

Trapping of an Electron due to Molecular Vibrations

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Here we first show that the nuclear motion of H_2^- generates a continuum of autoionization resonance states. The interference between them increases the lifetime of the trapped electron in the e^-/H_2 scattering experiments and leads to asymmetric oscillations in the phase of the excitation probability amplitude. This collective coherent interference resonance phenomenon is very different from any known mechanism in quantum mechanics which reveals the fingerprints of overlapping resonances in scattering cross section and results from the non-Hermitian properties of the H_2^- Hamiltonian.

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So far, Ericson fluctuations [1] in the cross section are the only known fingerprints of overlapping resonances. However, in this special case the structure in the scattering cross section appears as a result of *absence* of interference between different resonance states.

In this paper we propose another mechanism which is substantially different from the above one and yet leads to structure in the cross section even when the resonances are overlapping, i.e., $\Gamma_n > |\epsilon_n - \epsilon_{n\pm 1}|$, where ϵ_n is the energy position of the resonance state and Γ_n is the corresponding width. We will describe a case where the *interference* among resonance states results in sharp structure in the scattering cross section σ . This is very different from the known Fano interferences [2] which take place between a given resonance state and a weakly energy dependent background. Fano interferences lead to the distortion of the shape of the resonance peak in the cross section but not to a substantial increase of the lifetime of the trapped particle in the scattering process. In our case the structure is the result of the interference among resonances and consists of peaks where each one of them is much narrower than the width of a single resonance state Γ_n . Since the lifetime of the trapped particle is proportional to the inverse of the width of the peak in the cross section, it implies that the narrowing of the peak in the cross section increases the lifetime of the trapped particle. Moreover, the interference takes place between many resonances which are separated by a large energy interval as compared to the corresponding resonance widths i.e., $|\epsilon_n - \epsilon_m| \gg \max(\Gamma_n, \Gamma_m)$. *Therefore we may consider the new mechanism presented here as a collective coherent resonance phenomenon.* As will be discussed below, this phenomenon was first observed, without realizing it, in the experiments of inelastic electron scattering from an H_2 molecule [3]. The sharp structure in the experimental electron/hydrogen-molecule scattering cross section is associated with the short-lived vibrational states of the autoionizing H_2^- intermediate. We have calculated the positions and the widths of these H_2^- states within the local approximation and to our surprise we obtained that the width of the resonance states was 2–3 times larger than the widths of the peaks in the vibrational exci-

tation cross sections [4]. Yet, the mechanism that leads to this phenomenon remained unclear.

We will show here that the nuclear motion of H_2^- induces interference between resonances such that the structures appearing in the scattering cross section are narrower than the width of a single resonance state, Γ_n . First, however, we stress that the interference phenomenon between the resonance states itself is associated with the generalization of the inner product in quantum mechanics. This generalization is required when resonances, metastable states, are associated with complex rather than real eigenvalues of the Hamiltonian.

The transition probability amplitude, $t(E)$, for a scattering experiment where the initial and the final states are identical, i.e., $|\phi_i\rangle = |\phi_f\rangle = |0\rangle$, is given by the Lippmann-Schwinger equation,

$$t(E) = \langle 0|V + VGV|0\rangle = t_{\text{direct}}(E) + t_{\text{res}}(E). \quad (1)$$

The resonant term, $t_{\text{res}}(E)$, is given by

$$t_{\text{res}}(E) = \int d\epsilon \rho(\epsilon) a(\epsilon) / (E - \epsilon), \quad (2)$$

where $\hat{H}|\epsilon\rangle = \epsilon|\epsilon\rangle$, $a(\epsilon) = |\langle 0|V|\epsilon\rangle|^2 \geq 0$, and $\rho(\epsilon)$ stands for the density of states. However, when \hat{H} is a Hermitian operator the eigenvalues, ϵ , get real values only and the information about the resonance phenomena is spread over a large number of continuum states. There are several methods, such as complex scaling, which allow us to “concentrate” the information about the resonance phenomena into a *single square integrable state* which is associated with a complex energy eigenvalue, $E_n^{\text{res}} = \epsilon_n - \frac{i}{2}\Gamma_n$. That is, $\hat{H}|n\rangle = E_n^{\text{res}}|n\rangle$, where $|n\rangle$ is an eigenfunction which is *not* in the Hermitian domain of the Hamiltonian H . This enables us to replace the integral in the expression for the $t_{\text{res}}(E)$ by a sum over the discrete resonance states,

$$t_{\text{res}}(E) = \sum_n a_n / \left(E - \epsilon_n + \frac{i}{2}\Gamma_n \right). \quad (3)$$

