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Time-dependent resonant scattering: An analytical approach

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A time-dependent description is given of a scattering process involving a single resonance embedded in a set of flat continua. An analytical approach is presented which starts from an incident free particle wave packet and yields the Breit-Wigner cross-section formula at infinite times. We show that at intermediate times the so-called Wigner-Weisskopf approximation is equivalent to a scattering process involving a contact potential. Applications in cold-atom scattering and resonance enhanced desorption of molecules are discussed. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4825335>]

I. INTRODUCTION

Resonant scattering was examined in the early days of quantum mechanics by Fano¹ and by Breit and Wigner,² and is nowadays usually described in the framework of time-independent (on-the-energy-shell) collision theory.³ On the other hand, modern experimental techniques have progressed to the point where many physical and chemical processes can be observed in “real time.”^{4–6} The interest in time-dependent quantum theory has therefore been revived, in particular since it provides descriptions in line with intuitive expectations in many situations. To the best of our knowledge however, no complete analytical derivation of resonant scattering has ever been given which starts directly from the time-dependent Schrödinger equation. Numerical techniques, such as wave packet propagation, are of course perfectly capable of accounting for resonant scattering, but an analytical description is helpful in giving physical insight into the resonant processes and providing easily manageable expressions to describe the problem. In addition, the present treatment can clarify which properties of an observed time-dependent processes are general manifestations of resonant scattering, and which are specific to the system studied. The original treatment by Wigner and Weisskopf^{7,8} describes the decay into various continua of a bound state which has been populated “suddenly” at time $t = 0$. Our derivation takes a different point of view, corresponding more closely to an adiabatic description in which a wave packet, coming from the remote past, approaches the target and populates the bound state transiently during the collision. Notably, the manipulation and observation of quantum wave packets has grown in importance in tandem with experimental advances,⁹ and includes vibrational¹⁰ and electronic^{11,12} wave packets, as well as complicated combinations thereof.^{13,14} Further, scenarios associated with impulsive ionization by optical pulses such as time resolved Fano resonances have recently aroused interest.^{15,16}

The present development pertains to situations that involve particle pulses rather than photon pulses. Such pulses (on the picosecond scale) are used in ultrafast electron diffraction (UED).^{17–19} Particularly relevant to the present treatment is the rapid development of highly coherent sources of cold electrons.^{20–22} Cold-atom collisions can also be studied in

the time domain. Boesten *et al.*²³ have observed the time dependence of a cold-atom collision in a pulsed photoassociation experiment. Their experiment involves a g -wave shape resonance populated by cold colliding ⁸⁵Rb atoms. We shall outline below, for the sake of illustration, how the present formalism relates to these experiments. Finally, short electron pulses are also generated in surface science experiments when metal surfaces are irradiated by fast laser pulses.²⁴ It is known that chemical processes at surfaces are often enhanced by resonant scattering of such electrons from the molecules present on the surface. The possible control of such resonance-assisted hot-electron femtochemistry at surfaces is a subject of discussion.²⁵

II. TIME-DEPENDENT RESONANT SCATTERING

A. Solution of the time-dependent Schrödinger equation: Wigner-Weisskopf approximation

Consider the scattering of a wave packet due to its coupling to a resonant discrete state.⁸ The discrete state $|\phi\rangle$, with energy E_ϕ , interacts with a set of structureless continua $|\phi_{E\alpha}\rangle$ through an interaction V . Following Breit and Wigner² we assume that the interaction does not mix the continuum states, in other words, the resonant state dominates all processes.²⁶ The α indexes the channels and other properties, as for instance, the direction of the momentum which defines the direction of propagation of a plane wave.

We write the wave packet as a time-dependent superposition of the stationary discrete and continuum states:

$$\psi(t) = a(t)e^{-iE_\phi t/\hbar}|\phi\rangle + \sum_\alpha \int b_{E\alpha}(t)e^{-iEt/\hbar}|\phi_{E\alpha}\rangle dE. \quad (1)$$

Inserting the ansatz in Eq. (1) into the time-dependent Schrödinger equation yields the following coupled system for the amplitudes $a(t)$ and $b(t)$:

$$\begin{cases} \dot{a}(t) = -i\hbar^{-1} \sum_\alpha \int V_{E\alpha} b_{E\alpha}(t) e^{-i(E-E_\phi)t/\hbar} dE \\ \dot{b}_{E\alpha}(t) = -i\hbar^{-1} V_{E\alpha}^* a(t) e^{i(E-E_\phi)t/\hbar} \end{cases}, \quad (2)$$

where $V_{E\alpha} = \langle \phi | V | \phi_{E\alpha} \rangle$.

