Regular and resonant Auger decay in benzene

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X-ray based spectroscopies are used to probe the electronic structure of atoms and molecules. X-ray absorption creates electron vacancies in the core shell, leaving the molecule in a highly excited state. In case of molecules comprised of light atoms, they predominantly decay via Auger process. Auger decay is an autoionization process in which a valence electron fills the core hole and liberates sufficient energy to eject another electron to the ionization continuum. The theoretical modeling of Auger decay is challenging owing to the metastable nature of core-ionized (regular decay) or core-excited (resonant decay) states and the continuum nature of the ejected electron. One of the recent theoretical approaches for computing Auger decay rates is based on Feshbach-Fano theory combined with the equation-of-motion coupled-cluster (EOM-CC) framework [1, 2]. In our study, we use this approach to compute the Auger spectrum of the benzene molecule. Our theoretical spectrum can reproduce the main features of the experimental spectrum and shows the configuration mixing of decay channels. Our calculations also provide insights into the contribution of individual core-orbitals and decay channels to the Auger spectrum.

In the Feshbach-Fano approach, all the information about Auger decay from bound domain can be obtained from two-body Dyson functions. The two-body Dyson amplitudes connect the initial core-ionized or core-excited state with the final doubly or singly ionized valence states. Hence, an orbital picture analogous to the already existing Dyson orbitals (relevant for photoionization), or natural transition orbitals (relevant for absorption) is extremely beneficial for better understanding [3]. Therefore, we have developed an algorithm to obtain the most compact form of two-boy Dyson amplitudes using singular value decomposition.

References:

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