

Accurate thermochemistry with fixed node diffusion Monte Carlo

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QMC in the Apuan Alps – 27/07/2010



aim of this study

- ▶ fixed node error cancellation for reaction energies is a limiting factor when using FNDMC for chemistry
- ▶ to improve the nodes we can go beyond Hartree-Fock (HF) trial wave functions (TWFs) with
 - ▶ **density functional theory (DFT)**
 - ▶ **backflow wavefunctions**
 - ▶ **MO optimization**
 - ▶ multi-determinant TWFs
- ▶ how far do we have to go for accurate (CCSD(T)/cc-pVTZ level) thermochemistry (reaction energies)?

Helgaker benchmark set[1]

No.	reaction	cc-pVTZ[1]	cc-pVQZ	cc-pV5Z	cc-pV(Q5)Z	experiment
1	$CH_2 + H_2 \rightarrow CH_4$	-128.3	-128.76	-128.83	-128.97	-129.9(5)
2	$C_2H_2 + H_2 \rightarrow C_2H_4$	-49.4	-49.37	-49.32	-49.23	-48.5(5)
3	$C_2H_2 + 3H_2 \rightarrow 2CH_4$	-107.7	-107.42	-107.14	-106.89	-106.5(5)
4	$N_2H_2 \rightarrow N_2 + H_2$	-42.8	-41.85	-41.41	-41.18	-41.6(0)
5	$CO + H_2 \rightarrow H_2CO$	-3.8	-4.57	-4.93	-5.16	-5.0(2)
6	$N_2 + 3H_2 \rightarrow 2NH_3$	-34.9	-37.75	-38.87	-39.46	-39.2(2)
7	$F_2 + H_2 \rightarrow 2HF$	-130.2	-134.00	-134.93	-135.47	-134.5(2)
8	$O_3 + 3H_2 \rightarrow 3H_2O$	-217.8	-223.23	-224.85	-225.77	-222.8(5)
9	$H_2CO + 2H_2 \rightarrow CH_4 + H_2O$	-57.6	-59.03	-59.51	-59.77	-60.0(2)
10	$H_2O_2 + H_2 \rightarrow 2H_2O$	-83.8	-86.34	-87.15	-87.48	-87.2(2)
11	$CO + 3H_2 \rightarrow CH_4 + H_2O$	-61.4	-63.60	-64.45	-64.93	-65.0(2)
12	$HCN + 3H_2 \rightarrow CH_4 + NH_3$	-74.8	-76.09	-76.57	-76.76	-76.4(7)
13	$HNO + 2H_2 \rightarrow H_2O + NH_3$	-102.0	-104.86	-105.89	-106.47	-106.0(2)
14	$HNC \rightarrow HCN$	-15.0	-14.78	-14.82	-14.90	-15.3(0)
15	$H_2O + F_2 \rightarrow HOF + HF$	-27.5	-28.36	-28.50	-28.67	-30.8(10)
16	$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4$	-54.0	-56.85	-58.07	-58.63	-58.3(2)
17	$2CH_2 \rightarrow C_2H_4$	-198.2	-199.47	-199.83	-200.28	-201.6(7)
	MAD (to exp)	2.71	1.01	0.69	0.73	-

► CCSD(T)/cc-pVTZ usually considered 'accurate'

used error measures

- ▶ relative energies:
root mean square error (RMSE) over the complete set in kcal/mol
(statistical errors below 0.08 kcal/mol)
- ▶ absolute energies:

$$EC_X/EC_{ref} = \frac{E_{FNDMC}^X - E_{HF}^{reference}}{E_{FNDMC}^{reference} - E_{HF}^{reference}}$$

averaged over the complete set (statistical errors below $5 \cdot 10^{-4}$)
with PP-FNDMC(HF/BFD-VTZ) as reference

All-electron (AE) vs pseudo potential (PP) FNDMC

approach	RMSE
AE-FNDMC(HF/cc-pVTZ)[1]	8.7(2)
AE-FNDMC(HF/TZVP)	8.79(7)
PP-FNDMC(HF/Lester-TZ)	8.2(2)
PP-FNDMC(HF/BFD-VTZ)	4.10(5)
CCSD(T)/cc-pVTZ	3.1

