Ab-initio description of the free electron

Madhubani Mukherjee[1], Sarai Dery Folkestad[1,2], Anna I. Krylov[1]

[1]*Department of Chemistry, University of Southern California, Los Angeles, USA*
[2]*Department of Chemistry, Norwegian University of Science and Technology, N-7491 Trondheim, Norway*

The description of an ejected electron is essential in the modelling of photoelectron spectroscopies in the UV-Vis (UPS) and X-ray (XPS) regime, Auger and ICD processes, penning ionization, electron scattering etc. The interpretation of these experiments requires theoretical modeling, which relies on one- and two-particle Dyson orbitals and free-electron states[1,2]. While Dyson orbitals can be reliably computed using correlated wavefunctions, description of the free-electron is less established. The simplest description of free-electron states is given in terms of a plane or Coulomb wave, which do not properly account for the scattering of the outgoing electron from the molecular core[3]. Scattering interactions are important in the low energy regime and in describing the chiral response in the X-ray regime. There are several studies developing various models with explicit treatment of the ejected electron which often relies on relatively low-level treatment of molecular potential (e.g., DFT or Xα-like)[4,5]. We present an alternative approach to this problem where we are solving the Hartree-Fock like equation for the free electron in a basis consisting of products of plane-waves and GTOs (similar to London orbitals). We are using the ab-initio description of the free electron to model the photoelectron spectra, which offers detailed information about the electronic structure of the target molecule and the properties of the ejected electrons. We calculated experimentally important quantities such as the asymmetry parameter, total and differential cross sections, involved in the photoionization dynamics.

References

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