

Rigorous formulation of double hybrid density-functionals along the adiabatic connection

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We present a graphical analysis of the adiabatic connections underlying double-hybrid density-functional methods that employ second-order perturbation theory [1, 2]. Approximate adiabatic connection formulae relevant to the construction of these functionals are derived and compared directly with those calculated using accurate *ab initio* methods [3]. The discontinuous nature of the approximate adiabatic integrands is emphasized, the discontinuities occurring at interaction strengths which mark the transitions between regions that are: (i) described predominantly by second-order perturbation theory (ii) described by a mixture of density-functional and second-order perturbation theory contributions and (iii) described purely by density-functional theory. Numerical examples are presented for a selection of small molecular systems and van der Waals dimers. The impacts of commonly used approximations in each of the three sections of the adiabatic connection will be discussed along with possible routes for the development of improved double-hybrid methodologies.

[1] K. Sharkas, J. Toulouse, and A. Savin, *J. Chem. Phys.* **134**, 064113 (2011).

[2] E. Fromager, *J. Chem. Phys.* **135** 244106 (2011).

[3] Y. Cornaton, O. Franck, A. M. Teale, and E. Fromager, *Mol. Phys.* in press (2013).