

Ultra non-local response from a semi-local functional

A DFT functional for the electrical response of molecular chains

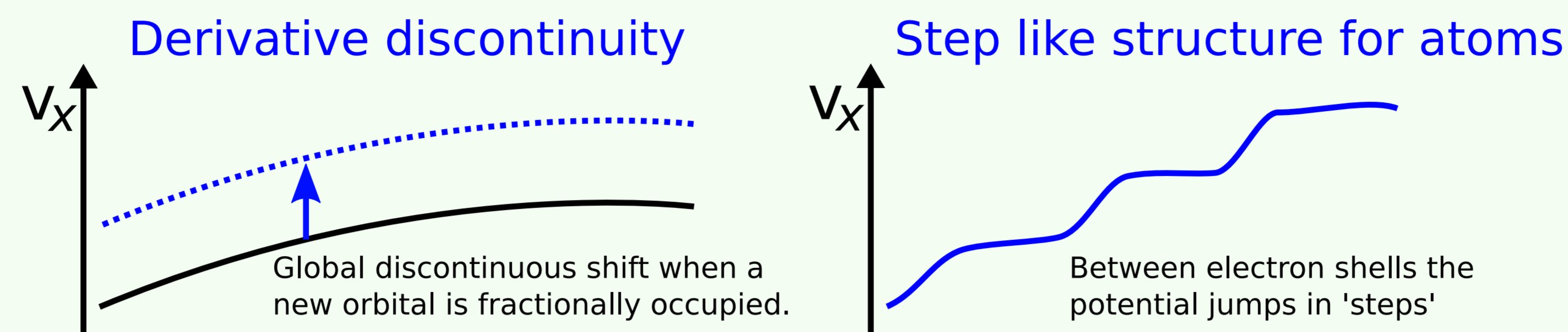
Rickard Armiento, Stephan Kümmel, Thomas Körzdörfer

Abstract

An exchange potential functional is constructed from semi-local quantities, and is shown to reproduce hydrogen chain polarizabilities with the same accuracy as exact exchange methods. We discuss the exchange potential features that are essential for accurate polarizability calculations, i.e., derivative discontinuities and the potential step structure. The possibility of a future generalization of the methods into a complete semi-local exchange-correlation functional is discussed.

Can a semi-local DFT functional reproduce relevant features of exact exchange?

- *Exact exchange DFT has certain features* in the exchange potential *that may seem related to its non-local nature*:



- These features are *important for the electrical response* of hydrogen chains (and thus likely also for general electrical response calculations.)

- Is it possible to construct *a semi-local DFT functional that reproduce these features?* And if so, will *polarizabilities come out right?*

Which exchange potential features are 'relevant'?

- The whole exchange potential *shifts discontinuously* when a new orbital is fractionally occupied.

- Atomic potentials show a *series of steps*, each step indicating a new shell.

