissociation implies the existence of at least one open channel the "quasi-energy" $E(t)$ is in fact a complex resonance energy of the form $E_R(t) - i\Gamma(t)/2$, $\Gamma(t)$ being the rate. The probability for the system to return to the initial vibrational bound state at the end of the pulse t_f is:

$$P_{bound} = \exp[-\frac{i}{\hbar} \int_0^{t_f} \Gamma(t') \, dt']$$

Critical intensities

Example with lower frequency $\lambda = 420$ nm. The Floquet rate is calculated versus intensity for the initial state $v_{diab} = 8$ of the molecular ion H_2^+. At an intensity $\sim 0.1335 \; 10^{13} \; W/cm^2$, the rate can be made practically zero by "zooming" in this region.
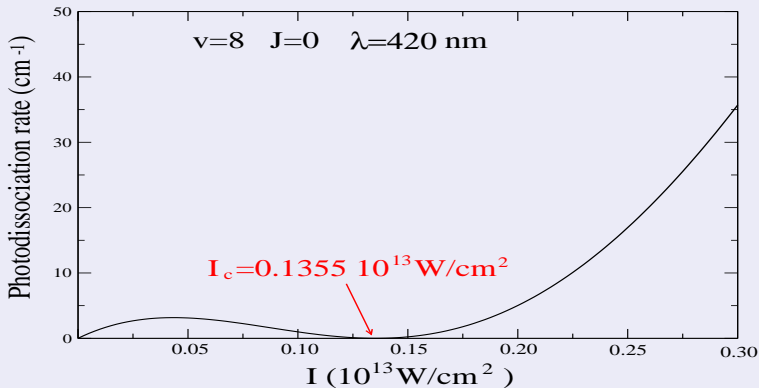
Adiabatic Floquet rates

The laser pulse shown in the upper panel is of duration 56 fs and maximum intensity $0.3 \, 10^{13} \, W/cm^2$. The Floquet rate is calculated as a function of time for four initial free-field states $v = 7$ to $v = 10$. The intensity passes twice through the critical intensity for $v = 8$, but is a little too low to reach the critical intensity for $v = 10$. The large widths of $v = 7$ and $v = 9$ are assigned to the shape character of these two resonances.
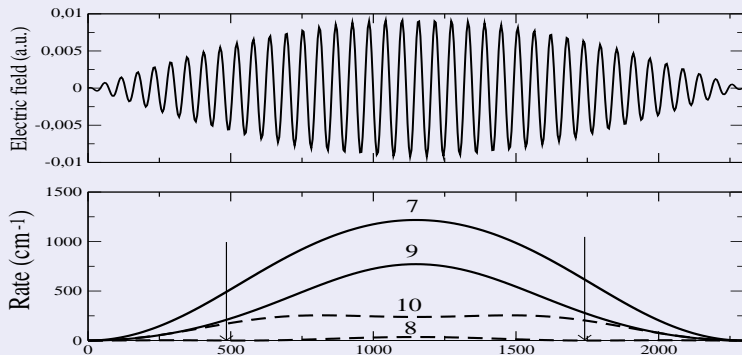
Survival probabilities

The initial states are in turn $v = 7$ to $v = 10$. The probability to remain in the initial state is calculated either with the wave packet formalism

$$P_v = | < \chi_v(R) | \chi_g(R, t_f) |^2$$

or according the expression given by the Floquet adiabatic treatment.
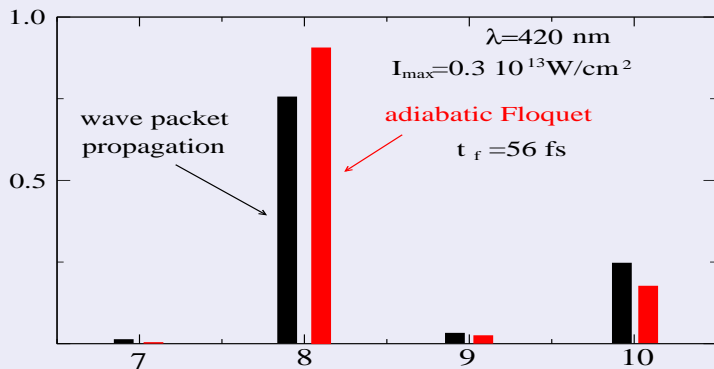
Filtering a vibrational state

