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Line shapes and relaxation effects in core-level photoelectron spectra of chemisorbed species

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Asymmetric broadening and relaxation shifts observed in the photoelectron spectra from adsorbate core levels are explained in terms of intra-atomic and extra-atomic relaxation effects. A simple model is set up in which the creation of a hole in an adsorbate core level in photoemission is followed by intra-atomic relaxation which pulls the adsorbate valence resonant states downward towards larger binding energies. It is shown that the response of the system to this perturbation involves singular shake-up and charge-transfer processes which give rise to shifts and drastic redistribution of the spectral weight in the core state. In addition we find that the latter effect is subject to the "zero-work sum rule" which states that the mean energy of the core level is unaffected by relaxation processes. As a consequence of this sum rule a maximum at the unrelated energy may appear in the core spectrum under the conditions which are briefly discussed. In systems in which the natural width of the adsorbate core level is negligible compared to that of the valence level, the core spectrum displays singular broadening at the relaxed (elastic) threshold and tailing off towards larger binding energies. In the case when the decay of the core hole must be taken into account this singularity is smeared out by lifetime broadening but the spectrum retains an overall asymmetric shape. The strength of these effects is found to depend strongly on the initial occupation of the adatom valence states and the magnitude of the intra-adatom relaxation shift.

I. INTRODUCTION

The decrease of electron binding energies and the spectral broadening observed in the levels of adsorbed atoms and molecules are general characteristics of all adsorption systems. Usually detected as upward relaxation shifts and broadening in the photoemission spectra of adsorbates with respect to the corresponding gas-phase levels, these effects may be explained in terms of electron shake up and final-state relaxation processes which take place in the vicinity of the photoexcited adatoms.[1]

In dealing with spectral properties of adsorbate core levels one may encounter several types of relaxation mechanisms. One must first consider intra-atomic relaxation from which, as discussed by Shirley,[2] one can estimate the relaxation-energy correction to the calculated atomic-core orbital binding energies. The philosophy behind this relaxation mechanism is simple: appearance of a core hole in an atomic orbital represents a sudden creation of a positive charge which interacts with electrons in the "passive" outer orbitals lowering their energy in the final state. The excess energy expressed as the difference between the energies of the initial (frozen) and final (relaxed) states should be then added to the atomic-core orbital energy to yield the measured electron binding energy observed in photoemission. Within the Hartree-Fock calculations this mechanism gives corrections to the Koopmans -theorem predictions of the electron binding energies in atomic core levels.

Another important relaxation mechanism discussed by Shirley is the effect of extra-atomic relaxation which appears when photoemission measurements are performed on molecules or condensed phases. Creation of a core hole will affect in this case also the electrons in the neighboring orbitals of a molecule or a solid. This will give rise to the flow and redistribution of the electronic charge in the vicinity of the photoexcited atom and further reduce the measured core-electron binding energy. In solids this effect can manifest itself roughly in two ways: (i) as polarization and screening around the photoexcited atom when the intra-atomic relaxation does not produce any new unoccupied states within the valence orbitals of the atoms, and (ii) as the flow of the electronic charge from the surrounding atoms to the photoionized atom when the relaxation of its valence orbitals gives rise to the appearance of unoccupied states below the Fermi level of the system.

The relaxation mechanisms described above also influence the electron binding energies in core levels of adsorbed species. Depending on the strength of adsorption (physisorption versus chemisorption) one may estimate whether the screening of the photoexcited core hole will be achieved only by polarization, or both polarization and charge-transfer effects. In physisorption, in which an atom is bound only by weak polarization forces to a metallic substrate, a photoexcited core hole will interact via Coulomb forces with the charge-density fluctuations in the substrate conduction band. This interaction which does not imply any charge transfer between the adatom and the substrate will lead to the well-known image-screening effects. By now both static and dynamic aspects of image screening and their role in relaxation of adsorbate levels have been elaborated by several authors.[3-5] Our aim in this paper is to investigate the role of electron shake-up and charge-transfer processes which follow the relaxation of adsorbate levels caused by the creation of a core hole in photoemission. Analogously to the case of image screening, we expect that both static and dynamic aspects of these processes will show up in the adsorbate core-level photoelectron spectra. In the following sections we shall pay a particular attention to the observed asymmetric broadening and large relaxation shifts of the adsorbate core levels as they can easily be interpreted qualitatively in terms of the proposed mechanism of intra- and extra-atomic relaxation. A preliminary report of some of the results presented in this paper has already been published.[6]

II. FORMULATION OF THE PROBLEM

In the presentation of the features of extra-atomic relaxation processes occurring in the photoemission spectroscopy of adsorbate core levels we shall start from a simple model of a chemisorption system. We consider a semi-infinite metallic substrate with a partly filled valence band which need not necessarily coincide with the metal conduction band responsible for the transport properties. An example are the transition metals which are the most common substrates. We shall also assume the simplest adsorbate, namely, a single atom whose valence orbital energies lie within the substrate valence band. The chemisorption bonding between the adatom and substrate valence orbitals gives rise to the lifetime broadening of the adatom valence levels into resonances. The lifetime of an electron in a resonant state is inversely proportional to the halfwidth Δ of the resonant level. In what follows we shall assume for simplicity a single valence orbital participating in the chemisorption bond. All other inner adatom orbitals which by our assumption are unaffected by chemical bonding will be hereafter referred to as core levels. Thus, any broadening mechanism of the adatom core levels will be a property of the adatom itself or due to the nonbonding interactions that lead to image effects.[3(b),4] To avoid complications we shall ignore the latter within the present model and restore them at the end, where in the discussion of the results we make contact with the situations in which their role may become important.