Eq. (8) we can rewrite Eq. (6) as

$$\begin{aligned} e^{i(E_0 - E_\phi)t/\hbar} \dot{a}(t) &= -i\hbar^{-1} V_{E_0\alpha_0} (\hbar \dot{c}(t) - i(E_0 - E_\phi)c(t)) \\ &= -i\hbar^{-1} V_{E_0\alpha_0} \left(f_\eta(t) - \frac{1}{\pi\hbar} c(t) \int \Gamma(E) \right. \\ &\quad \times \left. \left[\int_0^\infty e^{-i(E - E_0)\tau/\hbar} d\tau \right] dE \right). \end{aligned} \quad (9)$$

By using

$$\int_0^\infty e^{-ixt} dt = -i\pi \frac{1}{x} + \pi\delta(x), \quad (10)$$

where νp stands for the principal value integral and δ is the Dirac δ -function, we define the energy shift of the bound state at $E = E_0$ as $\Delta(E_0) = \sum_\alpha \nu p \frac{|V_{E\alpha}|^2}{E_0 - E}$, in addition to the half-width, which is $\Gamma(E_0) = \pi \sum_\alpha |V_{E_0\alpha}|^2 \approx \Gamma(E_\phi)$ with our assumptions. In the Wigner-Weisskopf approximation a resonance is thus characterized by a well defined complex energy $E_\phi + \Delta - i\Gamma$. Equation (9) now becomes

$$\hbar \dot{c}(t) - i(E_0 - E_\phi - \Delta + i\Gamma)c(t) = f_\eta(t). \quad (11)$$

The solution of Eq. (11) is

$$\begin{aligned} c(t) &= \hbar^{-1} \int_{-\infty}^t f_\eta(t') e^{i(E_0 - E_\phi - \Delta + i\Gamma)(t - t')/\hbar} dt' \\ &= \hbar^{-1} \int_0^\infty f_\eta(t - \tau) e^{i(E_0 - E_\phi - \Delta + i\Gamma)\tau/\hbar} d\tau, \end{aligned} \quad (12)$$

where in the second equation the integration variable has been changed to $\tau = t - t'$. Subsequently, we obtain the probability amplitude $b_{E\alpha}(t)$ by inserting $a(t)$ given by Eqs. (8) and (12) into Eq. (5). We begin by examining the limit $b_{E\alpha}(t \rightarrow \infty)$ with the purpose of recovering the scattering matrix.

B. Scattering matrix

We obtain the amplitude of probability $b_{E\alpha}(t)$ by inserting $a(t)$ given by Eqs. (8) and (12) into Eq. (5), and we examine the limit $t \rightarrow \infty$:

$$\begin{aligned} b_{E\alpha}(+\infty) &= b_{E\alpha}(-\infty) \\ &\quad - \hbar^{-2} V_{E\alpha}^* V_{E_0\alpha_0} \\ &\quad \times \int_{-\infty}^{+\infty} \left[\int_0^\infty f_\eta(t' - \tau) e^{i(E_0 - E_\phi - \Delta + i\Gamma)\tau/\hbar} d\tau \right] \\ &\quad \times e^{i(E - E_0)t'/\hbar} dt'. \end{aligned} \quad (13)$$

It appears tempting at this point to set $f_\eta(t' - \tau) = f_\eta(t')$ which yields a factorization of the two time integrals in Eq. (13). However, as shown below, this approximation consists in representing the incoming wave packet by a Dirac δ -function which is not the purpose here. Instead we take the Fourier transform $f_\eta(t' - \tau) = \int \hat{f}_\eta(E' - E_0) e^{-i(E' - E_0)(t' - \tau)/\hbar} dE'$ and we make use of Eq. (3) and the relation $\int_{-\infty}^{+\infty} e^{i(E - E')t'/\hbar} dt' = 2\pi\hbar\delta(E - E')$. We thus find

$$b_{E\alpha}(\infty) = \sum_{\alpha'} \left(\delta_{\alpha\alpha'} - 2\pi i \frac{V_{E\alpha}^* V_{E\alpha'}}{E - E_\phi - \Delta + i\Gamma} \right) b_{E\alpha'}(-\infty), \quad (14)$$

where we have set $V_{E_0\alpha}^* \simeq V_{E\alpha}^*$.

