Violation of The non-negativity of the target density in practical calculations

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Abstract

Tentative abstract

1 Introduction

- FDET equation

- shape of embedding potential.

- there is no possible embedding potential that can lead to non v-representable target densities

- if $\delta\rho_B(\mathbf{r})$ so that the extent of violation is reduced, the induced change in energy has to be non-positive ($\delta E^{FDET}[\Psi_A, \rho_B; v_B] \leq 0$

- if we somehow measure the extent of non-negativity, and this is reduced, the energy should also lower. This is true unless:

    - the violation reduces in a region of the space and increases somewhere else, with a larger energy effect in the latter than the former.

    - the contributions of the other sources of error (approximate functionals and potentials, basis set expansion) do not change significantly

- polarization and charge transfer can be expected to influence the extent of violation of the target density

2 Computational Details

- We study each of the 4 systems individually so that the changes in other error contributions are minimized

- The energy effect of density is far from easy

- Definition of M

- Definition of P

- pyscf to perform integration of M and P

- Qchem version

- ME vs SE, point-charge prepolarization only for ME

- labels for different densities

- in-house iterative procedure (Nico's fork of Alex's CCJob)

3 Results and discussion

3.1 Monomer Expansion

M vs E_{HF}

- When M decreases, so does the HF energy

- When we somehow prepolarize, we obtain a decrease in M, and the behavior is sensible (Mulliken ¡ ChelPG ¡ Freeze and Thaw, Mulliken sometimes no improvement)

M vs P

- When M decreases, so does the P

M vs E_{MP}

- When M decreases, so does the MP energy (obtained according to Wesolowski 2020)

- Small deviation from expected behavior is small and can be explained by the approximate correlation treatment, the approximate external potential, and the incomplete basis set

3.2 Supermolecular Expansion

M vs E_{HF} M vs P M vs E_{MP}

- same behavior for supermolecular expansion, where charge transfer is allowed

3.3 Freeze and Thaw cycles

N vs E_{HF}, SE

- the first freeze and thaw iteration leads to the largest energy decrease

- after 1-2 freeze and thaw iterations the energy is almost equal to the fully converged one

- the linearization is extremely accurate, Δ^{lin} decreases during freeze and thaw, and finally reaches zero

- same findings for ME (cf. SI)

4 Conclusions

- the negativity of the target density clearly increases $E^{FDET}[\Psi_A, \rho_B; v_B]$

- prepolarization techniques reduce negativity, and consequently $E^{FDET}[\Psi_A, \rho_B; v_B]$

- the negativity of the target density is a sizeable error contribution. Error analysis should account for this.

- Single-state properties require some type of prepolarization

- ESP-derived charges are a well-performing tradeoff between computation time and accuracy

- the error on excitation properties depends on the difference of negativity violation ΔM. This implies:

  - no-prepolarization can be expected to be much better than for single-state properties

  - the effect of prepolarization is hard to predict, and knowledge of the system is necessary

Supporting Information Available

The data is provided in csv.

- Filename: data as comma separated values. The labels are explaind below:

  - label: explanation

Graphical TOC Entry

TOC to be made. Probably isosurfaces of target density.