Since the eigenfunction $|n\rangle$ is not in the Hermitian domain of the Hamiltonian the definition of the inner product that

we use should be questioned. If we keep the usual definition of the scalar product in quantum mechanics the coefficients a_n in Eq. (3) will get real positive values only [as well as $a(\epsilon)$ in Eq. (2)] and the possibility of interference among different resonance states which leads to the trapping of an electron due to the molecular vibrations will be eliminated. The generalized definition of the inner product $(\dots | \dots)$ rather than the usual scalar product $\langle \dots | \dots \rangle$ has to be used when the Hamiltonian is not Hermitian [5,6]. For the sake of simplicity and without the loss of generality we define here $(f | g) \equiv \langle f^* | g \rangle$. Only the application of the generalized inner product can give rise to the complex coefficients, $a_n = (0|V|n)(n|V|0)$, in Eq. (3). The fact that $\{a_n\}$ can get complex and real negative values is essential to obtain the interference phenomenon which increases the lifetime of H_2^- intermediate in the e^-/H_2 scattering experiments.

In Figs. 1a and 1b we represent the electron- H_2 scattering cross section and the phase of the corresponding excitation probability amplitude. The widths of the peaks in Fig. 1a are 2–3 times narrower than the width of the H_2^- resonance states. The phase shows an oscillatory behavior similar to the behavior of the transition probability amplitude phase as measured in the experiments of an electron

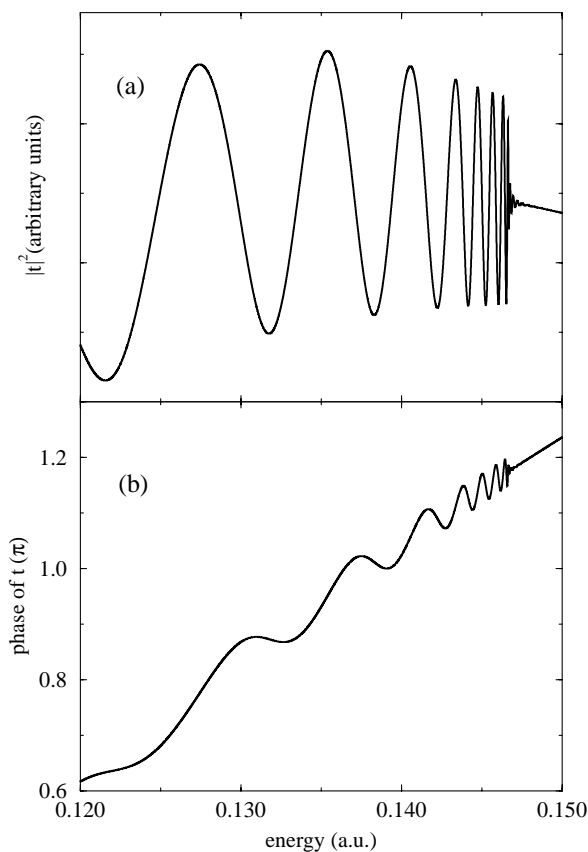


FIG. 1. (a) The behavior of the probability to excite the H_2 molecule from the ground vibrational $\nu = 0$ to the $\nu = 4$ excited state in e^-/H_2 collision. (b) The phase of the corresponding probability amplitude.

passing through a quantum dot [7]. Note that our numerical results presented in Fig. 2 are in a remarkable semi-quantitative agreement with the experimental cross section [3]. The experimental cross section was shifted up in energy by 0.45 eV to emphasize the agreement between the vibrational structures seen in the spectrum. Similar agreement was obtained earlier by Mündel *et al.* [8] using a different approach.

We now give a more detailed description of the electron trapping phenomena. It is known that the $^2\Sigma_u^+$ resonance of H_2^- which is responsible for the vibrational excitation in the low energy region is an extremely short-lived resonance with a lifetime comparable to the duration of the nonresonant scattering [9].