Another simplification we are going to introduce into the model is the neglect of the spin of the valence electrons. This, in effect, means that we ignore all intraorbital correlations in the adatom valence states, and these are known to be quite large in isolated atoms. However, as image screening effects considerably reduce the intraorbital correlations in adsorbates[4] the neglect of the latter is compatible with the neglect of the image effects. We shall return to the question of circumventing the problem of spin and intraorbital correlations later, in the discussion of the final results. With all these simplifications taken into account our model system may give a reasonable description of extra-atomic relaxation effects in alkali chemi-sorption on free-electron-like and transition metals but its qualitative predictions are believed to go beyond this limited number of adsorption systems.

Creation of a hole in an adatom core level during the photoemission process is followed by intra-atomic relaxation which shakes up the electrons in all outer "passive" orbitals and lowers their energy in the final state. In case when the lifetime-broadened adatom valence level is only partly occupied, the intra-adatom relaxation will be followed by a flow of electrons from the substrate into the empty states of the resonances which have been pulled below the Fermi level of the system (see Fig. 1). Viewed from the point of a many-body scattering process, sudden creation of a core hole represents a transient perturbation which gives rise to the emission of soft electron-hole excitations in the continuum of the adatom valence states. As has been known for some time, the emission of low-energy excitations by a transient localized perturbation displays some singular properties[7] which, as we expect, will strongly affect the photoemission spectra of adsorbate core levels.

In x-ray photoelectron spectroscopy (XPS) from atomic core levels the measured photoemission spectrum is to a good approximation proportional

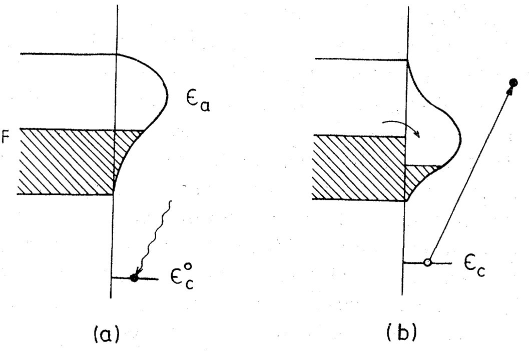

FIG. 1. Position of adatom resonant level with respect to the substrate valence band: (a) in the absence of core holes and (b) after photoemission when a hole is created in a core state.

to the core-level density of states:

$$N(\omega) \propto \rho_c(\omega) . \tag{1}$$

The relation (1) implies a sudden approximation to XPS in which all interactions between the photoemitted electron and the system may be neglected due to the sudden character of the photoelectron escape. This approximation will hold provided the removal of the electron from the core state is a fast event compared with the characteristic time of the substrate surface response which is of the order ω_s^{-1}, where ω_s is the surface plasmon frequency.[4] As we have already neglected the image effects which are characteristic of the surface response the sudden approximation and its implications will be used throughout this work.

The c-level spectral density is most conveniently obtained from the corresponding Green's function $G_c(\omega)$ on making use of the relation

$$\rho_c(\omega) = \pi^{-1} |\mathrm{Im}\, G_c(\omega)| , \tag{2}$$

where in the time representation G_c is defined in the standard way:

$$G_c(t, t') = -i \langle 0 | T[c_c(t) c_c^\dagger(t')] | 0 \rangle, \quad \epsilon_F = 0 . \tag{3}$$

Here $c_c^\dagger(t)$, T, and $|0\rangle$ stand for the c-level electron creation operator in the Heisenberg representation, the time-ordering operator, and the ground state of the system (with no core holes), respectively; ϵ_F is the Fermi energy. The time evolution of the operators $c_c^\dagger$ and c_c is governed by the Hamiltonian of the system

$$H = H_0 + H_{\mathrm{int}} , \tag{4a}$$

$$H_0 = H_{\mathrm{atom}} + H_{\mathrm{subs}} + H_{\mathrm{bond}} , \tag{4b}$$

in which the first two terms in H_0 describe the unperturbed adatom and the substrate (at infinite separation), respectively. H_{bond} describes the bonding interaction which gives rise to the formation of the chemical bond between the atom and the substrate upon bringing the adatom near to the substrate surface. The effect of this interaction is to broaden the initially discrete adatom valence level into a resonance. The last term in (4a) describes the relaxation of the adatom valence level upon the creation of a core hole. In our notation this may be written in the form

$$H_{\mathrm{int}} = -U n_a (1 - n_c) , \tag{5}$$

where U is an intra-atomic Coulomb integral which measures the magnitude of intra-atomic relaxation shift and n_a and n_c are the occupation operators corresponding to the adatom valence and core states $|a\rangle$ and $|c\rangle$, respectively. The interaction (5) is zero when acting on the system ground state $|0\rangle$ and is switched on with the creation of the core hole. In this and Sec. III we shall neglect virtual excitations and the decay of the c hole which implies infinite hole lifetime. This will be a realistic approximation in the case where the natural c-level width γ is much smaller than the width Δ of the adatom resonant level. The effect of the core-hole decay will be discussed in Sec. IV. Taking this into account $\langle 1 - n_c \rangle$ becomes a good quantum number: 0 before, and 1 after, photoemission. As regards the time evolution of the operators in the Green's function (3) this assumption transforms the interaction (5) into a time-dependent one-body scattering potential which acts only in the time interval (t', t) and is zero otherwise.

