SOME RECENT DEVELOPMENTS FOR ELECTRONIC RESONANCES, IN PARTICULAR ABOUT AUGER SPECTRA AND NON-ADIABATIC EFFECTS

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Traditionally, chemistry has focused on processes in which all electrons remain bound to the nuclei. However, state-of-the-art experimental techniques make it possible to create, in a controlled manner, environments where selected electrons are no longer bound to the nuclei. For example, core vacancies produced by X rays and temporary anions obtained by attachment of slow electrons undergo electronic decay.

The short-lived electronic resonance states that govern electronic decay processes are difficult to model with quantum-chemical methods designed for bound states because these methods do not describe the coupling to the continuum. An elegant treatment of resonances is, however, possible using non-Hermitian quantum chemistry [1]. Complex-variable techniques such as complex scaling, complex basis functions, and complex absorbing potentials (CAPs) describe resonances in terms of discrete states with complex energy and enable the application of concepts from bound-state quantum chemistry, for example, molecular orbitals and potential energy surfaces, to resonances.

In this talk, I will focus on two recent developments in field of non-Hermitian quantum chemistry: The *ab initio* modeling of molecular Auger spectra and the treatment of non-adiabatic effects.

Our approach for Auger spectra combines a generalization of the core-valence separation with complex-variable coupled-cluster methods [2,3]. Applications to ethane, ethene, acetylene, and benzene [4,5] illustrate the excellent performance of our approach, which avoids explicit treatment of the continuum. Further applications to molecular clusters show that the approach is also applicable to intermolecular Coulombic decay.

In the second part of the talk, I will discuss how the Born-Oppenheimer approximation and the theory of non-adiabatic couplings need to be modified for electronic resonances. Because there is always exact energetic degeneracy with continuum states, the standard Born-Oppenheimer picture is not applicable to such states. However, there is clear evidence from experiment that non-adiabatic couplings between resonances are important and do occur. I will discuss the modifications that are necessary in the theory and the implementation of non-adiabatic coupling vectors for complex-variable equation-of-motion coupled-cluster theory that we have developed. Pilot applications suggest that non-adiabatic couplings between resonances behave similarly to those between bound states.

References

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