Supporting Information for "Poisoning density functional theory with benchmark sets of difficult systems"

Tim Gould and Stephen Dale

Qld Micro- and Nanotechnology Centre, Griffith University, Nathan, Qld 4111, Australia

E-mail:

Abstract

Supporting Information for "Poisoning density functional theory with benchmark sets of difficult systems". Contains:

1. Technical details of the hybrid analysis
2. Supplementary Figure 1
3. Supplementary Figure 2
4. Supplementary Figure 3

1 Technical details of the hybrid analysis

We carry out self-consistent calculations of PBE0$_\alpha$ for $\alpha \in [0, 0.05, 0.1, 0.15, 0.2, 0.4, 0.6, 0.8, 1]$. All calculations are conducted using psi4,[1] the def2-SVP basis set,[2] and a global hybrid functional based on PBE as specified in Eqn. 6. The **P30-**N benchmark sets used in this work and code used to conduct these calculations are provided at `https://github.com/stephengdale/poison-set`.

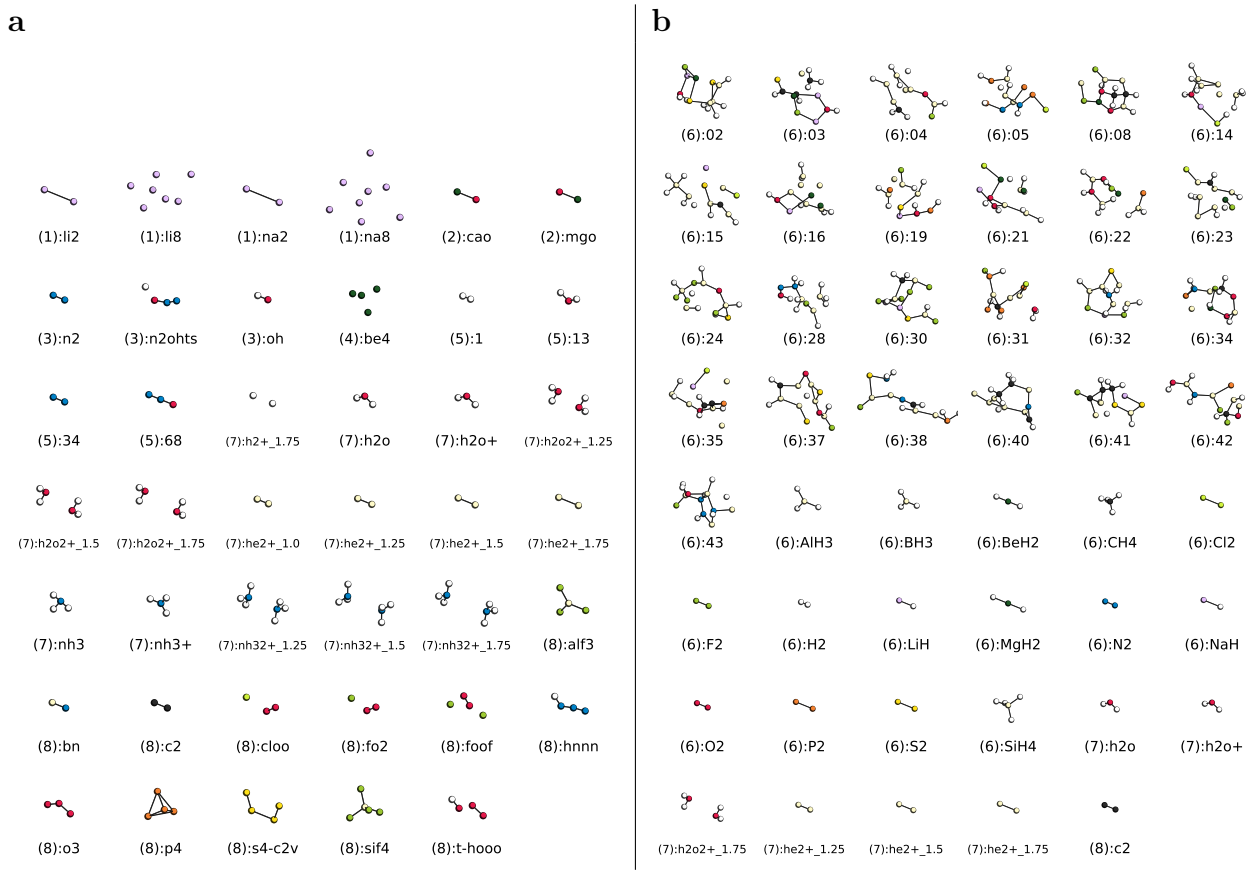
In most cases, the energy is almost linear ($\propto \alpha$) with only small corrections from the self-consistency cycle. Thefore, values of $0 \leq \alpha_0 \leq 1$ are determined by quadratic interpolation through the three points nearest the minimum, $\alpha_m = \arg\min_\alpha \mathrm{Err}(\alpha)$. When the resulting $\alpha_0 < 0$, it is re-evaluated by making a quadratic fit to values at $\alpha_{\mathrm{fit}} \in [0, 0.05, 0.1, 0.15, 0.2]$ and then finding the root. When initial $\alpha_0 > 1$, α_0 is re-evaluated by finding the root of a linear fit to $\alpha_{\mathrm{fit}} \in [0.8, 1]$.

