

# Non-Hermitian formulation of interference effect in scattering experiments

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Non-Hermitian quantum mechanics allows one to calculate a physical observable, e.g., scattering cross section, as a sum over a finite number of discrete resonance states. The coefficients in the sum can get complex and negative values even in cases where conventional scattering theory predicts real positive coefficients only. Consequently, structure (or absence of structure) in scattering cross section can be obtained as a result of interference between a small number of discrete resonance states; whereas, conventional scattering theory would require integration over the continuum of scattering states and therefore it is a heavy numerical task. We show here that in electron scattering experiments the interference between overlapping broad resonances leads to oscillations in the phase of transition probability amplitude and to enhancement of the transition state lifetime due to nuclear motion. © 2000 American Institute of Physics.

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## I. INTRODUCTION

In the theories of chemical reactions, transition state is usually associated with a quasibound state of the collision complex. Isolated resonance states have been observed in transition state spectroscopy experiments as finite width peaks in the cross sections. Whenever the resonance states have a short lifetime and strongly overlap (i.e., the distance between two consecutive resonances smaller than the inverse lifetime), their contribution to reaction dynamics is usually thought to be washed out and unimportant. So far, Ericson fluctuations<sup>1</sup> in the cross section are the only known fingerprints of overlapping resonances. The Ericson fluctuation model is based on an assumption that the initial state randomly populates all resonance states embedded within a given range of energy  $E_{\min} \leq \{\epsilon_n\} \leq E_{\max}$ . Another assumption of this model is that all of the overlapping resonances possess the same width,  $\Gamma$ . In such a case it can be shown that the terms in the expression for the scattering cross section,  $\sigma(E) = |\sum_n a_n / (E - \epsilon_n + (i/2)\Gamma)|^2$ , which are responsible for the interference among the different resonance states, are canceled out. Consequently,  $\sigma(E)$  is reduced to a sum over Lorentzian line shapes weighted by random positive numbers  $|a_n|^2$ ,  $\sigma(E) = \sum_n |a_n|^2 / ((E - \epsilon_n)^2 + (\Gamma^2/4))$ . This gives rise to fluctuations in the scattering cross section with a characteristic width which is equal to  $\Gamma$ . In this special case the structure in the scattering cross section appears as a result of the *absence* of interference between different resonance states.

In this paper we will 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.,  $\Gamma_n > |\epsilon_n - \epsilon_{n\pm 1}|$ . We will describe a case where the *interference* among resonance states results in sharp structure in the scattering cross section  $\sigma$ . This is very different from the known Fano interferences<sup>2</sup> which take

place between a given resonance state and a weakly energy dependent background. Fano interferences lead to 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  $\Gamma_n$ . 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 resonances which are separated by a large energy interval as compared to the corresponding resonance widths, i.e.,  $|\epsilon_n - \epsilon_m| \gg \text{Max}(\Gamma_n, \Gamma_m)$ . *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  $\text{H}_2$  molecule.<sup>3</sup> The sharp structure in the experimental electron/hydrogen-molecule scattering cross section is associated with the short-lived vibrational states of the autoionizing  $\text{H}_2^-$  intermediate. We have calculated the positions and the widths of these  $\text{H}_2^-$  states within the local approximation and to our surprise we obtained that the width of the resonance states were 2–3 times larger than the widths of the peaks in the vibrational excitation cross sections.<sup>4</sup> Yet, the mechanism that leads to this phenomenon remained unclear and only very recently the crucial role of the nuclear motion in the electron trapping mechanism has been pointed out.<sup>5</sup> In this paper this mechanism will be studied in more details. As we will show here the understanding of the increase of transition state lifetime due to the nuclear motion is based on the extension of quantum mechanics to deal with non-Hermitian operators and requires the replacement of the scalar inner

product by a more general definition of the inner product which is known as the  $c$ -product.<sup>6</sup>

## II. GENERALIZATION OF THE INNER PRODUCT IN QUANTUM MECHANICS AND INTERFERENCE BETWEEN RESONANCES STATES

We would like to 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, i.e., 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 an Hermitian operator the eigenvalues,  $\epsilon$ , 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 (CS), 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,  $E_n^{\text{res}} = \epsilon_n - (i/2)\Gamma_n$ . The resonance state is associated with a complex eigenvalue even when the Hamiltonian is not complex scaled and when no absorbing boundary conditions are imposed. 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  $H$ . The use of complex scaling does not effect the complex values of the resonance eigenvalues but does change the corresponding eigenfunctions to be square integrable functions. This enables us to replace the integral in the expression for the  $t_{\text{res}}(E)$  by a sum over the discrete resonance states,

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

Since the eigenfunction  $|n\rangle$  is not in the Hermitian domain of the Hamiltonian it is not clear at all what is the definition of the inner product that we should use. If we will 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 (...|...) rather than the usual scalar product (...|...) has to be used when the Hamiltonian is not Hermitian.<sup>7,6</sup> For the sake of simplicity and without loss of generality, we define here  $\langle f|g\rangle \equiv \langle f^*|g\rangle$ . Only the application of the generalized inner

product can give rise to the complex coefficients,  $a_n = \langle 0|V|n\rangle\langle n|V|0\rangle$ , 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  $\text{H}_2^-$  intermediate in the  $e^-/\text{H}_2$  scattering experiments.