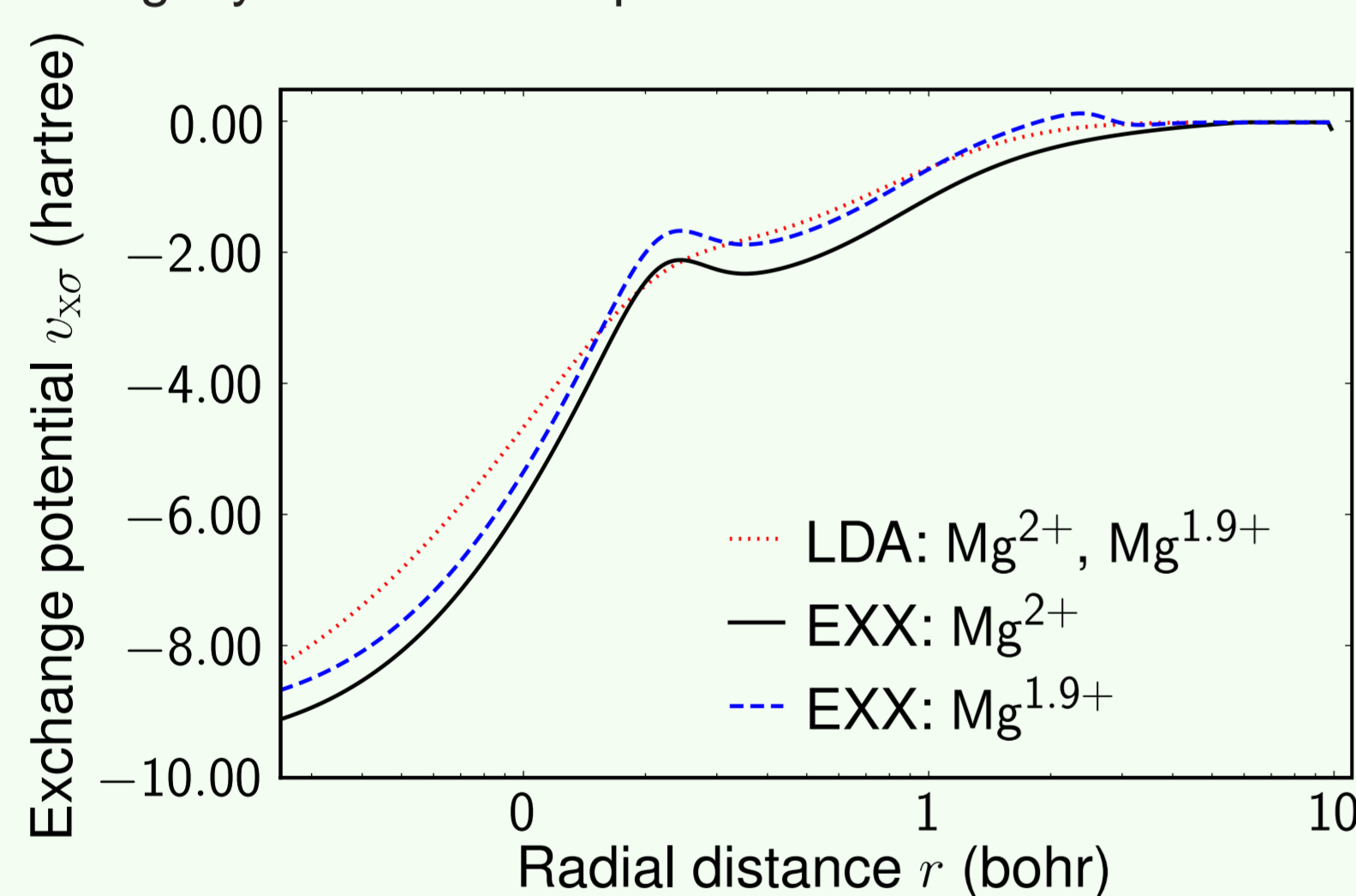
- DFT is not limited to integer electron numbers. Non-integer electron numbers 'simulate' sharing an orbital within a larger system. This can be used as a benchmark for functionals.

- In the ground state, two well separated atoms are both neutral. To reproduce this, a functional must have a discontinuity in dE/dN at integer electron numbers N .

- A related (but not the same) discontinuity is present in the exchange potential, i.e., $\delta E_x/\delta n(r)$ shifts discontinuously at integer electron numbers.

- The potential shift is further related to the successive steps visible in the potential vs. radial coordinate of atomic systems.

- Both features are illustrated by an Mg atom at two slightly different occupations:

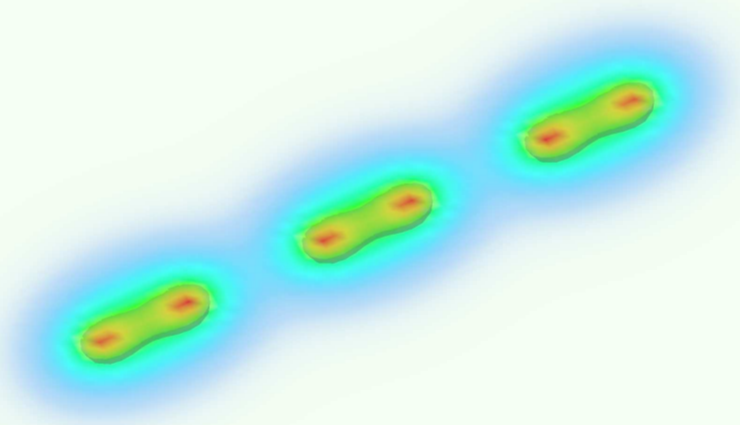


Why do we care about hydrogen chains?

- *Hydrogen atom pairs* are placed equidistantly *on a straight line*.

- The setup *mimics* electronic features of *polymers* like polyacetylene.

- *Common semi-local functionals* (LDA, ...) *fail to predict the electrical response*, which is linked to the relevant exchange features.



- The model mimics the electronic features of polymers like polyacetylene such as bond-length alternation, high and directional electron mobility, and large response coefficients.

- The electronic structure is still transparent enough to keep technical details (basis sets or grid parameters) well controlled.

