Calibration of DFT functionals for the $[Fe^{III}(SH)_4H]^0$ model system employing high-level *ab initio* methods

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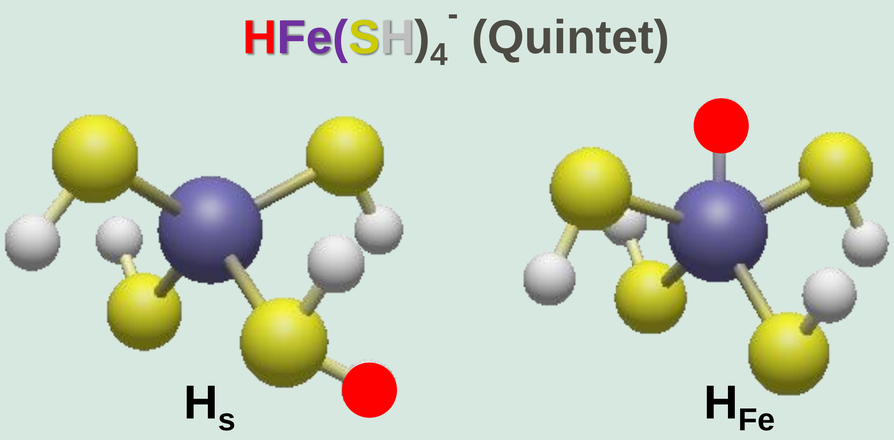
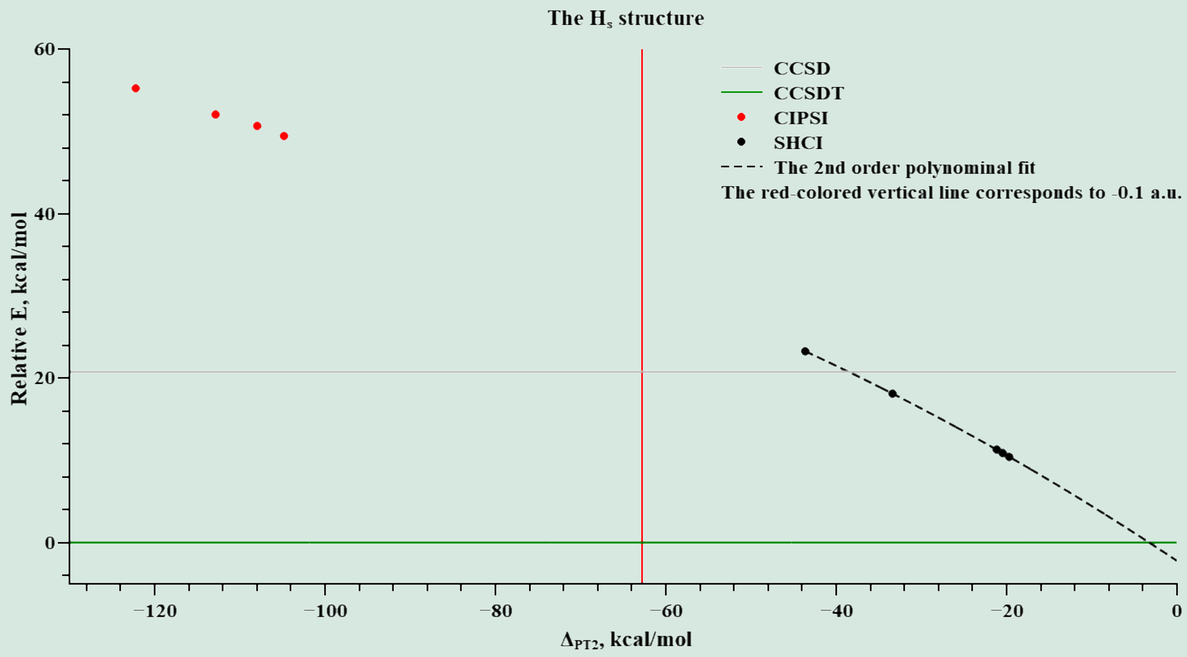
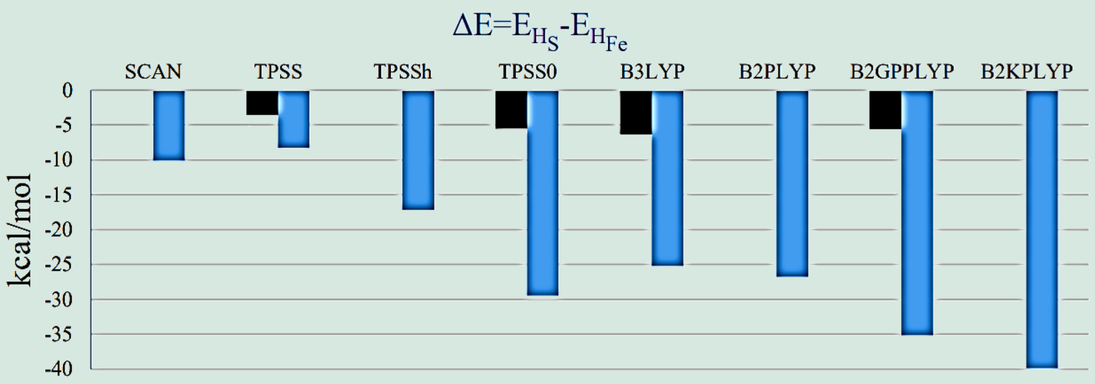
Two protonated model structures



