forces and response functions in QMC

Saverio Moroni
SISSA and DEMOCRITOS, IOM-CNR, Trieste, Italy

1) NEB calculation of minimum energy pathways

Collaborators: Sebastiano Saccani (Trieste), Claudia Filippi (Twente)
Special thanks to: Stefano Baroni

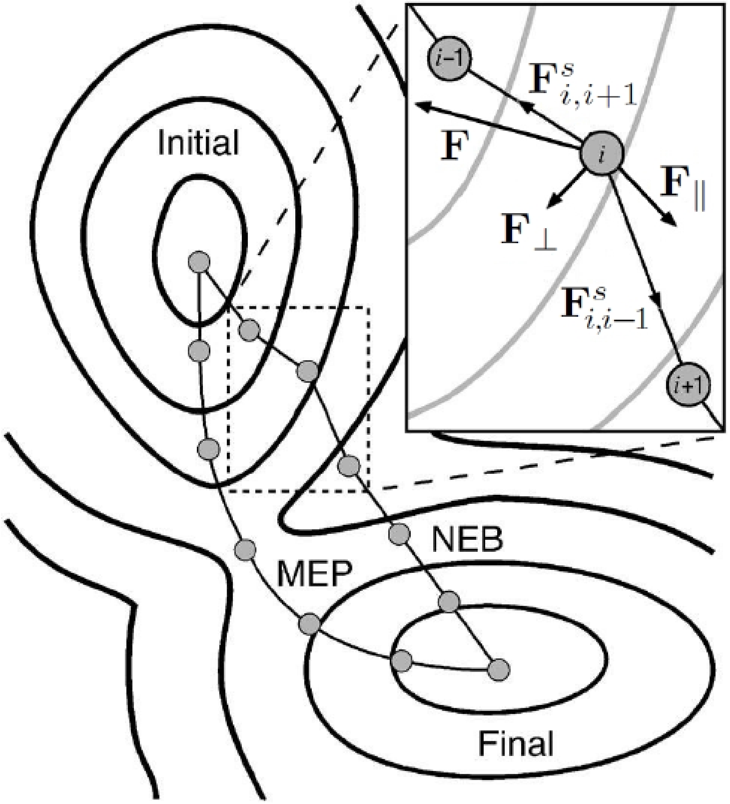
2) AFQMC calculation of imaginary-time correlations

Collaborators: Ettore Vitali, Mario Motta, Davide Galli (Milano)

Nudged Elastic Band

A local search method to find the minimum-energy path:

$$\begin{aligned}\mathbf{F}_\perp &= (\mathbf{F}\cdot\mathbf{n}_\perp)\,\mathbf{n}_\perp \\ \mathbf{F}_\parallel &= \left(\mathbf{F_s}\cdot\mathbf{n}_\parallel\right)\mathbf{n}_\parallel\end{aligned}$$



After convergence,
find transition state by
climbing image:

$$\begin{aligned}\mathbf{F}_\perp &= (\mathbf{F}\cdot\mathbf{n}_\perp)\,\mathbf{n}_\perp \\ \mathbf{F}_\parallel &= -\left(\mathbf{F}\cdot\mathbf{n}_\parallel\right)\mathbf{n}_\parallel\end{aligned}$$

G.Henkelman, B.P.Uberuaga, and H.Jonsson, JCP 113, 9901 (2000)

Nudged Elastic Band

- Extensively used for catalysis problems
- Mostly within DFT (especially GGA)

- Feasible/accurate with QMC?

▶ Test on reaction paths of small molecules

  - ✓ Reasonably automatic
  - ✓ Reasonably accurate (VMC, fixed-node DMC)

  - ✓ Presumably scalable

- ✓ Reasonably automatic: 1) finite-variance estimators of forces

$$I = \int_0^c p(x) f(x) dx$$

Monte Carlo evaluation requires that $\int_0^c p(x) f^2(x) dx$ be finite

If $p \propto x^2, \qquad f \propto 1/x,$ MC evaluation of I is OK (e.g. energy);

but $\nabla I = \int_0^c p(x) \left[\nabla f(x) + \cdots \ \right] dx$ and $\nabla f \propto 1/x^2, \qquad (\nabla f)^2 \propto 1/x^4$

MC evalutation of this estimator of ∇I is not possible (e.g. forces).

- A finite-variance estimator (S.Sorella and C.Attaccalite, PRL, 2008):

$$I = \int_0^c \tilde{p}(x) \left[p(x)/\tilde{p}(x) f(x) \right] dx \qquad \text{with} \qquad \lim_{x \to 0} \tilde{p}(x) = \mathrm{const}$$

$\tilde{p} \sim \mathrm{const.}, \quad \tilde{f} = p/\tilde{p} f \propto x,$ MC evaluation of both I and ∇I is OK

- finite-variance estimator available in both VMC and DMC

- ✓ Reasonably automatic: 2) low-enough variance in DMC

  DMC samples $\prod_{i=1}^{k} G_{dd}(R_i, R_{i-1}) e^{-\tau[E_L(R_i)+E_L(R_{i-1})]/2}$

  The drift-diffusion term G_{dd} gives high statistical noise in the calculation of forces.