The term in brackets (...) of Eq. (14) is independent of the shape of the initial wave packet and of the initially populated channel: it represents the scattering matrix $S_{\alpha\alpha'}(E)$ which is defined at each energy and summarizes the collision process inasmuch as it is independent of boundary conditions. It can be verified with Eq. (14) that $S_{\alpha\alpha'}(E)$ is unitary. In the case studied here, there is only one effective channel coupled to the bound state: the effective (weighted) continuum is

$$|\phi_{Eeff}\rangle = \sqrt{\frac{\pi}{\Gamma}} \sum_\alpha V_{E\alpha}^* |\phi_{E\alpha}\rangle. \quad (15)$$

All the eigenvalues of the scattering matrix in our example are equal to 1, except the one corresponding to ϕ_{Eeff} which is $\frac{E - E_\phi - \Delta - i\Gamma}{E - E_\phi - \Delta + i\Gamma}$. The scattering matrix corresponding to this single continuum channel is a scalar which may be written as $S(E) = e^{2i\delta(E)}$ where $\delta(E)$ is the phase-shift induced by the scattering. We obtain

$$\tan \delta(E) = -\frac{\Gamma}{E - E_\phi - \Delta}, \quad (16)$$

which is the well-known expression for the resonant phase underlying the Breit-Wigner² or Beutler-Fano³ cross section formulae. Following the derivation by Wigner²⁹ and Smith,²⁷ the time delay of the scattered wave packet is $\Delta t = \mathcal{R}[-iS^{-1}dS/dE]_{E_0} = 2\frac{d\delta}{dE}|_{E_0}$.

C. Solutions for $a(t)$ and $b(t)$ at intermediate times

We may formally extend the time integration in Eq. (12) from $-\infty$ to $+\infty$ by introducing the step function $\theta(t)$ (0 if $t < 0$ and 1 if $t > 0$) in the integrand. The complete solution of Eq. (12) then takes the form of a time convolution product which we denote by $*$:

$$c(t) = [f_\eta(t)] * [h(t) e^{i(E_0 - E_\phi)t/\hbar}] \hbar^{-1}. \quad (17)$$

Here $h(t) = \theta(t) e^{-i\Delta t/\hbar} e^{-\Gamma t/\hbar}$ is the amplitude of decay in the interaction picture of the discrete state prepared at $t = 0$ and coupled to the continua. $h(t)$ is obtained when the initial system, Eq. (2), is resolved with the boundary conditions $a(t = 0) = 1$ and $b_{E\alpha}(t = 0) = 0$. The term $e^{i(E_0 - E_\phi)t/\hbar}$ is a phase term due to the detuning of the discrete state from the center of the wave packet. We note that the term $e^{-\Gamma t/\hbar}$ contained in $h(t)$ acts as a cut-off function: since $1/\Gamma \ll 1/\eta$, $f_\eta(t - \tau)$ is a slowly varying function on a time scale proportional to $1/\Gamma$.

Based on these considerations we now derive an expression for the amplitudes of probability at intermediate times, which we obtain with the help of an approximate solution of Eq. (12). Setting initially $f_\eta(t - \tau) \approx f_\eta(t)$ we find that the leading term of $c(t)$, in zeroth order, becomes

$$c(t) \approx i \frac{1}{E_0 - E_\phi - \Delta + i\Gamma} f_\eta(t). \quad (18)$$

In this approximation the amplitude of the discrete state follows the evolution of the wave packet adiabatically. Notice, however, that this approximation does not give the correct energy dependence of the scattering matrix because Eq. (14)

is obtained with the wave packet energy E_0 in the energy denominator, instead of the energy E of the whole quantum system. The resonant contribution to the scattering matrix does therefore not go to zero as $E - E_0 \rightarrow \pm\infty$.

A better approximation is obtained when the first order term is kept in the expansion of $f(t - \tau)$:

$$c(t) = i \frac{1}{E_0 - E_\phi - \Delta + i\Gamma} f_\eta(t) + \frac{\hbar}{(E_0 - E_\phi - \Delta + i\Gamma)^2} \dot{f}_\eta(t). \quad (19)$$

According to our assumptions we have $\dot{f}_\eta(t) \lesssim (\eta/\hbar) f_\eta(t)$, and therefore the second term is a small correction which takes account of the fact that the energy is only approximately conserved, namely to within the interval defined by the initial dispersion η of the wave packet.

The probability amplitude $b_{E\alpha}(t)$ for intermediate times is derived directly from Eqs. (5) and (12):

$$b_{E\alpha}(t) = b_{E\alpha}(-\infty) - i \frac{V_{E\alpha}^* V_{E_0\alpha_0}}{E - E_\phi - \Delta + i\Gamma} \times (F(E, t) - c(t)e^{i(E-E_0)t/\hbar}). \quad (20)$$

This expression can be verified by direct time derivation. The coefficient $c(t)$ in Eq. (20) is given by Eq. (17) and vanishes at $t \rightarrow \pm\infty$. The term that contains $c(t)$ represents the transient population due to the resonance. The function $F(E, t)$ on the other hand represents the persistent population transfer,

$$F(E, t) = \hbar^{-1} \int_{-\infty}^t f_\eta(\tau) e^{i(E-E_0)\tau/\hbar} d\tau. \quad (21)$$

This term vanishes at $t \rightarrow -\infty$, while for $t \rightarrow \infty$ it converges to the wave packet energy distribution $2\pi \hat{f}_\eta(E - E_0)$. The energy width of this function depends on t , but only slightly so: it can be shown that for a symmetric energy distribution the width of $\text{Re} F(E, 0)$ is η , while $\text{Im} F(E, 0)$ varies as $\eta/(E - E_0)$, i.e., it decreases slowly with the energy. However, due to the second inequality in Eq. (7) the energy spread remains small compared to Γ .

