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Towards excitation spectra with the ensemble-generalized DFT approach

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Density functional theory (DFT) is an in-principle exact theoretical framework for any many-body system. It is particularly relevant for the warm dense matter (WDM) regime, where large systems have to be addressed at the electron-electron level, at relatively high temperatures and pressures. The high-temperature regime requires addressing not only the ground state, but (many) excited states of the system. It is well known, however, that the relation between excitation energies and Kohn-Sham energy-level differences is by no means straightforward, and usually involves discontinuities in the exact exchange-correlation potential [1], which are very difficult to model. The natural question that arises in this context is whether we can construct an xc functional that is suitable to predict excitation energies, preferably at a moderate computational cost. In my talk I present a thorough study of atomic systems throughout the periodic table [4] calculated with ensemble-generalized xc functionals [2,3] and examine, as a first step, their IP and fundamental gap, obtained from the Kohn-Sham spectrum. Analysis of the s-, p- and d-block systems vs experiment allows us to make a connection between the accuracy of the method and the position of the system in the Periodic Table and to suggest further steps to remove the remaining discrepancy. Generalization of the method to higher excitations and inclusion of temperature will be discussed.

[1] E. Kraisler, M. J. P. Hodgson, E. K. U. Gross, From Kohn–Sham to Many-Electron Energies via Step Structures in the Exchange-Correlation Potential, J. Chem. Theory Comput. 17, 1390 (2021)
[2] E. Kraisler, L. Kronik, Piecewise linearity of approximate density functionals revisited: Implications for frontier orbital energies, Phys. Rev. Lett. 110, 126403 (2013)
[3] E. Kraisler, L. Kronik, Fundamental gaps with approximate density functionals: The derivative discontinuity revealed from ensemble considerations, J. Chem Phys. 140, 18A540 (2014)
[4] S. Lavie, E. Kraisler, Ionization potentials and Fundamental Gaps in Atomic Systems from the Ensemble-DFT Approach, in preparation.

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