- A low-variance estimator of the DMC forces: replace

$$\nabla \prod_{i=1}^{k} G_{dd}(R_i, R_{i-1}) \to \nabla \Psi_T^2(R_k)$$

- Approximate but accurate (exact if Ψ_T is exact)

C.Filippi and C.J.Umrigar, PRB 61, R16291 (2000)

- ✓ Reasonably automatic: 3) forces as partial derivatives

$$\frac{dE}{d\lambda} = \frac{\partial E}{\partial \lambda} + \sum_i \frac{\partial E}{\partial c_i}\frac{\partial c_i}{\partial \lambda}$$

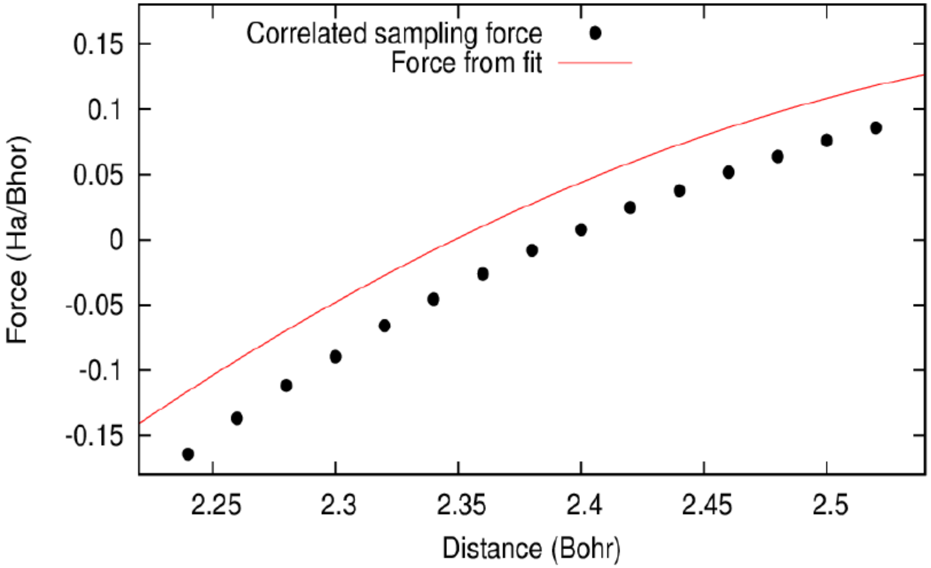
c_i variational parameters in Ψ_T

Optimize all variational parameters $\rightarrow \frac{dE}{d\lambda} = \frac{\partial E}{\partial \lambda}$

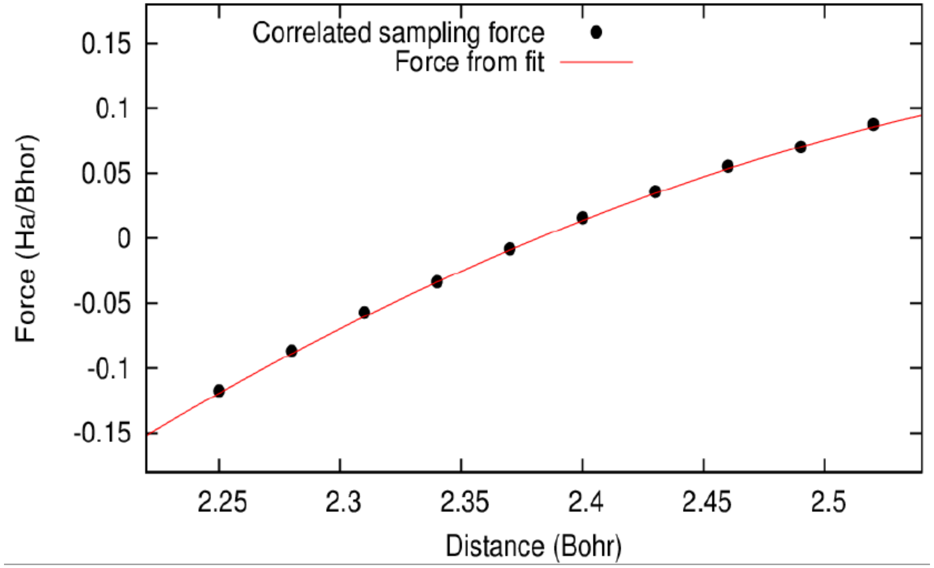
In the present study of reactions, optimization* and calculation of forces take approximately the same CPU time.

*C.J.Umrigar, J.Toulouse, C.Filippi, S.Sorella and R.G.Hennig, PRL 98, 110201 (2007).