1. Exact analytical solution for Gaussian distributions

If we choose an initial normalized Gaussian distribution for the wave packet, $\hat{f}_\eta(E - E_0) = N e^{-\frac{(E-E_0)^2}{2\eta^2}}$, $N = (\pi\eta^2)^{-1/4}$, we obtain

$$F(E, t) = N\pi e^{-\frac{(E-E_0)^2}{2\eta^2}} \text{erfc} \left[-\frac{1}{\sqrt{2}} \left(\frac{\eta t}{\hbar} - i \frac{E - E_0}{\eta} \right) \right], \quad (22)$$

where erfc is the complementary error function.³⁰ Figure 2 illustrates the amplitude $|F(E, t)|$ as a function of energy and time. Note that at large times t the coefficient $c(t)$ goes to zero so that only the amplitude $F(E, t)$ contributes to the wave packet. The probability amplitude of the effective continuum

FIG. 2. The amplitude $|F(E, t)|$ in Eq. (21) for the case of a Gaussian wave packet. The amplitude is plotted as a function of energy at various times separated by intervals corresponding to $0.2/\eta$ ($\hbar = 1$).

defined in Eq. (15) becomes, with Eq. (20),

$$b_{Eeff}(t) = \sqrt{\frac{\pi}{\Gamma}} V_{E_0\alpha_0} \left[\hat{f}_\eta(E - E_0) - i \frac{\Gamma/\pi}{E - E_\phi - \Delta + i\Gamma} \times (F(E, t) - c(t)e^{i(E-E_0)t/\hbar}) \right]. \quad (23)$$

In Fig. 3(a), the coefficient $|b_{Eeff}(t)|$ is shown as a function of time and energy when calculated using the analytical solution of $F(E, t)$ from Eq. (22) and the corresponding analytical form of $c(t)$ which is

$$c(t) = N\pi e^{-\frac{E^2}{2\eta^2} + i \frac{Et}{\hbar}} \text{erfc} \left[-\frac{1}{\sqrt{2}} \left(\frac{\eta t}{\hbar} + i \frac{\tilde{E}}{\eta} \right) \right], \quad (24)$$

where $\tilde{E} = E_0 - E_\phi - \Delta + i\Gamma$. The coefficient $c(t)$ reaches its maximum value at $c(t = 0) \approx N\sqrt{2\pi}(\eta/\Gamma)$. It is evident from Fig. 3(a) that the wave packet resides in the continuum for $t \ll 0$, then becomes transiently absorbed into the E_ϕ resonance around time $t \approx 0$, and finally decays back into the continuum for $t \gg 0$. The analytical solutions provided in Eqs. (22)–(24) offer the opportunity to examine the accuracy of the approximate form of $c(t)$ presented in Eq. (19). In Fig. 3(b) the percentage error in the amplitude of $b_{Eeff}(t)$ is calculated when the approximation in Eq. (19) is used instead of the exact form in Eq. (24). As expected, the asymptotic wave packets at both $t \ll 0$ and $t \gg 0$ are almost identical. The maximum error occurs around time $t = 0$, although it remains well below 1% at all times. It should be noted that the phase error persists to greater times, see Fig. 3(c), although it remains comparatively small throughout.

D. Coordinate representation of the wave packet

An alternative interpretation of Eq. (20) can be given in terms of a coordinate r -representation of the wave packet. We take free plane waves, $\langle \vec{r} | \phi_{E\alpha} \rangle = N_{pw} e^{ik\hat{k}_\alpha \cdot \vec{r}}$, with k the wavenumber relative to the threshold α , $\hat{k}_\alpha$ the unit vector

FIG. 3. The coefficient $|b_{E\alpha}(t)|$ evaluated as a function of energy E and time t , with parameters $E_\phi = 3.9$, $\Gamma = 1$, $E_0 = 3.90004$, and $\eta = 0.005$ ($\hbar = 1$). (a) Analytical solution of $|b_{E\alpha}(t)|$ for a Gaussian distribution, from Eq. (23). (b) Absolute error in percent for $|b_{E\alpha}(t)|$ when using the approximate rather than exact form of $c(t)$ [Eqs. (19) and (24)]. The percentage error is insensitive to the parameters. (c) Absolute error in percent of complex component of $b_{E\alpha}(t)$ when using the approximate form.

