Nuclear dynamics of decaying states: A time-dependent formulation

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The wave packet dynamics accompanying the excitation to a decaying electronic state and the subsequent decay to final electronic states are discussed. The cross sections for the excitation and for the production of final states are related to the corresponding wave packets. The time-dependent formulation adds insight into the process and is amenable to semiclassical approximations and interpretations. It can also be used to compute the gross features of the observed spectra via a spectral moment expansion. An illustrative application demonstrates the usefulness of the expansion.

I. INTRODUCTION

Most or even all excited electronic states possess a finite lifetime and decay by emitting either photons or other particles, e.g., electrons. The investigation of the excitation process and, in particular, of the emitted particles provide information on the decaying states as well as on the final states following the decay. The observed spectra and cross sections are greatly influenced by the nuclear dynamics in both the decaying and final states. If the excited state is long lived, the decay process is usually governed by the Franck-Condon principle or by straightforward extensions of it. A shorter lifetime which compares with typical times of the internal degrees of freedom of the system (e.g., vibrations), may give rise to interesting interference effects owing to the overlapping nuclear levels in the decaying electronic state. Further interesting effects are expected if a competition between different decaying channels is present. A vast number of processes involving the decay of states with a lifetime on the latter scale have been investigated of which we mention just a few. Energetically deep levels are preferably populated by photon or electron impact. The decay of those levels is studied by Auger and x-ray emission spectroscopies. In the photoionization cross sections of molecules the effects of short-lived resonance states constitute a common phenomenon in molecules and markedly influence the electron-molecules scattering cross sections.

In the present work we investigate the dynamics of the general situation shown in Fig. 1. The wave packet describing the nuclear motion in the target system is excited to a decaying electronic state where it propagates on the corresponding potential energy surface. During this propagation this wave packet gradually decays to the final electronic state. A relatively complex wave packet grows in time on the potential surface of the latter state to which new contributions are continuously added at later times. The knowledge of the wave packet in the decaying state is needed to compute the cross section for the production of this state. Clearly, the information on the cross section for the production of the final states of the decay is contained in the wave packet propagating on the corresponding surface. It is the major task of the present paper to investigate these wave packets and to relate them to the cross sections.

A time-dependent formulation of the theory is attempted. The reasons for this choice are twofold. First, a time-dependent picture leads to a better insight of the process itself. This is particularly relevant if several competing degrees of freedom are involved. As an example we mention the competition between dissociation and autoionization following inner-shell excitation of molecules. Second, a time-dependent formulation may also have technical advantages and be the appropriate tool for the computational evaluation of the cross sections. In the last years efficient time-dependent methods have been developed for propagating wave packets on potential energy surfaces. Although the present situation indicated in Fig. 1 is more complicated because of the two potential surfaces and two time scales involved, the available techniques will be useful. This applies the more the shorter the lifetime is of the decaying electronic state.

In Sec. II the cross sections for the production of the decaying and of the final electronic states are discussed within a time-dependent theoretical framework. These observables are related in Sec. III to the wave packet dynamics. In Sec. IV the gross features of the observed spectra are discussed in terms of spectral moments and a helpful semiclassical theory is presented. In many experiments the structures due to the nuclear dynamics are not resolved. Nevertheless, this dynamics can have strong impact on the gross features of the bands observed in the spectrum. Recently, it has been noticed theoretically that even the energetic positions of the bands can significantly depend on the nuclear dynamics making a reinterpretation of observed spectra necessary. A brief illustrative application to the Auger spectra of CO is presented in Sec. IV.
FIG. 1. The wave packet is excited from the initial electronic state to the decaying electronic state where it propagates on the potential energy surface of the latter. During this propagation the wave packet continuously decays to the final electronic state. The decayed components propagate on the surface of the final state and may interfere with one another.

II. TIME-DEPENDENT FORMULATION OF THE CROSS SECTIONS

Let us consider the following basic process. The target system is in the initial electronic state \(|i\rangle\) and vibrational state \(|n_i\rangle\). By impact with some projectile, e.g., photon, electron, the system is excited (or ionized) to the intermediate state \(|d\rangle\). The matrix element for this excitation is \(V\) and may depend on the nuclear coordinates of the target and on the difference between the energies of \(|d\rangle\) and of the projectile. The state \(|d\rangle\) is coupled to a continuum, the coupling matrix element being \(W\), and may thus decay via the emission of a photon or an electron. Clearly, \(W\) may also depend on the nuclear coordinates of the system and on the energy of the emitted particle.

The relevant quantity which describes the aforementioned general situation is the transition probability per unit time from the initial state to the final state of the decay. This transition probability reads\(^{11}\)

\[
P_{fi} = 2\pi \langle n_f | W (\mathcal{H} - \mathcal{H}_d)^{-1} V | n_i \rangle^2 \delta(E_i - E_F),
\]

where \(E_i\) and \(E_F\) are the total energies of the initial state plus incoming projectile and of the final state \(|f\rangle |n_f\rangle\) plus all the particles present at the end of the process, respectively. It should be noted that the electronic wave functions do not appear in expression (2.1). Their effect is in the transition and decay matrix elements \(V\) and \(W\). The energy \(E\) is the excess energy which has been absorbed into the system by the impact with the incoming projectile and is available for the decay. If this projectile is a photon and the intermediate state \(|d\rangle\) is a neutral state, \(E\) is just the photon energy. If \(|d\rangle\) is an ionic state, i.e., the primary process is photoionization, then \(E\) is the photon energy less the energy of the photoelectron. Analogously, if the projectile is an electron, the excess energy \(E\) is simply the energy loss through the impact in case the primary event is excitation and the energy loss less the kinetic energy of the ionized electron in the case of ionization. Unless otherwise stated, we choose the energy of the target system to be the zero of the energy scale.

\(\mathcal{H}_d\) is the complex and, in general, energy-dependent Hamiltonian describing the nuclear motion in the intermediate decaying state. It consists of the Hamiltonian \(H_f\) for the nuclear motion in the electronic state \(|d\rangle\) and terms \(\Delta - i\Gamma/2\) due to its interaction with the continuum

\[
\mathcal{H}_d = H_d + \Delta - i\Gamma/2.
\]

The imaginary part \(-\Gamma/2\) of \(\mathcal{H}\) represents the decay width and the real part \(\Delta\) the shift resulting from this interaction. These quantities read as

\[
\Gamma = 2\pi \sum_k W^* \delta(E - E_k - H_f) W, \tag{2.3a}
\]

\[
\Delta = P \sum_k W^* (E - E_k - H_f)^{-1} W, \tag{2.3b}
\]

where the summation is over the continuum states of the particle with energies \(E_k\) emitted in the decay and \(P\) denotes the Cauchy principle value. \(H_f\) is the Hamiltonian describing the nuclear motion in the final electronic states \(|f\rangle\). The operator properties of the width \(\Gamma\) and shift \(\Delta\) are only of relevance in situations where the decaying state and the final state are energetically very close together. Then nonadiabatic electron-nuclear energy transfer effects may take place, in particular, in targets with large dipole moments. A prominent example is found\(^{12}\) in the resonant low-energy electron scattering off HCl where interesting threshold peaks have been observed.\(^{13}\) Apart from such interesting but rare cases, the width \(\Gamma\) and shift \(\Delta\) can be considered to a good approximation as functions of the nuclear coordinates alone and independent of the energy. The quality of this so-called local approximation has been discussed in the literature.\(^{14}\) The local approximation is particularly excellent when the decaying state is energetically far from overlapping the final state. In the following we shall restrict ourselves to the local approximation and will return briefly to the general case in a subsequent publication.\(^{13}\)

It is clear that Eq. (2.1) is quite general and the cross sections for numerous experiments can be deduced from it. We may distinguish between two types of experiments. In the first type the primary excitation (or ionization) of the target is detected. Examples are photoelectron spectroscopy where the ionized states can decay, for instance, via Auger decay and electron energy loss spectroscopy involving the excitation of inner-valence or core electrons.
corresponding cross sections are determined from Eq. (2.1) by integrating over the momenta of the emitted particle and by summing over the vibrational states \(|n_f\rangle\) of the final electronic state. This leads to the cross section

\[
\sigma_f(E) \sim \langle n_f | W(E+H'_{nf}-\mathcal{H}_d) V | n_f \rangle.
\]

(2.4)

The proportionality factor contains kinematic quantities and a function of energy arising from the conversion of momentum \(dk\) into energy \(dk_E\). The quantity \(\sigma_f(E)\) describes the observation of a single vibrational band corresponding to the electronic state \(|d\rangle\). \(V\) is actually energy dependent, but since we do not consider overlapping states it can be assumed to be energy independent over the band. \(|W|^2\) is proportional to \(\Gamma\). In the case where the intermediate state can decay into several final states, all the previous equations still hold if we take \(\Gamma\) to be the total width and \(|W|^2\) in Eq. (2.1) to be proportional to the partial width for the final state \(|f\rangle\) under consideration (see Ref. 15 for more details).

