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Decay of the resonantly excited states of atomic Zn

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The $3p^{-1}\rightarrow 5s^1$ resonant excitation energy and decay width of the Zn atom are calculated by an *ab initio* Green's-function method. The agreement with experiment is reasonably good. The decay width and the dipolar relaxation energy shift of the $3p^{-1}\rightarrow 5s^1$ resonantly excited state of the Zn atom is predominantly due to the $3p^{-1}5s^1\rightarrow 3d^{-2}5s^1\varepsilon f(p)$ super-Coster-Kronig spectator decay and the corresponding virtual process. The calculated decay width is larger than the experimental one but smaller than that of the $3p^{-1}$ core-ionized state. It appears that the discrepancy is due to the overestimate of the $3p^{-1}5s^1\rightarrow 3d^{-1}4s^{-1}5s^1\varepsilon p$ Coster-Kronig decay by the present calculation.

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I. INTRODUCTION

The study of deexcitation mechanisms of resonantly excited states of atoms, molecules, solids, and surfaces by resonant photoemission [deexcitation electron spectroscopy (DES)] is a subject of current interest [1]. The resonant excitation from a core level (c) to an empty affinity level (a) leads to an intermediate resonantly excited state $|a\rangle(c^{-1}a)$, which decays by participant and spectator decay channels. In the former, the initially excited electron participates in the Auger decay channel ($c^{-1}a\rightarrow v^{-1}\varepsilon$), leading to a single ionization of the valence level ($v^{-1}\varepsilon$), identical to a singly valence ionized continuum state $|v\rangle$ observed as a main line state in the valence photoemission spectrum. At the resonance, the final state created either by the participant decay channel or by direct photoionization becomes indistinguishable. This leads to interference and in general a large enhancement of the main line intensity. In the latter the excited electron remains as a spectator in the Auger decay channel ($c^{-1}a\rightarrow j^{-1}k^{-1}a\varepsilon_s$) and leads to the two-hole one-particle ($2h1p$) state, corresponding to the $k^{-1}\rightarrow a$ shakeup satellite state observed in the valence photoemission spectrum. The spectral intensity of the final state is, in the case of direct photoemission, governed by the dipole excitation matrix element (and consequently the shakeup excitation matrix element), while in the resonant photoemission, it is given by Auger matrix element (Coulomb operator). Thus the resonant photoemission can be used to identify weak satellite lines in the valence photoemission spectrum.

It is often assumed that spectator decay width (decay width of a core hole in the presence of a nonparticipating resonantly excited electron) and normal Auger decay width are same. This assumption is justified because the spectator decay energy is often large so that the screening of the final-state two-hole potential by the presence of a resonantly excited electron (spectator) is not effective enough to influence the Auger electron wave functions. Consequently the spectator decay rate becomes the same as the Auger one. However, when the super-Coster-Kronig (SCK) spectator decay dominates (which is often the case with inner valence and core levels of free atoms [2]), the spectator decay width may differ from the normal Auger decay width. As the SCK decay energy is often small, the SCK decay rate is very sensitive not only to the SCK decay energy, but also to the final two-hole potential that the SCK electron experiences. If the screening of the final-state two-hole potential by the spectator is significant, the SCK electron wave function could be much different from the normal SCK one because of the final-state potential which is less attractive than in the case of normal SCK decay. Moreover, the energy shift between the spectator decay ($c^{-1}a\rightarrow j^{-1}k^{-1}a\varepsilon_s$) at the resonance and the Auger decay ($c^{-1}\rightarrow j^{-1}k^{-1}\varepsilon_A$) is given by $U_{ja}+U_{ka}-U_{ca}$. Here U is the effective hole-particle Coulomb interaction. The energy shift is often small (order of a few eV) because $U_{ca}\sim U_{va}$ (here v denotes a valence hole). As the SCK wave function depends critically also on the decay energy (when the decay energy is small), a small energy shift may also change the decay rate, even if the screening of the final-state two-hole potential by the spectator is not effective. Thus one may expect a competition between the spectator-Auger decay energy shift and the screening of the final-state two-hole potential by a spectator. The latter decreases the spectator SCK decay because of a less attractive potential. The former increases the spectator SCK decay rate (if the potential is not influenced by a spectator electron).

Recently Adam *et al.* [3] measured the resonant photoemission spectrum in the $3p^{-1}\rightarrow 5(n)s^1$ [and $4(n)d^1$] resonant excitation energy region of atomic Zn($Z=30$). Their experimental study shows that the resonant $3p^{-1}\rightarrow 5(n)s^1$ excitation decays dominantly by $3p^{-1}5(n)s^1\rightarrow 3d^{-2}5(n)s^1\varepsilon$ SCK spectator decay. The singly ionized final $2h1p$ state decays further to the doubly ionized $2h$ states. At or near the resonance, the $3d$ and $4s$ singly ionized states hardly resonate. Thus these states are created by direct valence ionization. This shows that the participant decay is negligible. Such a participant decay reduction may indicate that the excited electron is not strongly localized. Otherwise the participant decay is to have a significant intensity. The SCK

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spectator decay is similar to the SCK decay process of $3p$ ionized state $[3p^{-1}\rightarrow 3d^{-2}\varepsilon f(p)]$ and to strong $(3p^{-1}3d^{n+1}\rightarrow 3d^{n-1}\varepsilon f)$ deexcitation for the $3p$ edges of the $3d$ transition metals, first predicted by McGuire [4]. Adam *et al.* [3] obtained 1.5 eV for the decay width of resonantly excited state from the total electron yield. The width differs considerably from the $3p$ x-ray photoemission spectroscopy width of 2.2 eV. Such a difference is also observed in the case of copper. Jensen *et al.* [5] measured 2.2±0.3 eV for the width of $3p$ ionized state, whereas Bruhn *et al.* [6] obtained 1.75 eV for the $3p$ resonantly excited state.

