N-centered ensemble density-functional theory for open systems

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Résumé

Two (so-called left and right) variants of N-centered ensemble density-functional theory (DFT) [Senjean and Fromager, Phys. Rev. A 98, 022513 (2018)] will be presented. Unlike the original formulation of the theory, these variants allow for the description of systems with a fractional electron number. While conventional DFT for open systems uses only the true electron density as basic variable, left/right N-centered ensemble DFT relies instead on (i) a fictitious ensemble density that integrates to a central (integral) number N of electrons, and (ii) a grand canonical ensemble weight which is equal to the deviation of the true electron number from N. Within such a formalism, the infamous derivative discontinuity that appears when crossing an integral number of electrons is described exactly through the dependence in the ensemble weight of the left and right N-centered ensemble Hartree-exchange-correlation density functionals. Incorporating N-centered ensembles into existing density-functional embedding theories is expected to pave the way towards the in-principle-exact description of an open fragment by means of a pure-state N-electron many-body wavefunction.

Mots-Clés: ensemble density functional theory, open systems, embedding

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