COMMENTS AND ADDENDA

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Core-line asymmetries in the x-ray photoemission spectra of metals: A comment

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The interpretation of the core-line asymmetries found in x-ray photoemission spectra of transition metals is reexamined in the light of recent theoretical developments. The large asymmetries found in the spectra of d-group transition metals are interpreted in terms of an enhanced hole-electron scattering produced by the s-d interaction.

In a recent communication[1] the shapes of XPS (x-ray photoemission spectroscopy) lines of some core electron in the metals Au, Pt, Ir, Ag, Pd, and Rh were analyzed. This analysis was performed with a line-shape function derived by Doniach and Sunjic[2] (DS) using the exact solution for the core-hole–conduction-electron interaction given by Nozières and De Dominicis[3] (ND). It was found that the core lines could be well represented by the DS line-shape function, substantiating that the photoemission cross section has the form $1/\epsilon^{1-\alpha}$, which, for nonzero α, specifies the divergence in terms of the exponent, α.

In view of a recent series of papers by Kotani and Toyozawa[4] (KT), the physical interpretation of the exponent α has to be reexamined. These authors calculate the line shapes of transition-metal XPS spectra by a formalism similar to that of ND but use a different scattering mechanism. They argue that in transition metals the core hole produced in the photoemission process pulls down an empty d state close to or below the Fermi energy. This d state is highly localized and during the screening process acts as a scatterer for the conduction electrons, much in the same way as does the deep core hole in the simple metals in the ND approach, resulting in exactly the same functional form for the singularity $(1/\epsilon^{1-\alpha})$. The meaning of α is different, however, depending only on the s-electron phase shift δ_0,

$$\alpha = 2(\delta_0/\pi)^2. \tag{1}$$

δ_0, in turn, contains the s-d scattering matrix element V,

$$\delta_0 = \tan^{-1}\frac{\pi\rho V^2}{\epsilon_d - \epsilon_F}, \tag{2}$$

where ρ is the s-electron density of states at the Fermi energy and $\epsilon_d - \epsilon_F$ is the position of the empty d state with respect to the Fermi energy. The expression for α is identical to that of ND specialized for s-wave scattering only. This theoretical formulation makes it possible to gain some insight into the physical significance of the experimentally observed trends for α, namely, values of the order of 0.05 for Ag and Au, which have mainly s-p bands at the Fermi energy, and values between 0.10 and 0.20 for the transition metals which have large d-electron density of states.

If an analysis of the data is performed using s, p, and d phase shifts, δ_0, δ_1, and δ_2, constrained by the Friedel sum rule

$$\pi Z = \sum_{l=0}^{2} 2(2l+1)\delta_l, \tag{3}$$

the minimum value for the asymmetry parameter α, defined by

$$\alpha = 2\sum_{l=0}^{2}(2l+1)(\delta_l/\pi)^2, \tag{4}$$

realizable for $Z=1$ is 0.0556 (1/18). This value, obtained when all three phase shifts are equal to

$\frac{1}{18}\pi$, is close to those observed for Ag and Au. (The minimum α for s, p, d, and f phase shifts is $\frac{1}{32}$.) Phase shifts of $\delta_0 = 0.247$, $\delta_1 = 0.294$, $\delta_2 = 0.064$, obtained from the NMR Knight shift of Zn in Cu,[5] yield $\alpha = 0.069$, consistent with the observed α in noble metals. Arbitrarily setting $\delta_1 = 0$, it was found in Ref. 1 that for $Z = 1$, phase shifts of 0.60, 0, 0.19 yield $\alpha = 0.11$; 0.80, 0, 0.15 yield $\alpha = 0.15$; and 1.00, 0, 0.11 yield $\alpha = 0.22$—spanning the range of values observed in the transition metals. The interesting trend in these calculations is the *increase* in δ_0 required by the larger α found in the metals with large d-electron density of states at the Fermi energy. This comes about because one d electron gives a maximum α of only 0.10, while one s electron yields 0.50. This might already be interpreted as a manifestation of the s-d interaction leading to an increased s-electron contribution to the total phase shift. In the KT model the large value of α for the transition metals is an effect of just this s-d interaction. The actual magnitude is determined by the parameters contained in Eq. (2), but it is clear that large values are easily obtainable with entirely reasonable choices of ρ, V, and ϵ_d. For $\rho = 1$ eV^{-1}, $V = 1$ eV, and $\epsilon_d - \epsilon_F = 1$ eV, α is 0.32. Since δ_0 must fall between the limits of 0 and $\frac{1}{2}\pi$ in the KT formalism, the Friedel sum rule can always be satisfied with all phase shifts positive. Moreover, the value of α calculated for δ_0 from Eq. (1), and that obtained from Eq. (4) for the same δ_0, but with δ_2 added to satisfy the Friedel sum rule will not differ within our experimental accuracy when δ is greater than $\frac{1}{4}\pi$. Thus the two models lead to numerically similar results.

In summary, the models of ND and KT both give exactly the same analytical form for the description of the hole singularities in metals. The ND model is more general, and in a sense contains the KT result, but gives less insight into the physics of the screening process for the d-band metals. Moreover, it is not obvious that a process in which a deep hole is the active scatterer (Nozières and De Dominicis[3]) and in which the number of "s" electrons scattered is largely due to the s-d interaction (there being many d electrons available) is ultimately different from a process in which the deep hole creates a disturbance in the d band which in turn acts as the scatterer Kotani and Toyozawa[4]).

One can in fact argue that the two approaches are equivalent.[6] The time scale in which the d scattering center is produced in the KT approach is of the order of $1/|\epsilon_d - \epsilon_F|$, i.e., of the order of the inverse bandwidth. This is a time *much* shorter than those appearing in the ND formulation, because the power law describing an infrared divergence is valid only for times long compared to the inverse bandwidth. Thus for the purpose of the infrared divergence the creation of the d hole can be regarded as instantaneous, which removes the distinction between the ND and KT treatments of the problem.

The fact that the theoretical approaches are valid only in the limit of small excitation energy raises an interesting problem.[6,7] The fit of the DS lineshape function to the data is usually satisfactory for some eV from the center of the line; i.e., the function appears to be valid for excitations which are not "infrared" in the standard sense, and may in fact be of the order of the bandwidth. The question of why the ND theory in the DS formulation works so well in regions where it should break down deserves further theoretical and experimental consideration.

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