To proceed we note that

\[
(E-H_d)\langle n_f | W(E-H_d) V | n_f \rangle = \langle n_f | W(E+H'_{nf}-H_d) V | n_f \rangle
\]

which readily leads to

\[
\sigma_f(E) \sim \text{Re} \int_0^\infty \text{e}^{iE t} \langle n_f | V^{*} \text{e}^{-i\mathcal{H}_d t} V | n_f \rangle dt
\]

(2.6a)

which is nothing but the real part of the Fourier transform of the autocorrelation function. \(|\Psi_d(0)\rangle = V |n_f\rangle\) can be viewed as the wave packet transferred at time \(t=0\) to the potential energy surface of the intermediate state where it propagates via the Hamiltonian \(\mathcal{H}_d\), i.e., \(|\Psi_d(t)\rangle = \text{exp}(\text{-i}\mathcal{H}_d t) |\Psi_d(0)\rangle\). Consequently,

\[
\sigma_f(E) \sim \text{Re} \int_0^\infty \text{e}^{iE t} \langle \Psi_d(0) | \Psi_d(t) \rangle dt.
\]

(2.6b)

Equation (2.6) which is well known for real potential energy surfaces is seen to apply also for decaying states with complex surfaces which is not surprising. In the common Condon approximation the transition matrix element \(V\) is treated as a constant instead of a function of the nuclear coordinates and the equations simplify somewhat.

In the second type of experiment one measures the final states or, more precisely, the particle emitted due to the decay of the intermediate state. Examples are Auger spectroscopy, x-ray emission, as well as resonant Auger spectroscopy and the corresponding resonant x-ray emission. In the former two examples the system is ionized, for instance, by a photon, and one must integrate the transition probability, Eq. (2.1), over the photoelectron states in order to obtain the cross section for the secondary Auger electron. The result reads as

\[
\sigma_f(n_{f},E) \sim \langle n_{f} | W(E+E_{n_{f}}-\mathcal{H}_d) V | n_{f} \rangle^2.
\]

(2.7)

where \(E\) is now the energy of the Auger electron and \(E_{n_{f}}\) is the energy corresponding to \(|n_{f}\rangle\). In the latter two examples the system is excited, for instance, by a photon, and one integrates over the bandwidth of the photon source. If this bandwidth is broad, the cross section is again given by Eq. (2.7). On the other hand, if the bandwidth is narrow compared to the decay width \(\Gamma\), i.e., the photon source is monochromatic, then Eq. (2.7) must be multiplied by an apparatus function peaked around \(E = E_p - E_{n_{f}}\), where \(E_p\) is the energy of the exciting photon. In most experiments the cross section is not separately recorded for each final vibrational level \(|n_{f}\rangle\). The observed spectrum is rather obtained by summing over these levels:

\[
\sigma_f(E) \equiv \sum_{n_{f}} \sigma_f(n_{f},E).
\]

(2.8)

The cross section (2.4) for observations of the short-lived state does not exhibit interference effects; \(\sigma_f(E)\) can essentially be written as an incoherent superposition of Lorentzian lines. In the cross section (2.7) and (2.8) for observations of the final state, on the other hand, there are interference effects: If \(\Gamma \ll \omega\), where \(\omega\) is the typical vibrational spacing in the decaying state, its vibrational levels overlap and coherently contribute to the same final vibrational state \(|n_{f}\rangle\). These interference effects have been discussed in detail and identified in experimental spectra of small molecules.11,16,17

The question arises whether the cross section \(\sigma_f(E)\) can also be formulated in a time-dependent picture in which the interference effects can be unambiguously identified. To this end we express the denominator in Eq. (2.7) as an integral,

\[
(E+E_{n_{f}}-\mathcal{H}_d)^{-1} = \int_0^\infty \text{e}^{i(E+E_{n_{f}}-\mathcal{H}_d)t} dt,
\]

and rearrange the exponent using \(H|n_{f}\rangle = E_{n_{f}}|n_{f}\rangle\) and obtain

\[
\langle n_{f} | W(E+E_{n_{f}}-\mathcal{H}_d)^{-1} V | n_{f} \rangle
\]

\[
= -i \int_0^\infty dt \text{e}^{iE t} \langle n_{f} | e^{iH_{f}(t-r'(t'-r')} W e^{-i\mathcal{H}_d} V | n_{f} \rangle.
\]

Inserting into Eq. (2.7) immediately leads to

\[
\sigma_f(E) \sim \int_0^\infty dt' \int_0^\infty dt'' \text{e}^{iE(t'-t'')} \times \langle n_{f} | \text{e}^{i\mathcal{H}_{nf}} t' W e^{iH_{f}(t'-t'')} W e^{-i\mathcal{H}_d} V | n_{f} \rangle.
\]

(2.9a)

For several purposes it is convenient to introduce the times \(t-t'\) and \(T-t'+t''\) and obtain

\[
\sigma_f(E) \sim \int_0^\infty dT \int_{-T}^{T} dt \text{e}^{iE(t-t')} \times \text{W} e^{i\mathcal{H}_{nf} T} W e^{-i\mathcal{H}_d(T+t')/2} V | n_{f} \rangle.
\]

(2.9b)

While for the observation of the decaying state only a single time variable is relevant, see Eq. (2.6), we note from Eq. (2.9) that two time variables are essential for describing the dynamics leading to the final state. In the former
case the time is the propagation time of the initial wave-packet on the potential surface of the decaying state. In the latter case an additional time enters, namely the propagation time on the potential energy surface of the final state. In Sec. III we shall return to interpret this point in more detail.

Where are the interferences hidden in the time-dependent expression (2.9)? To keep the discussion as simple as possible we first introduce some simplifications which are of interest by themselves. Analogously to the Condon approximation for spectra of the $\sigma_f(E)$ type, we substitute the transition and decay matrix elements $V$ and $W$, which are functions of the target's nuclear coordinates, by their value at fixed nuclear coordinates. If $|n_2\rangle$ is the target's ground vibrational state, this will be at the equilibrium geometry of the target. In many cases the decay width will change only slightly with the nuclear coordinates. This is particularly true for all decay processes involving an energetically deep level, e.g., a core level. In these cases the decay width is essentially due to the atom corresponding to the deep level and $\Gamma$ is essentially a constant. Since $\Gamma \sim |W|^2$, a constant $\Gamma$ supports the Condon approximation. In the following we shall refer to the Condon plus constant $\Gamma$ approximations as the generalized Condon approximation.

Within the generalized Condon approximation the cross section simplifies to

$$\sigma_f(E) \sim \frac{\Gamma}{2} \int_0^\infty e^{-\Gamma T/2}dT \int_{-T}^T e^{iEt}(n_2) e^{iH_d(T-t)/2}$$

and by inserting complete sets of eigenstates between the operators we readily find

$$\sigma_f(E) \sim \frac{\Gamma}{2} \sum_{n'} |\langle n_f|n_{d'}\rangle\langle n_{d'}|n_2\rangle|^2$$

(2.10)

which is a well-known result.\cite{1,11,19} If $\Gamma$ is small compared to the spacings in $H_d$, all interferences are suppressed and $\sigma_f$ essentially becomes an incoherent superposition of Lorentzian lines. In the limit $\Gamma \to 0$ these Lorentzians become $\delta$ functions and the interferences have strictly disappeared

$$\sigma_f(E) \sim \sum_{n_f,n_{d'}} |\langle n_f|n_{d'}\rangle\langle n_{d'}|n_2\rangle|^2 \delta(E-E_{n_{d'}}+E_{n_f})$$

(2.12a)

Interestingly, putting the integration limits to infinity in the integral over $t$ in Eq. (2.10),

$$\sigma_f(E) \sim \frac{\Gamma}{2} \int_0^\infty e^{-\Gamma T/2}dT \int_{-T}^T e^{iEt}(n_2) e^{iH_d(T-t)/2}$$

$$\times e^{iH_f \tau}e^{-iH_d(T+\tau/2)}|n_2\rangle dt,$$

(2.12b)

and letting $\Gamma \to 0$ after the integrations recovers, Eq. (2.12a). In other words, in the time-dependent formulation the interference effects are due to the finite time intervals over which the Fourier transform must be performed.

Finally, we would like to mention that the time-dependent formulation of the cross sections provides some advantages over the time-independent one. We shall see later that the time-dependent picture amends itself to helpful interpretations of the underlying process. In addition, we shall be able to extract useful informations about the cross section starting with its time-dependent expression (see Sec. IV). Last but not least, in some cases, for example, if dissociative potential surfaces are involved, equations like Eq. (2.10) might be simpler to practically compute than the corresponding time-independent equations.

III. INTERPRETATION OF OBSERVATIONS BY WAVE PACKET DYNAMICS

The interpretation of the spectra $\sigma_d(E)$, where the short-lived state $|d\rangle$ is detected, is very straightforward, see Eq. (2.6), and there is no need for further discussion. On the other hand, the quantity $\alpha_{f}(E)$ is less obvious, it exhibits interference phenomena and its time-dependent formulation in Eqs. (2.9) and (2.10) involves two time variables. In the following we concentrate on the interpretation of $\sigma_f(E)$.