In the present work we discuss the deexcitation mechanism of the resonantly excited state, particularly how the core hole decay and its subsequent decay are manifested in DES spectra. Then we calculate the $3p^{-1}\rightarrow 5s^1$ resonant excitation energy and its spectator width by an *ab initio* Green's-function method. We describe the relaxation and decay of a resonantly excited state by the $1h1p$ (one-hole one-particle) spectral function. The advantage of the present many-body technique is that one can treat the decay width and the energy shift in a consistent manner. In the case of $3p^{-1}\rightarrow 5s^1$ resonant excitation, despite an increase of 5 eV in the decay energy, there is a decrease in the spectator decay width. We shall investigate the cause of the decrease.

II. THEORY

A. Resonant photoemission spectrum

We consider the resonant excitation from a core level c to an affinity level a. At or near the resonance, neglecting the direct emission amplitudes and considering only the resonant emission amplitudes, we obtain the resonant photoemission spectrum [7]

$$I(\varepsilon;\omega)\propto |Z_{ca}(\omega)|^2 A_a(\omega) \times \left\{ \frac{\Gamma_v}{\Gamma_a} A_v(\varepsilon-\varepsilon_v-\omega)+\frac{\Gamma_s}{\Gamma_a} A_s(\varepsilon-\varepsilon_s-\omega) \right\} . \tag{1}$$

Here for the sake of simplicity we consider only one spectator decay channel and one participant decay channel. The first term describes the participant decay from the resonantly core excited state $|a\rangle(c^{-1}a)$ to a singly valence ionized continuum state $|v\rangle(v^{-1}\varepsilon)$, whose decay width is Γ_v. The second term gives the spectator decay from $|a\rangle$ to a singly ionized $2h1p$ final state $|s\rangle(j^{-1}k^{-1}a\varepsilon)$, whose decay width is Γ_s. $Z_{ca}(\omega)$ is the effective dipole excitation $(c^{-1}\rightarrow a)$ matrix element, given by

$$Z_{ca}(\omega)=Z_{ca}+\sum_{\varepsilon}\frac{V_{va}Z_{v\varepsilon}}{\varepsilon_v-\varepsilon+\omega+i\Gamma_{fv}/2} . \tag{2}$$

Here the second term in Eq. (2) describes the configuration interaction between $|a\rangle$ and $|v\rangle$, which are coupled by V_{va}. ε_v is the ionization energy of the valence level v and ω is the photon energy. Γ_{fv} is the decay width of the valence hole state $|v\rangle$. $A_a(\omega)$ is the spectral function of the state $|a\rangle$, given by a Lorentzian profile with a width Γ_a,

$$A_a(\omega)=\frac{1}{\pi}\frac{\Gamma_a/2}{(\omega-\varepsilon_a+\varepsilon_c+U_{ca})^2+(\Gamma_a/2)^2} . \tag{3}$$

Here Γ_a is the total decay width and is a sum of Γ_s and Γ_v, ε_c is the ionization energy of a core level c, ε_a is the affinity energy of an empty level a, and U_{ca} is the effective core hole-excited electron Coulomb interaction. $A_v(\varepsilon-\varepsilon_v-\omega)$ is the spectral function of the state $|v\rangle$, given by a Lorentzian profile with a width Γ_{fv},

$$A_v(\varepsilon-\varepsilon_v-\omega)=\frac{1}{\pi}\frac{\Gamma_{fv}/2}{(\varepsilon-\varepsilon_v-\omega)^2+(\Gamma_{fv}/2)^2} . \tag{4}$$

$A_s(\varepsilon-\varepsilon_s-\omega)$ is the spectral function of the state $|s\rangle$, given by a Lorentzian profile with a width Γ_{fs},

$$A_s(\varepsilon-\varepsilon_s-\omega)=\frac{1}{\pi}\frac{\Gamma_{fs}/2}{(\varepsilon-\varepsilon_s-\omega)^2+(\Gamma_{fs}/2)^2} . \tag{5}$$

Γ_{fs} is the decay width of the $2h1p$ state $|s\rangle$. ε_s is the ionization energy of the final $2h1p$ state $|s\rangle$ and is given by

$$\varepsilon_s=\varepsilon_j+\varepsilon_k-U_{jk}-\varepsilon_a+U_{ja}+U_{ka} . \tag{6}$$

Here $\varepsilon_{j(k)}$ is the ionization energy of valence level $j(k)$ and U is the effective hole-hole (particle) Coulomb interaction.