The use of the generalized definition of the inner product has already lead to a remarkable agreement between the *ab initio* calculated scattering intensities of helium atoms from Cu(115) and the experimental scattering intensities.<sup>8</sup> As far as we know there is no other example where *ab initio* calculations for helium diffraction from a solid surface agreed so well with the experimental scattering intensities.

## III. INTERFERENCE MECHANISMS

We will now elaborate on the interference mechanism that could increase the lifetime of the trapped electron in the scattering experiment, and therefore could lead to a sharper structure in the scattering cross section as compared to a width of a single resonance state.

We will start illustrating this phenomena for the case of two overlapping resonances following closely discussion given by Bohm.<sup>9</sup>

Let us assume that  $E_1 = \mathcal{E}_1 - (i/2)\Gamma_1$  and  $E_2 = \mathcal{E}_2 - (i/2)\Gamma_2$  are two poles such that  $\Gamma_1 = \Gamma_2 = \Gamma$ ,  $\mathcal{E}_1 = 0$  and  $\mathcal{E}_2 = \Delta E$ . The cross section similar to Eq. (3) in the neighborhood of the poles is given by

$$\sigma(E) = \left| \frac{1}{E - \Delta E + (i/2)\Gamma} + \frac{C}{E + (i/2)\Gamma} \right|^2, \quad (4)$$

or,

$$\sigma(E) = \sigma_1(E) + \sigma_2(E) + \sigma_{12}(E), \quad (5)$$

where  $\sigma_1(E)$  and  $\sigma_2(E)$  are the first and the second pole contributions to the cross section:

$$\sigma_1(E) = \frac{1}{E^2 + \Gamma^2/4},$$

$$\sigma_2(E) = \frac{C^2}{(E - \Delta E)^2 + \Gamma^2/4}. \quad (6)$$

The last term in the Eq. (5),  $\sigma_{12}(E)$ , stands for the interference effect between the two poles:

$$\sigma_{12}(E) = \frac{2CE(E - \Delta E) + 2C\Gamma^2/4}{(E^2 + \Gamma^2/4)((E - \Delta E)^2 + \Gamma^2/4)}. \quad (7)$$

The interference can have a dual effect—it can be either destructive or constructive. For  $C = -1$  and for  $\Delta E \leq \Gamma$  the interference is constructive and there is a single peak in the cross section at  $E = \Delta E/2$ . For  $C = 1$  and  $\Delta E = \Gamma$  the interference term  $\sigma_{12}(E = \Delta E/2)$  gives a zero contribution to the cross section and we obtain two separated peaks in the cross section. However, if  $C$  is allowed to acquire a complex value of  $i$  and  $\Delta E = \Gamma$  a destructive interference occurs and  $\sigma(E = \Delta E/2) = 0!$  Consequently the two peaks in the cross section are very well separated. *As one can see the widths of the peaks in  $\sigma(E)$  are decreased due to the quantum interference effects.* Following the Heisenberg uncertainty principle

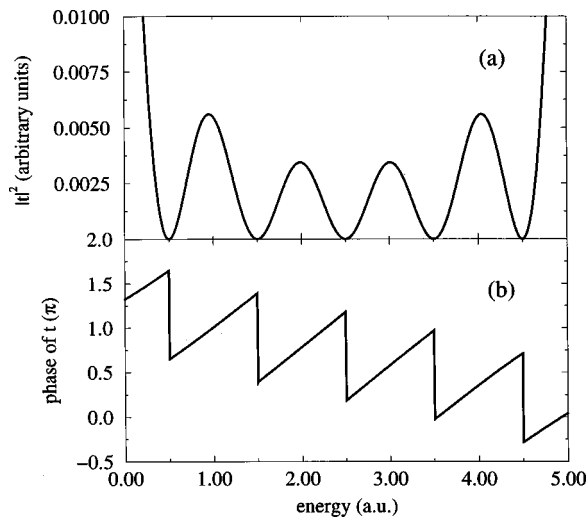


FIG. 1. The behavior of the transition probability (a) and its amplitude phase (b) in the case of six resonances contributing to the expansion of  $t_{\text{res}}(E)$ , Eq. (3). The complex coefficients  $a_n$ ;  $n=1, \dots, N-1$  are obtained by solving the set of linear equations given in the text with  $a_0=1$ ,  $\Delta=1$  a.u.,  $\Gamma=2$  a.u.

the uncertainty in energy times the lifetime of the system is larger than  $\hbar/2$ . Therefore we may say that by narrowing the widths of the peaks in  $\sigma(E)$  one increases the lifetime of the system. Note that the usual concept of the lifetime as the inverse of the decay rate is applicable only for isolated resonances and not in our case where there is a large overlap between the different resonances.

