PHYSICAL REVIEW A VOLUME 45, NUMBER 5 1 MARCH 1992

State interference in resonance Auger and x-ray emission

Amary Cesar and Hans Ågren
Institute of Quantum Chemistry, University of Uppsala, Box 518, S-75120, Uppsala, Sweden

(Received 6 February 1991; revised manuscript received 21 August 1991)

Starting from a scattering-theory formulation, cross sections for Auger and x-ray decay from energetically shifted inner-shell states are derived. Two situations are studied: (i) when there are several close-lying intermediate core-hole states with no vibrational excitations, in which case a *state interference* effect is identified; and (ii) when there are several close-lying intermediate states with vibrational excitations, in which case a *vibronic interference* effect is identified. In the latter case, the present formalism is a many-state generalization of the *vibrational interference effects* derived from the same type of scattering formalism in our previous paper [A. Cesar, H. Ågren, and V. Carravetta, Phys. Rev. A **40**, 187 (1989)]. Applications are carried out for spectra of some few-state model systems. It is found that a conventional analysis in terms of discrete noninteracting (noninterfering) states, such as the one-center decomposition model, is only valid when the ratio (R) between energy shift and lifetime is sufficiently large. For states with small R, a more complete theoretical account must be undertaken, including, e.g., the calculation of phases of the respective transition moments. The presented formalism applies to resonance Auger or x-ray emission spectra, to Auger and x-ray emission from core-electron shake-up states, and also, under certain circumstances, to emission from chemically shifted core-hole states.

PACS number(s): 32.80.Hd, 31.10.+z, 33.10.Cs, 32.70.Jz

I. INTRODUCTION

Intensities in radiative and nonradiative decay spectra of inner-shell hole states have traditionally been analyzed in terms of local selection models. These models provide the interpretability of the spectra in terms of electronic-structure theory of the ground-state molecule, and underlie much of the chemical utility of these spectroscopies. The use and limitations of these rules are by now rather well settled.

Along with spectroscopic innovations in terms of discrete excitation sources, attention has turned to resonance spectra of small and extended systems. In the present study we address such decay spectra (Auger and x-ray spectra), i.e., those emanating from energetically shifted core-hole states. We attempt to explore on a fundamental level the applicability of the type of intensity analysis usually applied to emission from isolated core-hole states. We start out from a scattering-theory formulation that has previously been used for deriving vibrational-lifetime interference in such spectra [1]. In the present case, we generalize this derivation to include many intermediate short-lived states. From the results of this derivation we identify the effect of *state interference* in decay spectra of inner-shell states. The expressions are evaluated for some few-state model systems with or without vibrational excitations, with the transition moments used as parameters. The intensities are then calculated for different ratios (R) between the energy shift and lifetime broadening. The consequences of the results for different values of R for the interpretation of decay spectra of close-lying states are discussed.

The effect of lifetime-vibrational interference in vibronic decay of molecular core-hole states has now been firmly established [2–7]. Several theoretical studies have been devoted to this effect. The first theoretical studies were given by Gel'mukhanov *et al.* [2,3], who started out from the Kramer-Heisenberg dispersion formula and derived an effective one-particle Green's function for the x-ray cross sections; Kaspar *et al.* [4], carried out a derivation that utilizes a scattering S matrix and vibronic coupling constants; while Correia *et al.* [5] derived the vibronic cross sections for x-ray and Auger emission by means of a time-dependent Franck-Condon formulation. Gunnarsson and Schönhammer [8] had earlier applied a quadratic response function formalism for Auger decay and shown that lifetime interference effects can be substantial for solid-state species. Common to these theoretical investigations is the assumption of non-post-collisional interaction (PCI), the Born-Oppenheimer (BO) approximation, and the local approximations for the nuclear Hamiltonian. The use of the general scattering formalism [9], rather than, e.g., the Feshbach projection operator approach, has the main advantage that interchannel and intrachannel interactions, nonadiabatic corrections, and many-body interactions may be introduced at progressively more sophisticated levels of approximations. This is an important motivation for the present work.

The present theory applies to resonant Auger and x-ray processes (fluorescence x-ray emission) as these generally occur from (Rydberg) series of close-lying core excited states embedded in a continuum. The spectra of such resonance processes are thus considerably more complex than the corresponding normal Auger or x-ray spectra from the main, well-isolated core-hole states. The theory applies equally well to decay from close-lying satellite, shake-up states, or to any situation with close-lying core-hole states, such as spin-orbit splitted states. Interesting systems for these studies are given by surface adsorbates where particularly intensive shake-up states lie close to the main lines. Under certain circumstances the theory also has a bearing on spectra from chemical shifted states of extended systems. The results indicate that, even for high-energy primary excitation, there may be shifts in energy levels derived from x-ray-emission-spectroscopy (XES) and Auger-electron-spectroscopy (AES) spectra in comparison with those derived from absorption-type spectroscopies.

II. THEORETICAL MODEL

Many phenomena associated with the atomic and molecular x-ray and Auger processes are successfully understood within the frame of the multichannel resonant scattering theory [9]. The presence of a set of N electronic discrete states embedded in the continuum of K degenerate electronic states causes the (angle-averaged) cross section for emission of (x-ray) photons or (Auger) electrons to show rapid variations within a certain range of the spectral energy centered about some values characteristic for the particular atomic or molecular system under consideration. Spectral parameters like the resonance width and level shift emerge from such theory as a measure of the strength of the configuration mixing between discrete and continuum states. Nonvanishing incoherent amplitudes of probability for the alternative direct and the diverse resonant events distort the line profile corresponding to a particular electronic transition from a usual Lorentzian-like shape to the so-called Fano profile.

The multichannel resonant scattering theory as applied for the atomic [9] and molecular [1] x-ray and Auger transitions has been formulated under the simplifying approximation of only one discrete electronic (vibronic) state embedded in many electronic (vibronic) continuum states. This refers to the normal situation when the decay takes place from one main core-hole state only. Within a broader context, solutions to the problem of configuration interaction between electronic states belonging to the discrete and continuum part of the spectrum of a Hamiltonian operator have been offered by Fano [10]. He considered the particular cases of (i) one discrete state in one continuum state, (ii) one discrete state in many continua, and (iii) many discrete states and one continuum. Solutions for the general case (iv) where many discrete states are embedded in many continua were first given by Mies [11]. The latter author emphasized the role of the overlap of neighboring resonances and the effects on a spectral line profile for a photoabsorption or a scattering process of the ratio between the relative (energy) position of the resonances and their widths. Later, Davis and Feldkamp [12] reconsidered the general case (iv) above and applied the theory to photoabsorption and photoemission of Cu in the region of the $3p$ threshold. The general problem of discrete states embedded in continuum states has also been treated in terms of projection operators by Feshbach [13], who presented an equivalent solution for the general case (iv) in his third paper of the series on the subject [14]. In the present work we consider x-ray and Auger emission as multichannel resonant scattering processes for the more general case (iv) formulated for the molecular case with a number of electronic states and with vibrational degrees of freedom included.