Nozières and De Dominicis[8] have shown that a Green's function of the form (3) in which the time evolution of the operators is subject to a transient one-body scattering potential can be written on making use of the linked cluster theorem in the form

$$G_c(t, t') = G_{c0}(t - t') e^{C(t - t')} . \tag{6a}$$

Here

$$G_{c0}(t) = i \Theta(-t) e^{-i\epsilon_c^0 t} \tag{6b}$$

is the unperturbed propagator for the c hole of energy ϵ_c^0, Θ is the step function, and $C(t)$ is the sum of all linked diagrams which represent the scattering of the a electrons by the localized perturbation within the time interval (t, t'). In the present case, this is obtained from the equation

$$C(t - t') = U \int_{t'}^{t} \varphi_a(\tau, \tau; t, t') \, d\tau , \tag{7}$$

where φ_a is the a-level propagator defined as

$$\varphi_a(\tau, \tau'; t, t') = -i \langle 0 | T[c_a(\tau) c_a^\dagger(\tau')] | 0 \rangle . \tag{8}$$

Here, $c_a^\dagger$ creates an electron in the a state and τ and τ' are subject to the condition that they lie within the time interval (t, t') during which the interaction (5) is switched on. Treating (5), again, as the one-body transient potential it may be shown that φ_a satisfies the integral equation[8]

$$\varphi_a(\tau, \tau'; t, t') = G_{a0}(\tau - \tau') - U \int_{t'}^{t} G_{a0}(\tau - \tau_1) \varphi_a(\tau_1, \tau'; t, t') \, d\tau_1 , \tag{9}$$

where G_{a0} is the unperturbed a-level propagator calculated in the initial state in the absence of the interaction H_{int}.

Several important properties of the c-level spectrum (2) emerge from the relations (6), (7), and (9). The relaxed threshold energy of the c level in the final state is obtained by summing up all the terms in (7) which are linear in $(t - t')$ in the limit

$t\to\infty$, $t'\to-\infty$ and adding them to the unperturbed energy ϵ_c^0. Making use of (9) we find

$$\lim \varphi_a(\tau, \tau, t, t') = G_a(\tau, \tau) = -i\langle n_a\rangle_f ,$$

$t\to\infty$, $t'\to-\infty$, where G_a is the a-level propagator in the final (equilibrium)state in the presence of the interaction H_{int}, and $\langle n_a\rangle_f$ is the corresponding final mean occupation of the adatom resonance. Hence, the relaxed energy of the c level is

$$\epsilon_c = \epsilon_c^0 + U\langle n_a\rangle_f , \tag{10}$$

where $U\langle n_a\rangle_f$ is the c-level relaxation shift.

Another quantity of importance in spectroscopic measurements is the mean energy $\langle\epsilon_c\rangle$ of the c level which is obtained by evaluating the first moment of the c-level spectrum

$$\langle\epsilon_c\rangle = \int_{-\infty}^{\infty} \omega\rho_c(\omega)\, d\omega . \tag{11}$$

Making use of (2) and (6) we find, after some calculation

$$\langle\epsilon_c\rangle = \epsilon_c^0 - \operatorname{Im} e^{C(0)}\partial C(0)/\partial t . \tag{12}$$

From Eqs. (7) and (9) we see that $C(0)=0$ and $\partial C(0)/\partial t = -i\langle n_a\rangle_0$, where $\langle n_a\rangle_0$ is the mean occupation of the adatom valence resonance in the initial unperturbed state (in the absence of the interaction U) because the integral in (9) is zero for $t=t'$. This means that the mean energy of the c state after photoemission equals the c-level energy in the absence of the extra-atomic relaxation:

$$\langle\epsilon_c\rangle = \epsilon_c^0 + U\langle n_a\rangle_0 . \tag{13}$$

Thus, whatever the role is of the extra-atomic relaxation in shifting and redistributing the weight in the c-level spectrum it must not, according to (13), affect the mean energy of the level. This statement, which may be termed "zero-work sum rule", has a plausible physical interpretation. In photoemission experiments involving fast electron transitions from the c level into the vacuum the energy uncertainity of the final state may be so large that one would measure only the mean energy of the core state.[9] Now if the relaxation time of the system largely exceeds the switching time of the applied perturbation, as is the case in the sudden limit, the measured energy will be the unrelaxed energy of the c state. Hence the zero effect of the extra-atomic relaxations on the mean energy in sudden transitions. A similar effect also has been found for image-screening relaxation processes in adsorption systems.[4]