For a fixed H-H distance the H_2^- molecule autoionizes with a rate depending on the H-H bond length, $\Gamma(R)$. This exponential decay can be described by a single resonance state possessing a *complex* electronic “energy” $V(R) - \frac{i}{2}\Gamma(R)$ (see Fig. 3) [10]. Therefore instead of using many real coupled electronic potential surfaces within the Born-Oppenheimer (BO) approximation we can solve the nuclear Schrödinger equation with a single complex potential energy surface [4], $\hat{H} = \hat{T}_{\text{nuclear}} + V(R) - \frac{i}{2}\Gamma(R)$.

By solving the nuclear H_2^- Schrödinger equation with the complex potential surface we obtained two distinctive types of resonance states which are presented in Fig. 3. The first one is associated with vibrationally bound motion of autoionizing H_2^- molecule, i.e., $H_2^- \rightarrow H_2 + e^-$. We will refer to these states as vibrationally discrete autoionization-resonance states. The second type of states is associated with the free motion of the nuclei and is referred to here as vibrationally continuum autoionization resonances where $H_2(\text{bound}) + e^- \xrightarrow{A} H_2^-(\text{continuum}) \xrightarrow{B} H^- + H$ (i.e., a branch cut of autoionizing states). Note that the autoionization (A) takes place at the inner classical turning point where the width of the complex potential surface is the largest. The

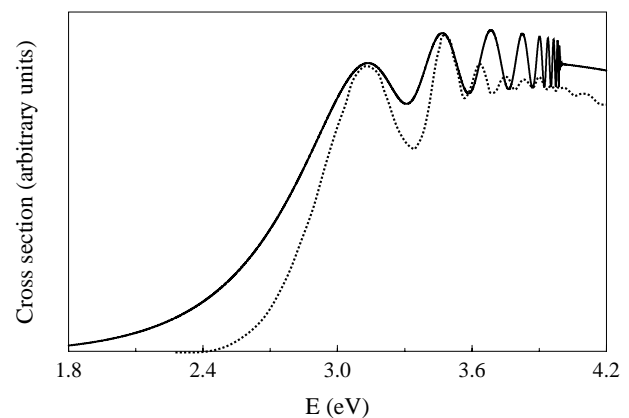


FIG. 2. Solid line shows the calculated probability to excite the H_2 molecule from the ground vibrational $\nu = 0$ to the $\nu = 4$ excited state in e^-/H_2 collision. Dotted line represents the shifted experimental results.

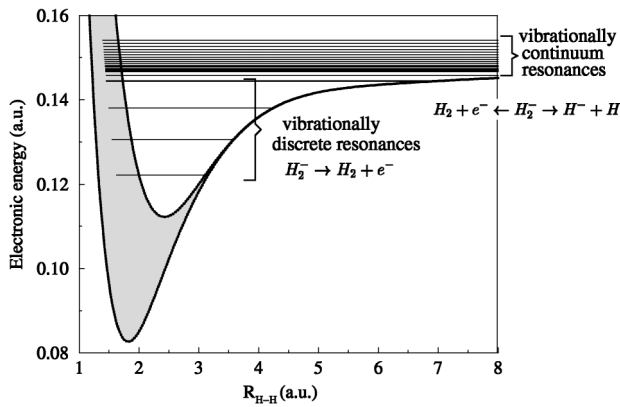


FIG. 3. The shaded area describes the electronic energy $\epsilon(R) \pm \Gamma(R)/2$ of autoionizing H_2^- as a function of the internuclear distance R . The horizontal parallel lines stand for the autoionization resonance energy levels (the resonance widths are not shown here). The continuum part of the spectrum is quantized due to the finite box approximation.

dissociation (B) occurs at the outer region where the width of the complex potential is zero. As we show below the formation of branch cut of resonances due to the nuclear motion plays the key role in the mechanism which is responsible for the enhancement of the electron trapping by the hydrogen molecule.

The initial state populates both types of resonance states of H_2^- . Interference between the vibrational discrete and the vibrational continuum autoionization resonances takes place although the resonance positions of the vibrationally discrete autoionization-resonance (disc-res) states and the vibrationally continuum autoionization-resonance states (cont-res) are very “far” from one another (as compared to their width). One may think that when $E \sim \epsilon_n(\text{disc-res})$ there is only one dominant term in the series resonance expansion of $t_{\text{res}}(E)$ [see Eq. (3)]. This is however not the case. The numerators associated with the branch-cut resonances, $a_n(\text{cont-res})$, get complex values where both the real and the imaginary parts are larger than the corresponding ones of $a_n(\text{disc-res})$ by *several orders of magnitude*. In the numerical calculations the amplitudes of the continuum-type resonances were found to be larger by 8–10 orders of magnitude than the discrete-type resonance amplitudes. Consequently, $|a_n(\text{cont-res})| \gg |a_n'(\text{disc-res})|$; however, at $E = E_n(\text{disc-res})$,

