Excitation energy dependence of core-level x-ray-photoemission-spectra line shapes in metals

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Creation of a deep localized hole in the process of x-ray photoemission from metals is followed by a drastic rearrangement of the surrounding electrons in the Fermi sea. This rearrangement in which low-energy electron-hole pairs are produced, in analogy with gas-phase atomic shake-up processes, gives rise to a low-energy tail in the hole spectral density with an integrable (Mahan) singularity at the energy corresponding to zero-energy pair production. When the usual (symmetric) broadening of the hole is included, the resulting hole line shape becomes a skew resonance, with the asymmetry indices growing with the strength of the electron-hole interaction. The case in which the hole potential is switched on instantaneously (the sudden or impulse limit) has been treated by Doniach and Šunjić. However, the potential switching-on time is a function of the speed at which the excited electron leaves the region of the hole. In this paper we calculate the skew line shapes for finite hole-creation times, going continuously from the adiabatic to sudden limits. The photoemission line shape, for a given hole state, varies smoothly from the symmetric result given in the adiabatic approximation to the asymmetric result of Doniach and Šunjić obtained in the sudden approximation, as the photon energy is increased above the photoionization threshold value.

I. INTRODUCTION

Interest is currently high in understanding the role of electronic relaxation phenomena upon creation of a localized hole in a metal, particularly in core-level x-ray-photoemission spectroscopy (XPS). Relaxation gives rise to shifts in apparent core-level binding energies (compared to single-particle Hartree-Fock orbital energies). Various aspects of the theories of relaxation-energy shifts have been discussed previously[1-5] and so, aside from some considerations on the role of time scales,[6] will not be dealt with here.

Another class of problems is concerned with the time dependence of the relaxation process and thus any possible observable consequences of the finite relaxation time.[6-13] Best[8] has given an excellent qualitative summary of the role of time scales in core-level spectroscopies. Meldner and Perez[7] have presented a theory of relaxation energies and relaxation times in the adiabatic and sudden limits, as follows. An electron in a Hartree-Fock single-particle orbital with orbital energy ϵ_0 is excited by a photon with energy $h\nu$. The time scale by which the remaining electrons of the atom feel and thus respond to the deficiency of an electron charge (a positive hole) is determined by the kinetic energy of the excited electron. As the kinetic energy approaches zero (the photoionization threshold, if delayed onsets due to centrifugual barriers are neglected[14]), the excited electron moves very slowly from the ion core, and the resulting hole potential can thus be imagined to be turned on adiabatically. The electrons in the ion lower their energy by slowly relaxing around the extra positive charge, while always remaining in the ground state of the instantaneous self-consistent potential. In order that energy is conserved, the ejected electron must pick up this "intra-atomic relaxation energy" ϵ_a, and thus it emerges with a total energy ϵ_a greater than that inferred from a picture in which the orbitals in the ion are frozen in the same configuration they had in the atom. The photoionization energy spectrum would thus be a δ function (neglecting hole lifetime decay processes) at the energy $\epsilon_t = h\nu + \epsilon_a - \epsilon_0$, as shown in Fig. 1(a). In the other extreme of very large kinetic energy, the ejected electron leaves quickly, and the hole potential appears to be switched on instantly. In this sudden limit, the wave functions of the electrons in the ion core are continuous functions of time, but now the eigenstates of the ion are eigenfunctions of a new Hamiltonian, the atomic Hamiltonian with a hole potential. Consequently, the ion wave functions have nonvanishing projections onto the excited eigenstates of the ion. There is thus the possibility of leaving the ion in an excited state,[15] and to conserve energy, the ejected electron must then emerge at discrete energies below the adiabatic energy as shown in Fig. 1(a). These peaks are called shakeup peaks. There is also the possibility of ejecting a second electron in this relaxation process, and the resulting continuous photoelectron spectrum is called a shakeoff satellite. The adiabatic limit is obtained when the switching-on time of the hole potential is $\tau \gg \hbar/E_x$, with E_x a typical ion excitation energy. Likewise, the sudden limit is valid when $\tau \ll \hbar/E_x$. Little theory seems to ex-