The Floquet picture shows that when applying a laser pulse the vibrational states of the molecule evolve in different aways, according to whether there is or not a ZWR on the way. This is confirmed by the time evolution of coherent combinations of vibrational functions. For an initial combination $3^{-\frac{1}{2}}[\chi_7 + \chi_8 + \chi_9]$ we have at the end of a pulse of duration $t_f = 56$ fs, of maximum intensity $I_{max} = 0.3 \ 10^{13} \ W/cm^2$ and for a wave length $\lambda = 420$ nm:

$$P_{bound} = \sum_v \ |<\chi_v(R)|\chi_g(R, t_f)|^2 = 0.2960$$

The populated channels are

$$P_7 = |<\chi_7(R)|\chi_g(R, t_f)>|^2 = 0.0021$$

$$P_8 = |<\chi_8(R)|\chi_g(R, t_f)>|^2 = 0.2852$$

$$P_9 = |<\chi_9(R)|\chi_g(R, t_f)>|^2 = 0.0044$$

Conclusions about the ZWRs

The various vibrational states behave quite differently when subjected to a high-intensity laser field. The classification into initial states leading or not to a ZWR is dependent on the laser frequency. This opens a route to filtration scenarios. If a coherent combination of field-free vibrational functions makes up the initial state, for a conveniently chosen pulse (duration, maximum intensity, frequency), only those states showing the ZWR phenomenon will survive.

Exceptional points in physics

Many problems of physics (classical and quantum) require the determination of complex frequencies or energies when dissipation is at work. Examples are coupled damped oscillators, field distributions in microwave cavities, ionization and dissociation processes, etc. When it is possible to modify the parameters of the system in such a way as to produce a degeneracy of two complex frequencies or energies, the corresponding point in parameter space is called an Exceptional Point (EP), after Kato. Many examples have been explored recently. For reviews, see Berry and Heiss.

T. Kato, *Perturbation Theory of Linear Operators* (Springer, Berlin, 1966).
M. V. Berry, Czech. J. Phys., **54**, 1039(2004)
W. D. Heiss, Czech. J. Phys., **54**, 1091(2004)

Exceptional points in molecular photodissociation

Our example is again the case of a molecule interacting with a cw laser field. We are now interested by the possibility, with an appropriate choice of laser frequency and intensity to provoke the coalescence of two Floquet quasi-energies, with an associated Exceptional Point (EP) in the parameter plane. The molecule Na_2 in the vibrational states of the $^3\Sigma_u^+$ electronic state reached by laser photoassociation and exposed to a laser producing photodissociation toward the $^3\Pi_g$ state serves as the example because of the importance of this species for molecular cooling.

OUTLINE

- The dressed picture for Na_2
- Energies and rates at the EP
- Transfer scenarios around an EP
- Check of the transfer scenario with the adiabatic Floquet formalism
- Clusters of EPs. Cooling scenarios
- Conclusions

