Data Review

Yi Xie

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Intermolecular Energies

- Supermolecular approach

$$E_{int} = E_{AB} - E_A - E_B$$

  - Straightforward, but cannot separate different types of interactions
  - Can adopt to different electronic structure methods
  - DFT-D3 with proper functional can be both cheap and accurate
- Symmetry-Adapted Perturbation Theory
  - Can give details about different types of interactions; important in understanding their nature
  - Not as cheap as DFT-D3
  - SAPT0 is somewhat cheap, but does not include intramonomer correlation

SAPT(DFT)

- Attempt to inlude intramonomer correlation in a cheap way
- Replaces HF orbitals with KS orbitals
- Needs to consider orbital response for dispersion terms
- Exchange-dispersion term needs to be estimated from scaling
- Investigate the accuracy and efficiency of SAPT(DFT)

Three-Body Interaction

- Crucial in computing lattice energies
- DFT-D3 does not perform well for three-body interaction
- MP2.5 scales as $O(N^6)$, MP2 is $O(N^5)$ but lacks three-body dispersion
- Three-body dispersion can be implemented with SAPT(DFT) in $O(N^5)$
- Combine MP2 with SAPT(DFT) dispersion to model three-body interaction

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Idea of SAPT(DFT)

- SAPT energy in orders of interaction and fluctuation potentials; n denotes order in V and k, l for W_A, W_B

$$H = F_A + F_B + V + W_A + W_B$$

$$E_{int} = \sum_{n=1}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \left(E_{pol}^{(nkl)} + E_{exch}^{(nkl)} \right)$$

- SAPT0: $n = 2, k = l = 0$, no intramonomer correlation, $O(N^5)$ cost
- Many-body SAPT: $k, l \geq 2$, $O(N^7)$ or higher cost
- SAPT(DFT): Use Kohn-Sham operator $K_{A,B}$ instead of Fock operator $F_{A,B}$, $O(N^5)$ cost
- Primitive SAPT(DFT) works well on 1st-order terms, but not 2nd-order terms (especially dispersion). Needs orbital response for them

Dispersion Term

- ALDA kernel good for pure GGA functional, but not for hybrid functional
- Exact exchange in $v_{xc} \rightarrow$ increased $\epsilon_{ij}^{ab} \rightarrow$ decreased $E_{disp}^{(2)}$

$$E_{disp,u}^{(2)} = -4 \sum_{ia \in A, jb \in B} \frac{|(ia|jb)|^2}{\epsilon_{ij}^{ab}}$$

- Hybrid ALDA kernel to compensate, or localized HF (LHF) exchange to avoid increase in ϵ_{ij}^{ab}

$$f_{xc} = \alpha f_{xc}^{HF} + (1 - \alpha) f_{xc}^{ALDA}$$

Equation for $E_{disp}^{(2)}$

- Computing coupled FDDS:

$$\boldsymbol{\chi} = \boldsymbol{\chi}_0' + \left(\boldsymbol{\chi}_0'\mathbf{S}^{-1}\mathbf{W} + \mathbf{K}\right)\left[\mathbf{S} - \left(\boldsymbol{\chi}_0'\mathbf{S}^{-1}\mathbf{W} + \mathbf{K}\right)\right]^{-1}\boldsymbol{\chi}_0'$$

$$\boldsymbol{\chi}_0' = \boldsymbol{\chi}_0 - \alpha\mathbf{K}_2\left(\lambda\right)$$

$$\mathbf{K} = \left[-\alpha\mathbf{K}_1\left(\lambda d\right) - \alpha\mathbf{K}_2\left(\lambda d\right) + \alpha^2\mathbf{K}_{21}\left(\lambda\right)\right]\left(\mathbf{R}^t\right)^{-1}\mathbf{S}$$

- $O(N^5)$ scaling is limited to forming $\mathbf{K}_1$, $\mathbf{K}_2$ and $\mathbf{K}_{21}$
- Separates nontrivial and trivial parts of the code, also highly reduces need of disk I/O operations
- $E_{disp}^{(2)}$ from coupled FDDS:

$$E_{disp}^{(2)} = -\frac{1}{2\pi}\int_0^\infty d\omega \int d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B \frac{1}{|\mathbf{r}_A - \mathbf{r}_B|}\frac{1}{|\mathbf{r}'_A - \mathbf{r}'_B|}\chi^A\left(\mathbf{r}_A, \mathbf{r}'_A|i\omega\right)\chi^B\left(\mathbf{r}_B, \mathbf{r}'_B|i\omega\right)$$