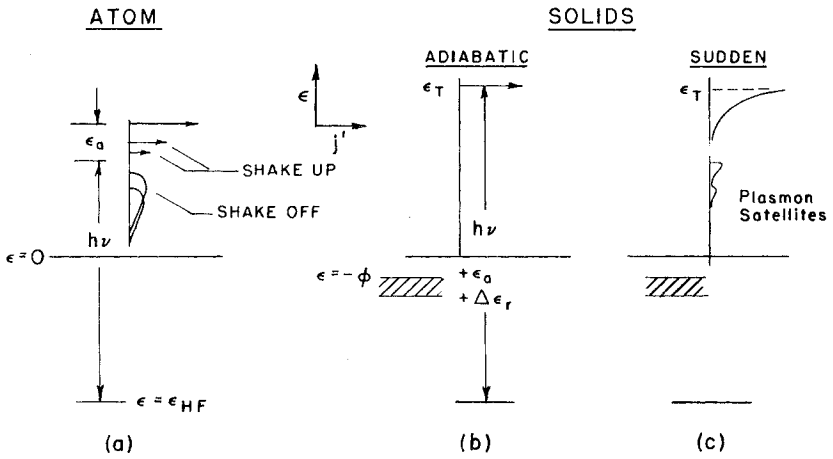

FIG. 1. Energy-level diagrams and photoemission energy distributions for core-level XPS. (a) Atomic photoionization showing the leading peak, shakeup peaks, and shake-off satellites. For adiabatic excitation, the intensity in all but the leading peak is zero. (b) Solid-state photoemission in a hypothetical adiabatic limit. Note that the leading peak has an additional relaxation-energy shift $\Delta\epsilon_r$ compared to the gas phase. (c) Solid-state photoemission in the sudden limit. The Mahan "shakeup" structure or the leading peak and intrinsic plasmon satellites are shown.

ist which goes smoothly between the two limits as τ varies. We will soon return to these ideas.

In solid-state physics, considerable attention has been focused on the long time response or relaxation of an electron gas when a localized potential such as a core hole is instantly switched on or off.[16–20] It has been shown that for certain simple hole potentials the sudden switching triggers a chaotic rearrangement of electrons in the conduction band, resulting in the excitation of many low-energy electron-hole pairs, the low-energy excited states of the metal. In fact, an infrared catastrophe should occur in which an infinite number of zero-energy pairs are created. The experimental ramifications of this effect have been predicted to be that x-ray emission or absorption spectra (obtained when core holes are switched off or on) should show singularities or exceptional rounding off at the threshold energies, where the spectra are predicted to have the functional form $D(\epsilon)\sim 1/(\epsilon_t - \epsilon)^{1-\alpha}$ where α is related to the phase shifts of Fermi-level electrons scattering from the screened hole potential. Whether such effects have been observed is still a subject of controversy.[16,20,21]

