Core-hole excitation and decay for continuum-coupled systems: The adsorbate case

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(Received 30 April 2001; published 28 August 2001)

In isolated atoms and molecules the resonant excitation and the subsequent decay of core-electron excitations are appropriately described as a coherent one-step process. Narrow-band excitation brings out its distinct features (linear dispersion and line narrowing for decay spectra in atoms; detuning effects such as vibrational collapse and turn-on and atomic versus molecular lines in molecules). Using the example of adsorbates on metal surfaces, we address the question if and how this is modified for systems in which discrete intermediate (core-excited) states are coupled to a continuum. The basic question of coherent versus incoherent processes is considered, and the more practical question is addressed as to what is the correct interpretation of the observed detuning effects for adsorbates. We demonstrate the inappropriateness of the usual wave function description based on the perturbative treatment of the time-dependent Schrödinger equation which leads to unphysical interferences and physically unacceptable features of the decay electron spectra and develop an appropriate density matrix approach. While its complications make a general solution impossible, we show that this approach leads in a systematic way to a picture in which coherent and incoherent excitation-decay channels compete but do not interfere with each other. The two-step description of the incoherent channel and the one-step character of the coherent one emerge from this analysis. The earlier interpretation of the observed variations of the relative strengths of the two channels upon detuning as the variation of the delocalization probability of the intermediate core excitation is justified by our treatment.

I. INTRODUCTION

Traditionally, the excitation of core holes and their following decay by x-ray photon or Auger electron emission have been viewed as a two-step process. This is adequate for broad-band excitation (where "broad" and "narrow" are defined by comparison to the lifetime width of the core-hole-excited state). Recent advances of experimentation with synchrotron radiation have made it possible to use much narrower excitation bandwidths.[1] If the resolution of the emitted decay photon or electron is sufficiently narrow as well, only a one-step description is appropriate for the entire excitation-decay sequence,[2] with the consequence that energy conservation applies only between the initial (ground) state and the final (decay) state. The experiments are then termed resonant inelastic x-ray scattering (RIXS) and resonant Auger-Raman (RAR, also ARR) spectroscopies.[1,3] Because of the strong dominance of Auger over radiative decays for light elements and the greater ease of high resolution for secondary electrons over secondary photons, a larger body of results on atoms and molecules exists for the Auger case which we will take as the example here. It should be noted that most arguments carry over to the x-ray emission case.

For isolated atoms and molecules with well-defined quantum states, consideration of the coupled excitation-decay process necessarily implies a one-step picture. The experimental signatures of experiments under such narrow-band ("Auger-Raman") conditions are[4] "linear dispersion" of the decay electron kinetic energy with the excitation photon energy and "line narrowing" (definition of the linewidth of the decay electrons by the photon energy resolution and the final-state lifetime, *not* the intermediate-state lifetime) for at-

oms. Both characteristics are direct consequences of energy conservation. For molecules additional very interesting "detuning effects" exist which derive from the fact that the time scale of nuclear motion determines the appearance of the decay spectra. Only exactly at resonance will the full lifetime of the core-excited state contribute to the final-state spectrum; detuning away from resonance leads to a shortening of the available time with potentially strong effects on the spectra.[5–9] For bound intermediate states detuning can—depending on the relative positions and shapes of the potential energy curves of the ground, intermediate, and final states—lead to the disappearance of vibrational structure ("vibrational collapse") (Refs. 7, 10, and 11), or the opposite effect.[7,11] For repulsive intermediate states "molecular" and "atomic" lines can arise which possess different dispersion behavior and can interfere in a very interesting and complicated way upon detuning;[12] and a Doppler effect for the emitted electrons can be observed.[13] All these effects can be described in a stationary formalism based on the Kramers-Heisenberg formula or in explicitly time-dependent formalisms which in some respects have the advantage of a more intuitive appeal. A large body of experimental and theoretical work exists, and extensive reviews as well as surveys have been given.[3,14,15] The basic one-step picture thus is unavoidable for isolated systems with well-defined quantum states. As long as no coupling to internal continua happens this picture is also appropriate for solids (see the RIXS case).[16] A basic question is if there are any changes for a system with coupling to a continuum (or to more than one continua). One might argue that the basic process should always be one-step, even if the particular conditions let it appear indistinguishable from the result derived from a two-step picture. This

opinion—that it is always a one-step process—has been voiced in the literature.[17]

An interesting case of a coupled discrete-continuum system is that of an adsorbate on a metal or semiconductor surface. Here the excitation-decay sequence of a core-hole excitation can in principle proceed in two ways which are easiest to visualize for a resonant, core-to-bound intermediate state which brings an electron from a core state of the adsorbate into a bound empty, dipole-coupled state of the system, in the simplest model into an empty orbital on the adsorbate. The electron in that excited adsorbate state can then delocalize into the bulk substrate. If this delocalization is slower than the core-hole decay, then the system does not know anything about this possibility, and the characteristics of the Auger-Raman conditions are expected to result. If, however, the electron transfer is competitive with or faster than the core-hole decay, a modification is expected; in the extreme it results in a breakdown of the Auger-Raman characteristics.[18] Experimentally it is indeed found that for a weakly adsorbed species like an Ar atom physisorbed on a transition metal surface,[19,20] both types of spectra occur: the linearly dispersing Raman spectrum and a spectrum called "normal Auger" because of its constant kinetic energies upon detuning and its equality to the Auger spectra obtained by primary excitation into the ionization continuum. Based on a simple rate approach, the ratio of the integrated intensities of the two spectra has been used to derive the ratio of the charge transfer time and the core-hole decay time and, since the latter is known reasonably well, to derive the absolute value of the former which turns out to lie in the range of some ten femtoseconds for different systems.[19,20] The ratio of channel intensities is often given in a normalized manner; i.e., the so-called Raman fraction is the strength of the Raman channel relative to the sum of both channels. For strongly coupled adsorbates such as chemisorbed molecules (CO, NO, N_2) the normal-Auger part overwhelmingly dominates[21] and the Raman fraction becomes very small. But using the different dispersion behavior of the two types of spectra, even here estimates of the (very short, below 1 fs) charge transfer or delocalization times are possible.

Such an analysis is based on a somewhat naive model of the clear separation into either decay before transfer or transfer before decay. It does not take into account the subtleties which the above-mentioned theories have demonstrated for ARR spectra of isolated molecules, in particular those revealed by detuning. Experimentally quite distinct but different variations of the Raman fraction with photon energy over the core-hole resonance have been observed in all systems examined in sufficient detail.[19–21] The question arises as to whether this variation is a signature of the one-step coherent processes and their interferences or whether it is connected to the way the resonant state is coupled to the internal continuum in the substrate, or whether both effects contribute. The *ad hoc* treatment mentioned assumes the second interpretation. We have endeavored to develop a treatment which would shed light on this question and hopefully also give a better picture of the basic processes in such a coupled system, as compared to isolated atoms and molecules. While we develop it for our adsorbate case, it would appear that many

arguments can be carried over to other continuum-coupled systems, such as, e.g., solids or large molecules in which a functional group is coupled to a large residual molecule.

In the following we will first demonstrate that the usual approach for coherent excitation-decay processes, a perturbative Schrödinger equation approach—here called the wave function approach—is inappropriate for our case,[19,20] since it does not permit one to incorporate the coupling to the substrate with efficient internal dissipation and dephasing and therefore leads to unphysical interference terms. We then develop a treatment based on the Liouville equation (the density matrix approach) designed to eliminate this difficulty. In this approach both excitation-decay channels are accounted for without making any prior assumptions as to their one- or two-step nature or whether they interfere or not. Unfortunately, however, a solution for the cases of a variable degree of coupling to a broad band of continuum states cannot be given. We have to be content with the treatment of limiting cases (either a single adsorbate state or a subset of adsorbate-substrate states coupled extremely strongly to a broad continuum band of variable density). Nevertheless, we believe that our treatment shows the essential correctness of the earlier naive model mentioned above: the competition of a coherent Raman-Auger channel as in the isolated atoms with an (intrinsically) incoherent normal-Auger channel. No interferences exist between the two channels, and therefore the observed detuning behavior must be connected with the variation of the delocalization probability of the intermediate excitation away from the adsorbate complex, which will be connected with the character and density of substrate states and their coupling to the adsorbate complex.

The paper is organized as follows. The processes are described in Sec. II; the results of the standard description based on the wave function approach are presented and discussed in Sec. III. The density matrix approach follows in Sec. IV. This section is divided into several subsections and the reader interested mainly in the results may concentrate on Sec. IV D where the results of the density matrix approach are confronted with those of the wave function approach. The discussion following Eqs. (24) in Sec. IV C should also be noted in this case. Finally, in Sec. V the density matrix approach is generalized to account for those parts of the adsorbate-substrate interaction which cannot be treated within the perturbation theory approach.

II. NORMAL-AUGER AND RAMAN-AUGER PROCESSES FOR AN ADSORBED ATOM

We start with the description of the processes involved. They are visualized in Fig. 1 in which the shaded areas to the left represent the Fermi sea of a metal and the levels on the right represent some selected orbitals of the adsorbed atom. An adsorbed atom in its ground state $|g\rangle$ with total energy E_g is subjected to the time-dependent nearly monochromatic synchrotron radiation field (angular frequency ω_L) which promotes one of its core electrons to the lowest unoccupied orbital, resulting in an atom in a core-hole-excited state $|d\rangle$ with energy E_d.
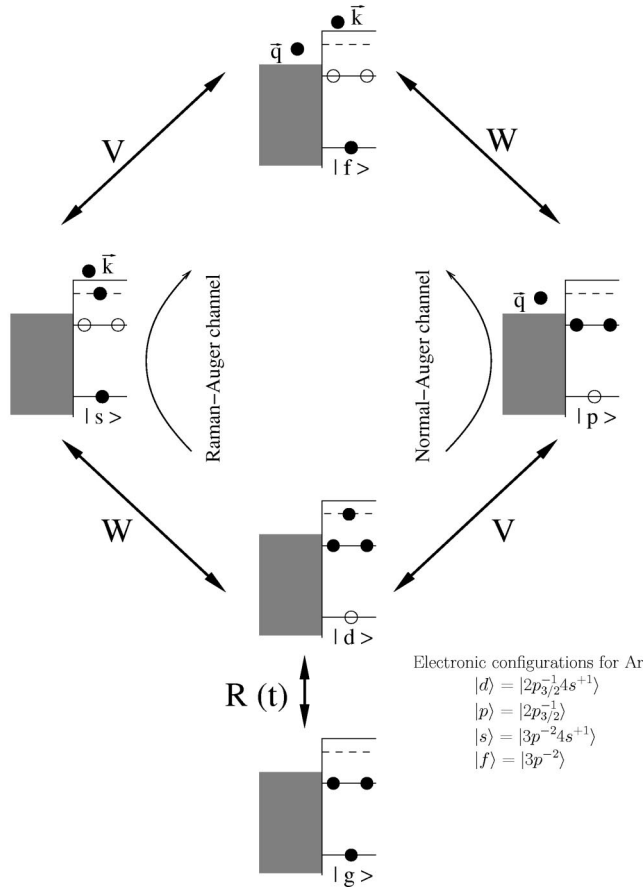
FIG. 1. Electronic configurations and excitation decay channels considered in this model. Inset: the electronic configurations for the Ar adsorbate.

By states of the atom, like $|g\rangle$, $|d\rangle$, and others to follow, we always mean quantum states of *all* electrons localized on the atom, possibly modified by the interaction with the substrate in comparison with the corresponding states of an isolated atom. To be specific we can consider, as an example, an Ar atom physisorbed at a surface of Ru, Pt, or Ag. The radiation promotes one of its core $2p$ electrons to the lowest unoccupied $4s$ orbital, so the core-hole-excited state $|d\rangle$ can be identified with $|2p_{3/2}^{-1}4s^{+1}\rangle$. This excited state of the atom is unstable against losing an electron into vacuum or into the substrate, which initiates the two distinct decay channels shown in Fig. 1 and described below.

The atom in the state $|d\rangle$ can lose an electron into a single-particle state $\vec{q}$ in the substrate, resulting in the adsorbed ion in a state denoted $|p\rangle$ with energy E_p (e.g., $|2p_{3/2}^{-1}\rangle$ for Ar), possibly screened by the substrate electrons. The energy of the electron in the substrate is denoted $\mathfrak{E}_{\vec{q}}$ and, for simplicity, a possible band index is incorporated into $\vec{q}$. Further Auger decay releases another electron into the vacuum state $\vec{k}$ (with kinetic energy $\mathcal{E}_{\vec{k}}$) while the atom ends up in a doubly ionized state $|f\rangle$ with energy E_f (e.g., $|3p^{-2}\rangle$). The decay channel from $|d\rangle$ through $|p\rangle$ to the final state $|f\rangle$ is termed the normal-Auger channel in Fig. 1.

The above process competes with the decay along the Raman-Auger channel, leading to the same final state of the combined system. In this process the state $|d\rangle$ decays first by a spectator Auger process in which the electron $\vec{k}$ is emitted into vacuum and the atom becomes an ion in a state $|s\rangle$ (e.g., $|3p^{-2}4s^{+1}\rangle$) with energy E_s. This is then followed by loss of another electron into the substrate state $\vec{q}$.

