Towards simple orbital-dependent density functionals for molecular dissociation

IGOR YING ZHANG\textsuperscript{1}, 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\textsubscript{2}\textsuperscript{+} and H\textsubscript{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 (PT\textsubscript{2}), but includes the self-consistent coupling of electron-hole pairs, which ensures the correct H\textsubscript{2} dissociation limit and gives a finite correlation energy for systems with a (near)-degenerate energy gap. This coupling PT\textsubscript{2}-like (CPT\textsubscript{2}) approximation delivers a significant improvement over all existing functionals for both H\textsubscript{2} and H\textsubscript{2}\textsuperscript{+} dissociation. We will demonstrate the reason for this improvement analytically for H\textsubscript{2} in a minimal basis. [1] A. J. Cohen et al., \textit{Chem. Rev.} \textbf{112} 289 (2012), [2] F. Caruso et al., \textit{Phys. Rev. Lett.} \textbf{110} 146403 (2013).