in the direction of the momentum, and $N_{pw} = \sqrt{\mu/2\pi\hbar^2 k_0}$ the energy normalization factor with μ the reduced mass. We examine the case of a single energy threshold. The scattered portion of the wave packet in a given channel α is denoted as $\psi_\alpha^s(\vec{r}, t)$ and may be calculated by use of Eqs. (5)

and (8):

$$\psi_\alpha^s(\vec{r}, t) = -N_{pw} e^{i(k_0 \hat{k}_\alpha \cdot \vec{r} - E_0 t / \hbar)} \int \hbar^{-1} V_{E\alpha}^* V_{E_0 \alpha_0} \times \int_{-\infty}^t c(\tau) e^{-i\hbar^{-1}(E - E_0)(t - \frac{\mu \hat{k}_\alpha \cdot \vec{r}}{\hbar k_0} - \tau)} d\tau dE. \quad (25)$$

Here the linear expansion $k = k_0 + \frac{\mu(E - E_0)}{\hbar^2 k_0}$ has been used while the quadratic (dispersion) term has been neglected. This is a good approximation as long as k_0 is sufficiently large, i.e., $\hbar^2 k_0^2 / \mu = 2E_0 \gg \Gamma$. This also means that threshold effects are disregarded: we do, in any case, not expect the Wigner-Weisskopf approximation to hold near threshold. The integration over the energy in Eq. (25) is carried out by taking $V_{E\alpha}^*$ as a constant. The result is a Dirac δ -function, $2\pi \delta(t - \frac{\mu \hat{k}_\alpha \cdot \vec{r}}{\hbar k_0} - \tau)$. The time integration then yields

$$\psi_\alpha^s(\vec{r}, t) = -2\pi N_{pw} V_{E_0 \alpha}^* V_{E_0 \alpha_0} e^{i(k_0 \hat{k}_\alpha \cdot \vec{r} - E_0 t / \hbar)} \times c \left(t - \frac{\mu \hat{k}_\alpha \cdot \vec{r}}{\hbar k_0} \right) \theta(\hat{k}_\alpha \cdot \vec{r}), \quad (26)$$

where the step function arises because only times $\tau \leq t$ contribute to the integral so that wave propagation occurs only for $\hat{k}_\alpha \cdot \vec{r} > 0$.

Equation (26) indicates that the resonant part of the scattered wave packet is *at all times* directly proportional to the amplitude of the discrete state. If the variation with energy of the coupling term $V_{E\alpha}^*$ was taken into account, one would instead of the step function obtain a time function with a very small width $\sim 1/L$. Under the present assumptions, then, the time during which the coupling of the continuum with the discrete state is effective does not exceed $1/L$. The discrete state therefore has no time to decay as long as the wave packet is present. Adopting the r -representation, we may say that the collision occurs as if the Hamiltonian seen by the free wave packet in the continuum was unchanged except in a range k_0/L near $r = 0$. In other words, the coupling with the discrete state is equivalent to a contact potential, and consequently there is no deformation of the shape of the scattered portion of the wave packet during the whole collision. This would no longer be exactly true if the energy dispersion term was included: with this improved approximation the familiar spreading with time of the wave packet may be obtained.

We finally examine the Eq. (26) for the situation where only a single channel is present ($\alpha = \alpha_0$ is omitted and $\hat{k}_\alpha \cdot \vec{r} = z$). The first term of Eq. (20) represents the propagation of the free wave packet:

$$\int b_E(-\infty) e^{i(kz - Et / \hbar)} dE = f_\eta \left(t - \frac{\mu z}{\hbar k_0} \right) e^{i(k_0 z - E_0 t / \hbar)}. \quad (27)$$

Combined with $\psi_\alpha^s(\vec{r}, t)$ from Eq. (26) it yields the forward scattered part of the wave packet

$$\psi(z, t) = e^{i[k_0 z - E_0 t / \hbar + 2\delta(E_0)]} \times \left[f_\eta \left(t - \frac{\mu z}{\hbar k_0} \right) - 2 \frac{d\delta}{dE} \Big|_{E_0} f_\eta \left(t - \frac{\mu z}{\hbar k_0} \right) \right] = e^{i[k_0 z - E_0 t / \hbar + 2\delta(E_0)]} f_\eta \left(t - \frac{\mu z}{\hbar k_0} - 2 \frac{d\delta}{dE} \Big|_{E_0} \right). \quad (28)$$

This expression is obtained by using $d\delta/dE|_{E_0} = \Gamma[(E_0 - E_\phi - \Delta)^2 + \Gamma^2]^{-1}$, where $\delta(E)$ is the scattering phase shift from, e.g., Eq. (16). The velocity and shape of the wave packet are seen to be the same before and after the collision, which simply adds a phase $2\delta(E_0)$ and a time delay $\Delta t = 2 \frac{d\delta}{dE}|_{E_0}$ ²⁹ to the wave packet. The delay is due to the interference between the part of the free wave packet in the effective continuum and the forward scattered wave. See also the discussion of time delay in Smith's 1960 paper²⁷ as well as more recent work in Ref. 31.

