Quantum Monte Carlo for Noncovalent Interactions

Advances in quantum Monte Carlo techniques for non-relativistic many-body systems (June 28, 2013, Seattle)

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Outline & Scope

- Numerical evidence
  - **FN-DMC in NCI – what can be achieved?**

// No method development, skip details on VMC & DMC & technical details //

FUNDAMENTAL QUESTIONS OF THIS MEETING ADRESSED: What is the current state of the art of QMC as compared to other many-body techniques? Is it possible to imagine QMC as a reliable standard to be used also by non- experts in the near future? What is the cost/benefit ratio compared, for instance, to DFT calculations?

http://www.int.washington.edu/PROGRAMS/13-2a/Questions.html

Noncovalent Molecular Interactions

- Chemical bonding without sharing of electrons
  - Hydrogen bonds
  - Van der Waals
    - Dipole-dipole, London dispersion
- Importance
  - Structure of biomacromolecules
  - Properties of liquids
  - Molecular recognition
  - ...

Typical strength: 0.5-30 kcal/mol

Levels of accuracy

- Depends on the problem
- Chemical accuracy
  - 1 kcal/mol ~ 0.04 eV
- Scale of NCI starts at 0.5 kcal/mol
    - Need less than 1 kcal/mol
- **Subchemical accuracy: 0.1 kcal/mol**
  - Target benchmark level for NCI
  - **One of the most challenging tasks in computational chemisty**

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OUR GOAL!

Noncovalent Interactions

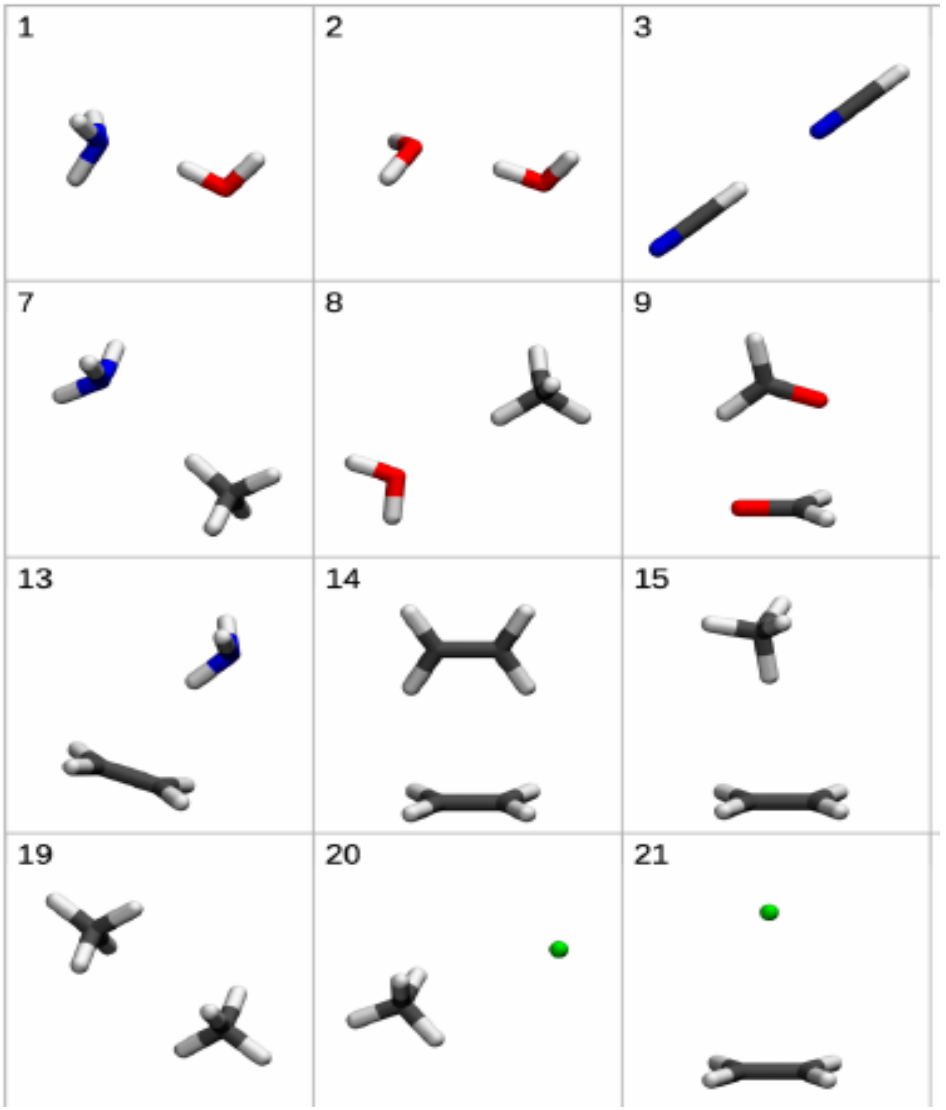
- Experiment
  - Strength on interactions
    - Dissociation & adsorption enthalpies
    - No direct info on nature of interactions
- Theory
  - Enthalpy
    - hard for anharmonicity
  - Interaction energy available from SSE in BO approx.
  - Other quantities of interest – fundamental understanding