Let us now propose a more general model that illustrates the increase of the lifetime of a trapped particle due to the collective interference resonance phenomenon. Assume that a given system consists of  $N$  equally spaced resonances  $E_n = n\Delta$ ;  $n=0, 1, \dots, N-1$ . All have the same width  $\Gamma$ , which is larger than the energy spacing  $\Delta$ , i.e.,  $\Gamma > \Delta$ . This is the case of  $N$  overlapping resonances. The goal is to find values of  $a_n$  in Eq. (3) such that the peaks associated with the resonances in the scattering cross section would be narrower than  $\Gamma$ . Clearly, if  $t_{\text{res}}(E)$  will vanish between two consecutive resonances, then the width,  $\gamma$ , of the resonance peaks in the cross section will be at most  $\Delta$  irrespective of the resonance width, i.e.,  $\gamma \leq \Delta < \Gamma$ .

Coefficients  $a_n$  that satisfy the condition of vanishing transition amplitude between each pair of resonances,  $t_{\text{res}}(E = (\epsilon_n + \epsilon_{n+1}/2)) = 0 \forall n$ , are the solutions of the following set of linear equations:  $\mathbf{B}\mathbf{a} = \mathbf{b}$ , where  $B_{m,n} = 2/(2(m-n) - 1 + i\Gamma/\Delta)$ ;  $b_m = 2a_0/(1 - 2m - i\Gamma/\Delta)$ ;  $\{n, m\} = 1, 2, \dots, N-1$ . The resulting transition probability,  $|t_{\text{res}}(E)|^2$ , is presented in Fig. 1(a) for the case of six resonances ( $N=6$ ). Note that even if  $a_0$  is chosen to be a real number coefficients  $a_1, \dots, a_{N-1}$  will get complex values.

It is easy to show that the vanishing of the complex transition amplitude is accompanied by the sharp (step-function like) drop ( $-\pi$ ) of the phase,  $\phi$ , of the transition amplitude  $t = |t|e^{i\phi}$ . For a simple proof see Ref. 10. This phenomena is illustrated in Fig. 1(b). Note that very similar results were obtained recently in the measurements of the phase of the transition probability amplitude for an electron

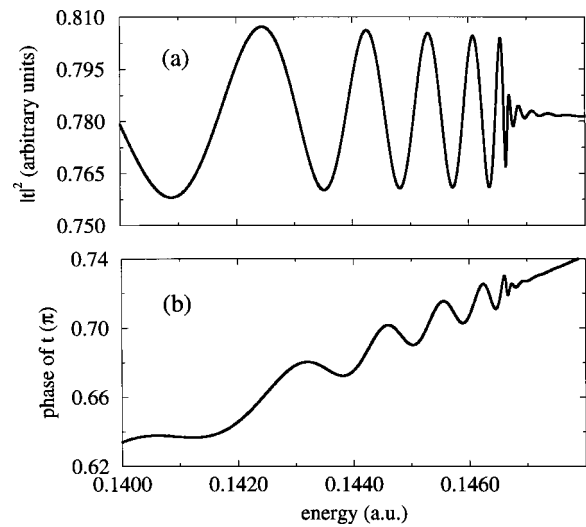


FIG. 2. (a) The behavior of the probability to excite H<sub>2</sub> molecule from the ground vibrational  $\nu=0$  to the  $\nu=4$  excited state in  $e^-/\text{H}_2$  collision. (b) The phase of the corresponding probability amplitude.

passing through a quantum dot.<sup>11</sup> The results presented in Figs. 2(a) and 2(b) were obtained for electron scattering from H<sub>2</sub> molecule. The similarity between the model and the physical system (compare Figs. 1 and 2) emphasizes the relevance of the interference mechanism to the  $e^-/\text{H}_2$  scattering experiments.

#### IV. DERIVATION OF VIBRATIONAL EXCITATION CROSS SECTION

Let us first derive the expression for the vibrational excitation cross section. We address ourselves to a scattering event where the electron, represented by  $\sqrt{(1/k_i)}e^{ik_i r}$ , collides with a molecule which has  $N$  internal electrons. We assume that the electronic state of the molecule is varied adiabatically during the collision. The molecular degrees of freedom are represented by coordinate  $R$ . Prior to collision the molecule is in its  $\nu$  vibrational state,  $\chi_\nu(R)$ , and in its  $n_0$ th electronic state,  $\phi_{n_0}(\{r\}_N; R)$ . Assuming adiabaticity, the initial state,  $\chi_\nu(R)\Phi_i(\{r\}_{N+1}; R)$ , properly antisymmetrized in the electronic coordinates such that  $\Phi_i(\{r\}_{N+1}; R) = \mathcal{A}(\phi_i(\{r\}_N; R)\sqrt{(1/k_i)}e^{ik_i r_{N+1}})$  is an eigenfunction of the interaction free Hamiltonian

$$H_0 = T(R) + T(\{r\}_{N+1}) + V_{\text{mol}}(\{r\}_N, R), \quad (8)$$

where  $T(\{r\}_{N+1})$  and  $T(R)$  are, respectively, the electronic and nuclear kinetic energy operators and  $V_{\text{mol}}(\{r\}_N, R)$  is the potential energy of the  $N+1$  electrons and nucleus of the molecule. After the inelastic collision the molecule is found in its vibrationally excited state  $\chi_{\nu'}(R)$  and the scattered electron is in a state defined by  $\sqrt{(1/k_f)}e^{ik_f r_{N+1}}$ . The final state of the noninteracting electron-molecule system is  $\chi_{\nu'}(R)\Phi_f(\{r\}_{N+1}; R)$  where  $\Phi_f(\{r\}_{N+1}; R) = \mathcal{A}(\phi_f(\{r\}_N; R)\sqrt{(1/k_f)}e^{ik_f r_{N+1}})$ . The energy of the scattered electron is given by the energy conservation law:

