Nuclear dynamics of several decaying overlapping electronic states:
A time-dependent formulation

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The nuclear dynamics accompanying the excitation of a polyatomic target to a manifold of
decaying overlapping electronic states and the subsequent decay to final electronic states are
discussed. Nonadiabatic interactions within the manifold of decaying states as well as of final
states are included. The cross sections for the excitation and for the production of final states are
derived. The wave packet dynamics are investigated for both the excitation and the decay and
related to the corresponding cross sections. Particular attention is paid to core levels of systems
with equivalent atoms. The time-dependent formulation is also used to compute the gross
features of the observed spectra via a spectral moment expansion. An interesting example is
investigated where the decaying as well as the final states have extremely localized electron
vacancies.

I. INTRODUCTION

Short lived electronic states play a central role in a vast
number of processes which have been investigated, for in-
stance, by Auger\textsuperscript{1} and x-ray emission\textsuperscript{2} spectroscopies as
well as by photoionization\textsuperscript{3} and electron–molecule scatter-
ing\textsuperscript{4} measurements. The observations are greatly influenced
by the nuclear dynamics in both the decaying state and the
final states of the decay. In a preceding study,\textsuperscript{5} we dis-
cussed the time-dependent nuclear dynamics accompany-
ing the excitation from an initial state to an intermediate
short-lived electronic state which decays to final electronic
states. The common Born–Oppenheimer approximation
was assumed to be valid.

In the present work, we generalize the theory\textsuperscript{5} to allow
us to treat the situation where several electronic states are
of relevance and nonadiabatic interactions may be present.
Several decaying states $|d\rangle$ are considered. Decaying states
are often highly excited neutral or ionized states lying in an
energy regime where the density of states is considerable.
In particular, in polyatomic systems, two or more decaying
states are then likely to be close together in energy and,
therefore, must be considered together to describe the final
state’s dynamics to which they may all contribute. Inter-
esting electronic interference phenomena may appear if the
decaying states overlap within their decay widths.\textsuperscript{6} Several
final states $|f\rangle$ are also considered. If they do not interact
nonadiabatically, it is sufficient to consider each final state
separately. Well-known cases of nonadiabatic or, synony-
mously, vibronic interactions are provided by the Jahn–
Teller and Renner–Teller effects (see, e.g., Refs. 7 and 8).
Other vibronic coupling cases involving nondegenerate
electronic states have been shown to occur in many sys-
tems (see, e.g., Ref. 9). To be complete, we consider vi-
broncoupling also in the initial state of the target, i.e.,
several electronic states $|i\rangle$ exist which are vibronically
coupled to each other. The target is, therefore, not in a
vibrational state of a specific electronic state, but rather in a
mixed vibrational-electronic state commonly termed vi-
broncoupling also in the initial state of the target, i.e.,

The paper is organized as follows: In Sec. II, the
Hamiltonian of the system is introduced and expressions
for the relevant cross sections are derived by standard
methods. The wave packets and their relation to the cross
sections are derived briefly in Sec. III in analogy to Ref. 5.
In Sec. IV, the cross sections are further discussed and the
gross features of the observed spectra are investigated in
terms of spectral moments. Section V is devoted to ener-
getically deep levels. Here, particularly interesting dynam-
ics arise in molecules containing equivalent atoms. An il-
ustrative application to MgF\textsubscript{2} is presented in Sec. VI.
II. HAMILTONIANS AND CROSS SECTIONS

In the Born–Oppenheimer picture, the initial state $|T_i\rangle$ of the target is written as a product $|i \rangle |n_j\rangle$ of an electronic state $|i\rangle$ and a vibrational state $|n_j\rangle$. If vibronic coupling prevails, the initial state reads

$$|T_i\rangle = |i\rangle |n_j\rangle = |i\rangle |n_{1j}\rangle + |i\rangle |n_{2j}\rangle + \cdots,$$  \hspace{1cm} (2.1a)

where $|n_j\rangle$ is a column vector of vibrational states in the various electronic states $|i_1\rangle, |i_2\rangle, \ldots$ vibronically coupled to each other. Here and in the following, bold faced quantities denote vectors, "t" stands for transposed, and sans serif quantities denote matrices. Thus, $|a\rangle$ is a column vector of kets $|a_j\rangle, j=1,2,\ldots$, its transpose $|a\rangle^t$ is the row vector of the same kets, and its adjoint $\langle a|$ is the row vector of the corresponding bras $\langle a_j|$. The Hamiltonians are represented as matrices in the basis of the electronic states. The eigenvalue equation for the initial state, for instance, then reads

$$H |n_j\rangle = E_{n_j} |n_j\rangle.$$ \hspace{1cm} (2.1b)

Analogously, we introduce the Hamiltonians $H_f$ for the nuclear motion in the vibronically coupled final electronic states $|f_1\rangle, |f_2\rangle, \ldots$ and the Hamiltonian $H_d$ for the nuclear motion in the decaying electronic states $|d_1\rangle, |d_2\rangle, \ldots$.

The Hamiltonians $H_t, H_d,$ and $H_f$ of course, also include the kinetic energy operator of the nuclei and are thus operators in nuclear space. In order to be able to handle the Hamiltonians easily, it is convenient to work in the so-called diabatic representation\textsuperscript{11} instead of the common adiabatic one. The electronic states $|i\rangle, |d\rangle,$ and $|f\rangle$ are, therefore, chosen to be diabatic states. The above Hamiltonians then essentially are a sum of the nuclear kinetic energy operator and a potential energy matrix.\textsuperscript{9,11}

The total Hamiltonian relevant for our process takes on the appearance

$$H = H_0 + H_1,$$ \hspace{1cm} (2.2a)

where

$$H_0 = |i\rangle \langle i| H_0 |f\rangle \langle f| + \sum_k |k\rangle \langle d| (E_k + H_d) |k\rangle \langle d|$$

$$\times \langle f| \langle k'| E_{k'} + H_f |k'\rangle \langle f| \langle f| \langle k'| \langle d| \langle k| \langle d| \langle f| |f\rangle + \text{h.c.} \rangle \langle f| \langle f| \langle f| \langle f| + \text{h.c.} \rangle.$$ \hspace{1cm} (2.2b)

describes the target (first term on the right-hand side), the incoming projectile (second term), the decaying state manifold together with the emitted primary particle with possible energies $E_k$ and momentum $k$ (third term), and the final state manifold together with the primary particle and the secondary particle emitted via the decay (last term).

The primary particle is, e.g., a photoelectron. In the case of an optical excitation followed by a decay, there is no primary particle and $|k\rangle$ can be discarded. The secondary particle is, e.g., an Auger electron.

The possible interactions of the states appearing in $H_0$ are described by

$$H_1 = \sum_k |k\rangle \langle d| V(|k\rangle \langle f| |k\rangle \langle f| + \text{h.c.} \rangle$$

$$+ \sum_{k',l'} |k\rangle \langle k'| W(|k'\rangle \langle d| |k'\rangle \langle l| \langle l| + \text{h.c.} \rangle.$$ \hspace{1cm} (2.2c)

Note that $|d\rangle^t$ is a column vector of bras $|d_1\rangle, \langle d_2|, \ldots$. The first term of $H_1$ is the interaction between the target and the projectile leading to the decaying states and a possible primary particle. The matrix elements for these excitations constitute the matrix $V$:

$$V = \begin{pmatrix} V_{d_1d_1} & V_{d_1d_2} & \cdots \\ V_{d_2d_1} & V_{d_2d_2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}.$$ \hspace{1cm} (2.2d)

The second term of $H_1$ is the coupling of the decaying manifold and the continuum of emitted particles. The coupling matrix elements are the elements of the matrix

$$W = \begin{pmatrix} W_{f_1d_1} & W_{f_1d_2} & \cdots \\ W_{f_2d_1} & W_{f_2d_2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}.$$ \hspace{1cm} (2.2e)

The transition probability per unit time from the overall initial state—target plus projectile $|f\rangle = |P\rangle |T_i\rangle$—to the final states plus the emitted particle reads\textsuperscript{12}
Here \( |F\rangle = |k_0\rangle |f_0\rangle |n_f\rangle \) and \( k_0 \) and \( f_0 \) are the momenta of the primary and secondary emitted particles, respectively. The \( T \) matrix has the usual appearance

\[
\hat{T} = H_1 + H_1 (E_f - H_0 + \hbar \omega^+)^{-1} \hat{T},
\]

where \( \hbar \omega^+ \) is a positive infinitesimal. The exact evaluation of \( P_{F\ell} \) with the Hamiltonian (2.2) is complicated. However, if we assume the golden rule to be valid for the excitation process \( |i\rangle \rightarrow |d\rangle \), the decay process can be calculated exactly. This implies that the excitation matrix \( V \) is considered in the \( T \) matrix only up to first order, whereas the decay matrix \( W \) to infinite order. This approximation is excellent if the incoming projectile is a photon or an electron scattered under dipole conditions and a very good approximation in many other cases.