Theory

- Problem: solve SNR-SE in BO approximation
- Golden standard of QCH: **CCSD(T)**
- Accurate in large basis and/or in CBS limit → 1 kcal/mol
- Problem: rapid scaling with system complexity ~O(N^7)
- Is the CCSD(T)/CBS reliable? How much?
- In general this is not settled
  - Single reference method! OK for NCI

Recent assessment of CCSD(T) on small complexes

- Rezac, Hobza ***JCTC*** 2013
  - Tests of various approximations on noncovalent interactions, test set A24:
    - Relativity
    - Excitation order by CCSDT(Q)
    - Ignoring core-valence correlation



Results

	system		CCSD(T)/CBS	ΔCCSDT(Q) (%)	
1	water···ammonia	C_s	−6.493	0.001	(0.01)
2	water dimer	C_s	−5.006	0.012	(0.23)
3	HCN dimer	C_s	−4.745	0.007	(0.15)
4	HF dimer	C_s	−4.581	0.017	(0.38)
5	ammonia dimer	C_{2h}	−3.137	−0.004	(0.13)
6	HF···methane	C_{3v}	−1.654	−0.006	(0.37)
7	ammonia···methane	C_{3v}	−0.765	−0.006	(0.80)

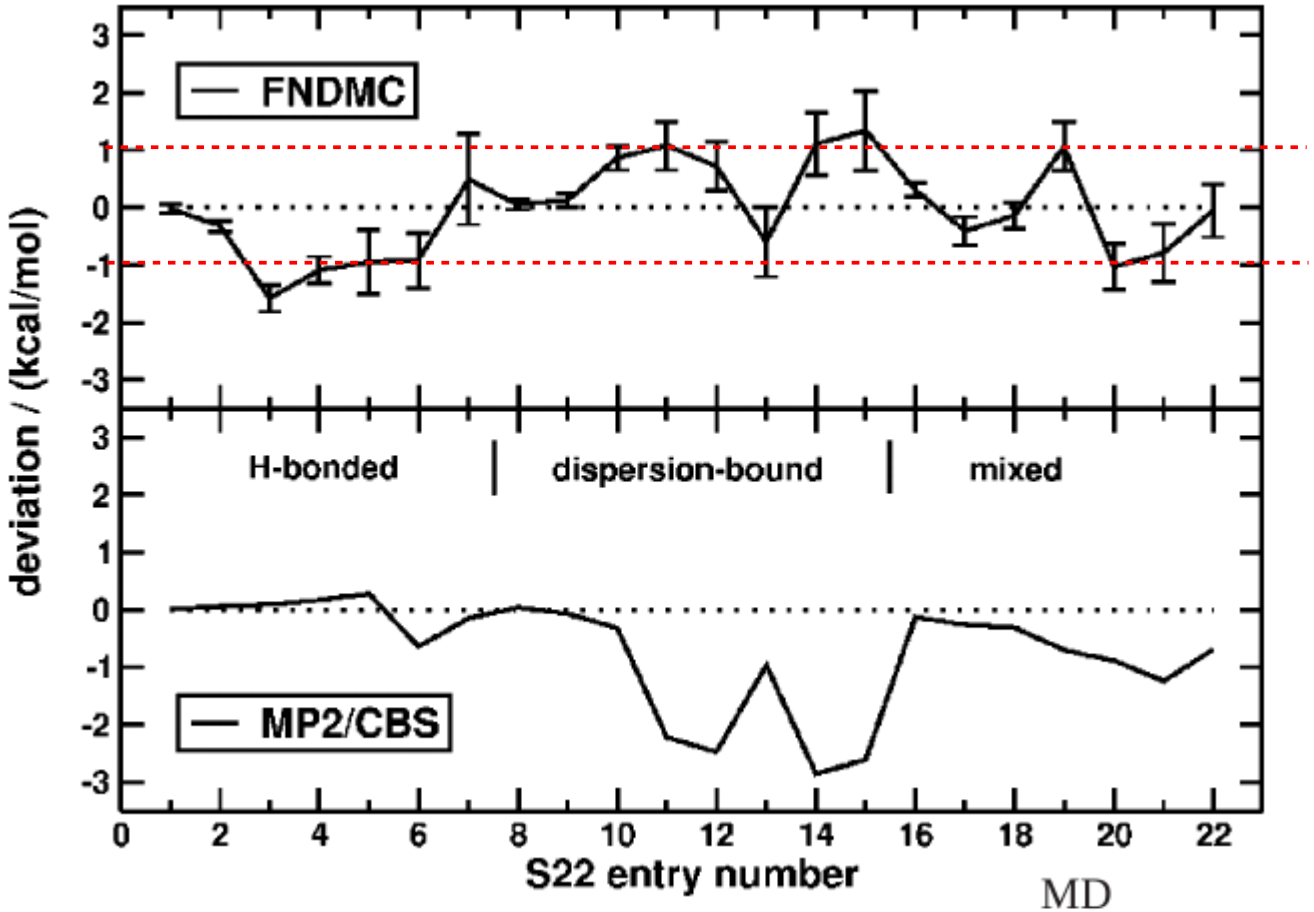
- **Subchemical accuracy is achieved within the whole set >20 mol's, total avg. error on IE is 1.5 % only**
- **Error compensation**
- **CCSD(T) is "converged" for IEs in small noncovalent complexes – our reference**