In the experiments at which we aim our approach, spectra of the decay electrons emitted into vacuum are measured and, in some cases, the decay channels can be identified as main contributors to different parts of the spectra. In such cases the "Raman fraction," defined as the ratio of the emission cross section of electrons emitted in a process along the Raman-Auger channel to the total electron emission cross section, can be determined[19,20] as a function of the exciting radiation frequency ω_L. In the Raman fraction the strong dependence due to the resonant character of the primary excitation is removed, leaving a relatively weak dependence due to other reasons like the energy dependence of the transition matrix elements and of the densities of states of electrons in vacuum and/or in the substrate. One of the aims of our approach is to identify possible reasons for such a dependence, as outlined above.

We would like to stress here that the specific designations, in terms of occupied and empty orbitals appropriate for Ar in the gas phase, do not have to be correct for adsorbed Ar because the transitions listed may involve many electrons at once; i.e., the holes created on the atom may be almost instantaneously screened by the substrate electrons. $R(t)$, W, and V in Fig. 1 refer to those parts of the Hamiltonian of the system which are responsible for the primary excitation, the Auger transitions, and the electron tunneling between the atom and the substrate, respectively. If the state $|s\rangle$ can no longer decay by releasing an electron into the substrate (either because the process leading to it was a participant Auger process or because the substrate screening pulls the excited orbital of the atom below the Fermi level of the substrate), then some of the issues discussed in this paper (e.g., the interference of both channels in the wave function approach) become mute. But the general approach, as we shall see, still accounts for such a possibility.

Our goal is to provide a consistent theoretical framework for a unified treatment of the above processes. The usual approach to be tried by anybody faced with this problem would be to use third-order perturbation theory (to account for three events: excitation, electron transfer, and decay—the latter two in either order) based on the time-dependent Schrödinger equation. In this approach, termed the wave function approach in this paper, the quantum states of interest can be collectively denoted by $|m,\vec{s},\vec{v}\rangle$, where m $= g$, d, s, p, or f denotes the state of the atom or ion; $\vec{s}$ can either be 0 (if no extra electron is present in the substrate) or $\vec{q}$ if the extra electron in the substrate is in a single-particle state $\vec{q}$ and, similarly, $\vec{v}$ can either be 0 or $\vec{k}$ depending on whether there is no electron in vacuum or there is one

with momentum $\hbar\vec{k}$. Specifically, the states are $|g,0,0\rangle$, $|d,0,0\rangle$, $|s,0,\vec{k}\rangle$, $|p,\vec{q},0\rangle$, and $|f,\vec{q},\vec{k}\rangle$. The wave function approach treats both continua involved, electron states in vacuum and in the substrate, in exactly the same way. Physically, this is not correct; while an electron in vacuum is truly free (possibly having its wave function differing from the plane wave form on the account of its interaction with the substrate), the electron in the substrate interacts strongly with all elementary excitations in it: other electrons, phonons, etc. The electron released into the substrate single-particle state $\vec{q}$ does not stay in it but dissipates its energy into the entire substrate. Consequently, the states $|p,\vec{q},0\rangle$ and $|f,\vec{q},\vec{k}\rangle$ are not stationary states, contrary to the assumption inherent in the wave function approach. In particular, in the wave function approach the time evolution of the relative phases between any two states taken into account explicitly in the expansion of the time-dependent wave function of the system is followed while, in fact, the phase coherence between any of the above two states and the remaining ones is lost on a time scale much shorter than the times over which the evolution of the system occurs which is relevant for the characteristics of the decay electron spectra. One of the consequences is the possibility—inherent in the wave function approach — that the same state $|f,\vec{q},\vec{k}\rangle$ might be reached along both decay channels, as explicitly shown in Fig. 1, so the electron spectrum exhibits signatures of a quantum interference between the channels. A truly correct wave function approach should, at least in principle, incorporate all other substrate electrons (and its other elementary excitations) into the considerations, i.e., take into account all relevant stationary states of the substrate in which the substrate with one extra electron in a single-particle state $\vec{q}$ may eventually end up. Such a version of the wave function approach is impractical and there does not seem to exist any systematic theoretical reduction scheme for its approximate treatment without losing the dynamical interactions within the substrate entirely. A physically equivalent description for which such a systematic reduction scheme exists is that in terms of the time-dependent Liouville equation for the density matrix of the combined system consisting of all electrons on the atom (or ion), the electron in vacuum (if present), and the electronic system of the substrate (including the electron transferred from the adsorbed atom). This method is specifically designed to deal with the dynamics of a small "dynamic system" (here the adsorbed atom, also referred to as the "primary system") interacting by exchanging energy and particles with a reservoir with very efficient internal interactions. In such an approach the internal degrees of freedom of the reservoir are effectively "projected out," leaving only an explicit reference to stationary states of the primary system (here $|m,\vec{v}\rangle$ with $\vec{v}=0$ or $\vec{k}$). We outline such a description and want to confront its results with those of the wave function approach.

We start with a short presentation of the wave function approach in Sec. III. We not only summarize its results there but also point out potential inconsistencies and difficulties inherent in it. Some of them we have identified only after

developing the density matrix approach, so several critical comments concluding Sec. III might seem unjustified when read for the first time. One of the conceptual difficulties with the wave function approach is the fact that, once certain of its most obviously incorrect features are ignored or corrected in an *ad hoc* manner, the remaining consequences look often "physically reasonable," resulting in unjustified confidence in the correctness of such an approach. It should eventually become clear, however, that some of these "physically reasonable" consequences are not, in fact, correct. The density matrix approach is presented in Sec. IV. The full theoretical development is quite a tedious task, so details will be omitted (and references to earlier works using similar schemes will be given), but all necessary simplifying assumptions and approximations will be spelled out explicitly. We then also confront the results of the density matrix approach with those of Sec. III. A systematic reduction of the full density matrix is possible only in the case of a sufficiently weak interaction between the core-hole-excited adsorbed atom and the substrate, which results in a loss of features of potential importance in actual systems. Therefore, we propose in Sec. V a phenomenological generalization of the density matrix approach for strongly coupled adsorbates.

III. WAVE FUNCTION APPROACH

We begin with the simplest possible treatment which is a direct generalization of the second-order perturbation theory approach to the Raman-Auger decay process for an isolated atom.

We start by assuming that the matrix elements of the Auger and the tunneling transitions depend on the state of the released electron (into a vacuum state $\vec{k}$ or into a substrate state $\vec{q}$, respectively) only via its energy, i.e.,

$$W_{s\vec{k},d}=W_{s,d}(\mathcal{E}_{\vec{k}}), \tag{1a}$$

$$V_{p\vec{q},d}=V_{p,d}(\mathfrak{E}_{\vec{q}}), \tag{1b}$$

and that the state of an electron already present in the substrate or in vacuum is neither affected by nor does it influence the subsequent emission of an electron into vacuum or into the substrate, respectively (this implies that post-emission interactions are eliminated from the model), i.e.,

$$W_{f\vec{q}\vec{k},p\vec{q}'}=\delta_{\vec{q},\vec{q}'}W_{f\vec{k},p}=\delta_{\vec{q},\vec{q}'}W_{f,p}(\mathcal{E}_{\vec{k}}), \tag{2a}$$

$$V_{f\vec{q}\vec{k},s\vec{k}'}=\delta_{\vec{k},\vec{k}'}V_{f\vec{k},s\vec{k}}(\mathfrak{E}_{\vec{q}})=\delta_{\vec{k},\vec{k}'}V_{f,s}(\mathfrak{E}_{\vec{q}}). \tag{2b}$$

In the wave function approach one usually starts from the third-order perturbation theory amplitudes for the normal-Auger and Raman-Auger channels, respectively,

$$\frac{W_{f,p}(\mathcal{E}_{\vec{k}})V_{p,d}(\mathfrak{E}_{\vec{q}})(-\vec{\mathcal{E}}_0\cdot\vec{D}_{d,g}/2)}{[E_g+\hbar\omega_L-E_d-i(\Gamma_d^v+\Gamma_d^w)/2](E_g+\hbar\omega_L-E_p-\mathfrak{E}_{\vec{q}}-i\Gamma_p^w/2)}, \tag{3a}$$

$$\frac{V_{f,s}(\mathfrak{E}_{\vec{q}})W_{s,d}(\mathcal{E}_{\vec{k}})(-\vec{\mathcal{E}}_0\cdot\vec{D}_{d,g}/2)}{[E_g+\hbar\omega_L-E_d-i(\Gamma_d^v+\Gamma_d^w)/2](E_g+\hbar\omega_L-E_s-\mathcal{E}_{\vec{k}}-i\Gamma_s^v/2)}, \tag{3b}$$

where $\vec{\mathcal{E}}_0$ and $\vec{D}_{d,g}$ are the radiation amplitude and the dipole transition matrix element between $|g\rangle$ and $|d\rangle$ states. Γ_m^w and Γ_m^v are the contributions to the lifetime width of a state $|m\rangle$ ($m=d,p,s$) due to the autoionizing Auger electron emission [the corresponding interaction Hamiltonian is $\mathbb{W}$ with matrix elements given in Eqs. (1a) and (2a)] and due to the electron transfer to the substrate [interaction $\mathbb{V}$, matrix elements in Eqs. (1b) and (2b)], respectively. Explicitly, the linewidth contributions are

$$\Gamma_p^w\equiv\hbar\gamma_p^w=2\pi\rho_V(E_p-E_f)|W_{f,p}(E_p-E_f)|^2, \tag{4a}$$

$$\Gamma_s^v\equiv\hbar\gamma_s^v=2\pi\theta(E_s-E_f-\epsilon_F)\rho_S(E_s-E_f)|V_{f,s}(E_s-E_f)|^2, \tag{4b}$$

$$\Gamma_d^w\equiv\hbar\gamma_d^w=2\pi\rho_V(E_d-E_s)|W_{s,d}(E_d-E_s)|^2, \tag{4c}$$

$$\Gamma_d^v\equiv\hbar\gamma_d^v=2\pi\theta(E_d-E_p-\epsilon_F)\rho_S(E_d-E_p)|V_{p,d}(E_d-E_p)|^2, \tag{4d}$$

where $\rho_S(\mathfrak{E})$ and $\rho_V(\mathcal{E})$ are the electron densities of states in the substrate and in vacuum, respectively, and the θ function assures that the electron transfer to the substrate is possible only into substrate states above the Fermi level ϵ_F.

Equations (3) are obtained when the time-dependent Schrödinger equation is solved in the lowest order in the interaction with radiation $\mathbb{R}(t)$ and in perturbations $\mathbb{V}$ and $\mathbb{W}$. The result of such an approach is that the amplitudes have a typical form for processes in which all three events—excitation-electron tunneling, Auger decay in Eq. (3a), or excitation-Auger decay, electron tunneling in Eq. (3b)—are coherent sequences of three events with no energy conservation required in any of them separately. Such a coherent sequence of events as a whole is referred to as a one-step process.

Both amplitudes must be added, the sum squared, and then multiplied by $2\pi/\hbar$, by the energy conservation Dirac's delta $\delta(E_g+\hbar\omega_L-E_f-\mathcal{E}_{\vec{k}}-\mathfrak{E}_{\vec{q}})$ (the only condition imposed by the energy conservation) and by $\rho_S(\mathfrak{E}_{\vec{q}})\theta(\mathfrak{E}_{\vec{q}}-\epsilon_F)$, and integrated over all possible energies $\mathfrak{E}_{\vec{q}}$ of the electron transferred to the substrate (this includes summation over all overlapping bands, if necessary). The result is the rate of emission of electrons into vacuum with energy $\mathcal{E}$

$$\dot{R}(\mathcal{E})=\frac{2\pi}{\hbar}\frac{|\vec{\mathcal{E}}_0\cdot\vec{D}_{d,g}/2|^2}{(E_g+\hbar\omega_L-E_d)^2+[(\Gamma_d^v+\Gamma_d^w)/2]^2}$$
$$\times[s_N(\mathcal{E})+s_R(\mathcal{E})+s_{NR}(\mathcal{E})], \tag{5}$$

with the contributions due to the normal-Auger and Raman-Auger processes being, respectively,

$$s_N(\mathcal{E})=\theta(E_g+\hbar\omega_L-E_f-\mathcal{E}-\epsilon_F)\rho_S(E_g+\hbar\omega_L-E_f-\mathcal{E})$$
$$\times\frac{|W_{f,p}(\mathcal{E})V_{p,d}(E_g+\hbar\omega_L-E_f-\mathcal{E})|^2}{(\mathcal{E}+E_f-E_p)^2+(\Gamma_p^w/2)^2}, \tag{6a}$$

$$s_R(\mathcal{E})=\theta(E_g+\hbar\omega_L-E_f-\mathcal{E}-\epsilon_F)\rho_S(E_g+\hbar\omega_L-E_f-\mathcal{E})$$
$$\times\frac{|V_{f,s}(E_g+\hbar\omega_L-E_f-\mathcal{E})W_{s,d}(\mathcal{E})|^2}{(\mathcal{E}+E_s-E_g-\hbar\omega_L)^2+(\Gamma_s^v/2)^2}, \tag{6b}$$

and $s_{NR}(\mathcal{E})$, which we do not quote, accounting for the interference of both channels.

It is worthwhile to note the following.

(i) The emitted electron spectra are proportional to $\rho_V(\mathcal{E})\dot{R}(\mathcal{E})$. It also is, obviously, proportional to the Lorentzian factor [in Eq. (5)] which accounts for the resonant character of the initial excitation process.