The evaluation of the transition probability can be carried out in analogy to the single-state case and we, therefore, only briefly sketch the derivation in the present several-state situation. A related derivation has recently been given for the case of several vibronically noninteracting decaying states and a single initial and final state. The \( T \) matrix is expanded in a series

\[
\langle F | \hat{T} | I \rangle = \langle F | H_1 | I \rangle + \langle F | H_1 G H_1 | I \rangle + \cdots,
\]

where the resolvent \( G \) reads

\[
G = (E_f - H_0 + \hbar \omega^+)^{-1}.
\]

The individual elements of the series are easy to compute, for instance,

\[
\langle F | H_1 | I \rangle = 0,
\]

\[
\langle F | H_1 G H_1 | I \rangle = \langle n_f | W(k_0') [(E_f - E_{k_0}) 1 - H_d + \hbar \omega^+]^{-1} V(k_0) | n_f \rangle.
\]

All higher terms are formal repetitions of the latter and can be identified as members of an operator geometric series. The final result can be cast in the following compact form:

\[
\langle F | \hat{T} | I \rangle = \langle n_f | W(k_0') [(E_f - E_{k_0}) 1 - H_d + \hbar \omega^+]^{-1} V(k_0) | n_f \rangle.
\]

Due to the matrix notation used, the formal similarity with the result in the single-state case is obvious.

The complex and, in general, energy dependent Hamiltonian \( \mathcal{H}_d \) describing the nuclear motion in the manifold of decaying states is now a matrix Hamiltonian of the dimension of this manifold. It reads

\[
\mathcal{H}_d = H_d + \sum_k W(k) [(E - E_{k}) 1 - H_f + \hbar \omega^+]^{-1} W(k),
\]

where \( E = E_f - E_{k_0} \) is the excess energy (see Sec. II of Ref. 5). The nonlocality and energy dependence of this Hamiltonian give rise to interesting effects which are not studied in this work. Here, we confine ourselves to the local approximation which is applicable in most cases (see Refs. 5 and 13 for details and further references). In this approximation, the shift \( \Delta \) and width \( \Gamma \) which result from the coupling of the discrete states \( |d_1\rangle, |d_2\rangle,... \) to the continuum are just functions of the nuclear coordinates \( Q \).

Note that in the present several-state problem, the shift and width are now, in general, full matrices.

### III. TIME-DEPENDENT FORMULATION

The present basic result (2.5) has the same formal appearance as the analogous result in the simpler single-state case. Therefore, with some care, all the equations in Secs. II and III of Ref. 5 can be formally transferred to the present several-state case and we do not wish to elaborate on the derivations in the following. Instead, we just present two explicit results as examples.

At time \( t = 0 \), the state \( |n_f\rangle \) is excited to the manifold of intermediate states and arrives there as \( V|n_f\rangle \). This wave packet describes the nuclear motion in the decaying manifold and propagates according to

\[
|\Psi_d(t)\rangle = e^{-i\mathcal{H}_d t}|n_f\rangle.
\]

The wave packet is obviously a vector with components on each of the electronic states \( |d_1\rangle, |d_2\rangle,... \). Each of these components is itself a wave packet, but because \( \mathcal{H}_d \) is in general nondiagonal, a component does not independently propagate on a potential energy surface of a single electronic state, i.e., the components mix as time proceeds. The cross section \( \sigma_d(E) \) for the production of the decaying state manifold is determined by the real part of the autocorrelation function

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

The wave packet on the final-state manifold \( \Psi_f(t) \) is a result of the decay of \( \Psi_d(t) \). In analogy to Sec. III of Ref. 5, we find

\[
|\Psi_f(E, t)\rangle = e^{-\mathcal{H}_f t} \int_0^t \exp[i(E + H_f) t'] W e^{-i\mathcal{H}_d t'} |n_f\rangle dt'.
\]

Clearly, this wave packet has components on all the participating final electronic states. It should be noted that \( \Psi_f \) depends on the energy \( E \) of the particle emitted in the decay. This energy enters as a phase in the integral describing the accumulation of the decaying contributions up to the time \( t \) of observation.

The cross section for the production of the final-state manifold is again as in Ref. 5

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

Using Eq. (3.2) immediately leads to the following expression:
\[ \sigma_f(E) \sim \int_0^\infty dT \int_{-T}^T dt \, e^{iE_t} \langle n_f | V^* \rangle \exp[i\mathcal{H}_d(T-t)/2] W^t \exp[-i\mathcal{H}_d(T-t)/2] V | n_i \rangle. \]  

(3.4h)

If the final states do not interact vibronically with each other, \( \mathcal{H}_f \) is diagonal and the cross section breaks into a sum of partial cross sections for each of the final electronic states \( | f_k \rangle \)

\[ \sigma_f(E) = \sum_k \sigma_{f_k}. \]  

(3.5)

The expression for \( \sigma_{f_k} \) is the same as in Eq. (3.4b) with \( H_f \) replaced by \( H_{f_k} \) describing the nuclear motion in the \( k \)th final states and \( W \) substituted by its \( k \)th row \( W_k \). If, on the other hand, the decaying states do not vibronically interact, the cross section \( \sigma_f \) does not in general break into a sum of incoherent contributions. That is, interference effects may arise because \( \Psi_f \) is a superposition of contributions from the various decaying states.

### IV. FURTHER PROPERTIES OF CROSS SECTIONS AND SPECTRAL MOMENTS

In many experiments, the structures due to the nuclear dynamics are not resolved. Nevertheless, the dynamics can have strong impact on the gross features of the bands observed in the spectrum. It has been noticed\(^5\) that even the energetic positions of the bands can significantly depend on the nuclear dynamics making a reinterpretation of observed spectra necessary. That the widths of the detected electronic bands depend strongly on the underlying nuclear dynamics is evident. The method of spectral moments\(^{14}\) is useful for describing the gross features of a spectrum. The general problem of evaluating the moments of spectra of short-lived states is solved in detail in Ref. 5.

The expressions for the spectral moments are more involved in the several-state situation than in the single-state case discussed in Ref. 5. The main reason is that the excitation and decay matrix elements \( V \) and \( W \) are matrices. The expressions for the moments can be derived from their definition using Eq. (3.4b). For transparency, we first assume that the elements of the matrices \( V \) and \( W \) are constant \( c \) numbers. At the end of this subsection, we then briefly discuss the general situation where these matrix elements are functions of the nuclear geometry and also depend on the angular distribution of the emitted particles. This discussion is also relevant in the single-state case and augments the discussion of Ref. 5.

In contrast to the single-state case, the zeroth moment which measures the total intensity is also of importance here. One readily finds

\[ \langle E^0 \rangle_f \equiv \int \sigma_f(E) dE = 4\pi \alpha \int_0^\infty dT \langle \Psi_d(T) | W^t W | \Psi_d(T) \rangle, \]  

(4.1)

where \( \alpha \) is the proportionality constant in Eq. (3.4b). Since \( W \) is a matrix, the integral cannot be evaluated without further specification of \( \mathcal{H}_d \). In the single-state case, the integral is readily evaluated. In the following, we choose \( \alpha \) to make \( \langle E^0 \rangle = 1 \), i.e., we work in units of the total integrated cross section.