What about Quantum Monte Carlo?

- First step, assess FN-DMC w.r.t. CCSD(T) in small complexes
  - Then test on larges systems
  - Learn what's possible: goal
- Chemistry: screening of large sets
  - Feasible and black-box approach required: goal
- How well are we able to reach the benchmark CCSD(T)/CBS data on small molecules?

Previous QMC attempt on a set S22

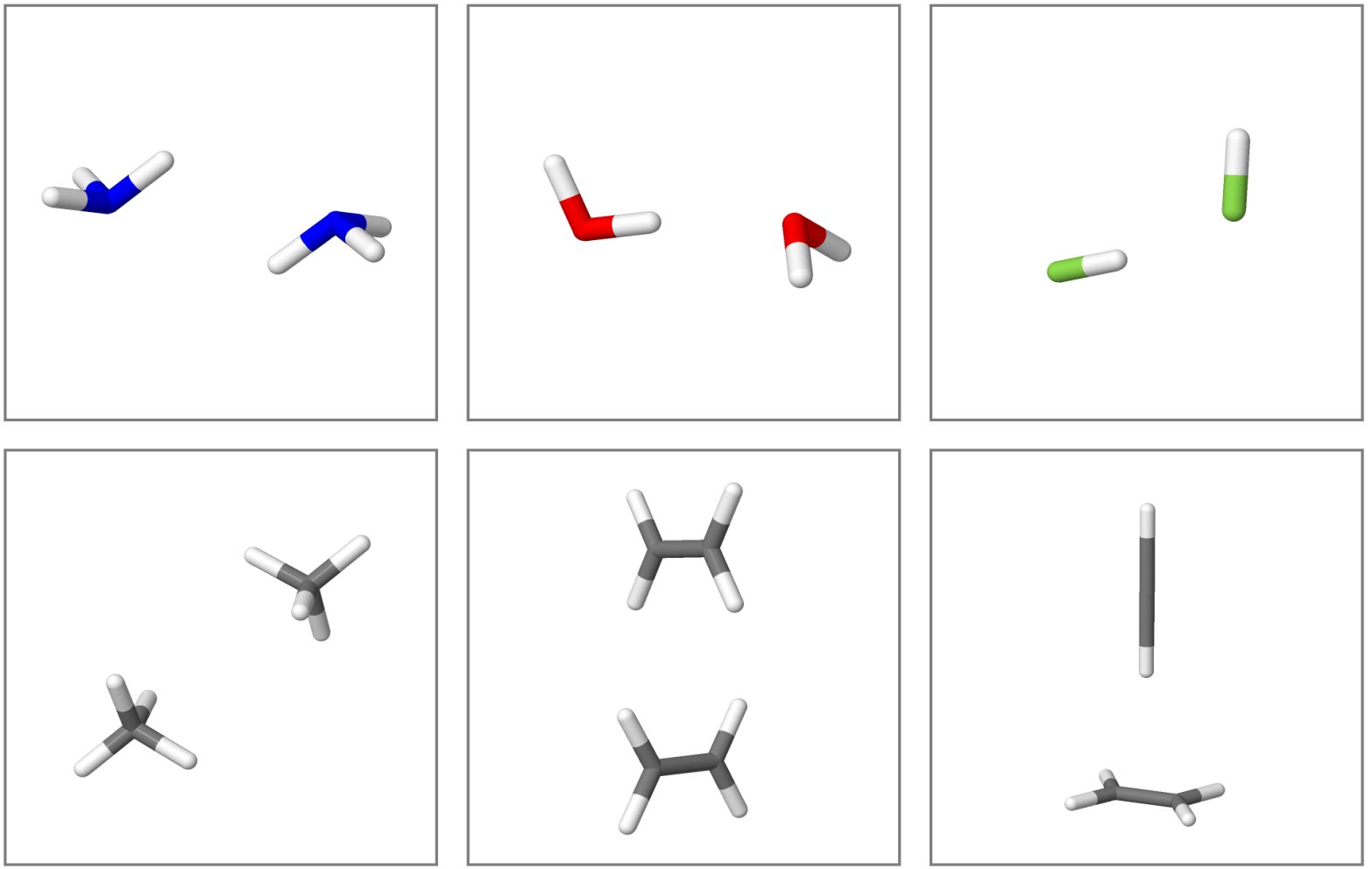
- Chemists are not satisfied with ~1 kcal/mol average error reported by Korth et al. JPCA 2008



