SHAKE UP AND RELAXATION EFFECTS IN CORE LEVEL PHOTOELECTRON SPECTRA OF CHEMISORBED SPECIES

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INTRODUCTION

Recent experimental investigations of the electronic properties of various chemisorbed species /1/ have revealed the existence of additional structures in the adsorbate XPS core level spectra which are not present in the corresponding spectra of atoms or molecules in gas phases. Here we present an outline of a theoretical description of electronic shake up and relaxation effects which may occur in chemisorption systems as a consequence of the sudden formation of a core hole in XPS. It is shown that this model enables a theoretical explanation of relaxation shifts, shake up and satellite structures observed in the XPS core spectra of adsorbates.

FORMULATION OF THE MODEL

The core level photoelectron spectrum in the sudden approximation is proportional to the core level density of states $\rho_c(\omega)$ which is obtained from the relation

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

Here $G_c(\omega)$ is the Fourier transform of the core level Green's function defined in the standard way. Creation of a core hole within the adsorbate in XPS suddenly switches on an interaction between the charge density fluctuations in the core and valence states which participate in the chemisorption bond. This interaction may be written in the form

$$H' = -Un_a(1-n_c), \qquad (2)$$

where n_a and n_c denote the occupation operators for the valence and core levels respectively. H' gives rise to the electron relaxation and shake up processes localized at the adsorbate, and as may be shown /2/, leads to the following form for G_c:

$$G_c(t-t') = g_c(t-t') \times \exp\left[U \int_{t'}^{t} dT\, \phi(T,T;t,t')\right] . \qquad (3)$$

Here g_c is the c-hole Green's function in the absence of the interaction (2) and ϕ describes the propagation of an electron in the adsorbate valence resonant state in the time interval when (2) is switched on:

$$\phi(T,T';\, t,t') = g_a(T-T') - U \int_{t'}^{t} dt_1\, g_a(T-t_1)\,\phi(t_1,T';t,t'). \qquad (4)$$

Here g_a describes the propagation of adsorbate valence electrons before (2) has been switched on.
The relations (1), (3) and (4) are the basic equations from which one can determine both static and dynamic properties of the adsorbate core level spectra without being restricted to any particular model of chemisorption.

RELAXATION SHIFTS IN THE CORE LEVELS

Appearance of a hole in an adsorbate core level pulls down the valence resonance which is then partially or completely filled up by the electrons from the substrate. This gives rise to an upward relaxation shift in the core level. Inspection of the long time behaviour of (3) and (4) yields the relaxed threshold energy of the c-level

$$\varepsilon_c' = \varepsilon_c^0 + U\langle n_a\rangle_f \,, \qquad (5)$$

where ε_c^0 and $\langle n_a\rangle_f$ are the unperturbed core level energy and the final occupation of the valence resonance respectively (3). On the other hand, as can be shown using (3) and (4) the mean energy or the centre of gravity of the c-spectrum remains unaffected by the relaxation processes and reads:

$$\langle\varepsilon_c\rangle = \varepsilon_c^0 + U\langle n_a\rangle_0 \,, \qquad (6)$$

here $\langle n_a\rangle_0$ is the occupation of the valence resonance before the creation of the core hole. This is the "zero work" sum rule which implies that since $\langle n_a\rangle_f \geq \langle n_a\rangle_0$ the major part of the spectral weight is located below the threshold energy (5).

SHAPES OF THE CORE SPECTRA

Qualitative estimates of the c-level spectral shapes can be made starting again from (3) and (4) and using some model function for the valence resonance density of states. A simpler case is that of an adsorbate valence resonance located close to the Fermi level (Fig.1). The transient interaction (2) causes in this case singular excitation of soft electron-hole pairs in the system which gives rise to divergent asymmetric behaviour of the c-spectrum near the threshold. Neglecting the decay of the core hole we find /3/:

$$\lim \rho_c(\omega) \propto (\varepsilon_c-\omega)^{(\delta/\pi)^2-1}\,\theta(\varepsilon_c-\omega) \qquad (7)$$

