

Abstract Submitted
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Towards simple orbital-dependent density functionals for molecular dissociation IGOR YING ZHANG¹, Fritz-Haber-Institut der MPG, Berlin, DE, PATRICK RICHTER, Aalto University, Helsinki, FI, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin, DE — Density functional theory (DFT) is one of the leading first-principles electronic-structure theories. However, molecular dissociation remains a challenge, because it requires a well-balanced description of the drastically different electronic structure at different bond lengths. One typical and well-documented case is the dissociation of both H_2^+ and H_2 , for which all popular DFT functionals fail [1,2]. We start from the Bethe-Goldstone equation to propose a simple orbital-dependent correlation functional which generalizes the linear adiabatic connection approach. The resulting scheme is based on second-order perturbation theory (PT2), but includes the self-consistent coupling of electron-hole pairs, which ensures the correct H_2 dissociation limit and gives a finite correlation energy for systems with a (near)-degenerate energy gap. This coupling PT2-like (CPT2) approximation delivers a significant improvement over all existing functionals for both H_2 and H_2^+ dissociation. We will demonstrate the reason for this improvement analytically for H_2 in a minimal basis. [1] A. J. Cohen *et al.*, *Chem. Rev.* **112** 289 (2012), [2] F. Caruso *et al.*, *Phys. Rev. Lett.* **110** 146403 (2013).

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