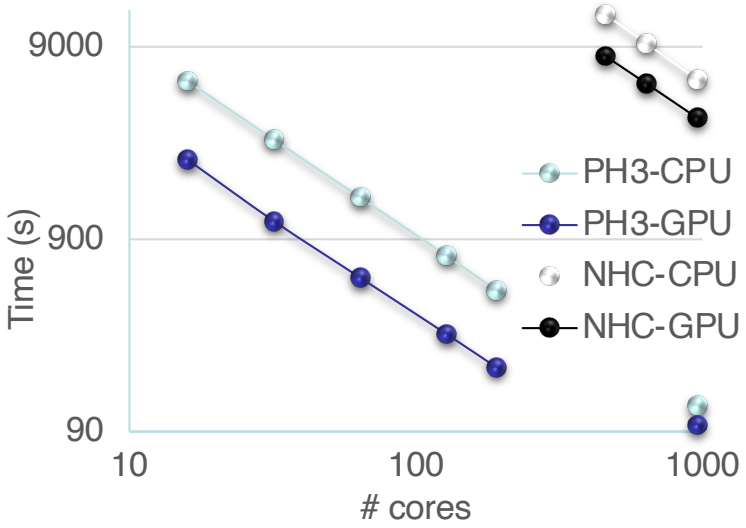
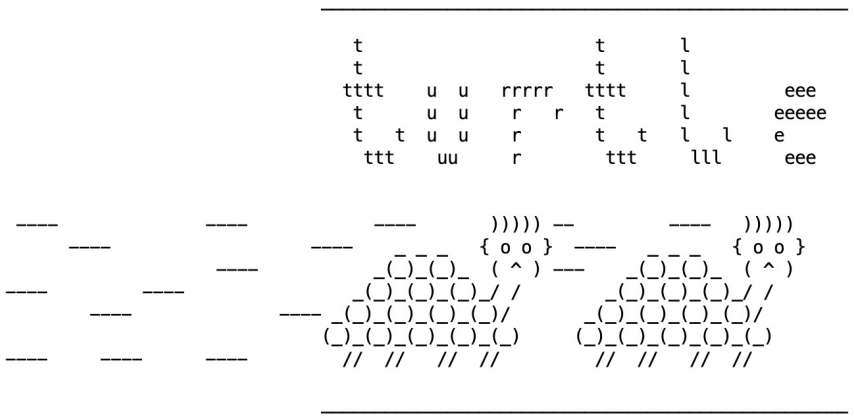
Accelerated chemistry





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university of groningen / faculty of science and engineering / stratingh institute for chemistry

Who am I?

- Theoretical chemist
- Interest in simulation of molecules and materials
- Approximate solutions to the Schrödinger equation
  - $H\Psi = E\Psi$
    - Eigenvalue equation

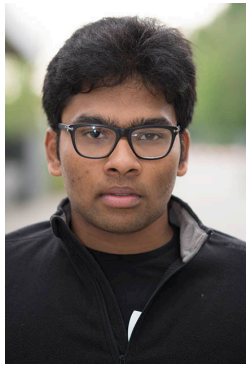
- Compute intensive

- Method development
  - Accuracy
  - Interpretability
    - Non-orthogonal theories

Collaborators

Johannes E.M.N. Klein

Ana V. Cunha



Kathir

Ria Broer

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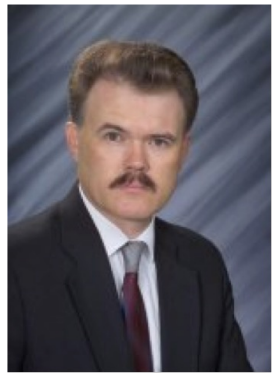

Tjerk Straatsma

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Computational Chemistry

- Find approximate solutions to the Schrödinger equation:
  - $H\Psi = E\Psi$
  - Eigenvalue equation
    - H is the Hamiltonian
    - Ψ the wavefunction (depends on the coordinates of the particles in the system)
    - E the energy