In analogy to Sec. IV of Ref. 5, the first moment which is the center of gravity of the observed structure takes on the appearance

\[ \langle E \rangle_f = 4\pi \alpha \int_0^\infty dT \langle \Psi_d(T) | \frac{1}{2} (\mathcal{H}_d^+ W W^t W + W^t W \mathcal{H}_d) \]  

\[ -W^t H_f W | \Psi_d(T) \rangle, \]  

(4.2)

which obviously reduces to the result (4.6b) of Ref. 5 in the single-state case. This also applies to the second moment which is related to the width of the structure. Although simple, the result is lengthy

\[ \langle E^2 \rangle_f = 4\pi \alpha \int_0^\infty dT \langle \Psi_d(T) | \frac{1}{4} [(\mathcal{H}_d^+)^2 W^t W \]  

\[ + 2 \mathcal{H}_d^+ W W \mathcal{H}_d + W^t W (\mathcal{H}_d^+)^2] \]  

\[ - [\mathcal{H}_d^+ W H_f W + W^t H_f W \mathcal{H}_d] \]  

\[ - W^t (H_f)^3 W | \Psi_d(T) \rangle. \]  

(4.3)

In the derivation of the moments, care has been taken not to commute any of the matrices. Consequently, the above equations (4.1)-(4.3) are also valid if \( W \) and \( V \) are functions of the nuclear coordinates. The expressions must be modified, however, if these matrices also depend on the directions of the emitted particles. In general, in the basic equation (2.5a), \( V (k_0) \) depends on the momentum of the primary emitted particle, e.g., photoelectron, and \( W (k_0) \) depends on the momentum of the secondary emitted particle, e.g., Auger electron. The cross section \( \sigma_f(E) \) has been obtained by integrating the basic equation over the states of the primary emitted particle. By writing

\[ dk_0 = (2E_{k_0})^{1/2} dE_{k_0} d\Omega; \]  

(4.4)

the integration over the energy \( E_{k_0} \) is readily performed and Eq. (3.4b) for \( \sigma_f(E) \) is recovered where \( V \) is now energy dependent—\( V = V(E, \Omega) \). Consequently, \( \sigma_f \) and hence also the computed spectral moments now also depend on \( \Omega \) and the analogous space angle \( \Omega' \) of the secondary particle: \( \sigma_f = \sigma_f (E, \Omega, \Omega') \). This cross section can be experimentally determined if both particles are measured in coincidence. If only the secondary particle is detected, the cross section must be integrated over \( \Omega \). For a molecule fixed in space, the resulting cross section depends on \( \Omega' \) and shows interesting interference structures.\(^{15}\) The cross section must be averaged over the molecular orientation if the molecule is free and the resulting \( \sigma_f \) will essentially not depend on \( \Omega' \).

As mentioned above, we have to integrate over \( \Omega \) if only the secondary emitted particle is measured. Of course, one can first compute the moments (4.1)-(4.3) and sub-
sequent integrate the result over $\Omega$. We may also proceed differently and first expand $V(k_o)$ in spherical harmonics

$$V(\Omega) = \sum_{l,m} V_{lm} Y_{lm}(\Omega). \quad (4.5)$$

Inserting this expansion into the expression (3.4b) and integrating over $\Omega$ leads to

$$\sigma_f = \sum_{l,m} \sigma_{f,lm}, \quad (4.6a)$$

where $\sigma_{f,lm}$ obeys the same expression (3.4b) with $V$ substituted by $V_{lm}$. All the spectral moments can now be computed from

$$\langle E^k \rangle_f = \sum_{l,m} \langle E^k \rangle_{f,lm}. \quad (4.6b)$$

Eq. (4.1)-(4.3) for the first moments are still valid for each $\langle E^k \rangle_{f,lm}$ if we define the wave packet $\Psi_d(t)$ as usual, but replace $V$ in Eq. (3.1) by $V_{lm}$. Integration over the second angle $\Omega'$ can be done analogously by expanding $W$.

In general, the above equation (4.6) cannot be further simplified even if $V$ and $W$ do not depend on the nuclear coordinates $Q$. The question arises why the results for the single-state case obtained in Ref. 5 are simpler and do not involve partial channel cross sections $\sigma_{lm}$. If $V$ and $W$ do not depend on $Q$, they can be taken out of the integral (3.4b) in the single-state case. It is immediately obvious that the integration over $\Omega$ (and $\Omega'$) only influences the proportionality factor in Eq. (3.4b)

$$|V(\Omega)|^2 \rightarrow \int |V(\Omega)|^2 d\Omega = \sum_{l,m} |V_{lm}|^2. \quad (4.7)$$

We expect interesting new interference effects as a function of energy in the several-state case where the integration over $\Omega$ is not just a change of a prefactor.

We would like to add two brief comments on the spectral moments in the several-state case. The calculation of moments is particularly useful if the final states do not interact vibronically. Then Eq. (3.5) is valid and, independent of the number of participating decaying states, each final state has its own cross section and moments. If the final states interact, the computed moments describe the properties of the interacting final manifold. The spectrum of this manifold might have several humps and the first moment, for instance, describes the center of gravity of the spectrum and does not tell us much on the individual humps. To know more about the humps, one may either compute higher moments or estimate the spectrum itself in some other way. The second comment concerns the semiclassical evaluation of the moments which has been found very useful in the single-state case (see Sec. IV B 3 of Ref. 5). The moments of the spectrum in the several-state case discussed here are complicated to compute quantum mechanically in general and a semiclassical theory would remedy the situation. It is well known, however, that it is difficult to derive satisfactory semiclassical approximations for coupled electronic states. Further work in this direction is needed.

V. CORE LEVELS

A. General aspects including interference effects

The general theory discussed in the preceding sections simplifies if the decaying states are localized in space. A particularly relevant class of localized states is that involving the excitation or ionization of core electrons. To demonstrate the impact of localization, let us first discuss the matrix Hamiltonian $H_d$ in Eq. (2.5) describing the nuclear dynamics in the decaying manifold of core levels. These states may interact directly via vibronic coupling. This interaction is included in $H_d$. In general, the states may also interact with each other indirectly via their common coupling to the same decay continuum. This interaction is in $\Delta(\Omega) - \Pi(\Omega)/2$. Hence, even if the direct interaction is negligible, i.e., $H_d$ is a diagonal matrix of operators, the continuum coupling will mix the states and complicated interference effects arise. In the case of core levels, this mixing is strongly quenched due to the localization in space as will be shown in the following.

In the local approximation, we may write for an element of the decay matrix $T(Q)$,

$$\Gamma_{d,d'}(Q) = 2\pi \sum_f dk W_{f,d'_n} W_{f,d_m} \delta[E_{d}(Q) - E_k]. \quad (5.1a)$$

This relation follows from Eqs. (2.5) under the assumption that the local approximation is valid. $E_d(Q)$ is the vertical Auger energy at geometry $Q$ and the sum over the states of the emitted particle is written as an integral over its momenta. Using Eq. (4.4), the integration over the energy $E_k$ is readily done leading to

$$\Gamma_{d,d'}(Q) = 1/2 \sum_f \int d\Omega |W_{f,d'_n}(\Omega) W_{f,d_m}(\Omega)| \quad (5.1b)$$

where the factor $[8\pi E_{d}(Q)]^{1/2}$ is incorporated into $W_{f,d}(\Omega)$.

Consider two equivalent core levels as, for instance, the two $1s$ levels of the nitrogen molecule $N_2$, one atom being at $R_1$, the other at the site $R_2$. Since the atoms are equivalent and the energy of the particle emitted by the decay of a core level is high, we find

$$W_{f,d_1} = e^{-ik_f R_1} W_{f,d}, \quad W_{f,d_2} = e^{-ik_f R_2} W_{f,d}, \quad (5.2a)$$

where $W_{f,d}$ depends only weakly on $\Omega$ and $k_f = k_f(Q)$ denotes the momentum of the Auger electron at the energy $E_{f}(Q)$. It follows that

$$\Gamma_{d_1,d_2} = 2\pi \sum_f |W_{f,d}|^2 \sin k_f R = \Gamma \sin k R / k R. \quad (5.2b)$$

Here, $k$ denotes the average absolute momentum of the emitted particle. $R$ is the internuclear distance between the atoms 1 and 2 on which the core levels $|d_1\rangle$ and $|d_2\rangle$ are localized. At typical energies of the emitted particles from the decay of core levels $kR \gg 1$ and, hence,
This relation holds better the larger is the distance between the atomic sites. For most practical purposes, we may neglect $\Gamma_{d,d_e}$, \( n \neq m \) in the following and consider $\Gamma(Q)$ to be diagonal. Since only core levels on atoms of one kind, e.g., nitrogen, have to be considered together and because of the atomic character of core levels, we may put all the diagonal elements of $\Gamma$ to be equal to a constant $\Gamma$. This assumption can be easily relaxed in the following calculations.

Having discussed the matrix Hamiltonian $H_d$, let us now turn to the cross section $\sigma_f$. In principle, two core levels $|d_1\rangle$ and $|d_2\rangle$ can decay to the same final state $|f\rangle$, i.e., $W_{fd_1}$ and $W_{fd_2}$ are both not equal to zero. An interesting exception is discussed in Sec. V B. Analogously, both $V_{d_1i}$ and $V_{d_2i}$ are generally not equal to zero, i.e., two core levels can be populated by the same excitation or ionization process. A relevant consequence is that mixed terms of the two core levels may contribute to the cross section even if these levels do not interact vibronically. Equation (3.4b) immediately gives

$$\sigma_f \approx \int_0^\infty d\tau e^{-\Gamma T/2} \int_0^\infty dt e^{\epsilon t}$$

$$\times \langle n_i | (A_{d_1} + A_{d_2}) e^{iH_f \tau} (B_{d_1} + B_{d_2}) | n_i \rangle,$$

(5.3a)

where

$$A_{d_i} = V_{d_i}^2 \exp\{iH_d(T-t)/2\} W_{fd_i}$$

(5.3b)

and $B$ is equal to $A^*_i$ with $t \rightarrow -t$. For transparency, we have assumed only one final and one initial electronic state. The $d_1 - d_2$ mixed terms obviously give rise to interference effects. The situation resembles the standard two slit experiment. The two core levels play the role of the slits and we cannot tell from which site the emitted particle came.