At the resonance $\omega_a=\varepsilon_a-\varepsilon_c-U_{ca}$, the participant (spectator) decay spectrum is given by a superposition of the spectral function $A_v(A_s)$, centered at $\varepsilon_v+\omega_a$ $(\varepsilon_s+\omega_a)$, weighted by the partial participant (spectator) decay ratio. The width of the participant (spectator) decay spectrum is $\Gamma_{fv(fs)}$, the same as that of valence photoemission spectrum main line (satellite line). Thus the deexcitation spectrum does not reflect the decay width Γ_a of the resonantly excited state. At the resonant excitation from a deep core level, the spectator decay is the fastest and dominates. As a result there is no decay channel which leads to the same final state as the direct valence photoemission main line state. Consequently there is no interference effect which may lead to Fano-type resonance or antiresonance behavior for the final state. In this case the x-ray absorption spectroscopy (XAS) spectrum represents the absorption from a discrete level broadened into a Lorentzian by the spectator decay:

$$I^{\mathrm{XAS}}(\omega)\propto |Z_{ca}|^2 A_a(\omega) . \tag{7}$$

Note that in this case the second term in Eq. (2) becomes negligible. The width Γ_a of XAS spectrum becomes the spectator decay width Γ_s.

Equation (1) shows that the total deexcitation spectral intensity obtained at a certain photon excitation energy is equal to the x-ray absorption spectral intensity at that photon energy. The constant ionic (final-) sate spectroscopy (CISS) spectrum obtained by collecting the emitted electrons at a constant final state binding energy $[-\varepsilon_s(\varepsilon_v)=\omega-\varepsilon]$ is a partial electron yield at constant binding energy. When the final-state lifetime broadening is negligible, the CISS spectrum for the final state $|s\rangle$

($|v\rangle$) is given by

$$I^{\mathrm{CISS}}(\omega)\propto|Z_{ca}|^2\frac{\Gamma_{s(v)}}{\Gamma_a}A_a(\omega)\ . \tag{8}$$

The CISS spectrum integrated over the whole binding energy scale of final states, in other words, summing over all decay channels in Eq. (8), gives the XAS spectrum in total electron yield. If the XAS spectrum consists of several structures, the CISS spectrum can be used to decompose the structures in the XAS spectrum by monitoring particular final states in the DES spectrum which can be reached only from a certain initial state.

When the outer valence levels are involved in the spectator decay, the $2h\,1p$ final state may decay further to the doubly ionized $2h$ state. This occurs dominantly by participant decay because it would not be energetically favored to create extra valence holes. The total decay width is Γ_{fs}. We consider the "second-step" resonant photoemission spectrum for the participant decay whose decay energy is ε'. The second step resonant photoemission spectrum is given by

$$I(\varepsilon';\omega)\propto|Z_{ca}(\omega)|^2A_a(\omega)\left\{\frac{\Gamma_s}{\Gamma_a}\sum_i\frac{\Gamma^i_{fs}}{\Gamma_{fs}}A_s(\varepsilon'-\varepsilon^i_f+\varepsilon_s)\right\}\ . \tag{9}$$

Here ε^i_f is the ionization energy of the doubly ionized final state $|f^i\rangle$, which is reached from $|s\rangle$ by the participant decay channel i whose decay width is Γ^i_{fs}. At the resonance, the second-step resonant spectrum is given by a superposition of the spectral function $A_s(\varepsilon'-\varepsilon^i_f+\varepsilon_s)$ centered at $\varepsilon'=-\varepsilon_s+\varepsilon^i_f$, weighted by the partial participant decay ratio ($\Gamma^i_{fs}/\Gamma_{fs}$). ε' is constant, independent of the excitation energy. From this viewpoint one may call the process Auger decay rather than participant decay. When the state $|s\rangle$ is reached dominantly by the spectator decay from $|a\rangle$, the second-step resonant photoemission spectral intensity will resonate also at the resonance energy ω_a. The CISS spectrum for the final state $|f^i\rangle$ is given by

$$I^{\mathrm{CISS}}(\omega)\propto|Z_{ca}|^2\left\{\frac{\Gamma_s}{\Gamma_a}\frac{\Gamma^i_{fs}}{\Gamma_{fs}}A_a(\omega)\right\}\ . \tag{10}$$

If the spectator decay from $|a\rangle$ is not dominant, then $|f^i\rangle$ can be reached also from the valence shakeup satellite state which is identical to $|s\rangle$. The valence shakeup satellite spectrum is given by

$$I(\varepsilon;\omega)\propto|Z_{cs}(\omega)|^2A_s(\varepsilon-\varepsilon_s-\omega)\ . \tag{11}$$

We consider further decay of the shakeup satellite state $|s\rangle$ to $|f^i\rangle$. The decay spectrum is given by

$$I(\varepsilon';\omega)\propto|Z_{cs}(\omega)|^2\left\{\sum_i\frac{\Gamma^i_{fs}}{\Gamma_{fs}}A_s(\varepsilon'-\varepsilon^i_f+\varepsilon_s)\right\}\ . \tag{12}$$

The spectrum is given also by a superposition of the spectral function A_s, centered at $\varepsilon'=\varepsilon^i_f-\varepsilon_s$, weighted by the participant decay ratio. However, the spectral intensity depends on the ionization cross section. Thus by studying whether there is significant enhancement in the second-step resonant photoemission spectrum (participant decay from $|s\rangle$ to $|f^i\rangle$) at the resonance, one can tell whether the final state $|s\rangle$ is due to the spectator decay or direct shakeup excitation.