Dressed picture for Na$_2$

The upper potential of the left panel has been lowered by 0.0879 a.u., corresponding to a photon wavelength 564 nm.
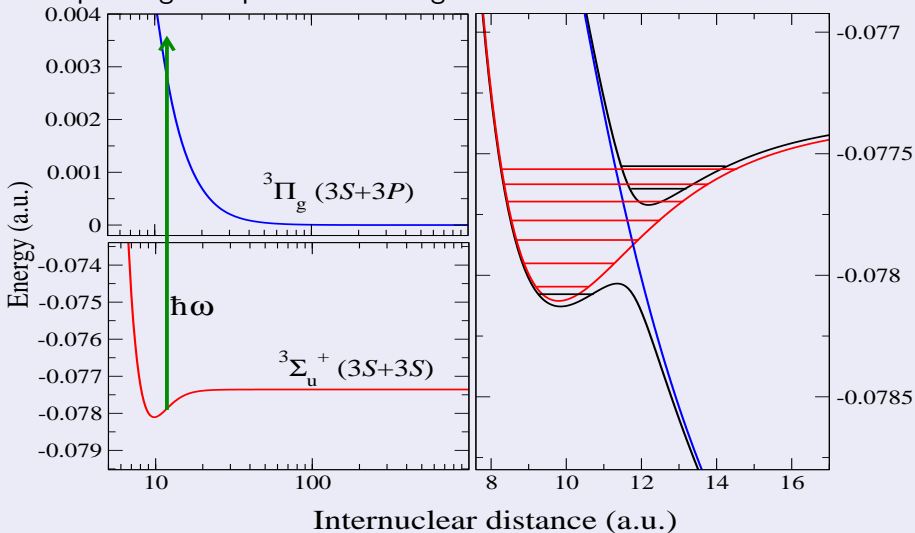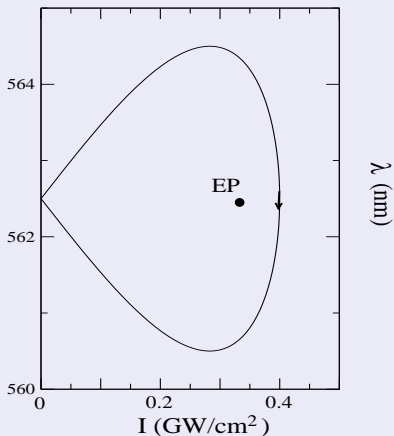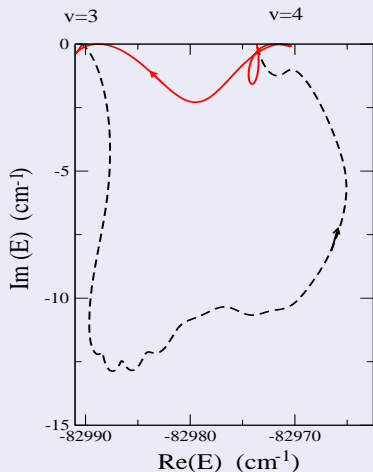
Generic picture near an EP

At the EP there is coalescence of the resonances issued from the field-free vibrational states $v = 3$ and $v = 4$.
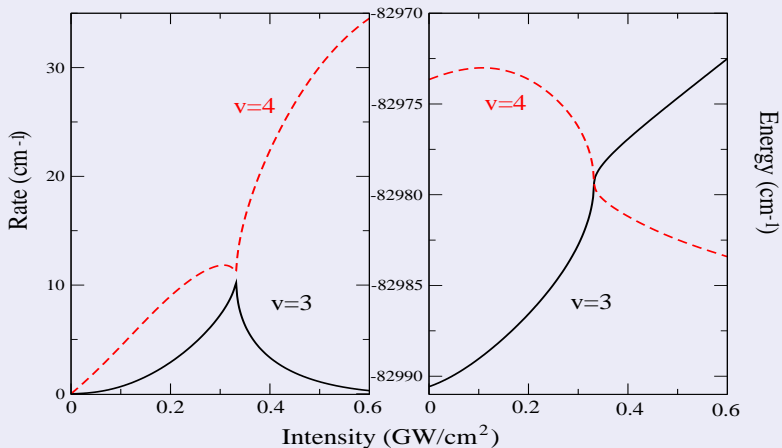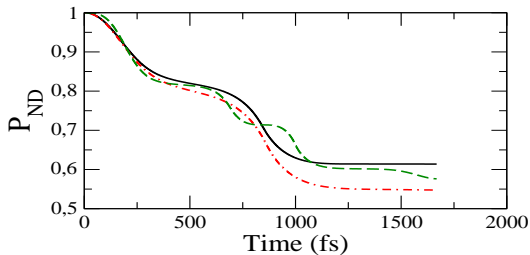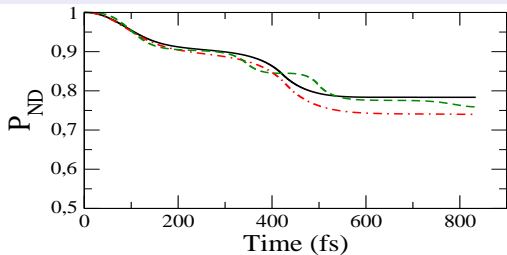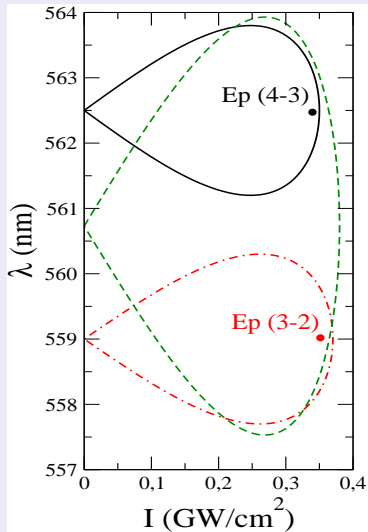
In the energy plane

