Extending Equation-of-Motion Coupled-Cluster Methods to Metastable States via Complex-Scaling and Complex Absorbing Potentials: Theory, Implementation, and Examples

Anna Krylov
University of Southern California

Autoionizing (or electron-detaching) states are ubiquitous in physics, chemistry, biology, and technology. Such meta-stable states (called resonances) belong to the continuum spectrum and can be represented either as an stationary exponentially diverging solution of time-independent Schrodinger equation or as a non-stationary solution of time-dependent Schrodinger equation. Theoretical description of resonances is exceptionally difficult, as their "wave functions" are not L2-integrable and, therefore, cannot be represented by expansions over gaussian basis sets. Moreover, the continuum part of the spectrum cannot be described by methods such as Davidson diagonalization formulated for discrete eigenproblems. Complex-scaling and complex absorbing potentials (CAP) formalisms result in an elegant and mathematically rigorous way to deal with the excited states embedded in the continuum (it can also be used for nuclear scattering problem). I will present an implementation of the complex-scaled and CAP EOM-CCSD methods. Theory of the complex-scaled EOM-EE/EA-CCSD methods will be described and salient features of this approach will be illustrated by benchmark calculations, with an emphasis on robustness of the protocols.