When speaking about the x-ray and Auger processes as scattering events, we will be referring to the solution of the Schrödinger equation

$$\hat{H}\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R})=E\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R}) \tag{1}$$

at a continuum interval of energy E lying well above the threshold for core ionization for the (atomic or molecular) system under consideration. The wave function $\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R})$ satisfies the usual outgoing boundary condition for scattering states,

$$\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R}) \underset{r\to\infty}{\sim} \sum_{\beta} \frac{\Omega_{\beta}(\mathbf{r}';\mathbf{R})\chi^{(\beta)}(\mathbf{R})}{2ir\sqrt{k_{\beta}}} \times[\bar{S}_{\beta\alpha}(E)e^{[k_{\beta}r+\theta_{\beta}(\epsilon)]}-\delta_{\beta\alpha}e^{-[k_{\beta}r+\theta_{\beta}(\epsilon)]}] , \tag{2}$$

where $\bar{S}_{\beta\alpha}(E)$ is the scattering matrix "on the energy shell" and $\theta_{\beta}(\epsilon)$ represents a phase shift related to the resonant scattering process.

The total Hamiltonian operator $\hat{H}$ in Eq. [1] is a sum of the Hamiltonian operators for the molecular system $\hat{H}_M$, the radiation field $\hat{H}_R$, and the radiation-molecule interaction term $\hat{H}_{MR}$, i.e.,

$$\hat{H}=\hat{H}_{\mathrm{M}}+\hat{H}_{\mathrm{R}}+\hat{H}_{\mathrm{MR}} . \tag{3}$$

It is convenient that we further divide the molecular Hamiltonian into

$$\hat{H}_{\mathrm{M}}=\hat{T}+\hat{H}_{\mathrm{el}} , \tag{4}$$

where $\hat{H}_{\mathrm{el}}$ is the electronic Hamiltonian and $\hat{T}$ is the kinetic-energy operator for the nuclei. In Eqs. [1] and [2], $\mathbf{r}$ and $\mathbf{R}$ stand collectively for the coordinates of, respectively, all electrons and nuclei present in the molecular system; r for the coordinate of the escaping particle; and $\mathbf{r}'$ (collectively) for the coordinates of the electrons remaining on the residual ion. We shall assume that the primary photoelectron is emitted with a high kinetic energy so that, according to the sudden approximation, final-state interaction between the escaping (photo)electron and the residual ions can be neglected. Also, we consider only angularly averaged cross sections, i.e., we do not consider any rotational degree of motion or rotational interaction for the whole scattering process. One energy label,

$$\epsilon_{\beta}=\tfrac{1}{2}k_{\beta}=E-I_{\beta} , \tag{5}$$

suffices therefore to identify the secondarily emitted x-ray photon or Auger electron. This energy refers to the βth singly (x-ray) or doubly (Auger) molecular ionization threshold $I_{\beta}=E^{\mathrm{ion}}_{\beta}-E^{\mathrm{neutral}}$. The core-hole ionization process proceeds by the intervening of one photon with energy $\hbar\omega$ impinging on the molecular system. Since in what follows we shall take the electronic energy of the neutral initial state E^{neutral} as the reference energy level, the total energy for the whole system will be $E=\hbar\omega$.

Throughout we assume the validity of the adiabatic Born-Oppenheimer factorized form for the asymptotic molecular wave functions for all relevant residual electronic states defining the possible continuum open channels. This means that

$$\underline{\psi}_\alpha(\mathbf{r},\mathbf{R})=\Omega_\alpha(\mathbf{r};\mathbf{R})\chi^{(\alpha)}(\mathbf{R}),\quad \alpha=1,2,\ldots,K \tag{6}$$

will be the approximated form for the (ground-state) electronic-vibrational wave function of the neutral molecule, the initial vibronic state in the scattering process, as well the electronic-vibrational wave function corresponding to the several final singly (x-ray) or doubly (Auger) charged ions. Analogously, the electronic-vibrational wave function of the discrete (core-hole) ionic states lying in the continuum is approximated as

$$\underline{\phi}_n(\mathbf{r},\mathbf{R}{:}\alpha E)=\varphi_n(\mathbf{r};\mathbf{R})\Upsilon_{\alpha nE}(\mathbf{R}) \tag{7}$$

(the reason for the α and E indices in the above equation will be made clear later).

The scattering functions on the subspace of the continuum background will be denoted by $\Psi^{\pm}_{\alpha\epsilon}(\mathbf{r},\mathbf{R})$ and they are chosen to satisfy the scattering outgoing or incoming wave boundary conditions, respectively,

$$\Psi^{\pm}_{\alpha\epsilon}(\mathbf{r},\mathbf{R})\underset{r\to\infty}{\sim}\sum_{\beta}\frac{\Omega_\beta(\mathbf{r}';\mathbf{R})\chi^{(\beta)}(\mathbf{R})}{2ir\sqrt{k_\beta}}\begin{cases}[\delta_{\beta\alpha}e^{k_\beta r+\theta_\beta(\epsilon)}-S_{\beta\alpha}(E)e^{-[k_\beta r+\theta_\beta(\epsilon)]}]\\ \{[S^{\dagger}(E)]_{\beta\alpha}e^{k_\beta r+\theta_\beta(\epsilon)}-\delta_{\beta\alpha}e^{-[k_\beta r+\theta_\beta(\epsilon)]}\}\end{cases} \tag{8}$$

($\alpha,\beta=1,2,\ldots,K$), where $S_{\beta\alpha}(E)$ is the scattering matrix on the shell related to the direct single- or double-ionization scattering process [1,2]. These functions form an orthogonal and noninteracting subset of continuum functions, orthogonal but not noninteracting to the subset of the discrete functions $\{\underline{\phi}_n(\mathbf{r},\mathbf{R})\}$:

$$\begin{aligned}&\langle(\Psi^{\pm}_{\beta\epsilon'}(\mathbf{r},\mathbf{R})|\Psi^{\pm}_{\alpha\epsilon}(\mathbf{r},\mathbf{R}))\rangle=\delta_{\alpha\beta}\delta(\mathcal{E}_\alpha+\epsilon-\mathcal{E}_\beta-\epsilon')\ ,\\ &\langle(\underline{\phi}_n(\mathbf{r},\mathbf{R})|\Psi^{\pm}_{\alpha\epsilon}(\mathbf{r},\mathbf{R}))\rangle=0\ ,\\ &\langle(\underline{\phi}_n(\mathbf{r},\mathbf{R})|\hat{H}|\Psi^{\pm}_{\alpha\epsilon}(\mathbf{r},\mathbf{R}))\rangle\neq 0\ .\end{aligned} \tag{9}$$

We shall not require more of the set of N discrete wave functions $\{\underline{\phi}_n(\mathbf{r},\mathbf{R}{:}\alpha E)\}$ than that they are linearly independent and that they fulfill the basic boundary conditions for discrete states,

$$\underline{\phi}_n(\mathbf{r},\mathbf{R})\to 0\quad\text{as } r\to\infty\ . \tag{10}$$