Test of force as partial derivative in VMC: Carbon dimer

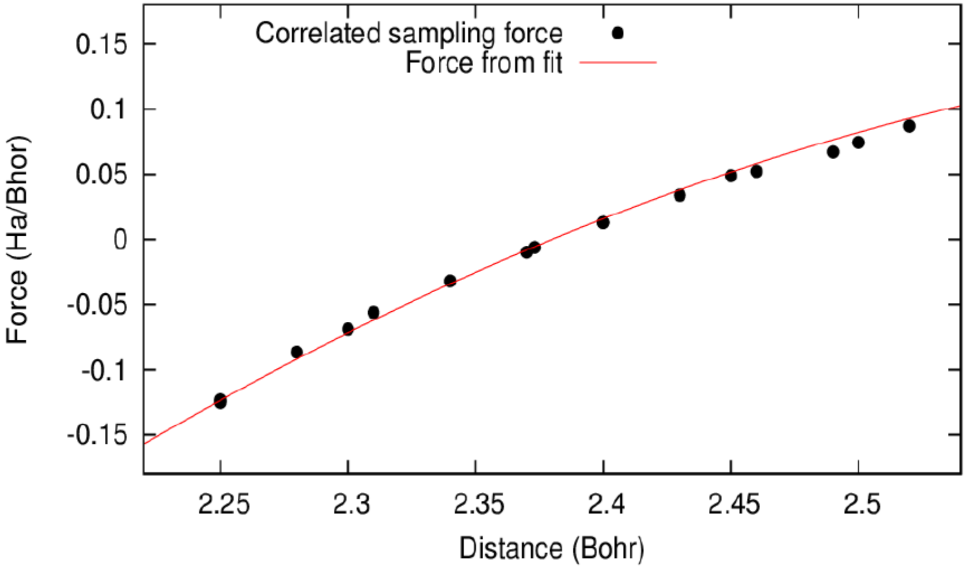


HF orbitals,
optimized Jastrow



optimized orbitals,
optimized Jastrow

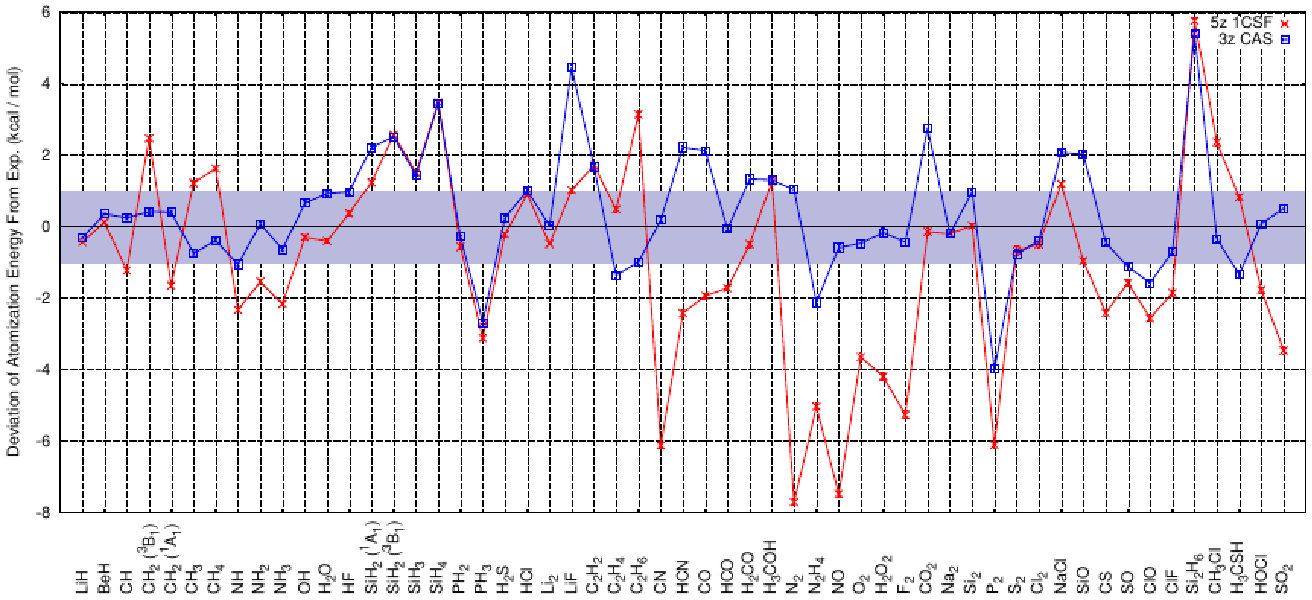
Test of approximation to DMC forces: Carbon dimer



DMC forces with replacement $\nabla \prod_{i=1}^{k} G_{dd}(R_i, R_{i-1}) \rightarrow \nabla \Psi_T^2(R_k)$

✓ Reasonably accurate:

DMC atomization energies for the G2 data set



5z 1CSF ✗
3z CAS ⊞

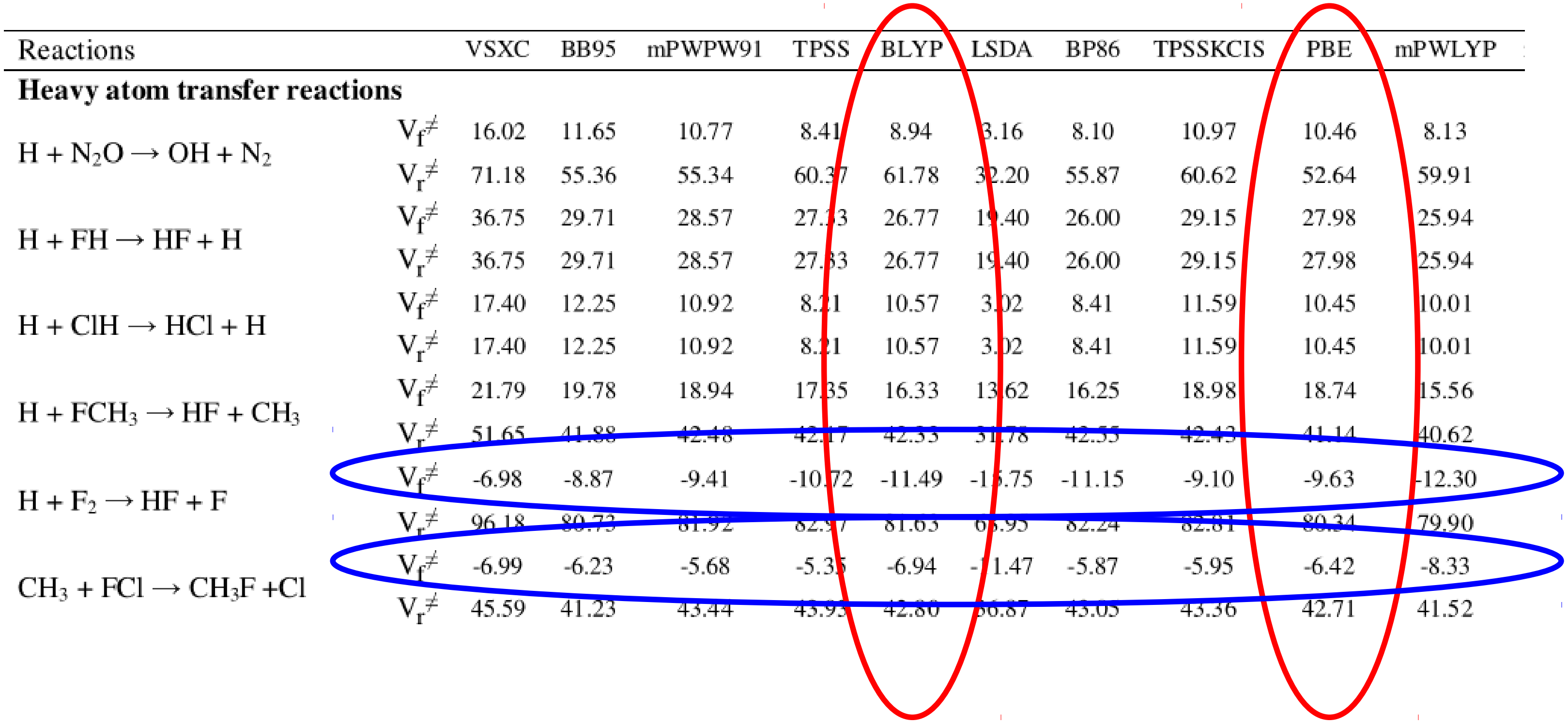
R.Petruzielo, J.Toulouse, and C.J.Umrigar, JCP 136, 124116 (2012)

