The Auger spectra of thiouracils

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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. Such molecules with core vacancies predominantly decay via Auger process when comprised of light atoms. 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 resonance theory combined with the equation-of-motion coupled-cluster (EOM-CC) framework [1, 2, 3]. We intend to compute the C-edge and S-2p edge Auger spectra of isomers, namely 2-, and 4-thiouracil. We show how a simple Koopmans theorem-based density of states approach can reproduce the experimental spectra. Consequently, we propose a weighted Koopmans approach, especially for the S-2p edge Auger spectra. Furthermore, we use the Feshbach-Fano approach to compute the partial Auger decay widths. Our calculations will also provide insights into the contribution of individual core-orbitals and decay channels to the Auger spectrum. We also computed the spin-orbit coupling (SOC) inclusive X-ray absorption spectrum (XAS) for the S-2p-edge case in thiouracils. The SOC variant agrees well with the experimental XAS, suggesting the need to include the same in S-2p Auger calculations. Hence, we propose the SOC variant of Feshbach-Fano approach based on EOM-CC theory. We anticipate how the SOC corrected partial decay widths would improve the agreement with experiments.

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. We employ the natural Auger orbitals (NAOs) to obtain the core holes, and valence holes for the Auger decay in thiouracils[4].

References:

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