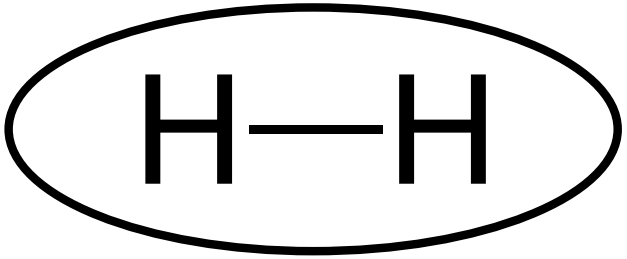
- Approximate solutions will give us access to “Chemistry”
  - Reaction mechanisms
  - Molecular properties
  - Spectra
  - Bonding in molecules

Finding approximate solutions

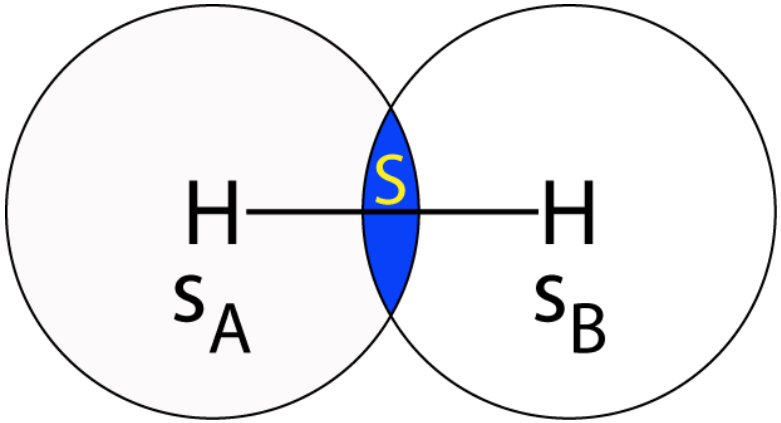
- The variational principle:
  - $\frac{\langle f|H|f\rangle}{\langle f|f\rangle} \geq E_0$ with *f* a trial wavefunction obeying the boundary conditions of the system
  - Expand *f* in a set of known functions: $f = \sum_\mu C_\mu \Phi_\mu$
  - Minimise energy to find the "best" C_μ
  - (**H**-E**S**)(**C**)=0
  - With $H_{\mu\nu} = \langle \Phi_\mu | H | \Phi_\nu \rangle$; $S_{\mu\nu} = \langle \Phi_\mu | \Phi_\nu \rangle$
  - The functions Φ are many- or 1-electron functions

Introduction to VB

- Alternative to MO theory
  - MO theory: delocalized, doubly occupied orbitals

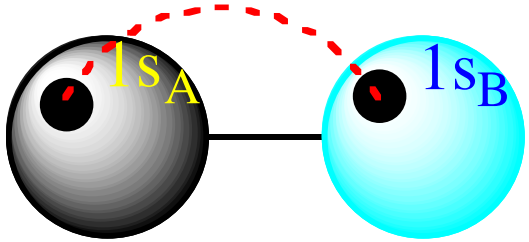


  - VB theory: atomic, singly occupied orbitals
    - Overlapping orbitals form a bond
    - Covalent, ionic contributions
    - Multiple resonance structures



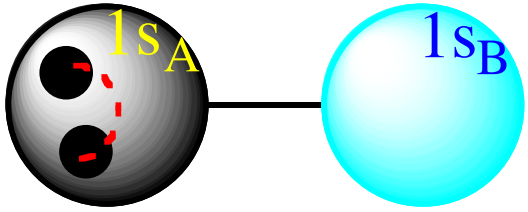
VB description of H_2

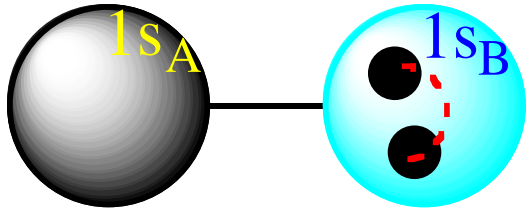
$$\Phi_{\text{cov}} = \left|s_A(1)\overline{s_B(2)}\right| - \left|\overline{s_A(1)}s_B(2)\right|$$