$$\frac{|\hbar k_i|^2}{2m_e} + E_\nu = \frac{|\hbar k_f|^2}{2m_e} + E'_{\nu'} \equiv E, \quad (9)$$

where  $m_e$  is the mass of an electron,  $E_\nu$  and  $E'_\nu$  are the energies of the initial and the final states of the molecule. The Hamiltonian during the collision process is given by

$$H = T(R) + T(\{r\}_{N+1}) + V_{\text{int}}(\{r\}_{N+1}; R), \quad (10)$$

where  $V_{\text{int}}$  is the  $N+1$  electron and nucleus interaction potential.  $V_{\text{int}}$  includes the coordinates of the colliding electron as well as the coordinates of electrons of the molecule. Since the electronic coordinate is much faster than the molecular one the Born–Oppenheimer (BO) approximation is applicable here. The adiabatic BO Hamiltonian is defined by

$$H_{\text{ad}}(\{r\}_{N+1}; R) = T(\{r\}_{N+1}) + V_{\text{int}}(\{r\}_{N+1}; R), \quad (11)$$

where the nuclear coordinate  $R$  is a parameter. The adiabatic Hamiltonian  $H_{\text{ad}}$  possesses  $R$ -dependent eigenenergies  $E_n^{\text{ad}}(R)$  and eigenfunctions  $\phi_n^{\text{ad}}(\{r\}_{N+1}; R)$  such that

$$H_{\text{ad}}(\{r\}_{N+1}; R) \phi_n^{\text{ad}}(\{r\}_{N+1}; R) = E_n^{\text{ad}}(R) \phi_n^{\text{ad}}(\{r\}_{N+1}; R). \quad (12)$$

The adiabatic energy  $E_n^{\text{ad}}(R)$  serves as a potential for the motion of the heavy nuclei:

$$(T(R) + E_n^{\text{ad}}(R)) \chi_{n,\alpha}^{\text{ad}}(R) = \epsilon_{n,\alpha}^{\text{ad}} \chi_{n,\alpha}^{\text{ad}}(R), \quad (13)$$

where  $\chi_{n,\alpha}^{\text{ad}}(R)$  and  $\epsilon_{n,\alpha}^{\text{ad}}$  are the nuclear vibrational wave function and energy. Within the Born–Oppenheimer approximation the total wave function is a product of the nuclear wave function and the electronic wave function which depends parametrically on the nuclear coordinate:

$$\Psi_{n,\alpha}^{\text{ad}} = \phi_n^{\text{ad}}(\{r\}_{N+1}; R) \chi_{n,\alpha}^{\text{ad}}(R). \quad (14)$$

According to the Lippman–Schwinger equation the probability to change the vibrational state of the molecule from  $\chi_\nu(R)$  to  $\chi_{\nu'}(R)$  due to the collision process is given by

$$\sigma = |\langle \Psi_f | V + VGV | \Psi_i \rangle|^2, \quad (15)$$

where, respectively, the initial and the final states are given by  $\Psi_i = \chi_\nu(R) \Phi_i(\{r\}_{N+1}; R)$  and  $\Psi_f = \chi_{\nu'}(R) \Phi_f(\{r\}_{N+1}; R)$ .  $V$  is defined as  $V = V_{\text{int}} - V_{\text{mol}}$ . The resonant part of the excitation probability is

$$\sigma_{\text{res}} = \left| \sum_{\alpha}^{\text{res}} \frac{\langle \chi_{\nu'} | \langle \Phi_i | V | \phi_{n_0}^{\text{ad}} \rangle_r \chi_{n_0,\alpha}^{\text{ad}} \rangle_R \langle \chi_{n_0,\alpha}^{\text{ad}} | \langle \phi_{n_0}^{\text{ad}} | V | \Phi_f \rangle_r \chi_\nu \rangle_R}{E - E_{n,\alpha}^{\text{ad}}} \right|^2. \quad (18)$$

Moiseyev and Peskin have shown that the integrals over the electronic coordinates in Eq. (18) are related to the partial widths. That is,

$$\begin{aligned} |\langle \Phi_i | V | \phi_{n_0}^{\text{ad}}(\{r\}_{N+1}; R) \rangle_r|^2 &= \Gamma_{n_0}^{(i)}(R) \\ |\langle \Phi_f | V | \phi_{n_0}^{\text{ad}}(\{r\}_{N+1}; R) \rangle_r|^2 &= \Gamma_{n_0}^{(f)}(R), \end{aligned} \quad (19)$$

$$\sigma_{\text{res}} = \left| \lim_{\epsilon \rightarrow 0^+} \left\langle \chi_{\nu'}(R) \Phi_i(\{r\}_{N+1}; R) \left| V \frac{1}{E - H + i\epsilon} V \right| \chi_\nu(R) \Phi_f(\{r\}_{N+1}; R) \right\rangle_{r,R} \right|^2. \quad (16)$$

