

2440-13

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Minimum energy pathways from Quantum Monte Carlo

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Minimum energy pathways from QMC

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An application of forces in QMC

- Methods: Variational and fixed-node Diffusion Monte Carlo
- Recent advances in forces and optimization
- Choice of the trial function: accuracy vs. size consistency
- Minimum energy pathways: Nudged Elastic Band
- Accuracy of DFT
- QMC improves geometries and barrier heights

Variational Monte Carlo

Expectation values on a correlated wave function Ψ

$$\Psi(R) = J(R)D(R); \quad R = \{r_1, \dots, r_N\}$$

J symmetric with one-, two- three-, ... body correlations

D antisymmetric:

- Slater determinant(s)

(linear combination of) - AGP

- Pfaffian(s)

(possibly with backflow transformations)

Variational Monte Carlo

$$E = \frac{\int dR P(R) E_L(R)}{\int dR P(R)}$$

$$P(R) = \Psi^2(R)$$

$$E_L(R) = \frac{H \Psi(R)}{\Psi(R)} \quad \text{local energy}$$

Multidimensional integrals by Metropolis method:

unbiased with known statistical errors if

$$\int dR P(R) E_L^2(R) \quad \text{is finite}$$

Diffusion Monte Carlo

$$\lim_{\beta \rightarrow \infty} \exp(-\beta H) \Psi = \Phi$$

imaginary-time evolution simulated by a branching random walk

Φ exact ground state; sign problem

Fixed-node approximation: $\Phi_{FN}(R) = 0$ if $\Psi(R) = 0$

→ Best energy **upper bound** given the nodes of Ψ

DMC less efficient, but more accurate, than VMC

Accuracy of Diffusion Monte Carlo

124116-4 Petruzielo, Toulouse, and Umrigar

J. Chem. Phys. **136**, 124116 (2012)

DMC
atomization energies
for the G2 set:
deviation from
experiment

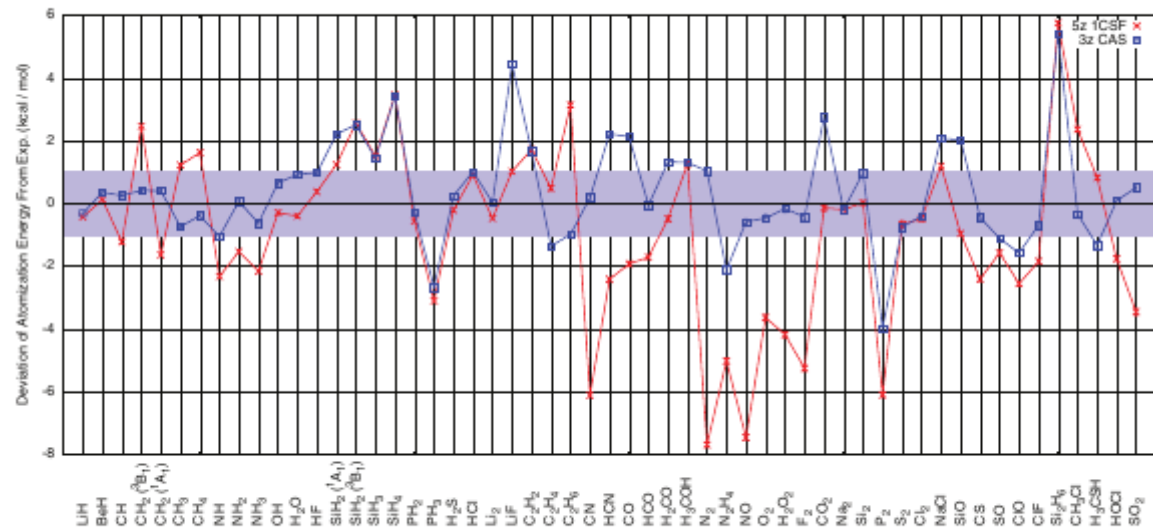


FIG. 4. Deviation of the DMC atomization energies from experiment for a single determinant SJ trial wavefunction composed of VMC optimized orbitals and a CAS SJ trial wavefunction. The MAD from experiment for the single determinant SJ trial wavefunction is 2.1 kcal/mol. The MAD from experiment for the CAS SJ trial wavefunction is 1.2 kcal/mol.

wavefunction	HF orbitals	optimized orbitals	CAS
MAD (kcal/mol)	3.0	2.1	1.2

Recent advances in forces

$$E = \int dR P(R) E_L(R) / \int dR P(R)$$

$$\nabla E = \int dR P(R) [\nabla E_L(R) + (E_L(R) - E) \nabla \ln P] / \int dR P(R)$$

$$E_L(R) \propto 1/d; \nabla E_L(R) \propto 1/d^2; P(R) \propto d^2$$

d is the nodal distance

the integral $\int dR P(R) [\nabla E_L(R)]^2$ diverges:

∇E has infinite variance

Recent advances in forces

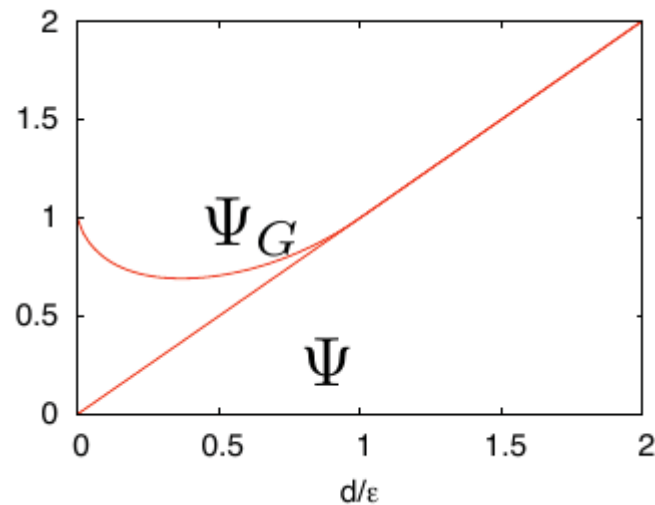
A finite-variance estimator (Attaccalite, Sorella 2008):

$$E = \int dR P_G(R) W(R) E_L(R) / \int dR P_G(R) W(R)$$

$$P_G = \Psi_G^2$$

$$W = \Psi^2 / \Psi_G^2$$

$$W E_L \propto d$$



Sample a guiding function with a finite value at the nodes

Recent advances in forces

The calculation of the forces on all the atoms does not change the scaling of the computational cost vs. system size
(Sorella and Capriotti, 2010)

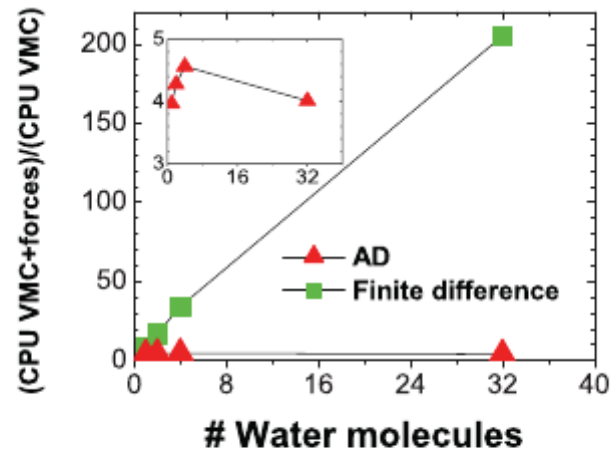


FIG. 2. Ratio of CPU time required to compute energies and all force components referenced to the one required for the simple energy calculation within VMC. The calculations refer to 1, 2, 4, and 32 water molecules. The inset is an expansion of the lower part of the plot.

This result can be obtained using algorithmic differentiation
(or equivalent algebraic manipulations)

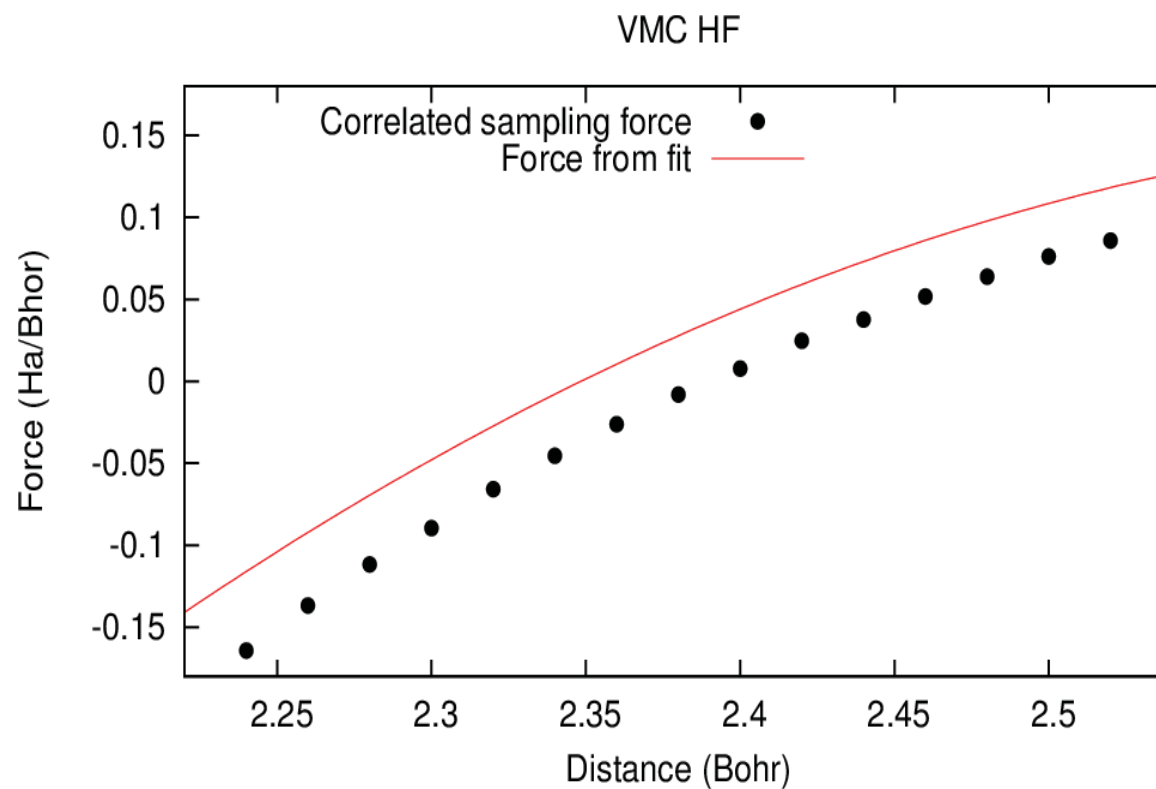
Recent advances in forces (VMC)