In minimal basis (STO-3G)
this equals FULL-CI

$$\Phi_{\text{ion}} = \left|s_A(1)\overline{s_A(2)}\right| + \left|s_B(1)\overline{s_B(2)}\right|$$





$$\Psi_{VB} = C_1\Phi_{cov} + C_2\Phi_{ion}$$

A structure

- A structure consists of a series of determinants (Δ) with fixed spincoupling coefficients (*s*):

$$\Phi_i = \sum_a s_a \Delta_a$$

- Determinants are antisymmetrised products of orbitals (ϕ):

$$\Delta = \left| \varphi_1 \cdots \varphi_n \right|$$

- Orbitals are linear combinations of basis functions (χ):

$$\varphi_i = \sum_a c_{ia} \chi_a$$

Final VB wavefunction

- Linear combination of structures:

$$\Psi_{VB} = \sum_i C_i \Phi_i$$

- Structure coefficients are determined in the usual way:

$$\left(\mathbf{H} - E\mathbf{S}\right)\mathbf{C} = 0$$

- Chirgwin-Coulson weights:

$$W_j = \sum_i c_i c_j S_{ij} \qquad \sum_j W_j = 1 = \sum_i \sum_j c_i c_j S_{ij}$$

- Gallup-Norbeck weights:

$$W_i = N\left|c_i\right|^2 / \left(\mathbf{S}^{-1}\right)_{ii}; \quad N^{-1} = \sum_i \left|c_i\right|^2 / \left(\mathbf{S}^{-1}\right)_{ii}$$

Needed in my research

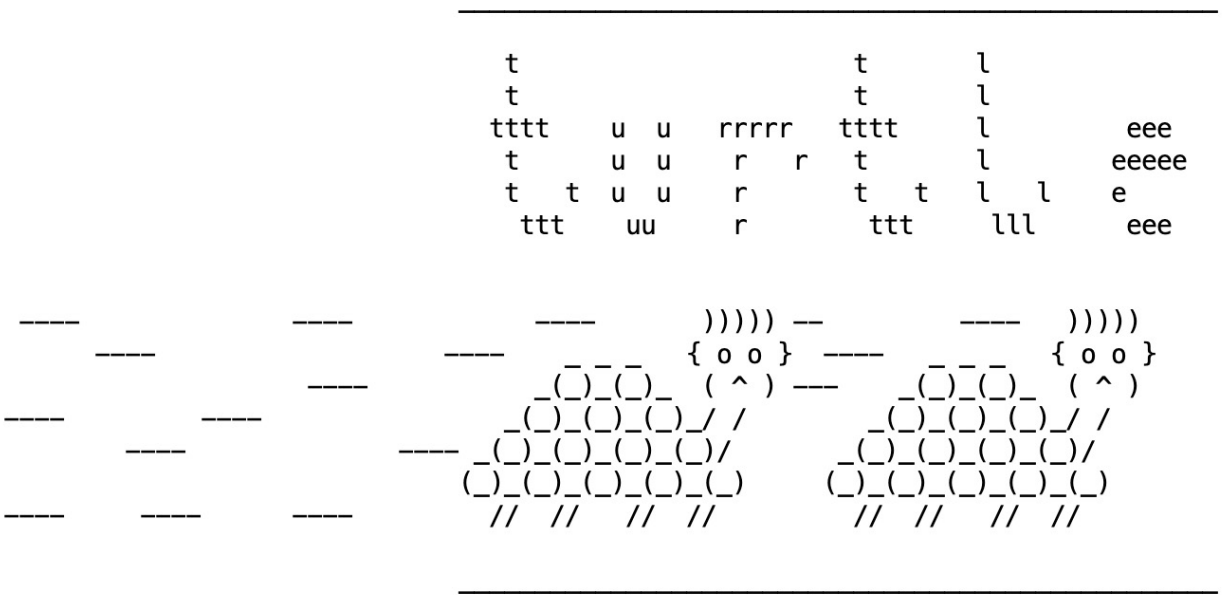
- Parallel codes that use accelerators

- Non-orthogonal theories:
  - MANY matrix elements of the type $\langle \Delta_\mu | H | \Delta_\nu \rangle$, with Δ an antisymmetrized product of orbitals, ϕ