The doubly ionized final state can be reached in one step in the case of open-shell atomic systems. Such an example studied recently is the decay of the $3p\rightarrow nl$ ($nl=ns,nd$) Rydberg excitations of atomic Cu, namely, a nearly total decay of these excitations into doubly ionized ($3d^9$ and $3d^84s^1$) final ionic states in contrast to the $3p\rightarrow 4s$ resonance which results into single ionization ($3d^84s^2$ state) [8]. The former double ionization occurs because $3d^84s^1nl$ states reached by the (S)CK spectator decay of the $3p^54s^1nl$ resonantly excited state are degenerate with $3d^84s^1$ continuum and above the $3d^{-1}4s^{-1}$ double-ionization limit. Thus one can see that the nl electron does not remain anymore as a spectator and becomes ionized at the same time as the (S)CK decay occurs [8]. The decay of the resonantly core-excited state to the doubly ionized state in one step can be seen also in more complicated systems such as molecules adsorbed on metal surfaces [9] and ionic insulators [10]. In these systems, the resonantly excited electron can delocalize to the empty substrate metal band or to the empty conduction band on the time scale of the core hole decay. Thus the Auger spectral feature (doubly ionized state) dominates in the DES spectrum measured at the resonance. Theoretical formulation of the competition between the delocalization of a resonantly excited electron and a core hole decay will be published elsewhere [11].

To summarize, the width of the spectator (participant) decay spectrum is due to the lifetime broadening of the final state reached by spectator (participant) decay from the resonantly excited state. The width is the same as that of the valence photoemission shakeup satellite line (main line), whose final state is identical to that reached by spectator (participant) decay. The lifetime broadening of the resonantly excited state by the spectator and participant decay does not manifest in the deexcitation spectrum because in the resonant excitation the "primary photoelectron" is excited to a particular bound level so that the "kinetic energy" is fixed. As a result the initial-state lifetime broadening is excluded. This is quite analogous to the case of Auger photoelectron coincidence spectroscopy (APECS) measurement. When the Auger electron is collected by fixing the primary photoelectron kinetic energy, the APECS spectrum excludes the lifetime broadening of the initial core hole state. In this case the width of the APECS spectrum is due to the two-hole final-state lifetime broadening [12].

B. Calculation of the XAS spectrum

We are particularly interested in describing the shift and broadening of the XAS spectrum. We rewrite $A_a(\omega)$ as

$$A_a(\omega)=\frac{1}{\pi}\frac{\mathrm{Im}\Sigma_a(\omega)}{[\omega-\omega^0_a-\mathrm{Re}\Sigma_a(\omega)]^2+[\mathrm{Im}\Sigma_a(\omega)]^2}\ . \tag{13}$$

Here ω^0_a is the $1h\,1p$ Koopmans resonant excitation energy and $\Sigma_a(\omega)$ is the self-energy for the $1h\,1p$ propagator. We treat explicitly only the dipole relaxation part $[\Sigma_a^D(\omega)]$ of the self-energy and approximate the monopole part $[\Sigma_a^M(\omega)]$ and the Fermi-sea (ground-state) correlation part $[\Sigma_a^c(\omega)]$ by the energy shifts Δ^M and Δ^c, respectively,

$$\Sigma_a(\omega)=\Delta^M+\Delta^c+\Sigma_a^D(\omega)\ . \qquad (14)$$

The broadening of the spectrum is dominated by (S)CK decay processes which are given by the imaginary part of dipole self-energy $\mathrm{Im}\Sigma_a^D(\omega)$. We approximate the monopole relaxation shift Δ^M by the Hartree-Fock (HF) ΔSCF (self-consistent-field) method

$$\omega_a^0+\Delta^M(\Delta\mathrm{SCF})=\omega_a(\Delta\mathrm{SCF})\ . \qquad (15)$$

The dipole part of the self-energy due to the spectator decay ($c^{-1}a\rightarrow j^{-1}k^{-1}a\varepsilon$) is given by

$$\Sigma_a^D(\omega)=\sum_{\varepsilon,j,k}\frac{|\langle c\varepsilon|1/r_{12}|jk\rangle|^2}{\omega+\varepsilon_s-\varepsilon+i\delta}\ . \qquad (16)$$

The method for evaluating the self-energy $\Sigma_a^D(\omega)$ is essentially the same as that for the $3p$ ionization, which is described in details elsewhere [12,13]. Here we only summarize the basic features of the zeroth-order nonrelativistic orbital basis: (i) occupied (hole) levels—the neutral $3p^{-1}5s^1$ excited-state relaxed SCF HF orbitals; (ii) unoccupied (particle) levels—orbitals calculated in a HF V^{n-2} potential constructed using the neutral $3p^{-1}5s^1$ excited-state relaxed SCF HF orbitals with two holes (j and k) in the final ionic states. For the $3d^{-2}5s^1n,\varepsilon f(p)$ excitation channel, the $[3d^{-1}n,\varepsilon f(p)]$ electron-hole pair excitations have been treated within the random-phase approximation with exchange (RPAE), which can be accomplished by calculating the excited discrete and continuum $f(p)$ states according to the $(3d^{-1}5s^1)_{\mathrm{av}}[3d^{-1}n,\varepsilon f(p)^1P]$ HF V^{n-2} potential and adding the Fermi-sea correlation. This potential describes the ionic excitation as $[3d^{-1}n,\varepsilon f(p)^1P]$ dipole excitation in a spherically averaged neutral $3d^{-1}5s^1 1h\,1p$ state [12,13].

