

Data Review

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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 include 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:

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

$$\chi'_0 = \chi_0 - \alpha \mathbf{K}_2 (\lambda)$$

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

- ▶ $O(N^5)$ 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:

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



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 $S22 \times 5$) fixed factor

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

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

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

LHF vs non-LHF orbitals

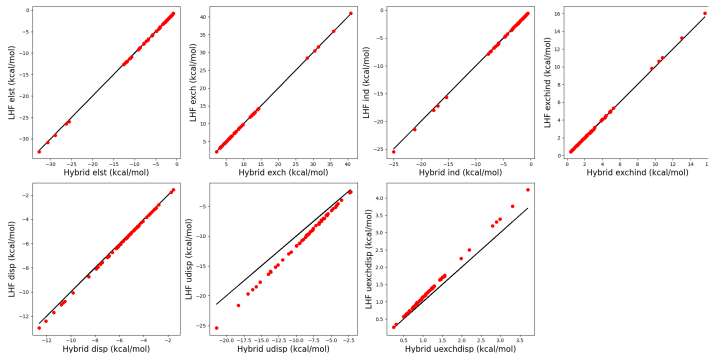


Figure: Hybrid vs. LHF values for each term for S66 data set ($E_{elst}^{(1)}$, $E_{exch}^{(1)}$, $E_{ind}^{(2)}$, $E_{exch-ind}^{(2)}$, $E_{disp,r}^{(2)}$, $E_{disp,u}^{(2)}$, $E_{exch-disp,u}^{(2)}$)



GRAC

- ▶ (Hybrid-)GGA functionals does not have correct long-range behavior
 $v_{xc}(r) \rightarrow -1/r + (I_p + \epsilon_{\text{HOMO}})$
- ▶ 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 $f[g(\mathbf{r})]$:

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

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

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

GRAC & Long-Range Behavior

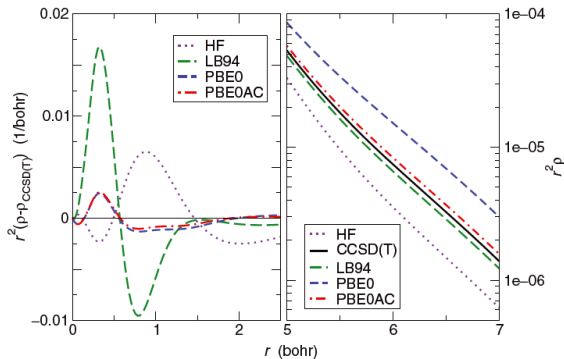


Figure: Radial densities $r^2 \rho(r)$ of Ne atom (right) and errors compared to CCSD(T) density (left) for various xc potentials.¹

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

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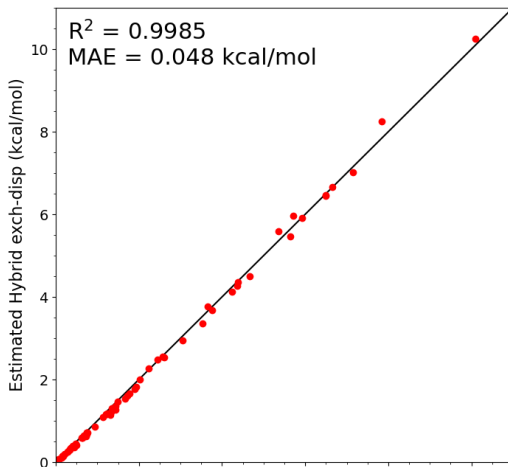
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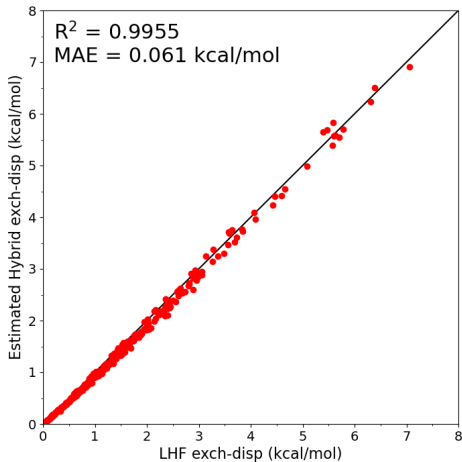
Exchange-Dispersion Refitting

- ▶ Need to fit the uncoupled $E_{exch-disp,r}^{(2)}$ with non-LHF orbitals on the coupled LHF orbital values (implemented in Molpro)
- ▶ Assuming coupled LHF and non-LHF orbital $E_{exch-disp,r}^{(2)}$ from the behavior of $E_{disp,r}^{(2)}$
- ▶ Exchange-related components depend heavily on distance between monomers, sets like S22×5 and S66×8 would be preferred
- ▶ Determine the scaling factor with S22×5, validate with S66×8