In the two slit experiment, the interference effects are most pronounced if the two slits are equivalent. The same is expected here. For instance, the two nitrogen atoms of the $N_2$ molecules are equivalent and hence also corresponding core levels. In this simple case, we may transform the localized $|d_1\rangle$ and $|d_2\rangle$ levels to “$g$” and “$u$” delocalized levels given by $|d_1\rangle \pm |d_2\rangle)/\sqrt{2}$. We notice that in this delocalized representation, the $g-u$ mixed terms in the cross section do not appear because of symmetry. All the interference effects have been transferred to the matrix elements $W_{fu}$ and $W_{fs}$ which are a superposition of $W_{fd_1}$ and $W_{fd_2}$. The pronounced interference effects predicted for $N_2$ are expected to decrease if the atoms are inequivalent and in particular if the core level energies are different.

The above discussed interference effects are suppressed to a substantial extent if the angles of the two emitted particles, e.g., photoelectron and Auger electron, are not measured, i.e., if we integrate over the spatial angle of one of the two electrons. Integrating $\sigma_f$ in Eq. (5.3a) over the angle of the primary particle, we immediately see with the help of Eq. (5.2) that the $d_1-d_2$ mixed term is suppressed by the factor $\sin kR/kR$ discussed above. A similar result holds if we integrate over the angle of the secondary particle. Consequently, for most purposes, we can neglect the mixed terms and consider $\sigma_f$ as an incoherent sum of contributions from the individual core levels. We shall see below that this finding also holds if the core levels interact vibronically. An interesting experiment where interference effects should be observable is resonant Auger (or resonant x-ray emission). The core electron is excited via a photon to a virtual orbital and no primary particle is emitted. The polarization of the light “selects” the position of the molecule in space and it is sufficient to detect the autoionized electron as a function of $\Omega$ relative to the light in order to see the above electronic interference, e.g., in $N_2$. Of course, if the molecule can be fixed in space, less averaging occurs and the effects are more pronounced. 15

B. Equivalent cores and their dynamical localization

1. General

Following symmetry requirements, the core orbitals of, e.g., benzene, are delocalized over all the six equivalent carbon atoms and transform like representations of the point group $D_{6h}$. Nevertheless, it is convenient to view the core hole, i.e., the benzene ion with a $1s_{1}$ vacancy, as localized on one carbon atom leading to $C_{2v}$ symmetry. This view simplifies the interpretation of the results and also makes the computation of the core hole easier. 16 However, the discussion of the nuclear dynamics is more transparent and helpful in the delocalized symmetry adapted representation. Delocalized core holes and core levels in general interact vibronically, and since this interaction is strongly dictated by symmetry, many useful results follow from symmetry considerations.

Let us briefly discuss some examples. The two $1s_{1}$ core vacancies in $CO_2$ transform as $\Sigma_g$ and $\Sigma_u$. Since the product $\Sigma_g \times \Sigma_u = \Sigma_u$, the antisymmetric CO stretching mode $Q_u$ which transforms like $\Sigma_u$ couples both states already linearly. Expanding the Hamiltonian for the core levels up to the linear term in all nuclear coordinates reads

$$(5.4a)$$

$$H_g = H_f + \left( E_g + \sqrt{2} \kappa_{sg} Q_g + \sqrt{2} \lambda_{sd} Q_u + \sqrt{2} \kappa_{ug} Q_u \right),$$

where $1$ is a unit matrix, $Q_g$ denotes the totally symmetric stretch coordinate, and $\sqrt{2}$ is introduced to have a consistent notation with Ref. 5. Because of the localized nature of core electrons, the vertical excitation energies $E_g$ and $E_u$ of the $\Sigma_g$ and $\Sigma_u$ states are essentially equal and this holds also for the coupling constant $\kappa_{ug}$. 17(a)

$$(5.4b)$$

$$E_d - E_i = E_g - E_u, \quad \kappa_{sg} = \kappa_{ug} = \kappa_{ug}.$$
This transformation implies nothing but the change from delocalized states \(|d_g\rangle\) and \(|d_u\rangle\) to localized ones \(|d_1\rangle\) and \(|d_2\rangle\) corresponding to the oxygen levels \(1\) and \(2\). The diagonal elements of the transformed Hamiltonian

\[
H_{dl} = S^+ H_d S
\]

(5.4d)
take on the appearance

\[
\begin{align*}
H_{d_1} &= H_i + E_d - E_i + \sqrt{2} \kappa_{dQ} Q_d + \sqrt{2} \lambda_{dQ} Q_u, \\
H_{d_2} &= H_i + E_d - E_i + \sqrt{2} \kappa_{dQ} Q_d - \sqrt{2} \lambda_{dQ} Q_u.
\end{align*}
\]

(5.4e)

These are oscillators shifted in the same direction by the totally symmetric and in opposite directions by the nontotally symmetric modes.

Similar results are found for all core hole states equivalent by symmetry. For instance, there are three \(\Gamma_1\)s vacancies states of BF\(_3\) which transform as \(E\) and \(A_1\) representations of \(D_{3h}\) symmetry. They are vibronically coupled by the degenerate Jahn–Teller modes. A localizing transformation similar to \(S\) in Eq. (5.4c) brings the three-dimensional Hamiltonian \(H_d\) to a diagonal form.\(^{17(b)}\) Each diagonal element represents a localized \(\Gamma_1\)s core hole and possesses its own particular combination of the coupling constants.

We would like to stress that not all core levels can be described by a single scalar Hamiltonian as \(H_{d_i}\) in Eq. (5.4e). Care must be taken if the core level is not a core vacancy, but a core excited state where the core electron is excited to a virtual orbital. If the virtual orbital is nondegenerate or the molecule is linear, the Hamiltonian still is a scalar. On the other hand, for a nonlinear molecule and a degenerate virtual orbital, \(H_{d_i}\) will still be a matrix Hamiltonian due to the vibronic coupling in the virtual orbital. For instance, there are six symmetry adapted states arising from the excitation of a \(\Gamma_1\)s electron to a doubly degenerate \(E\) virtual orbital in BF\(_3\). The six-dimensional Hamiltonian \(H_d\) in the symmetry adapted representation reduces with the aid of a suitable transformation to three two-dimensional matrix Hamiltonians \(H_{d_k}\), \(k=1, 2,\) and \(3,\) one for each \(\mathbf{F}\) atom. Because of the localization of the core electrons, the Jahn–Teller effect in the \(E\) virtual orbital has changed in the core excited state and the result has been termed the distorted Jahn–Teller effect.\(^{17(b)}\) Vibronic coupling may thus prevail even if the core electron is chosen to be localized.

As discussed above, the mixed terms in the total integrated cross section are strongly suppressed for core levels and each core level contributes incoherently to the spectrum. To a good approximation, we may write

\[
\sigma_f(E) \sim \sum_k \sigma_{f d_k}(E),
\]

(5.5a)

where the contribution of the \(k\)th localized core electron reads [see Eq. (3.4b)]

\[
\sigma_{f d_k}(E) \sim \int_0^\infty dT\, e^{-T^2/2} \int_{-T}^{T} dt\, e^{iE(t)} \langle n_i | V_{d_k} | n_f \rangle \times \exp[-iH_{d_k}(T-t)/2] W_{d_k} e^{iE(t)} \langle n_i | n_f \rangle.
\]

(5.5b)

Here, \(V_d\) and \(W_d\) are parts of \(S^+ V\) and \(W S\), respectively.

2. Specific examples

As discussed above, the angular integrated cross section is to an excellent approximation an incoherent superposition of cross sections of the individual localized core levels. In complicated cases, the corresponding Hamiltonians of the localized core levels and of the final states are matrices. The resulting cross section (5.5b) is then formally similar to the cross section discussed in Sec. V A for the general case and all the results obtained there including the expressions for the spectral moments can be used here.

In many cases, however, it is possible to obtain explicit working equations, in particular for the spectral moments, which are useful in practical applications. A few examples are given in the following subsections.

a. \(g-u\) coupling in the core. Here, we discuss two equivalent atoms whose core levels are vibronically coupled through nontotally symmetric modes. It is sufficient to consider two modes. A totally symmetric mode \(Q_g\) always present and a nontotally symmetric coupling mode \(Q_u\).