We note that for a description of the $3p$ ionization, we used two different types of approximations for evaluating the $3p$ hole self-energy. One (approximations C and D) is to use the neutral ground-state HF SCF orbitals (as described in detail in previous work [12,13]), while the other (approximations E and F) is to use the $3p$ ionized state relaxed HF SCF orbitals. One of the motivation for using the latter is to study the effect of the relaxation on the wave functions because in the former approximation the effect of the monopole relaxation is included only in terms of energy parameters. However, we note that there is no obvious justification for using relaxed orbitals when constructing potentials and calculating matrix elements. This is a nontrivial problem since it involves the dynamics of the primary photoionization process and the secondary (S)CK processes as well as interference between them. The screening charge grows from zero to full strength as the Auger electron leaves the system. The actual effect of relaxation on the potential corresponds to relaxation in the presence of a half hole in addition to the hole already present. In other words, using the completely relaxed ionic state with two holes overestimates the influence of relaxation effects, and a transition state type of calculation should be more appropriate. Therefore, the initial-state relaxed-state orbitals may represent a more realistic estimate of relaxation effects than using the final-state orbitals. The other motivation is to make a comparison with the results obtained for the $3p^{-1}\rightarrow 5s^1$ resonant excitation because in the cases of the resonant excitation, the resonantly excited-state relaxed SCF orbitals are used instead of the neutral ground-state SCF orbitals.

The average energies ε_s of the final $2h\,1p$ $3d^{-2}5s^1$ and $3d^{-1}4s^{-1}5s^1$ states for the spectator (S)CK decay of $3p^{-1}5s^1$ resonantly excited state are calculated using the HFΔSCF method. The multiplet splittings of the $3d^{-2}5s^1$ configuration are calculated by using the Coulomb integrals of the $3p^{-1}5s^1$ excited state. We estimate an average relativistic shift as in a previous article [12]. To evaluate the spectral function, in principle we need to know the correlation energy shifts Δ^c for the $1h\,1p$ and $2h\,1p$ states. Δ^c for the $3d$ and $4s$ levels are estimated as before [12]. However, Δ^c for the $3p^{-1}5s^1$ state is estimated to be 1.0 eV rather than $\Delta_{3p}^c=2.9$ eV, from a previous work [12], because of the $5s$ electron. The results for the $2h\,1p$ states are shown in Table 1, showing good agreement with experiment.

III. RESULTS AND DISCUSSIONS

In Table II we summarize the $3p^{-1}\rightarrow 5s^1$ resonant excitation energies and their spectator decay widths evaluated by the many-body technique described in Sec. II A.

In approximation A we used the theoretical $1h\,1p$ and $2h\,1p$ state energies listed in Table I. The calculated $3p_{1/2,3/2}$ widths are 2.0 and 1.9 eV, respectively. The Fermi-sea correlation introduced by RPAE reduces the SCK decay rate of the $1h\,1p$ state obtained by the Tamm-Dancoff approximation (TDA) by about 30% (from 2.54 to 1.78 eV for the $3p_{1/2}\rightarrow 5s^1$ resonant excitation and 2.38 to 1.67 eV for the $3p_{3/2}\rightarrow 5s^1$ resonant excitation). The introduction of the Fermi-sea correlation by RPAE (less attractive final-state potential) causes the

TABLE I. Theoretical (HFΔSCF) and experimental binding and excitation energies of atomic Zn (in units of eV). Asterisks means that Δ^c is not included.

Configuration	Expt. (Ref. [3])	Theory
$(3d^{-2}5s^1)_{\mathrm{av}}$		46.5
$(3d^{-2}5s^1)^2S$		52.1
^2G	46.6	46.6
^2P		45.9
^4P		45.7
^2D		45.1
^2F	43.3	43.0
^4F	43.3	42.9
$(3d^{-1}4s^15s^1)_{\mathrm{av}}$	30.1	30.5
$3p_{1/2}^{-1}5s^1$	96.0	97.9*
$3p_{3/2}^{-1}5s^1$	93.2	94.6*

TABLE II. Theoretical and experimental decay width (Γ) and excitation (binding) energy (E) of the $3p^{-1}5s^1$ and $3p^{-1}$ states of atomic Zn (in units of eV). E^0 is the unperturbed excitation (binding) energy which is a sum of the HFΔSCF excitation (binding) energy and the Fermi-sea correlation energy shift.

