

# Multi-configurational density functional theory by decomposition of the electron-electron interaction into long-range and short-range contributions

Julien Toulouse<sup>1</sup>, François Colonna<sup>2</sup>, Andreas Savin<sup>2</sup>

<sup>1</sup> *Cornell Theory Center, Cornell University, Ithaca, New York, USA.*

<sup>2</sup> *Laboratoire de Chimie Théorique, Université Pierre et Marie Curie,  
Paris, France.*

In electronic structure calculations of atomic and molecular systems using density functional theory applied within the Kohn-Sham scheme, the usual (semi-)local density functional approximations to the exchange-correlation energy (local density approximation, generalized gradient approximations) generally describe adequately the well-transferable interactions at short interelectronic distances but do not describe well the very specific interactions due to possible energetic near-degeneracies in the non-interacting Kohn-Sham system. Simple examples of systems in this latter situation include the Be atom where the  $2s$  and  $2p$  levels are near-degenerate and diatomic molecules at dissociation where the bonding and anti-bonding orbitals become degenerate.

In this context, we present a multi-configurational density functional theory based on a decomposition of the Coulomb electron-electron interaction into long-range and short-range contributions. The long-range part of the interaction is treated by a standard multi-determinantal wave function method like a multi-configurational self-consistent field (MCSCF) calculation, which properly takes into account the near-degeneracy correlation effects, while the short-range part of the interaction is treated by adequately-constructed (semi-)local density functional approximations.

We apply this multi-configurational density functional theory on simple electronic structure problems involving near-degeneracy correlation effects: ground-state energy of the Be atom, dissociation of the  $H_2$  and  $Li_2$  molecules, avoided crossing in the torsion of the ethylene molecule. In all these cases, the proposed method performs better than the standard *Restricted* Kohn-Sham scheme with the usual density functional approximations.

[1] J. Toulouse, F. Colonna, A. Savin, *Phys. Rev. A* **70**, 062505 (2004).

[2] J. Toulouse, F. Colonna, A. Savin, *J. Chem. Phys.* **122**, 014110 (2005).

**For more references, see [www.lct.jussieu.fr/toulouse/](http://www.lct.jussieu.fr/toulouse/)**