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Date: 01/04/2022 (but no, it's not an "April Fools!")
Topic: miscellanea concerning the non-negativity paper

Cycles and threshold

The conventional FDET macrocycles and the freeze-and-thaw procedure were interrupted when the change in the embedded SCF energy fell below $1\text{e-}09$ Ha.

The conventional FDET procedure converged in 5-6 cycles for both SE and ME (6 cycles for 7HQ-formate, 5 for the others).

Freeze and thaw with ME converged in 15, 19, 15, 17 cycles for 7HQ-2MeOH, 7HQ-formate, Uracil-5H₂O, PyrBnz-2HCOOH respectively.

Freeze and thaw with SE converged in 17, 27, 17, 19 cycles for 7HQ-2MeOH, 7HQ-formate, Uracil-5H₂O, PyrBnz-2HCOOH respectively.

Suggested sentence about FDET-HF (you may have to adjust references and LaTeX notation):

In Fig. * the interaction energies at the FDET-MP2 follow a general downward trend. This is consistent with the variational character of FDET-MP2, guaranteed by Eq. (38 of TAW 2020). There are nonetheless some deviations from this general trend, albeit small: in 3 out of 4 systems the results from the ChelPG prepolarised densities lie below those from ρ_B^{FAT} . It should although be noted that if only the self-consistent component of the FDET-MP2 energy expression, denoted as, FDET-MP2-sc is considered, such deviations from the trend disappear (figure available in the supporting information). This indicates that the terms

Grid specifications:

The integration of densities and the calculation of $E_k[\dots]$ was performed with pycscf, using a Lebedev-Laikov^[Lebedev1999] grid, where the "level" parameter was set to 4.

The integration within the individual Q-chem calculations used default grids and values.

bibtex:

```
@article{Lebedev1999,  
author = {Lebedev, Vyacheslav Ivanovich and Laikov, Dimitri N.},  
year = {1999},  
title = {A quadrature formula for the sphere of the 131st algebraic order of accuracy},  
journal = {Doklady Mathematics},  
volume = {59},  
pages = {477--481}  
}
```

The paper is hard to find, and in Russian. I attach it via email in case you find it interesting.

FDET optimising also with non-optimised environment density

Where there is the sentence "This is probably due to the variational character of densities obtained in FDET" I suggest to change to:

This is probably due to the variational character of densities obtained in FDET, which optimises ρ_A even when ρ_B^{isol} is used. This is highlighted by the fact that the FDET densities ρ_A^{iso} and ρ_B are remarkably more similar to the reference density than to the sum of isolated fragments, as can be shown by the values of P for the differences between these densities (cf. Supporting Information).

References for point-charges

the bibtex key for chelpg is already available and is Breneman1990

If we want we could mention the ChelP charges which pioneered the charges fit to the electrostatic potential. For this it would be:

```
@article{Chirlian1987,  
  abstract = {A new algorithm for fitting atomic charges to molecular electrostatic potentials is  
  presented. This method is non iterative and rapid compared to previous work. Results from a  
  variety of gaussian basis sets, including STO 3G, 3 21G and 6 31G*, are presented. Charges for  
  a representative collection of molecules, comprising both first and second row atoms and anions are  
  tabulated. The effects of using experimental and optimized geometries are explored. Charges  
  derived from these fits are found to adequately reproduce SCF dipole moments. A small split  
  valence representation, 3 21G, appears to yield consistently good results in a reasonable amount of  
  time. Copyright {\textcopyright} 1987 John Wiley & Sons, Inc.},  
  author = {Chirlian, Lisa Emily and Francl, Michelle Miller},  
  doi = {10.1002/jcc.540080616},  
  issn = {1096987X},  
  journal = {Journal of Computational Chemistry},  
  number = {6},  
  pages = {894--905},  
  title = {{Atomic charges derived from electrostatic potentials: A detailed study}},  
  volume = {8},  
  year = {1987}  
}
```

for mulliken charges:

```
@article{Mulliken1955,  
  author = {Mulliken, Robert Sanderson},  
  journal = {The Journal of Chemical Physics},  
  number = {January 1955},  
  pages = {1833--1840},  
  title = {Electronic Population Analysis on LCAO-MO Wave Functions.I},  
  volume = {23},  
  doi = {10.1063/1.1740588}  
  year = {1955}  
}
```

Mulliken has a long series of papers with this name (I, II, III, IV). The first one tackles "population breakdown", i.e. the charges.

Numerical values needed

The freeze and thaw values to adjust because of the one half factor before both kernels.

ME:

7HQ-2MeOH -13.465

7HQ-formate -28.272

Uracil-5H2O -37.680

PyrBnz-2HCOOH -32.789

SE

7HQ-2MeOH -14.590

7HQ-formate -33.680

Uracil-5H2O -40.281

PyrBnz-2HCOOH -35.334