Ensemble density functional theory of electrons and nuclei

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I will briefly review in this presentation a recent unified and in-principle-exact extension of density functional theory (DFT) to both charged and neutral electronic excitations [1]. The approach is based on the so-called *N*-centered ensemble formalism [2-4]. I will particularly focus on exchange-correlation derivative discontinuities associated to neutral excitation processes [1,5-8]. In a second part, I will discuss the derivation of an exact ensemble DFT of electrons and nuclei, starting from the Born-Huang expansion of the molecular wave function, with a particular focus on the description of non-adiabatic couplings [9]. This work is a first step towards the rationalization of computational non-adiabatic nuclear dynamics studies using electronic density-functional ensembles.

References

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