Besides the static properties (10) and (13) of the c-level spectrum, there exists an important dynamic effect arising from the transient character of the perturbation (5) which leads to the singular behavior of the c spectrum at the threshold. To demonstrate this we first point out that for large times the unperturbed a-level propagator behaves as

$$G_{a0}(t) \to -\rho_{a0}(0)/t, \quad t\to\infty ,$$

where $\rho_{a0}(\omega)$ is the a-level density of states in the absence of the interaction U. On noticing that in this limiting case the integral equation (9) becomes singular, Nozières and De Dominicis[8] have calculated the appropriate perturbative solution which is valid in the large t limit. Correspondingly, this suffices to calculate the limiting behavior of the c spectrum in the threshold region. Following their calculations we find

$$\lim_{\omega\to\epsilon_c} \rho_c(\omega) \propto (\epsilon_c - \omega)^{(\delta/\pi)^2-1}\Theta(\epsilon_c - \omega) , \tag{14a}$$

where the phase shift in the critical exponent is given by

$$\delta = \tan^{-1}\{U\rho_{a0}(0)/[1+Uy_a(0)]\} , \tag{14b}$$

and $y_a(\omega)$ is the Hilbert transform of ρ_{a0}. Hence, $\rho_c(\omega)$ displays a power-law divergence at the threshold and is sharply cut off above ϵ_c. The latter property is known as the Anderson orthogonality block[7] and indicates the orthogonality of the unrelaxed (initial) and relaxed (final) states of the system. The origin of the threshold singularity lies in the emission of a large number of low-energy electron-hole excitations by the localized transient perturbation (5). The mean number of these excitations is logarithmically divergent and this gives rise to the threshold divergence in the c spectrum.[10]

As is clear from (14b), the intensity of the threshold divergence will depend on the initial position of the adatom valence resonance with respect to the Fermi level. Thus, for smaller $\rho_{a0}(0)$ we may expect a redistribution of the spectral weight from the threshold towards $\langle\epsilon_c\rangle$ as is suggested by the zero-work sum rule (13). To demonstrate this we calculate the mean-square deviation σ of the c spectrum from its center of gravity given by (13). Starting from the definition

$$\sigma^2 = \int_{-\infty}^{\infty} d\omega\,(\omega - \langle\epsilon_c\rangle)^2\rho_c(\omega) ,$$

we calculate σ by applying the procedure analogous to that employed in the derivation of the mean energy (13). The problem amounts to evaluate $\partial^2 C(0)/\partial t^2$. Making use of (7) and (9), and taking the proper time limit in the latter expression, we find

$$\sigma^2 = U^2\langle n_a\rangle_0(1-\langle n_a\rangle_0) . \tag{15}$$

The interpretation of this expression is straightforward, for very small (or large) initial occupations of the valence resonance the c spectrum may exhibit an additional maximum at $\langle \epsilon_c \rangle$ provided $\sigma \ll \epsilon_c - \langle \epsilon_c \rangle$. This is a rather restrictive condition which is likely to be satisfied only for resonances located high above ϵ_F in the initial state and below ϵ_F in the final state.

The situation for observing the two peaks in the c spectrum is thus somewhat critical. Large U and small σ are required but the product $U\rho_{a0}(0)$ must not be too small in order to preserve the singular threshold behavior. What is more likely to occur in real systems is one of the following possibilities: (i) a strongly asymmetric peak at the threshold in the case where the coupling strength $U\rho_{a0}(0)$ of electron-hole excitations to the sudden perturbation (5) is large, i.e., when the maximum of $\rho_{a0}(\omega)$ is close to the Fermi level; (ii) a more or less symmetric peak at $\langle \epsilon_c \rangle$ when this coupling is small, as in the case of resonances lying well above or below the Fermi level. Only in the case of a "crossover" regime from strong to weak coupling would it be possible to encounter a doubly peaked structure in the c spectrum. In what follows we shall restrict our attention to the threshold properties and substantiate the above qualitative conclusions within the model calculations in Sec. III.

III. MODEL CALCULATION OF THE c-LEVEL SPECTRUM

In Sec. II we outlined how the assumption of the sudden intra-atomic relaxation of adsorbate valence levels enables one to obtain some general features of the c-level photoemission spectra without having specified any particular model of the chemisorption system. The only assumption used in the derivation of the expressions (10), (13), and (14) was the localized character of the adatom valence state $|a\rangle$ which is broadened into a resonance by the bonding interaction with the substrate. In this section we shall adopt Newns[11] model of chemisorption based on Anderson[12] Hamiltonian and calculate the shape of the c spectrum in the limit $U\rho_{a0}(0) < 1$.

Neglecting spin, the Hamiltonian of a chemisorption system consisting of a single adatom with a core, a valence state, and the substrate represented by its valence-band states $|k\rangle$, can be written in the form

$$H_0 = \epsilon_c^0 n_c + \epsilon_a^0 n_a + \sum_k \epsilon_k n_k + \sum_k (V_{ak} c_a^\dagger c_k + \text{H.c.}) . \tag{16}$$

Here $c_k^\dagger$ and c_k are the creation and annihilation operators for k electrons, $n_k = c_k^\dagger c_k$, and V_{ak} is the matrix element which is responsible for the tunneling of valence electrons between the adatom and the substrate. The halfwidth of the resonant a level in this model is given by

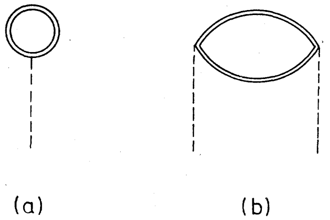

FIG. 2. (a) First- and (b) second-order diagrams in powers of U contributing to $C(t)$. Double and broken lines denote the propagator $G_{a0}(t)$ and the interaction U, respectively.