S22×5 Fitting Results



S66×8 Validating Results





Termwise results

- ▶ Compared the SAPT(DFT)/aug-cc-pVTZ results of our code to SAPT(CCSD)/aug-cc-pVTZ results from Korona S2², which consists of 14 small dimers
- ▶ Also comparing the results for S66. SAPT(CCSD) results are not available, used SAPT2+3(CCD) δ MP2/aug-cc-pVTZ as reference. Also added SAPT0/aug-cc-pVDZ, SAPT2+/aug-cc-pVDZ and SAPT2+(3) δ MP2/aug-cc-pVTZ into comparison as side-reference.
- ▶ Exchange-induction and exchange-dispersion not separated out for S66
- ▶ Errors of each system with respect to reference shown as vertical lines
- ▶ Mean absolute error (MAE) and mean unsigned relative error (MURE) listed for S2
- ▶ Color scheme for S66 systems: Hydrogen-bonded (HB, red), mixed-influence (MX, green), dispersion-dominated (DD, blue)

Korona S2 Results

Method ^a	MAE	MURE	Error Distribution ^b					
			4	OB	1	0	1	UB
Electrostatics								
SAPT(DFT) hybrid	0.112	2.39					█	
SAPT(DFT) LHF	0.114	3.68					█	
SAPT0	0.520	8.61					█	
Exchange								
SAPT(DFT) hybrid	0.251	3.38					█	
SAPT(DFT) LHF	0.258	3.09					█	
SAPT0	1.757	12.88	█	█				
Induction								
SAPT(DFT) hybrid	0.148	2.79					█	
SAPT(DFT) LHF	0.192	2.97					█	
SAPT0	1.993	16.83	█	█				
Exchange-Induction								
SAPT(DFT) hybrid	0.144	4.03					█	
SAPT(DFT) LHF	0.165	4.76					█	
SAPT0	1.551	26.80	█	█				

Dispersion

Exchange-Dispersion

Total[illegible]

S66 Results

Method ^a	Total	HB	MX	DD	Error Distribution ^b						
					4	OB	1	0	1	UB	4
Electrostatics											
SAPT(DFT) hybrid	0.374	0.556	0.177	0.311							
SAPT(DFT) LHF	0.423	0.666	0.196	0.319							
SAPT0	0.613	1.034	0.439	0.297							
SAPT2+	0.236	0.270	0.136	0.263							
SAPT2+(3) δ MP2	0.000	0.000	0.000	0.000							
Exchange											
SAPT(DFT) hybrid	0.886	1.127	0.426	0.926							
SAPT(DFT) LHF	0.886	1.121	0.431	0.928							
SAPT0	0.675	0.942	0.263	0.658							
SAPT2+	0.337	0.467	0.222	0.277							
SAPT2+(3) δ MP2	0.000	0.000	0.000	0.000							
Induction											
SAPT(DFT) hybrid	0.211	0.201	0.212	0.220							
SAPT(DFT) LHF	0.224	0.223	0.223	0.225							
SAPT0	0.241	0.200	0.261	0.271							
SAPT2+	0.327	0.384	0.250	0.318							
SAPT2+(3) δ MP2	0.152	0.179	0.121	0.145							

S66 Results

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Timing Performance

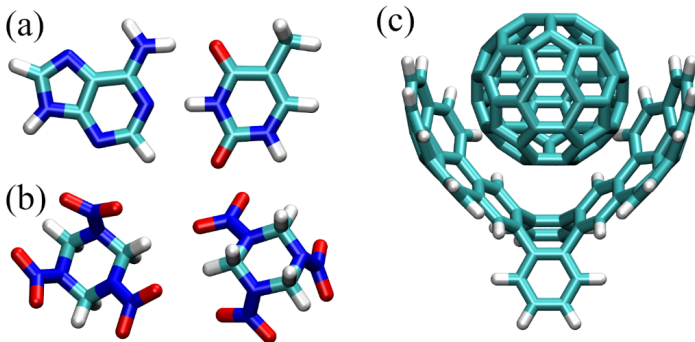
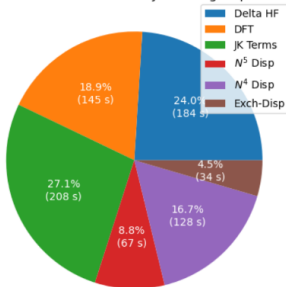


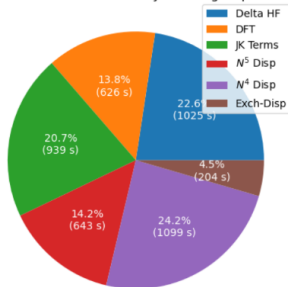
Figure: Dimer systems for timing: (a) Watson-Crick adenine-thymine complex, (b) RDX dimer, (c) C_{60} -buckycatcher complex.

Watson-Crick Adenine-Thymine

(a) Watson-Crick Adenine-Thymine aug-cc-pVDZ



(b) Watson-Crick Adenine-Thymine aug-cc-pVTZ



Fram without Columns

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Even more text here