MD	−0.03
MAD	0.68

Our work...

Test set



Results

Complex	Reference	FN-DMC^a	Δ^a	FN-DMC^b	Δ^b
Ammonia dimer	-3.15	-3.19±0.09	0.04	-3.22±0.10	0.07
Water dimer	-5.07	-5.34±0.09	0.27	-5.15±0.10	0.08
HF dimer	-4.58	-	-	-4.68±0.10	0.10
Methane dimer	-0.53	-0.48±0.08	-0.05	-0.44±0.10	-0.09
Ethene dimer	-1.48	-1.38±0.13	-0.10	-1.47±0.09	-0.01
Ethene/ethyne	-1.50	-1.22±0.12	-0.28	-1.56±0.10	0.06

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CCSD(T)/CBS
ATZV - AQZV
Takatani et al. JCP 2010

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Korth et al. JPCA 2009

ME: -0.008
MUE: 0.116

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ALL HIT

Korth et al. JPCA 2009

ME: -0.008
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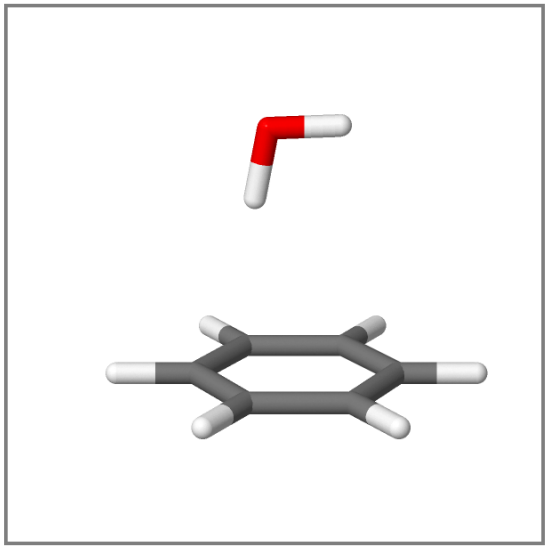
ME: 0.035
MUE: 0.068

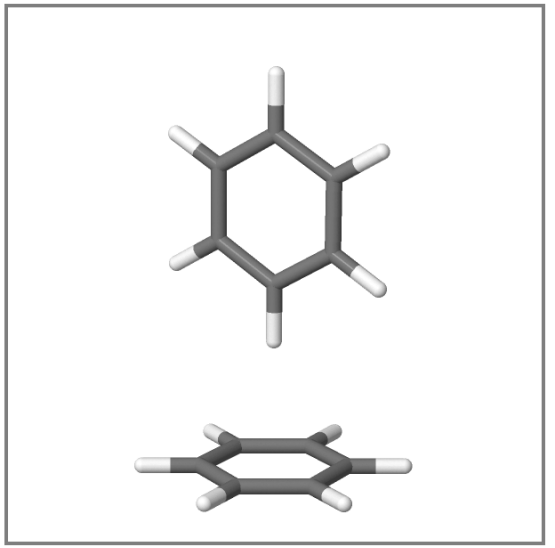
I.e. FN-DMC agrees to within subchemical accuracy w.r.t. benchmark data believed to be (esentially) exact.