$$\left| \frac{a_n(\text{disc-res})}{\frac{i}{2}\Gamma_n(\text{disc-res})} \right| \approx \left| \frac{a_n'(\text{cont-res})}{\Delta E + \frac{i}{2}\Gamma_n'(\text{cont-res})} \right|, \quad (4)$$

where

$$\Delta E = E_n(\text{disc-res}) - E_n'(\text{cont-res}) \quad (5)$$

even when the difference between the $H_2^-(\text{disc-res}) \rightarrow H_2 + e^-$ resonances and $H_2 + e^- \leftarrow H_2^-(\text{cont-res}) \rightarrow H^- + H$ resonances is much larger than the corresponding resonance widths, $\Delta E \gg \max(\Gamma_n, \Gamma_n')$.

The number of dominant terms in the expression for $t_{\text{res}}(E)$ [Eq. (3)] determines the number of effective indirect scattering events in the scattering experiment. In our case due to the large amplitudes of the branch-cut (continuum) resonances this number is large and therefore we deal with a multiple scattering process and a collective resonance phenomenon. By collectiveness we mean that even at the resonance energy, $E = \epsilon_n$, a large number of resonances have dominant contributions to the expansion of t_{res} given in Eq. (3).

The large amplitude of the continuum resonance states is a direct result of the non-Hermitian properties of H_2^- Hamiltonian (i.e., the resonance eigenfunctions which are associated with complex eigenvalues are not in the Hermitian domain of the molecular Hamiltonian). Let us explain this point in some more detail. Moiseyev and Friedland [11] have proved that if two $N \times N$ real symmetric matrices H_1 and H_2 do not commute, there exists at least one value of parameter $\lambda = \lambda_b$ such that matrix $H_1 + \lambda H_2$ possesses incomplete spectrum. The spectrum is incomplete when the number of independent eigenvectors of a matrix is smaller than N . For $\lambda \neq \lambda_b$, $(H_1 + \lambda H_2)\psi_n = \epsilon_n \psi_n$, where the N eigenvectors are linearly independent; $(\psi_n | \psi_{m \neq n}) = 0$. However, as $\lambda \rightarrow \lambda_b$ there are at least two specific eigenstates i and j for which $\lim_{\lambda \rightarrow \lambda_b} (\epsilon_i - \epsilon_j) = 0$ and also $\lim_{\lambda \rightarrow \lambda_b} (\psi_i - \psi_j) = 0$. Since ψ_i and ψ_j are orthogonal [within the general inner product definition, i.e., $(\psi_i | \psi_j) \equiv \langle \psi_i^* | \psi_j \rangle = 0$ and not in the usual scalar product definition] upon coalescence their length is reduced to zero, $\langle \psi_i^* | \psi_i \rangle = \epsilon$, $\epsilon \rightarrow 0$. When $\lambda \neq \lambda_b$ but is very close to it we still require normalization of ψ_i , $\langle \psi_i^* | \psi_i \rangle = 1$. Therefore the components of the corresponding eigenvectors are divided by a small number $\epsilon^{1/2}$ and the amplitude of ψ_i becomes enormously large.

We show here that the phenomenon of spectrum incompleteness is inherent in the case of H_2^- . The Hamiltonian of the intermediate H_2^- within the BO approximation is given by $H(R) = T(R) + V(R) - \frac{i}{2}\Gamma(R)$. We can rewrite this Hamiltonian introducing an autoionization strength parameter λ in the following way: $H(R) = T(R) + V(R) - \lambda \frac{i}{2}\Gamma(R)$. For $\lambda = 1$ we obtain the original physical Hamiltonian of H_2^- . Using real basis functions or finite grid methods the matrices representing the operators $T(R)$, $V(R)$, and $\Gamma(R)$ are real symmetric ones. The H_2^- Hamiltonian in the matrix form is $\mathbf{H} = \mathbf{T} + \mathbf{V} - \lambda \frac{i}{2}\mathbf{\Gamma} = \mathbf{H}_{\text{Re}} - \lambda \frac{i}{2}\mathbf{\Gamma}$. Since matrices \mathbf{H}_{Re} and $\mathbf{\Gamma}$ do not commute it follows from the theorem proved by Moiseyev and Friedland that there exists λ , such that the spectrum of \mathbf{H} is incomplete. In order to find the values of λ where the spectrum is incomplete in the case of H_2^- we have studied the λ dependence of the spectrum. In Fig. 4 we present the spectrum of H_2^- obtained while varying λ from 0 to 1 (i.e., increasing the strength of the ionization phenomenon). There are 9 bound vibrational states of H_2^- when the