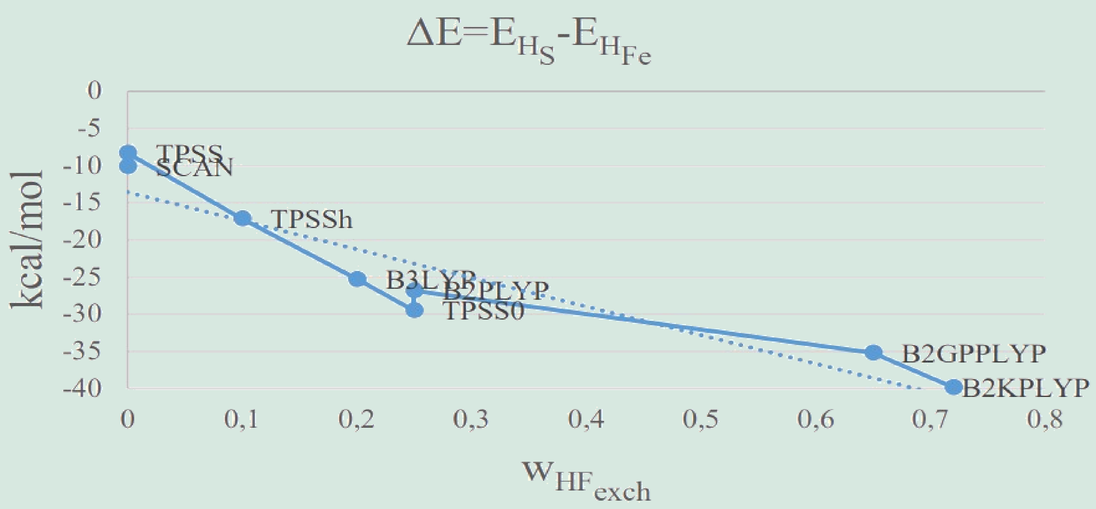


The frozen-core sCI and CC results on the H_S structure computed using the cc-pVDZ basis set. All energies are plotted in relation to the total CCSDT energy. For the best CIPSI and SHCI energies, the corresponding number determinants read 65M and 434M, respectively.