This makes FN-DMC competitor of CCSD(T) and in large complexes, it will benefit from the scaling.

Larger complexes

**CCSD(T) not yet assessed! Just best energy estimates...
believed to be OK ~+-0.3 kcal/mol**





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Benzene/water	-3.29	-3.69±0.24	0.40	-3.50±0.15	0.21
Benzene/methane	-1.50	-0.63±0.21	-0.87	-1.32±0.12	-0.18
Benzene dimer T	-2.71	-3.77±0.39	1.06	-2.94±0.15	0.23

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Korth et al. JPCA 2009

MUE: 0.76

MUE: 0.213

Optimal Protocol

- Geometries from S22 (except HF dimer)
- BFD ECP's
- Augmented bases TZV – aug part is a must!
- B3LYP orbitals (no orbital opt)
- VMC opt of J only, 3 body Schmidt-Moskowitz, Poly pade
  - Linear combination of Energy & Variance
    - esentially energy minimization / 95% of energy
- DMC: T-moves, conservative dt=0.005 a.u.,
  - 0.1 kcal/mol or smaller error bar

Just accepted in JCTC
http://pubs.acs.org/doi/abs/10.1021/ct4006739

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- Energy differences are converged
- Why?
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  - Closed shells – no multireference nature of the wave functions arises upon dissociation of the molecular complexes constituents – equal footing description
  - Other...

FN error cancellation

Anderson, Korth et al, ...

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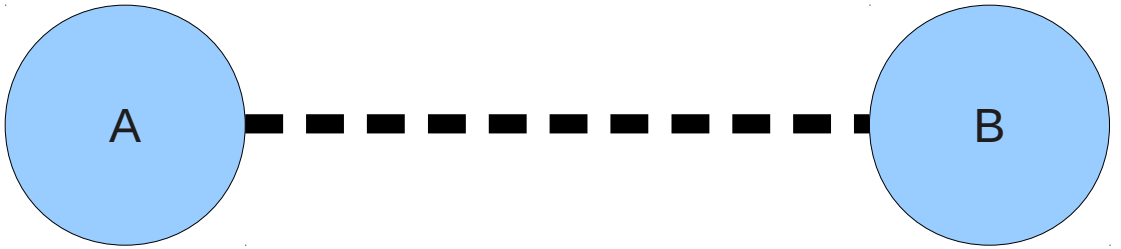
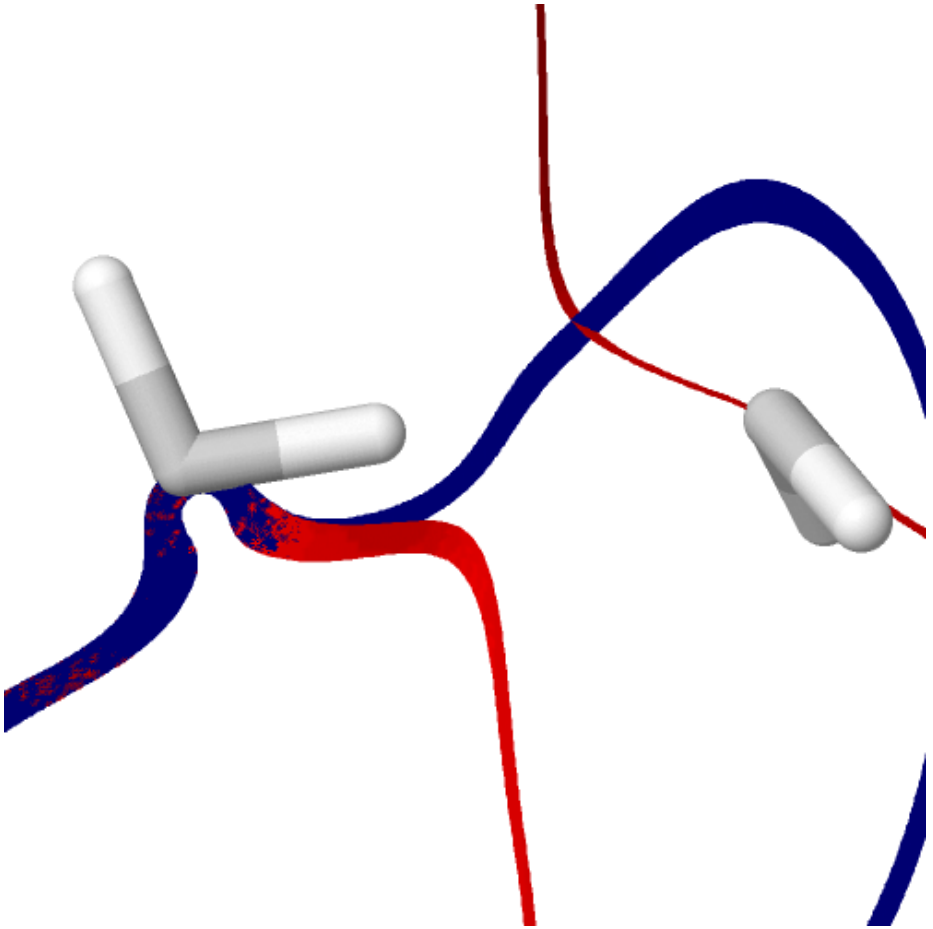
Weak interation => FN error constant, cancels out



