

An ab initio multiconfigurational description of core hole and shake up excited states in small molecules

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Synopsis In this contribution, equilibrium geometries and potential energy curves computed at the CASSCF level of theory for the core hole and shake up superexcited states of small size molecules will be presented. The effect of dynamic correlation on the description of these species will be discussed based on preliminary multireference configuration interaction energetics.

Recent experimental progresses in the development of sub-femtosecond extreme ultraviolet light sources have opened the way to monitor the ultrafast dynamics of nuclei and electrons in atomic and molecular systems in their natural attosecond time regimes [1].

Extreme UV radiation induces inner-shell ionization and results in core hole states or shake up excited states, if valence electron excitation follows the hole creation. The embedding of these electronic states in the electronic continuum and their complex open shell electronic structure, with close lying near degenerate states, hamper the electronic structure description from a theoretical viewpoint. Furthermore, the characterization of these superexcited electronic states is subject to the variational collapse of the wavefunction, invalidating standard quantum chemical procedures designed for the description of low-lying excited states.[2]

With the long-term aim of achieving a quantitatively reliable description of photoionization processes, here we present a multiconfigurational approach based on CASSCF[3] wavefunctions, and which relies on the control of the occupancy of the core orbital for the electronic characterization of the superexcited parent ions.

The performance of this method will be illustrated by comparing the equilibrium geometries, harmonic frequencies, anharmonicity constants, ionization potential and potential energy curves along selected coordinates computed with our approach and those obtained with other methods or extracted from experiments. Preliminary energetics including dynamic correlation by means of the Multireference Configuration Interaction method will be also presented.

Finally, the bonding in these superexcited electronic states will be analyzed on the basis of the Atoms in Molecules Theory of Bader [4] and will be compared to that of their valence cations, ground and valence excited state analogues.

References

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