(ii) The Raman-Auger contribution in Eq. (6b) has roughly a Lorentzian shape with the full width at half maximum (FWHM) controlled by the lifetime width of the "final" state $|s\rangle$. An extra width would be provided by the linewidth of the exciting radiation which in this treatment, assuming monochromatic radiation, is ignored. Its inclusion is a trivial matter but, in view of the fact that present experiments aim at minimizing the radiation linewidth, we ignore it because we are not specifically aiming at effects related to a finite but small linewidth of the radiation. The position of the kinetic energy peak of the Raman-Auger contribution changes linearly with the radiation frequency (the effect called linear dispersion) and its width is not affected by the lifetime width of the intermediate state $|d\rangle$. These two properties are the expected consequences of the fact that the Raman-Auger process is a one-step process in which the sequence of excitation and electron emission events is a single quantum process. The third event, the electron transfer from the two-valence-hole-excited state $|s\rangle$ to the substrate, contributes the "final-state lifetime" width Γ_s^v to the spectrum in Eq. (6b). This is also expected. However, the fact that both the frequency of the exciting radiation, ω_L, and the energy of the emitted electron, $\mathcal{E}$, appear explicitly in the energy argument of the substrate density of states ρ_S and of the tunneling matrix element $|V_{f,s}|^2$ in Eq. (6b) is contrary to physical intuition. It is surprising because once the electron is emitted into the vacuum its distribution should not be sensitive to that into which states of the substrate the other electron is *subsequently* released from the excited orbital of the

atom. Note that it is not the *presence* of $\rho_S|V_{f,s}|^2$ as a multiplying factor in Eq. (6b) which is questioned, but the fact that their energy argument contains the energy of the absorbed photon and the energy of the decay electron. The presence of the factor $\rho_S|V_{f,s}|^2$ is actually necessary to convert the Lorentzian factor in Eq. (6b) into the Dirac's δ function in the limit of a stable state $|s\rangle$, i.e., when $V_{f,s}\to 0$ [implying $\Gamma_s^v\to 0$; cf. Eq. (4b)].

(iii) In contrast, the normal-Auger contribution in Eq. (6a), also having nearly Lorentzian shape, does not move with the radiation frequency (i.e., no dispersion at all). Its FWHM is controlled by the lifetime width of the core-hole-ionic state $|p\rangle$ (whose Auger decay leads directly to the emission of the detected electron), does not depend on the lifetime width of the intermediate core-hole-excited state $|d\rangle$, and would not be affected by the linewidth of the incident radiation [except for the trivial dependence described in (i) above]. These properties are usually attributed to the fact that the normal-Auger process is a sequence of independent quantum events. This, however, is not how it is treated in the wave function approach. As seen in Eqs. (3), the normal-Auger and the Raman-Auger channels are treated in exactly the same way: as a one-step process being a coherent sequence of three events. The behavior of the normal-Auger contribution seen in Eq. (6a), different from that of the Raman-Auger one in Eq. (6b), is solely due to the averaging over the continuum of the final states of electrons in the substrate which must be done because only states of electrons emitted into the vacuum are resolved in the experiments while the electrons lost to the substrate are not observed at all. In other words, the contribution (6a) to the decay electron spectrum due to the normal-Auger process only mimics the behavior expected from the sequence of three independent events with energy being conserved (within the lifetime widths) separately in each event. Still, based on physical intuition, it may be argued that, while the fact that the energy argument of $\rho_S|V_{p,d}|^2$ contains the energy of the photon initiating the process is understandable, the reasons why it also contains the energy of the decay electron are not entirely clear. One would rather expect that the energy of the electron released into the substrate should be equal to the difference between the total energy of the system after the photon is absorbed, $E_g+\hbar\omega_L$, and the energy E_p left on the atom after the tunneling event. Consequently, the energy argument of $\rho_S|V_{p,d}|^2$ in Eq. (6a) would be $E_g+\hbar\omega_L-E_p$ rather than $E_g+\hbar\omega_L-E_f-\mathcal{E}$. In any event, the argument should not contain the energy $\mathcal{E}$ of the decay electron released into vacuum *after* the tunneling event if these two events are truly independent.

(iv) The consequence of treating both channels as one-step processes which seems most objectionable — on intuitive grounds—is the presence of the interference term $s_{NR}(\mathcal{E})$ in Eq. (5). Physical intuition would dictate that such interference between both channels should be absent in the presence of the substrate (see the detailed discussion of this point in the second last paragraph of Sec. II). However, the interference term cannot be avoided in the perturbative wave function approach based on the Schrödinger equation. Admittedly, its influence on the shape of the spectra is very small in

systems in which the normal-Auger and Raman-Auger peaks are well resolved under conditions of optimal resonant excitation (for $\hbar\omega_L\approx E_d-E_g$). Large detuning away from the resonance is then needed to merge the peaks close enough for the interference effects to be visible, but then the entire signal hardly rises above the noise level.

Still, as we have argued in Sec. II, the interference effects should not be present, even in principle, because once the electron is transferred into the solid all phase relations between pre- and post-transfer states of the system are quickly lost. One might either account for this by ignoring the interference term, arguing perhaps that for the Raman-Auger channel the final state is, in fact, $|s\vec{k}\rangle$ rather than $|f\vec{k}\rangle$; i.e., it is not identical with the final state along the normal-Auger channel, so one should just add the probabilities along both channels, not their amplitudes. By such a procedure one loses, however, the possibility of accounting for the finite lifetime of the Raman-Auger channel "final" state $|s\vec{k}\rangle$. It can be re-introduced *ad hoc* in the final expression by, effectively, replacing the energy conservation Dirac's δ function for this process by the appropriate Lorentzian, but this procedure is as unsatisfactory as just ignoring the interference term in Eq. (5). Using the wave function approach with *ad hoc* corrections is unsatisfactory not only because of its inconsistency but also because the correctness of the retained expressions for the normal-Auger and Raman-Auger contributions is doubtful. We have seen already in paragraphs (ii) and (iii) above that, indeed, the way in which the decay electron energy and the photon energy appear in the energy argument of the substrate density of states and of the tunneling matrix element is problematic.

As indicated above, the competition between the Raman-Auger and normal-Auger channels can be conveniently parametrized by the Raman fraction which is defined as a ratio of the integrated Raman-Auger contribution to the electron spectra to the total integrated spectrum (another possibility would be just the ratio of integrated Raman-Auger to the integrated normal-Auger contributions). The Raman fraction can be determined experimentally for systems for which both contributions can be clearly separated due to their different dispersion behavior with respect to the varying frequency of the incoming radiation. A benefit from measuring the Raman fraction is that the strong resonant dependence of the spectra on the radiation frequency, represented by the Lorentzian factor in Eq. (5), cancels out, allowing us to access much weaker dependences due to the energy dependence of the matrix elements and/or densities of states. Note, however, that the Raman fraction contains less information than the full spectra, and its experimental determination may be affected by assumptions concerning line shapes of contributions due to both channels, in particular those concerning the presence or lack of the interference terms.

An analytic evaluation of the Raman fraction can be done only approximately. We multiply $\dot{R}(\mathcal{E})$ by the density of states in vacuum, $\rho_V(\mathcal{E})$, and integrate over $\mathcal{E}$. Doing this, the Lorentzian resonant excitation factor in Eq. (5) can be ignored (this is not an approximation: it will cancel out when the fraction is taken). When the integrals of $s_N(\mathcal{E})\rho_V(\mathcal{E})$ and

of $s_R(\mathcal{E})\rho_V(\mathcal{E})$ are evaluated we assume that all non-Lorentzian factors in the integrands vary slowly as a function of $\mathcal{E}$ in comparison with the fast variation by the strongly peaked Lorentzian factor. These non-Lorentzian factors can, therefore, be pulled outside the integrals with $\mathcal{E}$ replaced with the peak value of the corresponding Lorentzian, and only the Lorentzians are integrated. The integrals of the Lorentzians in Eqs. (6a) and (6b) then result in $2\pi/\Gamma_p^w$ and $2\pi/\Gamma_s^v$, respectively. On the other hand, the factors which were pulled outside the integrals are the same factors as those present in Eqs. (4a) and (4b), which result in the lifetime widths Γ_p^w and Γ_s^v, respectively, to appear in the numerators. Consequently, the lifetime widths cancel and we get

$$
\begin{aligned}
S_N &\equiv \int \rho_V(\mathcal{E}) s_N(\mathcal{E}) d\mathcal{E} \\
&\approx \theta(E_g + \hbar\omega_L - E_p - \epsilon_F) \\
&\quad \times \rho_S(E_g + \hbar\omega_L - E_p)|V_{p,d}(E_g + \hbar\omega_L - E_p)|^2,
\end{aligned}
\tag{7a}
$$

$$
\begin{aligned}
S_R &\equiv \int \rho_V(\mathcal{E}) s_R(\mathcal{E}) d\mathcal{E} \\
&\approx \rho_V(E_g + \hbar\omega_L - E_s)|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2.
\end{aligned}
\tag{7b}
$$

The interference term merely redistributes the intensities between the Lorentzian peaks so the integral of $s_{NR}(\mathcal{E})\rho_V(\mathcal{E})$ vanishes. The Raman fraction then is

$$
\begin{aligned}
f &\equiv \frac{S_R}{S_R + S_N} \\
&= \frac{\rho_V(E_g + \hbar\omega_L - E_s)|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2}{\theta(E_g + \hbar\omega_L - E_p - \epsilon_F)\rho_S(E_g + \hbar\omega_L - E_p)|V_{p,d}(E_g + \hbar\omega_L - E_p)|^2 + \rho_V(E_g + \hbar\omega_L - E_s)|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2}
\end{aligned}
\tag{8}
$$

which is a quite complicated function of ω_L.

The forms of Eqs. (7) and (8) indicate again that both the normal-Auger and Raman-Auger channels are treated on equal footing in the wave function formalism: the radiation frequency and the energy of the ground state enter the energy argument of the Auger emission matrix element $W_{s,d}$ and of the tunneling matrix element $V_{p,d}$ and both densities of states, in exactly the same manner in Eqs. (7). This is not surprising because evaluating the Raman fraction we have to integrate over all possible states of electrons emitted into vacuum exactly like was already done for electrons transferred to the substrate: the difference in the way in which both types of electrons are treated disappears. On the other hand, the objections listed in paragraphs (ii) and (iii) below Eqs. (6), concerning the presence of $\mathcal{E}$ and/or $\hbar\omega_L$ in the energy arguments of the substrate density of states and the tunneling matrix element, have become now irrelevant, at least as long as the approximations used to evaluate the integrals in Eqs. (7) are justified. Indeed, the product $\rho_S|V_{f,s}|^2$ has disappeared altogether along with the final-state lifetime width Γ_s^v, and the energy argument of $\rho_S|V_{p,d}|^2$ is $E_g + \hbar\omega_L - E_p$, i.e., that argued for in paragraph (iii).

The next step one would make is to assume that the energy dependence of $\rho_V|W_{s,d}|^2$ is much weaker than that of $\rho_S|V_{p,d}|^2$ because the assumption of an energy-independent $\rho_V|W_{s,d}|^2$ usually leads to good agreement of measured and calculated electron decay spectra for isolated atoms. Consequently, the *frequency dependence* of the Raman fraction becomes almost exclusively due to the *energy dependence* of the atom–substrate-electron transfer process, i.e., to the energy dependence of the product $\rho_S(\mathcal{E})|V_{p,d}(\mathcal{E})|^2$. This conclusion, although physically reasonable, should be reexamined in view of the fact that it was obtained using a method in which the intermediate results are in doubt and in which

the loss of quantum coherence in the process involving the electron transfer to the substrate cannot be not accounted for.

IV. DENSITY MATRIX APPROACH

The derivation leading to general expressions for the decay electron spectra for adsorbed species must be done within the framework appropriate for studying properties of a primary system interacting with a dissipative system (the reservoir). The formalism to be used should allow one to account for the loss of coherence in the primary system when an act of energy-particle exchange with the dissipative system occurs. The separation of the system into primary and dissipative subsystems is not unique and is not always easy to do. We assume initially that the primary system is just the adsorbed atom alone while the electronic system of the substrate together with its interactions with phonons, etc., is the reservoir. Generalization to another possible separation scheme will be examined in Sec. V with special attention being paid to the issue of how such a separation affects the predicted spectra.

The starting point is the time-dependent Liouville equation

$$
\frac{d}{dt}\hat{\rho}(t) + \frac{i}{\hbar}[\mathbb{H}(t),\hat{\rho}(t)] = 0
\tag{9}
$$

for the density matrix of the combined system, rather than the time-dependent Schrödinger equation for its quantum state. The time-dependent Hamiltonian $\mathbb{H}(t)$ will be specified in Sec. IV A. Then, the procedure to be followed consists of three steps.

First, one derives an *approximate Liouville* equation, i.e., the equation for the reduced density matrix which accounts for the dynamics of the primary system (i.e., the atom) only.

The outline is provided in Sec. IV B. The reduced density matrix is the trace of the density matrix for the entire system over the states of the reservoir. Under certain conditions, the properties of the reservoir and the reservoir-primary system interactions enter the approximate Liouville equation only in an averaged way, while the internal dynamics of the primary system and its interaction with the radiation field are still treated exactly. The approximate Liouville equation is no longer equivalent to the time-dependent Schrödinger equation in the usual sense in which the former can be derived from the latter by defining the elements of the density matrix as $\psi_m \psi_n^\star$ and getting the equations for their time evolution from the Schrödinger equations for the time evolution of the wave functions ψ_m.