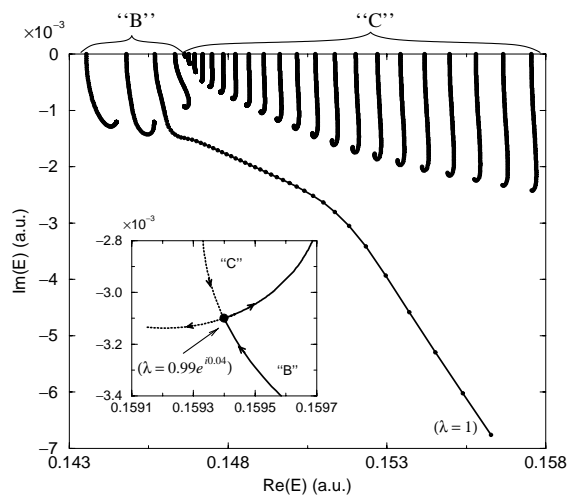


FIG. 4. λ -trajectory calculations of the complex eigenvalues of $\text{Re}(\mathbf{H}) - i\lambda \text{Im}(\mathbf{H})$, where \mathbf{H} is a matrix representation of the nuclear H_2^- Hamiltonian with complex electron potential surface. For $\lambda = 0$ the autoionization is artificially suppressed and the real eigenvalues obtained are divided into vibrationally bound states (denoted by "B" and into dissociative continuum solutions denoted by "C" (note that the discretization is due to the finite box approximation). The inset shows that very close to $\lambda = 1$ (the physical solution) one of the continuum solutions and the 8th "B" solution coalesce.

autoionization process is neglected, i.e., $\lambda = 0$. They all acquire finite width whenever the value of λ is increased. However, the width and the position of each state changes at a very different rate. The most dramatic change occurs to the 8th bound state ($\lambda = 0$). This state is "pushed out" above the energy threshold for the dissociation. Interestingly, whenever the position of the bound state crosses the threshold energy the behavior of the continuum states changes as well. That is, the width of the continuum states starts to decrease with increasing λ . The reason for this behavior is that for some complex values of the parameter λ close to $\lambda = 1$ the bound state which enters the continuum part of the spectrum crosses the continuum states one by one. Since the crossing does not happen at $\lambda = 1$, the picture we see at the physical value of $\lambda = 1$ is that of avoided crossing. It should be stressed that the crossing here implies coalescence of two eigenstates, one eigenstate originating from the bound state at $\lambda = 0$ and the second one from the continuum at $\lambda = 0$. *Indeed, we found several branch points associated with the coalescence of bound and continuum states which are in the vicinity of $\lambda = 1$.* For example, in the inset in Fig. 4 we show the branch point at $\lambda = 0.99145098 + i0.04006515$. The trajec-

tory approaching from below is associated with the 8th "bound" state and the trajectory approaching from above is associated with the "continuum" state. This branch point is the closest one to $\lambda = 1$ and the two states that cross at this point are very close to be self-orthogonal for the physical value of $\lambda = 1$. Consequently, the amplitudes of these states are by several orders of magnitude larger than the amplitudes of the discrete resonance states that are not involved in the crossings with the continuum states. As we have shown above this effect plays a crucial role in the mechanism that leads to the electron trapping by the H_2 molecule.

We conclude by saying that here we show that the lifetime of the trapped electron in the electron scattering experiment can be dramatically increased due to the coupling between the nuclear and the electronic motions. It should be stressed that this coupling takes place between molecular autoionizing states over a very large energy range. This unusually strong coupling is due to the existence of a continuum of short lifetime autoionizing resonance states of H_2^- , located at an energy above the threshold energy of dissociation. This branch cut of resonances is generated by the nuclear motion.

It seems to us that this phenomenon is a general one and should be observed in other systems and in other types of experiments.

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