Examples are the oxygen levels of CO\(_2\) discussed above and the core levels of ethylene and acetylene. We note that inversion symmetry is not necessarily needed and the notations "\(g\)" and "\(u\)" are only used for convenience. Vibronic coupling in the initial and final states is not considered. The vibrational state \(|n_i\rangle\) is chosen to be the ground state.

Following the discussion in Sec. V B 1, the Hamiltonian of the coupled core levels can be diagonalized explicitly. In the framework of linear coupling, the result has been given in Eq. (5.4e). Since each of the localized states leads to the same spectrum, it is sufficient to consider one of them which we call \(H_{d_k}\).

\[
H_{d_k} = H_i + E_d(R_0) - E_i(R_0) + \sqrt{2} \kappa_{dQ} Q_d + \sqrt{2} \lambda_{dQ} Q_u.
\]

(5.6)
obviously vanishes. The final state Hamiltonian reads
\[ H_f = H_i + E_f(R_0) - E_i(R_0) + \sqrt{2\kappa_{fg}} Q_g. \] (5.8)

With these Hamiltonians, the first two moments readily follow from Eq. (4.20) of Ref. 5
\[ \langle E \rangle_f = \langle E_d(R_0) - E_i(R_0) \rangle - \frac{2\kappa_{dg} \beta_g}{\omega_g} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_g^2} \right) \]
\[ \langle T \rangle = \langle T_d(R_0) - T_i(R_0) \rangle - \frac{2\lambda_{du}}{\omega_u} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_u^2} \right). \] (5.9a)
\[ C_f^2 = C_g^2 + C_u^2 + \frac{\kappa_{dg} \beta_g^2}{\omega_g \omega_u} \left[ \frac{\Gamma^2}{\Gamma^2 + (\omega_g + \omega_u)^2} \right] \]
\[ + \frac{\Gamma^2}{\Gamma^2 + (\omega_g - \omega_u)^2} - \frac{2\Gamma^4}{(\Gamma^2 + \omega_g^2)(\Gamma^2 + \omega_u^2)} \], (5.9b)
where
\[ C_g = \langle E^2 \rangle_f - \langle E \rangle_f^2 - \Gamma^2/8 \ln 2, \] (5.9c)
and the contributions of the individual modes to the bandwidth are
\[ C_g^2 = \beta_g^2 + 2\kappa_{dg} \beta_g^2 \left[ 1 + \frac{\Gamma^2}{\Gamma^2 + 4\omega_g^2} - 2 \left( \frac{\Gamma^2}{\Gamma^2 + \omega_g^2} \right)^2 \right], \] (5.9d)
\[ C_u^2 = \lambda_{du}^2 + 2\lambda_{du}^2 \left[ 1 + \frac{\Gamma^2}{\Gamma^2 + 4\omega_u^2} - 2 \left( \frac{\Gamma^2}{\Gamma^2 + \omega_u^2} \right)^2 \right]. \]

The coupling constant \( \lambda_{du} \) of the nontotally symmetric mode enters all moments quadratically. We note that the inclusion of additional totally symmetric and coupling modes is straightforward. Furthermore, since the only ingredient entering the calculation is the scalar form of \( H_d \), the present results are also valid in all those cases of more than two equivalent atoms where the Hamiltonian of the decaying manifold can be transformed to scalar \( H_d \). This, in particular, comprises all cases where the core levels under consideration are core vacancies.

**b. g-u coupling in the core and in the final states.** In addition to the \((g+u) \otimes (g+u)\) case discussed in the preceding subsection, we now also consider vibronic coupling in the final states. In contrast to the core case, vibronic coupling in the final states is much less trivial because the matrix Hamiltonian \( H_f \) cannot be explicitly diagonalized in general. For simplicity, we consider the coupling of two electronic states \( f_g \) and \( f_u \) in the linear approximation
\[ H_f = H_{fg} + \sqrt{2\kappa_{fg}} Q_g + \sqrt{2\lambda_{fu}} Q_u \]
\[ \left( E_{fg} + \sqrt{2\kappa_{fg}} Q_g \right) \left( \sqrt{2\lambda_{fu}} Q_u + E_{fu} + \sqrt{2\kappa_{fg}} Q_g \right). \] (5.10)

This basic Hamiltonian may serve to describe several cases. As mentioned above for the core Hamiltonian, \( g \) and \( u \) must not necessarily denote "gerade" and "ungerade." In general, \( Q_g \) denotes a totally symmetric and \( Q_u \) a coupling mode. However, assuming certain relations to hold between the coupling constants and energies, the Hamiltonian (5.10) can even describe the Jahn–Teller effect. Then \( Q_g \) and \( Q_u \) denote the components of the degenerate nuclear coordinate.

In analogy to the single-state situation, we introduce the time-dependent Hamiltonian
\[ H_f(T) = e^{iH_d T} H_f e^{-iH_d T}, \] (5.11)
which is now a matrix. Note that there is such a Hamiltonian for each localized core level. The general expressions (4.1) (4.3) for the spectral moments reduce to the following appearance in the present core case:
\[ \langle E \rangle_f = \frac{\Gamma}{|W_d|^2} \int_0^\infty dT \ e^{-\Gamma T} \]
\[ \times \langle n_i | W_d H_d 1 - H_f(T) | W_d | n_i \rangle, \] (5.12a)
\[ \langle E^2 \rangle_f = \frac{\Gamma}{|W_d|^2} \int_0^\infty dT \ e^{-\Gamma T} \]
\[ \times \langle n_i | W_d H_d 1 - H_f(T) | W_d | n_i \rangle. \] (5.12b)

These equations are valid for any number of coupled final states and are applicable to each core level separately. Note that \( W_d \) is now a column vector with elements \( W_{f,g} \), \( W_{f,d} \),... or \( W_{f,g}, W_{f,d} \) in our specific example of \((g+u) \otimes (g+u)\).

The computation of \( H(T) \) is carried out in analogy to the computation in the single-state case described in Ref. 5 (Sec. IV B 2). The fact that \( H_f \) is now a matrix Hamiltonian makes the calculations somewhat more tedious. We obtain the following result:
\[ H_f(T) = H_f \]
\[ + \begin{bmatrix} A_{gg}(T) + A_{du}(T) & A_{uu}(T) \\ A_{ug}(T) + A_{du}(T) & A_{uu}(T) \end{bmatrix}, \] (5.13a)
where the time-dependent operators \( A(T) \) read
\[ A_{gg}(T) = \beta_g (1 - \cos \omega_g T) \left[ \frac{2\kappa_{dg}}{\omega_g} + (b_g + b_g^*) \right] \]
\[ + i\beta_g \sin \omega_g T (b_g - b_g^*), \] (5.13b)
\[ A_{uu}(T) \] is obtained by the substitution \( \omega_g \rightarrow \omega_u, b_g \rightarrow b_u, \kappa_{dg} \rightarrow \lambda_{du}, \) and \( \beta_g \rightarrow -\beta_u; A_{du} \) is obtained by \( \omega_g \rightarrow \omega_u, b_g \rightarrow b_u, \) and \( \kappa_{dg}, \beta_g \rightarrow -\lambda_{du}, A_{ug} \) is obtained by replacing \( \beta_g \rightarrow -\beta_g = \kappa_{dg} \rightarrow \kappa_{du}. \) For convenience, we have introduced

annihilation operators $b_g$ and $b_u$ for the quanta of the $Q_g$ and $Q_u$ modes. The relation of $A_g(T)$ to the corresponding quantity [Eq. (4.15) in Ref. 51 in the single-state case is evident. It is interesting to note that whereas the $Q_g$ mode appears only in the diagonal elements of $H(T)$, the coupling mode $Q_u$ contributes to all elements.

Using Eq. (5.12a) with the Hamiltonian $H_d$ from Eq. (5.6) and $H(T)$ given above leads to the first moment

$$
\langle E \rangle_f = \left| W_{fgd} \right|^2 \left[ E_d(R_0) - E_{fg}(R_0) \right] - \frac{2 \kappa_{gde}}{\omega_g} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_g^2} \right) E_d(R_0) - E_{fg}(R_0) + \left| W_{fgd} \right|^2 \left[ E_d(R_0) - E_{fg}(R_0) \right] - \frac{2 \kappa_{ude}}{\omega_u} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_u^2} \right) E_d(R_0) - E_{fg}(R_0) + \left( W_{fgd} W_{fgd}^* + \text{h.c.} \right) \left[ \frac{2 \kappa_{gde} \lambda_{fgd}}{\omega_u} \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_u^2} \right) \right].
$$

The vector $W_d$ has been normalized such that $|W_d|^2 = 1$. Although the expression is somewhat lengthy, it has a simple structure. It consists of three terms. The first term would be the first moment of the $f_{gfg}$ final state weighted by its population probability $|W_{fg}|^2$ if there was no vibronic coupling between the final states. Analogously, the second term corresponds to the first moment of the $f_{gfg}$ final state weighted by its probability to be a product of the decay. The third term is a result of vibronic coupling and disappears if there is no vibronic coupling in either the final or decaying state manifolds. It also vanishes if one of the final states possesses a negligible population probability, but this would be rather unusual. It is worth noting that the two core levels are shifted in a different direction in $Q$, space, i.e., if Eq. (5.14) holds for one of them, then we have to replace $\lambda_{du}$ by $-\lambda_{du}$ to obtain the expression for the other core level [see Eq. (5.4e)]. Nevertheless, the first moment $\langle E \rangle$ remains invariant because $W_{fgd}$ also changes its sign. The equivalent cores thus have the same moments.

