

17.2.1 The photoelectron emission spectroscopies

Photoelectron emission from isolated atoms or molecules in the gas phase is predominantly a direct one-electron emission into the continuum and the electron energy spectrum maps the initially occupied energy levels. Solid state photoemission is a more complex process than this. In the solid state the one-step process is replaced by a three-step process. Firstly, the electron is promoted from its initial state in the valence band or core levels to a final state in the unoccupied conduction band. Then the electron must travel to the surface and finally escape through the surface potential barrier. Thus, surface photoelectron emission is not a direct mapping of the initial density-of-states function, as in the gas phase, but the final energy distribution rather represents a convolution of the initial density-of-states with the density-of-states of the conduction band and some energy-dependent surface escape function.

Some of the energy may appear in simultaneous excitation (a shake-up process) or even further ionization (a shake-off process) instead of all of the energy of the photon being employed in the primary photoionization process. In both of these processes the primary photoelectron has less kinetic energy than expected and in the shake-off process an extra electron appears in the spectrum. The probability of these processes is much less than that of primary photoionization.