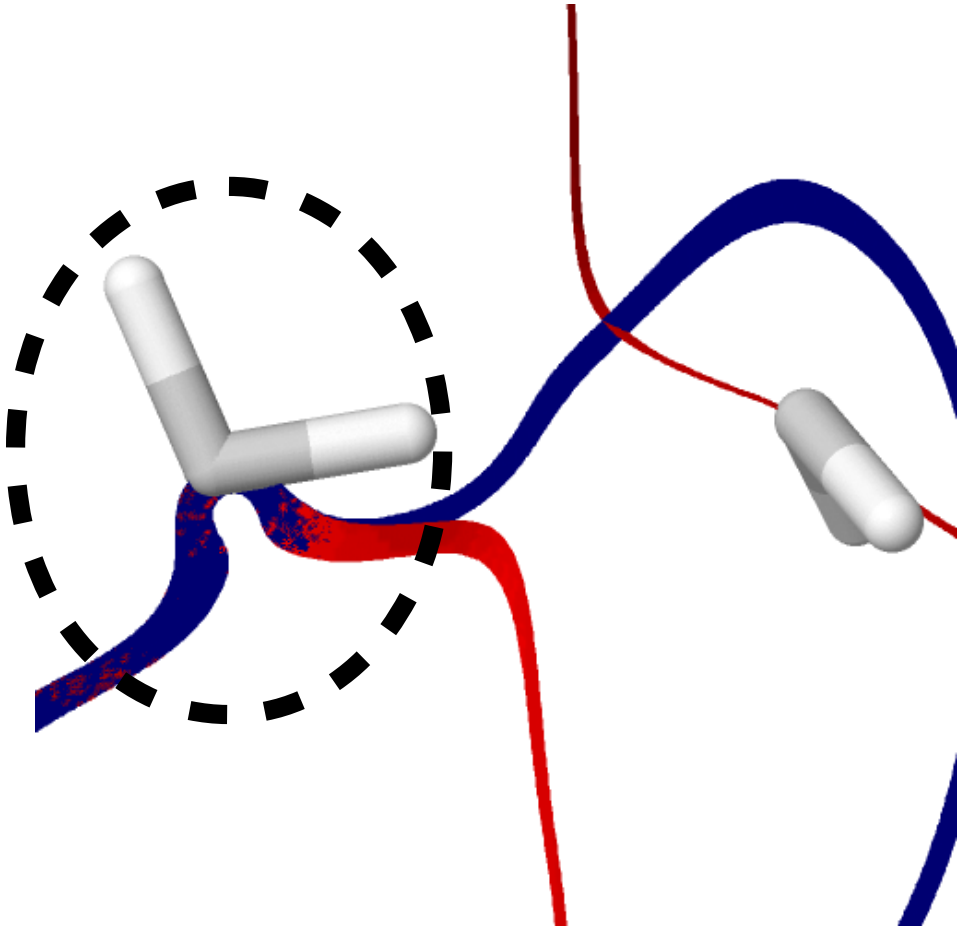
Visual evidence, water dimer

Slice cuts through multidimensional nodal surface



Monomer, **dimer**

