

# Theory of molecular photoionization and its applications

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**Synopsis** An overview of density functional theory based methods for the description of molecular continuum states is presented along with specific recent applications involving the calculation of photoelectron angular distributions and vibrationally-resolved cross section. We then introduce a stable and general close-coupling multichannel algorithm and provide sample applications of an initial implementation.

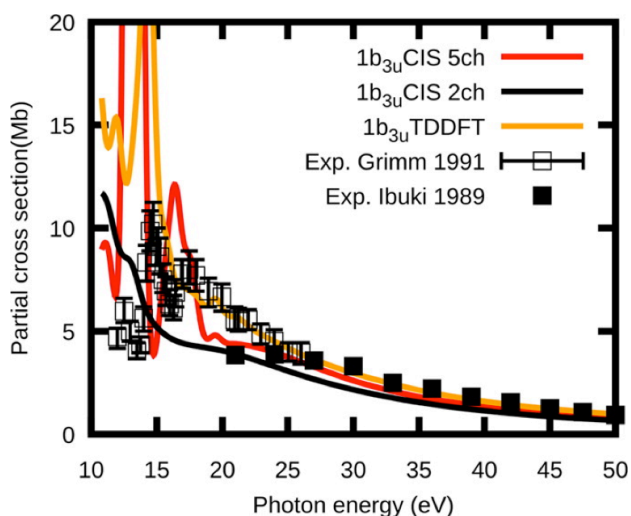
The description of the photoemission process provides a wealth of information on the nature of the ground and excited states of the target sample. Photoelectron and Auger electron spectroscopies are used not only for analytical purposes, but, for instance, to unravel the interplay of electron and nuclear dynamics following core excitation and decay in biological molecules, or as probe of ultrafast processes in pump-probe experiments in the femto- and attosecond time scale.

Compared to the rapid progress witnessed by the efficient implementation of LCAO based approaches of quantum chemistry, the theoretical description of the ionization dynamics is far less developed and standardized. Mean-field methods based on either (time-dependent) density functional theory (TDDFT) or static-exchange (SE) approximation are the more widely used approach in the community, affording a reasonably good and computationally affordable description of the ionization dynamics both in the linear, perturbative and strong-field regime.

In this progress report we will describe the implementation and capabilities of  $L^2$  DFT approaches to the calculation of molecular continuum states. Specific examples include the description of interference and diffraction phenomena in molecular photoionization, which are visible in both vibrationally-resolved cross sections and asymmetry parameter profiles [1].

A satisfactory interpretation of a large class of experiments requires a generalization of existing algorithms allowing a balanced inclusion of correlation in both bound initial and final target states and in the continuum. To this aim, we are developing a general least-squares B-spline basis set approach to the multichannel scattering problem. At this stage the algorithm has been

implemented within the configuration interaction singles (CIS) approximation [2] and its accuracy has been tested on medium-sized molecular systems such as ethylene. Further *in-fieri* developments include the use of a multicentric basis set and the its generalization for the use of correlated wave functions for the initial and final target states. Initial applications to small poly-atoms in both linear and strong-field ionization regimes will also be presented.



**Figure 1.** Photoionization cross section for the  $1b_{3u}^{-1}$  state of ethylene.

## References

- [1] S. Nandi *et al.* 2016 *Phys. Chem. Chem. Phys.* **18** 3214-3222
- [2] D. Toffoli and P. Decleva, 2016 *J. Chem. Theory Comput.* **12** 4996-5008

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