Massive parallel Quantum Chemistry: Quantum Monte Carlo at Home

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20.09.2006

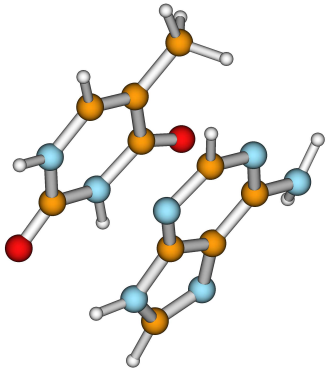
Part I

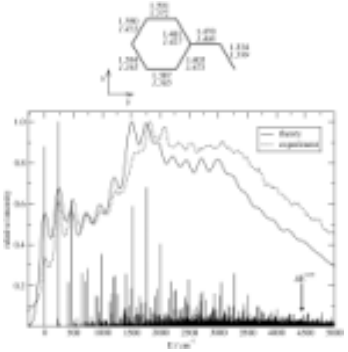
From Chemistry to QMC

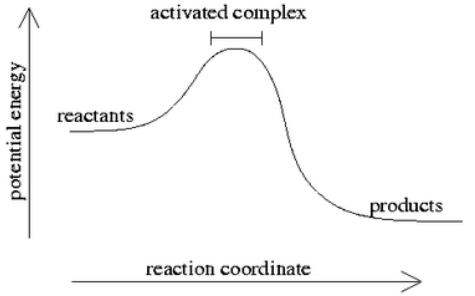
From Chemistry to QMC

Chemistry

- the science of matter at the atomic to molecular scale
- main focus: structure and reactivity of molecules
- properties of materials determined by their atomic scale structure
- atomic scale structure determined by basic interactions







From Chemistry to QMC

Theoretical Chemistry

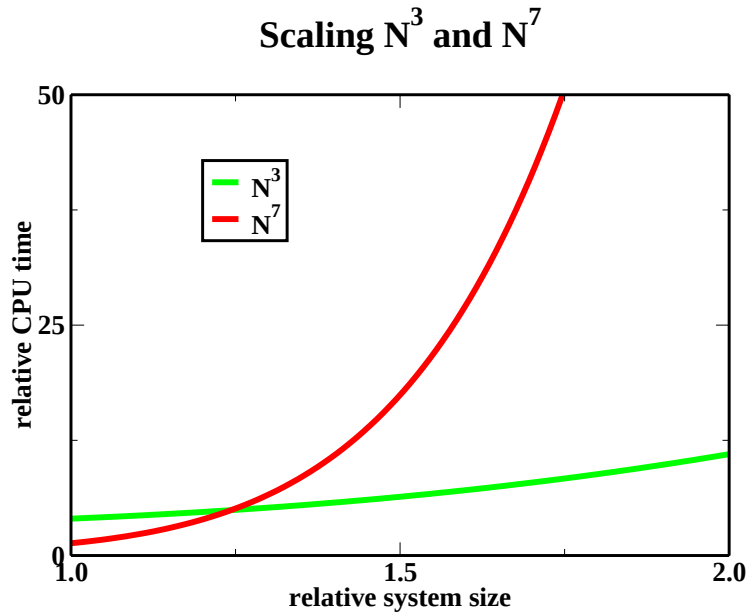
- theoretical chemistry is the use of reasoning to explain or predict chemical phenomena
- nowadays primarily 'quantum chemistry', the application of quantum mechanics to problems in chemistry

'The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.' (P.A.M. Dirac)

From Chemistry to QMC

Quantum Chemistry

- 'chemical accuracy' (1 kcal/mol) can be acquired within the framework of the non-relativistic Schrödinger equation and the Born Oppenheimer approximation
- efficient methods at hand (DFT) have known deficiencies
  $\longrightarrow$ high accuracy calibration methods needed
- common high accuracy methods (CCSD(T)) hit the 'scaling wall'



From Chemistry to QMC

Quantum Monte Carlo

- direct stochastic solution of the full Schrödinger equation
- exact within the 'fixed node approximation'
- favorable scaling behavior ($\propto N_{El}^{2-3}$) avoids the scaling wall
- exceptional high parallelizability

Part II

Quantum Monte Carlo

Quantum Monte Carlo

Quantum Monte Carlo

- solution of the electronic Schrödinger equation via a Monte Carlo type quantum simulation
- approximation of the unknown Greens function e.g. through the mathematical equivalence of the time-dependent Schrödinger equation in imaginary time ($\tau = it$) with a generalized diffusion equation