At time $t=0$ the initial vibrational state $|n_1\rangle$ is excited to the intermediate electronic state and arrives there as $V|n_1\rangle$. This wave packet propagates via the Hamiltonian $H_f$ on the potential surface of the final state: $|\Psi_f(t)\rangle = \exp(-iH_f t) V|n_1\rangle$. At every small time interval $dt$ it looses a part which decays to the final state. Since $W$ is the matrix element for the decay and $F$ is the energy carried away by the emitted particle, the “loss” arrives on the potential surface $f$ of the final electronic state at an energy $E$ below its starting point and takes on the appearance

$$-ie^{iEt}W|\Psi_d(t)\rangle dt$$

Now we are able to set up a differential equation for the resulting wave packet on the final potential surface. Let this wave packet be $\Psi_f(E,t)$ at time $t$. At a later time $t+dt$, this function has propagated via $H_f$ and the resulting change obviously is

$$(e^{-iH_f(r+dt)} - e^{-iH_f})\Psi_f(0) = -iH_f\Psi_f(t)dt.$$

To find the true change of the wave packet $d\Psi_f(E,t)$, we have to superimpose to this obvious change by propagation the aforementioned contribution of the decay in the time interval $dt$. The final result thus reads as

$$d|\Psi_f\rangle = -iH_f|\Psi_f\rangle dt - ie^{iEt}W|\Psi_d\rangle dt$$

(3.1a)

or, equivalently,

$$i\tilde{\Psi}_f - (H_f + E)\tilde{\Psi}_f + W\Psi_d$$

(3.1b)

where $\Psi_f$ and $\tilde{\Psi}_f$ differ by a phase factor $\tilde{\Psi}_f = \exp(iEt)|\Psi_f\rangle$. The inhomogeneous first order differential equation is readily solved by multiplying it from the left by $\exp(iH_f t)$ and subsequently rewriting it to give

$$d(e^{iH_f t}|\Psi_f\rangle)/dt = -ie^{iEt}e^{iH_f t}W|\Psi_d\rangle.$$

Since $\Psi_f$ is a consequence of the decay, the initial condition is
and the wave packet acquires the appearance

\[ |\Psi_f(E,t)\rangle = -ie^{-iH_f t} \int_0^t e^{i(E+H_f)t'} W e^{-i\mathcal{P}_d'} V |n_i\rangle dt'. \]  

(3.2b)

An alternative and instructive derivation of this wave packet follows from the ansatz

\[ \Psi(t) = \Psi_d(t) \phi_d + \int \tilde{\Psi}_f(E,t) \phi_f(E) dE \]  

(3.3)

for the total wave function \( \Psi \) of the system describing the nuclear motion and the electrons. \( \phi_d \) denotes the electronic wave function of the state \( |d\rangle \) and \( \phi_f(E) \) the energy normalized electronic wave function of the final state \( |f\rangle \) and emitted particle. Clearly, \( \Psi(t) \) obeys the usual time-dependent Schrödinger equation with the total Hamiltonian of the system. Multiplying this Schrödinger equation by \( \phi_f^*(E) \) and integrating over the electronic coordinates recovers the differential Eq. (3.1b).

As can be seen from Eq. (3.2b), the quantity which is propagated by \( \exp(-i H'_f t) \) is itself an integral over time. This integral represents the contribution which has accumulated on the final surface via the decay up to time \( t \). That strong interferences can take place is seen at hand because of the superposition of the two contributions in Eq. (3.1) each being connected to the motion in a different potential. Due to this superposition, the norm of the wave packet can vary strongly with \( E \) and for short times \( t \leq 1 \) also with \( t \). In particular, we notice from Eqs. (3.2b) and (2.9a) that

\[ \sigma_f(E) \sim \langle \Psi_f(E,\infty) | \Psi_f(E,\infty) \rangle. \]  

(4.4)

The norm of the wave packet at \( t \to \infty \) is proportional to the cross section. Note that in actual calculations of the cross section there is no need to compute the full wave packet \( \Psi_f \): The exponential in front of the time integral in Eq. (3.2b) does not contribute to the cross section and the integration itself is only needed up to \( t = 2 \Gamma^{-1} \).

For the sake of comparison we briefly also consider the norm of the decaying wave packet \( \Psi_d(t) \):

\[ N_d(t) = \langle \Psi_d(t) | \Psi_d(t) \rangle = \langle n_i | W e^{i\mathcal{P}_d} e^{-i\mathcal{P}_d'} V |n_i\rangle. \]  

(3.5)

Because of the decay this norm is not conserved. Unless \( \Gamma \) is a constant, this expression cannot be simplified considerably. The change of the norm with time, i.e., the "loss" of norm, is

\[ \frac{dN_d(t)}{dt} = \langle \Psi_d(t) | \Gamma | \Psi_d(t) \rangle. \]  

(3.6)

One might be tempted to express \( \sigma_f(E) \) as the real part of a Fourier transform of some effective autocorrelation function similarly to Eq. (2.6) for \( \sigma_d(E) \). This is indeed possible. The result is

\[ \sigma_f(E) \sim \text{Re} \int_0^\infty e^{i\omega t} \langle \Psi_f(0) | \Psi_f(t) \rangle dt, \]  

(3.7a)

where the effective "wave packet" \( \Psi_e(t) \) reads as

\[ |\Psi_e(t)\rangle = \int_0^\infty e^{i\omega t} e^{i\mathcal{P}_d} W e^{-i\mathcal{P}_d'} V |n_i\rangle \]  

(3.7b)

This result can be verified by inserting complete sets of eigenstates between the operators. Performing the integrations recovers Eq. (2.7). Care must be taken because \( \mathcal{H}_d \) is non-Hermitian. \( \Psi_e(t) \) has no obvious physical interpretation, at least we could not find one, but it is surprising and interesting that it exists at all. \( \Psi_e(0) \) is meaningful and can be computed by noting that for \( t = 0 \) the integrand is essentially the derivative of \( \exp(i\mathcal{P}_d T) \times \exp(-i\mathcal{P}_d T) V |n_i\rangle \) with respect to \( T \) [see also Eqs. (3.5) and (3.6)]. The result reads as

\[ |\Psi_e(0)\rangle = V |n_i\rangle. \]  

(3.7c)

At very large times \( t \) the "wave packet" \( \Psi_e(t) \) disappears in contrast to the true wave packet \( \Psi_f(t) \) which is zero at \( t = 0 \).

IV. PROPERTIES OF THE SPECTRA

A. Exactly solvable cases

There are only very few idealized cases where the spectra can be given explicitly in a closed analytical form. This applies to the spectra \( \sigma_d(E) \) where the decaying state is the state under observation and in particular to the much more complicated spectra \( \sigma_f(E) \) detecting the final states \( |f\rangle \). In the simplest case we can conceive of, all the potential curves involved are harmonic potentials of the same frequency but with different minimum positions and, in addition, the generalized Condon approximation (i.e., constant \( \Gamma, W, V \)) is assumed. The spectrum \( \sigma_d(E) \) then consists of a sum of equidistant Lorentz curves weighted by a Poisson distribution. The cross section \( \sigma_f(E) \) can also be given in this simple case of shifted harmonic oscillators, the resulting expression (which is useful for numerical computations) is, however, still too complicated to allow one to "see" how the spectrum looks like.

In general, the cross sections can be given explicitly whenever the Franck-Condon factors as well as energy differences between the vibrational levels are known explicitly and the generalized Condon approximation applies. If \( \Gamma \) is a function of the nuclear geometry, it can be incorporated into the potential which becomes complex. The energies and the Franck-Condon factors are then complex. In the case of harmonic oscillators, the expansion of \( \Gamma \) up to the quadratic term in the geometry leads to complex harmonic oscillators. The complex harmonic oscillator and its Franck-Condon factors have been discussed in the multimode case.\(^1\)

Three electronic states, the initial, the decaying, and the final states are involved in the process leading to \( \sigma_f(E) \). We can expect the spectrum to simplify considerably only if two of the surfaces are parallel and the generalized Condon approximation applies. The situation is particularly simple if the surfaces of the decaying and final states are parallel, i.e.,
where $E_0$ is a constant energy separation. In this case the final wave packet $\Psi_f(E,t)$ propagates essentially with the same Hamiltonian (up to an energy shift and imaginary decay part) as the decaying wave packet $\Psi_d(t)$ on the potential surface of the decaying state. Using Eq. (3.2b), we readily obtain the final wave packet

$$|\Psi_f(E,t)\rangle \sim \frac{e^{i(E-E_0+i\Gamma/2)t}}{E-E_0+i\Gamma/2} e^{-iH_d't} |n_0\rangle,$$  \hspace{1cm} (4.1h)

and, according to our general expression (3.4), the cross section takes on the appearance of a single Lorentz curve centered at $E_0$

$$\sigma_f(E) \sim \frac{1}{(E-E_0)^2 + (\Gamma/2)^2}.$$  \hspace{1cm} (4.1c)

Of course, this cross section can be computed directly from Eq. (2.11), but the wave packet view adds insight (see Sec. IV B 3).

