Quantum Chemistry on the Supercomputers of Tomorrow

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Smokey Mountain

Computational Sciences and Engineering Conference

Chemistry :

- Modeling's and simulations integrated part of experimental investigation
- Interplay between theory and experiment more important in the future

Example : *Molecular manufacturing*

- Synthesize materials of desired properties by manipulating individual atoms
- Embraces the potential of altering the future of technology

National Science Foundation

http://www.nsf.gov/pubs/reports/sbes_final_report.pdf

Report 2007 : Simulation-Based Engineering Science

- Seldom have so many independent studies been in such agreement:

Simulation is a key element for achieving progress in engineering and science

Foresight Nanotech Institute and Battelle

http://www.foresight.org/roadmaps/

Report 2007 : Technology road map for productive Nano systems

p.17 "*Extending the **scale, scope, and accuracy** of atomistic modeling techniques is **a high priority** and can greatly facilitate atomically precise technologies design and implementation*"

Todays modeling on Nano systems use models of low accuracy

- Density functional theory, Force field

p.152 '*While quantum mechanical methods exist that approach the absolute limits of accuracy, the use of these methods is currently limited to diminutive chemical systems (< 20 atoms)"*

What have the high accuracy calculation on small systems shown ?

Small Molecules: *Accomplishments using high accuracy models*

- Calculations changed how many experimental investigation are carried out,

  A theoretical investigation often precede an experimental

- Calculations broadening the understanding of the investigated phenomena

- In some cases calculations have replaced experiment :

  Who would nowadays try to determine equilibrium geometries for small molecules experimentally?

Large molecules: *Challenges for high accuracy models*

- The scaling in conventional implementations prohibit applications
- Restructure calculations for lower scaling
- Even the low scaling algorithms require large computational resources
- The low scaling models have to be massively parallel
- Development and implementation of low scaling methods must go together with access to modern computational facilities
- Expect similar development with respect to interplay with experiment as for small molecules

Development of code for large molecules

Theoretical challenges

- Restructure high scaling models to become lower scaling
- The low scaling models have to be massively parallel
- Parallelism at several levels (Coarse, medium and fine grained)

Challenges in connection with implementations

- Memory available
- Data traffic
- Many many more

Problems facing developers of new methods

Granting agency :

- Which chemical problem can you solve (using available methods)
- Equally important: Development of the methods for the future

For the future : *Close contact between developers of tomorrows code and tomorrows supercomputer software and hardware*

- Open new horizon we have not even dreamed about

30 years of research on small molecules have shown

a) Coupled cluster theory is the method of choice

b) Hierarchies of coupled models with improved accuracy

MP2 : Second order Møller Plesset theory , N^5 scaling

CCSD : Coupled sluster singles and doubles model , N^6 scaling

CCSD(T) : CCSD with perturbative triples corrections ,N^7 scaling

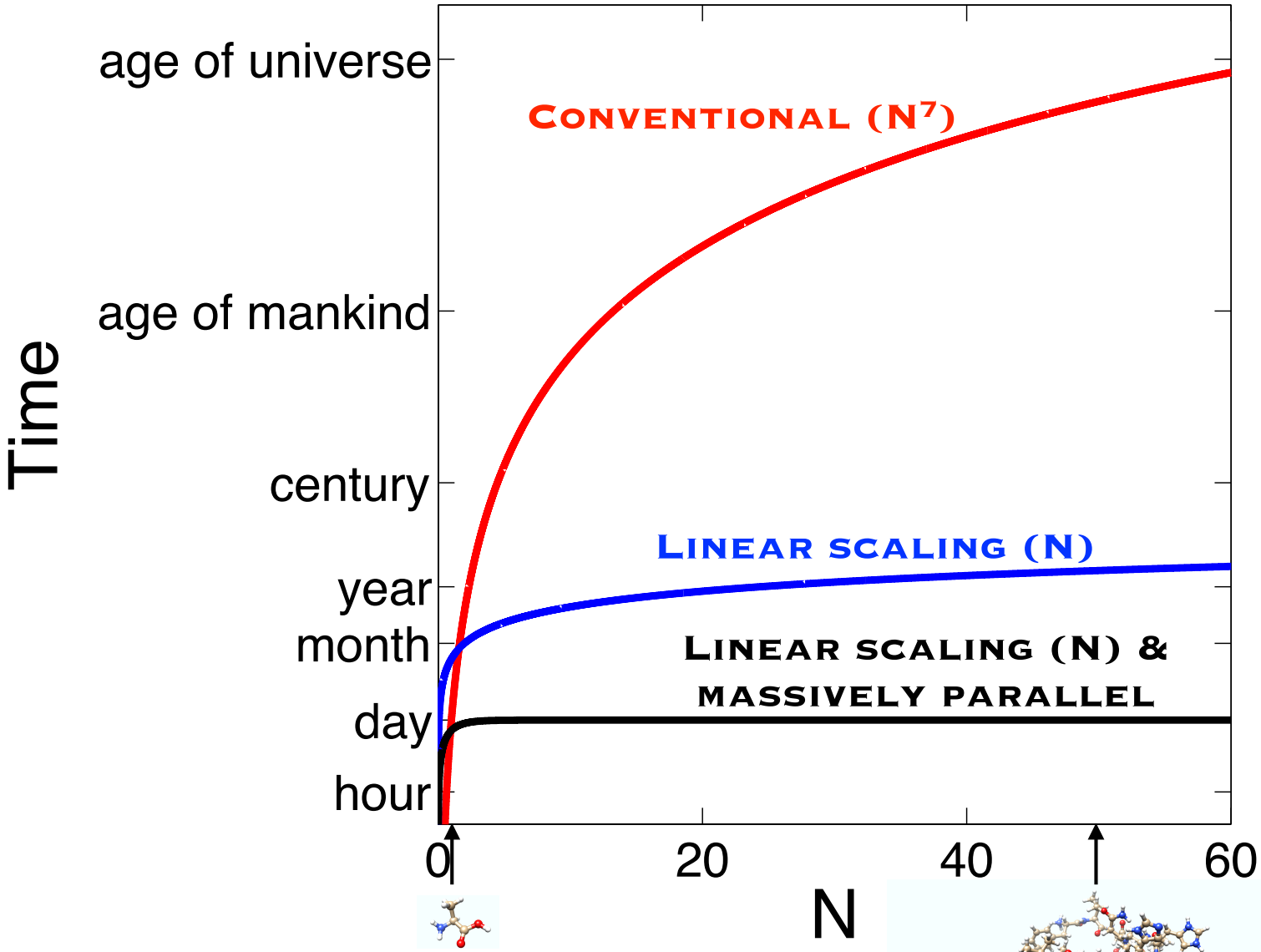
(N denote system size)

CCSD(T) is the gold standard of quantum chemistry

Many molecular properties are described to experimental accuracy or better e.g. equilibrium geometries and reaction enthalpies

Problem: The scaling in standard implementations

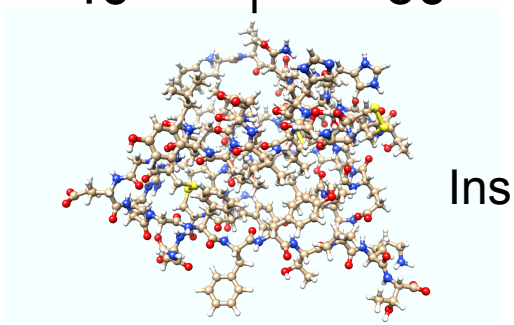
Scaling in Coupled Cluster theory *CCSD(T)*



Standard
Coupled Cluster
Canonical HF orbitals

DEC
Coupled Cluster
Local HF orbitals

One amino acid



Insuline (51 amino acids)

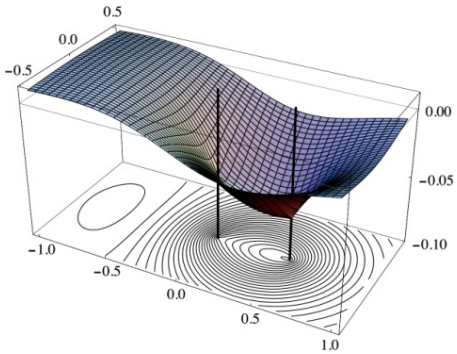
Coupled cluster wave function calculation