Now consider the case of core-level XPS of metals. We shall follow the same arguments used to discuss the Meldner and Perez[7] relaxation theory of atoms. If it were possible to switch on the hole potential adiabatically, then the energy-level diagram shown in Fig. 1(b) would apply. In addition to the intra-atomic relaxation-energy shift another shift, the extra-atomic relaxation energy $\Delta\epsilon_r$, occurs owing to the fact that the ion core is embedded in a polarizable electron gas. The conduction-band electrons lower their energy by screening the positive ion core, and this energy is picked up by the excited electron. Now consider the sudden limit. In analogy with atomic shakeup peaks, it is expected that the solid might be left in some excited states, and thus the photoejected electrons could emerge with energies $< \epsilon_T$. For a solid of infinite extent, the electron-hole pair excited states form a continuum with $0 \le \epsilon_{e-h} < \infty$. (Note that for a finite solid, the excited states would still be discrete, and thus there would be a small but finite gap between the ground state and first excited state.) If the atomic shakeup peaks are then allowed to merge together, the photoelectron spectrum shown in Fig. 1(c) would result. Here shakeup plasmon satellites are also shown.[18,22] An interesting connection exists between the pair "shakeup peak" and the Anderson theorem.[23] One aspect of this theorem states that the ground state of an *infinite* electron gas is orthogonal to the ground state of the same electron gas with a localized hole potential somewhere within it. Thus no matter how slowly the localized potential is turned on, electron-hole pairs and thus the infrared catastrophe will result. In other words, since the ground states are orthogonal, the electron gas with the localized potential must be in some excited state in order to project onto the initial ground state. Viewed as a shakeup process, the origin of this result is quite clear. For the electron gas of infinite (as opposed to large but finite) extent, there are always some excited states with sufficiently low energy that the switching-on time $\tau \ll \hbar/E_x$. Consequently, those states see the switching on as sudden, no matter how large τ is, and thus the infrared divergence occurs. For a finite system, τ can (in principle) be made larger than $\hbar$ divided by ΔE_x, a small but finite minimum excitation energy, and thus it would be possible to adiabatically turn on the localized potential.

Returning now to the question of XPS on core levels in solids, Doniach and Šunjić[24] (DS) noticed that the actual line shape of a photoemitted electron should include the (assumed symmetric) broadening due to the finite lifetime of the core hole, not just the shakeup or Mahan structure shown in Fig. 1(c).

Working in the sudden limit, they presented a theory in which asymmetric line shapes, skewed towards the high-binding-energy (low-kinetic-energy) side, were predicted. Such line shapes have since been observed.[25] In fact, the asymmetric XPS line may be one of the strongest confirmations of the Mahan singularity.[21]

In the present paper, we consider the effect of finite and variable hole switching times on the asymmetry of an XPS line. Experimentally, the switching time can be varied by varying the photon frequency and thus the kinetic energy of the excited electron. For photon energies near the photoionization threshold, the excited electron remains near the hole for a longer time, and thus the potential which the electron gas responds to, that one due to the lack of an electron, is switched on slowly. As the photon energy is increased, the hole potential is switched on more rapidly, tending to the sudden limit. Müller-Hartmann, Ramakrishnan, and Toulouse[19] (MHRT) have presented a theory of the particle-hole excitation spectrum obtained when a localized potential in an electron gas is turned on at a finite rate. Here we combine the works of DS and MHRT to obtain expressions and numerical values for asymmetry indices of XPS lines as a function of many parameters, with special emphasis on the switching rate. The switching rate and resulting asymmetry of an XPS line should be a function of $h\nu$. Thus systematic photoemission experiments with synchrotron radiation should be useful in providing additional data on this relaxation effect.

II. THEORY

As first suggested by Doniach and Šunjić, the observable XPS line shape, which takes into account core-hole lifetimes, is to a good approximation the convolution of the Mahan shakeup structure with the core lifetime broadening function[26]

$$\frac{dN}{d\epsilon} \equiv I_{\rm obs}(\epsilon) = \int_0^\infty \rho_{\rm hole}(\epsilon+\epsilon')D(\epsilon')\,d\epsilon' , \tag{1}$$

with

$$\rho_{\rm hole}(\epsilon+\epsilon') = \frac{1}{\pi}\frac{\gamma}{(\epsilon+\epsilon')^2+\gamma^2} \tag{2}$$

and γ the hole lifetime.[27] With this energy scale $\epsilon = 0$ at the adiabatic emergence energy $\epsilon_T = h\nu + \epsilon_a + \epsilon_r - \epsilon_0$. As mentioned previously, when using the sudden approximation, the Mahan shakeup structure has the form $D(\epsilon') \sim 1/(\epsilon')^{1-\alpha}$ where, for only s-wave scattering off the hole potential, $\alpha = (\delta/\pi)^2$ with δ the s-wave phase shift.