If the potential energy surfaces of the initial and the decaying states are parallel,

$$H_d = H_i + H_d,$$  \hspace{1cm} (4.2a)

the final wave packet is somewhat more complicated, but again its propagation depends only on $H_f$. At large times $t$ it takes on the appearance (the energy of the initial vibrational state $|n_0\rangle$ is chosen to be the origin of the energy scale)

$$|\Psi_f(E,t)\rangle \sim e^{-iH_f't} (E-E_d+H_f+i\Gamma/2)^{-1} |n_0\rangle.$$  \hspace{1cm} (4.2b)

The cross section can be written as an incoherent superposition of Lorentzians or, equivalently, as the real part of an autocorrelation function

$$\sigma_f(E) \sim \text{Re} \int_0^\infty e^{(E-H)^t} (n_1) e^{-i(H_d-H_f)t} |n_0\rangle dt.$$  \hspace{1cm} (4.2c)

By comparing with the general expression (2.6) for $\sigma_d(E)$, we note that, apart from the appropriate definition of the detected energy, $\sigma_f(E)$ just appears as the spectrum of a “decaying” state with the Hamiltonian $H_f-i\Gamma/2$. The true decaying state has transferred its decay width to the final state and is irrelevant otherwise. No essential simplifications arise if the potentials of the initial and of the final state are parallel.

**B. Appearance of the bands in the spectrum**

1. **General aspects**

   The cross section $\sigma_f(E)$ for the production of the final state $|f\rangle$ of the decay has been seen to possess a relatively complicated structure. It is thus not surprising that only a few calculations on diatomics are available\cite{11,16,17} within the Condon approximation. In polyatomics several nuclear degrees of freedom are usually of relevance making the accurate determination of $\sigma_f(E)$ prohibitively difficult. Even approximated cross sections are likely to be computed only for a few cases of particular interest. In various kinds of experiments, however, several or even many final states appear and even questions concerning the gross features of the whole spectrum are of relevance, such as, at what energies do the corresponding peaks (bands) appear and how large are their widths. Obviously, the gross features of the peaks are those needed to analyze low resolution or unresolved spectra.

   A distribution can be approximated in terms of its moments. The first few moments describe the gross features of the distribution. The $k$th moment of $\sigma(E)$ is defined as

   $$\langle E^k \rangle = \int E^k \sigma(E) dE.$$  \hspace{1cm} (4.3)

   The center of gravity of a band in the spectrum is given by the first moment $\langle E \rangle$ and the width of the band is related to $\langle E^2 \rangle - \langle E \rangle^2$.

   In the following we discuss the first and second moments of the cross sections $\sigma_d(E)$ and $\sigma_f(E)$ analyzing the decaying and final state, respectively. For the sake of simplicity we assume the generalized Condon approximation and write

   $$\sigma_d(E) \sim \frac{1}{2\pi} \text{Re} \int_0^\infty e^{(E+i\Gamma/2)t} (n_1) e^{-iH_d't} |n_0\rangle dt,$$  \hspace{1cm} (4.4)

   $$\sigma_f(E) \sim \frac{\Gamma}{4\pi} \int_0^\infty e^{-\Gamma t/2} dt \int_{-T}^T e^{iE_0t} (n_1) e^{iH_d(T-t)/\Gamma}$$

   $$\times e^{iH_f't} e^{iH_f(T-t)/\Gamma} |n_0\rangle dt,$$  \hspace{1cm} (4.5)

   where the prefactors $1/2\pi$ and $\Gamma/4\pi$ have been chosen such that the zeroth moment of the cross section, i.e., the total integrated intensity of the band, is unity apart from the remaining proportionality factors. Now, the matter of moments of decaying species presents a nontrivial problem. The zeroth and first moments exist and are well defined, but already the second moment diverges as one can easily see by replacing $\sigma(E)$ in Eq. (4.3) by a single Lorentzian: the integrand does not vanish for large $E$. The divergence of the high moments of $\sigma_d(E)$ and $\sigma_f(E)$ originates from the very long Lorentzian tail of the whole band far away from the peak constituting the band. Since this tail does not affect our observations of the band, we can ignore its effect on the observed quantities as, for instance, the full width at half maximum (FWHM) of the band. In the Appendix it is shown how this can be done unambiguously. All the moments of the cross sections defined in this way exist and are well defined. For the derivation of the moments we refer to the Appendix.

   The position of the band in the spectrum $\sigma_d(E)$ is simply the initial vibrational state expectation value of $H_d$:

   $$\langle E_d \rangle = \langle n_1 | H_d | n_0 \rangle.$$  \hspace{1cm} (4.6a)

   The analogous expression in the case of $\sigma_f(E)$ is substantially more involved reflecting the simultaneous dynamics on two potential energy surfaces:

   $$\langle E_f \rangle = \Gamma \int_0^\infty e^{-\Gamma T} (n_1) e^{itH_f (H_d-H_f)} e^{-iH_dT} |n_0\rangle dT.$$  \hspace{1cm} (4.6b)
The influence of the nuclear dynamics on the band position \( \langle E \rangle_f \) is much larger than on \( \langle E \rangle_d \) and gives rise to interesting phenomena (see Sec. IV B 2 for an explicit estimate and Sec. IV B 3 for the interpretation).

As mentioned earlier, the quantity \( \langle E^2 \rangle - \langle E \rangle^2 \) is a measure for the width of the band. Assuming that this electronic band takes on the appearance of a Gaussian, then its FWHM is explicitly given by

\[
\text{FWHM} = [8 \ln 2 (\langle E^2 \rangle - \langle E \rangle^2)]^{1/2}. 
\] (4.7)

The second moment needed to complete our general considerations reads

\[
\langle E^2 \rangle_d = \langle n_1 | (H_d)^2 | n_1 \rangle + \Gamma^2/8 \ln 2 
\] (4.8a)

for the cross section \( \sigma_d(E) \) and

\[
\langle E^2 \rangle_f = \int_0^\infty e^{-\Gamma T} \langle n_1 | e^{iH_dT} (H_d-H_f)^2 e^{-iH_dT} | n_1 \rangle dT 
\]

\[+ \Gamma^2/8 \ln 2 
\] (4.8b)

for \( \sigma_f(E) \). The origin of the small contribution \( \Gamma^2/8 \ln 2 \) is explained in the Appendix. \( \Gamma \) in this latter contribution may be chosen to also include the experimental resolution of the apparatus.

It should be noted that if the spectral band is highly asymmetric its position, \( \langle E \rangle \), i.e., its center of gravity, does not correspond to the maximum of the band. The asymmetry of the band can be computed using the third moment of the spectrum.

2. Working equations for the moments

In this subsection we derive approximate explicit expressions for the first two moments of the cross sections which can be used in practical calculations. The simpler expressions for \( \sigma_d(E) \) are not new, but are given for the sake of comparison. We first derive the expressions for the case of a single active nuclear coordinate and give the results for several coordinates at the end of the subsection.

In general, each of the three Hamiltonians \( H_i, H_d, \) and \( H_f \) describing the nuclear dynamics in the initial, decaying and final electronic states has a different potential energy. This severely complicates the calculation of the moments. The starting point of a systematic procedure to derive a useful expansion for the moments is to expand the difference between the potential energy expressions in the final and decaying states and that of the initial state about a reference geometry which we choose to be the equilibrium geometry of the system in the initial state. The merits of such a procedure have been discussed in connection with \( \sigma_d(E) \). Since the initial excitation \( |i\rangle \rightarrow |d\rangle \) is essentially vertical, it is the potential around the corresponding geometry which contributes and must be well estimated. In our present case of \( \sigma_f(E) \), the situation is more intricate. The wave packet on the decaying intermediate state propagates for a time \( \sim 1/\Gamma \) before decaying and the details of a larger portion of the potential energy surfaces become relevant. Nevertheless, the aforementioned expansion is still useful, in particular, if the lifetime \( 1/\Gamma \) of the decaying state is short.

In the spirit of the previous discussion, we now write the expansion

\[
H_d-H_i=E_d(R_0)-E_i(R_0)+\kappa_d(b+b^\dagger)+\cdots, 
\] (4.9a)

\[
H_f-H_i=E_f(R_0)-E_i(R_0)+\kappa_f(b+b^\dagger)+\cdots, 
\] (4.9b)

where \( b \) and \( b^\dagger \) are the usual annihilation and creation operators for vibrational quanta in the initial electronic state. \( E_d(R_0), E_f(R_0) \) and \( E_i(R_0) \) are the electronic energies of the decaying, final, and initial states, respectively, at the equilibrium geometry \( R_0 \) of the target (initial state). The coupling constants are the slopes of the electronic energies at \( R_0 \)

\[
\kappa_d=\frac{1}{\sqrt{2}} \left( \frac{\partial E_d(Q)}{\partial Q} \right)_0, \quad \kappa_f=\frac{1}{\sqrt{2}} \left( \frac{\partial E_f(Q)}{\partial Q} \right)_0 
\] (4.10)

with respect to the dimensionless normal coordinate \( Q=(b+b^\dagger)/\sqrt{2} \). We mention that in a diatomic molecule \( Q=R-\frac{1}{2} \) where \( R \) is the interatomic distance and \( \mu \) the reduced mass.