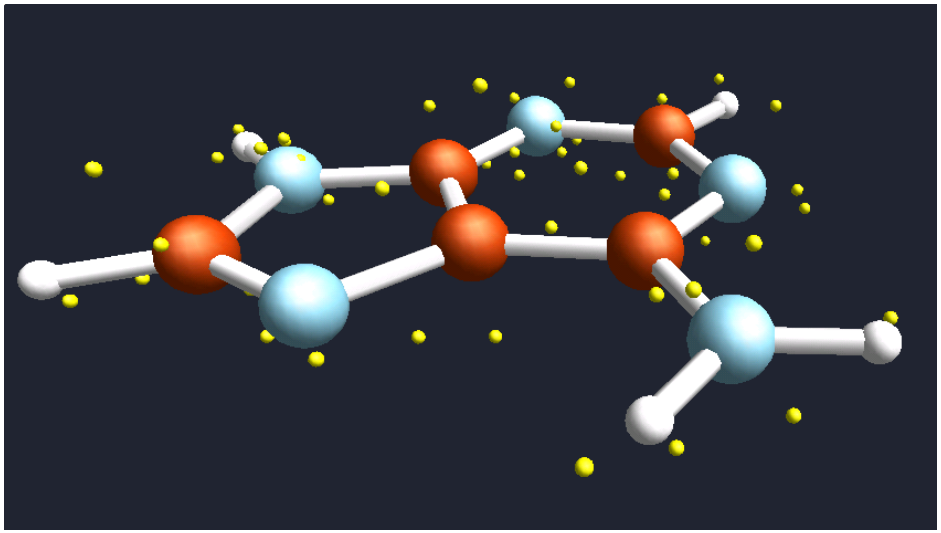
$$\frac{\partial \Psi(r,\tau)}{\partial \tau} = \frac{1}{2m}\nabla^2\Psi(r,\tau) - V(r)\Psi(r,\tau)$$

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t) - k(r)c(r,t)$$

Quantum Monte Carlo

Diffusion Monte Carlo

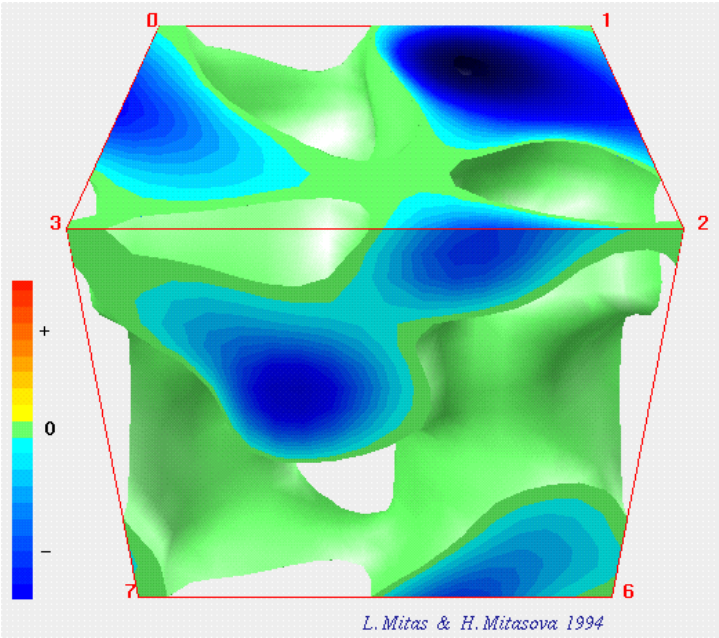
- random walk simulates a combined diffusion and rate process of electron configurations ('walkers')
- 'movement' in imaginary time: no real dynamics



Quantum Monte Carlo

Important Sampling and the Fixed Node Approximation

- effective treatment requires 'important sampling' with a 'guidance function'; at the same time the 'fixed node approximation' introduces fermion antisymmetry $\longrightarrow$ fermion sign problem



3D cut through a 59 dimensional nodal hypersurface

Quantum Monte Carlo

Fixed Node Diffusion Monte Carlo

1. create a start ensemble of walkers (electron configurations)
2. 'move' walkers according to the Greens function of the corresponding Schrödinger equation
   - diffusion step (random movement of the walkers)
   - drift step (important sampling guides the diffusion process)
   - branching step (create / annihilate walkers)
3. after an initial equilibration phase the walker distribution resembles the ground state electron density
4. the ground state energy can be calculated as a 'mixed estimator' over walkers and steps