for ω close to ε_c. The phase shift δ in the critical exponent is found to diminish as the resonance moves away from the Fermi level. In such a case part of the spectral weight is transfered from the threshold singularity towards $\langle\varepsilon_c\rangle$ where a new maximum may appear. To demonstrate this we calculate the mean square deviation of the c-spectrum from its centre of gravity and find:

$$\langle(\omega - \langle\varepsilon_c\rangle)^2\rangle = U^2\langle n_a\rangle_0(1-\langle n_a\rangle_0) \,, \qquad (8)$$

which means that for systems where the valence resonances lie high above (below) the Fermi energy in the initial state, the corresponding core spectra will exhibit a sharp maximum at the unrelaxed energy (6) and consequently much weaker singular structure at the threshold. Recent model calculations of the c-spectra based on the Anderson Hamiltonian and the simple Lorentzian-like resonances confirm these predictions /3,4/ (Fig.1).

A more complicated situation regarding relaxation and shake up processes may occur in chemisorption on transition metal substrates like tungsten or nickel where one may encounter valence resonance density of states sketched in Fig.2. The latter represents a combination of a pair of bonding and antibonding states below and above the Fermi level and some band structure around it. Expressions for the magnitude of the relaxation shift(5) and the mean energy (6) apply also to the present case whereas the spectral shape which reflects a variety of shake up processes occuring in the system turns out to be more complicated. In the limit $U < |\varepsilon_a|$, $|\varepsilon_b|$ it is possible to calculate shapes of the c-spectra analytically in a certain approximation (see Fig.2). Note here the appearance of multiply peaked satellite structure below the threshold due to the possibility of various shake up transitions between the levels ε_b, ε_a and ε_F.

At the end we point out that another possible mechanism which may give rise to the satellite structure and asymmetric broadening in the adsorbate core spectra are multiple surface plasmon and electron-hole shake up losses induced by image screening processes in the substrate /5/.

REFERENCES:

/1/ J.C.Fuggle et al, To be published in Solid St.Comm. and references therein.

/2/ P.Nozieres and C.T.DeDominicis, Phys.Rev.178,(1969)1097

/3/ B.Gumhalter, J.Phys.C10(1977) L219, and to be published.

/4/ K.Schönhammer and O.Gunnarsson, Solid St.Comm.23(1977)691.

/5/ B.Gumhalter and D.M.Newns,Phys.Lett. 53A(1975)137; J.Phys.(Paris)38(1977)1117.

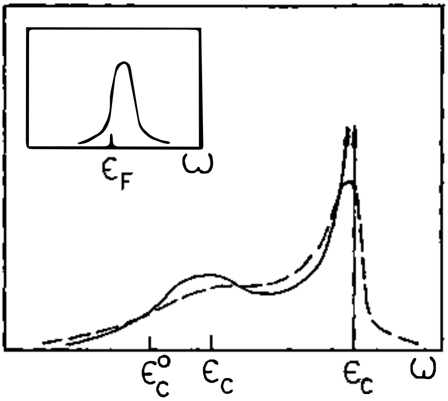

Fig.1. Top left: simple valence resonance density of states in the initial state; bottom: the adsorbate core level spectrum. Dashed lines denote the effect of the c-level lifetime broadening.

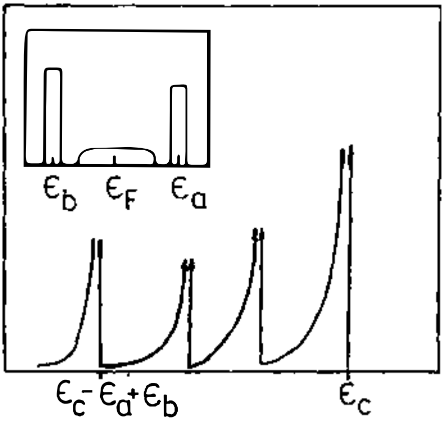

Fig.2. Top left: valence resonance density of states with a pair of bonding (b) and antibonding(a) states; bottom: corresponding multiply peaked core level spectrum.