By virtue of the factorizations of Eqs. (6), we construct the usual nuclear Born-Oppenheimer potential energy for the several possible electronic states defining the K open continuum and N discrete resonant channels as

$$\begin{aligned}&E_\alpha(\mathbf{R})=(\Omega_\alpha(\mathbf{r};\mathbf{R})|\hat{H}_{\mathrm{el}}|\Omega_\alpha(\mathbf{r};\mathbf{R}))\ ,\\ &E_n(\mathbf{R})=(\varphi_n(\mathbf{r};\mathbf{R})|\hat{H}_{\mathrm{el}}|\varphi_n(\mathbf{r};\mathbf{R}))\ ,\end{aligned} \tag{11}$$

and the corresponding nuclear born-Oppenheimer Hamiltonian operators

$$\begin{aligned}&\tilde{H}_\alpha=\hat{T}_N+E_\alpha(\mathbf{R})\ ,\\ &\tilde{H}_n=\hat{T}_N+E_n(\mathbf{R})\ .\end{aligned} \tag{12}$$

Throughout we shall reserve the use of parenthesis (|) and angular brackets ⟨ | ⟩ for integrations over the electronic and nuclear coordinates, respectively. We write the vibrational eigenfunctions of the nuclear Hamiltonian of Eq. (12) as $\chi^{(\alpha)}(\mathbf{R})$,

$$\tilde{H}_\alpha\chi^{(\alpha)}_i(\mathbf{R})=\mathcal{E}_{\alpha i}\chi^{(\alpha)}_i(\mathbf{R}),\quad \alpha=1,2,\ldots,K \tag{13}$$

where $\mathcal{E}_{\alpha i}$ corresponds to the electronic-vibrational energy of the several states α which include the initial neutral and the final single or doubly ionized molecular species. The yet unspecified functions $\Upsilon_{\alpha nE}(\mathbf{R})$ describe the nuclear motion of the molecular system in the nth core ionized intermediate states. One important aspect of the theory at this point is that these functions, unlike the vibrational wave functions $\chi^{(\alpha)}(\mathbf{R})$, are not required to be eigenfunctions of the nuclear Born-Openheimer operators $\tilde{H}_n$. Another important aspect of the theory is that it is developed in such a way that nonadiabatic corrections to the Born-Oppenheimer approximation can progressively be included in the scattering functions $\Psi^{\pm}_{\alpha\epsilon}(\mathbf{r},\mathbf{R})$ of the subspace of the continuum background functions. The inclusion of nonadiabatic effects is certainly relevant considering the density of the single or, more crucially, the doubly ionized final states.

We seek a solution for the Schrödinger equation (1) with the eigenfunctions satisfying the boundary condition of Eq. (2) in the space of functions spanned by the K continuum $\{\Psi^{+}_{\alpha E}(\mathbf{r},\mathbf{R})\}$ and N discrete $\{\underline{\phi}_n(\mathbf{r},\mathbf{R}{:}\alpha E)\}$ linearly independent functions. This solution is written as

$$\begin{aligned}\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R})=&\sum_n\varphi_n(\mathbf{r};\mathbf{R})\Upsilon^{+}_{\alpha nE}(\mathbf{R})\\ &+\sum_\beta\int d\epsilon'\Psi^{+}_{\beta\epsilon'}(\mathbf{r},\mathbf{R})B^{+}_{\beta\alpha}(\epsilon',E)\ .\end{aligned} \tag{14}$$

The coefficients $B^{+}_{\beta\alpha}(\epsilon',E)$ are determined by requiring that

$$\langle(\Psi^{+}_{\beta\epsilon'}(\mathbf{r},\mathbf{R})|\hat{H}-E|\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R}))\rangle=0 \tag{15}$$

and that $\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R})$ and $\Psi^{+}_{\alpha\epsilon}(\mathbf{r},\mathbf{R})$ satisfy the boundary conditions of Eqs. (2) and (8), respectively. We obtain

$$\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R})=\Psi^{+}_{\alpha\epsilon}(\mathbf{r},\mathbf{R})+\sum_{m}\left[\varphi_m(\mathbf{r};\mathbf{R})\Upsilon^{+}_{\alpha mE}(\mathbf{R})+\sum_{\beta}\lim_{\nu\to 0}\int\frac{d\epsilon'\Psi^{+}_{\beta\epsilon'}(\mathbf{r},\mathbf{R})\langle[\tilde{M}^{+}_{m\beta}(\epsilon',E)]^{\dagger}|\Upsilon^{+}_{\alpha mE}(\mathbf{R})\rangle}{(E-\mathcal{E}_{\beta}-\epsilon'-i\nu)}\right], \tag{16}$$

where we have made use of the equality

$$\lim_{\nu\to 0}\frac{f(x)}{(x+x_0\pm i\nu)}=\mathcal{P}\frac{f(x)}{(x-x_0)}\mp i\pi f(x_0)$$

($\mathcal{P}$ denotes the Cauchy principal value of the integral). The new introduced quantity $\tilde{M}^{+}_{m\beta}(\epsilon',E)$ is an element of the interaction matrix between the functions belonging to the discrete and the continuum subspace,

$$\tilde{M}^{+}_{m\beta}(\epsilon',E)=(\varphi_m(\mathbf{r};\mathbf{R})|(\hat{H}-E)|\Psi^{+}_{\beta\epsilon'}(\mathbf{r},\mathbf{R})) . \tag{17}$$

Notice that $\tilde{M}^{+}_{m\beta}(\epsilon',E)$ acts as a differential operator on the space of the nuclear wave functions. In addition to the wave function of Eq. (16), the above procedure also provides us with the elements of the resonant transition matrix:

$$\begin{aligned}\overline{T}_{\beta\alpha}(E,\epsilon',\epsilon)&=T_{\beta\alpha}(E,\epsilon',\epsilon)\\&\quad+\sum_{n}\langle[\tilde{M}^{-}_{n\beta}(\epsilon',E)]^{\dagger}|\Upsilon^{+}_{\alpha nE}(\mathbf{R})\rangle .\end{aligned} \tag{18}$$

$T_{\beta\alpha}(E,\epsilon',\epsilon)$ in the above equation is an element of the transition matrix for the direct single- or double ionization scattering process. The continuum indices $\epsilon\equiv\epsilon_\alpha$ and $\epsilon'\equiv\epsilon_\beta$ correspond, respectively, to the energy of the incoming photon ($\epsilon=\hbar\omega$) and the energy of the scattered x-ray photon ($\epsilon'=\hbar\omega^{\text{x-ray}}$) or Auger electron ($\epsilon'=\epsilon^{\text{Auger}}$). The solution for the proposed problem will be completed as soon as we find the wave equation to be satisfied by the nuclear wave functions $\Upsilon^{+}_{\alpha nE}(\mathbf{R})$. To this end, if we require that

$$\sum_{m}(\varphi_m(\mathbf{r};\mathbf{R})|(\hat{H}-E)|\Phi^{+}_{\alpha E}(\mathbf{r},\mathbf{R}))\rangle=0 \tag{19}$$

