Theory of resonant photoemission and photoelectron diffraction

Resonant photoemission is the photoelectron emission process that occurs in the vicinity of a x-ray absorption threshold, that is with a photon energy around the binding energy of a core-level. Here we are focus on resonant photoemission from valence states. In the photoemission process a photon is absorbed whereby one electron is excited from a valence state into the continuum and is detected at some energy ϵ_p. The process may be written as

$$|\Psi_g\rangle + \hbar\omega \xrightarrow{\text{rad}} |\Psi_f(\underline{v}), \phi_p\rangle$$

where Ψ_g is the N-electron ground state with energy E_g, $\Psi_f(\underline{v})$ a N-1-electron final state with a valence hole ($\underline{v}$) and energy E_f, ϕ_p the photoelectron wave function, and $\xrightarrow{\text{rad}}$ denotes a radiative (absorption) process. From energy conservation we have $\epsilon_p = \hbar\omega - E_f + E_g$ and the spectral intensity is given by

$$I(\epsilon_p, \omega) = \sum_f |\langle\Psi_g|T(\omega)|\Psi_f(\underline{v}), \phi_p\rangle|^2 \delta(\hbar\omega - \epsilon_p - E_f + E_g) \tag{1}$$

In off-resonant photoemission, there is only the direct process where the transition operator $T(\omega)$ corresponds the interaction of the electrons with the photon field $V_{\text{rad}} \equiv -\frac{e}{mc}\mathbf{A}.\mathbf{p}$ where $\mathbf{A}$ is the vector potential of the light and $\mathbf{p}$ is the electron momentum. V_{rad} does not explicitly depend on the photon energy ω.

For photon energies around and above an absorption threshold, a new transition channel opens up, namely the photoabsorption from a core-level followed by the decay of the core-excited (intermediate) state through autoionization. In the latter process the excited electron and one valence electron scatter by Coulomb interaction such that one electron fills the core-hole and the other one is ejected as the photoelectron. In resonant photoemission the core-excitation and auto-ionization have to be considered as a coherent (one-step) process which leads to the same final state as the direct photoemission process. The resonant process is

$$|\Psi_g\rangle + \hbar\omega \xrightarrow{\text{rad}} |\Psi_m(\underline{c}, k)\rangle \xrightarrow{\text{AI}} |\Psi_f(\underline{v}), \phi_p\rangle$$

where $|\Psi_m\rangle$ denotes a N-electron intermediate state with one core-hole ($\underline{c}$) and one electron in an excited state (k), and $\xrightarrow{\text{AI}}$ is the autoionization process. When the resonant process is included, the transition operator becomes, to lowest order [8, 9]

$$T(\omega) = V_{\text{rad}} + V_{\text{AI}} \sum_m \frac{|\Psi_m\rangle\langle\Psi_m|}{\hbar\omega + E_g - E_m + i\Gamma_m/2} V_{\text{rad}} \tag{2}$$

Here, $V_{\text{AI}} = e^2/r_{12}$ is the electron-electron Coulomb interaction which is responsible for the autoionization process and E_m and Γ_m are the energy and width of the intermediate state. The resonant denominator $\hbar\omega + E_g - E_m + i\Gamma_m/2$ gives rise to a fast variation of the intensity around threshold. Since the direct and resonant processes are added on the level of transition matrix elements (rather than intensities) they interfere which leads to the characteristic Fano profile as a function of photon energy.

Davies and Feldkamp [7] developed a theory of resonant photoemission based on the interaction between discrete states and continua. They applied the theory to the 3p-3d resonance of 3d transition metals whose electronic structure was described by either a simple band or charge transfer model. While the calculations had strong model character, general tendencies of the photon and binding energy dependence of resonant spectra could be explained. A much more realistic theory was presented by Tanaka and Jo [9] for resonant photoemission of transition metal oxides at the 2p threshold. The electronic structure was described with a charge-transfer cluster model which features full atomic multiplet interaction on the transition metal ion and hybridization to the oxygen ligand states. The many-electron hamiltonian was diagonalized numerically by configuration interaction. The method was applied successfully to various transition metal oxydes [9, 10]. The theory was extended by Garcia et al. [8] to multiatom resonant photoemission, which stands for photoemission from a core-level on some atom A which gets enhanced by a resonant process from a deeper core-level on a neighboring atom B. Using diagrammatic many-body perturbation theory in the Keldish formalism, Arai and Fujikawa [4] have developed a theory of core-level photoemission which includes single and multiatom resonant processes. All these theories have focussed on the photon and binding energy dependence of the resonant spectra but did not discuss the strong angular dependence of the valence band photoemission which manifests itself in angle-resolved photoemission spectroscopy (ARPES) and photoelectron diffraction (PED). To account for these phenomena a precise description of the delocalized nature of the valence band states and the photoelectron continuum states is required. For non-resonant ARPES and PED, band structure and multiple scattering methods have proved very succesful in this respect [1, 2, 3]. These methods are based on the independent particle approximation. When applying this approximation to resonant photoemission, all many-electron states $|\Psi_g\rangle$, $|\Psi_m\rangle$ and $|\Psi_f, \phi_p\rangle$ are taken as single Slater determinants and Eqs (1,2) become:

