Hybrid Basis Close-Coupling Interface to Quantum Chemistry Packages For The Treatment Of Ionization Problems

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Synopsis A new code to treat ionization in polyelectronic molecules is described (XCHEM code). Ionization cross section of H_2 is compared with benchmark calculations and preliminary calculation in N_2 are depicted.

The theoretical description of observables in attosecond pump-probe experiments requires a good representation of the system's ionization continuum. For polyelectronic molecules, however, this is still a challenge due to the complicated short-range structure of correlated electronic wave functions. Whereas calculations aimed to describe bound electronic states using Quantum Chemistry Packages (QCPs) are routine calculations nowadays; comparable tools for the continuum are not widely available yet. To tackle this problem we present a new approach developed in our group, the XCHEM method [2].

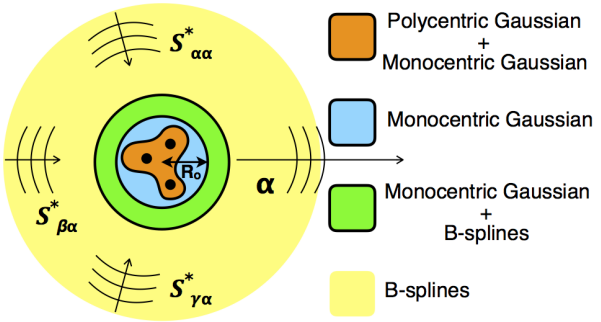

Figure 1. Schematic representation of the GABs basis set

In order to simulate ionization, the parent ions are obtained using a modified version of the MOLPRO package [4] with a Complete Active Space Self Consistent Field calculation (CASSCF) in the state average formalism. In this way a common set of orbitals is obtained to describe the $N-1$ bound electronic wavefunctions for all parent ions. These orbitals are exported to the MOLCAS code [3] and complemented with a Gaussian and B-splines basis set [1] (GABs) as depicted in Fig. 1. The molecular system is thus divided in two parts. On the one hand, the bounded part is treated by using standard polycentric Gaussian functions. On the other hand, the continuum is constructed with GABs functions [1], where the asymptotic part is represented by B-splines and the close range is described using monocentric Gaussians. Matrices elements of the Hamiltonian and dipole operators are also computed in two steps: calculation between Gaussian functions (handle by the MOLCAS code) and between monocentric Gaussian and B-splines (handle directly by the XCHEM code).

To illustrate the validity of this approach, we report results for the multichannel ionization of molecular Hydrogen that prove to be in excellent agreement with existing accurate benchmarks. Building on this we present results for molecular Nitrogen, the ionization of which cannot be easily treated by existing methods, thereby showcasing our method's usefulness in the study of ionization in polyelectronic, molecular system.

References

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