With the help of Eqs. (5.12) and (5.13), the second moment can also be computed quite straightforwardly. Since the final result is lengthy, we refrain from presenting it here explicitly. It will be given in Sec. V B 2 d for an interesting special case. Finally, we would like to mention that the extension of the present calculations to include additional nuclear coordinates is obvious in the linear approximation.

c. Jahn-Teller coupling. If the final state is degenerate, it will usually be subject to a Jahn–Teller7 (or Renner–Teller4) effect. We distinguish between two relevant situations where the degenerate Jahn–Teller active mode does or does not participate in the vibronic coupling of the core levels. For instance, there is only one 1$s$ orbital in BF$_3$ and one 1$s$ orbital in CF$_4$. Correspondingly, there is no vibronic coupling in the core vacancy levels and the Jahn–Teller modes play only a minor role. On the other hand, the Auger decay of these vacancies populates final dicationic degenerate states of $E$ symmetry and in CF$_4$ also of $T$ symmetry, where Jahn–Teller coupling prevails. In the other situation where the F1s electron is ionized, there are several equivalent core levels which interact vibronically through the Jahn–Teller modes. Diagonalizing the corresponding matrix Hamiltonian $H_d$ similarly to the $g$–$u$ coupling case leads$^{17(10)}$ to the following Hamiltonian of one of the localized F1s core vacancy levels of BF$_3$:

$$
H_d = H_{gf} + \left[ E_d(R_0) - E_{fg}(R_0) \right] + 2 \sqrt{2} \kappa_{gde} Q_x.
$$

$Q_x$ and $Q_u$ are the Cartesian components of the degenerate Jahn–Teller active mode and $\kappa_{gde}$ is the Jahn–Teller coupling constant in the core level of $E$ symmetry. The Hamiltonians for the other two localized vacancies can be obtained$^{17(b)}$ by rotating the molecule by $2\pi/3$ and $4\pi/3$. Similar results hold for CF$_4$ and all other molecules with degenerate symmetry representations.

The spectral moments are readily obtained from Sec. V B 2 a and Eq. (5.15) if the final state under consideration is nondegenerate. If the final state is degenerate, the results of the preceding subsection can be used. The $E \otimes e$ Jahn–Teller effect in the final state is obtained from the $(g + u) \otimes (g + u)$ Hamiltonian (5.10) by setting

$$
E_{fg} = E_{fu} = E_{(R_0) - E_{(R_0)}},
$$

$$
-\kappa_{fg} = \kappa_{fu} = \kappa_{fg} \equiv \kappa_{fu},
$$

$$
\omega_g = \omega_u \equiv \omega_e
$$

and identifying $Q_g$ as $Q_x$ and $Q_u$ as $Q_y$. The calculated spectral moments (5.14) can be further simplified by noting that the decay matrix elements $W_{fgd}$ and $W_{gfd}$ are related by symmetry. The states $|f_{gfg}\rangle$ and $|f_{gfg}\rangle$ now play the roles of the two Cartesian components $|f_{gfg}\rangle$ and $|f_{gfg}\rangle$ of the degenerate final state. The choice of the localized core vacancy corresponding to Eq. (5.15) leads to particularly simple normalized decay matrix elements $W_{fgd} = 0, W_{gfd} = 1$.

Comparing the $(g + u) \otimes (g + u)$ core Hamiltonian (5.6) with the $E \otimes e$ core Hamiltonian (5.15) makes clear that the coupling constant associated with $Q_u$ vanishes. Consequently, if we use expression (5.14) for the first moment of the Jahn–Teller case, we have to put $\lambda_{du} = 0$. With the above simplifications due to symmetry, we finally find

$$
\langle E \rangle_f = \left[ E_d(R_0) - E_{fg}(R_0) \right] - 4 \kappa_{gde} (2 \kappa_{gde} - \kappa_{fu}) \left( 1 - \frac{\Gamma^2}{\Gamma^2 + \omega_e^2} \right).
$$

The result is thus formally very similar to that of a nondegenerate single-state case. The inclusion of several Jahn–
Teller active modes and also of totally symmetric modes is straightforward. The above formal similarity can be used to accomplish this goal.

Equation (5.12b) is used to compute the second moment. We start by noting that in our case
\[ W_d^T [H_d - H_f(T)]^2 W_d \]
\[ = [H_{fxy}(T)]^2 + [H_d - H_{fyy}(T)]^2, \tag{5.18a} \]
where \( H_{fxy}(T) \) and \( H_{fyy}(T) \) are the nondiagonal and the lower diagonal elements of the time-dependent Hamiltonian \( H_f(T) \) in Eq. (5.13), respectively. The relations (5.16) for the \( \delta \leftrightarrow e \) Jahn–Teller must be used, of course.

The vibrational ground state expectation values of the above terms are straightforwardly evaluated
\[ \langle n_i | [H_{fxy}(T)]^2 | n_i \rangle = k_{fxy}^2 \]
\[ \langle n_i | [H_d - H_{fyy}(T)]^2 | n_i \rangle \]
\[ = | E_d(R_0) - E_f(R_0) - 4 \kappa_{de} (2 \kappa_{de} - \kappa_{fe}) \]
\[ \times (1 - \cos \omega_e T) / \omega_e^2 + (2 \kappa_{de} - \kappa_{fe})^2. \tag{5.18b} \]
Inserting this result into Eq. (5.12b) leads to the following expression for the width determining quantity:
\[ C^2 = \kappa_{fe}^2 + (2 \kappa_{de} - \kappa_{fe})^2 + 2 \left( \frac{2 \kappa_{de} (2 \kappa_{de} - \kappa_{fe})}{\omega_e} \right)^2 \]
\[ \times \left[ 1 + \frac{\Gamma^2}{\Gamma^2 + 4 \omega_e^2} \right] \left( \frac{\Gamma^2}{\Gamma^2 + 4 \omega_e^2} \right)^2. \tag{5.19} \]
Since the component \( Q_e \) does not appear in \( H_d \) [Eq. (5.15)] the dynamical influence of this mode is suppressed. It does not contribute to the first moment and its contribution to the second moment is merely the static term \( k_{fxy}^2 \). Static terms do not originate from the motion of the wave packet, i.e., they do not disappear for vanishing lifetime of the decaying state (\( \Gamma \to \infty \)). We have checked that the results for the spectral moments are invariant to the choice of the core vacancy, i.e., that all equivalent cores have the same moments. These calculations are more lengthy than the one presented here for \( H_d \) in Eq. (5.15).

**d. Double localization—localization of core and final states.** Here we discuss the interesting case where in addition to the core levels, the final states are also localizable, each on an equivalent atom. At first, one might suspect that the final states in order to be localizable must be core levels themselves. However, there are classes of examples where the final states are levels of valence electrons and yet they are localizable to an extremely high degree of accuracy. For instance, the valence levels of the dication of the linear symmetric molecules BF\(_2\) and, in particular, MgF\(_2\) can be divided into two sets. In the first set, the states can be characterized by one valence vacancy on each fluorine atom. In the second set, the states have two vacancies on the same atom which are delocalized because of symmetry. Like the Fls core vacancies, these states come in pairs of practically degenerate states, one of \( g \) and one of \( u \) symmetry, which are vibronically coupled through the antisymmetric mode (see the next section for an explicit numerical study). The same simple linear transformation \( S \) of Eq. (5.16) used to localize the core levels transforms these states \( f_g \) and \( f_u \) to localized states \( f_1 \) and \( f_2 \).