We finally note that Eq. (20) may be obtained directly from the first order expansion of $c(t)$ in Eq. (19). The coefficient of $-i\hbar^{-1}F(E, t)V_{E_0\alpha_0}V_{E\alpha}^*$ is then obtained in the form

$$\frac{1}{E_0 - E_\phi - \Delta + i\Gamma} \left(1 - \frac{E - E_0}{E_0 - E_\phi - \Delta + i\Gamma} \right), \quad (29)$$

which coincides with the first order expansion of $(E - E_\phi - \Delta + i\Gamma)^{-1}$, valid because $E - E_0 \sim \eta \ll \Gamma$ by definition of the initial wave packet.

III. TWO ILLUSTRATIVE EXAMPLES

A. Shape-resonance in cold-atom scattering

The experiment of Ref. 23 monitors a photoassociation transition of cold colliding ⁸⁵Rb atoms. The colliding atoms are doubly spin polarized in the $^2S_{1/2}F = 3, M_F = 3$ atomic state. The upper state of the optical photoassociation transition is chosen such that it selects the $\ell = 4$ orbital component of the colliding ground state atoms. The centrifugal potential associated with their relative motion supports a g -type shape resonance whose temporal evolution is observed by producing the colliding atoms in a pulsed far-off-resonance optical trap. The resonance decays back into the entrance channel, but, as shown in Ref. 23, it can also inelastically decay into the translational continua associated with ground state hyperfine levels which lie lower than the entrance channel threshold. In the experiment described in Ref. 23 the photoassociating laser radiation excites the atoms captured in the shape resonance behind the potential barrier and removes them from the trap. A first pulse eliminates all molecules present in the resonant state, while a second pulse arrives at various delay times after the first and monitors the re-population of the shape resonance as well as its decay. The situation is therefore similar to the one assumed in the present work: α_0 (associated partial width Γ_0) corresponds to the channel of two colliding $^2S_{1/2}F = 3, M_F = 3$ atoms, while the channels α (associated width Γ_d) correspond to the channels associated with the lower lying hyperfine thresholds. The optical trap provides the colliding atoms on a time scale which is long compared to the lifetime of the resonance, exactly as assumed in this work. The energy level scheme is similar as that shown in Fig. 6 below and will not be given here.

In Ref. 23 it was shown that $\Gamma_0/\Gamma_d \approx 2$ in this specific example. Figure 4 presents the time evolution of the experiment calculated according to Eq. (20). The figure shows the initial amplitude $|b_{0E}(t)|$ in the elastic scattering channel impinging on the shape resonance and being depleted, then at

FIG. 4. Results for a shape resonance in cold-atom ⁸⁵Rb scattering, showing the elastic, $|b_{0E}(t)|$, and inelastic, $|b_{\alpha E}(t)|$, channel populations as functions of energy (in milli-Kelvin) and time (in μ s), using parameters from the experiment.²³ (a) Elastic scattering, $|b_{0E}(t)|$. (b) Inelastic scattering, $|b_{\alpha E}(t)|$.

$t > 0$ decaying back into $|b_{0E}(t)|$ elastically as well as into channel $|b_{\alpha E}(t)|$ inelastically. The probabilities for the various channels throughout the process are shown in Fig. 5, with the continuum channel coefficients $b_0(t)$ and $b_\alpha(t)$ integrated over energy to yield total time-dependent probabilities.

B. Resonance-enhanced surface desorption of molecules

The second example presented here concerns resonance-assisted hot-electron femtochemistry at surfaces. Our aim is not to discuss a specific application of the expressions derived in Secs. II A–II D, but rather to sketch a conceptual framework that might be useful in the field of surface desorption.

Surface desorption of molecules is usually discussed in the framework of time-dependent quantum mechanics, see Ref. 25 or the excellent review in Ref. 32. The physical picture of laser-induced resonance-enhanced surface desorption is the following: a pulsed laser beam incident on a metal surface excites electrons from the conduction band, thus creating

FIG. 5. The time-dependent probabilities corresponding to the cold-atom shape resonance in ^{85}Rb scattering, showing the energy-integrated probabilities in the elastic, $b_0(t)$, and inelastic, $b_a(t)$, channels as well as in the resonance, $a(t)$. The total probability is conserved.

a pulse of energetic free electrons. Some of the electrons collide with molecules that are adsorbed on the surface and excite them to form a temporary negative-ion shape resonance. The charge-transfer potential energy surface resulting from the molecule-metal interaction is significantly altered in the excited state as compared to the ground state. Decay of the resonance to the ground state is therefore accompanied by excitation of the molecule-surface vibrational mode, and leads to desorption if the vibrational energy in the final ground state exceeds the dissociation energy.