Müller-Hartman *et al.*[19] have presented a very comprehensive theory of the dynamic response of an electron gas to a localized perturbation, and in particular they consider the influence of switching rates. For a time-dependent potential of the form

$$V(\vec{r}, t) = \begin{cases} V(\vec{r})\,e^{\eta t}, & t \le 0 \\ V(\vec{r}), & t \ge 0 \end{cases}$$

they find (with certain technical approximations[28]) that the excitation spectrum of electron-hole pairs generated in the switching-on process is

$$D(\epsilon') = \frac{(1/\eta^2 + 1/\omega_c^2)^{\alpha/2}}{\Gamma(\alpha)}\left(\frac{\eta}{\epsilon'}\right)^{1-\alpha} e^{-\epsilon'/\eta}, \quad \epsilon' > 0 \tag{3}$$

where ω_c is a cutoff energy of the order of the Fermi energy, and all energies are given in units of Fermi energies. The only difference between this result and that of the sudden approximation is that those excited states with energies $> \eta$ are exponentially damped out.

As a first approximation to the time-dependent hole potential that is produced in an XPS experiment, we take

$$V_h(\vec{r}, t) = \begin{cases} 0, & t \le 0 \\ V_h(\vec{r})(1 - e^{-\eta t}), & t \ge 0 \end{cases} \tag{4}$$

where the photon excitation occurs at $t = 0$, and $V_h(\vec{r})$ is the screened, static long-time potential. The rate at which the hole potential is switched on depends on how fast the excited electron recedes from the positive ion core. Roughly speaking, $\eta \lesssim$ velocity of the excited electron divided by the range of the screened potential. We will return to a discussion of η later. The desirable feature about this time-dependent potential is that within the approximations used by MHRT the pair excitation spectrum given by Eq. (3) applies also to the time-dependent potential of Eq. (4). Thus the observable XPS line shape can be obtained by combining Eqs. (1)–(3). The details of the integration (courtesy of Dr. Jan Herbst) are given in the Appendix and the end result is

$$I_{\rm obs}(\epsilon) = \frac{1}{\pi}\left(\frac{1}{\eta^2}+\frac{1}{\omega_c^2}\right)^{\alpha/2} e^{\epsilon/\eta} \times \frac{\Gamma(1-\alpha)}{(\epsilon^2+\gamma^2)^{(1-\alpha)/2}}\cos\theta - \eta^{\alpha-1}\delta I(\epsilon) , \tag{5a}$$

where

$$\theta \equiv (\alpha-1)\tan^{-1}(\epsilon/\gamma) - \tfrac{1}{2}\pi\alpha - \gamma/\eta , \tag{5b}$$

$$\delta I(\epsilon) = A\cos(\gamma/\eta) - B\sin(\gamma/\eta) , \tag{5c}$$

$$A = \int_0^1 z^{-\alpha}\, e^{-\epsilon z/\eta}\sin(\gamma z/\eta)\,dz , \tag{5d}$$

and

$$B = \int_0^1 z^{-\alpha}\, e^{-\epsilon z/\eta}\cos(\gamma z/\eta)\,dz . \tag{5e}$$

In Eq. (5a), the term with $\delta I(\epsilon)$ is generally quite small relative to that one with $\cos\theta$ except in the asymmetric wings of the line.