The impact of this double localization on the cross section and hence on the spectral moments is easily seen by inserting the unit matrix \( SS' \) twice into Eq. (5.5b), once in front and once behind exp(\( iHf \)). Since \( S \) diagonalizes \( H_f \), the spectrum is found to be an incoherent sum of spectra, one for each localized final state. Confining ourselves to core vacancies (or more generally to scalar \( H_d \)) immediately leads to
\[ \sigma_{f_i f_m} (E) \sim | V_{d_k} |^2 | W_{d_m} |^2 \int_0^\infty dT \ e^{-\Gamma T/2} \int_T^\infty dt \ e^{iE \Gamma T/2} \exp[-iHd_k (T - t)/2] e^{iHd_k} \]
\[ \times \exp[-iHd_k (T + t)/2] | n_i \rangle, \tag{5.20} \]
where \( W_{d_m} \) is the mth element of \( S' W_d \). The above \( \sigma_{d_k f_m} \) is the partial cross section for the production of the final state \( f_m \) localized on the mth equivalent atom via the decay of the core level localized on the kth equivalent atom.

Expression (5.20) is formally identical to the cross section obtained in the single-state case discussed in Ref. 5. We would like to stress that Eq. (5.20) is a general result for localizable final states and is not restricted to \( g \) and \( u \) states. To be specific, let us evaluate in the following this \( g-u \) situation with two equivalent atoms. We have already seen in Sec. V B 1 that the Hamiltonians of the core localized states read
\[ H_{d_1} = H_f + [E_d(R_0) - E_f(R_0)] + \sqrt{2} \kappa_{de} Q_\delta \pm \sqrt{2} \lambda_{de} Q_u. \tag{5.21} \]
Analogously, we may put in \( H_f \) of Eq. (5.10)
\[ \kappa_{fg} = \kappa_{fg} - \kappa_{fg}, \quad E_f(R_0) - E_i(R_0) = E_{f_g} - E_{f_u} \tag{5.22} \]
and apply the transformation \( S \) to diagonalize \( H_f \). Hence, the Hamiltonians of the localized final states have a similar appearance
\[ H_{f_1} = H_f + [E_f(R_0) - E_i(R_0)] + \sqrt{2} \kappa_{fg} Q_g \pm \sqrt{2} \lambda_{fg} Q_u. \tag{5.23} \]
The general situation addressed here is illustrated in Fig. 2. The initial wave packet \(| n_i \rangle \) is excited to the vibronically coupled decaying states \(| d_g \rangle \) and \(| d_u \rangle \) which decouple by localization to \(| d_1 \rangle \) and \(| d_2 \rangle \). These core levels decay to the vibronically coupled final states \(| f_{g1} \rangle \) and \(| f_{u1} \rangle \), which also decouple upon localization to \(| f_1 \rangle \) and \(| f_2 \rangle \). In principle, there are four partial cross sections \( \sigma_{af_{g1} f_{g2}} \) which are pairwise equal \( \sigma_{f_{g1} f_{g2}} = \sigma_{f_{u1} f_{u2}} \) and \( \sigma_{f_{u1} f_{u2}} \).
VI. ILLUSTRATIVE APPLICATION—DOUBLE LOCALIZATION IN MgF₂

The situation of double localization discussed in Sec. V B 2 d and illustrated in Fig. 2 sounds, at first glance, to be very idealized. One is well acquainted with localized deep core levels, where the split of the energies in the presence of symmetry equivalent atoms, e.g., the two O1s states of CO₂ (\(^{2}Σ_g^+\) and \(^{2}Σ_u^+\)), is substantially smaller at the equilibrium molecular geometry than the vibrational frequencies. For the description of the nuclear dynamics in these states it is, therefore, possible to neglect this split, i.e., to consider the states as degenerate, and the situation simplifies considerably by transforming to localized states (each state is localized on one atom). Then, the vibronic coupling of the delocalized states is easily solved and the dynamics of the non totally symmetric coupling mode can be treated analogously to that of a totally symmetric mode. We shall show below that a similarly simple situation of ideal localization can be found in nature even for valence states involving the outermost orbitals.

The explicit example we discuss here is MgF₂, which is a linear symmetric (\(D_{∞h}\)) molecule. We have computed the dicationic states of this molecule up to an energy of 75 eV above the ground state of the neutral system. The calculation is done using the \(ab\ initio\) Green’s function method discussed in Ref. 18, where all references can be found. The Gaussian basis set used is a double zeta plus polarization (DZP) basis consisting of \([7s, 4p]\) functions for Mg and \([4s, 2p]\) functions for F. Polarization functions (one set of d functions per atom) have been taken from Ref. 21.

The computed vertical double ionization potentials (DIPs) of MgF₂ corresponding to the first 24 dicationic states are collected in Table I. Also shown are the two-hole populations \(^{18}\) which describe the distribution of the two vacancies over the atoms in the system. The table clearly demonstrates that the states can be divided into two distinct classes. The first 12 states are seen to be two-site states where the two vacancies are on the two fluorine atoms (dominating \(F, F, \rho\) populations). These states come in pairs of states with different parity and arise as triplet and singlet combinations of the two vacancies located on the two fluorine atoms. Since these atoms are far apart, the exchange matrix elements for these vacancies are very small and, consequently, the energy split of states of each pair is nearly negligible. It is smaller than \(10^{-3}\) eV for the first pair and is \(3 \times 10^{-3}\) eV for the sixth pair. The following 12 states belong to the second class and are clearly one-site states where both vacancies are on the fluorine atom (see Table I). Again, these states come in pairs of states with different parity, but now of the same spin multiplicity. The energy splits between the states of a pair are surprisingly small, indicating the presence of ideal localization. The energy splits are even smaller than for deep core levels of many molecules. The vertical energy split in the first pair is \(10^{-4}\) eV and the split in the energy of, for instance, the O1s orbitals in CO₂ is \(1.5 \times 10^{-3}\) eV. We mention that the above classification of pairs of nearly degen-
TABLE I. Computed vertical DIPS corresponding to the lowest 24 dicationic states of MgF₂. Also shown are the two-hole populations in these states. In the first 12 states, each vacancy is dominantly localized on a different F atom (two-site states—dominating F⁻¹F⁻¹ population). In the last 12 states, both vacancies are localized on a single F atom (one-site states—dominating F⁻¹ population).

<table>
<thead>
<tr>
<th>State</th>
<th>DIP (eV)</th>
<th>Mg⁻¹</th>
<th>F⁻²</th>
<th>Mg⁻¹F⁻¹</th>
<th>F⁻¹F⁻¹</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Σ⁺</td>
<td>29.6046</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0573</td>
<td>0.8151</td>
<td>0.8734</td>
</tr>
<tr>
<td>3Σ⁺</td>
<td>29.6052</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0573</td>
<td>0.8152</td>
<td>0.8735</td>
</tr>
<tr>
<td>3Δ⁺</td>
<td>29.6064</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0573</td>
<td>0.8151</td>
<td>0.8734</td>
</tr>
<tr>
<td>1Δ⁺</td>
<td>29.6070</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0573</td>
<td>0.8152</td>
<td>0.8735</td>
</tr>
<tr>
<td>3Σ⁻</td>
<td>29.6080</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0573</td>
<td>0.8151</td>
<td>0.8734</td>
</tr>
<tr>
<td>2Σ⁺</td>
<td>29.6088</td>
<td>0.0010</td>
<td>0.0000</td>
<td>0.0573</td>
<td>0.8152</td>
<td>0.8735</td>
</tr>
<tr>
<td>1Π⁺</td>
<td>30.4004</td>
<td>0.0021</td>
<td>0.0003</td>
<td>0.0785</td>
<td>0.7839</td>
<td>0.8739</td>
</tr>
<tr>
<td>1Π⁻</td>
<td>30.4019</td>
<td>0.0021</td>
<td>0.0000</td>
<td>0.0789</td>
<td>0.7839</td>
<td>0.8739</td>
</tr>
<tr>
<td>3Π⁺</td>
<td>30.4053</td>
<td>0.0021</td>
<td>0.0002</td>
<td>0.0786</td>
<td>0.7838</td>
<td>0.8736</td>
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<tr>
<td>1Π⁺</td>
<td>30.4076</td>
<td>0.0022</td>
<td>0.0000</td>
<td>0.0787</td>
<td>0.7840</td>
<td>0.8738</td>
</tr>
<tr>
<td>2Σ⁺</td>
<td>31.2100</td>
<td>0.0048</td>
<td>0.0006</td>
<td>0.1143</td>
<td>0.7546</td>
<td>0.8742</td>
</tr>
<tr>
<td>2Σ⁻</td>
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<td>0.0049</td>
<td>0.0000</td>
<td>0.1172</td>
<td>0.7535</td>
<td>0.8742</td>
</tr>
</tbody>
</table>

Using the constants of Tables II and III, we have calculated the dynamically induced shifts and widths of the bands in the Auger spectrum of MgF₂ for both Mg₁s and F₁s spectra (the equations are discussed Sec. V B 2 d). The vibrational frequencies entering the equations are taken from experiment

The computed shifts and widths are listed in Table II. Only the Q₂ mode contributes to the Mg₁s Auger spectrum. Because of the short lifetime of the decaying Mg₁s state compared to a vibrational period, the wave packet decays fast to the final states and does not have sufficient time to substantially move along the potential energy curve. Consequently, the induced shifts are relatively small (they are of the order of 0.2 eV). The vibrational widths of the bands are ~1.5 eV. Since MgF₂ is essentially an ionic molecule, one a priori expects the shifts and widths to be similar for all states of the Mg₁s transition. The resulting total widths of the two-site levels in the fluorine spectrum are seen to be substantially smaller than in the magnesium spectrum, where only one mode is active.