is satisfied for $n=1,2,\ldots,N$. Then with help of Eqs. (16) and (17) we get

$$\sum_{n}[E\mathcal{S}_{mn}(\mathbf{R})-\tilde{H}_{mn}-\tilde{F}_{mn}(E)]|\Upsilon^{+}_{\alpha nE}(\mathbf{R})\rangle=|\tilde{M}^{+}_{m\alpha}(\epsilon,E)\rangle , \tag{20}$$

where

$$\mathcal{S}_{mn}=(\varphi_m(\mathbf{r};\mathbf{R})|\varphi_n(\mathbf{r};\mathbf{R}))$$

and

$$\tilde{H}_{mn}=(\varphi_m(\mathbf{r};\mathbf{R})|\hat{H}|\varphi_n(\mathbf{r};\mathbf{R}))$$

are, respectively, the overlap and the electronic Hamiltonian (energy) matrix elements within the subspace of the discrete functions $\{\varphi_n(\mathbf{r};\mathbf{R})\}$. The set of complex, nonlocal, and energy-dependent quantities $\tilde{F}_{mn}(E)$ are operators on the space of nuclear wave functions and are defined by

$$\begin{aligned}\tilde{F}_{mn}(E)&=\sum_{\beta}\lim_{\nu\to 0}\int\frac{d\epsilon'|M^{-}_{m\beta}(\epsilon',E)\rangle\langle[\tilde{M}^{-}_{n\beta}(\epsilon',E)]^{\dagger}|}{E-\mathcal{E}_{\beta}-\epsilon'-i\nu}\\&=\sum_{\beta}\lim_{\nu\to 0}\int\frac{d\epsilon'|M^{+}_{m\beta}(\epsilon',E)\rangle\langle[\tilde{M}^{+}_{n\beta}(\epsilon',E)]^{\dagger}|}{E-\mathcal{E}_{\beta}-\epsilon'-i\nu} ,\end{aligned} \tag{21}$$

which can be interpreted as a measure of the strength of configuration interaction between the discrete and continuum electronic states. More precisely, this discrete-continuum coupling enters in the effective nuclear optical Hamiltonian $\tilde{H}_{mn}-\tilde{F}_{mn}(E)$ through the diagonal part of $\tilde{F}_{mn}(E)$ while the nondiagonal terms give rise to a second-order contribution to the configuration mixing within the subspace of the discrete electronic functions $\varphi_n(\mathbf{r};\mathbf{R})$ due to the presence of the underlying continuum wherein the discrete electronic states are embedded.

Here one should note the relationship to the theoretical descriptions of resonant electron-molecule scattering experiments [15]. In the more elaborated formulations, such as the Feshbach projection operator method [13,14], or configuration interaction in the continuum states [16,11], the electron-molecule scattering cross sections for vibrational excitation and dissociative attachment are given by complex, energy-dependent, and nonlocal operators analogous to the $\tilde{F}_{mn}(E)$ operator appearing in Eq. (21). The use of a nonlocal versus a local operator has been rather extensively discussed in connection with resonant electron scattering, where the 2.3-eV resonance in N_2 is the prime example [17].

Without loss of generality, Eq. (20) can be simplified if we construct the electronic functions of the discrete set $\{\varphi_m(\mathbf{r};\mathbf{R})\}$ in such a way that they form a set of orthonormalized and noninteracting functions with respect to the *electronic* Hamiltonian matrix $(\hat{H}_{\text{el}})_{mn}$. Furthermore, if we neglect nonadiabatic couplings within this subspace of electronic functions, Eq. (20) reduces to

$$\sum_{n}[E-\tilde{H}_{n}-\tilde{F}_{mn}(E)]|\Upsilon^{+}_{\alpha nE}(\mathbf{R})\rangle=|\tilde{M}^{+}_{m\alpha}(\epsilon,E)\rangle , \tag{22}$$

where the objects $\tilde{F}_{mn}(E)$ and $\tilde{M}^{+}_{m\alpha}(\epsilon,E)$ have been redefined accordingly. The physical content of Eq. (22) is quite clear: $\Upsilon^{+}_{n\alpha E}(\mathbf{R})$ is a wave function that governs the nuclear motion of the molecular system in the metastable or quasidiscrete states n defined by the (diagonal) *shifted* nuclear Hamiltonian $H_n+\tilde{\Delta}_{nn}(E)$. It has a positive gain of probability amplitude from the right-hand-side source term $\tilde{M}^{+}_{n\alpha}(\epsilon,E)$ while it decays with a total rate of $\sim\hbar/\tilde{\Gamma}_{nn}(E)$ to all alternative x-ray or Auger final states $\beta=1,2,\ldots,K$. Since no effort has been made to diagonalize fully the optical Hamiltonian $\tilde{H}_n+\tilde{F}_{nm}(E)$, the N nuclear wave functions $\Upsilon^{+}_{n\alpha E}(\mathbf{R})$ will be coupled to each other by the residual interaction potential given by the nondiagonal elements of the level shift and width operators $\tilde{\Delta}_{mn}(E)$ and $\tilde{\Gamma}_{mn}(E)$, respectively. As a result of these couplings the position and width of the nth resonance will differ slightly from those obtained by an approximated treatment of only the diagonal part of the optical Hamiltonian $\tilde{H}_n+\tilde{F}_{mn}(E)$. As could be noticed, the imaginary and real parts of the $\tilde{F}_{nn}(E)$ operators have, above, received the proper symbols

$$\begin{aligned}\tilde{\Gamma}_{mn}(E)&=\sum_{\alpha}\tilde{\Gamma}_{mn;\alpha}(E)\\&=\operatorname{Im}\tilde{F}_{mn}(E)\\&=2\pi\sum_{\alpha}|\tilde{M}^{\pm}_{m\alpha}(\epsilon,\mathcal{E}_\alpha)\rangle\langle[\tilde{M}^{\pm}_{n\alpha}(\epsilon,\mathcal{E}_\alpha)]^{\dagger}|\ ,\\\tilde{\Delta}_{mn}(E)&=\operatorname{Re}\tilde{F}_{mn}(E)=\sum_{\alpha}\mathcal{P}\int\frac{d\epsilon\,\tilde{\Gamma}_{mn}(E,\epsilon)}{E-\mathcal{E}_\alpha-\epsilon}\ .\end{aligned}\tag{23}$$

Quite naturally, the index α in Eq. (22) should be associated to the set of quantum numbers of the initial vibronic (usually the ground state) of the neutral species, which, upon interaction with the radiation field, is resonantly promoted to a vibronic core-hole state. The decay, on the other hand, proceeds into each energetically open (continuum) channel $\alpha=1,2,\ldots,K$ at a partial rate $\tilde{\Gamma}_{mn;\alpha}$.

