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

Jesús González-Vázquez[*1] **Markus Klinker**[*] **Carlos Marante**[*] **Inés Corral**[*] **Luca Argenti**[*§] **Fernando Martin**[*†‡]

[*] Departamento de Química, Universidad Autónoma de Madrid
28049 Madrid, Spain [§] Department of Physics CREOL, University of Central Florida
Orlando, FL 32816-2385 [†] Insituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia)
28049 Madrid, Spain [‡] Condense Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid
28049 Madrid, Spain

Synopsis A new code to treat ionization in polielectronic 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 Quantum Chemistry Packages (QCP), implementing sophisticated methods to compute bound electronic molecular states, are routine calculations nowadays; comparable tools for the continuum are not yet widely available. To tackle this problem we present a new approach developed in our group, the XCHEM method [2].

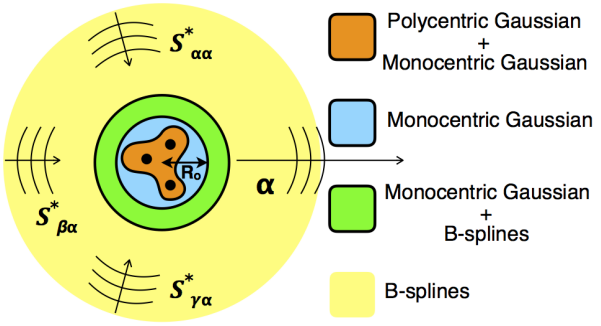

Figure 1. Schematic representation of the GABs basis set

In the XCHEM method, the problem is divided in two parts. On the one hand, the bound 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.

The parent ions are obtained using a modified version of the MOLPRO package [4] using multireference calculation (CASSCF)to create a set of orbitals common to all the parent ions is created. These orbitals are exported to the MOLCAS code [3] and complemented with a GABs basis set [1] as depicted in Fig. 1. Matrices elements of the Hamiltonian and dipole operators are 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 viability 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

[1] C. Marante, L. Argenti and F. Martin, 2014 *Phys. Rev. A.* **90** 012506.

[2] C. Marante, M. Klinker, I. Corral, J. González-Vázquez, L. Argenti and F. Marin 2016 *J. Chem. Theory Comput.* **13** 499.

[3] Aquilanti *et al. J. Comput Chem.* 2016 **37** 506.

[4] Werner *et al. WIREs Comput. Mol. Sci.* **2** 242.

[1] E-mail: jesus.gonzalezv@uam.es