Fixed-node DMC with multideterminant wavefunction approaches chemical accuracy

- For scalability we will use 2z one-determinant SJ wavefunction
- Expected accuracy ~a few kcal/mol: is that enough?

Y.Zhao, N.Gonzalez-Garcia, and D.G.Truhlar, JPC A 109, 2012 (2005)

Barrier heigths calculated by LSDA, GGA and Meta DFT methods:



Reactions		VSXC	BB95	mPWPW91	TPSS	BLYP	LSDA	BP86	TPSSKCIS	PBE	mPWLYP
Heavy atom transfer reactions											
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	16.02	11.65	10.77	8.41	8.94	3.16	8.10	10.97	10.46	8.13
	$V_r^{\neq}$	71.18	55.36	55.34	60.37	61.78	32.20	55.87	60.62	52.64	59.91
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	36.75	29.71	28.57	27.33	26.77	19.40	26.00	29.15	27.98	25.94
	$V_r^{\neq}$	36.75	29.71	28.57	27.33	26.77	19.40	26.00	29.15	27.98	25.94
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	17.40	12.25	10.92	8.21	10.57	3.02	8.41	11.59	10.45	10.01
	$V_r^{\neq}$	17.40	12.25	10.92	8.21	10.57	3.02	8.41	11.59	10.45	10.01
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	21.79	19.78	18.94	17.35	16.33	13.62	16.25	18.98	18.74	15.56
	$V_r^{\neq}$	51.65	41.88	42.48	42.17	42.33	31.78	42.55	42.43	41.14	40.62
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	-6.98	-8.87	-9.41	-10.72	-11.49	-15.75	-11.15	-9.10	-9.63	-12.30
	$V_r^{\neq}$	96.18	80.73	81.92	82.97	81.63	65.95	82.24	82.81	80.34	79.90
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	-6.99	-6.23	-5.68	-5.35	-6.94	-11.47	-5.87	-5.95	-6.42	-8.33
	$V_r^{\neq}$	45.59	41.23	43.44	43.93	42.80	56.87	43.05	43.36	42.71	41.52

Mean error: -14.66 -14.93

QMC calculation:

- Reactions studied [S.Saccani, C.Filippi and SM, JCP 138, 084109 (2013)]

H transfer: $H + OH \rightarrow H_2 + O$
Heavy atom transfer: $H + N_2O \rightarrow OH + N_2$
$H + F_2 \rightarrow HF + F$
Nucleophilic substitution: $F^- \cdots CH_3F \rightarrow FCH_3 \cdots F$
Association reaction: $H + CO \rightarrow HCO$

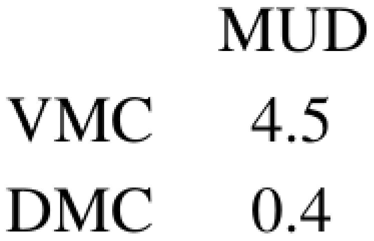
- Initial one-particle orbitals from GAMESS
- Pseudopotentials and optimized GTO VDZ basis from BFD*
- QMC energy and force calculations with CHAMP

---

* M.Burkatzki, C.Filippi and M. Dolg, JCP 126, 234105 (2007)

QMC results: Mean Unsigned Deviation from best estimates

forward barrier:



	MUD
VMC	4.5
DMC	0.4

reverse barrier:

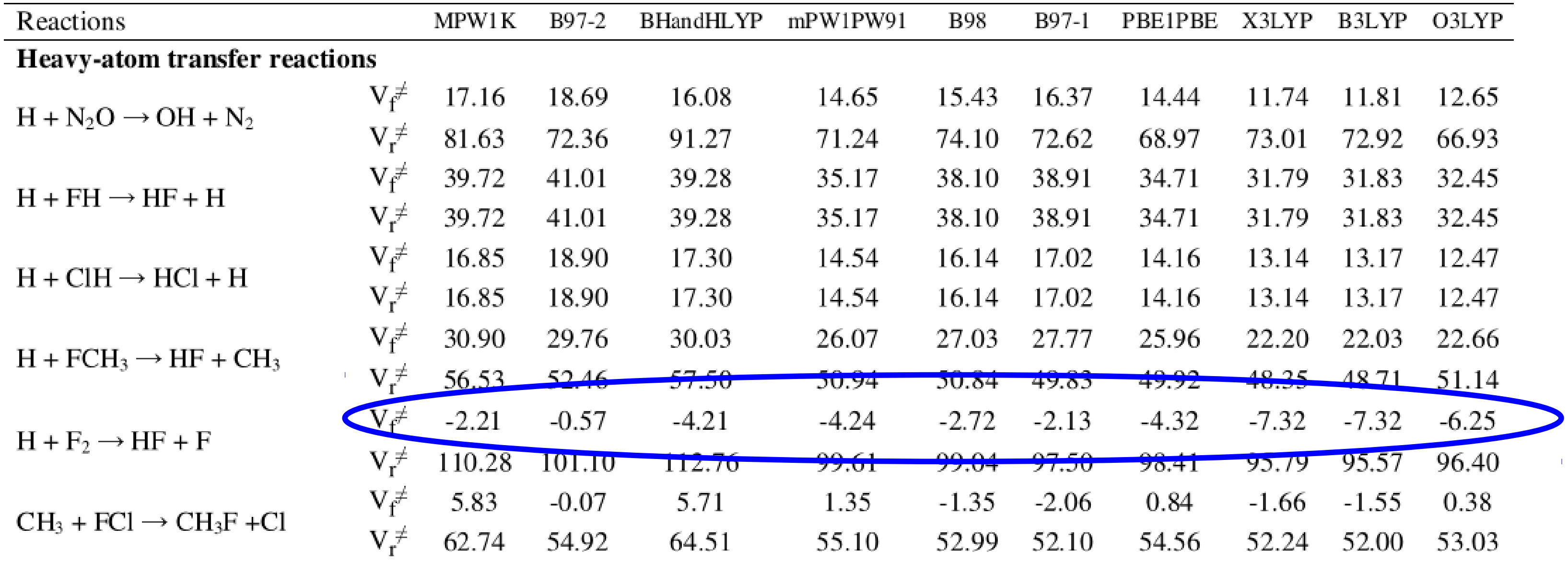
VMC	8.1
DMC	3.0

Significant improvement over GGA DFT

...but there exist better functionals

Y.Zhao, N.Gonzalez-Garcia, and D.G.Truhlar, JPC A 109, 2012 (2005)

Barrier heigths calculated by hybrid methods:



Reactions		MPW1K	B97-2	BHandHLYP	mPW1PW91	B98	B97-1	PBE1PBE	X3LYP	B3LYP	O3LYP
Heavy-atom transfer reactions											
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	17.16	18.69	16.08	14.65	15.43	16.37	14.44	11.74	11.81	12.65
	$V_r^{\neq}$	81.63	72.36	91.27	71.24	74.10	72.62	68.97	73.01	72.92	66.93
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	39.72	41.01	39.28	35.17	38.10	38.91	34.71	31.79	31.83	32.45
	$V_r^{\neq}$	39.72	41.01	39.28	35.17	38.10	38.91	34.71	31.79	31.83	32.45
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	16.85	18.90	17.30	14.54	16.14	17.02	14.16	13.14	13.17	12.47
	$V_r^{\neq}$	16.85	18.90	17.30	14.54	16.14	17.02	14.16	13.14	13.17	12.47
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	30.90	29.76	30.03	26.07	27.03	27.77	25.96	22.20	22.03	22.66
	$V_r^{\neq}$	56.53	52.46	57.50	50.94	50.84	49.83	49.92	48.35	48.71	51.14
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	-2.21	-0.57	-4.21	-4.24	-2.72	-2.13	-4.32	-7.32	-7.32	-6.25
	$V_r^{\neq}$	110.28	101.10	112.76	99.61	99.04	97.50	98.41	95.79	95.57	96.40
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	5.83	-0.07	5.71	1.35	-1.35	-2.06	0.84	-1.66	-1.55	0.38
	$V_r^{\neq}$	62.74	54.92	64.51	55.10	52.99	52.10	54.56	52.24	52.00	53.03

Mean unsigned error: 1.58 11.51

QMC results: geometries for the reaction $H + F_2 \rightarrow HF + F$

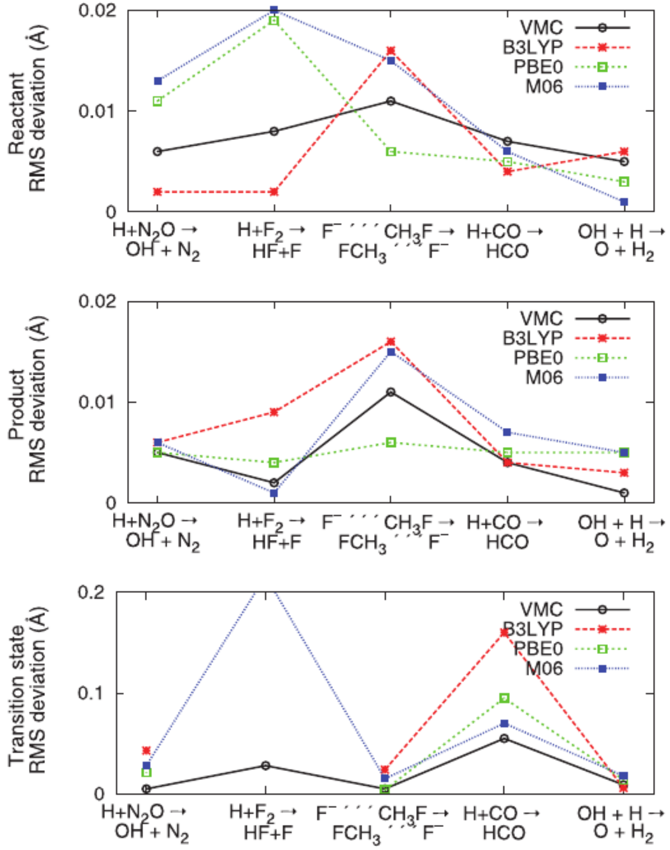
Root mean square deviation of all interatomic distances from best estimate in $\mathring{A}$