Hartree-Fock calculation determines the reference state

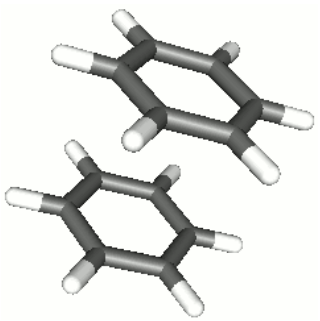
- Electrons move in an averaged field of the others
- Long range potential described to high accuracy
- **Give local orbitals for both occupied and virtual space**

Coupled cluster calculation describes local electron correlation effects

- Coulomb hole, Short range



- Dispersion forces, R^{-6}



Local phenomena described in **local basis** give linear scaling

The divide-expand-consolidate (DEC) coupled cluster method

Correlation energy MP2 and CCSD

Scaling

$$E_{corr} = \sum_{ijab} (t_{ij}^{ab} + t_i^a t_j^b)(2g_{iajb} - g_{ibja})$$

N^4

CCSD(T) energy correction

$$\Delta E^{CCSD(T)} = 2\sum_{ai} t_i^a T_i^a + 2\sum_{abij} (2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab}$$

N^4

CCSD and CCSD(T) energy has the same structure,

Summing over two occupied i,j and virtual a,b orbitals

$$T_i^a = \sum_{cdkl} (t_{ikl}^{acd} - t_{lki}^{acd}) L_{kcld}$$

N^6

$$T_{ij}^{ab} = \sum_{cdk} [L_{bckd} t_{ijk}^{acd} - g_{bckd} t_{kji}^{acd}] - \sum_{ckl} [L_{lckj} t_{ikl}^{abc} - g_{lckj} t_{lki}^{abc}]$$

N^7

$$\varepsilon_{ijk}^{abc} \; t_{ijk}^{abc} = -P_{ijk}^{abc} [\sum_d g_{ckbd} t_{ij}^{ad} - \sum_l g_{cklj} t_{il}^{ab}]$$

N^7

Correlation energy MP2 and CCSD

$$E_{corr} = \sum_{ijab} (t_{ij}^{ab} + t_i^a t_j^b)(2g_{iajb} - g_{ibja})$$

CCSD(T) energy correction

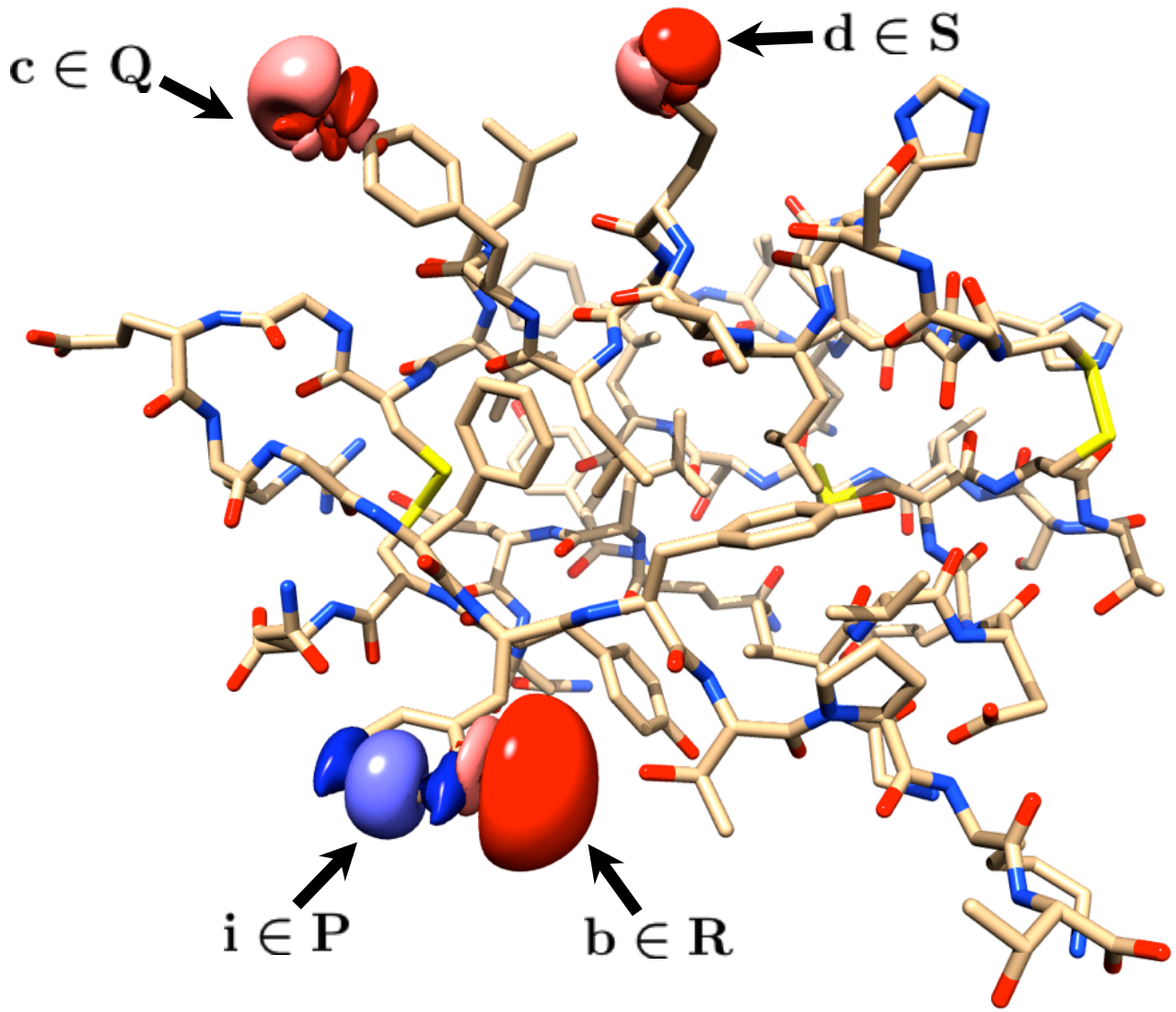
$$\Delta E^{CCSD(T)} = 2\sum_{ai} t_i^a T_i^a + 2\sum_{abij} (2t_{ij}^{ab} - t_{ji}^{ab}) T_{ij}^{ab}$$

DEC Strategy

Assign local orbitals to atomic sites P,Q,..

Replace summation over two occupied i,j (virtual a,b) orbitals with summations over sites P and pair sites P,Q and summations over orbitals belonging to these sites

Determine local Hartree-Fock orbitals



Occupied orbitals:
i,j,k,l

Virtual orbitals:
a,b,c,d

Atomic sites:
P,Q,R,S

Assign orbitals to atomic sites

INSULIN MOLECULE (HYDROGENS OMITTED)

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Occupied space partitioning of E_{corr}

Coulomb hole Dispersion energy

No approximation

$$E_{corr} = \sum_{P} E_P + \sum_{P>Q} \Delta E_{PQ}$$

Quadratic scaling

Occupied atomic fragment energy

$$E_P = \sum_{\substack{ij \in P \\ ab}} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left(2 g_{iajb} - g_{ibja} \right)$$

Occupied pair interaction energy

$$\Delta E_{PQ} = \sum_{\substack{i \in P, j \in Q \\ ab}} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left(2 g_{iajb} - g_{ibja} \right) + \quad P \leftrightarrow Q \ term$$