Partial vs. total derivatives: $\frac{dE}{d\lambda} = \frac{\partial E}{\partial \lambda} + \sum_i \frac{\partial E}{\partial c_i} \frac{dc_i}{d\lambda}$

all variational parameters c_i in Ψ
can be efficiently optimized in VMC by energy
minimization (Umrigar et al, 2007) so that the
last term vanishes

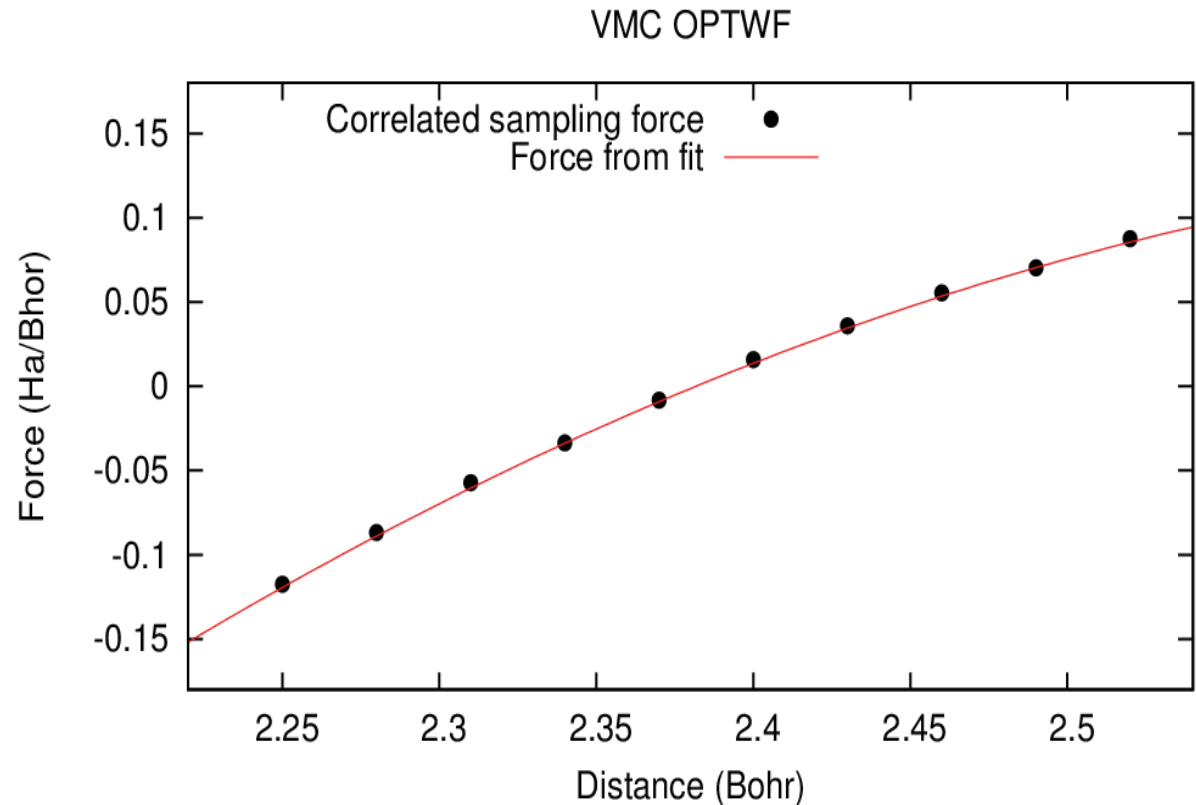
Neglect of the $\partial E / \partial c_i$ terms when using
unoptimized mean-field orbitals can lead to
inconsistencies between forces and PES

Recent advances in forces (VMC)



Carbon dimer with HF orbitals and optimized Jastrow

Recent advances in forces (VMC)



Carbon dimer with optimized orbitals and Jastrow

Forces in DMC

Unbiased calculations of ∇E in DMC are possible (e.g. Wagner and Grossman, 2010) but computationally demanding.

