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:
  
  ![Derivative discontinuity vs. Step like structure for atoms](image)

  - Global discontinuous shift when a new orbital is fractionally occupied.
  - Between electron shells the potential jumps in 'steps'.

- 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 \( \delta E/\delta N \) at integer electron numbers \( N \).
- A related (but not the same) discontinuity is present in the exchange potential, i.e., \( \delta E/\delta N \) 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:

![Exchange potential vs. Radial distance](image)

So, does it work?...

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

![Chain parallel coordinate \( z \) vs. hydrogen polarization](image)

... and the polarizabilities?

- As good as exact exchange!

  - Numerical polarizabilities in bulk 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):

<table>
<thead>
<tr>
<th>Method</th>
<th>( r_{pp} ) (amu)</th>
<th>( r_{pp} ) (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT, Cr, BJ</td>
<td>36.1</td>
<td>54.8</td>
</tr>
<tr>
<td>DFT, LDA</td>
<td>37.7</td>
<td>73.2</td>
</tr>
<tr>
<td>EXX-KLI</td>
<td>33.2</td>
<td>60.4</td>
</tr>
<tr>
<td>EXX-OPA</td>
<td>22.2</td>
<td>56.6</td>
</tr>
<tr>
<td>HF</td>
<td>32.0</td>
<td>56.4</td>
</tr>
<tr>
<td>MP4</td>
<td>29.5</td>
<td>51.6</td>
</tr>
</tbody>
</table>

- 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.

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.