Exchange-Dispersion Term

- Coupled exchange-dispersion requires storing 4-index tensors on disk
- Estimate from scaling uncoupled exchange-dispersion; Scale with ratio in dispersion term or with pre-fitted (with S22×5) fixed factor

$$\tilde{E}^{(2)}_{exch-disp,r} = E^{(2)}_{exch-disp,u} \cdot \frac{E^{(2)}_{disp,r}}{E^{(2)}_{disp,u}}$$

$$\tilde{E}^{(2)}_{exch-disp,r} = \alpha \cdot E^{(2)}_{exch-disp,u} (\alpha = 0.686361)$$

- The value above is fitted from $E^{(2)}_{exch-disp,u}$ with LHF orbitals
- Non-LHF orbitals have greater o-v gaps and smaller $E^{(2)}_{disp,u}$, needs to re-fit with non-LHF results

LHF vs non-LHF orbitals

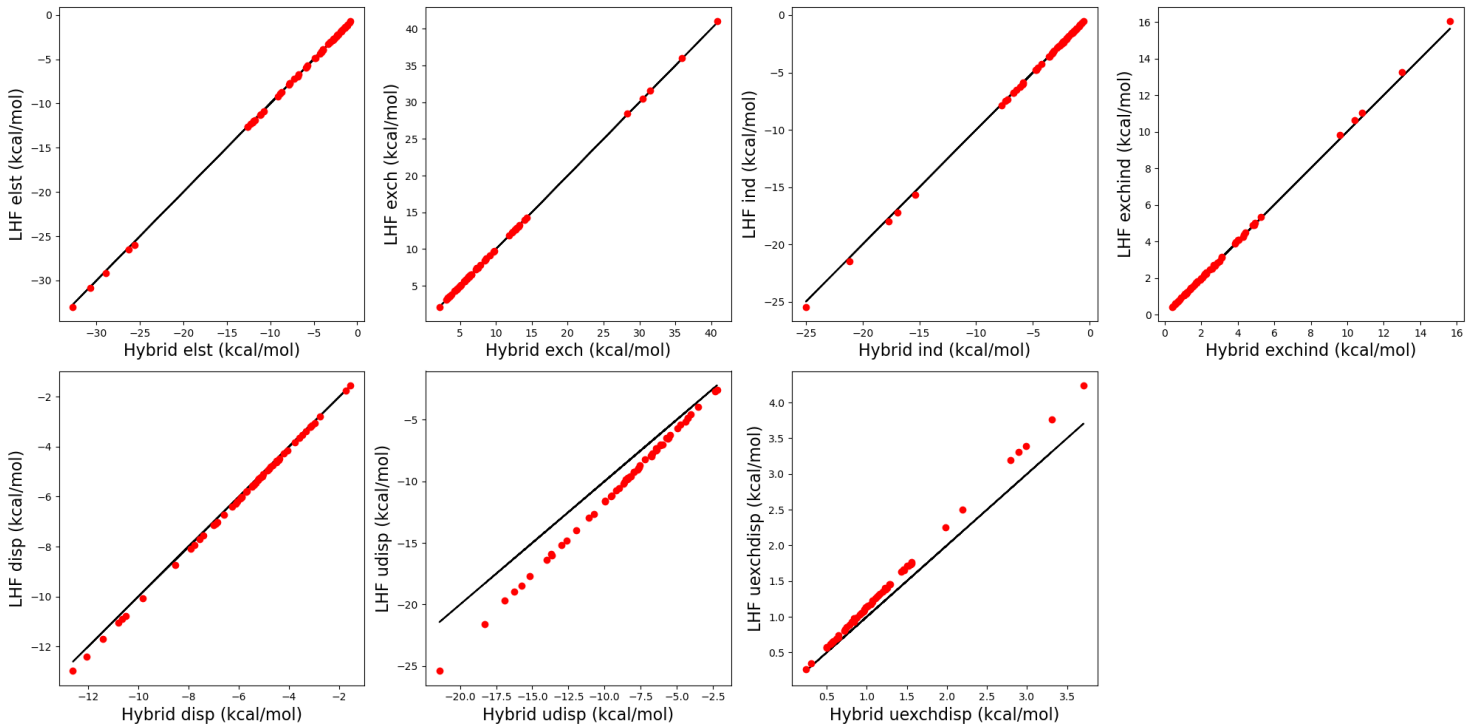

Figure: Hybrid vs. LHF values for each term for S66 data set ($E^{(1)}_{elst}$, $E^{(1)}_{exch}$, $E^{(2)}_{ind}$, $E^{(2)}_{exch-ind}$, $E^{(2)}_{disp,r}$, $E^{(2)}_{disp,u}$, $E^{(2)}_{exch-disp,u}$)

