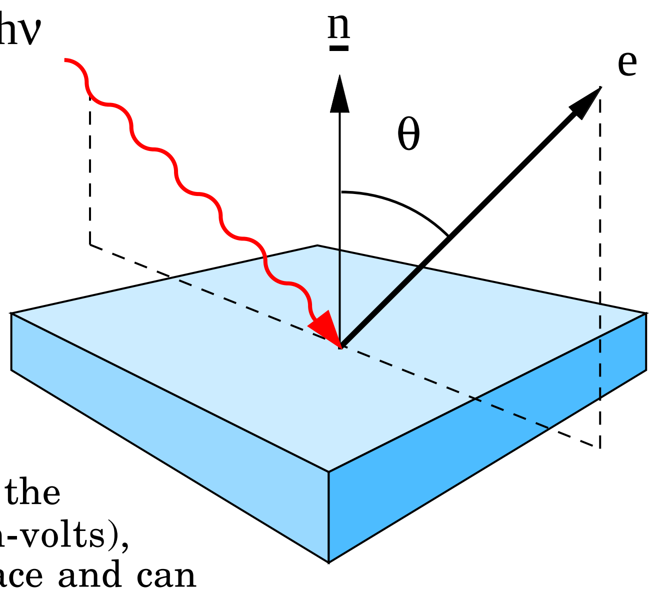
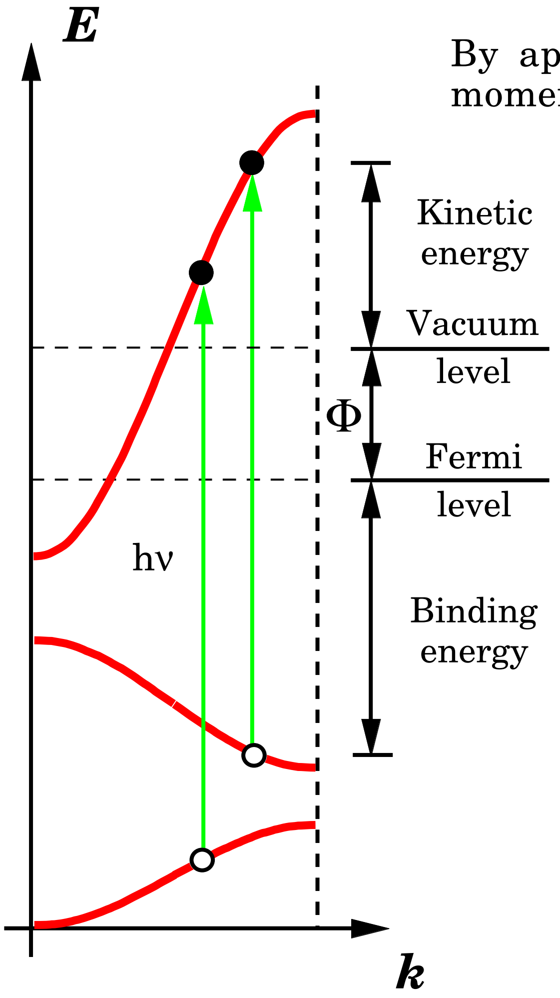
Photoelectron Spectroscopy

Electrons as particles

In the photoelectric effect, first explained by Einstein in 1905, a photon of light ejects an electron from the surface of a sample.



When the photon is absorbed by an electron, the kinetic energy of the electron is increased by an amount equal to the photon energy (by the conservation of energy). Some electrons will travel deeper into the sample, but some may head towards the surface. Providing that an electron is energetic enough to overcome the workfunction (Φ) of the sample (typically a few electron-volts), then it will leave the surface and can be detected.



By applying the conservation of energy and momentum, the state of the electrons before they were ejected by the photons can be deduced. Plotting the electron states of a crystalline material by their momentum (written as k) and energy (E) shows that they exist in bands of allowed energies, with energy gaps between them. The Fermi energy defines the energy of the most energetic electron in the material.

By absorbing a photon, an electron is kicked from a low energy state (○) inside an atom into a higher energy state (•) in which it is free to move through the sample.

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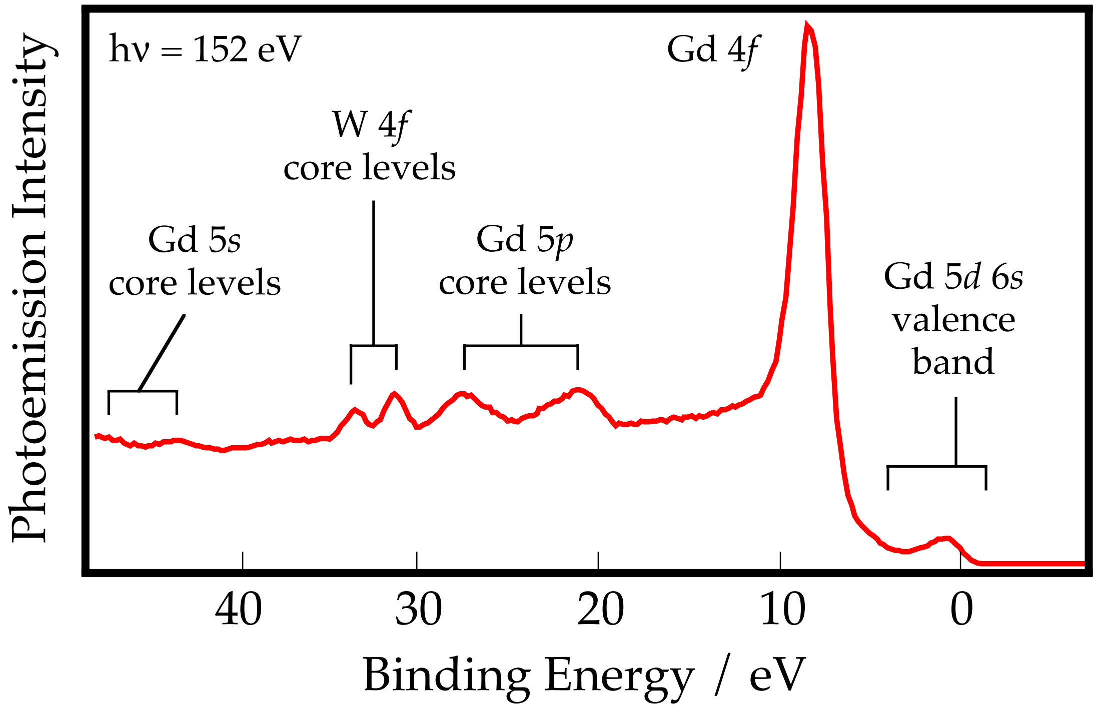
Some of the photoelectron's energy is used to free the electron from its parent atom (the binding energy), and some is used to overcome the workfunction. Whatever is left is measured as the kinetic energy of the photoelectron. Thus if we measure the kinetic energy of an electron, and we know the photon energy (hν) and the workfunction (Φ) of the sample, then we can calculate the binding energy of the electron.



The photoelectron spectra are often displayed as graphs of numbers of photoelectrons emitted per second (the photocurrent) plotted against kinetic energy or binding energy (above).

In this spectrum peaks are seen which correspond to electronic energy levels in atoms of tungsten and gadolinium. A binding energy scale has been used, so that zero corresponds to the most energetic electrons in the sample (the valence electrons in the outer electron shells of the atoms) and larger binding energies correspond to electrons more tightly bound to their parent atoms.

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