	VMC	DMC	BLYP	PBE	B3LYP	PBE0	M06
React	0.008	0.007	0.037	0.018	0.002	0.019	0.020
Prod	0.002	0.008	0.029	0.017	0.009	0.004	0.001
TS	0.028	0.013	-	-	-	-	0.216

- Within DFT only the M06 functional* does find a barrier
- VMC improves the geometry of the transition state significantly
- Further geometrical improvement with DMC is marginal

*constructed to fit (also) accurate barrier heights for the NHTBH38/04 database

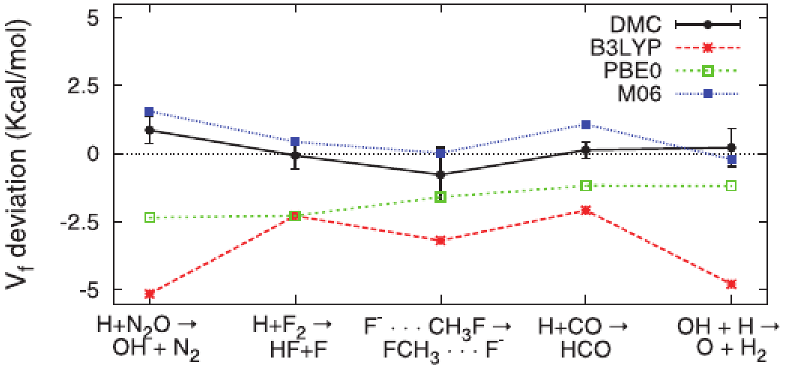
QMC vs DFT geometries



- QMC marginally better for reactants and products
- QMC significantly better for transition states

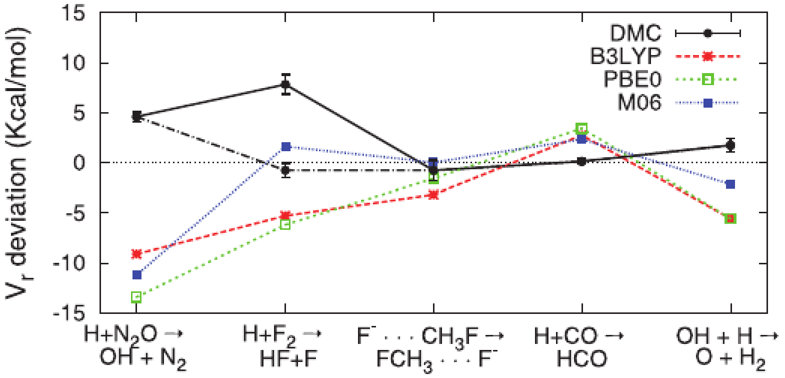
QMC vs DFT energies

	MUD
VMC	4.5
DMC	0.4
B3LYP	3.1
PBE0	2.0
M06	0.7



Forward barrier

VMC	8.1
DMC	3.0
B3LYP	5.2
PBE0	5.9
M06	3.5

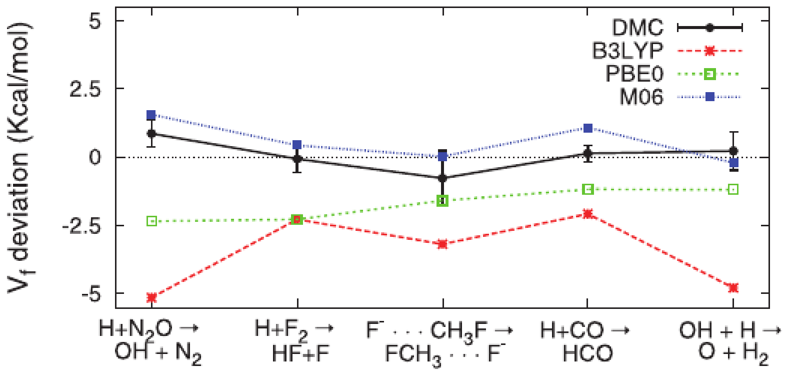


Reverse barrier

- DMC ~ M06

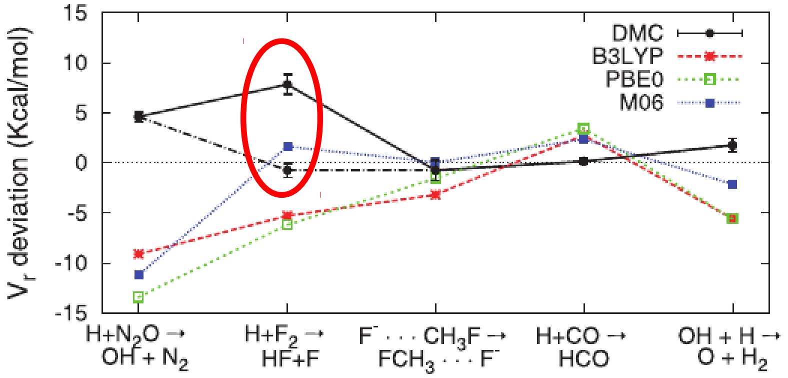
QMC vs DFT energies

	MUD
VMC	4.5
DMC	0.4
B3LYP	3.1
PBE0	2.0
M06	0.7



Forward barrier

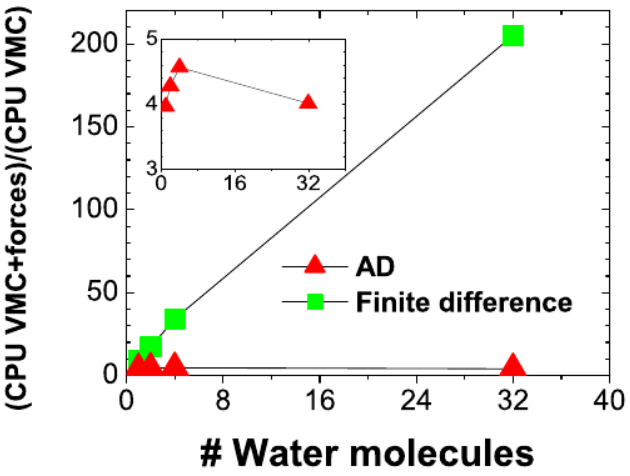
VMC	8.1
DMC	3.0 (1.8)
B3LYP	5.2
PBE0	5.9
M06	3.5