Both Q₂ and Q₄ modes contribute to the dynamically induced shifts and widths in the spectrum following the decay of the F₁s levels. As can be seen from Table II, the contributions of both modes to the shifts are small for the two-site states. The total shift is just the sum of the individual contributions of the two modes which tend to slightly compensate each other. In contrast, the width of a band arises from the individual contributions of the modes as well as from a term mixing the modes. In MgF₂, this mixing term reduces the width obtained by incoherently adding the widths induced by the individual modes. The resulting total widths of the two-site levels in the fluorine spectrum are seen to be substantially smaller than in the magnesium spectrum, where only one mode is active.

The dynamics in the one-site states is more interesting because of the double localization present. Here we encounter the situation illustrated in Fig. 2. In the localized picture, which is a suitable tool here, the primary core hole can be in the left or in the right fluorine atom. Each of these holes can, in principle, decay into both final valence states localized on the left and on the right fluorines. This leads to a substantially different dynamical behavior of the nuclei. As can be seen in Fig. 3, the one-site states which are degenerate at the equilibrium geometry split and the corresponding bands shift and broaden differently according to whether or not the intermediate and final states are localized on the same atom. The shifts of one group are about ~0.2 eV, and of the other ~0.4 eV, and the widths are about 1 and 2 eV, respectively. Although the latter group is difficult to detect experimentally with current Auger spectroscopy techniques, because of low intensity (see
TABLE II. Computed coupling constants and dynamically induced energy shifts and widths corresponding to the states in Table I. Shown are the slopes of the potential energy surfaces at the molecular equilibrium geometry along the totally symmetric and antisymmetric Mg–F stretching (dimensionless [Ref. 25]) normal coordinates $Q_s$ and $Q_a$. These slopes correspond to $\sqrt{2\alpha_s}$ and $\sqrt{2\alpha_a}$, respectively. In the cases of near degeneracy, the slopes of the crossing curves (see Fig. 2) along $Q_s$ are taken. The individual contributions of the modes to the shift and width are given. All the values are in electron volts.

<table>
<thead>
<tr>
<th>State</th>
<th>DIP</th>
<th>$Q_s$</th>
<th>$Q_a$</th>
<th>$\alpha_s$</th>
<th>$\alpha_a$</th>
<th>$\Gamma$</th>
<th>$\Delta E_{\text{shift}}$</th>
<th>FWHM</th>
<th>$\Delta E_{\text{width}}$</th>
<th>FWHM</th>
</tr>
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<tr>
<td>$^1\Sigma_g^+$</td>
<td>29.6064</td>
<td>-0.3833</td>
<td>0.1724</td>
<td>1.5201</td>
<td>-0.0238</td>
<td>0.1101</td>
<td>0.5707</td>
<td>0.5763</td>
<td>0.7548</td>
<td></td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>29.6052</td>
<td>-0.3874</td>
<td>0.1733</td>
<td>1.5281</td>
<td>-0.0241</td>
<td>0.1101</td>
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<td>0.7593</td>
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<tr>
<td>$^1\Delta_g$</td>
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<td>-0.3833</td>
<td>0.1724</td>
<td>1.5201</td>
<td>-0.0238</td>
<td>0.1101</td>
<td>0.5707</td>
<td>0.5763</td>
<td>0.7548</td>
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<tr>
<td>$^3\Sigma_u^+$</td>
<td>29.6080</td>
<td>-0.3833</td>
<td>0.1724</td>
<td>1.5201</td>
<td>-0.0238</td>
<td>0.1101</td>
<td>0.5707</td>
<td>0.5763</td>
<td>0.7548</td>
<td></td>
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<tr>
<td>$^1\Pi_u$</td>
<td>30.4004</td>
<td>-0.3389</td>
<td>0.1623</td>
<td>1.4311</td>
<td>-0.0206</td>
<td>0.1101</td>
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<td>0.5763</td>
<td>0.7548</td>
<td></td>
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<tr>
<td>$^3\Pi_u$</td>
<td>30.4019</td>
<td>-0.3430</td>
<td>0.1632</td>
<td>1.4392</td>
<td>-0.0209</td>
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<td>0.5707</td>
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<tr>
<td>$^1\Pi_g$</td>
<td>30.4076</td>
<td>-0.3389</td>
<td>0.1623</td>
<td>1.4311</td>
<td>-0.0206</td>
<td>0.1101</td>
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<td>0.7548</td>
<td></td>
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<td>30.4088</td>
<td>-0.3430</td>
<td>0.1632</td>
<td>1.4392</td>
<td>-0.0209</td>
<td>0.1101</td>
<td>0.5707</td>
<td>0.5763</td>
<td>0.7548</td>
<td></td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
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<td>-0.0175</td>
<td>0.1101</td>
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<td>0.7079</td>
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<tr>
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<td>0.4955</td>
<td>0.5763</td>
<td>0.7079</td>
<td></td>
</tr>
</tbody>
</table>

the preceding subsection), the prevailing dynamics is interesting and might be detectable using other experiments involving the same final states.

VII. SUMMARY

A target system is excited to a manifold of decaying electronic states which decay into a manifold of final states by emitting a particle (electron or photon). If the decaying states overlap, they contribute coherently to the cross section for the final states and must be considered simultaneously. A further substantial complication of the nuclear dynamics accompanying the decay comes from the fact that, in polyatomic systems, overlapping electronic states are likely to interact vibronically via the nuclear motion. Since the density of final electronic states in polyatomics cannot be considered low, nonadiabatic interactions among these states must also be considered in many cases. If the molecule is highly symmetric, decaying as well as final states can be degenerate and the presence of vibronic coupling is evident (various Jahn–Teller effects). In less sym-

![FIG. 3. Energy positions of the first electronic bands in the Auger spectra of MgF2. Depicted are the vertical transition energies and the band positions in the MgIs and FIs spectra corrected for dynamical effects. (A) shows the single-site states well separated energetically (notice the energy scale) from the two-site states shown in (B).](image)
metric systems, vibronic coupling may also prevail, but the situation is less transparent and the theoretical treatment is more involved.

The investigation of the nuclear dynamics accompanying the excitation and the subsequent decay is the central issue of the present work. The cross sections for the excitation and for the production of the final states are derived. Vibronic coupling is taken into account in the decaying and in the final state manifolds. Moreover, to allow for an excited target, vibronic couplings among the initial electronic states of the target are also considered.

The motions of the wave packets propagating on the coupled potential surfaces of the decaying and of the final state manifolds are discussed. These wave packets are related to the abovementioned cross sections and explicit expressions for these cross sections in a time-dependent framework are given. There are several advantages of a wave packet dynamical study, one being a simplified and informative interpretation of the decay process. Another advantage is the possibility to use a microscopic description of the system, allowing for a more detailed understanding of the decay process. Explicit wave packet propagations are desirable and will be done in the future. A further merit of the time-dependent picture is its suitability for deriving the spectral moments of the cross sections. Spectral moments are commonly used to approximate a distribution and are used here to describe the gross features of the cross sections.

Particular attention is paid to energetically deep lying decaying states. For several situations of interest, approximate explicit expressions for the position and width of bands observed in the spectrum are given in terms of the potential surfaces and their couplings. Vibronic coupling in the decaying and final states is considered for polyatomics possessing equivalent atoms. The cases studied include the Jahn–Teller effect in the final states and the distorted Jahn–Teller effect in the decaying manifold. An ab initio numerical application to the Auger decay in MgF₂ is presented. For this molecule, the decaying core levels as well as final dicatonic electronic states are strongly localized in space and exhibit vibronic coupling. Because of this double localization, approximate expressions for the spectral moments can be derived explicitly.

Interference effects arising from the presence of several overlapping core states are discussed in some detail. They are best detectable in the partial cross section as a function of the angular distribution of the emitted particle. Averaging over the distribution suppresses the interferences. Of particular interest are systems possessing atoms equivalent by symmetry.

ACKNOWLEDGMENTS

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