Correlated-sampling scheme of Filippi and Umrigar (2000):
The DMC probability density contains a branching factor

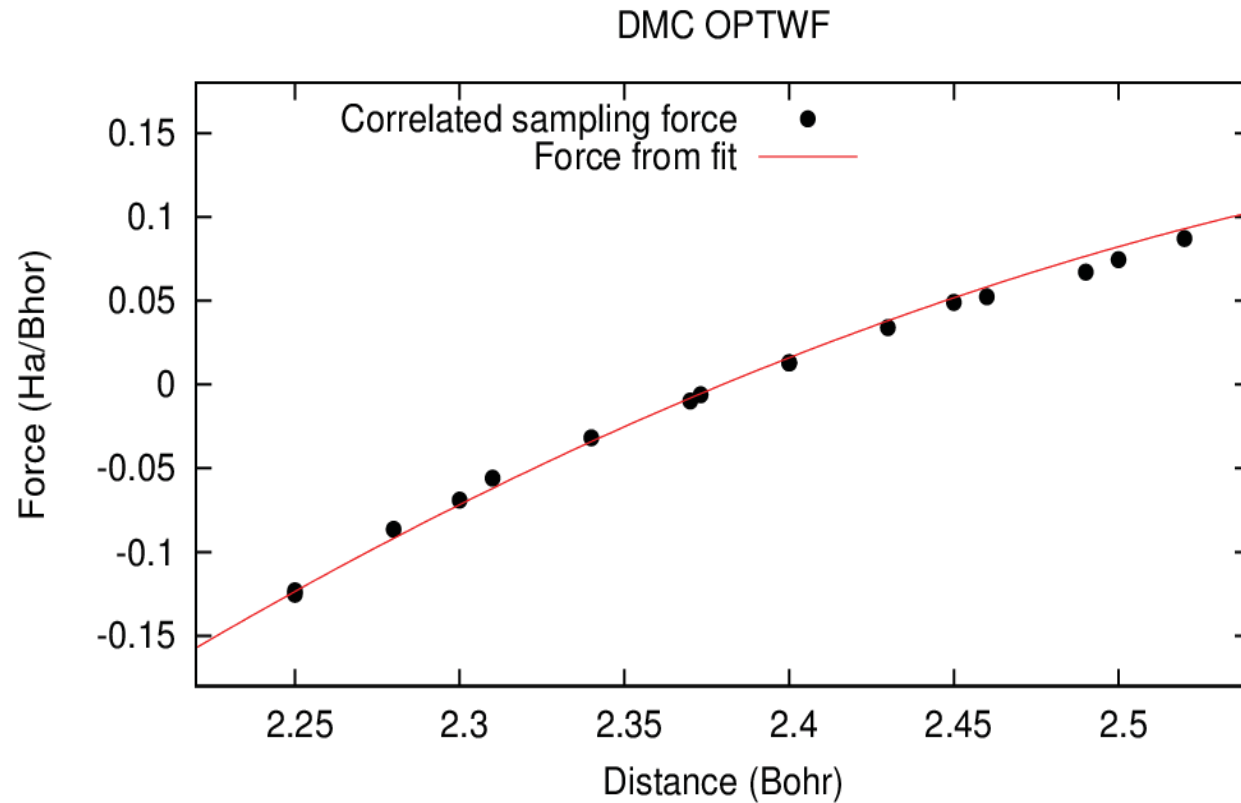
$$\exp(-\epsilon E_L(R))$$

and a drift-diffusion factor

$$\exp[-(R' - R - \epsilon \nabla \ln \Psi(R))^2 / 2\epsilon]$$

approximate the derivative of the latter.