Second, in the approximate Liouville equations, one has to simplify those (so far still exact) terms which account for the internal dynamics of the primary system and its interaction with the radiation field. The method is outlined and the results are presented in Sec. IV C. The result is the *effective Liouville* equation for the reduced density matrix [cf. Eqs. (24) below, followed by a discussion of its main features—a set of equations for its matrix elements rather than a single equation]. One of the attractive features of this result is that this equation can be expressed in terms of an effective non-Hermitian Hamiltonian [cf. Eq. (22)] which accounts for the internal interactions within the primary system and its interaction with radiation. This effective Hamiltonian generates all terms in the effective Liouville equations except those which account for the electron transfer to the substrate. The effective Hamiltonian could be taken as a starting point for the treatment of adsorbed systems which are more complicated than atoms, so that the internal molecular dynamics and/or the dynamics of their motion with respect to the substrate have to be accounted for.

Finally, the spectra of the decay electrons must be derived from the effective Liouville equation. Surprisingly, this step does not require any further approximations; the results are presented in Sec. IV D. The result is again Eq. (5) but $s_{NR}(\mathcal{E}) \equiv 0$ and $s_N(\mathcal{E})$ and $s_R(\mathcal{E})$ are given now in Eq. (26). A detailed discussion of the result and its confrontation with the results of Sec. III follows Eq. (26).

A. System and its Hamiltonian

The system consists of an atom with all its electrons (including an electron in vacuum, if present) and the electronic system of the metal substrate. In reference to Fig. 1, the relevant states of the atom are $|g\rangle$, $|d\rangle$, and $|p\rangle$, being the ground, core excited, and core ionic states, with energies E_g, E_d, and E_p, respectively. Rather than considering the two-valence-hole–one-electron-excited state $|s\rangle$ and the two-valence-hole state $|f\rangle$, we consider $|s\vec{k}\rangle$ and $|f\vec{k}\rangle$ by including an electron in vacuum with momentum $\hbar\vec{k}$ always associated with these states. The corresponding energies are $E_{s\vec{k}} = E_s + \mathcal{E}_{\vec{k}}$ and $E_{f\vec{k}} = E_f + \mathcal{E}_{\vec{k}}$ with $\mathcal{E}_{\vec{k}} = \hbar^2 k^2/2m$ (with energy zero at the vacuum level). With the free electron included, $|s\vec{k}\rangle$ and $|f\vec{k}\rangle$ belong to a continuum. In what follows we will reserve the indices l, m, and n and their primed counterparts to run through g, d, p, $s\vec{k}$, and $f\vec{k}$; i.e., Σ_l in-

cludes also summation over the wave vector of the free electron. All the states listed are assumed to form a complete set of states of the primary system.

We reserve Greek letters $\alpha, \beta, \ldots$ to label the general electronic states of the substrate (reservoir). The energy of the substrate state $|\alpha\rangle$ is E_α. Note that, in general, by $|\alpha\rangle$ we mean a many-electron state, not a state of a single electron in the substrate. Again, we assume that the $|\alpha\rangle$'s form a complete set of states of the reservoir.

The full Hamiltonian of the system is

$$\mathbb{H} = \mathbb{H}_0 + \mathbb{W} + \mathbb{R}(t) + \mathbb{H}_S + \mathbb{V}, \tag{10}$$

where $\mathbb{H}_S$ and $\mathbb{H}_0$ are, respectively, the Hamiltonian for the substrate electronic system and the Hamiltonian of an atom without the Coulomb interactions responsible for Auger processes; the latter are accounted for in $\mathbb{W}$. Here $\mathbb{R}(t)$ describes the atom-radiation interaction in the dipole approximation. In other words, $\mathbb{H}_0 + \mathbb{W} + \mathbb{R}(t)$ is the Hamiltonian necessary to treat the Raman-Auger process for a free atom. Finally, $\mathbb{V}$ accounts for the atom-substrate interactions responsible for the electron transfer between the subsystems. The explicit forms of each term are

$$\mathbb{H}_0 = \sum_m |m\rangle E_m \langle m|, \tag{11a}$$

$$\mathbb{W} = \sum_{m,m'} |m\rangle W_{m,m'} \langle m'|, \tag{11b}$$

$$\mathbb{R}(t) = \sum_{m,m'} |m\rangle R_{m,m'}(t) \langle m'|, \tag{11c}$$

$$\mathbb{H}_S = \sum_\alpha |\alpha\rangle \mathsf{E}_\alpha \langle \alpha| = \sum_{\vec{q}} \mathfrak{E}_{\vec{q}} c_{\vec{q}}^\dagger c_{\vec{q}}, \tag{11d}$$

$$\mathbb{V} = \sum_{m,m'} \sum_{\alpha,\alpha'} |m\alpha\rangle V_{m\alpha,m'\alpha'} \langle m'\alpha'|$$

$$= \sum_{\vec{q}} \sum_{m,m'} [V_{m,m'}(\mathfrak{E}_{\vec{q}}) c_{\vec{q}}^\dagger a_m^\dagger a_{m'} + \text{H.c.}]. \tag{11e}$$

We have assumed that the unperturbed electronic system of the substrate can be adequately represented by a Fermi sea of noninteracting (quasi)electrons occupying single-particle states $\vec{q}$ (which, if necessary, may include a band index), which results in the last form of $\mathbb{H}_S$, and of $\mathbb{V}$ to be in the second-quantization form. In the latter, $a_m^\dagger a_{m'}$ replaces an atom in the electronic state m' with an atom in the electronic state m. Extra restrictions are imposed on the matrix elements consistent with the model considered (cf. Fig. 1). Thus, it will be assumed that the radiation coupling matrix elements $R_{m,m'}(t)$ couple only $|g\rangle$ with $|d\rangle$. In the dipole approximation we have

$$R_{d,g}(t) = -\vec{\mathcal{E}}_0 \cdot \vec{D}_{d,g} \cos(\omega_L t) = -\frac{\hbar}{2} \Omega_{d,g}(e^{i\omega_L t} + e^{-i\omega_L t}), \tag{12}$$

where $\vec{\mathcal{E}}_0$ is the amplitude of the electromagnetic wave and ω_L is the radiation angular frequency. We have introduced the Bloch frequency $\Omega_{d,g}$ which we admit to be complex, so $\Omega_{d,g}^* = \Omega_{g,d}$. Similarly, the only nonvanishing matrix elements $W_{m,m'}$ are those in Eqs. (1a) and (2a) which connect state $|d\rangle$ with $|s\vec{k}\rangle$ and $|p\rangle$ with $|f\vec{k}\rangle$, respectively. More generally, the important point is that $\mathbb{W}$ and $\mathbb{R}(t)$ do not possess elements diagonal in the indices of the primary system (but they are both diagonal in and independent of the indices of the reservoir). On the other hand, $V_{m\alpha,m'\alpha'}$ is (i) off diagonal in the indices of the reservoir (i.e., it *vanishes* for $\alpha = \alpha'$) and (ii) it connects, as seen in Eqs. (1b) and (2b), either state $|d\rangle$ to $|p\rangle$ or $|s\vec{k}\rangle$ to $|f\vec{k}\rangle$ with *the same* $\vec{k}$. The latter restriction implies that the electron tunneling process from the atom to the substrate does not affect the state of a free electron already emitted. This is probably the most serious restriction in the model eliminating post-emission interactions from it: one might argue that if the tunneling is very effective, then the charge state change of the atom which it induces may catch up with the departing electron early enough to affect its state upon detection.

B. Approximate Liouville equation for the atom

The reduced density matrix is defined as the trace of $\hat{\rho}$ over the substrate degrees of freedom of the density matrix of the entire system:

$$\sigma_{m,n} = (\mathrm{Tr}_s \hat{\rho})_{m,n} = \sum_\alpha \rho_{m\alpha,n\alpha}. \qquad (13)$$

The derivation of the approximate Liouville equation for $\hat{\sigma}(t)$, using Zwanzig's projection operator method,[22] follows the path used in other contexts in Refs. 23. Here, we summarize the main assumptions needed in this derivation and present the result. The references quoted here should be consulted for technical details.

The main assumption is that the substrate relaxes to its own quasistationary state described by the reservoir density matrix $\hat{\rho}^{(S)}$ [i.e., here, its Fermi sea ground state; $\hat{\rho}^{(S)}$ should not be confused with the substrate density of states $\rho_S(\mathfrak{E})$] over the relaxation time τ^{res} which is much shorter than the characteristic time over which the slowly varying parts of the reduced density matrix for the primary system evolve. The relaxation time of the reservoir is determined by its internal interactions, its interaction with the phonon bath, etc. These interactions are not explicitly accounted for in the model. Instead, it is assumed that they are so strong that, effectively, they can be dropped from the Hamiltonian, and their effect is accounted for by averaging over the reservoir (i.e., over $\hat{\rho}^{(S)}$) the memory kernel in the resulting equation, linking the rate of change of $\hat{\sigma}(t)$ at an instant t to its earlier evolution. Summarizing, the main assumption requires that the intrareservoir interactions be much stronger than any other interactions accounted for explicitly in the model.

The next approximation deals with the memory kernel. Due to the averaging mentioned above, it is a Fourier integral over the energy spectrum of the reservoir with the char-

acteristic effective width Δ_S, and decays over a characteristic time $\tau_S = \hbar/\Delta_S$. If τ_S is much shorter than the characteristic time over which the slowly varying parts of the reduced density matrix $\hat{\sigma}$ significantly evolve or relax, then the Markovian approximation may be invoked and any reference to the past evolution is removed from the equation. The memory kernel is then replaced by a supermatrix[24] $\hat{\mathbb{S}}$ of transition rates. The characteristic evolution time of the slowly varying parts of $\hat{\sigma}(t)$ is itself determined by the strength of the interactions $\mathbb{V}$, $\mathbb{W}$, and $\mathbb{R}(t)$. So the condition for the Markovian approximation requires that these interactions be small compared to Δ_S.

This suggests the next approximation which allows us to treat these interactions in the Born approximation for the evaluation of the transition rate supermatrix $\hat{\mathbb{S}}$. The latter then becomes a bilinear function of the matrix elements of $\mathbb{V}$ which couple the primary system to the reservoir; it no longer depends on the interactions $\mathbb{W}$ and $\mathbb{R}(t)$ which affect only the primary system.

It is obvious from the above that a particular separation of the entire system into the primary one and the reservoir must be such that the reservoir-primary system interaction $\mathbb{V}$ is weak not only in comparison with the intrareservoir interactions; it must also be much smaller than the effective width of the reservoir energy spectrum. The effective width is determined by the width of the energy interval of $\mathfrak{E}_q^-$ over which the matrix elements of $\mathbb{V}$ do not vanish [cf. Eqs. (1b), (2b), and (11e)]. It may be considerably smaller than the actual width of the energy spectrum of the substrate. This is an important point: if some part of the atom-substrate interaction is strong and energy selective, then it has to be accounted for in the zeroth-order part of the Hamiltonian, i.e., in $\mathbb{H}_0$, and be used to determine the energy spectrum and electron configurations rather than be incorporated into $\mathbb{V}$ whose role is to account for the dynamics of transitions between these configurations. We will return to this point in Sec. V.

With all these simplifying assumptions the approximate Liouville equation for the reduced density matrix $\hat{\sigma}$ is obtained. Its convenient general form is

$$\frac{d}{dt}\hat{\sigma}(t) + \frac{i}{\hbar}[\mathbb{H}_0 + \mathbb{W} + \mathbb{R}(t), \hat{\sigma}(t)] = -\hat{\mathbb{S}}\hat{\sigma}(t), \qquad (14)$$

where the time-independent rate superoperator $\hat{\mathbb{S}}$ accounts for the dissipation into the substrate. With $\hat{\mathbb{V}} = 0$ we have $\hat{\mathbb{S}} = 0$, and the implications of the resulting Liouville equation would be the same as the implications of the time-dependent Schrödinger equation for a free atom in the radiation field, provided that initially the atom is in a pure state. The fact that the only nonvanishing matrix elements of $\hat{\mathbb{V}}$ are those between $|d\rangle$ and $|p\rangle$ and between $|s\vec{k}\rangle$ and $|f\vec{k}\rangle$ and that it has no diagonal elements in the reservoir (Greek indices) implies that many of the matrix elements of $\hat{\mathbb{S}}$ vanish. Some of the nonvanishing ones are real and can be expressed in terms of[23]

$$P_{m,l} = \frac{2\pi}{\hbar} \sum_{\alpha,\beta}^{\alpha \neq \beta} \rho_{\beta,\beta}^{(S)} |V_{m\alpha,l\beta}|^2 \delta(E_l + \mathsf{E}_\beta - E_m - \mathsf{E}_\alpha),$$

$$(15)$$

easily recognizable as the net transition rate from the atomic state $|l\rangle$ to $|m\rangle$, averaged over the quasistationary state of the substrate.[25] With all that, the equations for occupation probabilities $\sigma_{m,m}$ and correlations $\sigma_{m,n}$ (still referred to collectively as the approximate Liouville equation) are

$$\frac{d}{dt}\sigma_{m,m} + \frac{i}{\hbar}[\mathbb{W} + \mathbb{R}(t), \hat{\sigma}(t)]_{m,m}$$

$$= \sum_l^{l \neq m} P_{m,l}\sigma_{l,l} - \sum_l^{l \neq m} P_{l,m}\sigma_{m,m}, \qquad (16\text{a})$$

$$\frac{d}{dt}\sigma_{m,n} + i\omega_{m,n}\sigma_{m,n} + \frac{i}{\hbar}[\mathbb{W} + \mathbb{R}(t), \hat{\sigma}(t)]_{m,n}$$

$$= -\frac{1}{2}\sum_l^{l \neq (m,n)} (P_{l,m} + P_{l,n})\sigma_{m,n}, \qquad (16\text{b})$$

respectively. Here, $[\dots, \dots]_{m,n}$ denotes the (n,m)th matrix element of a commutator and

$$\omega_{m,n} = (E_m - E_n)/\hbar. \qquad (17)$$

The right-hand side of Eq. (16a) has the typical form encountered in linear master equations for occupation probabilities, but correlations still appear in the second term on the left-hand side. Consequently, Eq. (16b) for the correlations is needed. Its right-hand side accounts for dephasing due to the interactions with the substrate. The rates involved are just half of the rates with which the probabilities decay. Usually, another contribution to dephasing, called pure dephasing, exists. It would involve matrix elements of $\mathbb{V}$ diagonal in the reservoir indices, so it is absent from the present model.