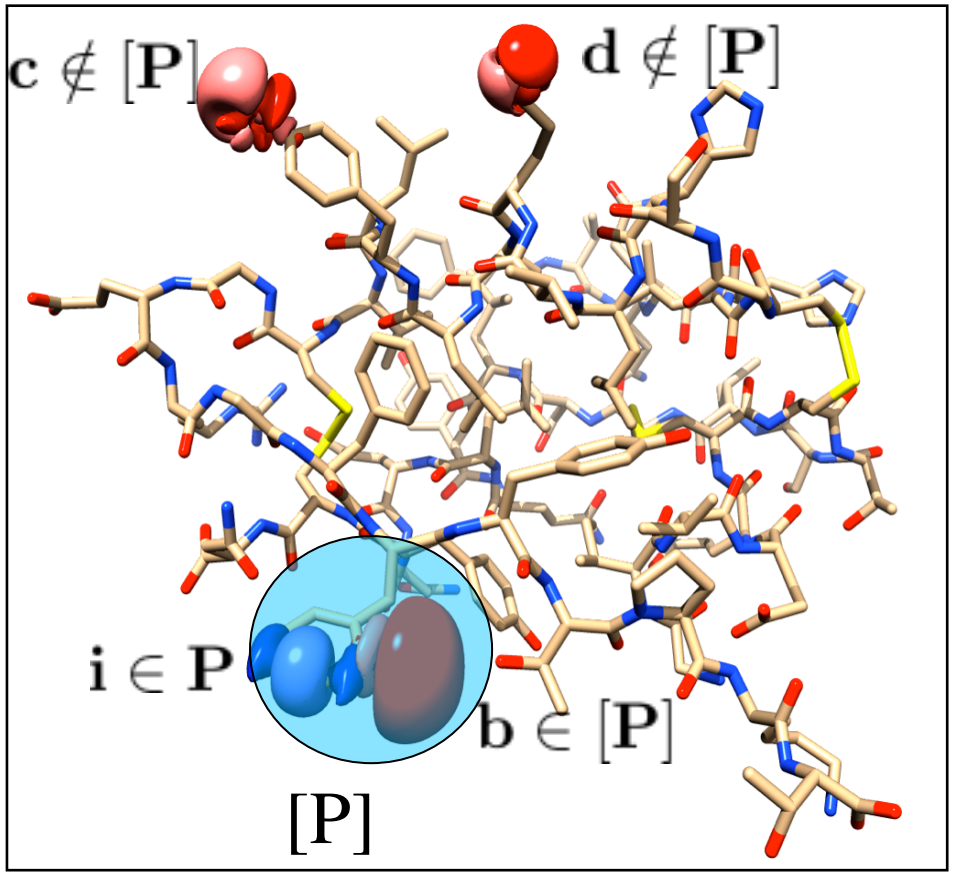
No approximations have so far been made, only a reorganization

Atomic fragment energy E_P

$$E_P = \sum_{ij \in P \; ab \in [P]} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left(2 g_{iajb} - g_{ibja} \right)$$

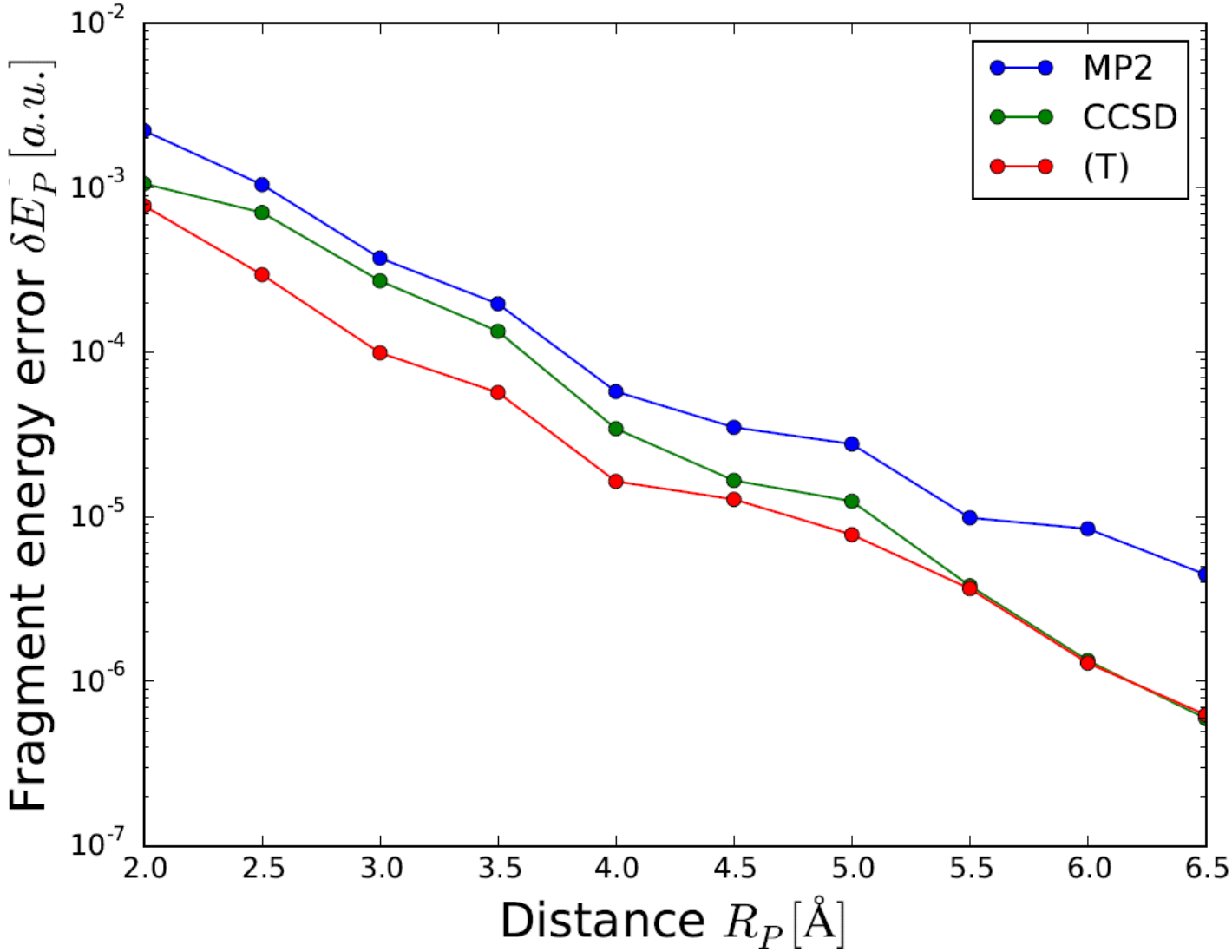
Charge distributions in integrals determine distance decay from site P

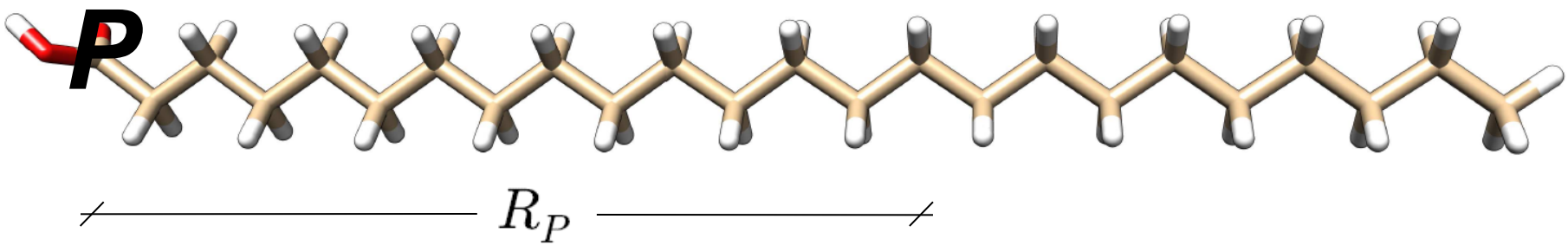
$$g_{iajb} \quad ; \; i, j \in P \quad , \; a, b \in [P]$$



Determine [P] in a black box manner such that errors in E_P is smaller than **Fragment Optimization Threshold (*FOT*)**

Distance decay of E_P





Occupied space partitioning of E_{corr}

Occupied atomic fragment energy

$$E_P^{\mathrm{O}} = \sum_{\substack{ij \in P \\ ab \in [P]}} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left(2 g_{iajb} - g_{ibja} \right)$$

(atomic fragment orbital space)