- Ab initio correlated wave function calculations are available for comparison.

- Current-DFT calculations have shown that among various molecular chains, hydrogen chains are the most difficult to describe accurately within DFT.

- It can thus be expected that, if they are described correctly, then other chains will be described correctly too.

- Hydrogen makes it possible to test new functional expressions without the need of creating new pseudopotentials.

A semi-local functional approach for the potential

- A *semi-local 'potential correction'* of Becke and Johnson gives a *step-like structure and derivative discontinuity*.

- The potential is modeled directly, the energy is given by the virial theorem.

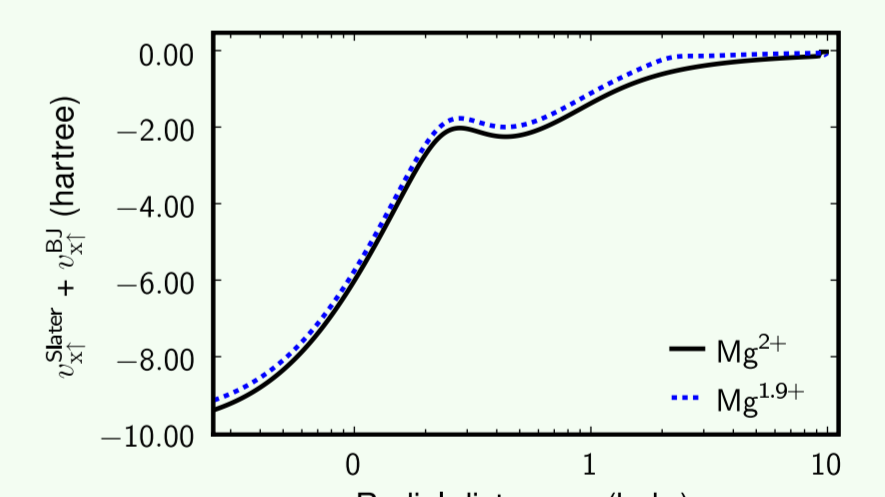
- New *understanding enables* the correction to be transformed to work for an *external electric field situation*.

- Becke and Johnson (BJ) started from (non-local) Slater exchange, which has no potential step structure, and added a semi-local correction term,

$$v_{x\sigma}^{\text{BJ}} = C_{\Delta v} \sqrt{2\tau_{\sigma}/n_{\sigma}}, \quad C_{\Delta v} = (1/\pi)\sqrt{5/12}. \quad (1)$$

Here: $\phi_{i\sigma}$ is the i :th Kohn-Sham-orbital of spin σ (up or down) with occupation $m_{i\sigma}$ and eigenvalue $\epsilon_{i\sigma}$; the total occupancy is $N = \sum_{\sigma} \sum_i m_{i\sigma}$; and the electron spin density $n_{\sigma} = \sum_i m_{i\sigma} |\phi_{i\sigma}|^2$; and the kinetic energy spin density $\tau_{\sigma} = \frac{1}{2} \sum_i m_{i\sigma} |\nabla \phi_{i\sigma}|^2$.

- For atoms, this introduces a step structure similar to exact exchange, and we also observe a potential derivative discontinuity that behaves correctly.



- Asymptotics of Kohn-Sham orbitals explain why: starting from orbital I , and occupying $J = I + 1$, induces a constant shift in the correction, independent of the occupation:

$$C_{\Delta v}(\sqrt{-2\epsilon_{J\sigma}} - \sqrt{-2\epsilon_{I\sigma}}). \quad (2)$$

- A similar examination when an external electric field F in the z -direction is present, shows that a new surplus field-related term must be removed. Final potential is:

$$v_{x\sigma} = v_{x\sigma}^{\text{Slater}} + C_{\Delta v} \left(\sqrt{\frac{2\tau_{\sigma}}{n_{\sigma}}} - \sqrt{-2\epsilon_{I\sigma}} - \frac{Fz}{\sqrt{-2\epsilon_{I\sigma}}} \right). \quad (3)$$

