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Combining strengths of DFT and wave functions: The short-range DFT-DMRG method

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Introduction

- Static electron correlation can be recovered with Complete Active Space (CAS) methods.
- Very large active spaces can be reached with the Denisty Matrix Renormalization Group Method (DMRG).

  S. R. White *Phys. Rev. Lett.* (1992), **69**, 2863.

  G. K. L. Chan, S. Sharma *Annu. Rev. Phys. Chem.* (2011), **62**, 465.

  S. Keller, M. Reiher *Chimia* (2001), **68**, 96
- Yet, dynamical correlation remains a problem.
- $\Rightarrow$ Combine DMRG with DFT, providing an efficient treatment of dynamical correlation.

  E. D. Hedegård *et al. J. Chem. Phys.* (Accepted; arXiv:1502.06157.)

CAS-CI/CASSCF energy and nomenclature

- CAS energy expression (p, q, r, s = general, i, j, k, l = inactive and u, v, r, s = active orbital indices)

$$E = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} P_{pqrs} + \hat{V}_{\mathrm{nn}}$$

$$E_{\mathrm{I}} = \sum_{i} \left(h_{ii} + f^{\mathrm{I}}_{ii} \right) + V_{\mathrm{nn}}$$

$$E_{\mathrm{A}} = \sum_{uv} f^{\mathrm{I}}_{uv} D_{uv} + \frac{1}{2} \sum_{uvxy} g_{uvxy} P_{uvxy}$$

- The 1-RDM and 2-RDM are:

$$D_{pq} = \langle \Psi | \hat{E}_{pq} | \Psi \rangle \qquad P_{pqrs} = \langle \Psi | \hat{e}_{pqrs} | \Psi \rangle$$

CAS-srDFT with DMRG

New energy expression with $\hat{g}(1,2) \longrightarrow g^{lr,\mu}(1,2) + g^{sr,\mu}(1,2)$

$$E_{\mathrm{DMRG}}^{\mathrm{srDFT}} = E_{\mathrm{I}}^{\mathrm{lr}} + E_{\mathrm{A}}^{\mathrm{lr}} + E_{\mathrm{H}}^{\mathrm{sr}}[\rho] + E_{\mathrm{xc}}^{\mathrm{sr}}[\rho]$$

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- $E_{\mathrm{I}}^{\mathrm{lr}}$ and $E_{\mathrm{A}}^{\mathrm{lr}}$ obtained with $g_{pqrs} \longrightarrow g_{pqrs}^{\mathrm{lr}}$ (with DALTON)
- Modified Fock matrix

$$f_{pq}^{\mathrm{I,lr}} = h_{pq} + \sum_{k} \left(2g_{pqkk}^{\mathrm{lr}} - g_{pkqk}^{\mathrm{lr}}\right)$$

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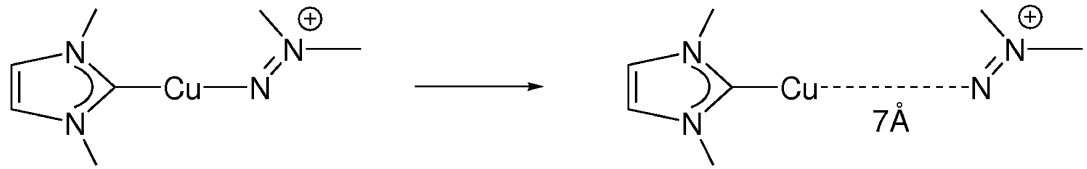
- $E_{\mathrm{xc}}^{\mathrm{sr}}[\rho]$ obtained throught tailored sr-DFT functionals

Ligand dissociation reactions with DMRG–srDFT



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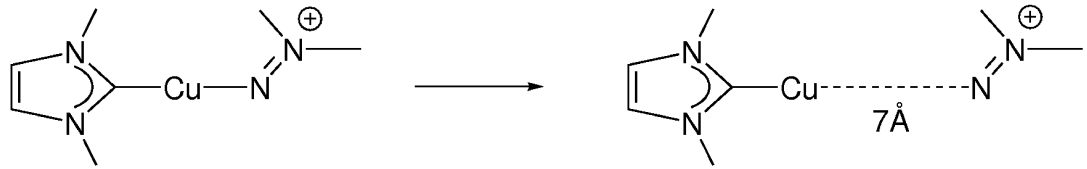

Table: Dissociation energies (D_0 is zero-point corrected)

Method	D_e (kJ/mol)	D_0 (kJ/mol)
DMRG[2000](30,22)	173.5	165.1
DMRG[2000](10,10)	132.8	124.3
DMRG[2000](30,22)-srPBE	225.1	216.6
DMRG[2000](10,10)-srPBE	216.5	208.0
PBE	240.2	231.8
Exp.	226.7	218.2

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- First applications for d-block complexes show improvement over regular DMRG
- Extension to open shell systems and excited states

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Thank you for your attention!