

Introduction to photoelectron spectroscopy in atoms, molecules and solids.

G. Stefani

CNR-ISM c/o Dipartimento di Scienze Università Roma Tre

Since availability of dedicated Synchrotron Radiation Sources, photoelectron spectroscopy (PES) has become one of the most widely used tools to investigate the electronic structure of matter in different states of aggregation, i.e. the electron binding energies [1]. PES is profitably applied in disciplines ranging from solid state physics, to surface science, material science, nano-technologies, chemistry, biology and geology, just to name a few.

Aim of these lectures, intended for beginners with different scientific background, is to introduce the general principles of the realization and interpretation of PES experiments [2]. This objective, common to all different applications of PES, will be pursued by the help of simple examples which explain what information can be deduced from the different structures characteristic of the photoelectron spectra.

Though the main features of PES can roughly be interpreted on the basis of an independent electron model, the many body behaviour of the quantum system under scrutiny (chemical shift, satellite structures and multiplet splitting) prevents from simply interpreting them in terms of single electron binding energies. The selected atomic, molecular and solid state examples, will show that on the one hand the complexity of the many particle response to the ionizing perturbation is a problem, but on the other hand it can be used to shine light on several different properties of the aggregates; among them the correlated behaviour of the valence electrons that is at the basis of technologically relevant phenomena, such as magnetism, superconductivity, chemical reactivity, etc.

Peculiarities of molecular PES spectra will be introduced before extending to the Energy Distribution Curve (EDC) in solids the interpretative framework elaborated in the simpler atomic case. To this end, the fundamental three step model will be outlined. Distribution in angle of the photoelectrons (ARPES) [3] will be also discussed and its application to investigation of the band structure in solids will be highlighted. The concept of resonant photoemission will be also introduced.

To conclude, a brief survey on the recent development of PES in: spin resolved (SR-PES) [4], time resolved (Tr-PES) [5] and high energy photon excited (HAXPES) [6] experiments will be provided.

This brief introduction to photoelectron spectroscopy with synchrotron radiation, will not rigorously and exhaustively treat the process and the scientific results. For in depth description of the photoelectron spectroscopy, the reader is addressed to the literature quoted in [1-6].

[1] Reinert, F., Hüfner, S., *New Journal of Physics* 7 (2005) 97

[2] Mariani, C., Stefani, G. In: *Synchrotron Radiation: Basics, Methods and Applications*, pp. 275-317. Springer Berlin Heidelberg (2015) DOI: 10.1007/978-3-642-55315-8_9

[3] Sobota, J., A., *Rev. Mod. Phys.* 93 (2021) 025006

[4] King, P., D., C., et al., *Chemical Reviews* 121 (2021) 2816

[5] Kutuyakhov, D., et al., *Rev. Sci. Instr.* 91 (2020) 013109

[6] Kalha, C., et al., *J. Phys. Cond. Matter* 33 (2021) 233001