When moving around the EP, there is an exchange of the two resonances. 3 goes to 4 and is shape all the way, while 4 goes to 3 and is Feshbach. This is a useful distinction to build efficient cooling scenarios.
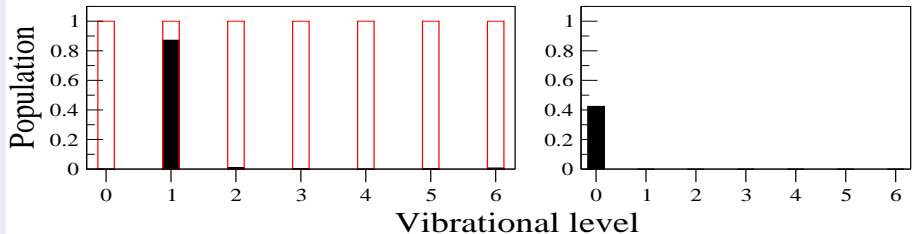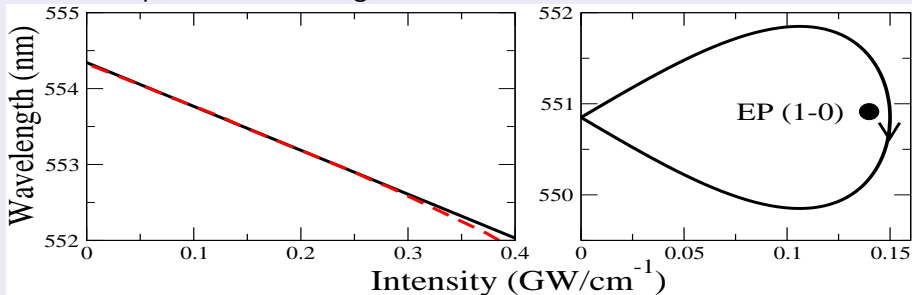
Cooling by encircling 2 EPs

Combining ZWRs with an EP

The first step is to follow in parameter plane the locus of ZWR points of level $v = 1$. All states except $v = 1$ disappear. The final step is to use an EP for the pair $1 - 0$ to bring the undissociated molecules down to $v = 0$.

General Conclusions

The one-dimensional model developped here has been the starting point in the past to describe several phenomena which received experimental confirmation, such as After Threshold Dissociation (ATD), Vibrational Trapping (VT) or Bond Softening (BS). This applies if the diatomic molecule can be assumed to be aligned in a given direction by a linearly polarized laser or if the rotational period exceeds the pulse duration. The ZWRs and the EPs offer a wide variety of scenarios to manipulate the molecule.

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