Occupied atomic pair interaction energy

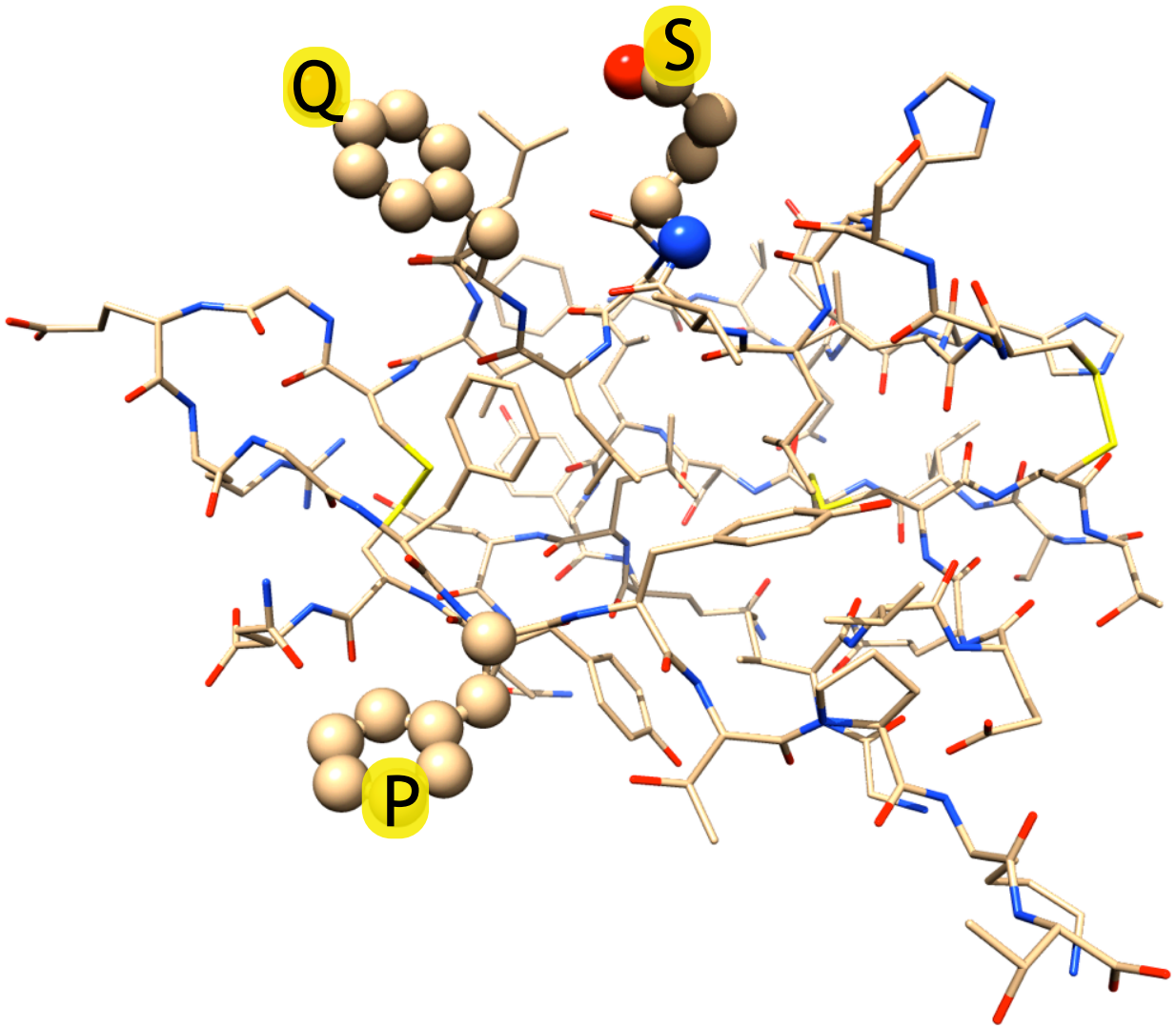
$$\Delta E_{PQ}^{\mathrm{O}} = \sum_{\substack{i \in P, j \in Q \\ ab \in [P] \cup [\Theta]}} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left(2 g_{iajb} - g_{ibja} \right) + \quad P \leftrightarrow Q \ term$$

(union of atomic fragment orbital spaces)

Insulin - three examples of atomic fragments

$$E_{\text{corr}} = \sum_{P} E_P + \sum_{P>Q} \Delta E_{PQ}$$

Quadratic scaling



$\mathbf{E_P}$ **determined to FOT precision**

↓

$\mathbf{\Delta E_{PQ}}$ **determined to FOT precision**

↓

$\mathbf{E_{corr}}$ **determined to FOT precision**

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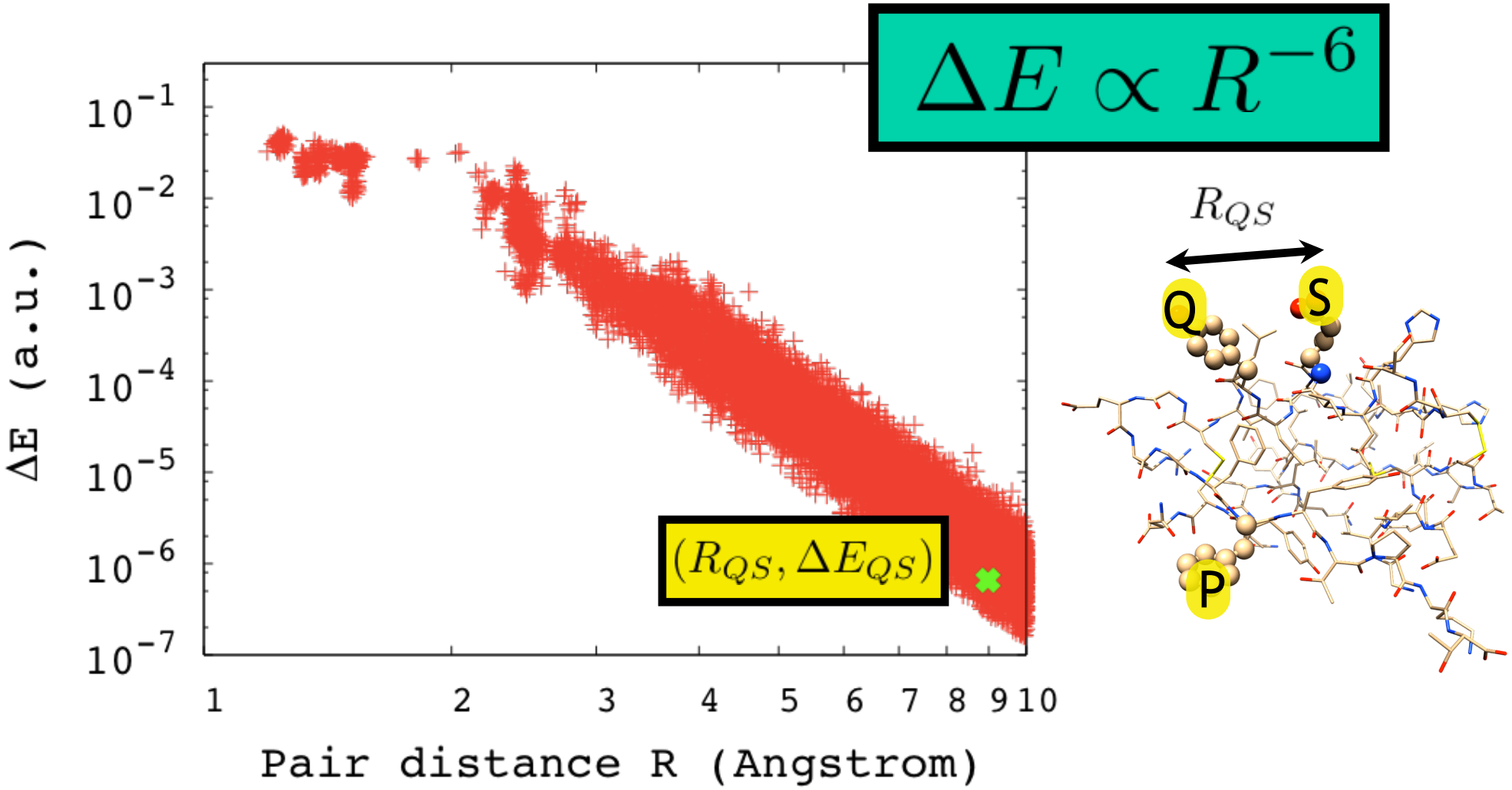
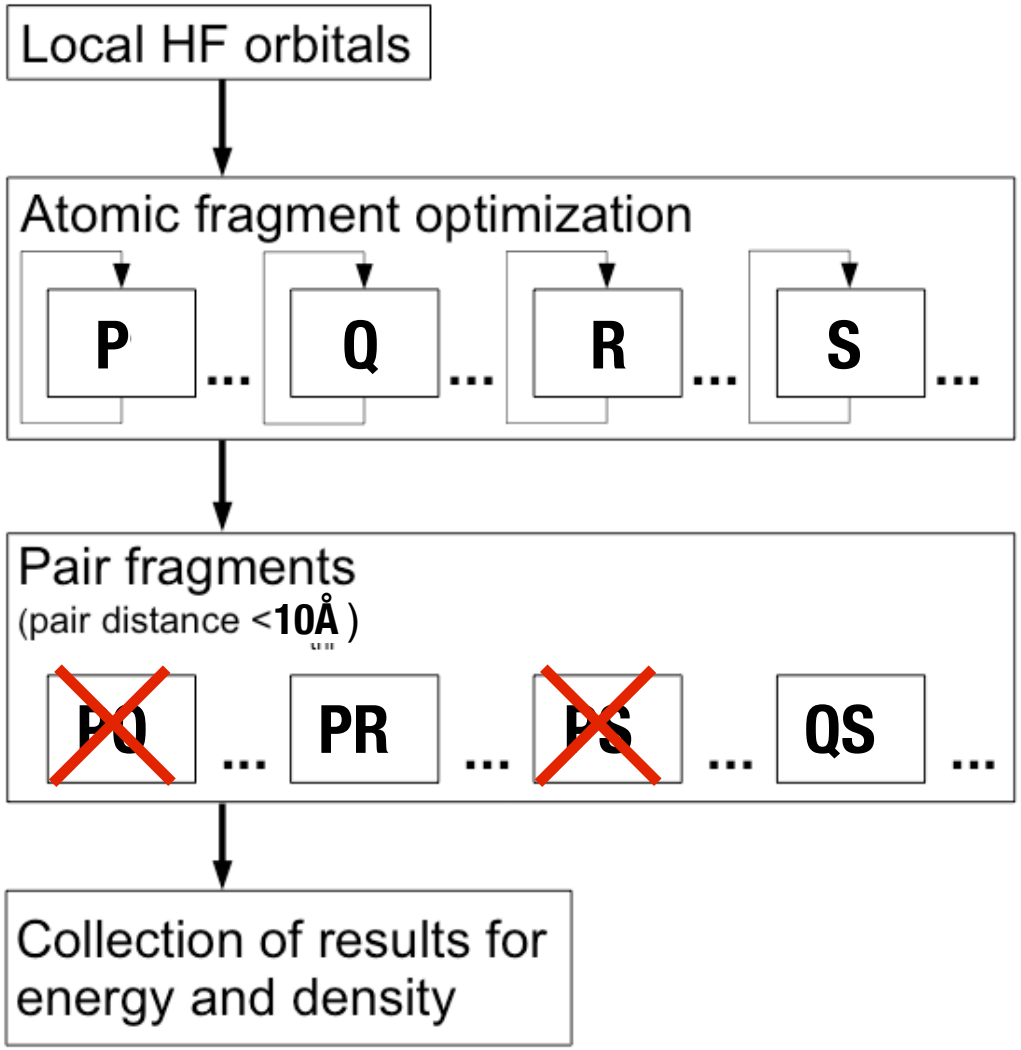
Insulin - pair interaction energies ΔE_{PQ}