Inspection of the basic Eqs. (4.5), (4.6b), and (4.8b) indicates that the time-dependent Hamiltonian

\[
H_f(T) \equiv e^{iH_fT}H_fe^{-iH_fT} 
\] (4.11)

is relevant for the computation. If we view the process under consideration as a single step process \( |i\rangle \rightarrow |f\rangle \), then the effective Hamiltonian describing the nuclear dynamics is time-dependent [compare Eqs. (4.6a) and (4.6b); see also Eqs. (3.7a) and (3.7b)]. To proceed we use the expansion (4.9) and expand \( H_f \) about \( R_0 \) as well

\[
H_f=T+(iT)^2/2! \cdots 
\] (4.12)

and note that the terms not shown explicitly are cubic and of higher order in the operators. For the evaluation of \( H_f(T) \) we now use the Baker–Hausdorff formula yielding

\[
H_f(T)=H_f+iT[H_d,H_f] \frac{(iT)^2}{2!} [H_d,[H_d,H_f]] + \cdots. 
\] (4.13)

where \([H_d,H_f]\) is the usual commutator. All the commutators appearing in expansion (4.13) can straightforwardly be evaluated with the aid of the relations

\[
[b,b^\dagger]=1, \quad [b\pm b^\dagger,b^\dagger b]=b \mp b^\dagger, 
\] (4.14)

\[
[bb\pm b^\dagger b^\dagger b]=2(bb\mp b^\dagger b^\dagger). 
\]
Using only the terms explicitly shown in Eqs. (4.9) and (4.12) for the Hamiltonians, the infinite series (4.13) can quite easily be written in closed form:

\[ H_f(T) = H_f + \beta(1 - \cos \omega T) \left( \frac{2k_d}{\omega} + (b+b^\dagger) \right) + i\beta \sin \omega T (b-b^\dagger), \quad (4.15) \]

\[ \beta \equiv \kappa_d - \kappa_f. \]

This time-dependent Hamiltonian describes the nuclear dynamics on a potential surface whose equilibrium geometry and the corresponding energy change periodically in time. Furthermore, a periodical change of momentum also takes place. If higher order terms in the expansion of the Hamiltonians, Eqs. (4.9) and (4.12), are included, additional terms will, of course, appear in the expression for \( H_f(T) \) which can be evaluated systematically.

Once \( H_f(T) \) and the initial vibrational state \( |n_i\rangle \) are known, all the moments of the spectrum can be determined. The moments we are usually interested in are those where \( |n_i\rangle \) is the vibrational ground state of the target. We choose the corresponding energy to be the zero of our energy scale. Considering only the terms explicitly shown earlier in the expansion of the Hamiltonians about \( R_0 \), the evaluation of the first moment is now very simple. Only the terms without annihilation and creation operators in \( H_f(T) \), Eq. (4.15), contribute. After performing the integration over \( T \) in Eq. (4.6b), the first moment reads as

\[ \langle E \rangle_f = \left[ E_d(R_0) - E_i(R_0) \right] - \frac{2\kappa_d\beta}{\omega} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega^2} \right). \quad (4.16a) \]

The first term on the right-hand side (r.h.s) is simply the vertical transition energy and the second term results because of the nuclear dynamics. A discussion of this contribution is given in Sec. IV B 3. Here we just remark that this dynamically induced contribution vanishes if the decaying state has zero lifetime \( \Gamma \rightarrow \infty \), i.e., the nuclei have no time to move before the decay takes place.

The first moment of the spectrum \( \sigma_d(E) \) measuring the decaying state is simply given by

\[ \langle E \rangle_d = E_d(R_0) - E_i(R_0). \quad (4.16b) \]

In words, the center of the band in the \( \sigma_d \) spectrum is just the vertical transition energy and is not affected by the nuclear dynamics. Here we mention that the dynamically induced contribution in Eq. (4.16a) for the \( \sigma_f \) spectrum can be large. Our numerical calculations indicate that it can amount even up to a few eV.

Using the closed-form expression (4.15) for \( H_f(T) \), the second moment also follows easily. The expectation value in Eq. (4.8b) is evaluated most straightforwardly if \( [H_d - H_f(T)] \) is first applied to \( |n_i\rangle \) and, subsequently, the self-scalar product is performed. Introducing the abbreviation \( C_f^2 = \langle E^2 \rangle_f - \langle E \rangle_f^2 \), we obtain

\[ C_f^2 = \beta^2 + \frac{2\kappa_d^2\beta^2}{\omega^2} \left[ 1 + \frac{\Gamma^2}{\Gamma^2 + \omega^2} - 2 \left( \frac{\Gamma^2}{\Gamma^2 + \omega^2} \right)^2 \right], \quad (4.17a) \]

which has the following expansions for long and short lifetime,

\[ C_f^2 = \beta^2 + \frac{2\kappa_d^2\beta^2}{\omega^2} \left( \frac{\Gamma^2}{\Gamma^2 + \omega^2} \right)^{1/2} \times \left\{ \begin{array}{ll}
1 + \frac{\Gamma^2}{\omega^2}/4 - 33(\Gamma/\omega)^4/16 + \cdots & \Gamma/\omega \ll 1 \\
10(\omega/\Gamma)^4 + \cdots & \Gamma/\omega \gg 1
\end{array} \right. \]

If we neglect the motion of the wave packet, i.e., if dynamic effects are not present, only the first term \( \beta^2 \) on the r.h.s. of the previous equations contributes. The width of the band would then be FWHM = \( (\beta^2/2 + \Gamma^2/2)^{1/2} \) as can be seen from \( \Gamma \rightarrow \infty \) in Eqs. (4.17a) and (4.7). The dynamically induced contribution to the second moment, given by the second term on the r.h.s. of Eq. (4.17a), is always positive and can be large and even exceed the static contribution \( \beta^2 \) as long as the lifetime of the decaying state is not very short.

In the case of the \( \sigma_d(E) \) spectrum, the analogous quantity \( C_d^2 \) takes on the simple appearance

\[ C_d^2 = \kappa_d^2 \quad (4.17b) \]

giving rise to a band with the width FWHM = \( \sqrt{\kappa_d^2/2 + \Gamma^2/2} \). Clearly, no dynamical contributions of the wave packet’s motion to the width are present. The width of the spectrum is just the result of the fact that the initial wave packet itself possesses a width. The projection of the initial wave packet on the potential curve of the decaying state leads to the observed width of the band.

The expression derived previously for the position and width of a band in a spectrum are amenable to \textit{ab initio} computations. To be calculated are the electronic energies at a fixed geometry as well as the slope of the corresponding potential curves at this geometry. We would like to restate here that the aforementioned expressions are the leading terms of a systematic expansion. The corrections are also amenable to \textit{ab initio} computations.

In the following we briefly comment on the extension of the working equations (4.16) and (4.17) to the multimode situation. Now \( M \) normal coordinates \( Q_m = (b_m + b_m^\dagger)/\sqrt{2} \) with frequencies \( \omega_m \) are available in the initial electronic state. The explicit expansions (4.9) and (4.12) of the Hamiltonians must be reformulated. For instance,

\[ H_d - H_i = E_d(R_0) - E_i(R_0) + \sum_{m=1}^{M} \kappa_{dm}(b_m + b_m^\dagger) + \cdots, \quad (4.18) \]
where the coupling constant $\kappa_{dm}$ of the $m$th mode is defined in analogy to $\kappa_d$ in Eq. (4.10), but with $Q_m$ instead of $Q$. The expansions of $H_f - H_i$ and of $H_i$ are done analogously. The time-dependent Hamiltonian $H_f(T)$ in the multimode case takes on the appearance

$$
H_f(T) = H_f + \sum_{m=1}^{M} \left[ \beta_m (1 - \cos \omega_m T) \left( \frac{2\kappa_{dm}}{\omega_m} \right) + (b_m + b^*_m) + i\beta_m \sin \omega_m T (b_m - b^*_m) \right],
$$

$$
\beta_m = \kappa_{dm} - \kappa_{fm}.
$$

The moments can now be computed in analogy to the single mode case. The first moment reads as

$$
\langle E \rangle_f = \left[ E_d(R_0) - E_f(R_0) \right] + \sum_{m=1}^{M} \frac{2\kappa_{dm} \beta_m}{\omega_m} \times \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_m^2} \right),
$$

showing that the dynamically induced shift of the peak position can, in principle, be substantially enhanced by the presence of several nuclear degrees of freedom. Clearly, nontotally symmetric modes do not contribute on this level of theory since their coupling constants vanish. The influence of nontotally symmetric modes can be relevant if several decaying states are present (see Ref. 15).