Using the spectral representation of the Green operator  $(E - \hat{H})^{-1}$  in Eq. (16) within the Born–Oppenheimer approximation framework one gets:

$$\sigma_{\text{res}} = \left| \sum_{n,\alpha} \frac{\langle \chi_{\nu'} | \langle \Phi_i | V | \Psi_{n,\alpha}^{\text{ad}} \rangle_r \langle \Psi_{n,\alpha}^{\text{ad}} | V | \Phi_f \rangle_r | \chi_\nu \rangle_R}{E - E_{n,\alpha}^{\text{ad}}} \right|^2. \quad (17)$$

The molecular anion, which is formed when an electron collides with a neutral molecule, supports no bound states. However, the electron can be trapped for a finite period of time in the quasibound resonance state. There are several methods, such as complex scaling (CS), 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,  $E_n^{\text{res}} = \epsilon_n - (i/2)\Gamma_n$ . That is,  $\hat{H}_{\text{CS}}|n\rangle = E_n^{\text{res}}|n\rangle$ , where  $\hat{H}_{\text{CS}}$  is the complex scaled Hamiltonian. Note by passing that Hamiltonian possesses complex eigenvalues whenever the outgoing wave boundary conditions are imposed. Complex scaling allows to obtain these complex eigenvalues while forcing square integrability on the solutions associated with the resonances. The solution space of the complex scaled molecular anion Hamiltonian can be divided into subspace of resonance states and into the subspace of continuum scattering states. Whenever the resonance is isolated (the distance between two consecutive resonances is larger than the width,  $\Gamma$  of each resonance) and has a large lifetime ( $\Gamma/\hbar$  is larger than any characteristic frequency of the system) we can make an assumption that a scattering event involves a single resonance state.

A common situation is that  $\Delta E_{\text{vib}} \leq \Gamma < \Delta E_{\text{elec}}$ , where  $\Delta E_{\text{elec}}$  and  $\Delta E_{\text{vib}}$  are, respectively, the energy spacing between electronic levels and vibrational levels. In such a case scattering event proceeds via a single *electronic* resonance state,  $n_0$ . However it involves a number of vibrational states  $\{\chi_{\nu'}^{\text{ad}}\}$  belonging to the same electronic resonance state,  $n_0$ . Consequently the sum over electronic energy levels,  $n$ , can be omitted from the sum in the expression for the resonant part of the excitation probability in Eq. (17):

where  $\Gamma_{n_0}^{(i)}(R)$  is the partial width of the electronic resonance state  $n_0$  as function of the nuclear coordinate  $R$ . The products of this decay channel are neutral molecule and a free electron associated with a wave number  $k_i$ .  $\Gamma_{n_0}^{(f)}(R)$  is the partial width for the decay channel that results in a neutral molecule and a scattered electron associated with  $k_f$  wave number.



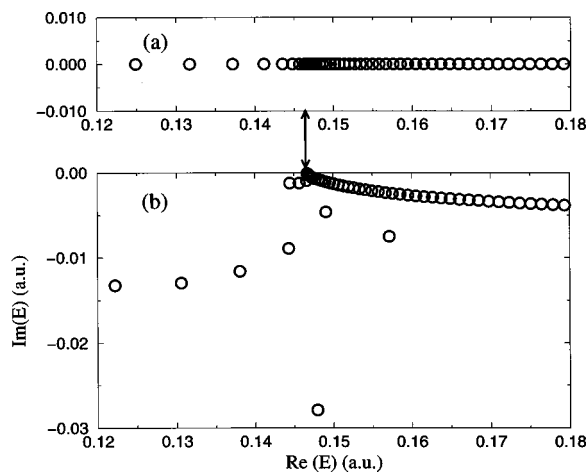


FIG. 3. The vibrational eigenstates of  $H_2^-$  obtained: (a) ignoring the imaginary part of the potential; (b) with the full complex potential. The arrows stand for the threshold energy to dissociation at  $E_{\text{threshold}}=0.1467$  a.u.

Within the local approximation the energy dependence of the partial widths (via the scattered electron wave number  $k$ ) is neglected and  $\Gamma_{n_0}^{(i)} = \Gamma_{n_0}^{(f)}$ . Using this approximation and Eqs. (18), (19) one gets

$$\sigma_{\text{res}} = \left| \sum_{\alpha} \frac{\langle \chi_{\nu'} | \Gamma_{n_0}^{1/2}(R) | \chi_{n_0, \alpha}^{\text{ad}} \rangle_R \langle \chi_{n_0, \alpha}^{\text{ad}} | \Gamma_{n_0}^{1/2}(R) | \chi_{\nu} \rangle_R}{E - E_{n_0, \alpha}^{\text{ad}}} \right|^2. \quad (20)$$

Since  $\Gamma_{n_0}$  is the width of the electronic resonance state  $n_0$  it is related to the imaginary part of the adiabatic electronic energy  $E_{n_0}^{\text{ad}}$ :

$$\Gamma_{n_0}(R) = -2 \text{Im} E_{n_0}^{\text{ad}}(R). \quad (21)$$

Equation (20) given above not only simplifies the calculation of  $\sigma$  but also provides a simple physical insight to the problem of electron scattering from a neutral molecule. Since the final expression for the vibrational excitation cross section does not depend on the electron coordinates, we can say that the electron-neutral molecule collision prepares a nuclear wave packet on the potential energy surface of the molecular anion intermediate (see Figs. 3–5). The prepared wave packet is propagated via the nuclear Born–Oppenheimer molecular anion Hamiltonian with the complex potential  $E_{n_0}^{\text{ad}}(R)$ . Finally, the anion undergoes autoionization process resulting in the molecule in a vibrationally excited state. The probability amplitude to obtain a specific vibrational state  $\nu$  of the molecule is given in Eq. (20). This expression is in a complete agreement with the results obtained by Domcke and Cederbaum<sup>12</sup> by applying the local approximation to the exact expression for  $\sigma$ .

