Recent progress about complex-scaled coupled-cluster methods: Rydberg states, Coster-Kronig decay, and interatomic Coulombic decay

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The interaction of molecules with energetic radiation can produce metastable electronic states that decay non-radiatively by means of autoionization. Prominent examples are core-ionized and core-excited states that are subject to Auger decay. The theoretical modeling of Auger decay and other autoionization processes is difficult owing to the metastable nature of the initial states, which are embedded in the ionization continuum. Conventional quantum chemistry methods are formulated for discrete bound states with L^2-integrable wavefunctions and thus cannot describe states subject to electronic decay.[1,2]

Most methods for modeling autoionization rely on partitioning the Hilbert space into a bound part and a continuum part.[3,4] This approach works well as long as the partitioning is straightforward, for example, by means of core-valence separation for K-shell Auger decay.[5] However, it faces problems if the distinction between the bound part and the continuum part is less clear, which is the case for many other types of metastable states that are, as a consequence, more challenging to describe: In this talk, I will focus on 1) L-shell vacancies in third-row elements, which can undergo Coster-Kronig decay,[6] 2) Rydberg states above the first ionization potential,[7] and 3) ionization of loosely bound clusters, which can result in interatomic Coulombic decay.[8]

To describe these decay processes, we apply equation-of-motion coupled-cluster (EOM-CC) theory in a basis set that includes functions with complex-scaled exponents.[9] This approach does not involve partitioning the Hilbert space but rather relies on analytic continuation of the Hamiltonian to the complex plane. It results in a Schrödinger equation with complex eigenvalues from which total and partial decay widths can be extracted.[10,11] Our numerical results indicate that complex-scaled EOM-CC methods are well suited for a broad range of autoionization phenomena.

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