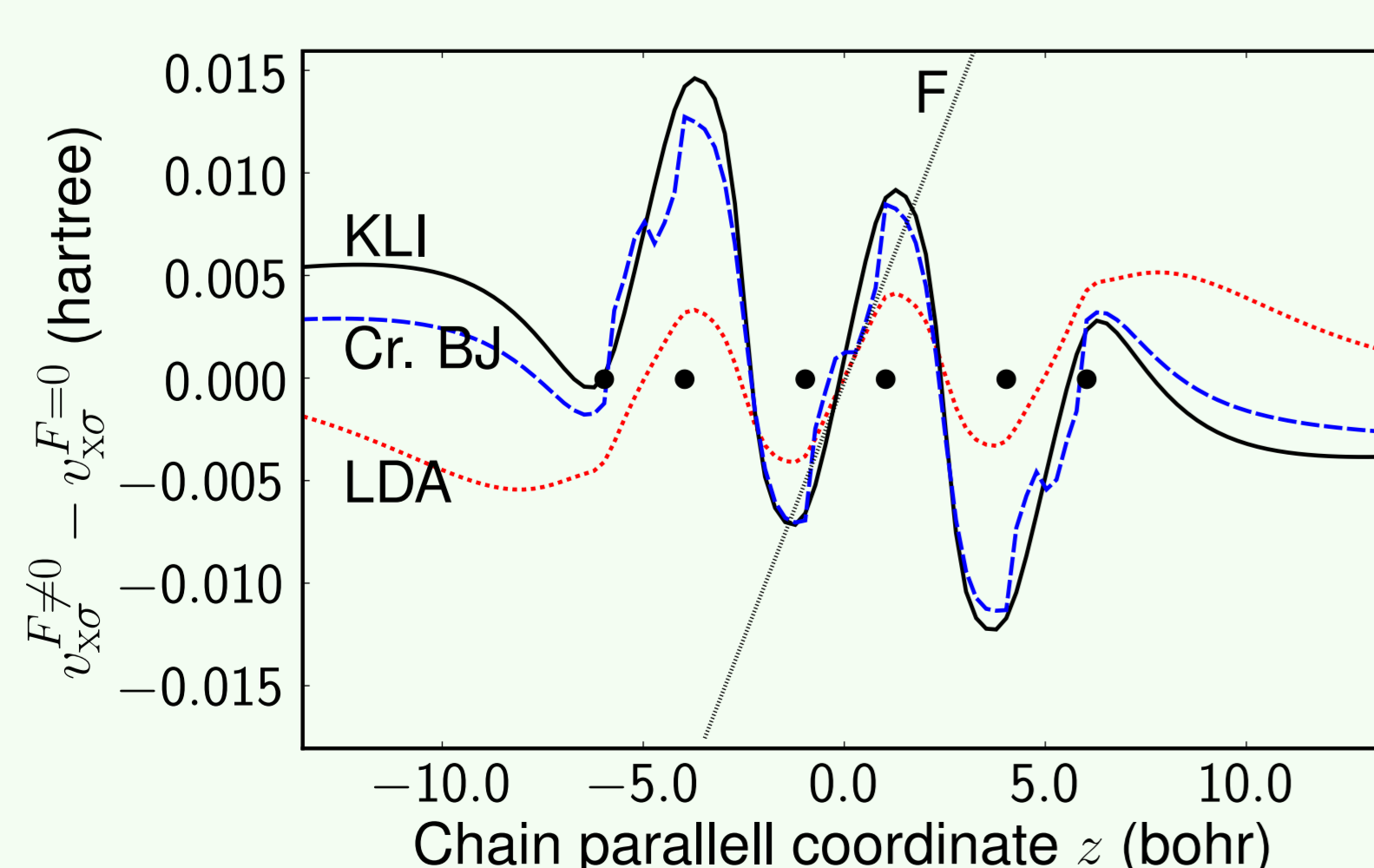
Conclusions and outlook

- We have a *semi-local correction* that *reproduces relevant features of exact exchange*; unlike common semi-local functionals.

- We are currently developing it into the form of a regular semi-local DFT functional.

So, does it work?...

- The result is a potential surprisingly close to exact exchange methods.



- Black circles are Hydrogen atoms.
- Exact exchange (in the KLI approximation) and the corrected BJ both slope to counteract the field, whereas LDA – similar to other common semi-local functionals – slopes weakly with the field.

... and the polarizabilities?

- *As good as exact exchange!*

- Numerical polarizabilities in bohr³ of DFT using the Slater potential + our adjusted BJ term, compared to other methods; local density approximation (LDA), Hartree-Fock (HF) and Møller-Plesset (MP4):

	H ₄	H ₆
DFT, Cr. BJ	30.1	54.8
DFT, LDA	37.7	73.2
EXX-KLI	33.2	60.4
EXX-OEP	32.2	56.6
HF	32.0	56.4
MP4	29.5	51.6

- The large overestimation of LDA is typical for DFT with semi-local functionals. The HF and MP4 methods are generally considered to reproduce polarizabilities well.