Part III

QMC@HOME

QMC@HOME

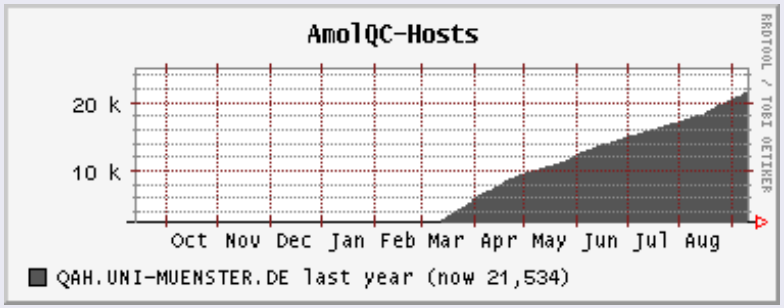
Quantum Monte Carlo at Home

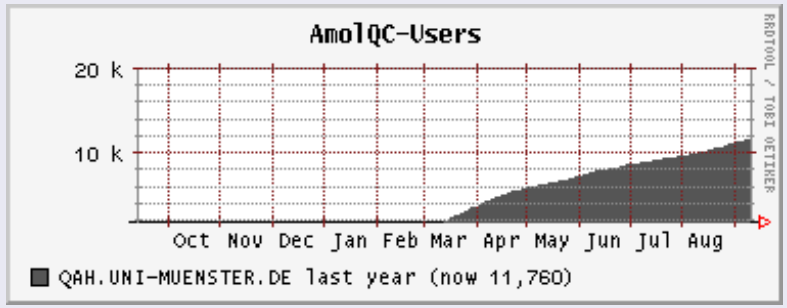
- first large scale distributed computing project in *ab initio* quantum chemistry
- based on BOINC and Amolqc (QMC program by Lüchow et al.)
- ultimate goal: find a solution for the fermion sign problem

http://qah.uni-muenster.de

Status

- since April 2006 alpha
- since June 2006 beta (with screen-saver)





QMC@HOME

QMC
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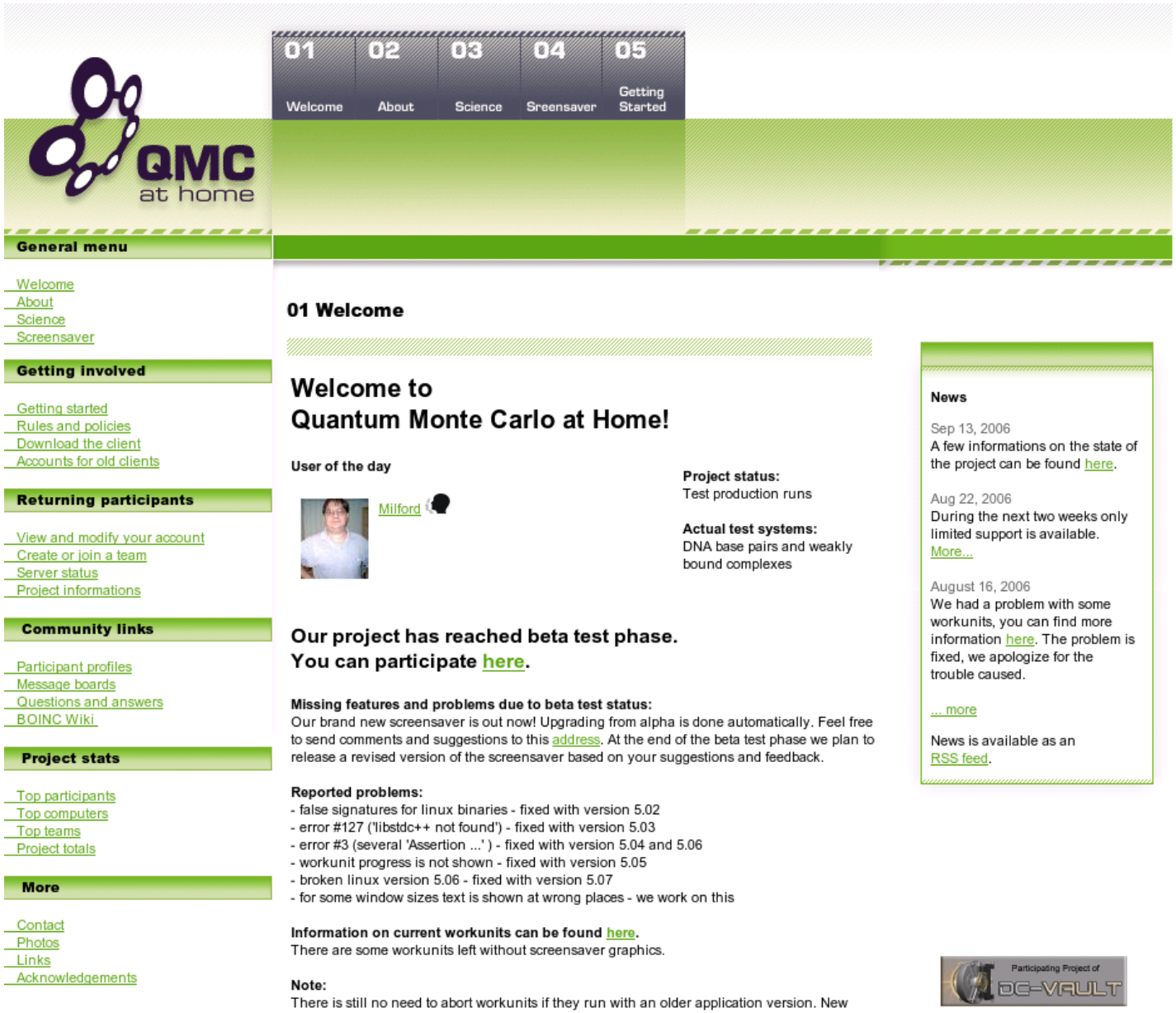