Visual evidence:
FN error cancellation



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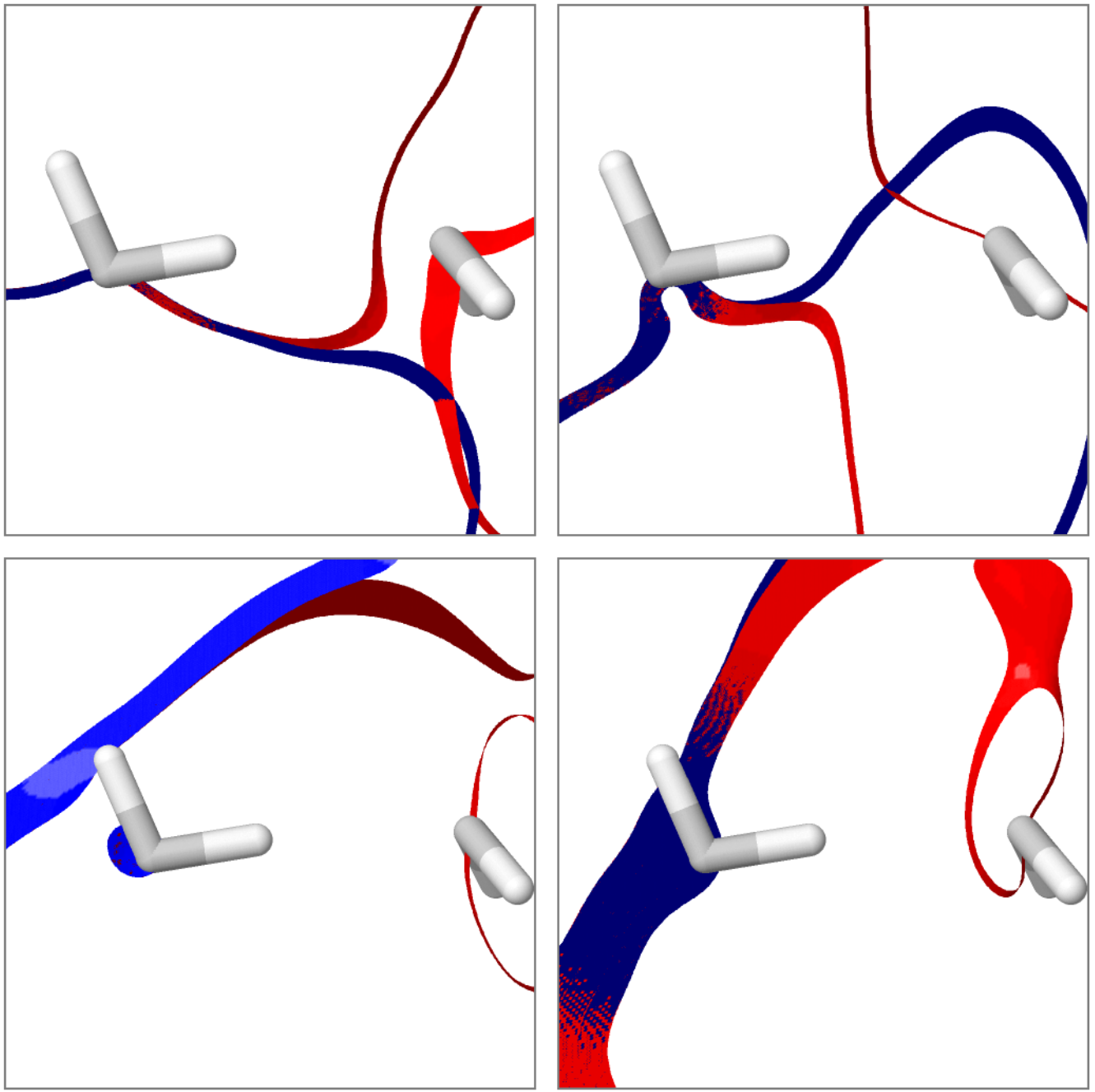