The hottest possible electrons of the pulse initiated by the incident radiation have an energy $E_F + h\nu$ where E_F is the Fermi level of the substrate and $h\nu$ is the energy of the laser pulse. As in one of the situations considered in Ref. 33, we assume here that the incident electrons in channel α_0 have a rather sharply defined energy E_0 , with a distribution given by $\hat{f}_\eta(E - E_0)$ as in Sec. II (Ref. 33 used a Dirac distribution, cf. Eq. (23) given therein).

We label the ground state of the metal-adsorbate complex as MA . As argued by Gadzuk,³⁴ the continuum of substrate electron states excited by the photon pulse acts like a single-electron continuum and shall be labeled as M^-A . In the notation of the present paper we thus have $\alpha_0 = M^-A$. The ionic excited level created by substrate $\rightarrow$ adsorbate electron transfer is labeled MA^- . It may decay to MA in two ways, either by electron transfer back to the substrate, $MA^- \rightarrow M^-A \rightarrow MA$, or directly, by “non-adiabatic interaction”³² without participation of the metal, through emission of an electron into the vacuum, $MA^- \rightarrow MA + e^-$. The partial widths associated with the two processes are $\Gamma^{(M)}$ and $\Gamma^{(A)}$, respectively. Based on the general principles of molecular theory we anticipate that $\Gamma^{(A)}$ is not likely to exceed any vibrational frequency because in the isolated small molecule one can always find a representation (diabatic or adiabatic) which minimizes the effective interaction.

The surface desorption experiments carried out over the past decades have shown that the resonance widths of electronically excited adsorbates may vary in wide limits, from 10^{-16} to 10^{-6} s,³² depending on the substrate and the adsorbate. Here we briefly consider two limiting cases.

1. Fast quenching of electronic excitation by the substrate

If $\Gamma^M \gg \Gamma^{(A)}$ the electron transfer back into the substrate will be “sudden” in the sense that nuclear motion is slow on the time scale of the quenching process. Desorption occurs only to the extent that the adsorbate manages to stay long enough in the resonant state which gives access to desorption. The limiting yield for desorption in this situation is therefore $\Gamma^{(A)}/(\Gamma^{(M)} + \Gamma^{(A)}) \approx \Gamma^{(A)}/\Gamma^{(M)}$, i.e., the larger the quenching by the substrate, the smaller the yield of desorption. This is the situation which has been assumed in most theoretical models and which indeed is encountered in many experiments. The above analysis is valid for the initial nuclear equilibrium configuration of the metal-adsorbate complex MA . The evolution of the system towards desorption requires use of wave packet propagation techniques as done, e.g., in Ref. 35. In a time-independent approach such a treatment would amount to coherently superposing many vibrational substates of the shape resonance, and therefore is beyond the scope of this paper.

2. Slow quenching of electronic excitation by substrate

When $\Gamma^M \ll \Gamma^{(A)}$ account of nuclear motion is taken as follows. The entrance channel α_0 now corresponds to $M^-A(v_0)$ with v_0 referring to the ground state vibrational wave function. The M^-A electronic continuum is in fact split into a *set of continua* because different vibrational excitations $M^-A(v)$ occur in addition to v_0 , and each vibrational threshold gives rise to a continuum. The ionic excited levels created by substrate $\rightarrow$ adsorbate electron transfer then are $MA^-(v')$ and the decay paths are $MA^-(v') \rightarrow M^-A(v'') \rightarrow MA(v'')$ and $MA^-(v') \rightarrow MA(v'') + e^-$.

We see that the continuum channels α correspond to free electron states associated with the various vibrational levels of the adsorbed molecule. The latter includes the levels of the molecule-surface vibrations as well as the internal modes of the adsorbate. Only a finite range of these is accessible owing to the energetics of the experiment, and only a subclass $\{\alpha_d\}$ is actually desorptive. The remaining thresholds, denoted $\{\alpha_i\}$, correspond either to the excitation of internal modes of the adsorbed molecule or to vibrationally bound levels of the metal-adsorbate modes. Figure 6 schematically illustrates this situation.

