Diving into the continuum with resonances

DAMOUR Yann;[A] **KOSSOSKI Fábris**;[A] **SCEMAMA Anthony**[A], **LOOS Pierre-François**[A]

A) Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France

ydamour@irsamc.ups-tlse.fr

In quantum chemistry, the Hamiltonian spectrum contains continuum states in addition to the usual bound states. Among those continuum states can be found the so-called "resonances", which are metastable states resembling bound states.[1] However, due to their metastability, resonances have a finite lifetime which makes them differ from the regular bound states and lead to interesting properties. For this reason, resonances are studied in various fields involving electron-molecule collisions, from biochemistry (DNA damage induced by ionizing radiation or the development of radiosensitizers against cancer) to interstellar chemistry (extraterrestrial synthesis of prebiotic molecules).[2,3]

The unbound nature of resonance states creates various theoretical challenges because of the necessity of accounting for the coupling of the bound part of the wave function with the continuum. Several methods have been specifically developed to describe accurately such states and notably their lifetimes. However, at the current stage, one of the state-of-the-art methodologies to describe resonances of medium-sized molecules remains the complex absorbing potential (CAP) technique (which consists in the addition of a complex one-electron potential to the usual Hamiltonian) combined with coupled-cluster with singles and doubles (CCSD).[4] Unfortunately, the resulting errors for resonances are one to two orders of magnitude larger than obtained with state-of-the-art methods for bound states. This aspect underlines the necessity of improving the description of the electronic structure of resonances. Answering this call, we propose to combine the CAP technique with selected configuration interaction (SCI). This choice is motivated by the ability of SCI to provide highly-accurate excitation energies for bound states, allowing to faithfully benchmark more approximate methods.[5] In this contribution, we will give a concise overview of resonance states, the CAP methodology, and the SCI method, before investigating the performances of CAP-SCI and CAP-CCSD on various ubiquitous resonance states.

Keywords: Electronic Structure Theory, Excited States, Resonances, Complex Absorbing Potential, Selected Configuration Interaction.

[1] S. Klaiman and I. Gilary, Advances in Quantum Chemistry 63 (2012) 1-31.

[2] Q. T. Wu, H. Anderson, A. K. Watkins, D. Arora, K. Barnes, M. Padovani, C. N. Shingledecker, C. R. Arumainayagam, J. B. R. Battat, ACS Earth Space Chemistry 8 (2024) 79-88.

[3] E. Alizadeh, T. M. Orlando, L. Sanche Annual, Review of Physical Chemistry 66 (2015) 379-398.

[4] D. Zuev; T.-C. Jagau, K. B. Bravaya, E. Epifanovsky, Y. Shao, E. Sundstrom, M. Head-Gordon, A. I. Krylov, Journal of Chemical Physics 141 (2014)

[5] Y. Garniron *et al.*, Journal of Chemical Theory and Computation 15 (2019) 3591-3609