Pairs separated by more than ~10 Å can be neglected without affecting the precision of the calculation

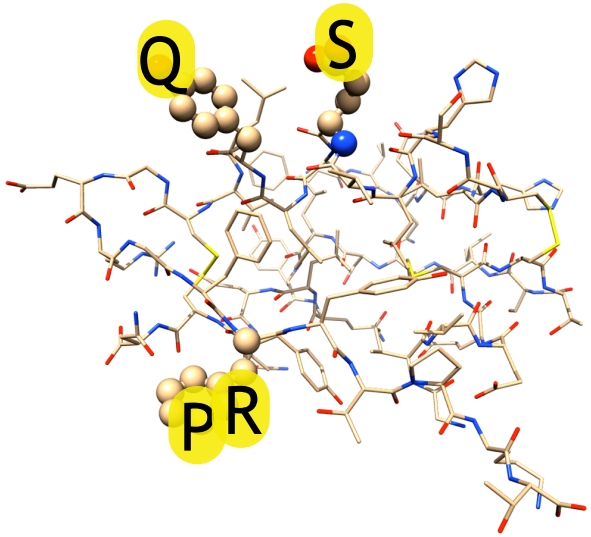
Linear scaling algorithm 19L

Summary of the DEC scheme



N atomic fragments

Formally: N*(N-1)/2 pair fragments
Use cut-off: const*N pair fragments



DEC is linear scaling and massively parallel

Parallelism in DEC calculation

Parallelism at three levels

Coarse grained parallelism

All fragment calculations E_P and ΔE_{PQ} carried out independently

Medium grained parallelism

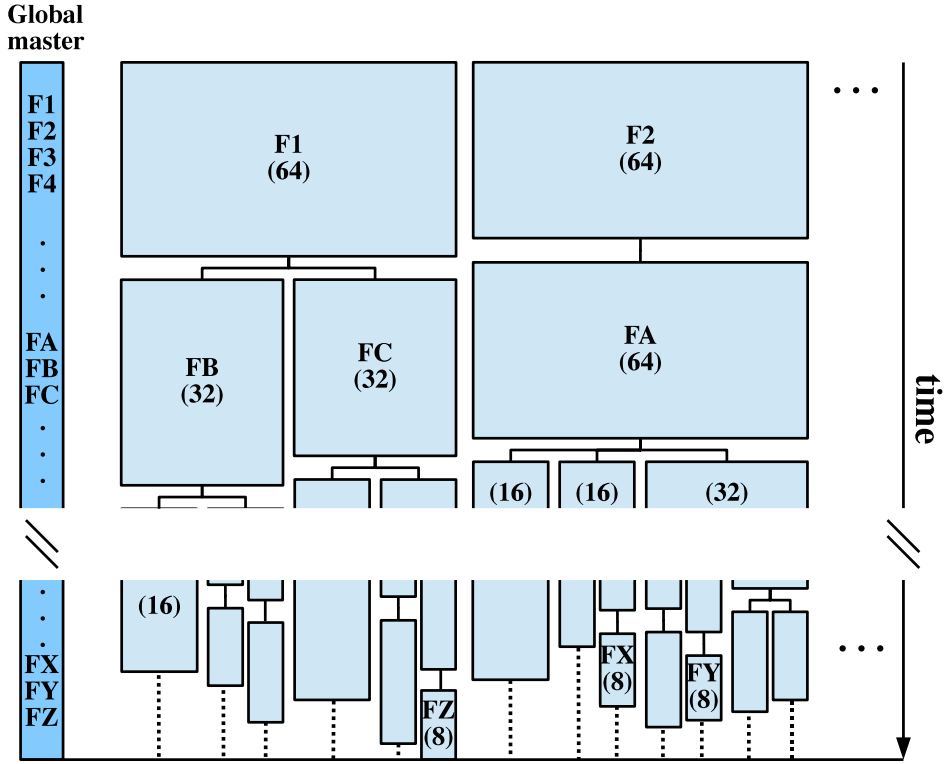
Individual fragment calculations (MPI)

Parallelism as for standard CC calc.

Fine grained parallelism

Exploiting multiple core(OpenMP)and GPU accelerators (OpenACC)

Parallelism in DEC calculation



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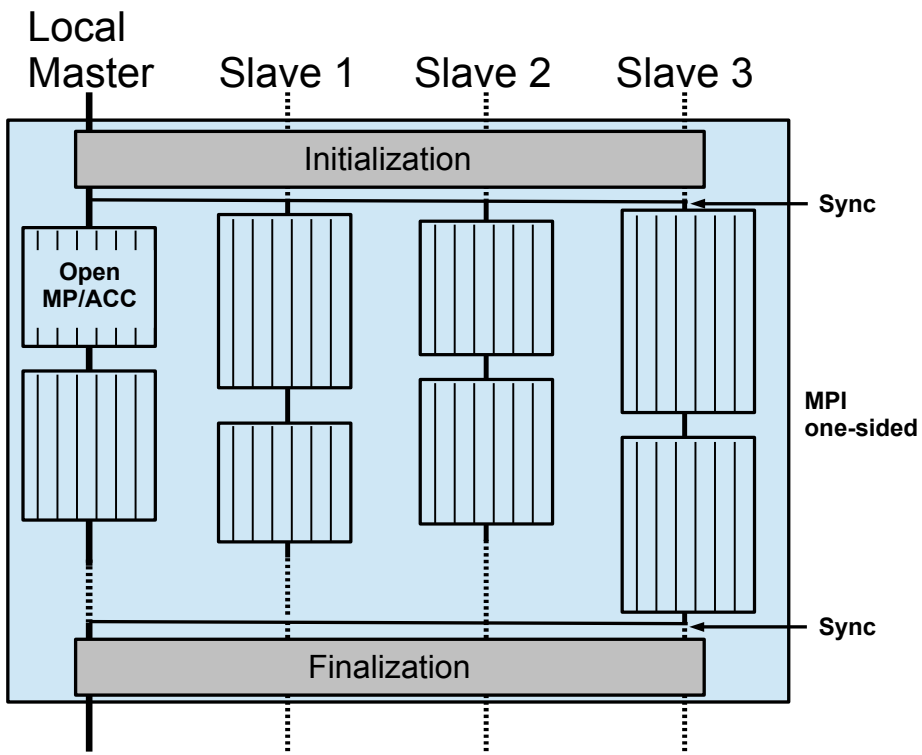