The second moment is somewhat more involved in the multimode situation since $H_f(T)$ appears quadratically in $H_f(T)$. We find

$$
\langle \Delta Q^2 \rangle_f = \sum_{m=1}^{M} C_{fm}^2 + \sum_{m > n} \alpha_m \alpha_n \left( \frac{\Gamma^2}{\Gamma^2 + (\omega_m + \omega_n)^2} + \frac{\Gamma^2}{\Gamma^2 + (\omega_m - \omega_n)^2} - \frac{2\Gamma^4}{(\Gamma^2 + \omega_m^2)(\Gamma^2 + \omega_n^2)} \right),
$$

where $\alpha_m = 2\beta_m \kappa_{dm}/\omega_m$ and $C_{fm}^2$ denotes the individual contribution of the $m$th mode and is given by Eq. (4.17a) if we insert the index $m$ on $\beta$, $\omega$, and $\kappa_d$. It is eye catching that the dynamically induced contribution in the multimode case is not just an incoherent sum of contributions of the individual modes. The second term on the r.h.s. of Eq. (4.20b) describes the interaction of modes already on this level of theory where the Hamiltonians, see Eq. (4.18), do not exhibit such mode-mode interactions. These interactions arise from the motion of the multidimensional wave packet and disappear if this motion cannot take place because the lifetime is too short ($\Gamma \to \infty$) and also if the lifetime is very long ($\Gamma \to 0$). The case where two frequencies are accidentally degenerate is noteworthy. Then, the term $\Gamma^2/[(\Gamma^2 + (\omega_m - \omega_n)^2)^2 - 1$ and the mode-mode interaction becomes particularly relevant also when the lifetime is long.

Let us briefly compare with the results on the spectrum $\sigma_d(E)$ of the decaying state. The first moment $\langle E \rangle_d$ is identical to the one found for the single mode case, Eq. (4.16b). The second moment is just a sum over the individual moments of the modes

$$
C_d^2 = \sum_{m=1}^{M} \kappa_{dm}^2.
$$

Clearly, this expression does not contain mode–mode interaction terms because dynamical effects do not contribute.

3. Interpretation

At time $T=0$ the wave packet is vertically excited from the initial state to the potential surface of the decaying state where it propagates and decays to the final state. At any time $T > 0$ the center of the wave packet is at a normal coordinate position $Q(T)$ and the momentaneous energy of the particle ejected via the decay is

$$
\Delta[Q(T)] = E_d[Q(T)] - E_f[Q(T)]
$$

as indicated in Fig. 2. Since the wave packet is not located at a single point but describes a distribution of positions, the correct energy is obtained by averaging over this distribution. The wave packet decays continuously and, hence, we have to average over the decay probability as well. Our energy which is the band position, therefore, reads as

$$
\langle E \rangle_f = \Gamma \int_0^\infty dq \int_{-\infty}^\infty dT e^{-\Gamma T} \int_{-\infty}^\infty dq |\Psi(q,T)|^2 \Delta(q),
$$

where $\Psi$ is the wave packet [compare with Eq. (4.6b) and notice that $\Psi_d(T) = \Psi(T) \exp(-\Gamma T/2)$].

To simplify the expression we note that

$$
Q(T) = \int |\Psi(q,T)|^2 dq
$$

and approximate $|\Psi|^2$ semiclassically by neglecting the spreading of the wave packet with time which should be an
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\[ A(T) = \frac{\omega^2}{2} + \frac{\kappa_d}{2} Q + \frac{\kappa_f}{2} f(R_0), \]  

(4.24)

\[ E_f(Q) = \frac{\omega^2}{2} Q^2 + \sqrt{2} \kappa_f Q + E_f(R_0). \]  

(4.21)

The equation of motion (4.23) under the initial condition for vertical excitation \([Q(0) = 0, dQ(0)/dt = 0]\) has the solution

\[ Q(T) = -\sqrt{2} \kappa_d/\omega (1 - \cos \omega T). \]  

(4.25a)

To evaluate the integrals in Eq. (4.22b) we need \(\Delta[Q(T)]\) which follows from Eq. (4.24):

\[ \Delta[Q(T)] = [E_d(R_0) - E_f(R_0)] + \sqrt{2}(\kappa_d - \kappa_f) Q(T). \]  

(4.25b)

The integrals are readily calculated and we find

\[ \langle E_{\text{sc}} \rangle_f = \Delta(0) - \frac{2\kappa_d(\kappa_d - \kappa_f)}{\omega} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega^2} \right) \]  

(4.26a)

which is identical with the result (4.16a) of the full quantum mechanical calculation.

Inserting Eq. (4.25) into Eq. (4.22), we straightforwardly find

\[ \langle E_{\text{sc}}^2 \rangle_f - \langle E_{\text{sc}} \rangle_f^2 = \langle E^2 \rangle_f - \langle E \rangle_f^2 = T^2/8 \ln 2. \]  

(4.26b)

Up to a usually irrelevant contribution the semiclassical width of the band is identical with the quantum result of the preceding section. Because the potential \(E_d(Q)\) is harmonic, \(Q(T)\) is exact. At first sight, it seems surprising that the spreading of the wave packet neglected in our calculation does not contribute at all. However, the wave packet at \(T=0\) corresponds to an eigenstate of \(E_f(Q)\) which according to Eq. (4.24) has the same frequency as \(E_d(Q)\) on which it propagates and, hence, no spreading occurs (see, e.g., Ref. 24). If \(E_f(Q)\) and \(E_d(Q)\) are still harmonic but with different frequencies, spreading of wave packet with time takes place. In this case the spreading contributes even to the position of the band. We compared \(\langle E_{\text{sc}} \rangle_f\) with \(\langle E \rangle_f\) and identified the term due to spreading (see Sec. IV C). This term will usually be small. We mention that the effect of spreading can be incorporated into the basic semiclassical equations (4.22b) and (4.22c) if the curves are harmonic: one just has to replace \(\exp(-\varphi^2)\) by \(\exp(-\alpha(T) \varphi^2)\), where \(\alpha(T)\) can be given explicitly.24

The aforementioned semiclassical expressions (4.22b) and (4.22c) are useful in practice also when the potentials \(E_d(Q)\) and \(E_f(Q)\) are anharmonic. Although the classical equation of motion for \(Q(T)\) is not strictly valid in this case, the time scale of the decay is usually sufficiently short to ensure satisfactory accuracy. An advantage of the semiclassical theory or modifications of it is that they can be applied at relatively low cost to polyatomic systems with many degrees of freedom.
C. Harmonic and linear potentials

In this subsection we derive the time-dependent Hamiltonian $H_f(T)$ and the position and width of a band in the spectrum for two explicit cases: (1) all three potential curves are harmonic and $E_d(Q)$ is harmonic and $E_f(Q)$ and $E_f(Q)$ are linear. The results are presented for a diatomic molecule, but can be easily transferred to a normal coordinate of any system. The calculations which have been carried out are quite lengthy and tedious. Here, we only sketch the main steps of the derivation.

We begin with the harmonic potentials. Each curve $E_i$, $E_d$, and $E_f$ has its own frequency $\omega_i$, $\omega_d$, and $\omega_f$ and its own equilibrium geometry $R_i$, $R_d$, and $R_f$, respectively. To compute $H_f(T)$ of Eq. (4.11) via the series (4.13) it is convenient to express both Hamiltonians $H_d$ and $H_f$ in terms of the destruction and creation operators of $H_d$. This is done by a nonunitary linear transformation

$$
\begin{pmatrix}
  b^\dagger_f \\
  b_f
\end{pmatrix} =
\begin{pmatrix}
  \alpha & \beta \\
  \beta & \alpha
\end{pmatrix}
\begin{pmatrix}
  b^\dagger_d \\
  b_d
\end{pmatrix},
$$

(4.27)

where $\alpha^2 - \beta^2 = 1$ and $\alpha$ is chosen to reproduce the frequencies correctly. After some algebra the series (4.13) can be written in closed form. Thereby, one makes extensive use of the commutator relations (4.14) and of the following:

$$
\begin{align}
&[b^\dagger b^\dagger + b^\dagger b, b^\dagger b^\dagger b^\dagger + b^\dagger b + b^\dagger b^\dagger ] = 2(b^\dagger b^\dagger), \\
&[b^\dagger b^\dagger + b^\dagger b, (b^\dagger b^\dagger)^2] = 4(b^\dagger b^\dagger)^2,
\end{align}

(4.28)

The Hamiltonian $H_f(T)$ describes an harmonic oscillator with time-dependent coordinate, momentum, frequency, equilibrium geometry, and energy shift. To determine these quantities explicitly the matrix in Eq. (4.29a) must first be diagonalized.

Once $H_f(T)$ is known, the moments of the spectrum $\sigma_f(E)$ can be computed straightforwardly. Using Eq. (4.6b) the position of the electronic band in the spectrum reads as

$$
\begin{align}
\langle E \rangle_f &= [E_d(R_0) - E_f(R_0)] + (\omega_d^2 - \omega_f^2)/4\omega_d \\
&\quad + \mu \omega_f^2 (R_d - R_0) (R_f - R_d) \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_d^2} \right) \\
&\quad + \frac{\omega_d^2}{4\omega_d} \left[ \mu \omega_f^2 (R_d - R_0)^2 + (\omega_d^2 - \omega_f^2) / 2\omega_d \right]
\times \left( 1 - \frac{\Gamma^2}{\Gamma^2 + 4\omega_d^2} \right),
\end{align}

(4.30)

The first two terms on the r.h.s. of Eq. (4.30) are due to the vertical transition, the other terms are purely dynamical in origin. It is interesting to note that the dynamical term which depends only on the frequencies (and $\Gamma$) is a result of the spreading of the wave packet as a function of time (see Sec. IV B 3). If $\omega_d$ is either close to $\omega_0$ or to $\omega_f$ then the impact of the spreading on the band position is negligible.