GRAC

- (Hybrid-)GGA functionals does not have correct long-range behavior $v_{xc}(r) \to -1/r + (I_p + \epsilon_{\text{HOMO}})$
- Underestimates o-v gap as a consequence
- Functionals like LB94 have correct asymptotic behavior, but poor in bulk region
- Using gradient-regulated asymptotic correction (GRAC) scheme to connect PBE0 and LB94 with the switching function $f[g(\boldsymbol{r})]$:

$$v_{xc}^{\text{GRAC}} = \{1 - f[g(\boldsymbol{r})]\} v_{xc}^{\text{PBE0}} + f[g(\boldsymbol{r})] v_{xc}^{\text{LB94}}$$

$$f[g(\boldsymbol{r})] = \left(1 + e^{-\alpha[g(\boldsymbol{r}) - \beta]}\right)^{-1}$$

$$g(\boldsymbol{r}) = \frac{|\nabla \rho(\boldsymbol{r})|}{\rho^{4/3}(\boldsymbol{r})}$$

GRAC & Long-Range Behavior

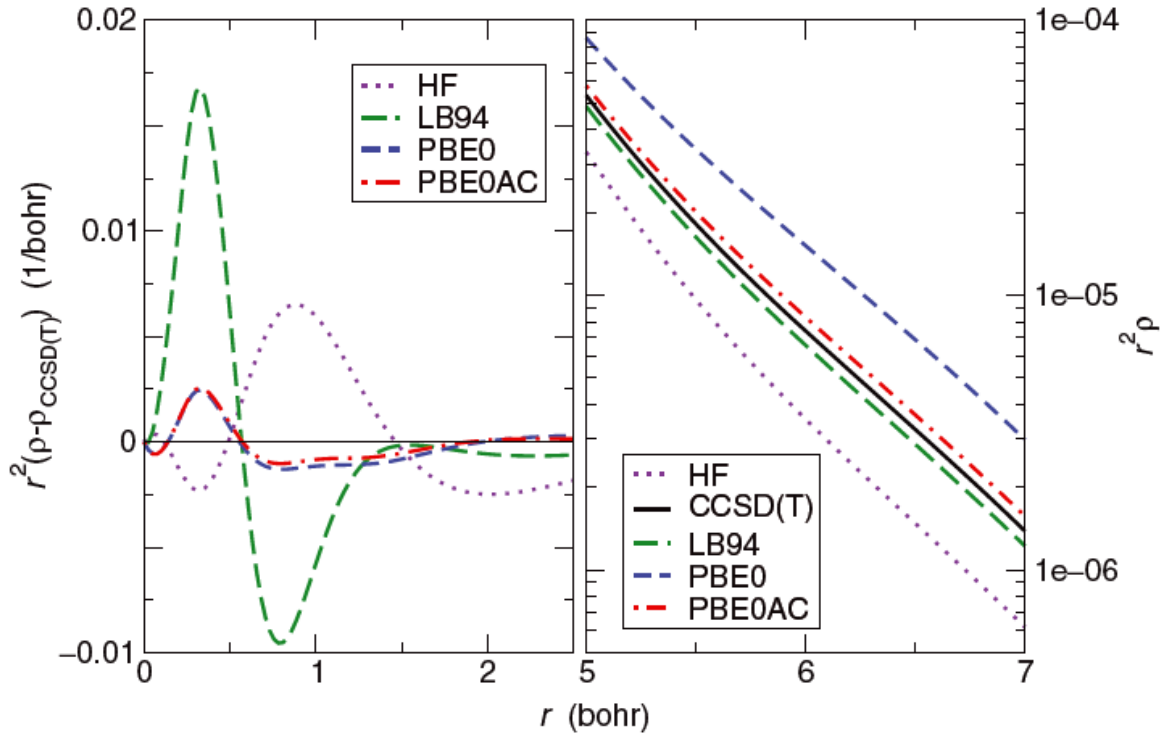

Figure: Radial densities $r^2\rho(r)$ of Ne atom (right) and errors compared to CCSD(T) density (left) for various xc potentials.[2]

[1] G. Jansen, WIREs Comput. Mol. Sci. **4**, 127 (2014).

Test 5

Test0	Test1	Test2
Test1	Test2	Test3 LaTeX
Test4	Test5	Test6

Test 6

Example block

Test0	Test1	Test2
Test1	Test2	Test3 LaTeX
Test4	Test5	Test6

Block

Test0	Test1	Test2
Test1	Test2	Test3 LaTeX
Test4	Test5	Test6

Test 7

Block A

short	Short stuff
long	Longer stuff
longest label	Longest stuff (insert cat)

- item1
- item2
- item3

Frame with Columns

Block 1

Text here

Block 2

More text here

Frame without Columns

Block

Even more text here