Almost all α_0 lie between -0.75 and 1.25. Exceptions are $\alpha_0 = -2.02$ for G2RC:11, 3.335 for ALK8:2. In the case of MB16-43:5 there is no way to make the error go to zero, and thus α_0 is undefined.

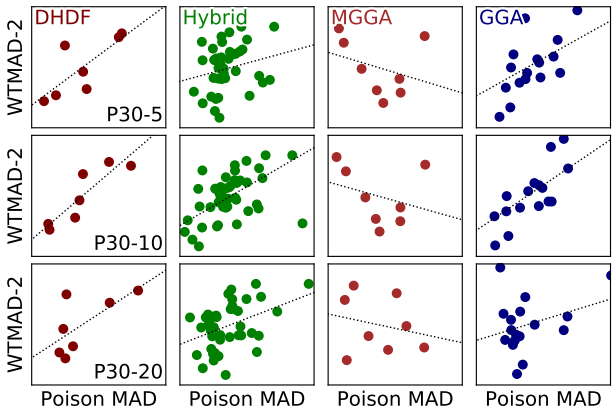
References

(1) Smith, D. G.; Burns, L. A.; Simmonett, A. C.; Parrish, R. M.; Schieber, M. C.; Galvelis, R.; Kraus, P.; Kruse, H.; Di Remigio, R.; Alenaizan, A.; et al, PSI4 1.4: Open-source software for high-throughput quantum chemistry. *J. Chem. Phys.* **2020**, *152*, 184108.

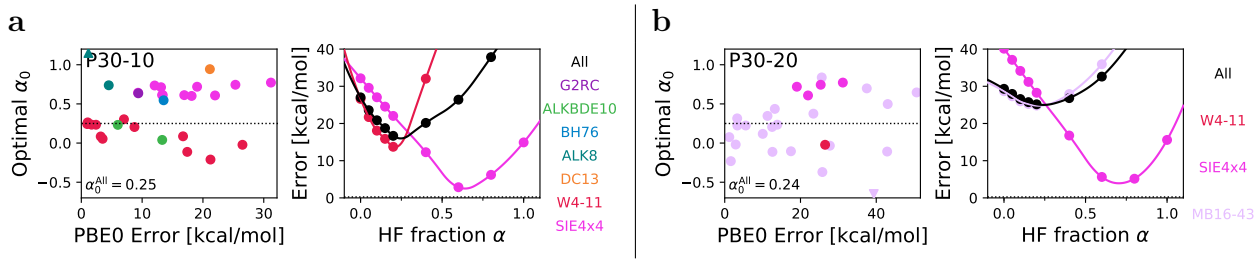
(2) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.



SUPPLEMENTARY FIGURE 1: The molecules (atoms not shown) used to form the 30 "poison" reactions in the **P30-10** (a) and **P30-20** (b) benchmark sets.



SUPPLEMENTARY FIGURE 2: Scatter plots of WTMAD-2 versus $\mathrm{MAD}_{\mathrm{P30}\text{-}N}$ for the three benchmark sets and the four rungs. All plots use normalized units and the line of best fit is indicated by dotted lines. The colour of dots indicates the rung: double-hybrid (reds), hybrid (greens), meta-GGAs (earth tones) and GGAs (blues)



SUPPLEMENTARY FIGURE 3: Optimal HF exchange mixing parameter, α_0, for the thirty reactions in **P30-10** (a) and **P30-20** (b). The left plots show α_0 as a function of the PBE0 error for each reaction. The right plots show the MAD for each subset as a function of α, and across the full poison set. Colours indicate the subset. Arrows indicates α_0 outside of the reported range.