$$\underbrace{\langle \Delta_\mu | H | \Delta_\nu \rangle}_{\sim 10^6} = \sum_{i,j} h_{ij} S^{(i,j)} + \sum_{i<j} \sum_{k<l} \underbrace{[(ij|kl) - (ik|jl)]}_{\sim 10^{10}} S^{(i,j,k,l)}$$

  - Matrix elements are independent; distribution of integrals
- Computer codes:
  - TURTLE
  - GronOR

TURTLE



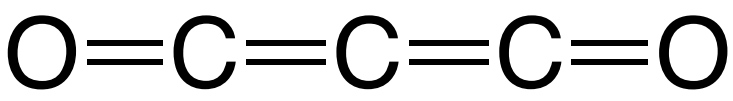
- General VBSCF program, developed in Utrecht (Dr. J.H. van Lenthe)
- Fortran 77, parallelized using MPI
- Accelerated using openACC (in collaboration with Dr. A. Varbanescu, UvA)

Challenges in accelerating the code

- It is an old code, written by many different people
- Optimized for older machines and serial execution
- MPI parallelized later
- Time consuming part: two, six nested loops that have to be executed in the same order
  - Restructuring the code to combine the loops and to remove the order dependency at the cost of serial performance

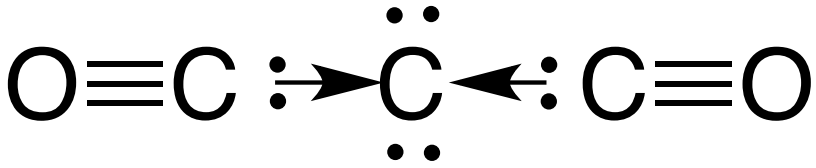
Carbonsuboxide

- OC=C=CO
  - Conventional bonding



or

  - Dative bonding?

