Efficient linear-response calculations without unoccupied states: The Sternheimer approach as an alternative to real-time methods and the Casida scheme

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Abstract
Time-dependent density functional theory (TDDFT) is among the most frequently used methods to calculate and understand the electronic excitations of, e.g., molecules and nanostructures. In the linear regime, its most common formulation (sometimes called the "Casida approach") relies on an expansion of the response into particle-hole excitations, which requires the computation of unoccupied Kohn-Sham (KS) orbitals and the exchange-correlation (xc) kernel f_{xc}. The former often becomes the computationally limiting step, as the space of unoccupied states grows rapidly with system size. Using orbital-dependent approximations to the xc potential in the KS scheme turns the construction of f_{xc} into another major hurdle. We here discuss an alternative approach based on solving the frequency-dependent Sternheimer equation [1]. It does not require unoccupied orbitals and can excellently be parallelized. Furthermore, the approach allows to include orbital functionals into DFT in the Kohn-Sham framework without having to construct their kernel explicitly [2]. It thus makes it easy to work with orbital-dependent KLI and CEDA potentials in linear-response calculations, and it may be an efficient way for solving the long-standing problem of the time-dependent optimized effective potential.

References

[1] F. Hofmann. I. Schelter and S. Kümmel, *Linear Response Time-Dependent Density Functional Theory without unoccupied states: The Kohn-Sham-Sternheimer Scheme revisited*, J. Chem. Phys. 149, 024105 (2018).

[2] F. Hofmann. I. Schelter and S. Kümmel, *Efficiently evaluating the Krieger-Li-Iafrate and common-energy-denominator approximations in the frequency-dependent Sternheimer scheme*, Phys. Rev. A 99, 022507 (2019).

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