$$\Delta(\omega) = \pi \sum_k V_{ak}|^2 \delta(\omega - \epsilon_k) , \tag{17a}$$

and its Hilbert transform

$$\Lambda(\omega) = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\Delta(\omega')}{\omega - \omega'} d\omega' , \tag{17b}$$

yields the bonding shift of the a level upon chemisorption. The unperturbed a-level density of states is given by

$$\rho_{a0}(\omega) = \Delta(\omega)/\pi^{-1}[(\omega - \epsilon_a)^2 + \Delta^2(\omega)] , \tag{18}$$

where the chemical shift Λ has been already included in ϵ_a. To obtain the c-level spectrum in the limit $U\rho_{a0}(0) < 1$ we again start from the relation (6a) and calculate $C(t)$ exactly up to the order $[U\rho_{a0}(0)]^2$. This is achieved by taking the first two terms in the diagrammatic expansion of $C(t)$ which are sketched in Fig. 2. These diagrams differ from the ordinary ones that describe systems in equilibrium since the times associated with the interaction vertices U are constrained to the time interval (t, t'). It is easily verified that the diagram (a) of Fig. 2 yields

$$C_a(t) = -iU\langle n_a \rangle_0 t , \tag{19a}$$

and as it is linear in t it can only contribute to the shift of the c level. The dynamic effects of relaxation arise first in the diagram (b) of Fig. 2, in which terms oscillatory in t appear together with the linear ones. Taking into account the restriction on the intermediate times associated with the two U vertices[13] we find

$$C_b(t) = -U^2 \int_0^\infty d\omega \frac{S(\omega)[1 - \exp(i\omega t) + i\omega t]}{\omega^2} , \tag{19b}$$

where $S(\omega)$ is the energy spectrum (imaginary part) of the electron-hole pairs denoted by the polarization bubble in Fig. 2(b). It can be calculated by taking the imaginary part of the convolution

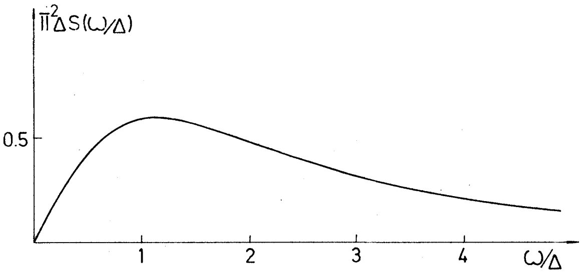

FIG. 3. Spectral function $\pi^2\Delta S(\omega)$ of electron-hole excitations calculated in the limit of a half-filled resonance and Δ=const.

of the function $G_{a0}(\omega)$ with itself. On expressing $G_{a0}(\omega)$ in the spectral representation and making the convolution we get

$$S(\omega)=\int_0^{\omega} d\omega'\,\rho_{a0}(\omega')\rho_{a0}(\omega'-\omega)\,. \tag{20}$$

In the low-frequency limit the function $S(\omega)$ behaves as

$$\lim_{\omega\to 0} S(\omega)=\omega\rho_{a0}^2(0)+(\omega^3/3!)\times\{2\rho_{a0}''(0)\rho_{a0}(0)-[\rho_{a0}'(0)]^2\}+O(\omega^5)\,, \tag{21}$$

where primes denote derivatives with respect to ω. In the opposite limit of large frequences $S(\omega)$ falls off as ω^{-2} provided $\Delta(\omega)\ll\omega<W$ where W is the bandwidth of Δ. To get a qualitative estimate of $S(\omega)$ we shall henceforth assume a very slow variation of $\Delta(\omega)$ over the whole bandwidth W. This assumption does not affect the appearance of the threshold divergence in the c spectrum which is connected with the existence of a linear ω behavior of $S(\omega)$ for small frequences. In this limit $\rho_{a0}(\omega)$ tends to a Lorentzian-shaped density of states centered at ϵ_a. In the model Δ=const it is possible to derive an analytic expression for $S(\omega)$,[14] and its behavior is sketched in Fig. 3. In order to make the integration in (19b) feasible we shall introduce an ansatz for $S(\omega)$ which coincides with the linear term in (21) for small frequences so as to produce the correct threshold singularity given by (14). However, this linear behavior must be properly cutoff near the maximum of the electron-hole spectrum so that the zero-work sum rule (13) is obeyed. The function which satisfies such requirements is

$$S(\omega)=\omega\rho_{a0}^2(0)\exp[-\omega\rho_{a0}(0)]\,, \tag{22}$$

and enables the analytic solution of (19b). Thus, we get

$$C_b(t)=-iU^2\rho_{a0}(0)t-[U\rho_{a0}(0)]^2\ln[1-it/\rho_{a0}(0)]\,. \tag{23}$$

The first term in (23) contributes to the relaxation shift of the c level while the logarithmic term gives rise to threshold divergences. Combining (19a) with (23) and neglecting in the weak-coupling limit other logarithmic terms in $C(t)$ proportional to higher powers of the coupling constant $U\rho_{a0}(0)$,[15] the calculation of the c spectrum becomes straightforward and yields

$$\rho_c(\omega)=\frac{\exp[(\omega-\bar{\epsilon}_c)\rho_{a0}(0)](\bar{\epsilon}_c-\omega)^{\alpha-1}\Theta(\bar{\epsilon}_c-\omega)[\rho_{a0}(0)]^{\alpha}}{\Gamma(\alpha)}\,. \tag{24}$$

Here Θ and Γ denote step and gamma functions, respectively, the critical exponent takes the form

$$\alpha=[U\rho_{a0}(0)]^2\,, \tag{25}$$

and the threshold energy is given by

$$\bar{\epsilon}_c=\epsilon_c^0+U\langle n_a\rangle_0+U^2\rho_{a0}(0)\,. \tag{26}$$

Note that α and $\bar{\epsilon}_c$ are just the terms up to the order $[U\rho_{a0}(0)]^2$ in the power expansion of the exact critical exponent $(\delta/\pi)^2$ defined by (14b) and the relaxed threshold energy ϵ_c given by (10). Besides the threshold power-law divergence, the relaxation shift and the orthogonality block already discussed in Sec. II, the spectrum (24) exhibits an exponential attenuation towards higher binding energies and is correctly normalized to unity. A plot of (24) is given in Fig. 4(a).