According to this picture the total resonance width Γ may be partitioned into contributions: $\Gamma = \Gamma_i^{(M)} + \Gamma_d^{(M)} + \Gamma_i^{(A)} + \Gamma_d^{(A)}$. The values of the coupling elements $V_{E\alpha}$ in this situation are modulated according to the Franck-Condon principle:

$$V_{E\alpha_{i/d}}^{(M/E)} = \sqrt{\frac{[\Gamma_i^{(M/E)}(E) + \Gamma_d^{(M/E)}(E)]}{\pi}} \int \chi^{(-)}(R) \chi_{\alpha_{i/d}}(R) dR, \quad (30)$$

where R is the coordinate associated with a particular adsorbate-surface or internal adsorbate mode, $\chi_{\alpha_{i/d}}(R)$ are the (bound or dissociative) vibrational wave functions v'' of the ground adsorption state, while $\chi^{(-)}(R)$ is the (generally displaced) vibrational wave function v' of the negative-ion

FIG. 6. Energy level diagram pertaining to an electron-induced resonant desorption of a molecule adsorbed on a metal surface (DIET). Continua are indicated by boxes, while the associated thresholds are indicated by dotted lines. Adsorbate vibrational levels are represented by the thresholds (α_i internal modes and/or non-dissociative substrate-adsorbate modes, α_d desorptive substrate-adsorbate modes). E_F is the Fermi level of the metal. The continua associated with each such state are electronic.

resonance state. For simplicity we have assumed that the couplings $V_{E\alpha_i}^{(M/A)}$ and $V_{E\alpha_d}^{(M/A)}$ are independent of R , and that it is sufficient to consider a single value v' at a time. The yield for desorption in this limit is $[\Gamma_d^{(M)} + \Gamma_d^{(A)}]/[\Gamma_d^{(M)} + \Gamma_d^{(A)} + \Gamma_i^{(M)} + \Gamma_i^{(A)}]$, that is, unlike in the fast-quenching case, the yield should scale with the sum of the desorptive Franck-Condon factors, but be independent of the relative strengths of the substrate and non-adiabatic quenching processes.

The main feature in this picture is the interaction of the resonant negative-ion state with the conduction band as well as with the electronic continuum of the neutral ground state of the adsorbed molecule. We shall not discuss in detail the associated time-dependent aspects here, we just stress that the time-dependent resonant scattering approach presented in this paper does provide a conceptual framework for resonantly enhanced surface desorption, although it is obviously not appropriate for all situations that may be encountered. For the purpose of comparison we note that previous theoretical approaches to resonantly enhanced surface desorption range from a phenomenological rate equation treatment²⁵ (where the electron flux is multiplied with the time-independent Breit-Wigner cross section expression), and elaborate multi-dimensional wave packet calculations on *ab initio* potential energy surfaces describing the molecule-surface interaction.³⁵ Our approach might help to render the simple model calculations more realistic.

IV. CONCLUSION

The present development is intended to analytically bridge the gap between the time-dependent and time-independent formulations of quantum mechanics for a fundamental scattering event, that of a free particle wave packet interacting with an isolated bound state coupled to a set of flat continua. An important aspect here is the fact that we make no “sudden” approximation, but let the incoming wave packet evolve nearly adiabatically at all times. It turns out that in the framework of the Wigner-Weisskopf approximation the

discrete-continuum interaction takes the character of a contact potential. The bound state remains continually populated during the passage time $\sim 1/\eta$ of the wave packet [Eqs. (8) and (19)] and scatters the incoming wave packet inelastically into all channels coupled to it [Eqs. (20) and (21)]. We have further shown that an isolated resonance embedded in a set of flat continua corresponds, in the time dependent picture with free propagation of plane waves, to a wave packet that proceeds with unchanged velocity and shape at all times, and simply undergoes a phase shift and a time delay during the collision [Eqs. (26) and (28)].

All presented expressions should prove simple to handle — in particular in situations where the incoming wave packet may be approximated by a Gaussian shape — and should lend themselves to straightforward interpretation of resonant collision experiments monitored in real time. As an example we have outlined the application of the formalism to two processes which are studied experimentally. The first concerns time-resolved measurements of cold-atom scattering, and illustrates how competing elastic and inelastic time-dependent processes can be modeled very easily using the theoretical results in this paper together with experimental parameters. The second example is the surface desorption induced by electronic transitions (DIET). The purpose here is obviously not to compete with sophisticated theoretical developments such as presented in Refs. 35 and 36, based on elaborated *ab initio* potential surfaces³⁵ and accounting for multiple electron transitions as well as nonlinear effects induced by high laser intensities.³⁶ However, the basic Breit-Wigner approach extended into the time domain allows us to separate the resonance phenomena that are of a *general* nature from the specific characteristics of the DIET process embodied in electronic interactions, potential surfaces, and vibrational motion.

Currently, there is rapid progress in new electron sources capable of delivering cold electron bunches of arbitrary energy, shape, and duration.^{20–22} At the moment, these sources are primarily intended for the use in electron diffraction experiments on molecules.³⁷ As the electron energies are progressively lowered, effects of resonant scattering such as discussed here should become observable. Finally, we are in the process of adapting the formalism presented in this paper to problems associated with impulsive ionization by optical pulses such as time resolved Fano resonances,^{15,16} electron correlation times, and photo-emission time.³⁸

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