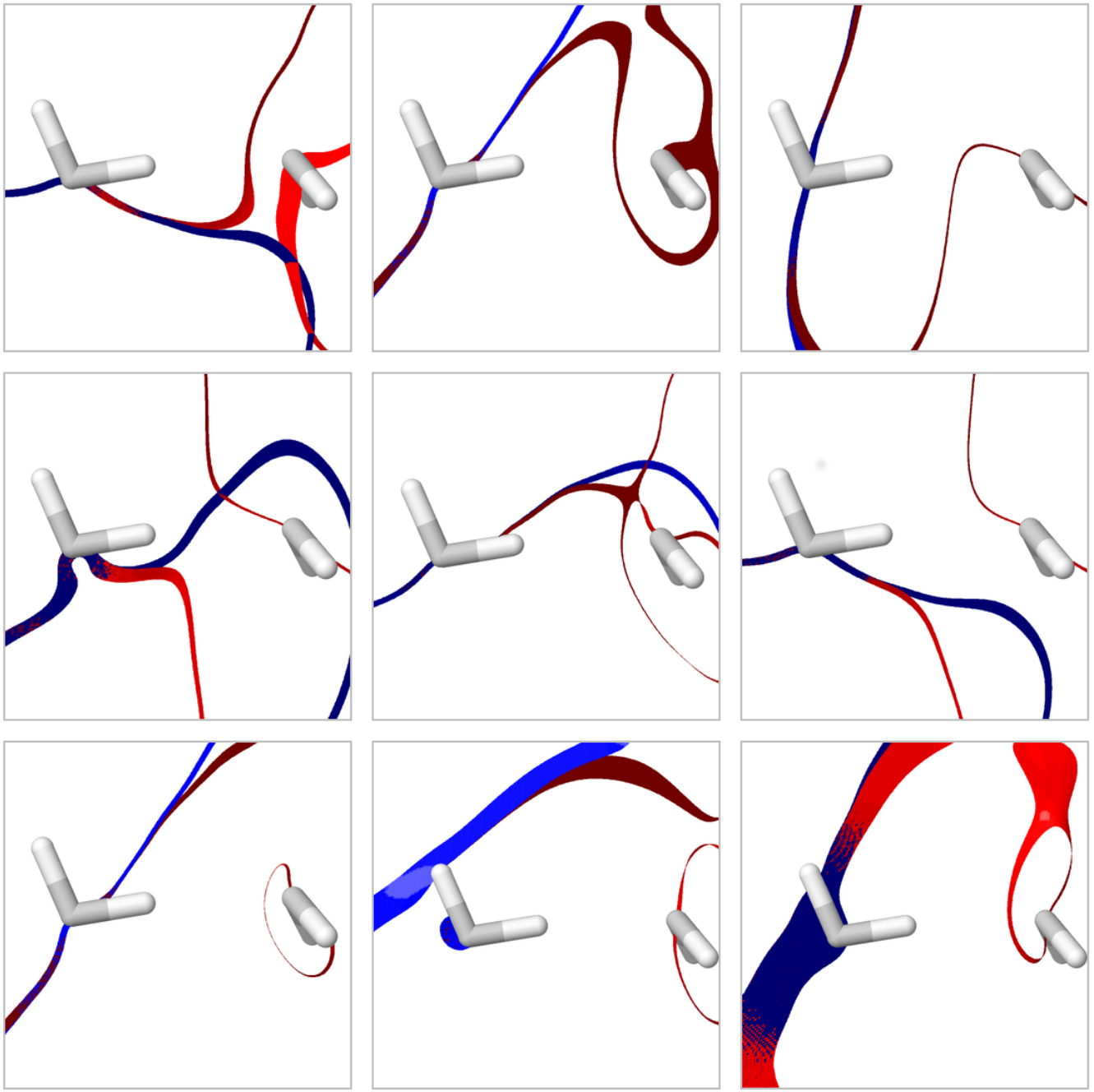

Too fresh...
quantitative analysis under way...

FUNDAMENTAL QUESTIONS AGAIN

What is the current state of the art of QMC as compared to other many-body techniques? Is it possible to imagine QMC as a reliable standard to be used also by non-experts in the near future? What is the cost/benefit ratio compared, for instance, to DFT calculations?

Modified from http://www.int.washington.edu/PROGRAMS/13-2a/Questions.html

My answer in domain of NCI

- QMC now allows routine use & attains predictive power with benchmark accuracy as CCSD(T)
  - At least for comparable closed shell complexes with comparably complex bonding pattern/s
- I believe that NCI may be easily studied by non-QMC-expert using this approach as the provided protocol is esentially a black-box recipe
- More work required/under way, to support...
  - Testing on more complexes, (S22, cd, …)
  - Predictive calculations
  - Physics – nodes, nonlinearities?

Thank you!

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