Extracting Chemistry From X-Ray Photoemission Spectroscopy: Orbitals, Multiplets, and More

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The use of orbital based analyses, which provide an important fundamental basis for interpreting and understanding the features in X-ray photoelectron spectroscopy, XPS, is described. In particular, the physical meaning of Koopmans' theorem is shown to allow the separation of the interesting initial state contributions to XPS binding energies, BEs, from the less interesting properties of the highly excited ionic states. The use of orbitals and orbital occupations provide the critical basis for understanding resolved and unresolved multiplets in the XPS of open shell systems, both isolated molecules and condensed matter. The standard approximation to determine the XPS intensities is based on the ionization of electrons from specific orbitals. Furthermore, orbital models allow the different losses of intensities to satellites for ionization of shallower and deeper shells to be understood.

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