Improving the exchange and correlation potential in density-functional approximations through constraints

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I shall review briefly work in our group to impose constraints on the effective Kohn–Sham (KS) potential of local and semi-local density-functional approximations[1]. Constraining the minimisation of the approximate total energy density-functional invariably leads to an optimised effective potential (OEP) equation, the solution of which yields the KS potential.
I shall argue theoretically, and demonstrate with examples, that the solution of the finite basis OEP equations is numerically robust. Then, I shall demonstrate that appropriately constraining the 'screening charge' which corresponds to the Hartree, exchange and correlation potential not only corrects the asymptotic behaviour of the KS exchange and correlation potential, but also allows it to exhibit a non-zero derivative discontinuity, a feature of the exact KS potential that is necessary for the accurate prediction of band-gaps in solids but very hard to capture with semi-local approximations.
Finally, time permitting, I shall present a new generalised Kohn-Sham or constrained hybrid method, where the exchange potential is the (equally weighted) average of the nonlocal Fock exchange term and the self-interaction-corrected exchange potential, as obtained from our constrained minimisation method of semi-local approximations. The new method gives an accurate single- particle eigenvalue spectrum with an average deviation between (the negative of) the valence orbital eigenvalues and the experimental ionisation potentials of about 0.5eV, while the deviation of core orbitals is within 2eV. The improvement in the eigenvalue spectrum is achieved with a minimal increase in the total energy.

1. Nikitas I. Gidopoulos, and Nektarios N. Lathiotakis. "Constraining density functional approximations to yield self-interaction free potentials." The Journal of Chemical Physics **136,** no. 22 (2012): 224109.
2. Timothy J. Callow, Benjamin J. Pearce, Tom Pitts, Nektarios N. Lathiotakis, Matthew JP Hodgson, and Nikitas I. Gidopoulos. "Improving the exchange and correlation potential in density-functional approximations through constraints." *Faraday Discussions* **224** (2020): 126-144.
3. Thomas C. Pitts, Nektarios N. Lathiotakis, and Nikitas Gidopoulos. "Generalized Kohn–Sham equations with accurate total energy and single-particle eigenvalue spectrum." *The Journal of Chemical Physics* **155**, no. 22 (2021): 224105.