Forces in DMC



Carbon dimer with optimized orbitals and Jastrow

Recent progress in optimization

Energy optimization (Umrigar, Toulouse, Filippi, Sorella, Hennig, 2007)

$$\Psi_i = \partial \Psi / \partial c_i, \quad i > 1; \quad \Psi_0 = \Psi; \quad \Omega = \{\Psi_i\}$$

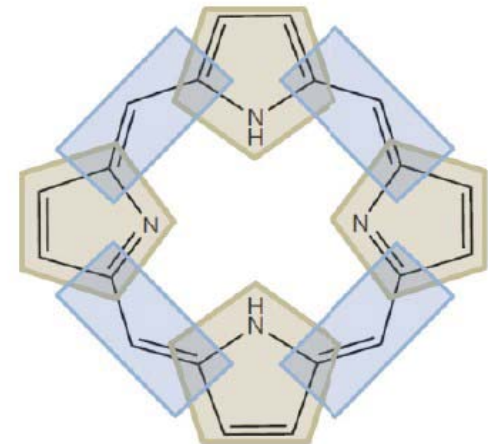
Linear method: find lowest-energy eigenstate in Ω solving

$$\sum \langle \Psi_i | H | \Psi_j \rangle x_j = E \sum \langle \Psi_i | \Psi_k \rangle x_k$$

update variational parameters $c_i' = c_i + x_i / x_0$

Neuscamman, Umrigar, Chen (2012)

~10000 parameters for free-base porphyrine



Nudged Elastic Band

A method for finding the minimum-energy path

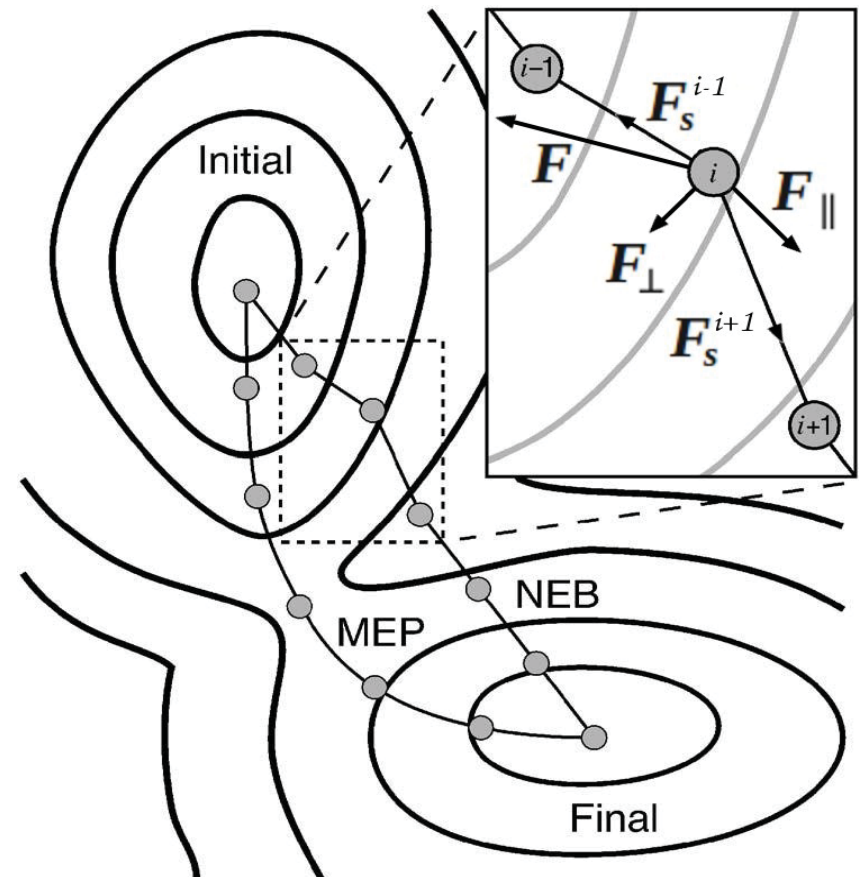
$$\mathbf{F}_{\perp} = (\mathbf{F} \cdot \mathbf{n}_{\perp}) \mathbf{n}_{\perp}$$

$$\mathbf{F}_{\parallel} = (\mathbf{F}_s \cdot \mathbf{n}_{\parallel}) \mathbf{n}_{\parallel}$$

After convergence,
find transition state by
climbing image:

$$\mathbf{F}_{\perp} = (\mathbf{F} \cdot \mathbf{n}_{\perp}) \mathbf{n}_{\perp}$$

$$\mathbf{F}_{\parallel} = -(\mathbf{F} \cdot \mathbf{n}_{\parallel}) \mathbf{n}_{\parallel}$$