			Theory		Expt.	
State	Approx.	E^0	E	Γ	E	Γ
$3p_{1/2}^{-1}5s^1$	*A*	98.9	97.0	2.04	96.0[a]	
	B	98.9	97.0	1.93		
$3p_{3/2}^{-1}5s^1$	*A*	95.6	93.7	1.93	93.2[a]	> 1.5[a]
	B	95.6	93.7	1.82		
$3p_{1/2}^{-1}$	*C*	102.5	100.5	2.13 (2.33)	98.9[a]	2.2[a]
	D	100.6	98.6	2.05 (2.24)	98.7[b]	2.1±0.2[b]
	E	102.5	100.6	2.04		
	F	100.6	98.7	1.98		
$3p_{3/2}^{-1}$	*C*	99.5	97.5	2.00 (2.18)	96.1[a]	2.3[a]
	D	97.6	95.6	1.93 (2.10)	96.1[b]	2.1±0.2[b]
	E	99.5	97.6	1.94		
	F	97.6	95.6	1.87		

[a] Reference [3].
[b] Reference [14].

continuum wave function to move radially outwards. As a consequence the level width distribution becomes shifted to higher energies. A less attractive potential leads to a decrease in the SCK decay rate. The TDA is not a consistent approximation and not sufficient for the evaluation of the decay rate [12,13]. The excitation energies are 97.0 and 93.7 eV, respectively. The dipole relaxation shift of the resonantly excited state is 1.9 eV, which is almost the same as that of the $3p$ ionized state (2.0 V, according to the present many-body calculation). The dipole relaxation shift is due to $3p^{-1}5s^1 \rightarrow 3d^{-2}5s^1\varepsilon f(p)$ SCK virtual processes. As the relaxation beyond the HFΔSCF picture (the dipole relaxation) of the $1h\,1p$ state is due to the $3p$ core relaxation rather than that of $5s$ electron, the term value $(-\varepsilon_a+U)$ can be quite accurately evaluated even at the level of the TDA. The calculated term values are listed in Table III. The agreement with experiment is excellent. Note that the resonant excitation energies presented in Table II are evaluated by solving the Dyson equation

$$\omega-\omega_a(\Delta\mathrm{SCF})-\mathrm{Re}\Sigma_a(\omega)=0\ . \tag{17}$$

The preliminary theoretical investigation shows that $l \rightarrow l-1$ excitation is much stronger than $l \rightarrow l+1$ excitation. Thus the assignment of $3p \rightarrow ns$ to the dominant resonant excitation spectral features of atomic Zn by Adam *et al.* [3] is correct.

In approximation *B* we used the experimental average $2h\,1p$ level energies. The calculated width decreases by about 0.1 eV; however, the excitation energy is fairly independent of the approximations. The widths are still slightly overestimated.

In Table II we present the results also for the $3p$ ionization, obtained by four different approximations. We refer to a previous work for a list of the experimental and theoretical $1h$ and $2h$ state energies [12].

Approximation *C* is essentially the same as approximation *A* (use of the theoretical final-state energies), except for the $\Delta^c=2.9$ eV used for the $3p$ levels. The width agrees well with experiment, although the experimental data by Adam *et al.* [3] show that the $3p_{3/2}$ width is slightly larger than the $3p_{1/2}$ width. This is opposite the present prediction. The peak energies are overestimated by about 1.5 eV because of overestimated Δ^c for the $3p$ levels.

Approximation *D* is essentially the same as approximation *B* (use of the experimental final-state energies). The energy positions are significantly improved, because $\Delta^c=1.0$ eV is used for the $3p$ levels. However, the widths seem to be underestimated. This must be due to an underestimate of the $3p^{-1} \rightarrow 3d^{-1}4s^{-1}$ CK decay rate by a factor of 3 by the present calculation. The theoretical $(3p^{-1} \rightarrow 3d^{-2})/(3p^{-1} \rightarrow 3d^{-1}4s^1)$ decay rate ratio is 100:6, while the experimental one is 100:16 [14]. Using the experimental decay ratio to estimate the correct $3p^{-1} \rightarrow 3d^{-1}4s^{-1}$ decay rate, we obtain 2.2 and 2.1 eV for $3p_{1/2}$ and $3p_{3/2}$ levels, respectively. The results are in good agreement with experiment. This is also the case

TABLE III. Theoretical and experimental term values for atomic Zn (in units of eV).

		Term value	
Initial state	Final state	Theory	Expt. (Ref. [3])
$3p$	$5s$	2.85	2.90
	$6s$	1.32	1.30
	$7s$	0.76	
	$8s$	0.50	
	$4d$	1.62	
	$5d$	0.9	
	$6d$	0.57	
	$7d$	0.39	

with the results obtained by approximation *C* (see the values inside the parentheses).

Approximations *E* and *F* are the same as approximations *C* and *D*, respectively, except for a choice of basis sets (see Sec. II B). The energy positions and the widths are quite similar to those obtained by approximations *C* and *D*. However, a detailed analysis shows that the present theoretical $(3p^{-1}\rightarrow 3d^{-2})/(3p^{-1}\rightarrow 3d^{-1}4s^{-1})$ spectrum intensity ratio is about 100:17, in good agreement with experiment. This is due to a decrease of the $3p^{-1}\rightarrow 3d^{-2}$ SCK decay rate by about 10% and an increase of the $3p^{-1}\rightarrow 3d^{-1}4s^{-1}$ CK decay rate by a factor of 2.3. The core relaxation will screen and reduce the attractive Hartree-Fock potential of the final-state holes and causes the continuum wave function to move radially outwards. As a consequence the level width distribution becomes shifted to higher energies. A less attractive potential leads to a small decrease in the SCK decay rate, while the CK decay rate width increases very much. In other words, the relative change of the CK decay rate is fairly sensitive to a choice of orbitals. Although the $(3p^{-1}\rightarrow 3d^{-2})/(3p^{-1}\rightarrow 3d^{-1}4s^{-1})$ decay ratio is well reproduced by using the relaxed orbitals, the total decay widths are slightly underestimated.