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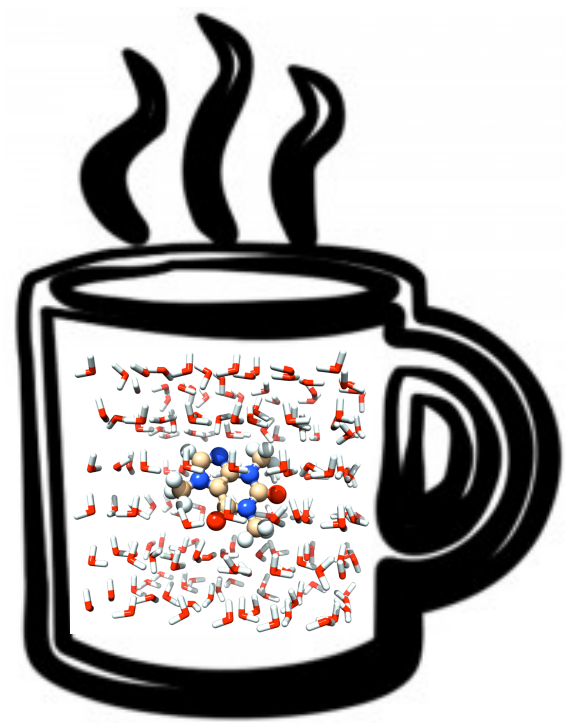
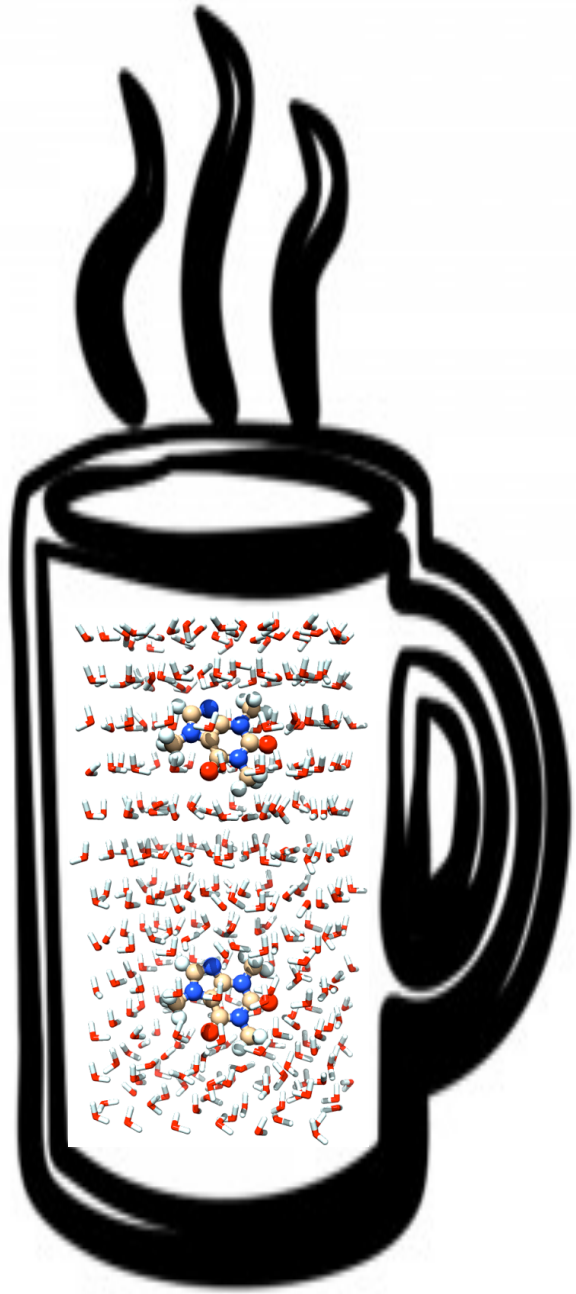
Exploiting multiple cores(OpenMP)and GPU accelerators (OpenACC)

“A nano-cup of coffee...”

- Calculate MP2 correlation energy and density using cc-pVDZ basis.
- Nanospresso (system **1**): 528 atoms (4278 BF.)
- Nanospresso Doppio (system **2**): 1056 atoms (8556 BF.)



Nanospresso



Nanospresso doppio

Time to solution (TTS)

System	#fragments	#nodes	TTS(hours)
1	7136	5890	1.66
1	7136	11780	0.93
2	16151	5890	4.49
2	16151	11780	2.37

- Calculations on Titan, Oak Ridge National Laboratory* using 8 OpenMP threads per MPI process. Nodes refer to NUMA nodes

- **Scaling with system size?**

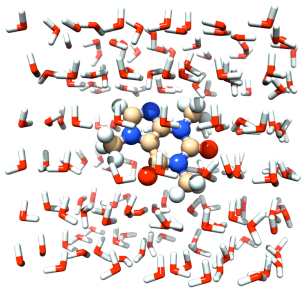
  #frags(2) / #frags(1) = 2.26 (ideal)
  TTS(2) / TTS(1) = 2.70 (5890 nodes)
  TTS(2) / TTS(1) = 2.55 (11780 nodes)

- **Parallel (strong) scaling** (ideal: 0.5)

  TTS(11780) / TTS(5890) = 0.56 (system 1)

  TTS(11780) / TTS(5890) = 0.53 (system 2)

1



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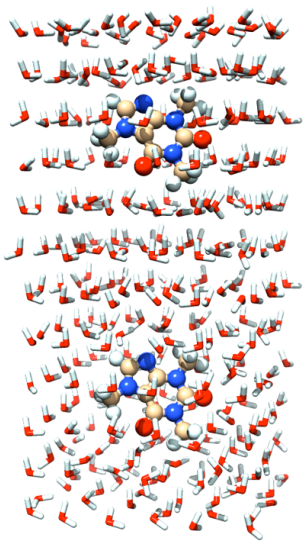
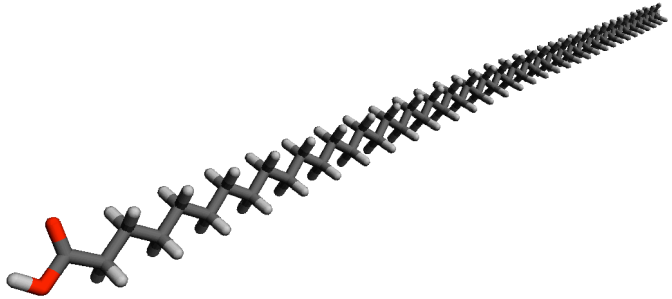


*https://www.olcf.ornl.gov/

DEC Correlation energy(au) vs. FOT

FOT	10^{-3}	10^{-4}
MP2	-11.41503	-11.59505
CCSD	-12.18642	-12.25120
CCSD(T)	-12.63602	-12.74882



$C_{64}O_2H_{128}$

cc-pVTZ

3772 AOs

- We expect to carry out a 10^{-5} calculation in the close future

- 10^{-4} DEC-CCSD(T) is possible with current computer facilities for large systems

- At the *SUMMIT 2018 supercomputer Oak Ridge National Laboratory* DEC-CCSD(T) becomes routine on large molecules with FOT 10^{-4} and 10^{-5}

Number of basis functions for which calculations have been carried out

Hartree-Fock (HF)	~40 000
MP2	~10 000
RI-MP2	~15000
CCSD	~4000
CCSD(T)	~4000

Precision of Coupled Cluster calculation

Standard Coupled Cluster

- Residual norm (***R***) of amplitude equation

DEC Coupled Cluster (new strategy which exploit locality efficiently)

- Fragment optimization threshold (***FOT***) for atomic fragment energies

Standard and DEC Coupled Cluster on par with respect to precision

- Single parameter (***R*** or ***FOT***) define the precision of energy, density, ...

Wish list for future computer

Hardware

- Larger fast-access memory
- Fast networks
- Accelerators (easy to use)

Operating environment

- System well tested and stable

- Many issues on previous machines,
  solved in collaboration with liaisons and vendors

- Problems should preferably be identified and
  solved before machine delivery

- Not all problems can be identified before machine delivery,
  support from liaisons and vendors has high priority

Libraries

- High level libraries for simple implementation of mathematical expressions using parallelism (example: general tensor contractions)

- Unified memory spaces (easy use of distributed data)

- Libraries with full control over memory footprint (either passive or active)

- Improved one-sided MPI performance (MPI_ACCUMULATE)

Exascale computing !!!