Equations (5a)–(5e) possess the necessary feature of reducing to all the appropriate limiting cases: (i) $\eta \to \infty$, the sudden approximation. Then Eqs. (5a)–(5d) become

$$I_{\rm obs}(\epsilon) = \frac{\Gamma(1-\alpha)}{\pi}\frac{1}{\omega_c^{\alpha}}\frac{\cos[(\alpha-1)\tan^{-1}(\epsilon/\gamma)-\pi\alpha/2]}{(\epsilon^2+\gamma^2)^{(1-\alpha)/2}},$$

which is the result of Doniach and Šunjić.[24] (ii) $\gamma \to 0$, no broadening. Then

$$I_{\rm obs}(\epsilon) = \frac{1}{\Gamma(\alpha)}\left(\frac{1}{\eta^2}+\frac{1}{\omega_c^2}\right)^{\alpha/2}\frac{e^{\epsilon/\eta}}{|\epsilon|^{1-\alpha}}, \quad \epsilon<0 .$$

From (ii) we can recover the limits: (iii) $\gamma \to 0$, $\eta \ll \omega_c$; the adiabatic limit of MHRT:

$$I_{\rm obs}(\epsilon) = -\frac{1}{\Gamma(\alpha)}\frac{1}{\epsilon}\left(\frac{|\epsilon|}{\eta}\right)^{\alpha} e^{\epsilon/\eta}, \quad \epsilon<0 .$$

(iv) $\gamma \to 0$, $\eta \gg \omega_c$; the transient limit of Nozières and de Dominicis[17]:

$$I_{\rm obs}(\epsilon) = -\frac{1}{\Gamma(\alpha)}\frac{1}{\epsilon}\left(\frac{|\epsilon|}{\omega_c}\right)^{\alpha}, \quad \epsilon<0 .$$

(v) $\alpha = 0$, no relaxation limit, $\eta \to \infty$:

$$I_{\rm obs}(\epsilon) = \frac{1}{\pi}\frac{\gamma}{(\epsilon^2+\gamma^2)},$$

a Lorentzian shape; $\gamma \to 0$:

$$I_{\rm obs}(\epsilon) = e^{\epsilon/\eta}\delta(\epsilon) .$$

It is gratifying that the single expression, Eq. (5), contains all these limits.

Proceeding towards the numerical consequences of finite switching times on the shakeup relaxation, Eqs. (5a)–(5d) have been evaluated for a typical set of parameters: $\alpha = 0.3$, $\omega_c = 1$, $\gamma = 0.1$, and η treated parametrically (with all energies in units of the Fermi energy), and $I_{\rm obs}(\epsilon)$ vs ϵ/γ is shown in Fig. 2, where the curves have been normalized to unity at the peak maximum. As can be noted, the transition from the adiabatic Lorentzian ($\eta = 0$) to the sudden-limit shape of DS ($\eta = \infty$) occurs mostly as η varies from 0 to 1. Line shapes with other reasonable parameters demonstrate similar trends. A convenient measure of the η-dependent skewness is the asymmetry index used by x-ray spectroscopists: the ratio of the absolute value of peak energy minus $\frac{1}{2}$-height energy on the low-energy to that on the high-energy side of the line. Asymmetry indices calculated numerically from Eqs. (5a)–(5d) for some typical parameters spanning the physically realized range and for a large range of values of η are given in Table I. The discussion and interpretation of these results will be given in Sec. III.

III. DISCUSSION

The ultimate hope of the present theory is to show that information on the electron-gas relaxation pro-