## V. INCOMPLETE SPECTRUM OF NON-HERMITIAN OPERATORS

Moiseyev and Friedland<sup>13</sup> 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  $\lambda$  such that matrix

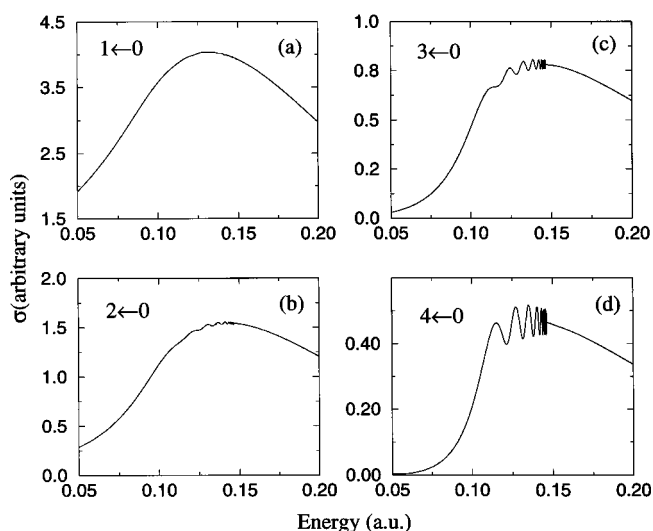


FIG. 4. Vibrational excitation cross sections  $\nu=0 \rightarrow \nu=1, 2, \dots, 4$ .

$H_1 + \lambda H_2$  possesses incomplete spectrum. The spectrum is incomplete when the number of independent eigenvectors of a matrix is smaller than  $N$ . We will explain this phenomena using a following example. Suppose that non hermitian Hamiltonian,  $H$ , which depends on some parameter  $\lambda$  can be represented by complex symmetric matrix  $3 \times 3$

$$H(\lambda) = \begin{pmatrix} 6 & e^{i\lambda} & -1 \\ e^{i\lambda} & 5 & 2e^{i\lambda} \\ -1 & 2e^{i\lambda} & 1 \end{pmatrix}. \quad (22)$$

The fact that the matrix that represents a non-Hermitian operator is complex symmetric is the direct result of the use of the generalized inner product as was discussed in the Sec. II. One can easily see that the matrix given in Eq. (22) has three distinctive eigenvalues and eigenvectors for all but one value of parameter  $\lambda$ . When the parameter approaches value of  $\lambda = \pi/2$  two of the eigenvalues and eigenfunctions approach each other and finally coalesce, i.e.,  $E_2 \rightarrow E_3$  and  $\Psi_2 \rightarrow \Psi_3$  as  $\lambda \rightarrow \pi/2$ . For  $\lambda = \pi/2$  matrix [Eq. (22)] has only two distinct eigenvectors:

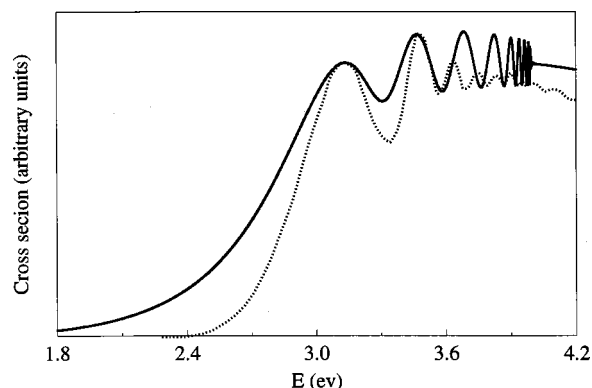


FIG. 5. Solid line shows the calculated probability to excite  $H_2$  molecule from the ground vibrational  $\nu=0$  to the  $\nu=4$  excited state in  $e/H_2$  collision. Dotted line represents the shifted experimental results.

$$E_1=6, \quad \Psi_1 = \begin{pmatrix} 1 \\ i/3 \\ -1/3 \end{pmatrix}, \quad E_2=E_3, \quad \Psi_2=\Psi_3 = \begin{pmatrix} 0 \\ 1 \\ i \end{pmatrix}. \quad (23)$$

Whenever two eigenvectors approach each other they gradually become self-orthogonal within the definition of the generalized inner product, i.e.,  $(\Psi_2|\Psi_2) \rightarrow 0$ . In our example eigenvector  $\Psi_2$  is self orthogonal for  $\lambda = \pi/2$ :

$$(0 \ 1 \ i) \cdot \begin{pmatrix} 0 \\ 1 \\ i \end{pmatrix} = 0. \quad (24)$$

If we will try to normalize the eigenvector  $\Psi_2$  such that  $(\Psi_2|\Psi_2)=1$  we will have to divide its components by 0!