Only a few equations in the entire set (16) will have terms generated by the rates $P_{m,n}$. Assuming that the electron system of the reservoir remains always in the ground state $|\alpha_F\rangle$ of the Fermi sea at $T=0$ we have $\hat{\rho}^{(S)} = |\alpha_F\rangle\langle\alpha_F|$. Using the last form in Eq. (11e) and accounting explicitly for all nonvanishing matrix elements of $\mathbb{V}$, one can show that the only nonvanishing rates in Eq. (15) are

$$P_{f\vec{k},s\vec{k}} \equiv \gamma_s^v = \frac{2\pi}{\hbar} \sum_{\vec{q}} \theta(\mathfrak{E}_{\vec{q}} - \epsilon_F)|V_{f,s}(\mathfrak{E}_{\vec{q}})|^2 \delta(E_s - E_f - \mathfrak{E}_{\vec{q}})$$

$$= \Gamma_s^v/\hbar, \qquad (18\text{a})$$

$$P_{p,d} \equiv \gamma_d^v = \frac{2\pi}{\hbar} \sum_{\vec{q}} \theta(\mathfrak{E}_{\vec{q}} - \epsilon_F)|V_{p,d}(\mathfrak{E}_{\vec{q}})|^2 \delta(E_d - E_p - \mathfrak{E}_{\vec{q}})$$

$$= \Gamma_d^v/\hbar, \qquad (18\text{b})$$

i.e., the rates already encountered in Eqs. (4b) and (4d), respectively [this is seen by replacing $\Sigma_{\vec{q}}$ in Eqs. (18) with the integration over $\mathfrak{E}_{\vec{q}}$ with the substrate density of states $\rho_S(\mathfrak{E}_{\vec{q}})$].

The decay electron spectra are expressed in terms of $d(\sigma_{s\vec{k},s\vec{k}} + \sigma_{f\vec{k},f\vec{k}})/dt$. So only equations for those occupation probabilities and correlations have to be considered which couple directly or indirectly to the equations for the two occupation probabilities given above. Examining the structure of the commutators and the nonvanishing tunneling rates in Eqs. (16) one can show that the equations for all occupation probabilities ($\sigma_{g,g}$, $\sigma_{d,d}$, $\sigma_{p,p}$, $\sigma_{s\vec{k},s\vec{k}}$, and $\sigma_{f\vec{k},f\vec{k}}$), and only for certain correlations ($\sigma_{g,d}$, $\sigma_{g,s\vec{k}}$, $\sigma_{d,s\vec{k}}$, $\sigma_{s\vec{k},s\vec{k}'}$, $\sigma_{p,f\vec{k}}$, and $\sigma_{f\vec{k},f\vec{k}'}$ and correlations complex conjugated to those) form a closed set of equations: the equations for these occupation probabilities and correlations do not contain correlations not listed.[26]

All equations are listed explicitly in the Appendix together with some comments concerning their structure. They should be solved subject to the initial conditions

$$\sigma_{g,g}(t=0) = 1, \qquad (19\text{a})$$

$$\sigma_{m,n}(t=0) = 0 \quad \text{for} \quad m, n \neq g. \qquad (19\text{b})$$

The electron emission rate $\dot{R}(\mathcal{E})$ is equal to the long-time limit of $d(\sigma_{s\vec{k},s\vec{k}} + \sigma_{f\vec{k},f\vec{k}})/dt$ with $\mathcal{E}$ substituted for $\mathcal{E}_{\vec{k}}$.

C. Effective Liouville equation for the atom

The approximate Liouville equation (16) [or, explicitly, Eqs. (A1)] is a set which still has to be simplified to be tractable. The approximations to be made affect only terms on the left-hand side of Eqs. (14) or (16), and are similar to those usually made in a set of coupled time-dependent Schrödinger equations for an isolated atom to arrive at the amplitude of the Raman-Auger process [Eq. (3b)] in third-order perturbation theory. Technically, they are considerably more difficult to do for the Liouville than for the Schrödinger equations. These approximations involve three steps.

(a) First, we modify the equations in such a way that their solutions automatically account only for contributions due to the lowest nonvanishing order in the radiation coupling (we temporarily use $\sigma_{m,n}^{(j)}$ to denote the contribution of order j to $\sigma_{m,n}$). With the initial conditions (19) it is easy to see, by inspecting Eqs. (A1), that the leading nonvanishing order contribution to the ground-state occupation probability is $\sigma_{g,g}^{(0)}$ (the radiation can affect it only in the second order). As to correlations involving the ground state $|g\rangle$, they are of first order, and among them only $\sigma_{g,d}^{(1)}$ and $\sigma_{g,s\vec{k}}^{(1)}$ are relevant. For all other occupation probabilities and correlations the lowest-order nonvanishing contributions are of second order. In all cases the order of the next nonvanishing contribution is always higher by 2 than the lowest nonvanishing one. If we keep only contributions of the lowest nonvanishing order to $\sigma_{m,n}$, we can ignore the superfluous superscript (j) denoting the contribution's order. This approximation substitutes $\sigma_{g,g}(t) = 1$ in any equation where $\sigma_{g,g}(t)$ is needed; i.e., the depletion of the ground state due to the excitation process is ignored. It also removes the last term on the right-hand side of Eq. (A1c) for $\sigma_{g,s\vec{k}}(t)$—it would contribute $\sigma_{g,s\vec{k}}^{(3)}$ to the solution.

(b) Second, we employ the rotating-wave approximation (RWA) in which rapidly oscillating terms on the right-hand side of the equations (for occupation probabilities and slowly varying parts of correlations) are ignored. This step assumes $|\omega_L - \omega_{d,g}| \ll \omega_{d,g}$, i.e., that the detuning of the radiation frequency away from the excitation resonance is moderate. It is very well met in all cases of interest in which the excitation energy is usually of the order of a few hundred eV while the detuning is not larger than a few eV. Technically, the RWA requires merely dropping the $\exp(+i\omega_L t)$ term in Eq. (12) for the radiation coupling matrix element $R_{d,g}(t)$.

(c) Third, some equations [like Eqs. (A1b), (A1d), (A1f), (A1h), and (A1j)] couple the rate of change of a particular $\sigma_{m,n}(t)$ to all correlations involving configurations $|s\vec{k}\rangle$ or $|f\vec{k}\rangle$. A typical term responsible for such a coupling is, for example, $\Sigma_{\vec{k}} W_{s\vec{k},d} \sigma_{g,s\vec{k}}$. A systematic procedure is developed which allows us to replace such terms with expressions linking the rate of change of this particular $\sigma_{m,n}(t)$ to its own time evolution at all times earlier than t. The memory kernels present in such expressions are Fourier-type integrals over the effective width Δ_V of the electron spectrum in vacuum [determined by the width of the $\mathcal{E}_{\vec{k}}$ dependence of $W_{s\vec{k},d}$ or $W_{f\vec{k},p}$—cf. Eqs. (1a) and (2a)], so they vanish over a characteristic time $\tau_V = \hbar/\Delta_V$. If the characteristic time over which all occupation probabilities and slowly varying parts of correlations relax or significantly evolve [the time determined by the strength of $\mathbb{W}$ and $\mathbb{R}(t)$, the lifetime due to the interaction with the substrate, and by the radiation detuning away from the excitation resonance], i.e., when

$$\tau_V \equiv \hbar/\Delta_V \ll 1/\gamma_d^v, \quad \hbar/|W|, \quad 1/|\omega_L - \omega_{d,g}|, \quad (20)$$

then the Markovian approximation may be invoked and any reference to the past evolution is removed by replacing each memory kernel with either one of the two following decay rates:

$$\gamma_d^w = \frac{2\pi}{\hbar} \sum_{\vec{k}} |W_{s\vec{k},d}|^2 \delta(E_d - E_s - \mathcal{E}_{\vec{k}}) \equiv \Gamma_d^w/\hbar, \quad (21a)$$

$$\gamma_p^w = \frac{2\pi}{\hbar} \sum_{\vec{k}} |W_{f\vec{k},p}|^2 \delta(E_p - E_f - \mathcal{E}_{\vec{k}}) \equiv \Gamma_p^w/\hbar. \quad (21b)$$

These are the rates already encountered in Eqs. (4c) and (4a), respectively, as can be seen when Eqs. (1a) and (1b) are used and $\Sigma_{\vec{k}}$ in Eqs. (21) is replaced with integration over $\mathcal{E}_{\vec{k}}$ with the free-electron density of states $\rho_V(\mathcal{E}_{\vec{k}})$. More precisely, the limits $\gamma_d^v \to 0$ and/or $\gamma_s^v \to 0$ must be taken at some point to get the above rates and corrections to $E_d, E_p, \ldots$ due to $\mathbb{W}$ are ignored. The conditions (20) are easy to satisfy in view of the assumed weakness of both $\mathbb{V}$ and $\mathbb{W}$ and the moderate amount of detuning.

These three approximation steps convert the *approximate* Liouville equations (16) [or, explicitly, Eqs. (A1)] into the *effective* Liouville equations. Formally, these equations still can be written in the same form as Eqs. (16) but with the interaction Hamiltonians $\mathbb{W}$ and $\mathbb{R}(t)$ replaced with non-Hermitian effective interaction Hamiltonians $\mathcal{W}$ and $\mathcal{R}(t)$ given by

$$\mathcal{W} = |d\rangle \left(-\frac{i}{2} \Gamma_d^w \right) \langle d| + |p\rangle \left(-\frac{i}{2} \Gamma_p^w \right) \langle p|$$

$$+ \sum_{\vec{k}} (|s\vec{k}\rangle W_{s\vec{k},d} \langle d| + |f\vec{k}\rangle W_{f\vec{k},p} \langle p|), \quad (22a)$$

$$\mathcal{R}(t) = |d\rangle \left(-\frac{\hbar}{2} \Omega_{d,g} e^{-i\omega_L t} \right) \langle g|, \quad (22b)$$

where $\Gamma_d^w \equiv \hbar \gamma_d^w$ and $\Gamma_p^w \equiv \hbar \gamma_p^w$ are the Auger decay linewidths ($\hbar \times$ rates) defined in Eqs. (21) [or Eqs. (4c) and (4a), respectively]. For non-Hermitian effective Hamiltonians the commutator in Eqs. (16) (i.e., the action of the Liouville operator) must be replaced as follows:

$$[\mathbb{W} + \mathbb{R}(t), \hat{\sigma}(t)] \to \mathcal{H}(t)\hat{\sigma}(t) - \hat{\sigma}(t)\mathcal{H}(t)^\dagger, \quad (23)$$

where $\mathcal{H}(t)$ stands for $\mathcal{W} + \mathcal{R}(t)$.

In comparison with $\mathbb{W}$ given in Eq. (11b) the effective interaction $\mathcal{W}$ does not contain the matrix elements $W_{d,s\vec{k}}$ and $W_{p,f\vec{k}}$ but, instead, has diagonal imaginary matrix elements $-i\Gamma_d^w/2$ and $-i\Gamma_p^w/2$ which act as the Auger decay widths for the levels $|d\rangle$ and $p\rangle$, respectively. Similarly, $\mathcal{R}(t)$ does not contain the matrix element $R_{g,d}(t)$ which eliminates the radiation-induced transitions from $|d\rangle$ back to $|g\rangle$ [this takes care of the simplification (a) listed in the initial paragraph of this section], and the surviving matrix element $R_{d,g}(t)$ has lost its part proportional to $\exp(+i\omega_L t)$ on the account of the rotating-wave approximation. Although we here arrived at the effective Hamiltonians $\mathcal{W}$ and $\mathcal{R}(t)$ by considering the approximate Liouville equations (A1), it is quite comforting to realize that for the case of an isolated atom, for which the Liouville equation approach is unnecessary, one gets almost exactly the same effective Hamiltonian [i.e., without the terms involving $|p\rangle$] by starting from the time-dependent Schrödinger equation. One may speculate that for molecular adsorbates for which the intramolecular motion affects the dynamics of the electron transfer to the substrate or the electron emission events, and in cases in which they are affected by the motion with respect to the substrate, one can start considerations from a phenomenological non-Hermitian effective Hamiltonian in which the width parameters $-i\Gamma_d^w/2$ and $-i\Gamma_p^w/2$ are replaced with optical potentials depending on these coordinates. In such cases, however, also the electron transfer widths Γ_s^v and Γ_d^v appearing on the right-hand side of Eqs. (16) should be replaced with some coordinate-dependent functions. In any case, starting a model from the effective non-Hermitian Hamiltonian from which the effective Liouville equation can be constructed is an attractive proposition.