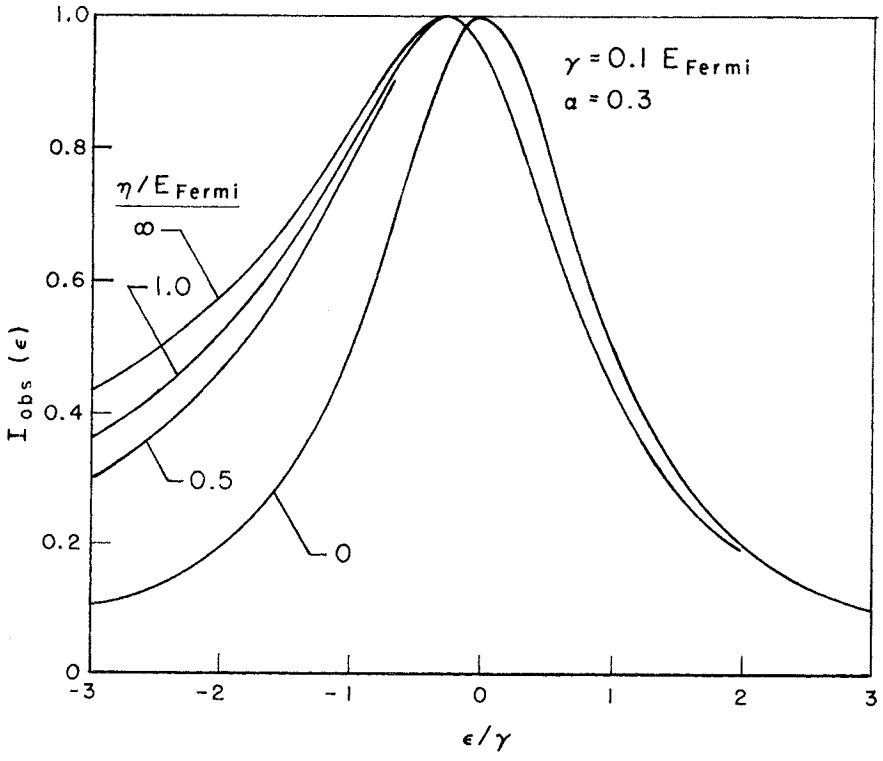

FIG. 2. Typical asymmetric XPS line shape vs ϵ/γ with η treated parametrically (in units of $E_{\rm Fermi}$). For this figure, $\omega_c = 1$, $a = 0.3$, and $\gamma = 0.1$.

TABLE I. XPS line-shape asymmetry indices $\alpha(a, b, c)$.

$b=\omega_c/\eta$ \ $\alpha=V^2$	0.00	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24	0.26	0.28	0.30	$c=\gamma/\omega_c$
0	1.000	1.033	1.068	1.106	1.147	1.191	1.240	1.292	1.349	1.412	1.480	1.555	1.637	1.727	1.827	1.937	0.1
	1.000	1.033	1.068	1.106	1.147	1.191	1.240	1.292	1.349	1.412	1.480	1.555	1.637	1.727	1.827	1.937	0.02
0.1	1.000	1.032	1.067	1.104	1.144	1.188	1.235	1.287	1.341	1.401	1.467	1.538	1.616	1.702	1.795	1.898	0.1
	1.000	1.033	1.068	1.105	1.146	1.191	1.239	1.291	1.348	1.410	1.477	1.551	1.633	1.722	1.820	1.929	0.02
0.2	1.000	1.032	1.066	1.102	1.142	1.184	1.230	1.280	1.333	1.391	1.454	1.523	1.597	1.678	1.766	1.862	0.1
	1.000	1.032	1.067	1.105	1.146	1.190	1.238	1.290	1.346	1.408	1.475	1.548	1.628	1.717	1.814	1.921	0.02
0.5	1.000	1.030	1.063	1.098	1.135	1.174	1.217	1.263	1.312	1.364	1.421	1.482	1.547	1.617	1.692	1.772	0.1
	1.000	1.032	1.067	1.104	1.144	1.188	1.235	1.286	1.341	1.401	1.467	1.538	1.616	1.702	1.795	1.898	0.02
1.0	1.000	1.028	1.058	1.090	1.124	1.160	1.198	1.239	1.281	1.327	1.375	1.426	1.479	1.536	1.596	1.659	0.1
	1.000	1.032	1.066	1.102	1.142	1.184	1.230	1.280	1.333	1.391	1.454	1.523	1.597	1.678	1.766	1.862	0.02
2.0	1.000	1.025	1.051	1.078	1.107	1.137	1.168	1.201	1.234	1.270	1.306	1.344	1.383	1.424	1.466	1.509	0.1
	1.000	1.031	1.064	1.099	1.137	1.178	1.221	1.268	1.319	1.373	1.432	1.495	1.563	1.636	1.715	1.800	0.02
5.0	1.000	1.017	1.035	1.053	1.072	1.091	1.110	1.130	1.149	1.169	1.189	1.210	1.231	1.251	1.272	1.293	0.1
	1.000	1.028	1.058	1.090	1.124	1.160	1.198	1.239	1.281	1.327	1.375	1.426	1.479	1.536	1.596	1.659	0.02
10.0	1.000	1.011	1.021	1.031	1.042	1.052	1.063	1.073	1.084	1.094	1.105	1.115	1.126	1.135	1.145	1.156	0.1
	1.000	1.025	1.051	1.078	1.107	1.137	1.168	1.200	1.234	1.270	1.306	1.344	1.383	1.424	1.466	1.509	0.02

