CORE-HOLE RELAXATION IN X-PHOTOEMISSION FROM ATOMS ADSORBED ON METAL SURFACES

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Core-level electron spectroscopy is a very useful method both for elemental identification and for chemical characterization of solid surfaces(1). In general, an incident beam of photons (or electrons) excites the solid in a way which ultimately leaves at least one hole in some core state and an electron in a high kinetic energy state. In addition, the solid can be left in an excited state due to the creation of plasmons (bulk and surface), electron-hole pairs or phonons(2). The ejected electrons emerge at discrete energies which are, to a first approximation, characteristic of the elemental nature of the source atom. However, there are small (∿1-10 eV) shifts of these characteristic energies which depend on the immediate chemical environment of the source atom. These "chemical shifts" arise from the differing electrostatic potentials at the core site in various chemical situations.

On the other hand, the core hole polarizes the remaining electrons in the system. The Coulomb interaction between the polarization and the hole charge changes the total energy of the ionized system. Therefore, the ejected electron emerges with different kinetic energy than would be inferred from a "frozen electron" picture. This shift is called "relaxation energy". The ejected electron is observed at an energy which is displaced both by chemical and by relaxation shifts. To extract chemical shifts from observed spectra, one must know the relaxation shift.

The relaxation shift can be divided in two parts. The first part is the intra-atomic relaxation of all electrons on the source atom. It is usually assumed that the intra-atomic relaxation is identical in atoms and solids for which accurate calculational schemes are available(3). The response of the rest of the system causes an extra-atomic relaxation-energy shift. In the following, this extra-atomic relaxation we would simply call relaxation.

In this work we consider a system consisting of a thin inert dielectric film adsorbed on the surface of a semi-infinite metal. By inert we mean a dielectric whose properties are well described by the dielectric constant ε. (A physical realization of such a system could be, e.g. a layer of a noble gas physisorbed on a metal substrate). Furthermore, we consider a core hole which is outside of the metal, either in a dielectric or outside of it (e.g. a deep level of some atom adsorbed onto the dielectric layer).

In our case, the relaxation energy consists of two contributions. The first contribution (W_p) is due to screening by surface plasmons(4) and the other (W_d) is due to the response of the dielectric. If the thickness of the dielectric is denoted by a and the distance of the core hole from the metal surface by z, the relaxation shifts are as follows(5):

a) for $0<z<a$:

$$W_p(K) = -\frac{e^2}{\varepsilon+1}\,\frac{e^{-2Kz}}{2\pi K}\,\frac{[1+be^{-2K(a-2z)}]^2}{(1+be^{-2Ka})(1-b^2e^{-2Ka})} \quad ,$$

$$W_d(K) = \frac{e^2}{\varepsilon}\,\frac{be^{-2Kz}}{4\pi K}\,\frac{[1+be^{-2K(a-z)}]}{1-b^2e^{-2Ka}} \tag{1}$$

$$\times \left\{1 + \frac{(b+e^{2Kz})\,e^{-2K(a-z)}}{[1+be^{-2K(a-z)}]}\right\} \quad ;$$

b) for z>a

$$W_p(K) = -\frac{e^2}{\varepsilon+1}\,\frac{1}{2\pi K}\,(1+b)^2\,\frac{e^{-2Kz}}{(1+be^{-2Ka})(1-b^2e^{-2Ka})}\,,$$

$$W_d(K) = -\frac{e^2}{4\pi K}\,b\,\frac{e^{-2K(z-a)}-e^{-2Kz}}{1-b^2e^{-2Ka}}\,, \qquad (2)$$

where

$$b = \frac{\varepsilon-1}{\varepsilon+1}\ .$$

The total energy shift (W) is obtained by integrating over the two-dimensional wave vector $\vec{K}$.

Figure 1 shows the relaxation energy as a function of z. The substrate is taken to be aluminum ($\hbar\omega_B$=15.2 eV), the thickness of the dielectric is a=2Å and its dielectric constant ε=4.

It is also worth mentioning that in the limit of a very thick dielectric (formally $a\to\infty$) and large z, the energy shift approaches the results of a classical electrodynamics for a point charge near the metal-dielectric interface.

References:

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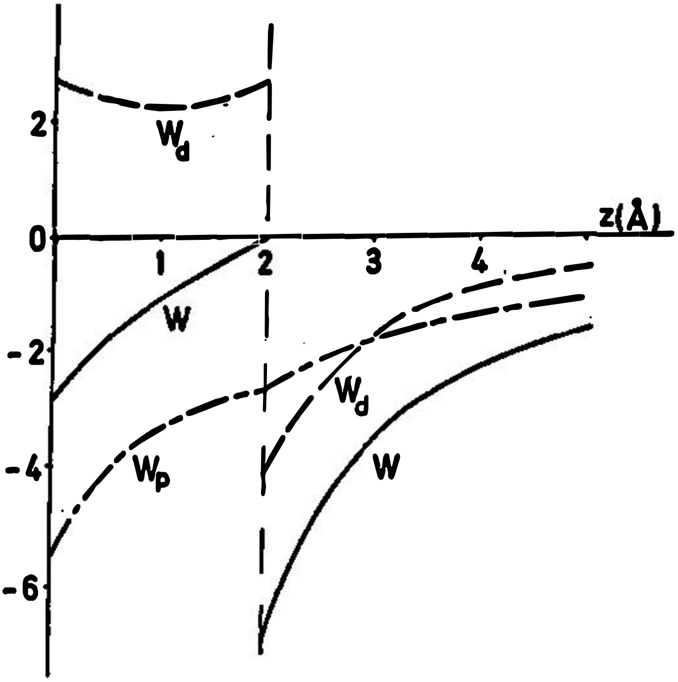

Fig. 1. Relaxation shifts for the system described in the text. (Note: The small value of W for z close to the dielectric-vacuum interface is due to the choice of parameters. For different ε and/or a, W has a significant non-zero value.)