If we now formally solve Eq. (22) for $\Upsilon^{+}_{\alpha mE}(\mathbf{R})$,

$$|\Upsilon_{\alpha mE}(\mathbf{R})\rangle=\sum_{n}[E-\tilde{H}_n-\tilde{F}_{mn}(E)]^{-1}|\tilde{M}^{+}_{n\alpha}(\epsilon,E)\rangle\ ,\tag{24}$$

and substitute this result into Eq. (18), we obtain the explicit expression for the elements of the resonant transition matrix in terms of a number of computable parameters, namely, the vibronic transition moments for the excitation and deexcitation processes, $\tilde{M}^{+}_{n\alpha}(\epsilon,E)$ and $\tilde{M}^{-}_{n\beta}(\epsilon',E)$, respectively; the resonance positions and their widths (the diagonalized form of) $\tilde{H}_n+\tilde{\Delta}_{mn}(E)$ and $\tilde{\Gamma}_{mn}(E)$, respectively; and the smoothly energy-varying transition amplitude for the direct single- or double-ionization process $T_{\beta\alpha}(E,\epsilon',\epsilon)$:

$$\bar{T}_{\beta\alpha}(E,\epsilon',\epsilon)=T_{\beta\alpha}(E,\epsilon',\epsilon)+\sum_{mn}\langle[\tilde{M}^{-}_{n\beta}(\epsilon',E)]^{\dagger}|\left[E-\tilde{H}_n-\tilde{\Delta}_{mn}(E)-\frac{i}{2}\tilde{\Gamma}_{mn}(E)\right]^{-1}|\tilde{M}^{+}_{n\alpha}(\varepsilon,E)\rangle\ .\tag{25}$$

At the expected energy range for x-ray photon or Auger electron decay, the amplitudes for the resonant events overwhelm the amplitudes for the direct single- or double-ionization processes. This means that the transition amplitude for the whole scattering process can be well approximated by only the second term in the right-hand side of Eq. (25)

$$\bar{T}_{\beta\alpha}(E,\varepsilon',\varepsilon)\approx\sum_{mn}\langle[\tilde{M}^{-}_{n\beta}(\varepsilon',E)]^{\dagger}|\left[E-\tilde{H}_n-\tilde{\Delta}_{mn}(E)-\frac{i}{2}\tilde{\Gamma}_{mn}(E)\right]^{-1}|\tilde{M}^{+}_{n\alpha}(\varepsilon,E)\rangle\ .\tag{26}$$

In order to get an explicit functional expression for the resonant transition amplitude, we insert the spectral resolution of the optical nuclear Hamiltonian,

$$\begin{aligned}&\tilde{H}_n+\tilde{\Delta}_{mn}(E)+\frac{i}{2}\Gamma_{mn}(E)=\sum_{\nu}|\xi^{(n)}_{\nu E}(\mathbf{R})\rangle Z_{n\nu}(E)\langle\chi^{(n)}_{\nu E}(\mathbf{R})|\ ,\\&Z_{n\nu}(E)=\mathcal{E}_{n\nu}(E)+\frac{i}{2}\gamma_{n\nu}(E)\ ,\end{aligned}\tag{27}$$

into Eq. (26) to obtain

$$\bar{T}_{\beta\alpha}(E,\varepsilon',\varepsilon)\approx\sum_{n}\sum_{\nu}\langle[\tilde{M}^{-}_{n\beta}(\varepsilon',E)]^{\dagger}|\xi^{(n)}_{\nu}(\mathbf{R})\rangle[E-Z_{n\nu}(E)]^{-1}\langle\xi^{(n)}_{\nu}(\mathbf{R})|\tilde{M}^{+}_{n\alpha}(\varepsilon,E)\rangle\ .\tag{28}$$

The energy dependence on the transition matrices $\tilde{M}^{-}_{n\beta}(\varepsilon',E)$ and $\tilde{M}^{+}_{n\alpha}(\varepsilon,E)$, as well on the eigenvalues $Z_{n\nu}(E)$ of the nuclear optical Hamiltonian, can be removed from our further considerations since the resonances we are addressing are relatively narrow. The apparent symmetry of the electronic and vibrational indices (quantum numbers) in the above equation is remarkable. It implies that for the ordinary cases where the energy difference between two adjacents vibrational levels is smaller than the corresponding difference for the electronic levels, it is expected that vibrational rather than electronic interference will be the leading effect distorting and shifting a vibronic band profile from its standard (Lorentzian) form and position. Quite interesting, however, is the case where a pair of vibronic bands of the decaying core-hole electronic states have an energy shift comparable to the displacement between two (populated) adjacent vibrational levels. In this case the competing decay will show an equal contribution from the two groups of possible vibrational and electronic interferences.

The cross section for the x-ray or Auger decay will be proportional to the square of the (approximated) amplitude of transition of Eq. [28], summed over all final channels and averaged over the initial channels. We will let the initial channel correspond to a single electronic state α, usually the electronic ground state of the neutral molecule, in the zero vibrational level. The set of final channels will be spanned by all singly (x-ray) or doubly (Auger) ionized electronic states β and populated vibrational level λ that are energetically reachable from the intermediate core-hole states n:

$$\sigma_\alpha(E,\varepsilon',\varepsilon)\propto\sum_{\beta\lambda}\left|\sum_{n\nu}\frac{\langle\chi_\lambda^{(\beta)}(\mathbf{R})|(\tilde{M}^-_{n\beta})^\dagger|\xi_\nu^{(n)}(\mathbf{R})\rangle\langle\xi_\nu^{(n)}(\mathbf{R})|\tilde{M}^+_{n\alpha}|\chi_0^{(\alpha)}\rangle}{E-\mathcal{E}_{n\nu}-\frac{i}{2}\gamma_{n\nu}}\right|^2\delta(\mathcal{E}_{\beta\lambda}+\varepsilon'-E) \tag{29}$$

or

$$\sigma_\alpha(E,\varepsilon',\varepsilon)\propto\sum_{\beta\lambda}\left[\sum_{n\nu}\frac{|\mathcal{M}^-_{\beta\lambda,n\nu}\mathcal{M}^+_{n\nu,\alpha 0}|^2}{(\varepsilon'+\mathcal{E}_{\beta\lambda}-\mathcal{E}_{n\nu})^2+\frac{1}{4}\gamma^2_{n\nu}}+\sum_{n,\nu(\neq n',\nu')}\frac{(\mathcal{M}^-_{\beta\lambda,n\nu}\mathcal{M}^+_{n\nu,\alpha 0})(\mathcal{M}^-_{\beta\lambda,n'\nu'}\mathcal{M}^+_{n'\nu',\alpha 0})^*}{\left[\varepsilon'+\mathcal{E}_{\beta\lambda}-\mathcal{E}_{n\nu}-\frac{i}{2}\gamma_{n\nu}\right]\left[\varepsilon'+\mathcal{E}_{\beta\lambda}-\mathcal{E}_{n'\nu'}+\frac{i}{2}\gamma_{n'\nu'}\right]}\right]$$

$$=\sum_{\beta\lambda}\left[\mathcal{L}^{\beta\lambda}_{n\nu}(\varepsilon',\varepsilon)+\sum_{n,\nu(\neq n',\nu')}\mathcal{J}^{\beta\lambda}_{n\nu,n'\nu'}(\varepsilon',\varepsilon)\right], \tag{30}$$

where, for sake of clarity, we have employed

$$\mathcal{M}^{\pm}_{ak,bl}=\langle\chi_k^{(a)}(\mathbf{R})|(\tilde{M}^{\pm}_{ba})^\dagger|\xi_l^{(b)}(\mathbf{R})\rangle\ . \tag{31}$$