Zoo of DFT results

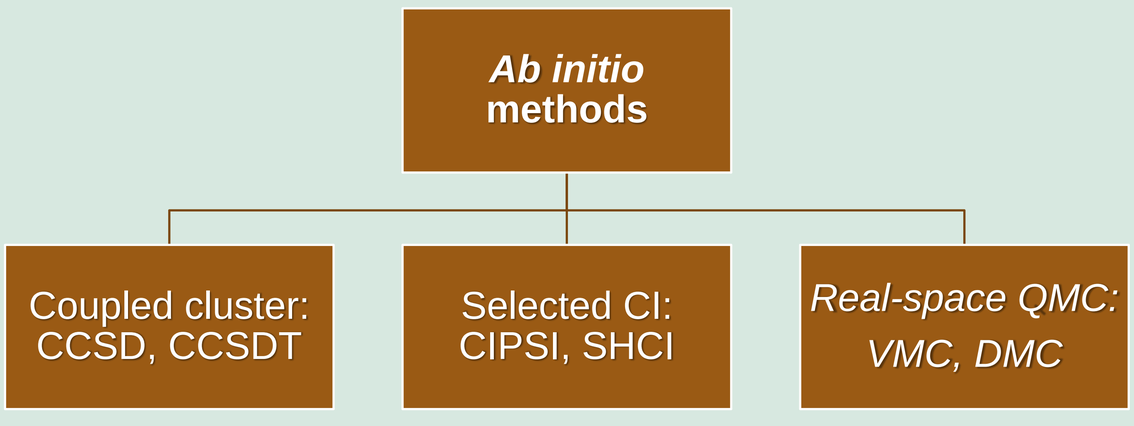


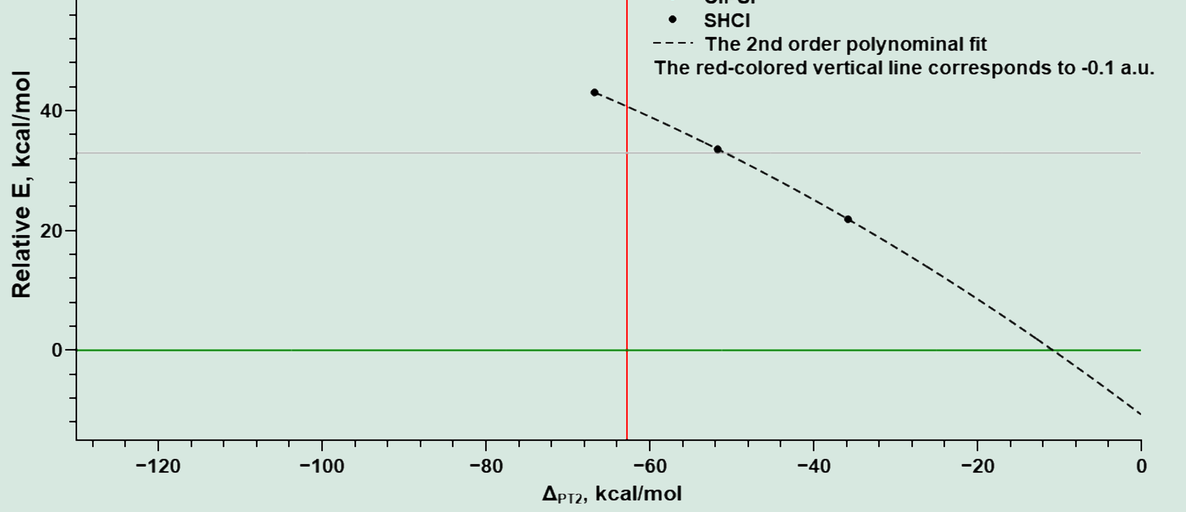
The spin-polarized UKS total energy gap between the H_S and H_{Fe} structures computed by different exchange-correlation (XC) functionals and ANO-RCC basis set (Fe:VQZP; S,H+: VTZP; H: VDZP). Electronic energy gaps ΔE for target protonated structures are colored in blue. For a representative set of XC functionals, single-point energy gaps between deprotonated skeleton $Fe(SH)_4^{2-}$ structures are depicted in black color.



At the UKS level of theory, ΔE correlates with the weight of exact HF exchange contribution to the XC. With (meta-)GGA XC functionals, the Self-Interaction Correction to energy drastically (~10x) increases the energy gap between protonated structures. The SIC and HF exchange posses a similar trend, regardless of the atomic basis set used.

Ab initio reference results





The frozen-core sCI and CC results on the H_S structure computed using the cc-pVDZ basis set. All energies are plotted in relation to the total CCSDT energy. For the best CIPSI and SHCI energies, the corresponding number determinants read 84M and 428M respectively.

Conclusions

According to the frozen-core SHCI/cc-pVDZ results extrapolated to *the FCI limit*, the energy gap between two protonated structures is *-16 kcal/mol* while the H_S structure is the most stable one. The CCSDT/cc-pVDZ predicts an energy gap of -24 kcal/mol. The discrepancy between CCSDT and SHCI is because the H_{Fe} structure exhibits multi-reference character.

Future perspectives

The memory requirement of selective CI approaches is ultimately high. At present, one can easily allocate thousand(s) of CPU cores but it might problematic to allocate dozen of fat memory nodes equipped by 3TB of RAM each. Therefore, we are going to apply QMC methods to study an influence of basis set on the energy gap.

Contact

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