To make contact with the working equation in Sec. IV B 2 we mention that the final and intermediate state coupling constants $\kappa_f$ and $\kappa_d$ have a simple appearance in the harmonic case:

$$
\kappa_f = \frac{1}{2\mu \omega_d} \left( \frac{\partial E_d}{\partial R} \right)_{R_0} = \frac{\mu}{2\omega_0} \omega_f^2 (R_0 - R_f),
$$

(4.31)

where $\gamma$ stands for $f$ and $d$. It should be clear that the potential surfaces addressed in Sec. IV B 2 are not har-
monic in general and that there the second equality in Eq. (4.31) does not hold, the surfaces may even not possess a minimum.

The width of the band has also been computed using $H_f(T)$ in Eq. (4.29) and the expression for the second moment (4.8b). The resulting equation consists of simple terms, but is extremely lengthy and we refrain from giving it here explicitly.

Let us briefly discuss our second explicit example where the curves $E_f(Q)$ and $E_d(Q)$ are linear. In this case the structure of $H_f(T)$ remains as in Eq. (4.29a), but the time-dependent quantities simplify considerably:

$$\mathcal{H}(T) = E_f(R_0) + \kappa_d(k_d-\kappa_f)\omega_0(T)^2,$$

$$\gamma(T) = k_f + f(k_d-\kappa_f)\omega_0 T,$$

$$\lambda(T) = \omega_0/4, \quad \nu(T) = -\omega_0/4.$$

Since the potentials are linear, the slopes are constant. $\kappa_d$ and $\kappa_f$ are the slopes with respect to the dimensionless normal coordinate $Q$ in the initial electronic state ($Q = \sqrt{\mu \omega_0} (R - R_0)$ in a diatomic). Because of the simple form of $\lambda$ and $\nu$ the central term on the r.h.s. of Eq. (4.29a) for $H_f(T)$ becomes $-(b - b^2)\omega_0/4$ which is nothing but the usual kinetic energy operator.

The moments are easily calculated:

$$\langle E \rangle_f = \frac{2k_d(k_d-\kappa_f)}{\omega_0} \left( \frac{\omega_0}{\Gamma} \right)^2,$$

$$\langle E^2 \rangle_f - \langle E \rangle_f^2 = \frac{20k_d^2(k_d-\kappa_f)^2}{\omega_0} \left( \frac{\omega_0}{\Gamma} \right)^4. \quad (4.33b)$$

As anticipated, the band position derived in Eq. (4.16a) is identical to the result for linear potentials if the lifetime $1/\Gamma$ is very short. It is interesting to note that this is not the case for the bandwidth. As can be seen from the comparison of Eq. (4.17a) for $H_f(T)$ becomes $-(b - b^2)\omega_0/4$ which is nothing but the usual kinetic energy operator.

For a linear potential the wave packet always propagates in the same direction and the dynamically induced shift of position and width of the band can be severe. Indeed, Eq. (4.33) is valid for all $\omega_0/\Gamma$ and if the lifetime of the decaying state is long, the moments can exceed any limit. In reality the potential, even if unbound, will level off at some distance. Nevertheless, Eq. (4.33) and the developed semiclassical interpretation indicate that one may expect dramatic dynamical effects for strongly repulsive curves.

V. ILLUSTRATIVE APPLICATION OF SPECTRAL MOMENTS

To illustrate the practicability of spectral moments, we apply the theory of the Sec. IV to the Auger spectra of carbon monoxide which have been discussed many times in the literature, one due to the creation of a Cls hole and the other following the ejection of a 01s electron. Although the same final dicaticionic states of CO$^{++}$ are populated by the decay, the bands observed in the two spectra appear at different energies because of dynamical effects. This has been discussed for the first time recently. The computed positions of the bands corresponding to the first states of CO$^{++}$ are depicted in Fig. 3. They are calculated using the expression for the first moment given in Eq. (4.16a). The ab initio data for the vertical transition energies as well as for the coupling constants $\kappa_d$ and $\kappa_f$ are taken from Ref. 10, where all details can be found. We just mention that the latter two constants are calculated as the slopes of the energy curves of the decaying and final states, respectively, at the equilibrium geometry of CO in its ground state [see Eq. (4.10)]. There is a formal difference between the expression for the first moment used in Ref. 10 and that derived here. In Ref. 10 the term $\Gamma^2/(\Gamma^2 + \omega^2)$ shown in Eq. (4.16a) is missing because of the incomplete derivation of the moments carried out for $\Gamma \to 0$. For CO, however, $\Gamma = 0.1$ eV (Ref. 26) and $\omega = 0.21$ eV (Ref. 27) and, hence, the contribution of this term is small. During the lifetime of the core hole states the nuclei perform a fraction $\omega/(2\pi\Gamma) \approx 0.4$ of a vibrational period.

The vertical transition energies are also shown in Fig. 3. It is clearly seen that the dynamical shifts of the band positions can be substantial. For the Auger Cls spectrum many of the shifts exceed 2 eV. The shifts can also be quite different for different states in the same spectrum. The
based on vertical transition energies and the second is calculated using the formulas of Sec. IV B 2 derived from the time-dependent formulation. The substantial difference between these two computed spectra and the eye catching agreement of the latter with experiment demonstrates the relevance of dynamical effects and the usefulness of spectral moments.

VI. SUMMARY

The motions of the wave packets propagating on the potential surface of a decaying electronic state and on the surface of a final electronic state are discussed. The latter wave packet is found to depend on the energy of the particle emitted by the decay. Its dynamics is relatively complex and interference effects can take place. The cross sections for the production of the decaying state and of the final state can be related to the corresponding wave packets. Explicit expressions for these cross sections in a time-dependent framework have been given. The latter cross section $\sigma_f$ is represented as an integral over two time variables. A one time variable is needed for the description of the decay, the other is related to the propagation on the final state's potential surface. The interference effects known to appear in $\sigma_f$ can be identified in the time-dependent picture used.

Simplified interpretation of the decay process is one advantage of a wave packet dynamical study; computational effort is another. In particular, if the lifetime of the decaying state is short. In the present case the time-dependent picture is, in addition, suitable for deriving the spectral moments of the cross sections. Spectral moments are commonly used to approximate a distribution and can be used here to describe the gross features of the cross sections, like the energetic positions and widths of electronic bands observed in the spectrum under consideration, e.g., autoionization spectrum. However, relevant moments of cross sections involving exponentially decaying states diverge. The time-dependent formalism enabled us to identify and to unambiguously eliminate the divergencies and determine well-defined moments. Approximate explicit expressions for the position and width of a band are given in terms of properties of the potential energy surfaces of the decaying and final states. An illustrative application to the Auger spectra of carbon monoxide is briefly discussed demonstrating the usefulness of spectral moments. It is shown that even the ordering of the electronic bands in the spectra can change due to the dynamics.

The time-dependent formulation is amenable to semiclassical approximations which also add insight into the decay process and its dynamics. This is demonstrated here for the spectral moments as an example. The semiclassical approximations are of practical relevance, in particular, for polyatomic molecules. Propagation of the wave packets in the framework of the present formulation are currently being computed and will be used to interpret the dynamics of the decay process.
APPENDIX: SPECTRAL MOMENTS OF CROSS SECTIONS OF DECAYING STATES

To discuss the problem of constructing spectral moments of cross sections involving decaying states we first consider the following incoherent superposition of Lorentzians

\[
\sigma_d(E) = \sum_n |a_n|^2 L(E-E_n),
\]

where

\[
L(E) = \frac{\Gamma/2}{E^2 + (\Gamma/2)^2}, \quad \sum_n |a_n|^2 = 1.
\]

The kth spectral moment of the distribution \(\sigma_d(E)\) can be evaluated directly using the binomial expansion

\[
\langle E^k \rangle_d = \int E^k \sigma_d(E) dE = \sum_{m=0}^{k} \binom{k}{m} \langle E^{k-m} \rangle L_m,
\]

where \(\langle E^m \rangle_L\) is the mth moment of a single Lorentzian

\[
\langle E^m \rangle_L = \int E^m L(E) dE
\]

and \(\langle E^0 \rangle\) denotes the sth moment of the auxiliary cross section

\[
\sigma(E) = \sum_n |a_n|^2 \delta(E-E_n)
\]

which is obtained from \(\sigma_d(E)\) for \(\Gamma \to 0\), i.e., \(\sigma(E)\) is the cross section one would obtain if the decaying state \(d\) possesses infinite lifetime. Usually all the moments of \(\sigma(E)\) exist.