The labels (a,b) stand here for the electronic and (k,l) for the vibrational levels. Equations (29) or (30) show that an x-ray or Auger emission spectral function (cross section) is composed of two factors: (1) a series of $(\beta\times\lambda)\times(n\times\nu)$ Lorentzian functions $\mathcal{L}^{\beta\lambda}_{n\nu}(\varepsilon',\varepsilon)$, with a full width at half maximum (FWHM) $\gamma_{n\nu}$ and centered at $\varepsilon'=\mathcal{E}_{n\nu}-\mathcal{E}_{\beta\lambda}$, due to the *independent* electronic decay events from the several intermediate electronic-vibrational $(n\nu)$ core-hole states to the manifold of singly or doubly ionized final electronic-vibrational $(\beta\lambda)$ open channels; and (2) the interference terms $\mathcal{J}^{\beta\lambda}_{n\nu,n'\nu'}(\varepsilon',\varepsilon)$ which account for the occurrence of incoherent resonant events whereupon the excitation (creation of a core-hole) and electronic decay processes are "mediated" by distinct intermediate electronic-vibrational levels $n\nu$ and $n'\nu'$. The latter terms are naturally denoted as state interference terms, and emerge only because the lifetime of the states is finite.

III. DISCUSSION

In this section we discuss some of the implications and the physical interpretations of the expressions arrived at in Eq. (30) which is the main result of the present many-state generalization for interference effects in x-ray (XES) and Auger (AES) decay. As potential areas of applica-

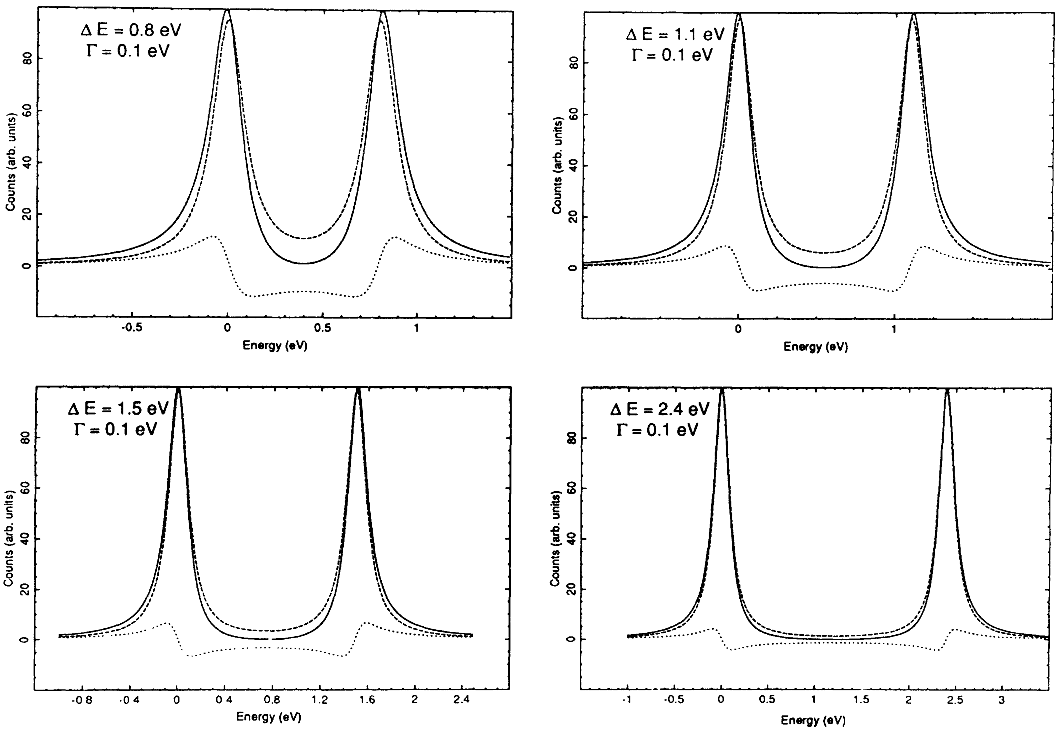

FIG. 1. Two-level state interference. Dotted, dashed, and solid lines correspond to the interference spectrum, the direct spectrum, and the total spectrum, respectively.

tions we list (1) resonance x-ray and Auger emission, (2) XES and AES emission from core electron shake-up states, (3) autoionization of a member of a Rydberg series converging to a common ionization potential of the ground or excited state, and (4) XES and AES decay from adsorbed species, for which relatively strong "main" and "satellite" states fall close to each other in the photoelectron spectrum. Under certain circumstances, as discussed below, the theory also concerns (5) XES and AES decay from close-lying chemically shifted states.

We chose here to illustrate to which extent the *state* interference changes the XES or AES spectral line profile of energetically shifted close-lying states. We also focus on the more general case of a molecular system, where two or more close-lying intermediate core-hole states and the final electronic states are vibrationally populated. We carry out some numerical simulations of the model systems starting out from Eq. (30). The simulation of this equation requires several quantities: the excitation energies and transition moments, the lifetimes, and the phases of the decay transition moments. We assume in all cases that the core-hole states have equal lifetimes. For the final transition moments, we consider only one final state at a time. This is because the total cross section will be summed over all final β states after the squaring, thus as a straight superposition of noninterfering spectra. In reality, the crowded manifold of the final states can make it difficult to distinguish the effects we are discussing here on purely experimental grounds. The transition moments and their phases are used as parameter input. In particular, we study the cases when $M_{1\beta}=M_{2\beta}$ and when $M_{1\beta}=-M_{2\beta}$, i.e., when the deexcitations occur with equal or opposite phases. We also study the case when $|M_{1\beta}| \ll |M_{2\beta}|$. In the list of examples given below, R denotes the ratio between energy shift and lifetime.

(1) Two-state-model systems with varying R. Here $R=8$, 11, 15, and 24 (Fig. 1). Equal transition moments and equal phases are assumed. For $R=24$ one discerns only a minor displacement of the Lorentzian profiles, and a conventional intensity analysis can be carried out. For $R=8$, however, some effect of state interference can be discerned on the Lorentzian tails, e.g., a decrease of intensity in between the peaks and an asymmetrization of the line profiles.

(2) Two-state model systems with fixed R and different transition moments (Fig. 2). Different ratios of transition moments $(R_M)=1,\frac{1}{2},\frac{1}{3},\frac{1}{4}$, are assumed for an energy-lifetime ratio $R=11$. For smaller values of R_M, the relative effect of state interference increases for the weak transition but decreases for the strong transition.