- ▶ error cancellation much better with BFD-PPs

Mean field model and basis set dependence

	method	basis[1]	RMSE	EC/EC_{ref}
PP-FNDMC with	HF	BFD-VDZ	7.55	0.998
		BFD-VTZ(-f)	3.90	0.999
		BFD-VTZ	4.10	1.000
		BFD-VQZ(-g)	4.30	1.003
	DFT	BFD-VDZ	5.19	1.000
		BFD-VTZ	3.86	1.003
		BFD-VQZ(-g)	3.60	1.006
AE-FNDMC with	HF	TZVP	8.79	-
	DFT	TZVP	6.44	-
	DFT	QZVP	...	-

- ▶ DFT TWFs become more favorable with larger basis sets

DFT functionals along Jacob's ladder

	method	RMSE	EC/EC_{ref}	DFT RMSE
PP-FNDMC with	LDA	3.77	1.004	13.80
	PBE	3.84	1.003	12.05
	TPSS	3.86	1.003	18.07
	PBE0	3.75	1.004	6.43
	TPSSH	3.83	1.004	14.12
	B3-LYP	3.85	1.003	9.23
AE-FNDMC with	...			

- ▶ large differences with DFT, largely leveled for FNDMC

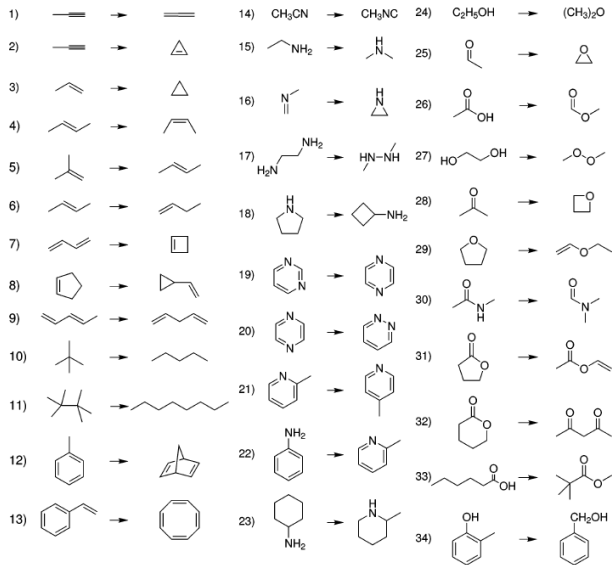
Backflow wavefunctions[1]

	method	RMSE	$F=EC/EC_{ref}$
PP-FNDMC with	HF	4.10	1.000
	HF+BF	3.88	1.007
	DFT	3.86	1.003
	DFT+BF	4.15	1.012
AE-FNDMC with	...		-

- ▶ good for absolute energies, less so for relative?

[1] P. Lpez Ros, A. Ma, N.D. Drummond, M.D. Towler and R.J. Needs, *Phys. Rev. E*, **2007**, 74, 066701.

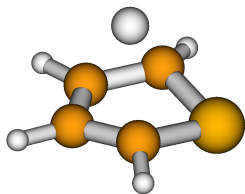
The ISO34 benchmark set



The ISO34 benchmark set[1]

method	RMSE
PP-FNDMC(B3LYP/BFD-VQZ)	...
PP-FNDMC(B3LYP/BFD-VTZ)	1.3(1)
AE-FNDMC(HF/cc-pVTZ)	2.2(1)
CCSD(T)/cc-pVTZ	0.95
MP2/TZVPP	2.04
CCSD(T)/6-31G(d)	2.78
B3-LYP/TZVPP	3.27
HF/TZVPP	3.79
BLYP/TZVPP	4.43

[1] S. Grimme, M. Steinmetz and M. Korth, *J. Org. Chem.*, **2007**, 72, 2118.



The lithium–thiophene interaction revisited

method	TWF	interaction energy (kcal/mol)
CCSD(T)/AVTZ	-	-7.5 [1]
AE-FNDMC	HF/AVTZ	+1.3 ± 1.7 [1]
PP-FNDMC	HF/BFD-VQZ	-7.17 ± 0.12
	B3LYP/BFD-VTZ	-8.27 ± 0.11
	PBE/BFD-VTZ	-8.24 ± 0.11
	PBE/BFD-VQZ	-8.61 ± 0.12

[1] Caffarel *et al.*, *Theor. Chem. Acc.*, **2010**, 126, 275–287.

Conclusions

- ▶ PP-FNDMC(DFT/BFD-VQZ) seems to allow for accurate 'everyday' thermochemistry
- ▶ more benchmark data to come ...

Acknowledgments

Money

- ▶ German National Academy of Sciences Leopoldina, Leopoldina postdoc stipend LPDS 2009-18



People

- ▶ Mike Towler (TCM)
- ▶ Stefan Grimme (University of Münster)