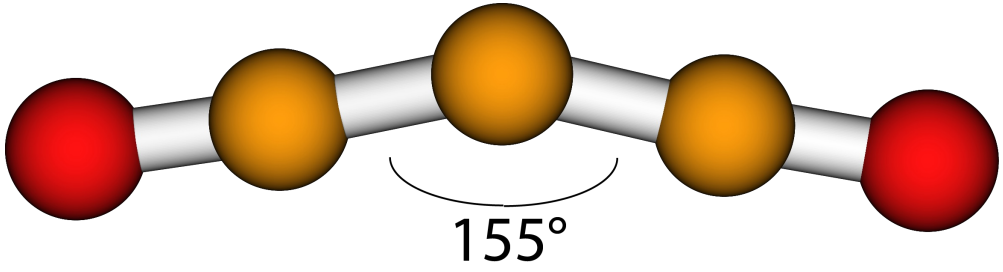


- Compare with CO_2, $CH_2{=}C{=}CH_2$, and $(OC)Au(CO)^+$

R. Tonner, G. Frenking, *Chem. Eur. J.*, **14** (2008), 3260-3272

Geometry of carbonsuboxide

- CO_2
  - Linear
- OCCCO
  - Slightly bent



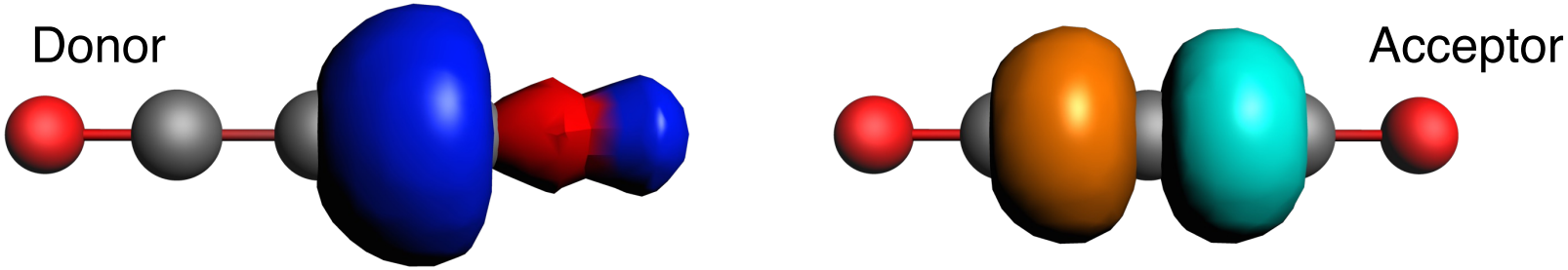
Energy decomposition analysis

- Orbital interaction energy (BP86/TZ2P)
  - CO_2

Fragment 1	Fragment 2	ΔE_{orb} (kcal/mol)
^{3}P(O)	^{5}S(C)	-1051.23
^{1}D(O)	^{1}D(C)	-1079.92

  - OC=C=CO

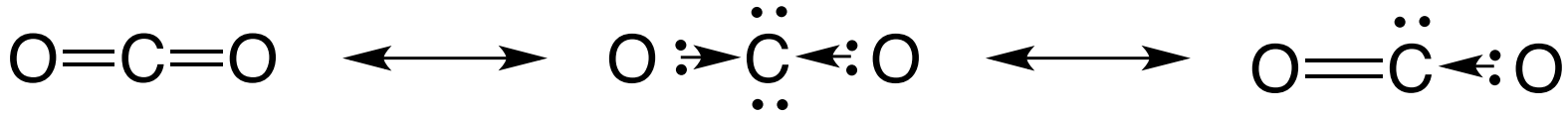
Fragment 1	Fragment 2	ΔE_{orb} (kcal/mol)
^{3}(CO)	^{5}S(C)	-609.91
^{1}(CO)	^{1}D(C)	-603.80