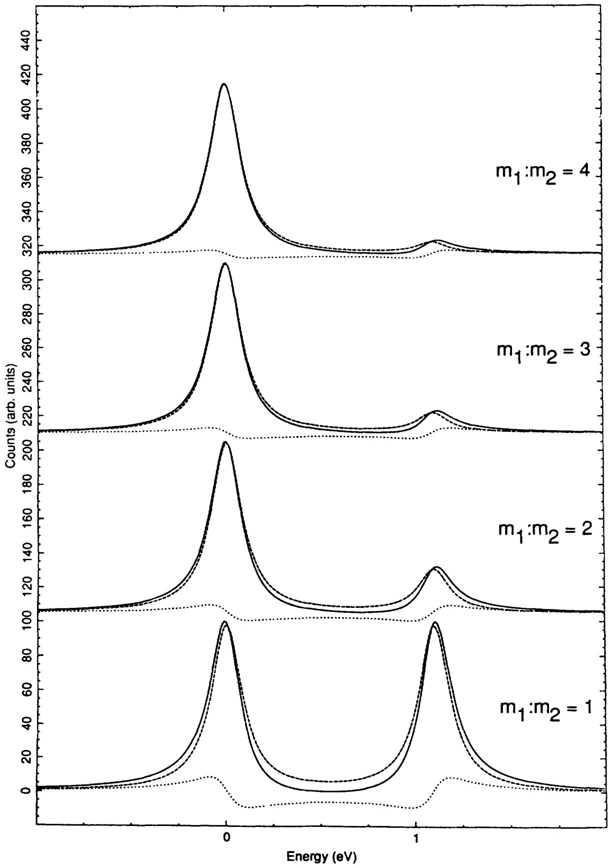

FIG. 2. Two-level state interference. Varying transition moments. See caption to Fig. 1.

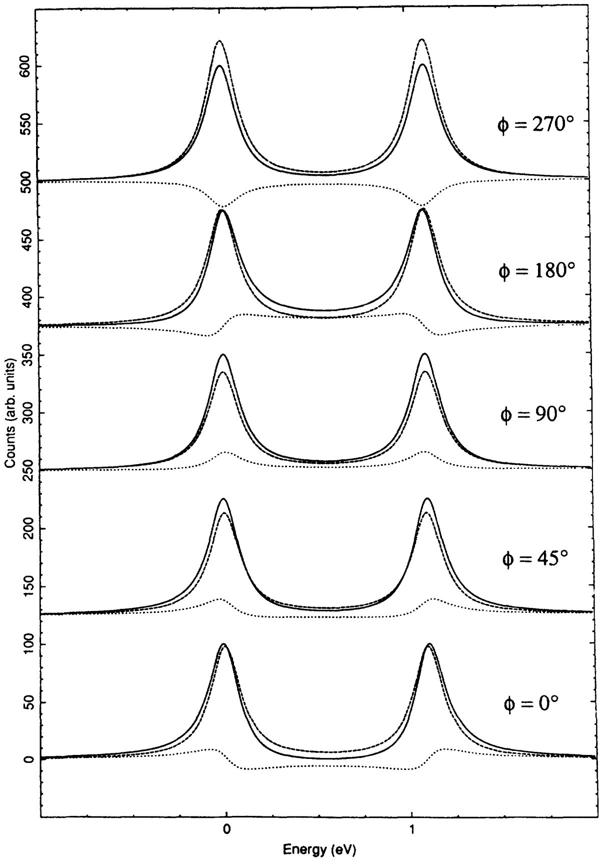

FIG. 3. Two-level state interference. Varying phase. See caption to Fig. 1.

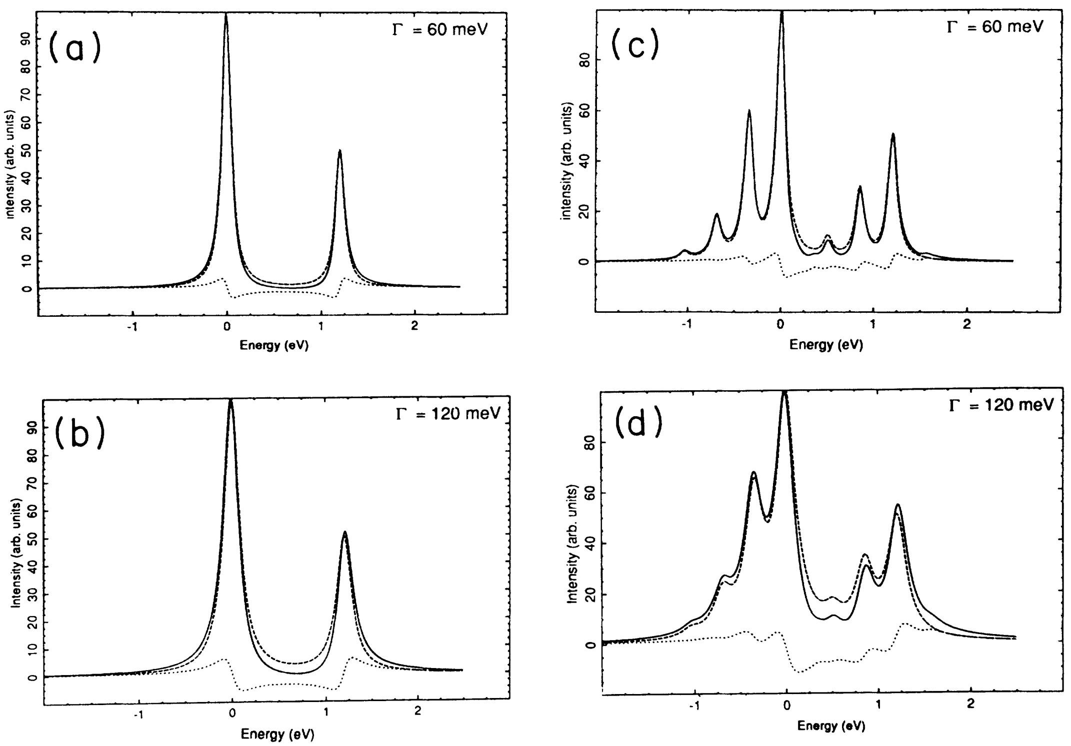

FIG. 4. Electronic and vibronic state interference in the Auger spectrum of the $S2p_{3/2,1/2}$ spin-orbit splitted states of H_2S. See caption to Fig. 1. (a) Electronic interference for $\Gamma = 60$ meV; (b) electronic interference for $\Gamma = 120$ meV; (c) vibronic interference for $\Gamma = 60$ meV; (d) Vibronic interference for $\Gamma = 120$ meV.

(3) Two-state-model systems with fixed R and different phases for the transition moments (Fig. 3). Phases are varying as 0° (no phase change), 45°, 90°, 180°, and 270°. $R = 11$ as in example 2. Equal absolute values for the transition moments (R_M) are considered. The interference pattern changes smoothly; at 180° the interference is reversed with respect to the case of equal phases (0°).

(4) Two-state-model systems with vibrational excitations: The $S2p_{3/2,1/2}$ spin-orbit split states of H_2S *(Fig. 4).* The spectrum [18] consists of two bands originating from the $2p_{3/2}$ (L_{III}) and $2p_{1/2}$ (L_{II}) levels to the outermost double hole $1b_1^{-2}$ state of H_2S^{2+}. It shows a simple vibronic progression, repeated for the two spin-orbit components, along the bending mode. The progression is built up by nonresolved superpositions of subprogressions, emerging from the $^2B_1$, $^2B_2$, and $^2A_1$ levels of the (spin-orbit splitted) $2p^{-1}$ core-hole states. The two last levels are virtually degenerate while the $^2B_1$ differed by about 0.08 eV according to calculations carried out in Ref. [19].

