SINGLE-CENTER FRAMEWORK IN CALCULATION OF MOLECULAR PHOTOIONIZATION PROCESS

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Photoionization is a process where interaction of matter with photons of sufficiently high energy removes electron(s) from the target. The phenomenon is one of the main tools used in material sciences, because if the energy of the incident radiation E_p is known and the kinetic energy E_k of the emitted electron can be measured, the binding energy E_b of the emitted electron in the matter is $E_b=E_k-E_p$. Then the spectrum of photoelectrons (E_b versus intensity) provide insight to the chemical environment and the electronic structure of the studied target.

Despite of its importance, calculation of photoelectron spectra of materials is a notoriously difficult task. The complete picture requires calculation of both, binding energies and photoionization matrix elements, which can be then used to obtain further properties, such as angular dependence or spin polarization of photoelectrons. One of the main challenges in the calculation of photoionization is the description of the continuum wavefunction of the emitted electron. Even after of decades of research, the problem remains to challenge theoretical physicists. The continuum problem is fairly well understood in spherically symmetric systems, such as atoms, but even for the smallest many-center systems description of continuum states remain as one of the main bottlenecks in theoretical calculations of photoionization.

Different approaches and levels for describing continuum wavefunctions of molecules have been developed over the years. Recently one of the less known methods, known as single-center (SC) method has been investigated and revived [1]. SC method was developed in the 1960s [2] and was therefore one the first ways for treating the continuum problem. However, due to its considerable computer memory demands, it remained nearly unused until the very recent years. The method is based on the fact that spatial molecular orbitals can be always expanded with respect to a chosen single center as a linear combination of spherical harmonic functions. The expansion allows writing the 3-dimensional molecular Hartree-Fock (HF) equations to an infinite (but converging) set of atomic-like radial HF equations, which are straightforward to solve using matrix algebra. The method has been recently used to predict photoelectron spectra, photoionization energy dependence and angular distribution parameters for small molecules (see, references in [1]) and lithium clusters [3]. The presentation to be given at the physics days will describe the mathematical formalism behind the SC method, recent results obtained for small lithium clusters and future development plans at Oulu university.

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