cess around localized potentials can be extracted from the observed asymmetry of XPS line shapes. In particular, the asymmetry has been seen to be a strong function of the switching-time parameter η, which is an experimentally controllable parameter. A zeroth-order approximation to η might be the velocity of the excited electron (far from the ion core) divided by the range of the hole potential. Unfortunately, for a potential with ~1-Å range, $\eta = 1$ corresponds to an electron with a kinetic energy of about 1 Fermi energy with respect to the bottom of the conduction bond. In order for the electron to get out of the solid, at least another 5 eV is required to overcome the work-function barrier. Thus it would appear that all experimentally observable electrons would originate from events in which $\eta \geq 2$. However, as seen from Fig. 2 or Table I, the most dramatic and consequently most observable changes in asymmetries occur as η varies between 0 and ~2.

As it turns out, the proposed definition of η is much too restrictive and thus $0 < \eta \lesssim 2$ might still occur for electrons with several E_{Fermi}'s of kinetic energy. η is really the inverse time delay[29,30] for an electron wave packet to pass through the region of the strongly attractive ion-core potential. As the electron proceeds to the edge of the attractive potential, it can be reflected back towards the ion core and oscillate back and forth for quite long times before finally escaping.[29,30] At least in the case of electron scattering from atoms, this time delay for the lth partial wave has been shown to be $\langle \Delta t \rangle_l = 2\hbar\, d\delta_l/dE$, with δ_l the energy-dependent lth-wave phase shift.[30] This time delay is always longer than the simple expression, range/velocity. Furthermore, centrifugal barriers are known[14] to provide attractive wells for metastable localized final states with large l values which would tend to further reduce η. Lastly, the interesting possibility of exciting two electron autoionizing states in the solid, in analogy with extensive gas-phase results,[31,32] would again provide a mechanism for localizing the excited electron around the ion core for quite a long time, accompanied by a concomitant $\eta \ll 1$. With sufficient mechanisms available which result in small values of η, it seems quite possible that experimentally determined line-shape asymmetries, as a function of $h\nu$ and thus η, could be quite a useful new technique for studying electron relaxation processes due to localized core-hole potentials. Experimental facts are enthusiastically awaited.

Mention should also be made of the connection between the time-*dependent* relaxation effects discussed here and the time *independent* extra-atomic relaxation energy discussed elsewhere.[1-5,9,10,21,22] Experimentally, the core-state binding energy is usually taken to be $h\nu$ less than the kinetic energy