At this stage it would be appropriate to question the validity of the ansatz (22) for the spectral function (20). As has been already mentioned, (22) coincides with exact $S(\omega)$ for small ω and satisfies the sum rule (13). On the other hand it gives a too large $\sigma(=U)$ and hence does not allow for the splitting off of the possible maximum at $\langle\epsilon_c\rangle$ from the threshold singularity. Thus, our conclusion is that the ansatz (22) correctly describes the shape of the c spectrum when the adatom valence resonance lies close to the Fermi level in the initial state whereas it may not be a reliable approximation in the opposite situation. In the latter case, it may be necessary to treat the interaction (5) on a completely different footing.[14]

IV. LINE SHAPES IN PRESENCE OF FINITE CORE-HOLE LIFETIME

Up to now we have ignored all decaying mechanisms which could lead to the finite lifetime of adsorbate core holes created in photoemission. This approximation, which would work well in case of core states sufficiently deep to avoid band broadening, may become increasingly worse in the case of very deep levels for which there is a high probability that the hole captures an electron from an adjacent inner shell of the adatom.

This decaying process through which the c hole acquires a finite lifetime will broaden the discrete c state into a level of finite halfwidth γ which is inversely proportional to the hole lifetime.

Intra- and extra-atomic relaxation processes will also influence the XPS spectra of adsorbates whose core levels are already broadened by lifetime effects. On introducing certain restricting assumptions on the evolution of a c hole it is possible to demonstrate within the present model how the shake-up and relaxation processes are affected by lifetime effects. Thus depending on whether the ratio γ/Δ is larger or smaller than unity we may anticipate that the line-shape broadening will be due mainly to the lifetime or shake-up effects, respectively.

To introduce the effect of the c-level broadening we extend the unperturbed adatom Hamiltonian in (4b) by a new term

$$\tilde{H}_{\text{atom}} = H_{\text{atom}} + H^{\text{decay}}_{\text{hole}}, \tag{27}$$

which accounts for the finite lifetime of the c hole. To calculate the c propagator (3) under these conditions we assume that only the hole produced by the x-ray photon needs to be considered and all virtual excitations of the hole may be neglected due to the large energy separation between ϵ_c^0 and ϵ_F. This implies that the unperturbed Green's function $\tilde{G}_{c0}(t)$ still describes the propagation only in the direction of negative times and is obtained from (6b) on multiplying it by a phenomenological attenuating factor $e^{(\gamma t)}$.[16,17] Taking this into account the full propagator $G_c(t, t')$ upon switching on the interaction H_{int} takes again the form (6a) with G_{c0} replaced by $\tilde{G}_{c0}$. As can be easily shown[18] this form of the c propagator in the t space leads to the expression for the c-level spectrum which is given as a convolution:

$$\rho_c(\omega) = \int_{-\infty}^{\infty} d\omega' \rho_{c0}(\omega') D(\omega - \omega'). \tag{27a}$$

Here ρ_{c0} is the unperturbed c-level density of states corresponding to $\tilde{G}_{c0}$ and $D(\omega)$ is the spectrum of the shake-up structure

$$D(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp[i\omega t + C(t)]. \tag{27b}$$

An exact calculation of the interference of lifetime broadening and shake-up and relaxation processes can be performed using the results of Sec. III. We first note that in the present case $\rho_{c0}(\omega)$ takes a form of a Lorentzian of the halfwidth γ in accordance with the assumption of the c-hole decay. Convoluting this form of the unperturbed c spectrum with the expression (24) in which $\bar{\epsilon}_c$ is replaced by ω', we find that the c-level spectral density in presence of lifetime and relaxation effects reads

$$\begin{aligned}\rho_c(\omega) = \pi^{-1}[\rho_{a0}(0)]^{-\alpha} \operatorname{Im} \{&(\omega - \bar{\epsilon}_c - i\gamma)^{\alpha-1} \\ &\times \exp[(\omega - \bar{\epsilon}_c - i\gamma)\rho_{a0}(0)] \\ &\times \Gamma(1-\alpha, (\omega - \bar{\epsilon}_c - i\gamma)\rho_{a0}(0))\}, \end{aligned} \tag{28}$$

where $\Gamma(x, y)$ is the incomplete gamma function and other quantities are the same as defined in (24). The most prominent feature of the spectral density (28) is its pronounced asymmetric shape near the maximum which is located very close to the threshold energy $\bar{\epsilon}_c$. The origin of this asymmetry lies in the shake-up processes which give rise to the singular broadening and the orthogonality block appearing in the c spectrum in the absence of the core-hole decay.