In the case studied by Moiseyev and Friedland the parameter  $\lambda$  was related to the complex scaling parameter and the incompleteness of the spectrum was an artifact of the use of the complex scaling method.

We will 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,

$$H(R) = T(R) + V(R) - (i/2)\Gamma(R). \quad (25)$$

We can rewrite this Hamiltonian introducing an autoionization strength parameter  $\lambda$  in the following manner:

$$H(R) = T(R) + V(R) - \lambda(i/2)\Gamma(R). \quad (26)$$

For  $\lambda=1$  it is reduced to the original physical Hamiltonian of  $H_2^-$ . Using the real basis functions or DVR representation 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

$$\mathbf{H} = \mathbf{T} + \mathbf{V} - \lambda(i/2)\mathbf{\Gamma} = \mathbf{H}_{\text{Re}} - \lambda(i/2)\mathbf{\Gamma}. \quad (27)$$

Since matrices  $\mathbf{H}_{\text{Re}}$  and  $\mathbf{\Gamma}$  do not commute, it follows from the theorem proved by Moiseyev and Friedland that there exists  $\lambda$ , such that the spectrum of  $\mathbf{H}$  is incomplete. In order to find the values of  $\lambda$  where the spectrum is incomplete in the case of  $H_2^-$  we have studied the  $\lambda$  dependence of the spectrum. In Fig. 6 we present the spectrum of  $H_2^-$  obtained while varying  $\lambda$  from 0 to 1 (i.e., increasing the strength of the ionization phenomenon). There are nine bound vibrational states of  $H_2^-$  when the autoionization process is neglected, i.e.,  $\lambda=0$ . They all acquire finite width whenever the value of  $\lambda$  is increased. However, the width and the position of each state changes at a very different rate. The most dramatic change occurs to the eighth 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  $\lambda$ . We suspected that the reason for this behavior is that for some

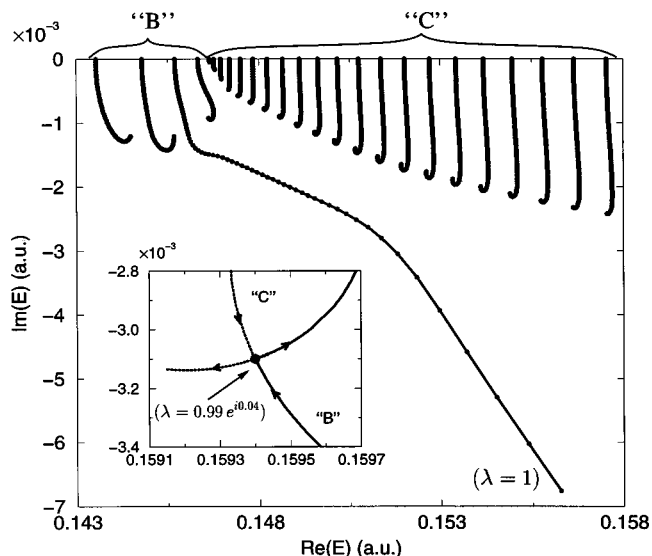


FIG. 6.  $\lambda$ -trajectory calculations of the complex eigenvalues of  $\text{Re}(\mathbf{H}) - i\lambda \text{Im}(\mathbf{H})$ , where  $\mathbf{H}$  is a matrix representation of the nuclear  $H_2^-$  Hamiltonian with complex electron potential surface. For  $\lambda=0$  the autoionization is artificially 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 eighth "B" solution coalesce.

complex values of the parameter  $\lambda$  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 see the inset of Fig. 6 where we show the branch point at  $\lambda=0.99145098 + i0.0406515$ . The trajectory approaching from below is associated with the eighth "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 several orders of magnitude larger than the amplitudes of the discrete resonance states that are not involved in the crossings with the continuum states. We show below that this effect plays a crucial role in the mechanism that leads to the electron trapping by the  $H_2$  molecule.

## VI. RESULTS: EIGENVALUES OF $H_2^-$ AND EXCITATION CROSS SECTIONS

In Fig. 3(a) we represent the energy levels of  $H_2^-$  when the autoionization process is neglected, i.e.  $\Gamma(R)=0$  in the Hamiltonian given in Eq. (13). There are nine infinite-

lifetime vibrational bound states of  $H_2^-$ . In Fig. 3(b) we show the results obtained when the complex nonlocal Hamiltonian of  $H_2^-$  is diagonalized [i.e.,  $\Gamma(R) \neq 0$  in Eq. (13)]. The complex nonlocal potential,  $E_{n_0}^{ad}(R) = V(R) - (i/2)\Gamma(R)$ , was taken from Ref. 14. As one can see when the imaginary part of the potential is taken into account, each vibrational state of  $H_2^-$  acquires a finite width. The vibrationally bound states become discrete resonance states and the dissociative continuum now becomes dissociative continuum of resonances. The discretization of the continuum is due to the usage of the finite basis set. The actual situation is of a branch cut. That is, a continuum of singular points of the scattering matrix.