- Only meaningful with massively parallel code
- Shifts of algorithms
- Very few groups are taking up that task
- Difficult task; requires skilled specialist programmers
- Recognition from outside world

Change of Granting agency policy together with exascale initiative :

- Which chemical problem can you solve (using available methods)
- Equally important: Development of the methods for the future

For the future : *Close contact between developers of tomorrows code and tomorrows supercomputer software and hardware*

- Open new horizon we have not even dreamed about

RI MP2

- Fast and efficient MP2 method
- Small errors compared to standard MP2 from the finite auxiliary basis
- Special design of auxiliary basis has reduced the cost and error

DEC RI MP2 (Thomal Kjaergaard)

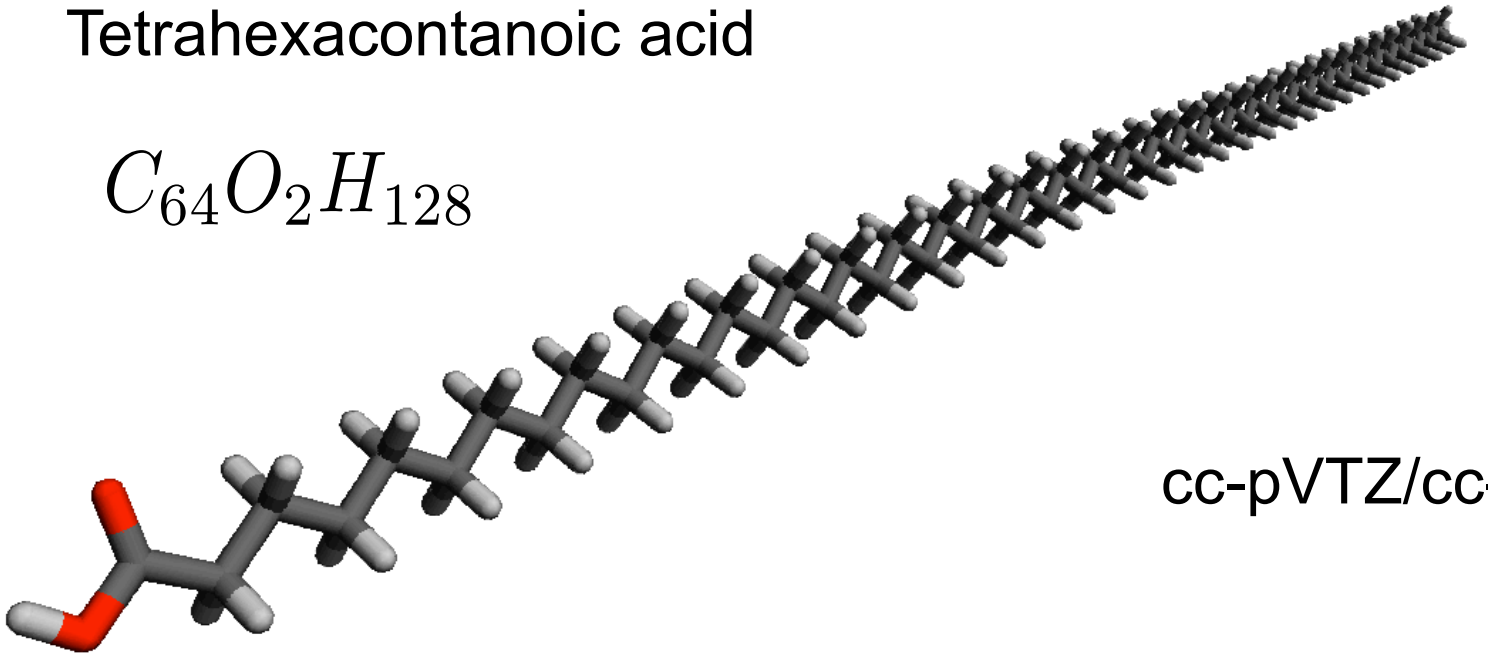
- Apply the RI approximation for individual fragment

  (corresponds to a local domain fitting)

DEC-RI-MP2: Results

Tetrahexacontanoic acid

$C_{64}O_2H_{128}$



cc-pVTZ/cc-pVTZ-RI

Number of Atomic Orbitals: 3772

Number of Auxiliary Atomic Orbitals: 9186

Number of Occupied Orbitals: 264

Number of Virtual Orbitals: 3508

DEC-RI-MP2: Results

FOT	Speedup	Error $[E_h]$
$1.0 \cdot 10^{-3}$	25.8	0.1193
$5.0 \cdot 10^{-4}$	24.8	0.06359
$1.0 \cdot 10^{-4}$	17.2	0.01404
$5.0 \cdot 10^{-5}$	14.6	0.008400
$1.0 \cdot 10^{-5}$	6.7	0.001803
$5.0 \cdot 10^{-6}$	3.7	0.0008282
$1.0 \cdot 10^{-6}$	0.99	0.0001728

$$\mathrm{RI} - \mathrm{error} \approx 0.00202748200$$

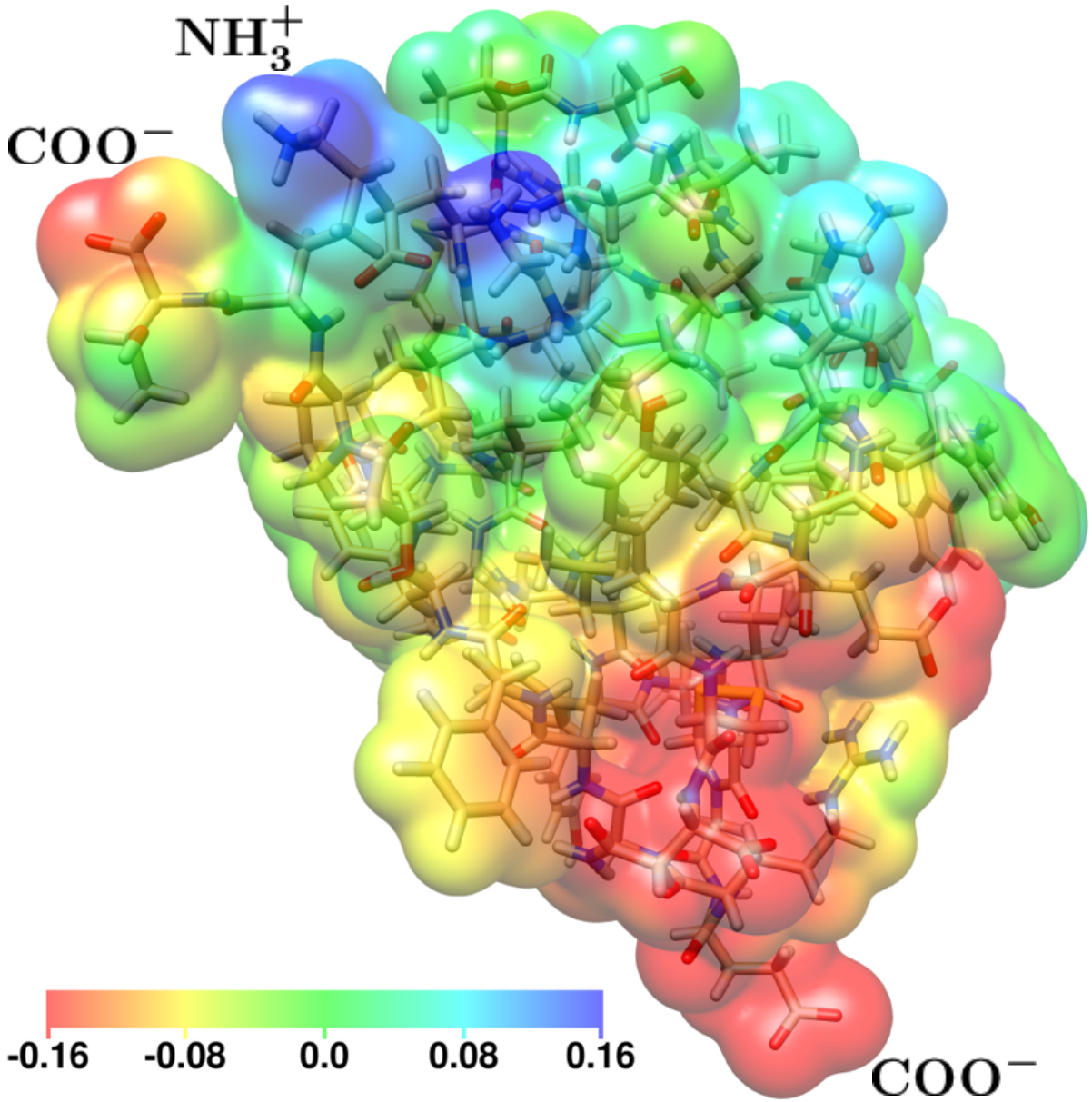
DEC-RI-MP2 calculation can be carried out provided the Hartree-Fock calculation can be performed