However, the singularity is, in the present case, smeared out by the lifetime effects. For energies far away from the threshold the spectrum (28) tends to a Lorentzian, as can be easily checked by using the asymptotic limit of the incomplete gamma function for large argument: $\Gamma(1-\alpha, z) \to z^{-\alpha} e^{-z}$. This is an expected property because within a very short time interval (large ω) the electrons in the system cannot relax and respond to the suddenly created scattering potential introduced by the core hole.

A closed-form expression for $\rho_c(\omega)$, albeit in a form of a series, can be obtained using the power expansion for the incomplete gamma function. After a somewhat lengthly but straightforward calculation we get

$$\begin{aligned}\rho_c(\omega) = \pi^{-1}\rho_{a0}(0) &\exp[(\omega - \bar{\epsilon}_c)\rho_{a0}(0)] \\ &\times \Bigg\{\Gamma(1-\alpha)\{[(\omega - \bar{\epsilon}_c)^2 + \gamma^2]\rho_{a0}^2(0)\}^{(\alpha-1)/2} \cos\left[(1-\alpha)\tan^{-1}\left(\frac{(\omega - \bar{\epsilon}_c)}{\gamma}\right) + \gamma\rho_{a0}(0) + \frac{\alpha\pi}{2}\right] \\ &\quad + \sum_{k=0}^{\infty} \frac{(-1)^k\{[(\omega - \bar{\epsilon}_c)^2 + \gamma^2]\rho_{a0}^2(0)\}^{k/2}}{k!(k+1-\alpha)} \sin\left[\frac{k\pi}{2} - k\tan^{-1}\left(\frac{(\omega - \bar{\epsilon}_c)}{\gamma}\right) - \gamma\rho_{a0}(0)\right]\Bigg\}. \end{aligned} \tag{29}$$

The first term on the right-hand side of (29) is responsible for the asymmetric shape of the spectrum near the threshold which becomes more pronounced with the decrease of γ. The second term suppresses the exponential for large $|\omega|$, thereby giving the correct Lorentzian limit in the tails of the spectrum. For $\gamma = 0$ this term vanishes and the expression (28), and hence (29) tend to the limit

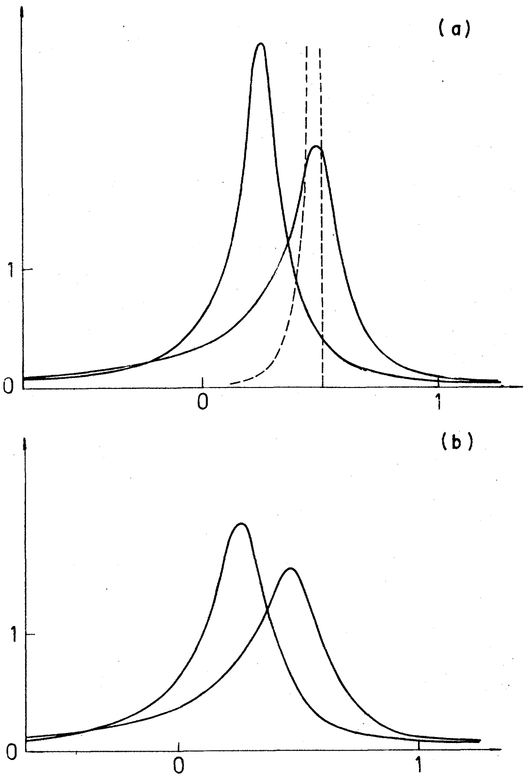

FIG. 4. Core-level spectra $\rho_c(\omega)/\rho_{a0}(0)$ obtained from (29) as functions of $(\omega-\epsilon_c^0)\rho_{a0}(0)$ for $\langle n_a\rangle_0=\frac{1}{2}$ and different values of $\beta=U\rho_{a0}(0)$ and $\eta=\gamma\rho_{a0}(0)$. (a) $\eta=0.09$, $\beta=0.315$ (left curve) and $\beta=0.5$ (right curve). Dashed curve is the spectrum (24) for $\gamma=0$ and $\beta=0.5$. (b) $\eta=0.14$, $\beta=0.315$ (left curve) and $\beta=0.5$ (right curve).

given by (24). However, it should be pointed out that this term must not be neglected for small but finite γ since the cosine function appearing in the first-term changes its sign for small γ in the threshold region.

Plots of $\rho_c(\omega)$ for several values of parameters U, γ, and $\rho_{a0}(0)$ (Ref. 19) are given in Fig. 4. Note the similarity between these analytical results and the numerical results obtained recently by Schönhammer and Gunnarsson[20] for an equivalent choice of parameters.

At this point it would be tempting to extend the result for the spectral shape (29) beyond the limit $U\rho_{a0}(0)<1$ by replacing α and $\bar{\epsilon}_c$ by $(\delta/\pi)^2$ and ϵ_c, respectively. Granted it is correct, this procedure does not lead to any qualitative changes in the shape of the c spectrum, i.e., it is again limited to the systems in which valence resonances lie close to the Fermi level when one has $\sigma\sim U$. Hence, the numerical approach of Schönhammer and Gunnarsson[20] proves necessary in the treatment of the crossover regime of intermediate coupling where the peak at the unrelaxed energy starts to split off from the threshold singularity (see the discussion at the end of Sec. II).

