Photoemission Process

Photo emission process

$\Psi_{tot}^{i}(N)$, $E_{tot}^{i}(N) \rightarrow \Psi_{tot}^{f}(N, K)$, $E_{tot}^{f}(N,K)$

$\Psi_{tot}^{f}(N, K) \rightarrow K^{th}$ final state of N electron system.

(involves both the emitter and the photoelectron)

Energy conservation equation.

$E_{tot}^{i}(N) + h\nu = E_{tot}^{f}(N, K)$

k refers to one electron orbital k from which electron emission occurred, in the simplest case. In general it should include all modes of excitation, electronic, vibrational and translational.

In general, it is assumed that the photoelectron is weakly coupled to the (N – 1) electron system so that separation of final state is possible

$\Psi_{tot}^i(N)$, $E_{tot}^i(N)$ $\xrightarrow{h\nu}$ $\Psi_{tot}^f(N-1, k)$, $E_{tot}^f(N-1, k)$ + $\phi^f(1)$ $\chi^f(1)$, E_{kin}
Initial state   Final state ion   Photoelectron

$\phi^f(1)$ is the spatial part and $\chi^f(1)$ is the spin part.

$\Psi_{tot}^f(N-1, k)$ and $\phi^f(1)$ can be combined suitably to yield correct antisymmetry. This can be done with antisymmetriying operator Â.

$\Psi_{tot}^f(N, K) = \hat{A} (\phi^f(1) \chi^f(1), \Psi_{tot}^f(N-1,k))$

The energy conservation equation then yields
$E_{tot}^i(N) + h\nu = E_{tot}^f(N-1, k) + E_{kin}$

The binding energy corresponding to producing the $\Psi_{tot}^f(N-1,K)$ state is,

$$E_b^v(K) = E_{tot}^{(f)}(N-1, K) - E_{tot}^i(N)$$

The photoelectron is referred w.r.t the vacuum level.
Line width $\rightarrow$ lifetime of initial and final states
Intial lifetimes are large, for a final state life time t the lorentzian width of the peak is $\sim\hbar/t = 6.58 \times 10^{-16}/t(s)$ in eV. For life time of 10^{-18}sec this width can be large (initial state lifetime in most cases is high and there is no contribution to line width)

System containing N electrons with spatial coordinates r_1, r_2 ….r_N and spin coordinates σ_1, σ_2, …. σ_N and p nuclei with coordination R_1, R_2 …. R_N the total wave function,

$$\Psi_{tot}(N) = \Psi_{tot}(r_1, \sigma_1, r_2, \sigma_2 \dots r_N \sigma_N; \quad R_1, R_2 \dots R_P)$$

Nuclear coordinates can be neglected in the resolution scale of electron spectroscopy. In the non-relativistic limit, the Hamiltonian in electrostatic units,

$$\hat{H}_{tot} = \hbar^2/2m \sum_{i=1}^{N} \blacktriangledown_i^2 - \sum_{i=1}^{N} \sum_{l=1}^{P} Z_l e^2/r_{il} + \sum_{i=1}^{N} \sum_{j>i}^{N} e^2/r_{ij}$$

      e-kinetic   e-n attraction   e-e repulsion

$$+ \sum_{l=1}^{P} \sum_{m>l}^{P} Z_l Z_m e^2/r_{lm} - \hbar^2/2 \sum_{l=1}^{P} {}_l \blacktriangledown_l^2 / M_l$$

        n-n repulsion   Nuclear kinetic

M – electron mass, Z_l charge of lth nucleus $r_{il} = |r_i - R_l|$, $r_{ij} = |r_j - r_j|$, $R_{lm} = |R_l - R_m|$, M_l – mass of lth nucleus.

To this relativistic effects may be added by perturbation. Hamiltonian most often added is due to spin-orbit splitting.