The asymmetric role played by the Auger decay and the electron tunneling to the substrate rates in the present formulation is now obvious: while the former can be incorporated into the effective non-Hermitian Hamiltonian, the latter [present as on the right-hand side of Eqs. (16)] cannot be incorporated into any effective non-Hermitian Hamiltonian. In other words, *it is impossible, even approximately, to describe the evolution of the primary system (the atom) in*

terms of a time-dependent Schrödinger equation with a non-Hermitian Hamiltonian. The effective Liouville equation must be used instead.

We can now list all relevant effective Liouville equations. First, as indicated before [paragraph (a) at the beginning of this section] we have $\sigma_{g,g}(t) = 1$. Then, solutions for $\sigma_{s\vec{k},s\vec{k}'}$ and for $\sigma_{f\vec{k},f\vec{k}'}$ for $\vec{k} \neq \vec{k}'$ are no longer needed. So the minimum set of equations needed is

$$\frac{d}{dt}\sigma_{g,d} + [i\omega_{g,d} + (\gamma_d^v + \gamma_d^w)/2]\sigma_{g,d} = -\frac{i}{2}\Omega_{g,d}e^{i\omega_L t}, \tag{24a}$$

$$\frac{d}{dt}\sigma_{g,s\vec{k}} + [i\omega_{g,s\vec{k}} + \gamma_s^v/2]\sigma_{g,s\vec{k}} = \frac{i}{\hbar}W_{d,s\vec{k}}\sigma_{g,d}, \tag{24b}$$

$$\frac{d}{dt}\sigma_{d,d} + (\gamma_d^v + \gamma_d^w)\sigma_{d,d}$$
$$= \frac{i}{2}(\Omega_{d,g}e^{-i\omega_L t}\sigma_{g,d} - \Omega_{g,d}e^{i\omega_L t}\sigma_{d,g}), \tag{24c}$$

$$\frac{d}{dt}\sigma_{d,s\vec{k}} + [i\omega_{d,s\vec{k}} + (\gamma_s^v + \gamma_d^v + \gamma_d^w)/2]\sigma_{d,s\vec{k}}$$
$$= \frac{i}{\hbar}W_{d,s\vec{k}}\sigma_{d,d} + \frac{i}{2}\Omega_{d,g}e^{-i\omega_L t}\sigma_{g,s\vec{k}}, \tag{24d}$$

$$\frac{d}{dt}\sigma_{s\vec{k},s\vec{k}} + \gamma_s^v\sigma_{s\vec{k},s\vec{k}} = -\frac{i}{\hbar}(W_{s\vec{k},d}\sigma_{d,s\vec{k}} - W_{d,s\vec{k}}\sigma_{s\vec{k},d}), \tag{24e}$$

$$\frac{d}{dt}\sigma_{p,p} + \gamma_p^w\sigma_{pp} - \gamma_d^v\sigma_{d,d} = 0, \tag{24f}$$

$$\frac{d}{dt}\sigma_{p,f\vec{k}} + [i\omega_{p,f\vec{k}} + \gamma_p^w/2]\sigma_{p,f\vec{k}} = \frac{i}{\hbar}W_{p,f\vec{k}}\sigma_{p,p}, \tag{24g}$$

$$\frac{d}{dt}\sigma_{f\vec{k},f\vec{k}} - \gamma_s^v\sigma_{s\vec{k},s\vec{k}} = -\frac{i}{\hbar}(W_{f\vec{k},p}\sigma_{p,f\vec{k}} - W_{p,f\vec{k}}\sigma_{f\vec{k},p}), \tag{24h}$$

The initial conditions are given in Eq. (19b).

We must solve Eqs. (24) and extract the long-time limit of $d(\sigma_{s\vec{k},s\vec{k}} + \sigma_{f\vec{k},f\vec{k}})/dt$. Before presenting the solution we discuss the structure of Eqs. (24) to make the obtained result intuitively plausible on physical grounds:

(i) The structure of Eqs. (24) is transparent enough to permit guessing some generalizations without going through all the mathematical machinery used to derive them. For example, the possible decay of the final state $|f\vec{k}\rangle$ can be accounted for by adding $\gamma_f/2$ inside the square brackets on the left-hand side of Eq. (24g) and a term $\gamma_f\sigma_{f\vec{k},f\vec{k}}$ to the left-hand side of Eq. (24h).

(ii) Inspecting Eqs. (24e) and (24h) we note that in the sum $d(\sigma_{s\vec{k},s\vec{k}} + \sigma_{f\vec{k},f\vec{k}})/dt$ the term $\gamma_s^v\sigma_{s\vec{k},s\vec{k}}$, responsible for direct flow of the occupation probability from state $|s\vec{k}\rangle$ into $|f\vec{k}\rangle$ cancels out. This does not imply, however, that the life-

time of the state $|s\vec{k}\rangle$ drops out entirely because $\gamma_s^v/2$ still contributes to the dephasing of correlations in Eqs. (24b) and (24d).

(iii) It is easy to guess that the contribution to the electron spectra due to the normal-Auger process is entirely due to the right-hand side of Eq. (24h) for $d\sigma_{f\vec{k},f\vec{k}}/dt$, and the contribution due to the Raman-Auger channel is due to the right-hand side of Eq. (24e) for $d\sigma_{s\vec{k},s\vec{k}}/dt$. The latter is physically appealing because it indicates that, in fact, it is the state $|s\vec{k}\rangle$ rather than $|f\vec{k}\rangle$ which should be considered as the final state along the Raman-Auger channel. The subsequent electron transfer decay from $|s\vec{k}\rangle$ to $|f\vec{k}\rangle$ affects this spectrum [through $\gamma_s^v/2$ in Eq. (24b)] by broadening the spectral line, as seen later in Eq. (26a). In the limit $\Gamma_s^v \to 0$ the Lorentzian in the first line of Eq. (26a) becomes Dirac's delta function $\delta(\mathcal{E} + E_s - E_g - \hbar\omega_L)$ of the energy conservation in a coherent one-step Raman-Auger process consisting of two virtual transitions (events): the primary excitation followed by the Auger decay.

(iv) The modification mentioned in comment (i) would introduce an extra lifetime broadening of the normal-Auger spectral line but would not affect the Raman-Auger line because the rate of decay of $|f\vec{k}\rangle$ does not affect any equation needed for the solution of Eq. (24e). This is a quite obvious conclusion: whether $|f\vec{k}\rangle$ decays or not does not influence the decay rate of $|s\vec{k}\rangle$ or any correlation between this state and any other state involved along the Raman-Auger channel.

(v) Note also the particularly simple structure of Eq. (24f) for the rate of change of the occupation probability of state $|p\rangle$: it is due to direct competition between its increase due to electron transfer into the substrate at a rate $\gamma_d^v\sigma_{d,d}$ from the state $|d\rangle$ and its Auger decay at a rate $\gamma_p^w\sigma_{p,p}$. This equation involves only occupation probabilities but not correlations and, consequently, the electron transfer into the substrate is phase decoupled from the primary photoexcitation along the normal-Auger channel. The electron transfer to the substrate (increasing the occupation probability of $|p\rangle$) and the Auger decay (decreasing it) are truly independent events from the perspective of the occupation probability of state $|p\rangle$. The energy is conserved for *each* of them because each of the rates in Eq. (24f), γ_d^v and γ_p^w, is a rate for an energy conserving event, as seen in Eqs. (18b) and (21b), respectively. Note, however, that the occupation probability $\sigma_{p,p}$ does not affect the rate of change of the final state along this channel ($|f\vec{k}\rangle$) directly, but rather through the correlations $|\sigma_{p,f\vec{k}}\rangle$ between these two states. In other words, although it is possible to use Eq. (24g) to eliminate $\sigma_{p,f\vec{k}}$ from Eq. (24h) in favor of the occupation probability $\sigma_{p,p}$, the relation obtained in this way links the rate of change of $\sigma_{f\vec{k},f\vec{k}}$ at an instant t to the entire past evolution of $\sigma_{p,p}$ rather than to its value at t—i.e., the right-hand side of Eq. (24h) *cannot* be written in a trivial rate form $\gamma\sigma_{p,p}$, indicating again that the Auger decay event does not scramble phase relations between states it involves even along the normal-Auger channel.

(vi) Note also that the primary initial excitation affects the

occupation probability of the state $|d\rangle$ only indirectly by continuously building up correlations between the ground and the core-hole-excited state [cf. Eqs. (24a) and (24b)]. The radiation field also has a combined direct and indirect influence on all correlations between the state $|d\rangle$ and any other state, but none of them, except for the correlation between $|d\rangle$ and $|s\vec{k}\rangle$ along the Raman-Auger channel, influences the electron decay spectra. Correlations of $|d\rangle$ with any state along the normal-Auger channel are irrelevant. This supports the earlier conclusion [in comment (v)] that the primary excitation and the electron transfer into the substrate along the normal-Auger channels are two independent processes. One important implication of this fact is that the electron density of states in the substrate $\rho_S(\mathfrak{E})$ and the electron transfer matrix element $V_{m,n}(\mathfrak{E})$ will enter the decay electron spectra only through the rates γ_s^v and γ_d^v. So, as seen from Eqs. (4b) and (4d), the energy of the primary excitation photon ($\hbar\omega_L$) will not appear anywhere in the energy arguments of ρ_S and $V_{m,n}$. We will return to this point at the end of the next section and in Sec. V.

D. Decay electron spectra

We must solve Eqs. (24) extracting the long-time limit of $d(\sigma_{s\vec{k},s\vec{k}}+\sigma_{f\vec{k},f\vec{k}})/dt$. This can be done *without* any further approximations, most efficiently by taking the Laplace transform of all equations in Eqs. (24) and proceeding with a systematic solution of the obtained set of algebraic equations. The long-time limit of interest is

$$
\lim_{t\to\infty}\left\{\frac{d}{dt}[\sigma_{s\vec{k},s\vec{k}}(t)+\sigma_{f\vec{k},f\vec{k}}(t)]\right\}
$$
$$
=\lim_{z\to 0}\{z(z[\hat{\sigma}_{s\vec{k},s\vec{k}}(z)+\hat{\sigma}_{f\vec{k},f\vec{k}}(z)])\}, \quad (25)
$$

where $\hat{\sigma}_{m,n}(z)$ denotes the Laplace transform of $\hat{\sigma}_{m,n}(t)$ [note the difference in notation: $\hat{\sigma}(t)$, e.g., in Eq. (14), denotes the reduced density matrix *operator* while $\hat{\sigma}_{m,n}(z)$ here denotes the Laplace transform of one of its matrix elements]. This is a quite tedious but rather straightforward calculation and we stress again that no approximations are involved in it.

For the rate of emission of electrons with energy $\mathcal{E}$ we get again Eq. (5) but now *without* the interference term; i.e., we get $s_{NR}(\mathcal{E})\equiv 0$. For the normal-Auger and the Raman-Auger contributions $s_N(\mathcal{E})$ and $s_R(\mathcal{E})$ we get [compare with Eqs. (6) obtained in the wave function approach]

$$
s_N(\mathcal{E})=\frac{\Gamma_d^v}{\Gamma_p^w}|W_{f,p}(\mathcal{E})|^2\frac{\Gamma_p^w/2\pi}{(\mathcal{E}+E_f-E_p)^2+(\Gamma_p^w/2)^2}
$$
$$
=\theta(E_d-E_p-\epsilon_F)\rho_S(E_d-E_p)
$$
$$
\times\frac{|W_{f,p}(\mathcal{E})V_{p,d}(E_d-E_p)|^2}{(\mathcal{E}+E_f-E_p)^2+(\Gamma_p^w/2)^2}, \quad (26a)
$$

$$
s_R(\mathcal{E})=|W_{s,d}(\mathcal{E})|^2\frac{\Gamma_s^v/2\pi}{(\mathcal{E}+E_s-E_g-\hbar\omega_L)^2+(\Gamma_s^v/2)^2}
$$
$$
=\theta(E_s-E_f-\epsilon_F)\rho_S(E_s-E_f)
$$
$$
\times\frac{|V_{f,s}(E_s-E_f)W_{s,d}(\mathcal{E})|^2}{(\mathcal{E}+E_s-E_g-\hbar\omega_L)^2+(\Gamma_s^v/2)^2}, \quad (26b)
$$

where one uses Eqs. (4b) and (4d) for Γ_s^v and Γ_d^v, respectively, to go from the first to the second line in both expressions.

Note that in Eqs. (26) (the second line of each one), in contrast to the expressions in Eq. (6), the θ function, the substrate density of states ρ_S, and the matrix elements for the electron transfer to the substrate $V_{m,n}$ (i.e., all quantities related directly to the substrate) contain neither the energy of the emitted electron ($\mathcal{E}$) nor the energy of the absorbed photon ($\hbar\omega_L$). This is the result of the loss of coherence between the photon absorption and the electron emission process if the electron transfer to the substrate is sliced in between them. In other words, coherence between the photon absorption and the electron emission is preserved in the Raman-Auger channel because the electron transfer to the substrate is here the last event which merely contributes to the lifetime width of the post-emission state $|s\rangle$, but the coherence is destroyed in the normal-Auger channel because the electron transfer to the substrate intervenes between them. The symmetry between both channels, present in the wave function approach, does not occur here.