QMC@HOME

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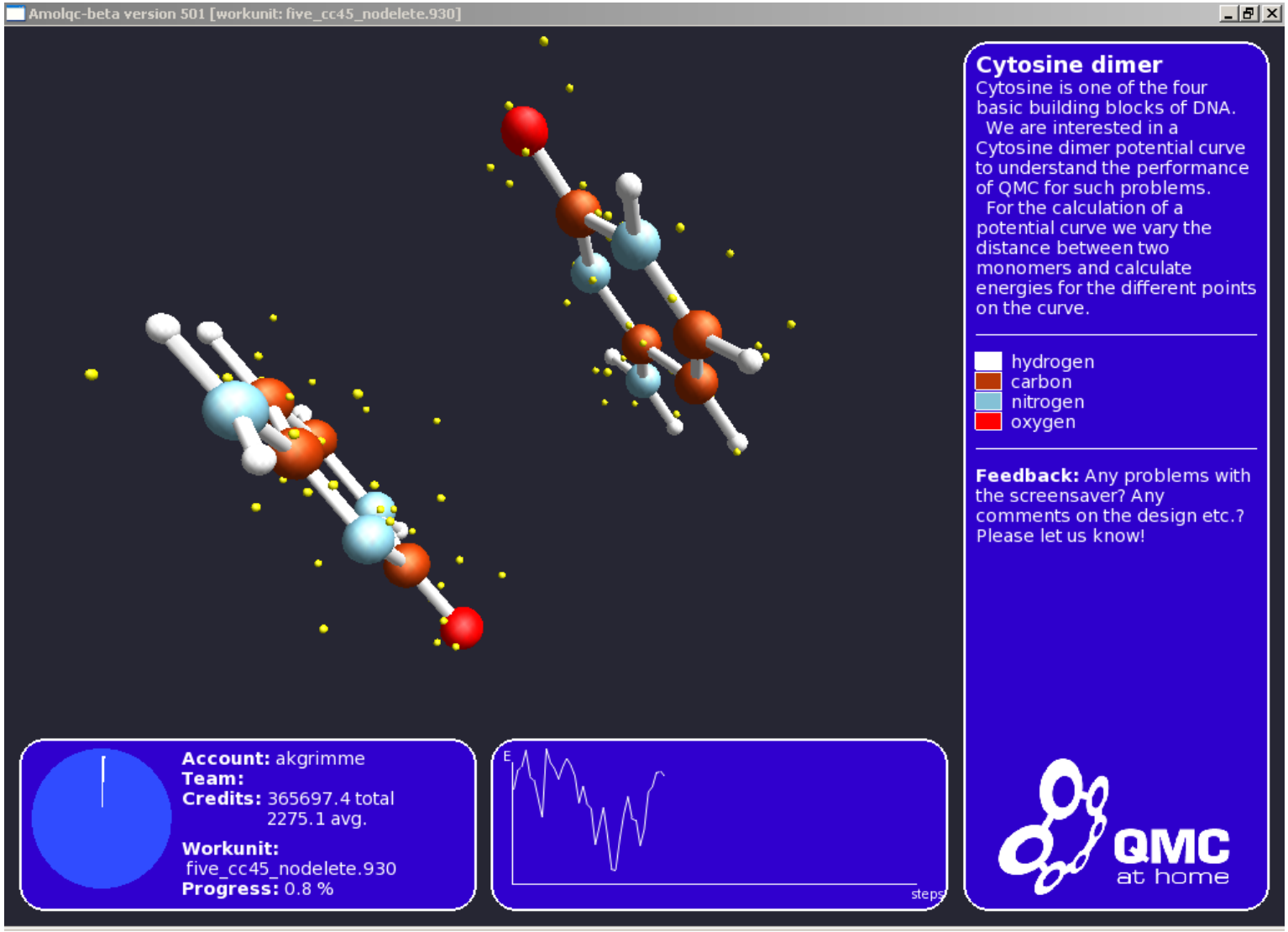


