Exploration of the Core Valence Separation approximation to obtain the ionization potentials of the core electrons by the EOM-CCSD method according to a 4-component relativistic approach

Loïc Halbert*[1], Marta Lopez Vidal[2], Avijit Shee[3], Sonia Coriani[2], and André Severo Pereira Gomes[1]

[1]Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique : UMR8523 – France
[2]Department of Chemistry, Technical University of Denmark – Danemark
[3]Department of Chemistry, University of Michigan – États-Unis

Résumé

Advances in X-ray spectroscopy, both in high-energy and in resolution, now allow us to reach the ionization potentials (IP) of the core electrons of many systems [3, 5]. In quantum chemistry, these electrons must be treated using relativistic Hamiltonians (Dirac-Coulomb, Dirac- Coulomb-Gaunt), as well as for electrons belonging to molecular orbitals (MO) having a strong Spin-Orbit coupling. In addition, the Ionization Potential - Equation of motion Coupled-Cluster (IP-EOM-CCSD) method has many advantages both by the precision of the results [6] and by its explanatory and predictive nature [2]. However, its computational cost in N6 quickly makes it inapplicable.

We then explore the Core Valence Separation approximation (CVS-EOM- CCSD) [4] based on the flexible separation between core and valence MO to be taken into account in the EOM calculation. In parallel, we were interested in the Frozen Core (FC) approximation whose role is to make certain MO inactive during the preliminary Coupled-Cluster (CC) calculation. These different technics, recently implemented by our team in Dirac [1], have been applied to X– and HX systems (X : Cl, Br, I, At) and a systematic examination shows the advantage of using these different methods to obtain the IP of the core electrons.

DIRAC, a relativistic ab initio electronic structure program (available at http://dx.doi.org/10.5281/zenodo.3572669, see also http://www.diracprogram.org)

Bouchafra, Y., Shee, A., Réal, F., Vallet, V., and Gomes, A. S. P. Physical Review Letters 121, 2018, 26

Boudjemia, N., Jänkälä, K., Gejo, T., Nagaya, K., Tamasaku, K., Huttula, M., Piancastelli, M. N., Simon, M., and Oura, M. Physical Chemistry Chemical Physics 21, 2019, 5448.

*Intervenant

Coriani, S., and Koch, H. The Journal of Chemical Physics 143, 2015, 181103.

Oura, M., Gejo, T., Nagaya, K., Kohmura, Y., Tamasaku, K., Journel, L., Pian- castelli, M. N., and Simon, M. Hard New Journal of Physics 21, 2019, 043015.

Shee, A., Saue, T., Visscher, L., and Gomes, A. S. P. The Journal of Chemical Physics 149, 2018, 174113.

Mots-Clés: Core, valence separation, ionization energies, halogens, equation of motion coupled cluster, relativistic electronic structure