The total (partial) decay widths for the resonantly excited state and core ionized state obtained by using the initial-state relaxed orbitals are almost same. This is because the monopole relaxation of the occupied orbitals in both initial ionized and excited states described by the average configuration HF SCF approximation is similar. Moreover, this is also the case with the monopole relaxation of the occupied orbitals in the two-hole finite-states of both resonant excitation and core ionization. At the level of the average configuration HF SCF approximation, the resonantly excited 5*s* electron does not seem to act as a screening electron in both initial and final states of the resonant excitation. The screening of the final-state two-hole potential by the resonantly excited 5*s* electron does not seem to be significant. Otherwise, there should be a substantial difference between the decay width calculated for the resonantly excited state and that for the core ionized state. This is also in accord with the argument that the negligible participant decay implies the diffused (nonlocalized) 5*s* electron orbital. However, the experiment shows that there is a decrease of 0.7 eV in the decay width from the core ionized state to the resonantly excited state.

The present theoretical $(3p^{-1}5s^{1}\rightarrow 3d^{-2}5s^{1})/(3p^{-1}5s^{1}\rightarrow 3d^{-1}4s^{-1}5s^{1})$ decay ratio is about 100:16 and agrees well with the experimental ratio for the 3*p* ionization. The $3p^{1}5s^{1}$ resonant emission spectrum [3] shows that the $3p^{-1}5s^{1}\rightarrow 3d^{-1}4s^{-1}5s^{1}\varepsilon$ decay rate is negligible because the spectral intensity of the $3d^{-1}4s^{-1}5s^{1}$ final state does not increase at all at the resonance. The $3d^{-1}4s^{-1}5s^{1}$ singly ionized state is created dominantly by the $4s\rightarrow 5s$ shakeup excitation associated with the 3*d* ionization. The $3d^{-1}$ and $4s^{-1}$ final states do not resonate either, indicating that the $3p^{-1}5s^{1}$ resonantly excited state decays dominantly by the $3p^{-1}5s^{1}\rightarrow 3d^{-2}5s^{1}\varepsilon f(p)$ SCK decay. Then the $3p^{-1}5s^{1}\rightarrow 3d^{-1}4s^{-1}5s^{1}$ CK decay rate is much overestimated by the present calculation. If the CK decay rate for the resonantly excited state is negligible as the experiment shows, we obtain 1.67 and 1.56 eV for the $3p_{1/2}\rightarrow 5s$ and $3p_{3/2}\rightarrow 5s$ resonant excitations, respectively (approximations *C* and *D*). They are in good agreement with experiment.

Combet-Farnoux [15] performed the *R*-matrix calculation for the $3p\rightarrow 4s$ resonant decay of atomic Cu and found that the decay rate for $3p^{5}3d^{10}4s^{2}(^{2}P)$ to $3p^{6}3d^{8}4s^{2}$ is 20 times larger than that for $3p^{5}3d^{10}4s^{2}$ to $3p^{6}3d^{9}4s^{1}$. This indicates that the present many-body calculation overestimates the CK spectator decay rates. The CK decay rates are also very sensitive to a choice of approximations. A less attractive final-state potential leads to an increase in the CK decay rate, while it leads to a decrease in the SCK decay rate. In the present work the CK decay rates are calculated by the TDA for both core ionization and resonant excitation. The introduction of the Fermi-sea correlation by RPAE (less attractive final-state potential) is expected to increase the CK decay rate. In the case of the 3*p* ionization (approximation *C* and *D*), this probably leads to better agreement with experiment. For the core ionized state case the use of the relaxed orbitals underestimates the SCK decay rate because of a less attractive potential. Thus in the case of core ionization, the frozen-core approximation with RPAE for both SCK and CK processes (improvement for approximations *C* and *D*) may provide a reasonably good description of the core hole decay. This may indicate that in the case of core ionization the relaxation effects in both initial and final states are small. In the case of the resonantly excited state, the increase of the CK decay rate by the introduction of RPAE leads to an overestimate of the total decay width.

From a viewpoint of the spectator Auger energy shifts, the (S)CK spectator decay energy is about 5 eV larger than the normal (S)CK decay energy. If the final-state potential for the spectator decay is the same as that for the Auger decay, in other words, if the presence of the spectator 5*s* electron is negligible, then the total decay width increases by about 0.25 eV. The experiment shows a decrease of 0.7 eV. Thus the possibility that the width decreases because of the decay energy shifts can be excluded.

In the present work the presence of a spectator (5*s* electron) is treated within the framework of average configuration. We cannot exclude the possibility that this may provide an inaccurate description of the relaxation in both initial and final states of resonant excitation. The presence of the 5*s* electron may be underestimated by the approximation because of lack of explicit coupling between the excited electron and a hole (or holes). Using the neutral ground-state orbitals as a starting point for the perturbation scheme to describe the resonant excitation and its subsequent decay (as in approximations *C* and *D* for the 3*p* ionization) and include the explicit coupling of the 5*s* electron with a hole (holes) may provide a more accurate description of the excitation. However, such a numerical procedure is beyond the present scope.