Grimme

QMC@HOME

Technical requirements

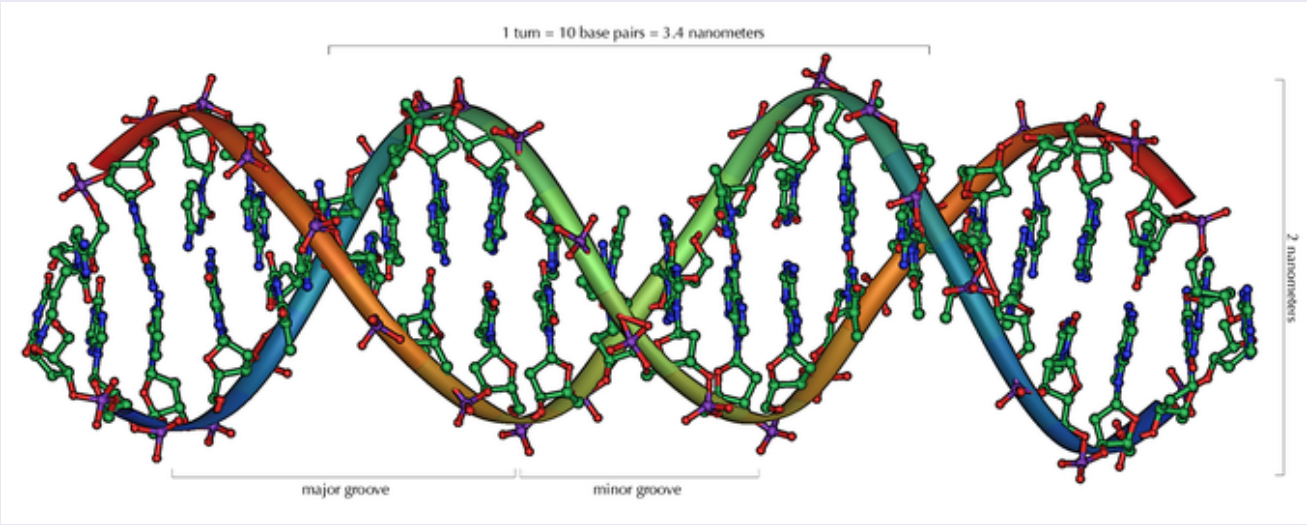
- BOINC works perfectly well for FNDMC
  - Monte Carlo algorithm
  - moderate CPU/disk requirements
  - small input/output files
- WU length kind of problematic
  - approx. 2000 WUs (statistically independent runs) needed for the evaluation of the groundstate energy of a molecule
  - minimal length of a WU related to system size due to the scaling behavior of the FNDMC algorithm ($\propto N_{El}^{2-3}$)
  - greatly differing minimal WU lengths (for different molecules) unexpected from the user side

Part IV

First results - DNA base pair interactions

DNA base pair interactions

DNA

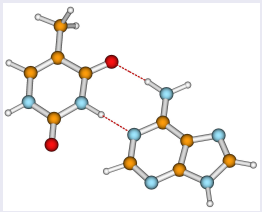


DNA bases

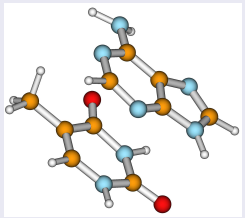
structure of biomacromolecules (DNA, RNA, proteins) highly influenced by nonconvalent interactions between the basic building blocks (DNA/RNA bases, amino-acids)