Going into more details, the factor $\rho_S(E_s-E_f)|V_{f,s}(E_s-E_f)|^2$ in the Raman-Auger contribution to the spectra not only does not contain $\hbar\omega_L$ and $\mathcal{E}$ in the energy argument [their presence was found troublesome in paragraph (ii) below Eqs. (6)] but it introduces also the lifetime width directly into the numerator, as seen in the first line of Eq. (26b). In the limit of a free atom, obtained by setting $\rho_S\to 0$, we have $\Gamma_s^v\to 0$ which leads to $s_R(\mathcal{E})\to|W_{s,d}(\mathcal{E})|^2\delta(\mathcal{E}+E_s-E_g-\hbar\omega_L)$ [best seen from the first line of Eq. (26b)]. This is exactly the expected result for the Raman-Auger process for an isolated atom. At the same time, we have $s_N(\mathcal{E})\to 0$ for $\rho_S\to 0$ because the Lorentzian in Eq. (26a) is not affected by taking the limit. As required, the normal-Auger process can only occur in the presence of a substrate.

We have argued in paragraph (iii) below Eqs. (6) that for the normal-Auger process the energy argument of $\rho_S|V_{p,d}|^2$ should not contain the energy $\mathcal{E}$ of the electron emitted into vacuum but it should contain the energy $\hbar\omega_L$ of the photon initiating the process. This is not what we see in Eq. (26a) in which the energy argument is just E_d-E_p. In comparison with Eq. (6a) the argument has lost both $\mathcal{E}$ and $\hbar\omega_L$ dependence rather than only the former. We will return to this point in Sec. V.

Turning our attention to the Raman fraction we again evaluate the integrals defined in Eqs. (7) doing the same approximation as there: replace $\mathcal{E}$ in all slowly varying factors [here only in $\rho_V(\mathcal{E})$ and in $|W_{m,n}(\mathcal{E})|^2$] with the peak value of the corresponding Lorentzian factor and then integrate the Lorentzian only. Using Eqs. (4) one gets

$$S_N \approx \theta(E_d - E_p - \epsilon_F)\rho_S(E_d - E_p)|V_{p,d}(E_d - E_p)|^2 = \Gamma_d^v/2\pi, \tag{27a}$$

$$S_R \approx \rho_V(E_g + \hbar\omega_L - E_s)|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2. \tag{27b}$$

We see that while S_N is just the contribution to the lifetime width of the core-excited state $|d\rangle$ by electron transfer to the substrate and is not equal to S_N obtained in the wave function approach [Eq. (7a)], S_R is the same as in the wave function approach [i.e., the same as in Eq. (7b)] and it is *not* equal to $\Gamma_d^w/2\pi$ [given in Eq. (4c)], the contribution to the lifetime width of the core excited state by the Auger decay.

The lack of symmetry between S_N and S_R is now obvious. The Raman fraction defined in the first line of Eq. (8) becomes

$$f = \frac{2\pi\rho_V(E_g + \hbar\omega_L - E_s)|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2}{\Gamma_d^v + 2\pi\rho_V(E_g + \hbar\omega_L - E_s)|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2}. \tag{28}$$

In contrast to the expression obtained in Eq. (8) the Raman fraction depends on the frequency of the exciting radiation only through the energy argument of the product of the vacuum density of states and the Auger decay matrix element: $\rho_V(\mathcal{E})|W_{s,d}(\mathcal{E})|^2$ with $\mathcal{E} = E_g + \hbar\omega_L - E_s$. As argued, however, in the two last sequences of paragraph (iii) below Eqs. (6), S_N and, consequently, the Raman fraction are expected (and found experimentally) to contain $\rho_S(\mathfrak{E})|V_{p,d}(\mathfrak{E})|^2$ with $\mathfrak{E} = E_g + \hbar\omega_L - E_p$, rather than $\mathfrak{E} = E_d - E_p$ as obtained in Eqs. (27a) and (28). Paradoxically, the Raman fraction obtained within the physically unacceptable—because of its neglect of coupling-induced phase loss—wave function approach seems to make more physical sense than that obtained using the density matrix method. A way to remedy this is proposed next.

V. GENERALIZATIONS

One of the essential assumptions made in deriving the results (26)–(28) in the preceding section is that the excited atom-substrate interaction is weak enough to be treated within the Born approximation. In this approach the entire effect of this interaction on the core-excited state $|d\rangle$ of the atom is to merely provide it with a lifetime width. Consequently, the substrate density of states $\rho_S(\mathfrak{E})$ and the tunneling matrix element $V_{p,d}(\mathfrak{E})$ appear in the expression (26a) for the normal-Auger contribution to the electron spectra with their energy argument $\mathfrak{E}$ equal to the energy difference $E_d - E_p$ between states $|d\rangle$ and $|p\rangle$, irrespective of whether the primary excitation is tuned precisely to or away from the $|d\rangle$ resonance. This is adequate for broad excitation linewidths for which the degree of exact tuning of the radiation within the excitation resonance has a small effect on the electron decay spectra. For nearly monochromatic excitation with a linewidth substantially smaller than the broadening of the core-excited state one should allow for the fact that the interaction of the latter with the substrate is not necessarily weak. In such a case it is not valid to consider this interaction within the perturbation approach.

To account for the strongly interacting case we can try to divide the entire atom-substrate system into three rather than two subsystems: (i) the atom, (ii) the cluster of substrate atoms adjacent to the adsorbed-atom (referred to as the adsorption-site cluster) with which the atom interacts strongly, and (iii) the rest of the substrate (the reservoir) with which the atom interacts only indirectly through the adsorption-site cluster. In principle, one could generalize the density matrix approach to such a case, but the necessity of treating the atom-adsorption-site cluster interactions nonperturbatively renders such an approach intractable. One can, however, attempt a much simpler treatment, basically identical to the density matrix approach leading to the results from the previous section, in which the atom plus the adsorption-site cluster is treated as the dynamic primary system interacting, now weakly, with the rest of the substrate. This approach is expected to be valid when the interactions between the atom and the adsorption-site cluster are so strong that an electron transfer between the atom and the cluster happens on time scales much shorter than any other electronic process which we want to account for explicitly. This is the case at least for chemisorbed atoms or molecules. The price paid by such an approach is the necessity of dealing with a substantially increased number of electronic configurations (states) of the primary dynamic system (i.e., the states to be accounted for in the zeroth-order Hamiltonian), in comparison with the situation in which the primary dynamic system was merely an atom. As long as, however, these configurations are treated phenomenologically with parameters describing them taken from experiment or treated as free-fitting parameters, the problem is still tractable.

The zeroth-order description requires then to consider the quasistationary electronic states of an atom interacting with the adsorption-site cluster. One can visualize that each electronic configuration of the atom considered so far (i.e., $|g\rangle$, $|d\rangle$, $|p\rangle$, $|s\rangle$, and $|f\rangle$) hybridizes with the electronic states of the cluster. For the purpose of this model we account only for the hybridization of the core-excited state $|d\rangle$: hybridization of the ground state is not of importance (because if present it still leads to a sharp ground state), and that of the final state $|f\rangle$ influences the results trivially (this is why we have ignored in our model the possibility that this state interacts with the substrate at all, despite the certain presence of screening). Hybridization of the $|p\rangle$ and $|s\rangle$ states can be easily accounted for without leading to any interesting effects. The core-excited state of the atom hybridized with the states of the adsorption-site cluster leads to a series of states distributed in energy over a certain interval and spatially localized on the atom *and* the cluster. Formally, we can incorporate this into our formalism by considering the index d as an index running through all these states. It is important to note that the wave function of each of these states contains, as an admixture, the wave function of the original core-excited state. So each of them is coupled to the ground state $|g\rangle$ by the radiation field, and direct radiative excitation from the latter to any of the $|d\rangle$ states is possible.

Before continuing we should note that the given picture in which the strong atom-substrate interaction is attributed to the atom-adsorption-site cluster interaction does not have to

be the only possibility. We have already seen in Sec. IV B [cf. discussion in several paragraphs leading to Eq. (14)] that one of the necessary conditions allowing us to replace the interaction $\mathbb{V}$ in the exact Liouville equation (9) with the rate superoperator $\hat{\mathbb{S}}$ in the approximate Liouville equation (14) is that matrix elements of $\mathbb{V}$ effectively allow tunneling into the substrate states distributed over an energy continuum so broad that memory effects could be ignored. One might, however, visualize a situation in which some parts of $\mathbb{V}$ couple the core-hole-excited state only to substrate states distributed over an energy interval Δ_S, which is small enough to be comparable to the typical magnitude of the matrix elements $\mathbb{V}$ themselves. Symmetry selection rules may play a role here. It is obvious that these parts of $\mathbb{V}$ cannot be incorporated into $\hat{\mathbb{S}}$ and cannot be treated as a perturbation. They must be included in the zeroth-order Hamiltonian, leading again to a relatively narrow band of $|d\rangle$ states localized partially on the adsorbed atom but having substantially delocalized components. The interaction of these states with truly delocalized states of the substrate distributed over a much broader energy interval is represented by the matrix elements $V_{p,d}(\mathcal{E})$ entering $\hat{\mathbb{S}}$ and then treated within the formalism developed in Sec. IV.

If the individual $|d\rangle$ states are not coupled to each other, then any correlations between theses states are irrelevant and the theoretical approach described in Secs. IV C and IV D still applies. Effectively, the result for the electron decay spectrum, which is obtained, is again Eq. (5) with $s_N(\mathcal{E})$ and $s_R(\mathcal{E})$ given in Eqs. (26a) and (26b), respectively [and, obviously, $s_{NR}(\mathcal{E})\equiv 0$], but now summed over all possible d's. There are several quantities which in these expressions depend on the index d. First, as seen in Eq. (5), we have the radiative excitation dipole matrix element $|\mathcal{E}_0\cdot\vec{D}_{d,g}|^2$. It will be replaced with an average $\overline{|\mathcal{E}_0\cdot\vec{D}_{d,g}|^2}$ over all d's and pulled outside the summation. Next, we have the linewidths Γ_d^v and Γ_d^w as well as the related matrix elements $V_{p,d}(E_d-E_p)$ and $W_{s,d}(\mathcal{E})$ [cf. Eqs. (26a) and (26b)]. The subscript d refers to individual states, so $\Gamma_d^v+\Gamma_d^w$ is the lifetime width of a dth state due to the Auger decay and due to the tunneling interaction of the atom-adsorption-site cluster with the rest of the substrate. This linewidth can be smaller than or comparable with the exciting radiation linewidth and it *does not* determine the x-ray absorption linewidth directly. The latter, Γ_A, is determined by the strong interaction between the atom and the adsorption-site cluster.

Performing the summation we will assume that the d-states form a quasidiscrete continuum with the density of states $\rho_A(E_d)$, spread over the interval of width Γ_A around some central energy $\langle E_d\rangle$. Summation over d will thus be replaced with the integration $\int dE_d\rho_A(E_d)\ldots$. Because $\Gamma_d^v+\Gamma_d^w$, determined by weak interactions, is much smaller than Γ_A (determined by the strong one) and because the energy dependence of $|V_{p,d}(\mathcal{E})|^2$ and $\rho_S(\mathcal{E})$ is expected to be rather weak over an energy interval width of the order of $\Gamma_d^v+\Gamma_d^w$, we will approximate the resonant absorption-excitation factor in Eq. (5) with Dirac's δ function:

$$\frac{1}{(E_g+\hbar\omega_L-E_d)^2+[(\Gamma_d^v+\Gamma_d^w)/2]^2}$$

$$\approx\frac{2\pi}{\Gamma_d^v+\Gamma_d^w}\delta(E_g+\hbar\omega_L-E_d), \qquad (29)$$

which allows us to evaluate the integral analytically. Performing the integration we will take into account only the E_d dependence of various quantities in Eqs. (5) and (26) but ignore a possible dependence on d implied by the subscript d in $|V_{p,d}|^2$ and $|W_{s,d}|^2$; i.e., we pull them outside the integral as certain matrix elements squared $\overline{|V_{p,d}|^2}$ and $\overline{|W_{s,d}|^2}$, respectively, averaged over all d's. Similarly, Γ_d^v and Γ_d^w will be pulled outside the integral as $\bar{\Gamma}_d^v$ and $\bar{\Gamma}_d^w$ defined in Eqs. (4d) and (4c), respectively, but now in terms of the averaged matrix elements.