$$I(\omega, \epsilon_p) = \sum_v \left| \langle \phi_p | V_{\mathrm{rad}} | \phi_v \rangle + \sum_{c,k} \frac{\langle \phi_p \phi_c | V_{\mathrm{AI}} | \phi_v \phi_k \rangle - [v \leftrightarrow k]}{\hbar\omega + \epsilon_c - \epsilon_k + i\Gamma_{ck}/2} \langle \phi_k | V_{\mathrm{rad}} | \phi_c \rangle \right|^2 \delta(\hbar\omega - \epsilon_p + \epsilon_v) \quad (3)$$

where ($[v \leftrightarrow k]$) denotes the exchange term and all other notation is obvious from the foregoing. Cho et al. [5, 6] have calculated Ga 3d-4p resonant photoemission spectra of a GaAs(110) surface using the independent particle theory (3). The intermediate states ($\Psi_m(\underline{c}, k)$), were limited to the surface core exciton which was treated as an atomic excitation. Using a tight-binding scheme for the valence band states (ϕ_v), on- and off-resonant angle resolved spectra were calculated for specific points in the Brillouin zone and good agreement with experiment was achieved [6].

For direct valence band photoemission, the observed angular dependence is influenced both by the character of the initial band states and by electron diffraction of the photoelectron final state, i.e. it is a combined initial and final state effect [13]. The initial state band dispersion leads to an angular dependence within the limited solid angle range corresponding to one Brillouin zone. The angular range decreases quickly with increasing kinetic energy (e.g. 7^o for 1000 eV and a lattice constant of 3Å). At high energy, the resulting fast angular variation becomes largely smeared out by various broadening effects (finite inelasting mean free path, phonon broadening, recoil, etc.). Therefore, at high energy the angular dependence is dominated by final state photoelectron diffraction.

For strong resonances, such as 2p-3d in transition metals, the direct term can be neglected at the maxiumum of the resonance curve. The remaining resonant process is element selective, since it involves x-ray absorption from a core-level. Therefore, a resonant photoemission spectra is approximately proportional to an element-projected density of states, rather than the total density of states. This property of resonant photoemission is routinely used to "decompose" the valence band spectrum of a compound into its elemental contributions.

The physical reason for this lies in the fact that the Coulomb matrix element $\langle \phi_p \phi_c | V_{\mathrm{AI}} | \phi_v \phi_k \rangle$ in Eq. (3) is dominated by the on-site contribution, i.e. it is by far largest when ϕ_v and ϕ_k are located on the same site as ϕ_c. As a consequence, in resonant photoemission, the initial valence states become effectively localized to the core-level site.

The foregoing arguments indicate that the angular dependence of resonant photoemission is, especially for strong resonances and high kinetic energy, mainly due to diffraction of the outgoing photoelectron, while the band dispersion and delocalization of the initial valence states have a much weaker effect. This suggests that resonant photoelectron diffraction patterns may approximately be modeled in the same manner as standard x-ray photoelectron diffraction, i.e. as an incoherent sum over multiply scattered photoelectron waves emitted from all sites on which the selected initial state is localized [3]. For core-level photoemission, this is a simple sum over all sites of the same element since the number of electrons in a core-shell is the same for all atoms of this element. For a selected valence state, however, the number of electrons depends furthermore on the crystallographic site, since the local density of states is different for inequivalent sites. So for photoelectron diffraction from valence states, the sum over emitter sites (of the same element) is to be weighted by the local density of states at the selected binding energy. This fact can be exploited to determine the charge distribution (among inequivalent sites of the same element) of specific states in the valence band.

This was shown by Krüger et al. [12] who analyzed the band gap state that appears upon reduction of a TiO2(110) surface. It is well established that this defect state is mainly of Ti-3d character but the location of the defect charge (that is the location of the Ti3+ ions) is a matter of on-going debate, especially in the theoretical literature. In Ref. [12] the photoelectron diffraction from the defect state was measured at the Ti 2p-3d resonance and analyzed using multiple scattering calculations. For each inequivalent Ti site in the surface and sub-surface layer, the photoelectron diffraction intensity for Ti-3d emission was calculated and the total intensity was taken as a weighted sum over the different Ti sites. The weights, which give the relative amount of defect charge on each site, were obtained from a least-square fit between the theoretical and experimental pattern. It was found that the majority of defect charge is located on the a specific Ti site on the first subsurface layer.

Magnan et al. [11] studied the electronic structure of Fe3O4 by resonant photoemission at the Fe L3 edge. Photoelectron diffraction was used to determine the relative contribution of octahedral and tetrahedral Fe sites in selected valence band peaks. In agreement with previous experimental and theoretical studies, it was found that the state at the Fermi level is essentially located on octahedral Fe sites.

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