With the aid of Eq. (A3) we readily find

\[
\langle E^0 \rangle_d = 1.
\]

\[
\langle E \rangle_d = \langle E \rangle = \sum_n |a_n|^2 E_n.
\]

\[
\langle E^2 \rangle_d = \sum_n |a_n|^2 E_n^2 + \int E^2 L(E) dE.
\]

The second moment is a sum of \(\langle E^2 \rangle\) and a divergent second moment \(\langle E^2 \rangle_L\) of a single Lorentzian \(L(E)\). The long slowly decaying tail of \(L(E)\) leads to the divergence. The second cumulant \(\langle E^2 \rangle - \langle E \rangle^2\) of a distribution is related to the width of the distribution and the observed width of a measured cross section should not depend on this long tail. It is usually dominated by the vibrational excitation peaks and not by the particular form of the single peaks. We, therefore, replace the single Lorentzian \(L(E)\) above by a Gaussian \(G(E)\) of the same FWHM \(\Gamma\), i.e., \(G(E, x) = \exp(-E^2 a^2)\alpha/\pi^{1/2}\), where \(\alpha^2 = 4 \ln \Gamma/\gamma^2\). The first moment does not change and the second moment now reads as

\[
\langle E^2 \rangle_d = \langle E^2 \rangle + \Gamma^2/8 \ln 2.
\]

All higher moments are also easily computed via Eq. (A3). The nontrivial quantities \(\langle E^s \rangle\) are determined using

\[
\langle E^k \rangle = \langle n_i | [H_d] \rangle \langle n_i | E \rangle,
\]

where \(H_d\) is the Hamiltonian of the decaying state [see Eq. (4.4)].

Let us now turn to the much more complicated spectrum \(\sigma_f(E)\) for the production of the final state \(|f\rangle\) of the decay. Following Eq. (4.5) we may write

\[
\sigma_f(E) \sim \frac{\Gamma}{4\pi} \int_0^\infty e^{-\Gamma t/2} dT \int_{-T}^T e^{iE t} F(t,T) dt,
\]

where \(\epsilon\) is a positive infinitesimal. It is relatively easy to show that all moments of \(\sigma_f(E)\) exist. The difference between this “cross section” and \(\sigma_f(E)\) originates from the fact that \(T\) can take on the value zero. We define

\[
\sigma_{f\epsilon}(E) \sim \frac{\Gamma}{4\pi} \int_0^\infty e^{-\Gamma t/2} dT \int_{-T}^T e^{iE t} F(t,T) dt,
\]

immediately leads to

\[
\langle E^k \rangle_{f\epsilon} = \int E^k \sigma_{f\epsilon}(E) dE = (-i)^k 2\pi d\delta(\epsilon)/d\epsilon^k
\]

which can be easily evaluated formally for our \(F(t,T)\). To establish the relationship between \(\sigma_f(E)\) and \(\sigma_{f\epsilon}(E)\), we first rewrite the former quantity to give

\[
\sigma_f(E) = \frac{\Gamma}{2\pi} \sum_{n_d,n_d'} \langle n_i | n_d \rangle \left\langle n_d \left| \frac{1}{(E+H_f-E_{n_d'}-i\Gamma/2)(E+H_f-E_{n_d'}+i\Gamma/2)} \right| n_d' \right\rangle \langle n_d' | n_i \rangle
\]

and represent the integrand of Eq. (A9) as

\[
F(t,T) = \langle n_i | e^{iH_d(T-t)/2} e^{iH_f} e^{-iH_d(T-t)/2} | n_i \rangle = \sum_{n_d,n_d'} \langle n_i | n_d \rangle \langle n_d' | e^{iH_f} \langle n_d' | n_d \rangle | n_d' \rangle \langle n_d' | n_i \rangle e^{i[H_d(E) - E_{n_d}-E_{n_d'}]/2}.
\]
Although these expressions are not particularly useful for evaluating the spectral moments, they are suitable for establishing the desired relationships. The moments of $\sigma_f(E)$ can be determined by integrating over the upper complex plane and subtracting the arc at infinite distance:

$$\langle E^k \rangle_f = \int_{-\infty}^{\infty} E^k \sigma_f(E) dE = \int_0^{\infty} E^k \sigma_f(E) dE - \int_{-\infty}^{0} E^k \sigma_f(E) dE.$$  \hspace{1cm} (A12)

On the other hand, the quantities $\langle E^k \rangle_{fe}$ are obtained by inserting $F(t,T)$ of Eq. (A14) into Eq. (A12) and integrating over time $T$.

For $k=0$ the integration over the arc vanishes and one readily arrives at

$$\langle E^0 \rangle_f = \langle E^0 \rangle_{fe} = 1.$$  \hspace{1cm} (A16)

For $k=1$ the integral over the arc gives $\pi$ which cancels the imaginary part of the first integral on the r.h.s. of Eq. (A15). A comparison of the remaining real part and (A12) shows after some straightforward algebra that

$$\langle E \rangle_f = \langle E \rangle_{fe}.$$  \hspace{1cm} (A17)

These results could have been anticipated since the zeroth and first moments of the exact cross section exist and the introduction of an infinitesimal $\epsilon$ does not have any consequences. The second moment of $\sigma_f(E)$ does not exist and here the $\epsilon$ trick plays a substantial role. Now the arc integral has two contributions. One of them again compensates the imaginary part of the integral over the upper complex plane and the other can easily be identified as the diverging second moment of a single Lorentzian. The final result reads as

$$\langle E^2 \rangle_f = \langle E^2 \rangle_{fe} + \int E^2 L(E) dE.$$  \hspace{1cm} (A18a)

In analogy to Eq. (A7) we may now write

$$\langle E^2 \rangle_f = \langle E^2 \rangle_{fe} + \Gamma^2/8 \ln 2.$$  \hspace{1cm} (A18b)

Analogously, all higher moments $\langle E^k \rangle_f$ can be expressed by the well-defined quantities $\langle E^k \rangle_{fe}$ for all the relevant physical contents of the cross sections is contained in these latter quantities.

It is illuminating to compute $\sigma_f(E)$ via Eq. (A9) for a hypothetical $F(t,T)=1$. The result is the Lorentzian

$$\sigma_f(E) = \frac{1}{\pi} \frac{\Gamma/2}{E^2 + (\Gamma/2)^2},$$  \hspace{1cm} (A19)

We repeat the calculation using the $\epsilon$ trick Eq. (A10) and obtain

$$\sigma_{fe}(E) = \frac{1}{\pi} \frac{\Gamma/2}{E^2 + (\Gamma/2)^2} \left( \frac{1 - e^{-r/2}}{1 + e^{-r/2}} \right),$$  \hspace{1cm} (A20)

For $r \to 0$ obviously the two quantities are identical. The latter quantity is a function of $E$ with surprising properties. Using

\begin{equation}
\int_{-\infty}^{\infty} \frac{\cos(eE)}{E^2 + (\Gamma/2)^2} dE = \frac{2\pi}{\Gamma} e^{-\Gamma e/2},
\end{equation}

\begin{equation}
\int_{-\infty}^{\infty} \frac{\sin(eE)}{E^2 + (\Gamma/2)^2} dE = \frac{4\pi}{\Gamma} (1 - e^{-\Gamma e/2}),
\end{equation}

one finds for integer $k$ that

$$\int_{-\infty}^{\infty} E^k \sigma_{fe}(E) dE = \begin{cases} 1 & \text{for } k=0 \\ 0 & \text{for } k>0 \end{cases}$$  \hspace{1cm} (A22)

Except for the zeroth moment, all moments vanish and this for any positive $\epsilon$ (that $\epsilon$ is an infinitesimal has not been used yet). Note that all odd moments of the Lorentzian $\sigma_f(E)$ vanish because of symmetry and that the even moments $k>0$ are divergent.

Finally, we remark that choosing

$$F(t,T) = \sum_n \left| a_n \right|^2 e^{-iE_n t}$$  \hspace{1cm} (A23)

in Eq. (A9) recovers $\sigma_f(E)$ introduced in Eq. (A1). Using the $\epsilon$ trick with this $F(t,T)$, we can immediately identify the resulting moments of $\sigma_{fe}(E)$ with those of $\sigma(E)$ in Eq. (A5). In general, the moments of $\sigma_{fe}(E)$ do depend on the value of $\Gamma$ and are much more involved than those of $\sigma(E)$ owing to the fact that $F(t,T)$, see Eq. (A14), is a function of both $t$ and $T$.

The removal of the divergencies of the spectral moments is a central issue of this Appendix and concluding remarks are in order. The divergencies are removed by replacing the integration range (0 to $\infty$) in Eq. (A9) by the range $\epsilon$ to $\infty$, where $\epsilon$ is a positive infinitesimal. This does not affect at all the zeroth and first moments [see Eq. (A17)]. The exact second moment is shown to be the sum of the second moment computed using the $\epsilon$ trick and the second moment of a single Lorentzian of FWHM $\Gamma$ [see Eq. (A18a)]. It is only this single Lorentzian, whose tail is identified to cause the divergence, which is replaced by a Gaussian of the same FWHM. $\Gamma$ is usually very small compared to the width of the band (in CO discussed in Sec. V this $\Gamma$ is 0.1 eV, while the widths range up to 7 eV) and the replacement of a single Lorentzian by a single Gaussian is of little impact anyway. In these cases one might even ignore the term due to the single Lorentzian.

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5. J. Nordgren, L. Selander, L. Pettersson, C. Nordling, K. Siegbahn, and...


L. S. Cederbaum and F. Tarantelli (to be published).


Dimensionless normal coordinates are obtained from the usual normal coordinates by dividing the latter by the square root of the corresponding frequency.