Reverse barrier

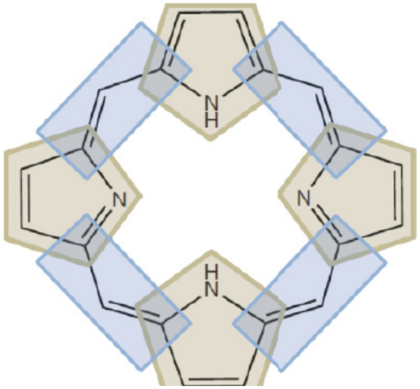
- DMC ~ M06
- DMC improves with a small CAS (~ten determinants)

- ✓ Presumably scalable (algorithmic differentiation, large optimizations):



S.Sorella and L. Capriotti,
JCP 133, 234111 (2010)

extra factor in CPU time to compute forces independent of the number of atoms



free base porphin

E.Neuscamman, C.Umrigar, and G. Chan,
PRB 85, 045103 (2012)

optimization of ~10,000 variational parameters

Summary part 1

- NEB calculation with full QMC forces reasonably automatic and stable

- Based on a few reactions:
  - VMC geometry improves DFT results
  - DMC energy at least as good as M06 with simple SJ wavefunctions

- At this level of accuracy, presumably scalable to large systems

- Improvements possible in specific situations using better wavefunctions

Response functions (work in progress)

$$F_{AB}(\tau) = \langle \hat{A}(\tau)\hat{B}(0)\rangle$$

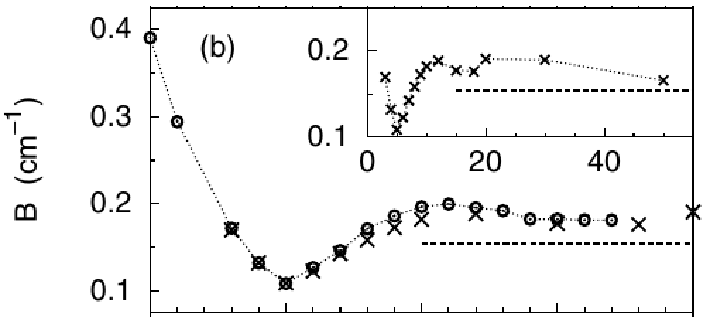
QMC simulation

$$F_{AB}(\tau) = \int d\omega e^{-\omega\tau} S_{AB}(\omega)$$

Inverse Laplace transform

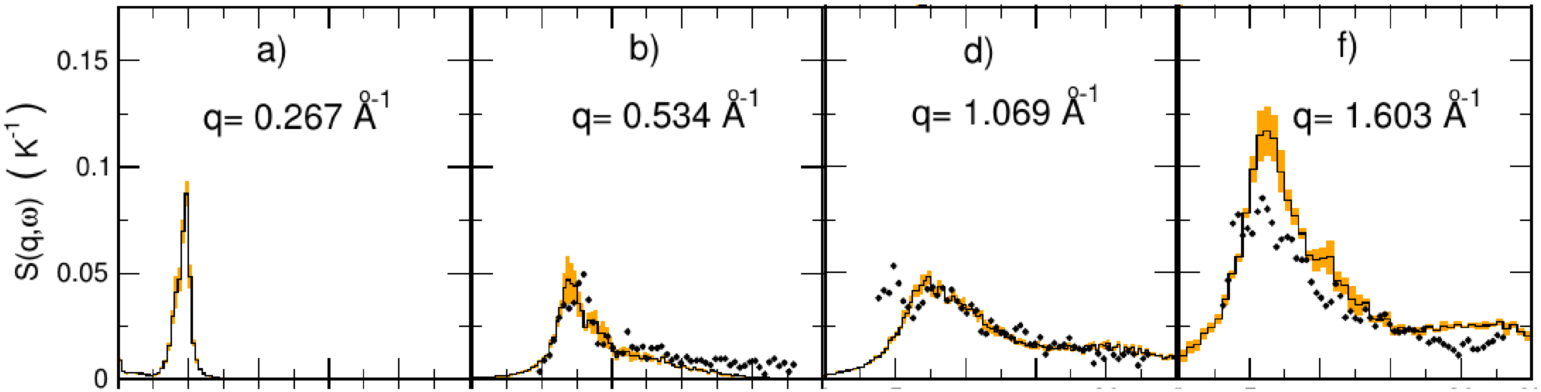
An example for a Bose system:

$$C(\tau) = \langle \mathbf{d}(\tau) \cdot \mathbf{d}(0)\rangle \;\longrightarrow$$ rotational spectrum with J=1



Effective rotational constant of CO2 in 4He clusters vs cluster size.
Circles, experiment; crosses, simulation.