The state and vibronic interference patterns are plotted in Fig. 4. A spin-orbit splitting of 1.2 eV and statistical population of initial states (2 to 1) is used. Auger transition moments with equal magnitudes and phases are likewise assumed [20]. The effect of the state interference or "intensity borrowing" is largest for the weak component. For 60 meV the effect is hardly discernible, while for 120 meV it implies a displacement of 17 meV.

Auger and x-ray decay from chemically shifted core-hole states. So far we have made no assumptions concerning the spatial distribution of the core-hole states. It is evident that even if the core-hole states are close in energy, they will not decay with state interference if they belong to species where not all are connected to each other. In order to apply the present theory for such systems, the transition matrix appearing in Eq. (30) must be made explicit in terms of a phase factor depending on the internuclear distance. Thus if the product $\bar{R}\bar{k}$ ($\bar{k}$ being the wave vector and $\bar{R}$ the internuclear distance) is small enough, then the conditions for interference prevail even between spatially separated core holes. If it is large, however, the frequent oscillations of the particle wave will effectively smear out any interference. Thus either the nuclei, to which the core-hole states are localized, are spatially close or the core-hole states have low energy, e.g., are situated closely above the threshold energy for autoionization or Auger emission. In such a case the decay particles will have small energies and small wave vectors. Thus for chemically shifted species, the possibility of an interference effect depends on the particular conditions, on spatial proximity, and on excitation energy.

IV. CONCLUSION

In the present work we have derived and explored the consequences of a scattering formulation of x-ray and Auger decay for many core-hole-state problems. The formalism applies to resonance or fluorescence spectra and to the decay of core-electron shake-up or shake-off satellite states. Applications in the present work are carried out for spectra of some few-state model systems, including or not vibrational excitations. In the former case we identify a *state interference* effect, in the latter case a *vibronic interference* effect. It is found that a conventional analysis in terms of discrete noninteracting states is only valid when the ratio (R) between energy shift and lifetime is sufficiently large. For states with small R, say $R < 5$, a more complete theoretical account must be undertaken. It is found that the vibrational degree of freedom in a molecule, leading to vibronic interference effects, enhances the effect of state interference in the corresponding atomic spectra. As pointed out, the present theory also has a (yet unexplored) bearing on decay spectra of chemically shifted states and that interference effects then depend on the particular conditions with respect to spatial proximity of states and excitation energies.

The findings presented in this work indicate that the resonance Auger and x-ray spectra (x-ray fluorescence spectra), as obtained, for example, by new synchrotron techniques, must be addressed at a higher theoretical level than the "normal" Auger or x-ray transitions emanating from the well-separated main core-hole states. The results also indicate that, even for high-energy primary excitation, i.e., in the absence of noticeable post-collision interactions, there will be distortions, although generally small, in the level diagrams obtained from these spectroscopies with respect to the corresponding level diagrams obtained from UV and x-ray photoexcitation [electron-energy-loss (EELS)] and photoelectron spectroscopy. This goes also for quantities like spin-orbit splittings, inner-shell lifetimes, satellite energetics, and core-state vibrational constants and conformations, the values of which may be different from the corresponding values obtained by XPS and EELS.

---

[1] A Cesar, H. Ågren, and V. Carravetta, Phys. Rev. A **40**, 187 (1989).

[2] F. K. Gel'mukhanov, L. N. Mazalov, and N. A. Shklyaeva, Zh. Eksp. Teor. Fiz. **69**, 1971 (1975).

[3] F. K. Gel'mukhanov, L. N. Mazalov, A. V. Nikolaev, A. V. Kondratenko, V. G. Smirnii, P. I. Wadash, and A. P. Sadovskii, Akad. Nauk SSSR **225**, 597 (1975); F. K. Gel'mukhanov, L. N. Mazalov, and A. V. Kondratenko, Chem. Phys. Lett. **46**, 133 (1977).

[4] F. Kaspar, W. Domcke, and L. S. Cederbaum, Chem. Phys. **44**, 33 (1979).

[5] N. Correia, A. Flores-Riveros, H. Ågren, K. Helenelund, L. Asplund, and U. Gelius, J. Chem. Phys. **83**, 2035 (1985); A. Flores-Riveros, N. Correia, H. Ågren, L. Pettersson, M. Bäckström, and J. Nordgren, *ibid.* **83**, 2053 (1985); errata to be published. Computational errors in these papers have been corrected by Carroll and Thomas (1987) in Ref. [6].

[6] L. Ungier and T. A. Thomas, J. Chem. Phys. **82**, 3146 (1985); T. X. Carroll, S. E. Anderson, L. Ungier, and T. D. Thomas, Phys. Rev. Lett. **58**, 867 (1987); T. X. Carroll, and T. D. Thomas, J. Chem. Phys. **86**, 5221 (1987); **89**, 5983 (1988).

[7] R. Murphy, Z.-W. Lyo, and W. I. Eberhardt, J. Chem. Phys. **88**, 6078 (1988).

[8] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **22**, 3710 (1980).

[9] T. Åberg, Phys. Scr. **21**, 495 (1980); T. Åberg and G. Howat, in *Encyclopedia of Physics,* edited by S. Flügge and W. Mehlhorn (Springer, Berlin, 1982), Vol. XXXI, p. 469.

[10] U. Fano, Phys. Rev. **124**, 1866 (1961).

[11] F. H. Mies, Phys Rev. **175**, 164 (1968).

[12] C. L. Davis, and L. A. Feldkamp, Phys. Rev. B **15**, 2961 (1977).

[13] H. Feshbach, Ann. Phys. (N.Y.) **19**, 287 (1962).

[14] H. Feshbach, Ann. Phys. (N.Y.) **43**, 410 (1967).

[15] N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980); M. A. Morrison, Aust. J. Phys. **36**, 239 (1983); A. K. Kazanskiĭ and I. I. Fabrikant, Usp. Fiz. Nauk **143**, 601 (1984) [Sov. Phys.—Usp. **27**, 607 (1984)].

[16] J. N. Bardsley, J. Phys. B **1**, 349 (1968).

[17] M. Berman, H. Estrada, L. S. Cederbaum, and W. Domcke, Phys. Rev. A **28**, 1363 (1983).

[18] S. Svensson, A. Naves de Brito, N. Correia, M. Keane, and L. Karlsson, Institute of Physics Report No. UUIP-1274, University of Uppsala; (unpublished).

[19] A. Cesar, H. Ågren, A. Naves de Brito, S. Svensson, L. Karlsson, M. P. Keane, B. Wannberg, P. Baltzer, P. G. Fournier, and J. Fournier, J. Chem. Phys. **93**, 918 (1990).

[20] Equation (30) also holds when the core-hole states are spin-orbit splitted. It is only to be assumed that the derivation includes a spin-dependent Hamiltonian and its discrete and continuum eigenfunctions.