Eigenstates of the  $H_2^-$  used in the calculation of the cross sections were obtained by diagonalization of the Hamiltonian matrix in the discrete variable representation (DVR) basis. Complex scaling (CS) of the H–H coordinate ( $R \rightarrow Re^{i\theta}$ ) which is equivalent to the usage of absorbing boundary conditions in that coordinate was employed.<sup>15</sup> Application of CS enabled us to get rid of nonphysical weak oscillations in the cross section above the threshold energy to dissociation obtained in previous calculations.<sup>14</sup> We used only 200 grid points in the interval of 20 a.u., while the CS parameter  $\theta = 0.25$  turned out to be the optimal one for our calculations (resonance positions were insensitive to the variation of  $\theta$ ).

Cross sections for vibrational excitations  $\nu=0 \rightarrow \nu = 1, 2, \dots, 4$  calculated using the simplified version<sup>4</sup> of Eq. (20) are represented in Fig. 4. The structures appearing under the dissociation threshold are in a good qualitative agreement with a previous results obtained for the nonlocal theory.<sup>16,14</sup> Since the electronic resonance state of  $H_2^-$  decays by  $p$ -waves, nonlocal effects will influence the scattering cross section, but not the quality of the interference effects due to nuclear dynamics. For discussion of local versus nonlocal effects, see Ref. 12. In Fig. 5 we present the comparison of the calculated cross section for the vibrational excitation  $\nu = 0 \rightarrow \nu = 4$  with the experimental cross section measured by Allan.<sup>3</sup> 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.

No structure is seen in the  $\nu=0 \rightarrow \nu=1$  cross section. However, peaks below the dissociation threshold energy first appear for  $\nu=0 \rightarrow \nu=2$  cross section and become even more pronounced for the excitations to higher vibrational levels.

The absence of the structure for the  $\nu=0 \rightarrow \nu=0, 1$  excitation and formation of it for higher ones could suggest that the structure of the final state introduces the structure in the cross section. This effect is known as the reflection principle.<sup>17</sup> This possibility, however, was ruled out by a following numerical experiment. The cross section for the  $\nu=0 \rightarrow \nu=0$  vibrational “excitation” was calculated then as the  $H_2^-$  Born–Oppenheimer potential was shifted in such a way that its minimum coincides with a minimum of the neutral  $H_2$  molecule. *The shift affected only the shape of the broad background line, leaving the fine structure in the cross section the same as obtained in Figs. 4(b)–(d). The conclusion is obvious: peaks in the cross section are unrelated to the structure of initial or the final states and cannot be explained by the reflection principle.*

Another possible explanation would be to relate the structure appearing in the vibrational excitation cross section to the discrete resonance states of  $H_2^-$  appearing at energies below the dissociation threshold energy. However, resonance positions do not coincide with the peak positions in the cross section. *Moreover, the widths of the peaks appearing in the cross section are 2 to 3 times smaller than the widths of the resonances calculated before.* The structure appears in the cross section although the resonances are broad and overlapping.

## VII. STRUCTURE IN THE CROSS SECTIONS AND INTERFERENCE

There is a similarity between Figs. 1(a) and 1(b) and Figs. 2(a) and 2(b) where the electron- $H_2$  scattering cross section and the phase of the corresponding excitation probability amplitude are shown. The phase shows an oscillatory behavior rather than sharp drops since the complex cross section amplitude does not exactly vanish. Note that our numerical results presented in Fig. 2(a) are in reasonable agreement with the experimental cross section.<sup>3</sup>

We will now give a more detailed description of this phenomena. By solving the nuclear  $H_2^-$  Schrödinger equation with the complex potential surface we obtained two distinctive types of resonance states, as discussed in the Sec. VI. 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  $H_2(\text{bound}) + e^- \xleftarrow{A} H_2^-(\text{continuum}) \xrightarrow{B} H^- + H$  (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 dissociation (B) occurs at the outer region where the width of the complex potential is zero. As we will 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. This is a direct result of the non-Hermitian properties of  $H_2^-$  Hamiltonian as was shown in Sec. V. Consequently,  $|a_n(\text{cont-res})| \gg |a_n(\text{disc-res})|$  but, however, at  $E = E_n(\text{disc-res})$ ,

$$\left| \frac{a_n(\text{disc-res})}{(i/2)\Gamma_n(\text{disc-res})} \right| \approx \left| \frac{a_{n'}(\text{cont-res})}{\Delta E + (i/2)\Gamma_{n'}(\text{cont-res})} \right|, \quad (28)$$

where

$$\Delta E = E_n(\text{disc-res}) - E_{n'}(\text{cont-res}), \quad (29)$$

even when the difference between the  $\text{H}_2^-(\text{disc-res}) \rightarrow \text{H}_2 + e^-$  resonances and  $\text{H}_2 + e^- \leftarrow \text{H}_2^-(\text{cont-res}) \rightarrow \text{H}^- + \text{H}$  resonances is much larger than the corresponding resonance widths,  $\Delta E \gg \text{Max}(\Gamma_n, \Gamma_{n'})$ .

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  $t_{\text{res}}$  given in Eq. (3).

### VIII. CONCLUSIONS

We can 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  $\text{H}_2^-$ , 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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