Conclusion for DEC

- New strategy for CC energy and properties which explore locality efficiently
- Full system in terms of CC calculations on small fragments of total orbital space
- Linear scaling and massive parallel algorithm
- Full control of errors in energy and cluster amplitudes
- Black box method

- Performance (speed) depends on locality of HF orbitals
- DEC on par with standard CC method,
  FOT defines precision as residual norm in standard CC

DEC MP2 electrostatic potential for insulin



Insulin monomer:

$C_{257}N_{65}O_{77}S_6H^-_{382}$

Red/blue regions indicate high/low potential energy for a positive point charge

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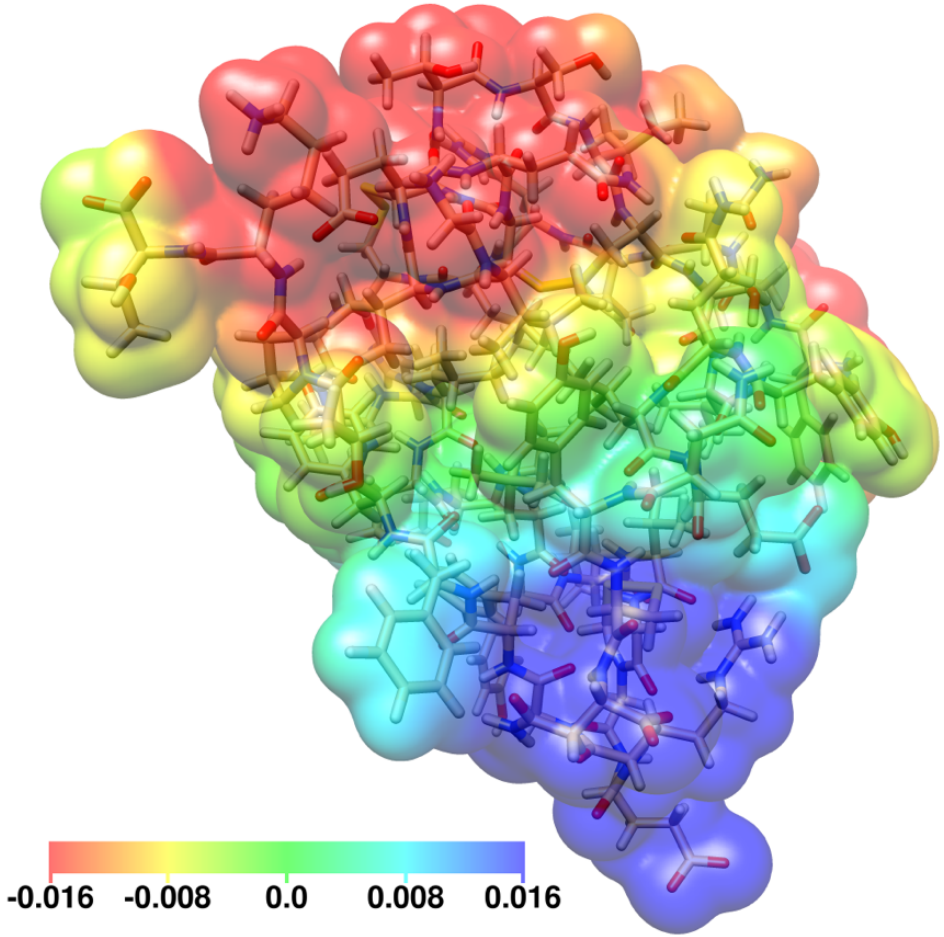
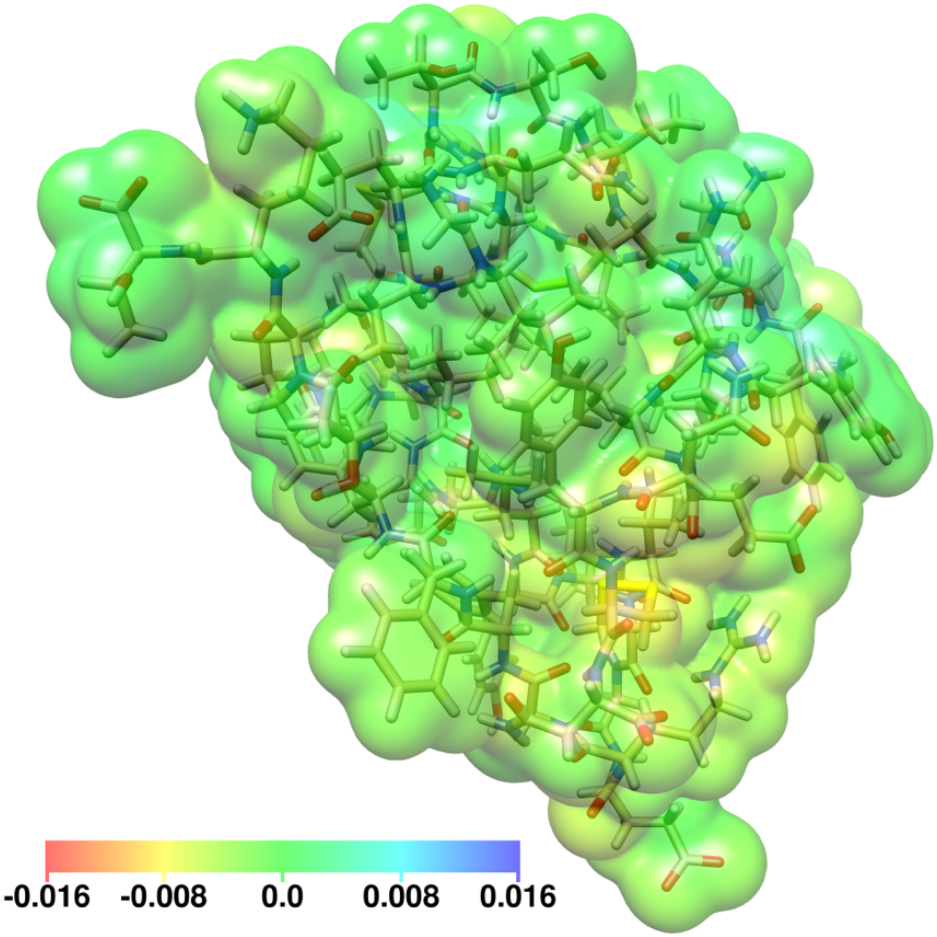
Benchmarking other models: DFT - MP2 difference in electrostatic potential

B3LYP - MP2
(no long-range correction)



CAMB3LYP - MP2
(long-range correction)



Red/blue regions correspond to increased/decreased electrostatic potential for DFT compared to MP2

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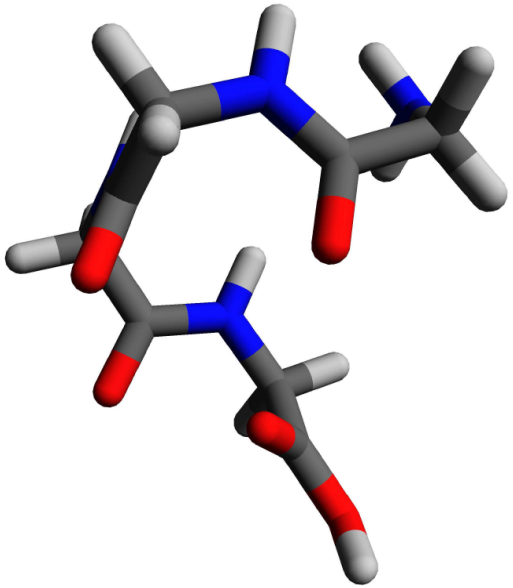
DEC Error vs. FOT



4 glycine residue in α-helix structure

cc-pVDZ

FOT	10^{-3}	10^{-4}	10^{-5}
ΔMP2	$3.61\ 10^{-2}$	$5.36\ 10^{-3}$	$3.99\ 10^{-4}$
ΔCCSD	$9.33\ 10^{-3}$	$1.16\ 10^{-3}$	$-6.03\ 10^{-4}$
ΔCCSD(T)	$2.06\ 10^{-2}$	$3.06\ 10^{-3}$	$-2.81\ 10^{-4}$