Accuracy of DFT

Zhao, Gonzalez-Garcia, and Truhlar (2005) NHTBH38/04

Table 1: Barrier Heights Calculated by LSDA, GGA and Meta DFT Methods^{a,b}

Reactions		VSXC	BB95	mPWPW91	TPSS	BLYP	SPW91	BP86	TPSSKCIS	PBE	mPWLYP
Heavy atom transfer reactions											
H + N ₂ O → OH + N ₂	V _f [‡]	16.02	11.65	10.77	8.41	8.94	3.16	8.10	10.97	10.46	8.13
	V _r [‡]	71.18	55.36	55.34	60.37	61.78	32.20	55.87	60.62	52.64	59.91
H + FH → HF + H	V _f [‡]	36.75	29.71	28.57	27.33	26.77	19.40	26.00	29.15	27.98	25.94
	V _r [‡]	36.75	29.71	28.57	27.33	26.77	19.40	26.00	29.15	27.98	25.94
H + ClH → HCl + H	V _f [‡]	17.40	12.25	10.92	8.21	10.57	3.02	8.41	11.59	10.45	10.01
	V _r [‡]	17.40	12.25	10.92	8.21	10.57	3.02	8.41	11.59	10.45	10.01
H + FCH ₃ → HF + CH ₃	V _f [‡]	21.79	19.78	18.94	17.35	16.33	13.62	16.25	18.98	18.74	15.56
	V _r [‡]	51.65	41.88	42.48	42.17	42.33	31.78	42.55	42.43	41.14	40.62
H + F ₂ → HF + F	V _f [‡]	-6.98	-8.87	-9.41	-10.72	-11.49	-15.75	-11.15	-9.10	-9.63	-12.30
	V _r [‡]	96.18	80.73	81.92	82.97	81.63	68.95	82.24	82.81	80.34	79.90
CH ₃ + FCl → CH ₃ F + Cl	V _f [‡]	-6.99	-6.23	-5.68	-5.35	-6.94	-11.47	-5.87	-5.95	-6.42	-8.33
	V _r [‡]	45.59	41.23	43.44	43.93	42.80	36.87	43.05	43.36	42.71	41.52

Mean error

-14.66

-14.93

Accuracy of DFT

Zhao, Gonzalez-Garcia, and Truhlar (2005) NHTBH38/04

Table 3: Barrier Heights Calculated by Hybrid Meta DFT Methods^{a,b}

Reactions		BB1K	MPWB1K	MPWK CIS1K	B1B95	MPW1B95	MPW1KCIS	TPSS1KCIS	TPSSH
Heavy-atom transfer reactions									
H + N ₂ O → OH + N ₂	V _f [‡]	17.99	17.80	16.69	16.00	15.86	12.82	12.86	9.85
	V _r [‡]	80.79	80.80	84.70	72.78	73.21	69.07	68.31	66.31
H + FH → HF + H	V _f [‡]	40.50	40.48	39.36	36.98	37.12	32.60	32.35	29.81
	V _r [‡]	40.50	40.48	39.36	36.98	37.12	32.60	32.35	29.81
H + ClH → HCl + H	V _f [‡]	18.18	18.10	17.24	16.33	16.34	13.66	13.32	9.48
	V _r [‡]	18.18	18.10	17.24	16.33	16.34	13.66	13.32	9.48
H + FCH ₃ → HF + CH ₃	V _f [‡]	31.57	31.66	29.64	27.76	28.04	22.40	22.49	20.04
	V _r [‡]	55.22	54.80	57.23	51.00	50.69	48.90	46.91	45.63
H + F ₂ → HF + F	V _f [‡]	-1.10	-1.34	-2.75	-2.96	-3.02	-6.59	-6.51	-8.76
	V _r [‡]	108.88	109.02	110.64	100.38	101.09	94.11	92.13	90.14
CH ₃ + FCl → CH ₃ F + Cl	V _f [‡]	4.95	4.63	5.32	1.46	1.26	-1.52	-2.24	-2.51
	V _r [‡]	62.13	62.22	62.10	56.15	56.57	50.58	49.52	48.67

MUE

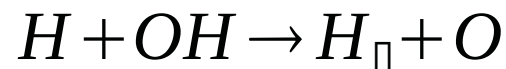
1.58

11.51

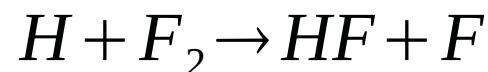
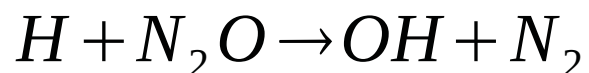
QMC results

Reactions studied:

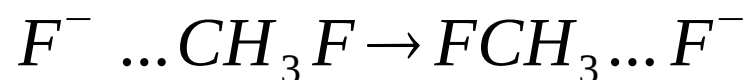
H transfer:



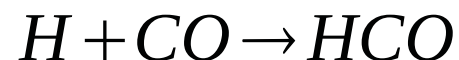
Heavy atom transfer:



Nucleophilic substitution:



Association reaction:



- Initial one-particle orbitals from GAMESS
- Pseudopotentials and optimized GTO VDZ basis from BFD
- QMC energy and force calculations with CHAMP