DNA base pair interactions

DNA base pairs



Watson/Crick



stacked

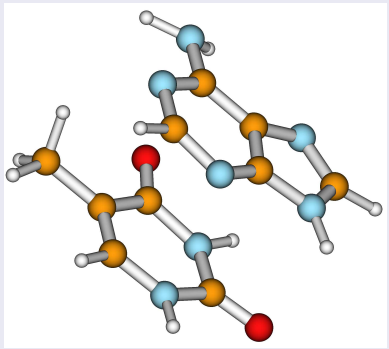
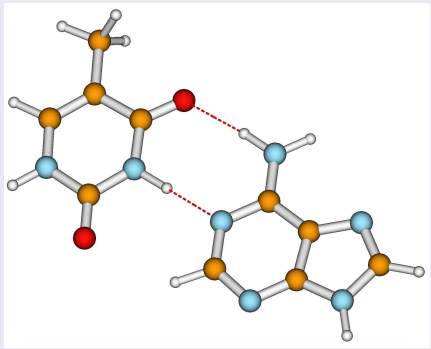
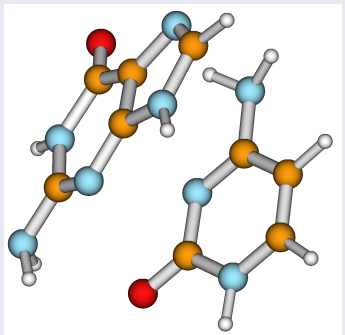
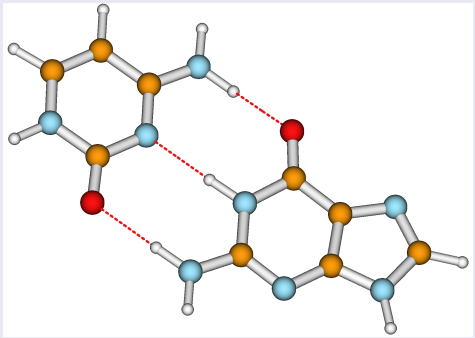
- hydrogen bonding, electrostatic and van der Waals interactions important $\longrightarrow$ very complex systems
- no experimental data available, despite fundamental importance

... as test systems

- far outside the reach of CCSD(T) with a sufficiently large AO basis (quantum chemistries 'gold standard' for calibration purposes)
- no fixed node error for weakly bound systems

DNA base pair interactions

DNA model systems

	stacked (st)	Watson/Crick (wc)
Adenine / Thymine		
Cytosine / Guanine		

DNA base pair interactions

QMC@HOME Results

DNA base pair interaction energies (kcal/mol):

(statistical (FNDMC) / estimated (CCSD(T)) error in parenthesis)

	FNDMC	CCSD(T)/CBS est.[1]
A/T, st	-11.0(1.0)	-11.64(1-2)
A/T, wc	-15.1(1.0)	-15.43(1-2)
C/G, st	-17.7(1.5)	-16.90(1-2)
C/G, wc	-31.3(1.0)	-28.80(1-2)

[1] Hobza *et al.*, Phys. Chem. Chem. Phys., **2006**, 8, 1985.

$\rightarrow$ most accurate nucleic acid base pair interaction energies reported up to now

Part V

Conclusion & Outlook

Conclusion & Outlook

Conclusion

- QMC@HOME is the first large scale distributed computing project in *ab initio* quantum chemistry
- FNDMC is a promising calibration method for medium to large systems
- high accuracy solutions for DNA base pair interaction possible with FNDMC

Outlook

- future development of FNDMC depends on further insight into the fermion sign problem
- QMC@HOME provides the necessary computing power

Acknowledgments

Grimme Workgroup

- especially C. Diedrich, C. Mück-Lichtenfeld and S. Grimme

Other Help

- Screen-saver - Jan Budde
- Web-site design - Martin Heinrich

Funding

- QMC@HOME is funded by the Sonderforschungsbereich 424 established by the Deutsche Forschungsgemeinschaft

Many thanks

- ... for your attention!

Further Acknowledgements

Pictures

- reaction scheme by Ian Craig (http://en.wikipedia.org/wiki/Image:Ac_com.png)
- picture of dices by Roland Scheicher (http://de.wikipedia.org/wiki/Bild:Craps.jpg)
- nodal hypersurface by L. Mitas and H. Mitasova (http://altair.physics.ncsu.edu/fnode.html)
- DNA overview by Michael Ströck http://en.wikipedia.org/wiki/Image:DNA_Overview.png released under the GFDL (http://en.wikipedia.org/wiki/WP:GFDL)