With all this and using Eqs. (5), (26), and (29), we get the following expression for the decay electron spectrum:

$$\dot{\bar{R}}(\mathcal{E})\equiv\int dE_d\rho_A(E_d)\dot{R}(\mathcal{E})$$

$$=\frac{(2\pi)^2}{\hbar}\frac{\overline{|\vec{\mathcal{E}}_0\cdot\vec{D}_{d,g}/2|^2}}{\bar{\Gamma}_d^v+\bar{\Gamma}_d^w}\rho_A(E_g+\hbar\omega_L)[\bar{s}_N(\mathcal{E})+\bar{s}_R(\mathcal{E})],$$

$$(30)$$

where

$$\bar{s}_N(\mathcal{E})=\theta(E_g+\hbar\omega_L-E_p-\epsilon_F)\rho_S(E_g+\hbar\omega_L-E_p)$$

$$\times\frac{|W_{f,p}(\mathcal{E})|^2\overline{|V_{p,d}(E_g+\hbar\omega_L-E_p)|^2}}{(\mathcal{E}+E_f-E_p)^2+(\Gamma_p^w/2)^2}, \qquad (31a)$$

$$\bar{s}_R(\mathcal{E})=\theta(E_s-E_f-\epsilon_F)\rho_S(E_s-E_f)$$

$$\times\frac{|V_{f,s}(E_s-E_f)|\overline{|W_{s,d}(\mathcal{E})|^2}}{(\mathcal{E}+E_s-E_g-\hbar\omega_L)^2+(\Gamma_s^v/2)^2}$$

$$=\overline{|W_{s,d}(\mathcal{E})|^2}\frac{\Gamma_s^v/2\pi}{(\mathcal{E}+E_s-E_g-\hbar\omega_L)^2+(\Gamma_s^v/2)^2}$$

$$(31b)$$

are the contributions to the spectra due to the normal-Auger and Raman-Auger processes, respectively. The factor $\rho_A(E_g+\hbar\omega_L)$ accounts for the overall x-ray absorption profile with width Γ_A. Note that the $\mathcal{E}$ and ω_L dependences in Eq. (31b), accounting for the contribution to the electron spectra by the Raman-Auger channel, are almost identical to those in Eq. (26b) because E_d is not explicitly present in the latter. In contrast, for the normal-Auger channel this same dependence is different in Eq. (31a) than it is in both Eq. (6a) and (26a). In fact, the energy argument of $\rho_S\overline{|V_{f,s}|^2}$ in Eq. (31b) contains neither $\mathcal{E}$ nor $\hbar\omega_L$, and that of $\rho_S\overline{|V_{p,d}|^2}$ in Eq. (31a) is equal to $E_g+\hbar\omega_L-E_p$, exactly as argued for in paragraphs (ii) and (iii) below Eqs. (6), respectively.

For the Raman fraction the same procedure as before, described above Eqs. (4), is followed. One gets

$$\bar{S}_N \equiv \int \rho_V(\mathcal{E}) \bar{s}_N(\mathcal{E}) d\mathcal{E}$$

$$\approx \theta(E_g + \hbar\omega_L - E_p - \epsilon_F)$$

$$\times \rho_S(E_g + \hbar\omega_L - E_p) \overline{|V_{p,d}(E_g + \hbar\omega_L - E_p)|^2},$$

(32a)

$$\bar{S}_R \equiv \int \rho_V(\mathcal{E}) \bar{s}_R(\mathcal{E}) d\mathcal{E}$$

$$\approx \rho_V(E_g + \hbar\omega_L - E_s)$$

$$\times \overline{|W_{s,d}(E_g + \hbar\omega_L - E_s)|^2},$$

(32b)

which, apart from the fact that they are expressed in terms of matrix elements averaged over all d's, are formally the same expressions as obtained in Eqs. (7a) and (7b) in the wave function approach. Therefore, an expression analogous to Eq. (8) [but not to Eq. (28)] is obtained.

The fact that eventually we obtain an expression for the Raman fraction which has formally the same structure as in the wave function approach does not, of course, mean that the latter approach is correct. For example, the interference term, represented by $s_{NR}(\mathcal{E})$ in Eq. (5), cannot be systematically eliminated within the wave function approach. The Raman fraction reflects only a global property of the electron decay spectrum, not its details: the spectra in Eqs. (30) and (31) are different from those in Eqs. (5) and (6).

VI. CONCLUSIONS

The competing decay channels of core-excited adsorbed atoms induced by nearly monochromatic x-ray synchrotron radiation have been theoretically investigated within the reduced density matrix approach which was confronted with the commonly employed wave function approach. The channels are the Raman-Auger channel in which the adatom Auger decay precedes the electron transfer to the substrate and the normal-Auger channel in which these events occur in the reverse order. Particular attention was paid to the presence or lack of quantum interference between the channels and the decay electron spectra and their photon energy dependence as the radiation is tuned across the excitation resonance.

In particular, the perturbative wave function approach, in which the Auger electron emission and the electron transfer into the substrate are not fundamentally different, leads to quantum interferences between both decay channels because each excitation decay channel is necessarily treated as a one-step quantum process which consists of a sequence of three coherent events not conserving energy individually.

We argue that the density matrix approach is necessary for an accurate description of the excitation decay sequences when they involve charge and energy transfer into the substrate with very efficient internal dissipation of the excitation energy. In such an approach the Auger decay and the electron transfer into the substrate are two fundamentally different elementary events. Consequently, the Raman-Auger decay channel is, similarly as for an isolated atom, a one-step quantum process involving core-hole excitation and Auger auto-ionization events, not conserving energy individually, followed by an uncorrelated electron transfer to the substrate which merely smears the overall energy conservation required in the preceding (two-event) step over the final-state lifetime width. Along the normal-Auger channel, however, the excitation, the charge transfer, and the Auger decay form a sequence of independent events with energy being conserved at each step [see, however, the detailed discussion following Eqs. (24)], because the coupling to the continuum in the solid destroys the coherence. Naturally, quantum interference between the channels does not occur in this approach.

Of more practical importance, the predicted details of the decay electron energies and the radiation frequency dependence of measured decay electron spectra and the related Raman fraction differ in the two approaches when at least one of the following—the single-electron density of states in the substrate, the electron density of states in vacuum, the matrix elements of interactions responsible for the charge transfer to the substrate, and/or those of the interactions responsible for the Auger autoionization of the adsorbed atom — depend on energy. The treatment justifies the earlier interpretation of the Raman fraction and its energy dependence given in the experimental work.

APPENDIX

All relevant equations forming the set of Equations (16) are

$$\frac{d}{dt}\sigma_{g,g} = -\frac{i}{\hbar}(R_{g,d}\sigma_{d,g} - R_{d,g}\sigma_{g,d}),$$

(A1a)

$$\frac{d}{dt}\sigma_{g,d} + [i\omega_{g,d} + \gamma_d^v/2]\sigma_{g,d}$$

$$= \frac{i}{\hbar}\sum_{\vec{k}} W_{s\vec{k},d}\sigma_{g,s\vec{k}} - \frac{i}{\hbar}R_{g,d}(\sigma_{d,d} - \sigma_{g,g}),$$

(A1b)

$$\frac{d}{dt}\sigma_{g,s\vec{k}} + [i\omega_{g,s\vec{k}} + \gamma_s^v/2]\sigma_{g,s\vec{k}} = \frac{i}{\hbar}W_{d,s\vec{k}}\sigma_{g,d} - \frac{i}{\hbar}R_{g,d}\sigma_{d,s\vec{k}},$$

(A1c)

$$\frac{d}{dt}\sigma_{d,d}+\gamma_d^v\sigma_{d,d}=\frac{i}{\hbar}\sum_{\vec{k}}\ (W_{s\vec{k},d}\sigma_{d,s\vec{k}}-W_{d,s\vec{k}}\sigma_{s\vec{k},d})$$

$$-\frac{i}{\hbar}(R_{d,g}\sigma_{g,d}-R_{g,d}\sigma_{d,g}),\qquad\text{(A1d)}$$

$$\frac{d}{dt}\sigma_{d,s\vec{k}}+[i\omega_{d,s\vec{k}}+(\gamma_s^v+\gamma_d^v)/2]\sigma_{d,s\vec{k}}$$

$$=\frac{i}{\hbar}W_{d,s\vec{k}}\sigma_{d,d}-\frac{i}{\hbar}\sum_{\vec{k}'}\ W_{d,s\vec{k}'}\sigma_{s\vec{k}',s\vec{k}}-\frac{i}{\hbar}R_{d,g}\sigma_{g,s\vec{k}},$$

$$\text{(A1e)}$$

$$\frac{d}{dt}\sigma_{s\vec{k},s\vec{k}}+\gamma_s^v\sigma_{s\vec{k},s\vec{k}}=-\frac{i}{\hbar}(W_{s\vec{k},d}\sigma_{d,s\vec{k}}-W_{d,s\vec{k}}\sigma_{s\vec{k},d}),$$

$$\text{(A1f)}$$

$$\frac{d}{dt}\sigma_{s\vec{k},s\vec{k}'}+[i\omega_{s\vec{k},s\vec{k}'}+\gamma_s^v]\sigma_{s\vec{k},s\vec{k}'}$$

$$=-\frac{i}{\hbar}(W_{s\vec{k},d}\sigma_{d,s\vec{k}'}-W_{d,s\vec{k}'}\sigma_{s\vec{k},d}),\quad\text{(A1g)}$$

$$\frac{d}{dt}\sigma_{p,p}-\gamma_d^v\sigma_{d,d}=\frac{i}{\hbar}\sum_{\vec{k}}\ (W_{f\vec{k},p}\sigma_{p,f\vec{k}}-W_{p,f\vec{k}}\sigma_{f\vec{k},p}),$$

$$\text{(A1h)}$$

$$\frac{d}{dt}\sigma_{p,f\vec{k}}+i\omega_{p,f\vec{k}}\sigma_{p,f\vec{k}}=\frac{i}{\hbar}W_{p,f\vec{k}}\sigma_{p,p}-\frac{i}{\hbar}\sum_{\vec{k}'}\ W_{p,f\vec{k}'}\sigma_{f\vec{k}',f\vec{k}},$$

$$\text{(A1i)}$$

$$\frac{d}{dt}\sigma_{f\vec{k},f\vec{k}}-\gamma_s^v\sigma_{s\vec{k},s\vec{k}}=-\frac{i}{\hbar}(W_{f\vec{k},p}\sigma_{p,f\vec{k}}-W_{p,f\vec{k}}\sigma_{f\vec{k},p}),$$

$$\text{(A1j)}$$

$$\frac{d}{dt}\sigma_{f\vec{k},f\vec{k}'}+i\omega_{f\vec{k},f\vec{k}'}\sigma_{f\vec{k},f\vec{k}'}$$

$$=-\frac{i}{\hbar}(W_{f\vec{k},p}\sigma_{p,f\vec{k}'}-W_{p,f\vec{k}'}\sigma_{f\vec{k},p}).\quad\text{(A1k)}$$

The equations for only half of the correlations $\sigma_{m,n}$ are listed; those for the remaining ones—$\sigma_{n,m}$—can be obtained by taking the complex conjugates.

The set of equations (A1) is quite intimidating, so several organizing comments are helpful. First, the radiation coupling enters only the equations for those occupation probabilities and correlations which involve either the ground or the core-excited states, $|g\rangle$ or $|d\rangle$, respectively. Second, the electron transfer from the atom to the substrate enters only through the rates γ_s^v and γ_d^v which appear as dephasing rates with which the correlations involving either states $|s\vec{k}\rangle$ or $|d\rangle$, respectively, decay (dephasing occurs at a half of these rates). They also enter as rates with which the occupation probabilities tend to decrease or increase. With these comments it should be a simple matter to modify the above set to account for the fact that the final state, with two valence holes, is also short lived due to possible electron transfers from the substrate which would fill or screen both holes. The decay of the occupation probability of $|f\vec{k}\rangle$ and of related correlations involves the charge transfer from the substrate, so it would add some extra rates to the supermatrix $\hat{\mathbb{S}}$ in Eq. (14). This would introduce terms in Eqs. (A1j) and (A1k) which are exactly the same terms as those described in paragraph (i) below Eq. (24). Their influence on the spectra is described in paragraph (iv) below Eq. (24).

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[24] We use the term *supermatrix* to denote a matrixlike object which, acting on a usual matrix, results in another usual matrix. Similarly, a *superoperator* is an operator acting in a Hilbert space of more familiar operators, like the density matrix or a Hamiltonian. The matrix elements of a superoperator form a supermatrix.

[25] In the equations for the correlations $\sigma_{m,n}$ the matrix elements of $\hat{\mathbb{S}}$ are complex. The imaginary parts of the matrix elements in retained terms contribute merely to the substrate-induced corrections to the energy levels E_m. They can be ignored if the energies are taken from experiment. Still other matrix elements of $\hat{\mathbb{S}}$ appear in certain "nonsecular" terms in equations for correlations $\sigma_{m,n}$, linking their rate of time evolution to other correlations $\sigma_{m',n'}$. These terms can be ignored if for all (m',n') we have $|\omega_{m,n} - \omega_{m',n'}| \gg \Sigma_l^{l \neq (n,m)}(P_{l,m} + P_{l,n})$ which again imposes limits on the strength of $\mathbb{V}$ [$\omega_{m,n}$ is defined in Eq. (17)]. For the discrete spectrum of the primary system $|\omega_{m,n} - \omega_{m',n'}|$ never approaches zero except in unlikely cases of accidental degeneracies, and the above condition is easy to meet. In our case where the free electron $\vec{k}$ is included in the primary system the spectrum contains a continuum part. One can show, however, that because $\mathbb{V}$ does not couple $|s\vec{k}\rangle$ to $|s\vec{k}'\rangle$ except when $\vec{k} = \vec{k}'$, the nonsecular terms for which $|\omega_{m,n} - \omega_{m',n'}|$ might approach zero do not appear in any of the equations. See, however, Ref. 26.

[26] One of the consequences of having to consider only some selected correlations is that the only equations (for the correlations $\sigma_{d,p}$ and $\sigma_{f\vec{k},s\vec{k}}$ and their complex conjugates) which might contain nonsecular terms in the case of $\omega_{d,p} \approx \omega_{s,f}$ are not needed for determining the spectra. Such degeneracy is very unlikely anyway because the screening experienced by the electron in the excited orbital of the atom in the state $|d\rangle$ is different from that for the ion in the state $|s\rangle$.