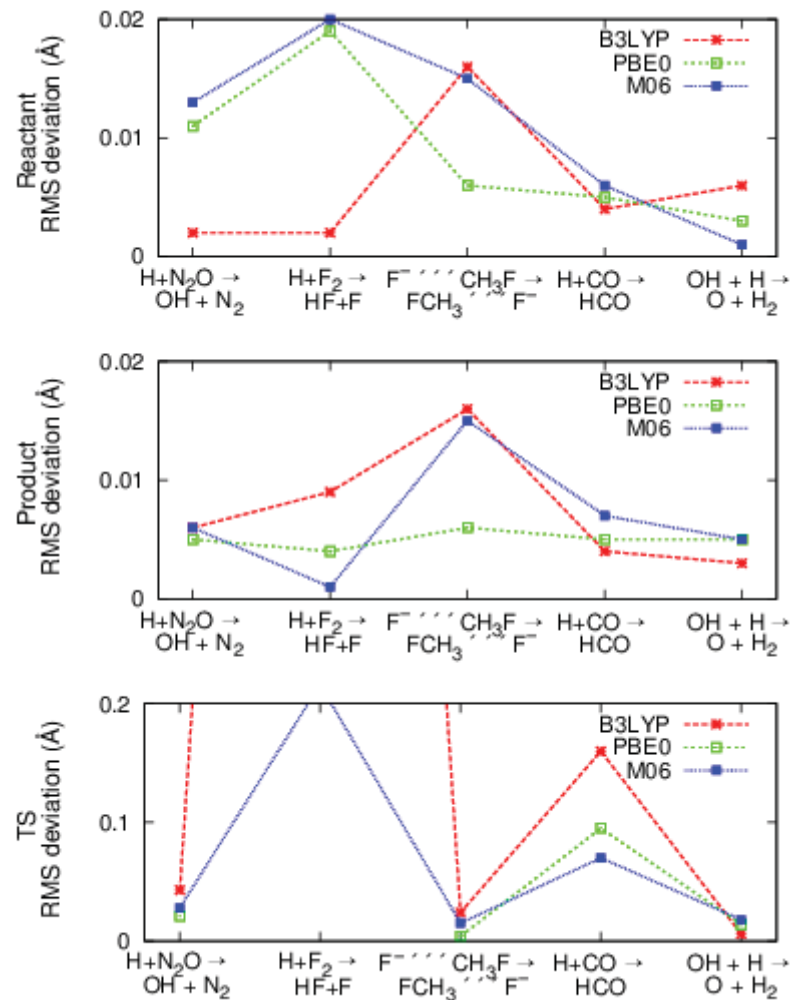
QMC results

Geometries for the reaction $H + F_2 \rightarrow HF + F$

$H + F_2 \rightarrow HF + F$		VMC	DMC	HF	LSDA	BLYP	B3LYP	PBE	PBE0	M06
RMS deviation (Å)	React	0.008	0.007	0.067	0.010	0.037	0.002	0.018	0.019	0.020
	Prod	0.002	0.008	0.016	0.018	0.020	0.009	0.017	0.004	0.001
	TS	0.028	0.013	-	-	2.193	1.792	-	-	0.216

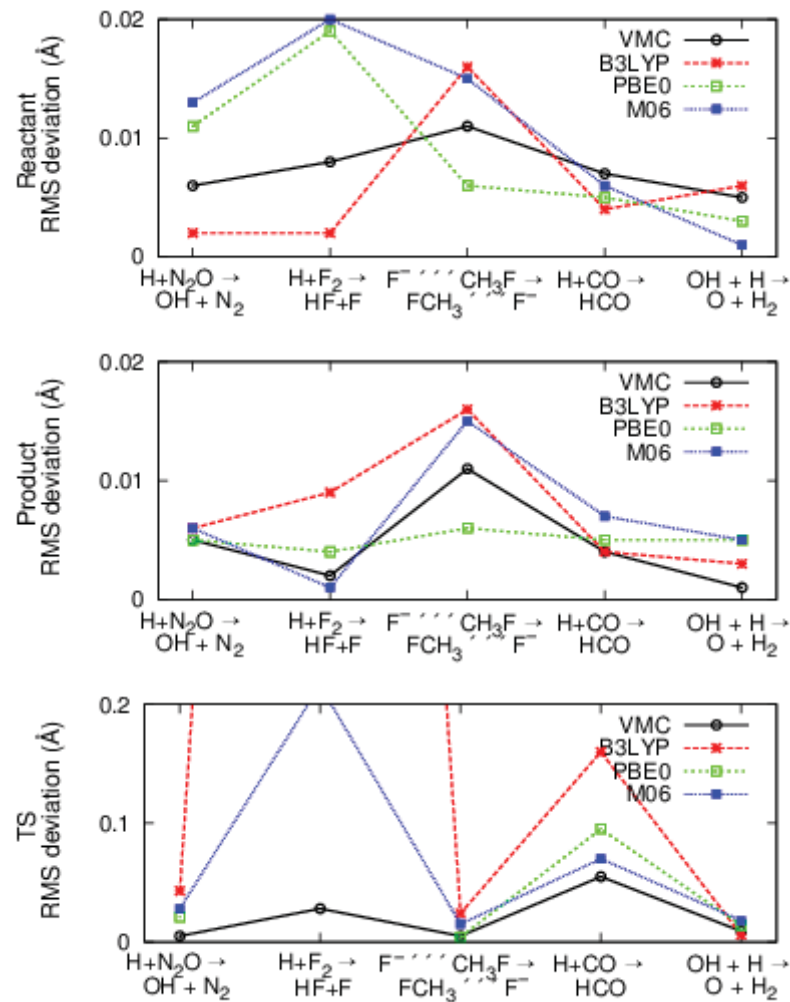
- M06 constructed to fit (also) accurate BHs from NHTBH38/04
- BLYP and B3LYP do find a barrier on their own TS geometry
- VMC improves the geometry significantly
- Further improvement from DMC is marginal