- In particular cases, for small enough systems this works well also for Fermions. An example: the dynamic structure factor of 2D 3He at freezing density (N=26)



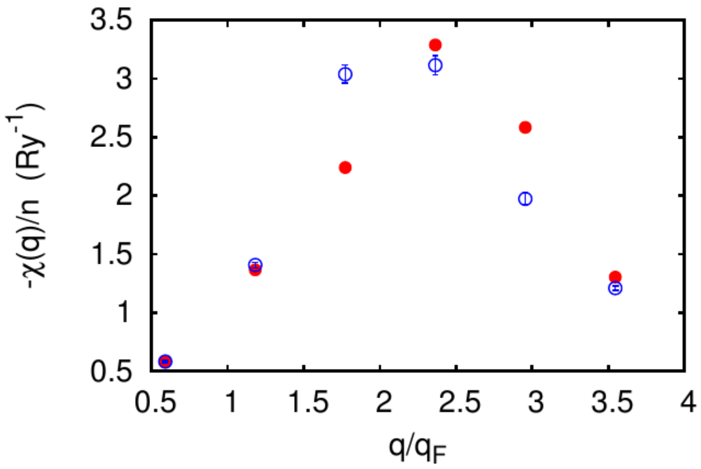
Histograms with errorbars: simulation; points: experiment

but in general Fermi systems require approximations to avoid the sign problem.

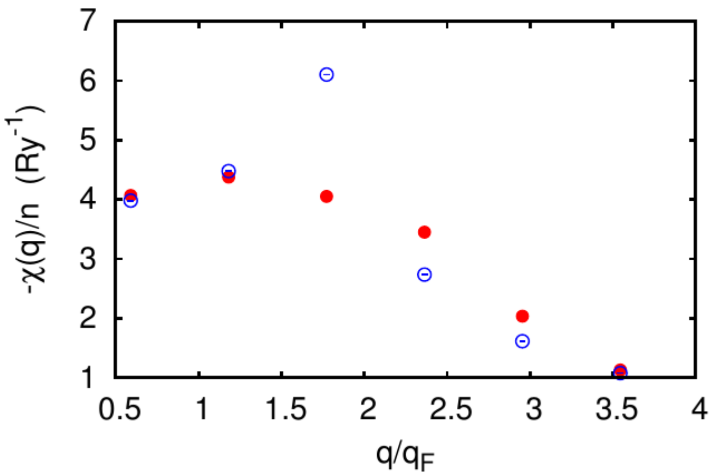
fixed node approximation not good for imaginary-time correlations

Static susceptibility $\chi(q) = \int F(q,\tau) d\tau, \qquad F(q,\tau) = \langle \rho_{-q}(\tau) \rho_q(0) \rangle$

2D jellium, rs=5



Non interacting



○ From fixed-node $F(q,\tau)$

● “exact”

a different nodal constraint: phaseless AFQMC
[S.Zhang and H.Krakauer, PRL 90, 136401 (2003)]

- Hubbard-Stratonovich transformation maps many-body propagator into one-body propagator with fluctuating auxiliary fields
- Imaginary time evolution simulated by a random walk in the space of Slater determinants

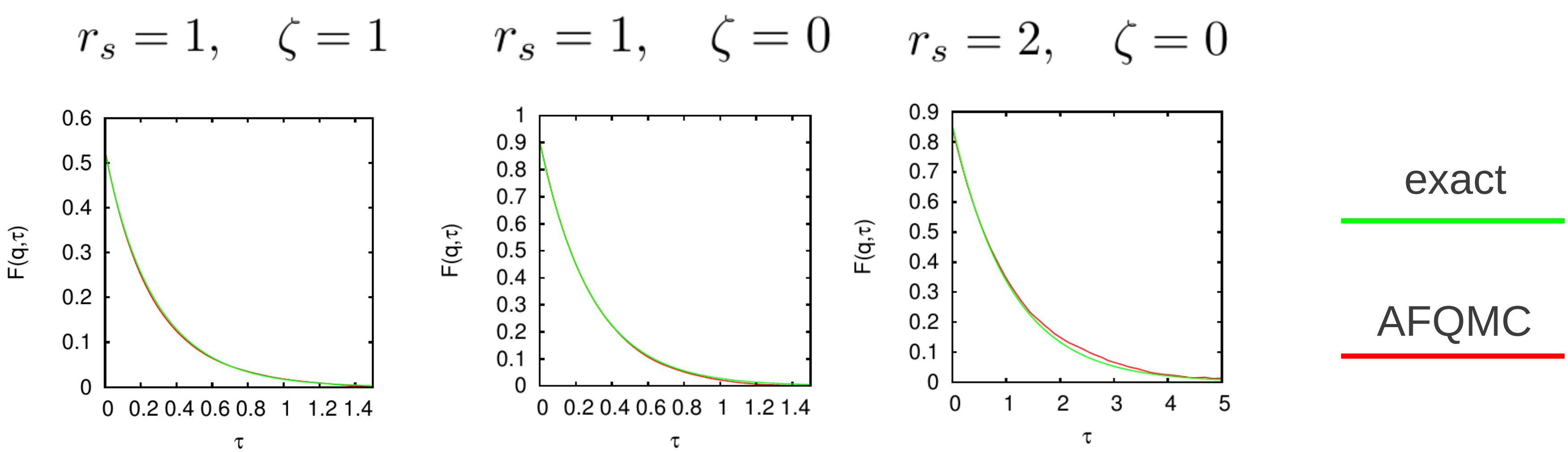
- Importance sampling enhances overlap between random walker $|\phi\rangle$ and trial function $|\Psi_T\rangle$
- Phaseless approximation: branching weight approximated by

$$\exp(-\tau \mathrm{Re}[E_L(\phi)])$$

→ Very good results for ground-state energy even with poor trial functions

How good for imaginary-time correlation functions?

$F(q,\tau)$ for 2D jellium (N=2)



Summary part 2:

- Phaseless AFQMC looks good for imaginary-time correlations
- Tests still very preliminary