V. CONCLUSION

Quite a few experimental works in which the adsorbate core-level spectra were recorded by photoemission or other spectroscopic techniques have been reported recently. All measured core spectra display shifts and broadening with respect to the corresponding levels in gas phases with a strong asymmetric spectral redistribution undoubtedly present in some cases. In systems where one can rule out the overlaps of the split off adsorbate core peaks the asymmetricity of the broadened c levels may be thought of as due to the shake-up and relaxation mechanisms proposed in this work. Thus, Fuggle *et al.*[21] detected skew-broadened O 1s XPS peak from oxygen and CO adsorbed on the rhutenium (001) surface which is in accordance with the results of Sec. IV. A similar effect has been also observed by Norton *et al.*[22] for oxygen chemisorbed on nickel and Bradshaw *et al.*[23] for oxygen on aluminum.

As was shown by Doniach and Šunjić[16] the asymmetry index of skew spectral lines increases with the increase of the critical exponent α. Hence, we may expect strongly asymmetric core line shapes in adsorption systems in which the product $U\rho_{a0}(0)$ is not negligible. Unfortunately, it is difficult to estimate this product in case of oxygen chemisorbed on transition metals due to the relatively large separation between the center of the resonant valence levels and the substrate Fermi level. The systems which would most obviously satisfy this requirement are those in which the adatom resonant levels are centered near the Fermi level of the substrate, in which case it becomes possible to approximate $\rho_{a0}(\omega)$ by a Lorentzian and hence obtain the maximum critical exponent $\alpha\approx(U/\pi\Delta)^2$. A suitable example are heavier alkaline and alkaline-earth atoms chemisorbed on transition metals since the ionization potentials of the former are comparable with the work functions of the latter. An estimate of α may be made for the photoemission from the 5s core levels of barium adsorbed on tungsten. From the data of Plummer and Young[24] we find $\Delta\lesssim 1$ eV and estimate U to be of the order 1–2 eV from the calculations of Shirley.[2] This gives $\alpha\approx 0.1-0.3$ which implies the asymmetry index approximately in the interval 1.2–1.8.[16]

The magnitude of the relaxation shift (10) also depends critically on the ratio U/Δ. For narrow resonances located entirely above the Fermi level and $U\ll\Delta$ we have $\langle n_a\rangle_0=0$ and $\langle n_a\rangle_f\ll 1$ and the relaxation shift will be very small. In the opposite limit $U\gg\Delta$ the shifted valence state will lie below ϵ_F and hence $\langle n_a\rangle_f\approx 1$. This gives the maximum relaxation shift of the order U though α is zero in this case and the asymmetricity of the c-level spectrum will disappear. The absence of asymmetricity under these circumstances is easily understood as the filling of a completely empty resonance by electron tunneling from the substrate proceeds at the time-rate Δ^{-1} and hence the sudden character of the perturbation $H_{\rm int}$ acting on the adatom valence electrons is lost. For resonances located close to the Fermi level in the initial state and $U \approx \Delta$ the relaxation shift will be of the order $\frac{1}{2}U$ and the asymmetricity of the core spectrum will be large.[25]

The effect of image screening which has been neglected throughout our calculations can also contribute to the enhancement of the spectral line asymmetry and the magnitude of the relaxation shift. In case when $\langle n_a\rangle_f - \langle n_a\rangle_0 < 1$ the charge accumulated on the adatom cannot completely screen out the core hole produced in photoemission and hence an image charge will be induced at the substrate surface. This will give rise to an additional upward relaxation shift v in the c level and reduction of the intra-atomic integral to the effective value $U_{\rm eff} = U - 2v$. The dynamic aspect of image screening which involves excitation of electron-hole pairs and collective modes in the substrate conduction band will also contribute to the skew broadening of the c spectrum at the threshold.[3(b),4] Thus the total critical exponent will be given as the sum $\alpha = \alpha_1 + \alpha_2$, where α_1 and α_2 describe the excitation of soft electron-hole pairs in image screening and atomic relaxation, respectively.

Our last comment concerns the neglect of spin within the present model. The inclusion of spin correlations into the problem requires the appropriate extension of the original Hamiltonain (16) by a term which would account for intra-orbital correlations. This may be written in the form[11,12]

$$H_{\rm corr} = U_{aa} n_{a\uparrow} n_{a\downarrow} , \tag{30}$$

where U_{aa} is the intra-orbital Coulomb integral whose magnitude in isolated atoms may be estimated as the difference between the atomic ionization and affinity potentials: $U_{aa} = I - A$. However, in adsorbed atoms this quantity will be reduced due to image screening to $(U_{aa})_{\rm eff} = U_{aa} - 2v$,[4] and hence the effective correlation strength measured by the ratio $(U_{aa})_{\rm eff}/\pi\Delta$ will be smaller. In chemisorption of heavier alkaline and alkaline-earth atoms this ratio becomes smaller than unity for most commonly found values of Δ and v which are of the order of 1 eV. In this case, it is justified to treat the correlation interaction (30) within the nonmagnetic limit of the Hartree-Fock approximation $\langle n_{a\uparrow}\rangle = \langle n_{a\downarrow}\rangle$.[12,26] The unperturbed a-level propagators $G_{a0}^{\uparrow}$ and $G_{a0}^{\downarrow}$ are then decoupled and the effect of spin will amount to the enhancement of the critical exponent and the relaxation shift since electrons of both spin directions will contribute equally to $C(t)$ in (7). This would favor the appearance of threshold divergence or assymetry in $\rho_c(\omega)$. However, the formal solution of the problem with spin correlations taken into account and arbitrary $U_{aa}/\pi\Delta$ is not at all straightforward and would require special treatments.[26]

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