DFT geometries for other reactions



Transition State particularly challenging

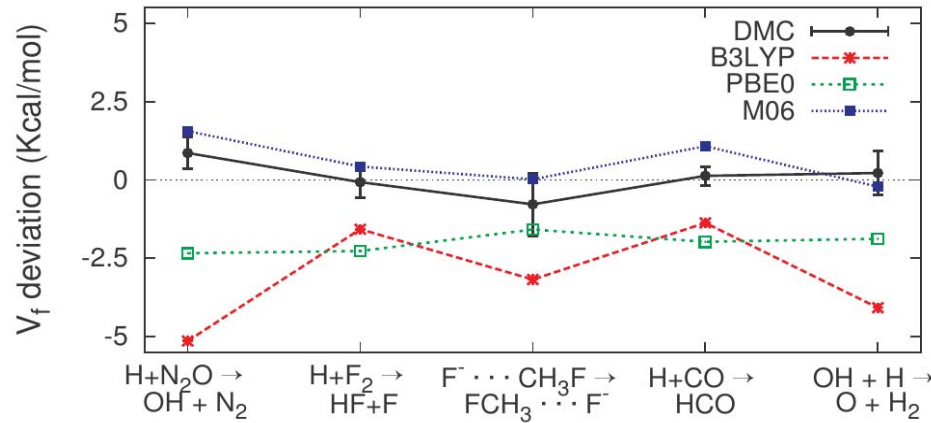
QMC vs DFT geometries



QMC marginally better for Products and Reactants,
significantly better for Transition States

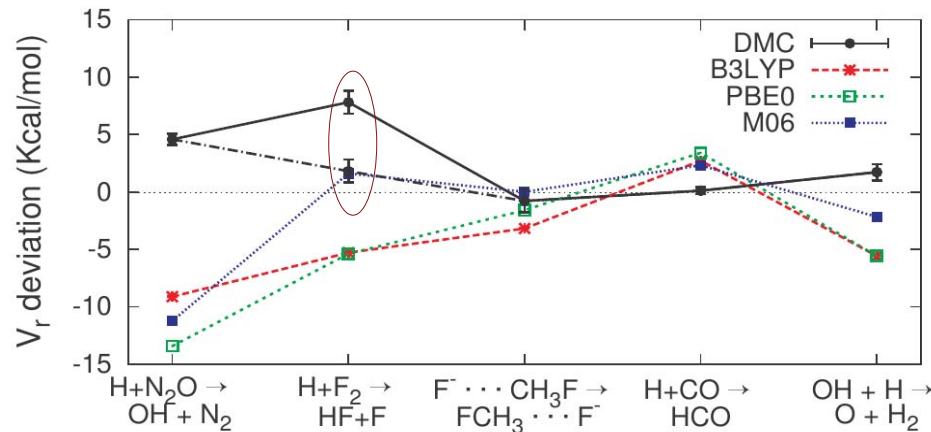
DMC vs DFT energies

	MUD
VMC	4.5
DMC	0.4
B3LYP	3.1
PBE0	2.0
M06	0.7



Forward
barrier

VMC	8.1
DMC	3.0 (1.8)
B3LYP	5.2
PBE0	5.9
M06	3.5



Reverse
barrier

- DMC ~ M06
- DMC improves with a small-CAS wavefunction (~tens determinants)

Conclusions

- Full, consistent applications of QMC forces reasonably automatic and stable
- CPU time scaling with system size (presumably) like a plain E calculation
- Based on a few reactions:
 - VMC geometry improves DFT geometry
 - DMC energy at least as good as DFT (M06) with SJ wavefunctions (this level of accuracy scalable to large systems)
- Further improvements possible by changing wavefunction