Total energy of excitations via ensemble density functionals

Stefano Pittalis
CNR-Istituto Nanoscienze, Via Campi 213A, I-41125 Modena, Italy

Ensemble-Density-Functional Theory (EDFT) was conceptualized with the intent of bringing cost-efficient methods from ground-state to stationary excited-state problems [1], but did not achieve the success of Time-Dependent DFT (TDDFT) due to challenges in developing approximations. Here I show that resolving these challenges involves a fundamental revision of the DFT perspective on Hartree, exchange, and correlation energies:

- The traditional definition of Hartree and exchange energy functionals must be abandoned in favor of extended forms involving non-interacting yet multi-determinant auxiliary states [2];
- A new form of correlation, the so-called density-driven correlation, must also be dealt with [3];
- The fluctuation dissipation theorem for ensembles allows us to break down all the novel key energy components into further elementary contributions which are amenable to well-developed or developable approximations [4];
- Rules for functional constructions have been derived, which bring the calculation of double excitations within reach at the level of Hybrid functional forms [5];
- The extended density functionals must interpolate between the recently discovered high- and low-density limits for ensembles of excited states [6].

As a result, excitations which remain difficult to be tackled by (linear-response) TDDFT may now be computed via EDFT.

[1] E. K. U. Gross, L. N. Oliveira, W. Kohn *"Density-functional theory for ensembles of fractionally occupied states. I. Basic formalism"* Phys. Rev. A **37** 2809 (1988)
[2] T. Gould and S. Pittalis *"Hartree and Exchange in Ensemble Density Functional Theory: Avoiding the Nonuniqueness Disaster"* Phys. Rev. Lett. **119**, 243001 (2017)
[3] T. Gould and S. Pittalis *"Density-Driven Correlations in Many-Electron Ensembles: Theory and Application for Excited States"* Phys. Rev. Lett. **123**, 016401 (2019)
[4] T. Gould, G. Stefanucci, S. Pittalis *"Ensemble density-functional theory: Insight from the fluctuation-dissipation theorem"* Phys. Rev. Lett. **125**, 233001 (2020)
[5] T. Gould, L. Kronik, and S. Pittalis *"Double Excitations from Ensemble Density Functionals: Theory and Approximations"* Phys. Rev. A **104**, 022803 (2021)
[6] T. Gould, D. P. Kooi, P. Gori-Giorgi, S. Pittalis *"Electronic excited states in extreme limits via ensemble density functionals"* arXiv:2205.07136 (2022)