(plus emitter work function when referenced to the emitter Fermi level) of electrons at the energy of the maximum intensity in the XPS line. As Doniach and Šunjić demonstrated, in the $\eta \to \infty$ limit, Eq. (5) has a maximum at

$$\epsilon_{\max} = -\gamma \cot\left(\frac{\pi}{2-\alpha}\right) \tag{6}$$

which is obviously strongly dependent on both the hole lifetime and the scattering strength of the hole. In fact, since $0 \le \alpha \le 1$, Eq. (6) shows that $\gamma \le \epsilon_{\max} \le 0$ and thus the "apparent" binding energy (defined in terms of the position of the peak maximum) depends on the parameters of the relaxation process. The expression for $\epsilon_{\max}$ when $\eta < \infty$ is unwieldy but does depend on η. Thus the apparent relaxation energy, as commonly defined, also depends on the dynamics or time dependence of the relaxation process. This is due to the fact that the finite hole lifetime causes a core-state broadening which in turn forces us to average over the η-dependent shakeup spectrum, and this always results in a center of gravity displaced below the maximum energy. For phase shifts $\delta \approx \pi/2$, which are not unreasonable, $\epsilon_{\max}$ can be displaced by as much as γ below the true maximum energy, with no pair shakeup. Typically $\gamma \sim O(1\text{ eV})$, so theoretical studies, in which experimentally "determined" relaxation energies are compared with detailed theoretical calculations,[3,5] should include the influence of the "shakeup shift" on the experimental energies, if they are defined as the energy at the XPS peak maximum.

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APPENDIX

The basic integral from Eqs. (1)–(3) is

$$A(\epsilon) \equiv \int_0^\infty d\epsilon' \frac{e^{-\epsilon'/\eta}}{(\epsilon')^{1-\alpha}[(\epsilon'+\epsilon)^2+\gamma^2]}$$

$$= \frac{1}{2i\gamma}\int_0^\infty d\epsilon' (\epsilon')^{\alpha-1} e^{-\epsilon'/\eta} \times\left(\frac{1}{\epsilon'+\epsilon-i\gamma} - \frac{1}{\epsilon'+\epsilon+i\gamma}\right).$$

Integrals of this form are given in tables[33] and the result is

$$A(\epsilon) = \frac{1}{2i\gamma}[(\epsilon-i\gamma)^{\alpha-1} e^{(\epsilon+i\gamma)/\eta}\Gamma(\alpha)\Gamma(1-\alpha, (\epsilon-i\gamma)/\eta) - (\epsilon+i\gamma)^{\alpha-1} e^{(\epsilon+i\gamma)/\eta}\Gamma(\alpha)\Gamma(1-\alpha, (\epsilon+i\gamma)/\eta)]$$

$$= \frac{\Gamma(\alpha)}{\gamma} e^{\epsilon/\eta}\,\mathrm{Im}[(\epsilon-i\gamma)^{\alpha-1} e^{-i\gamma/\eta}\Gamma(1-\alpha, (\epsilon-i\gamma)/\eta)]. \tag{A1}$$

Making use of the relations

$$\Gamma(1-\alpha, z) = \Gamma(1-\alpha) - \gamma(1-\alpha, z)$$

and

$$\gamma^*(1-\alpha, z) = \frac{z^{\alpha-1}}{\Gamma(1-\alpha)}\gamma(1-\alpha, z),$$

where $z = (\epsilon - i\gamma)/\eta$, a little algebraic manipulation is then required to express Eq. (A1) in the form displayed in Eqs. (5a)–(5d).

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[26]Note that although the expression given by DS appears algebraically quite different from Eq. (1), in fact it is just the time Fourier transform of the hole propagator $G_{\text{hole}}(t)$ and $D(t)$, where $\rho_{\text{hole}}(\epsilon+\epsilon') = (1/\pi)\text{Im}G_{\text{hole}}(\epsilon+\epsilon') = (1/\pi)\text{Im}\int e^{i(\epsilon+\epsilon')t}G_{\text{hole}}(t)\,dt$.
[27]By taking $\rho=\rho(\epsilon+\epsilon')$ rather than $=\rho(\epsilon-\epsilon')$, the sign of ϵ, the ejected-electron energy, is positive on the high-kinetic-energy side of the XPS line, as is the experimental convention.
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