Resonance Energies and Lifetimes from Extrapolation Methods: Robust Algorithms and a Critical Analysis

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Abstract:

An electronic resonance is an electronic state of an $(N + 1)$-electron system that lies energetically above the N-electron system, and therefore in the scattering continuum of the N-electron state. Examples are temporary anions such as N_2^-, the Be^-, or the benzene anion, small dianions in the gas phase such as CO_3^{2-} or SO_4^{2-}, core-ionized atoms and molecules decaying via the Auger process, and the Auger-like decay of inner-valence ionized clusters. Resonances are characterized by their so-called resonance position, E_r, that is, the energy above the N-electron state, and by their width, Γ, which plays—cum grano salis—the role of a first-order decay constant. In other words, there is a typical decay time, $\tau = \hbar/\Gamma$, which is inversely proportional to the width.

Characterizing a resonance with standard—or at least more or less standard—quantum chemistry methods is a challenge. If a standard basis set is used, the continuum is so poorly described that any description of the decay is suppressed, because the excess electron is effectively trapped in a basis set box. Using more and more diffuse functions gives a better and better discretization of the continuum, however, then the resonance state mixes with the continuum states, and from a straightforward calculation one obtains at best a rough idea of the resonance position but at worst the lowest energy of the discretized continuum. Almost from the beginning of computational chemistry, various so-called L^2–methods have been put forward to address this challenge. All L^2–methods have one thing in common: The original Hamiltonian is parametrized, and E_r and Γ are extracted from a study of the behavior of the eigenvalues of the parametrized Hamiltonian as functions of the parameter. One example are extrapolation methods. Here an artificial stabilizing potential is added to the Hamiltonian, the stabilization is increased until the resonance state is turned into a bound state, and then further increased until enough bound state data have been collected so that these can be extrapolated back to vanishing stabilization. The lifetime of the resonance can be obtained from the same data, but only if the extrapolation is performed by analytic continuation (ACCC). Here we outline progress regarding the ACCC method, and critically examine the dependence of the results on the following: The artificial stabilizing potential used in the data collection step, different ACCC variants, and the energy-range of input data for the extrapolation.

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