The calculation for the resonantly excited state with one 3*d* hole final-state HF V^{n-1} potential, simulating the complete screening of $3d(4s)$ hole by the $5s$ electron, together with the excited-state SCF relaxed orbitals, shows the decay width of about 1.2 eV. This is smaller than the experimental value (1.5 eV). Despite an increase of 5 eV in the SCK decay energy for the spectator decay, the SCK decay rates calculated for the resonant excitation by the relaxed orbital approximation show a decrease (0.25 eV) in comparison to the SCK decay rates calculated for the $3p$ core ionized states by the frozen-core approximation (approximations C and D). Thus one may conclude that the present results indicate that the screening of the final-state double hole ($3d^{-2}$) by the resonantly excited electron is not very significant, but there is indeed a small decrease in the spectator SCK decay width in comparison to normal SCK decay width. It appears that it is the CK rather than the SCK decay rate which changes substantially from the core ionized state to the resonantly excited state.

The second-step resonant photoemission spectrum due to the decay from $3d^9 4s^1 5s^1$ to $3d^{10}$ appears around $\varepsilon' = 2.75$ eV [3]. The spectrum does not show any significant enhancement at the resonance, indicating that the $3d^9 4s^1 5s^1$ state is created mainly by the shakeup excitation associated with the $3d$ valence ionization [3]. In other words, the spectator decay $3p^{-1}5s^1 \to 3d^{-1}4s^{-1}5s^1$ is negligible. This is in accord with nonresonant behavior of the $3d^9 4s^1 5s^1$ final state in the "first-step" resonant photoemission spectrum. The width of the second-step decay spectrum does not change at the resonance and appears to be the same as that (≈ 1.0 eV) of the first-step decay spectrum corresponding to $3p^{-1}5s^1 \to 3d^{-1}4s^{-1}5s^1$. As discussed in Sec. II, this is because the width reflects the lifetime broadening of the final $2h1p$ state. The second-step resonant photoemission spectrum due to decay from $3d^8 4s^2 5s^1$ to $3d^9 4p^1$ (or $3d^9 4s^1$) is expected around ($\varepsilon' \approx 5$ eV). There is a significant enhancement at the resonance [3]. The width of this second-step decay spectrum should be the same as that of the first-step decay spectrum for $3p^{-1}5s^1 \to 3d^{-2}5s^1$ (1.6 eV).

Adam *et al.* [3] observed the prominent two structures (A and B in Fig. 4 of Ref. [3]) at 43.3 and 46.6 eV around the $3p_{3/2}^{-1} \to 5s^1$ resonance. These two structures can be assigned as $3d^{-2}5s^{1\;2(4)}F$ and ${}^2G$ configurations, respectively (see Table I). At the resonance (93.1 eV), an extra structure (C in Fig. 4 of Ref. [3]) appears at 50.7 eV. With an increase of the photon energy (from 93.9 to 94.2 eV) above the resonance maximum, the spectral intensity of A and B begins to decrease while the intensity of structure C increases gradually. Structure C is most likely $3d^{-2}6s^{1\;2}G$ due to SCK decay of $3p^{-1}6s^1$ resonantly excited state (note that the energy separation between $3p^{-1}5s^1$ and $3p^{-1}6s^1$ resonance maxima is 1.6 eV, while the width of $3p^{-1}5s^1$ is 1.5 eV, so there is a significant overlap between two resonances). Structure B may contain partly $3d^{-2}6s^{1\;2(4)}F$.

IV. CONCLUSION

The SCK decay of the resonantly core-excited state in the presence of an extra electron (spectator) is expected to be influenced by the screening of the final-state two-hole potential by the spectator. The degree of screening depends on the localization of the spectator electron. The stronger the localization, the less attractive the final-state potential. However, at the same time, in general the spectator decay energy increases in comparison to the normal Auger decay energy. As the (S)CK decay rate is often sensitive to both final-state potential and decay energy, an *ab initio* many-body calculation may be useful to determine which factor is the most important for the variation of decay width from core-ionized state to resonantly excited state. In general such a calculation of the decay widths needs a highly developed systematic scheme for an accurate description of many-body effects. The decay width (1.5 eV) of the $3p^{-1} \to 5s$ resonantly excited state of free atom Zn is substantially smaller than that of the $3p^{-1}$ core-ionized state. The present *ab initio* many-body calculations show that the resonantly excited state decays dominantly by $3p^{-1}5s^1 \to 3d^{-2}5s^1\varepsilon f$ SCK decay. This is in agreement with the experimental observation. The SCK spectator decay rate seems not to be much influenced by the presence of the extra $5s$ electron, although there is a decrease of 0.2–0.3 eV in the width. The present calculation seems to overestimate the CK spectator decay, which is in fact negligible. When the CK decay is neglected, we obtain good agreement with experiment.

Thus it appears that it is CK rather than SCK decay rate which changes substantially from the core-ionized state to the resonantly excited state. The increase of spectator decay energy in comparison to the Auger decay energy increases the SCK decay rate if the final-state potential is not influenced at all by the presence of the extra $5s$ electron. This excludes the possibility that the widths are decreased due to the decay energy changes. The decay width of the both first-step and second-step resonant photoemission spectra reflects the lifetime broadening of the final state of the spectator and participant decay which are identical to the valence photoemission satellite states and main line states, respectively. Thus the decay widths of the resonant photoemission spectra should be the same as those of the valence photoemission spectra. The differences are the intensities, which are determined by different excitation mechanisms.

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