R. Tonner, G. Frenking, *Chem. Eur. J.*, **14** (2008), 3260-3272

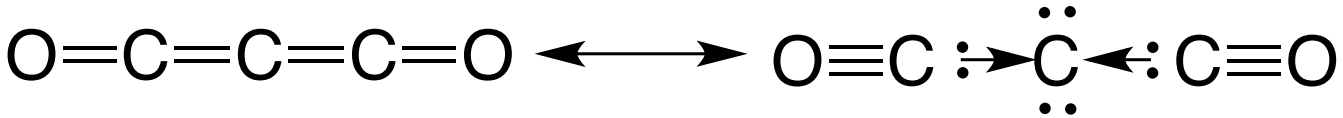
VB wavefunction composition

- CO_2

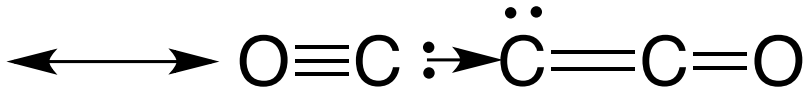


0.88 0.01 0.11

- OC=C=CO



0.64 0.02



0.35

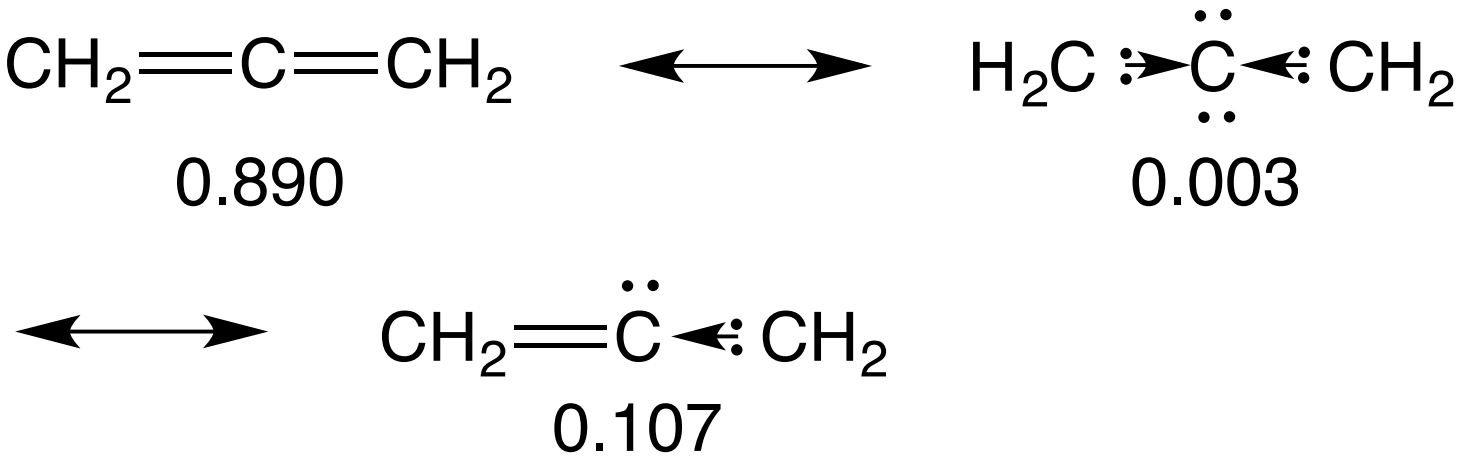
- Carbene character, but not a full carbone!

$H_2C{=}C{=}CH_2$

- Energy decomposition

Fragment 1	Fragment 2	ΔE_{orb} (kcal/mol)
$^3(CH_2)$	$^5S(C)$	-514.27
$^1(CH_2)$	$^1D(C)$	-697.34

- VB wavefunction

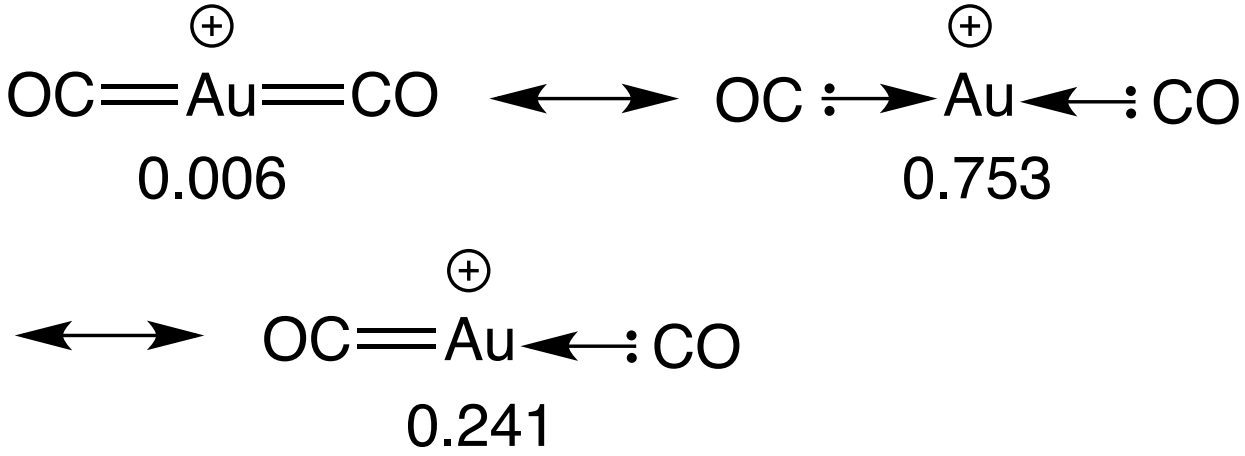


OC:Au:CO$^+$

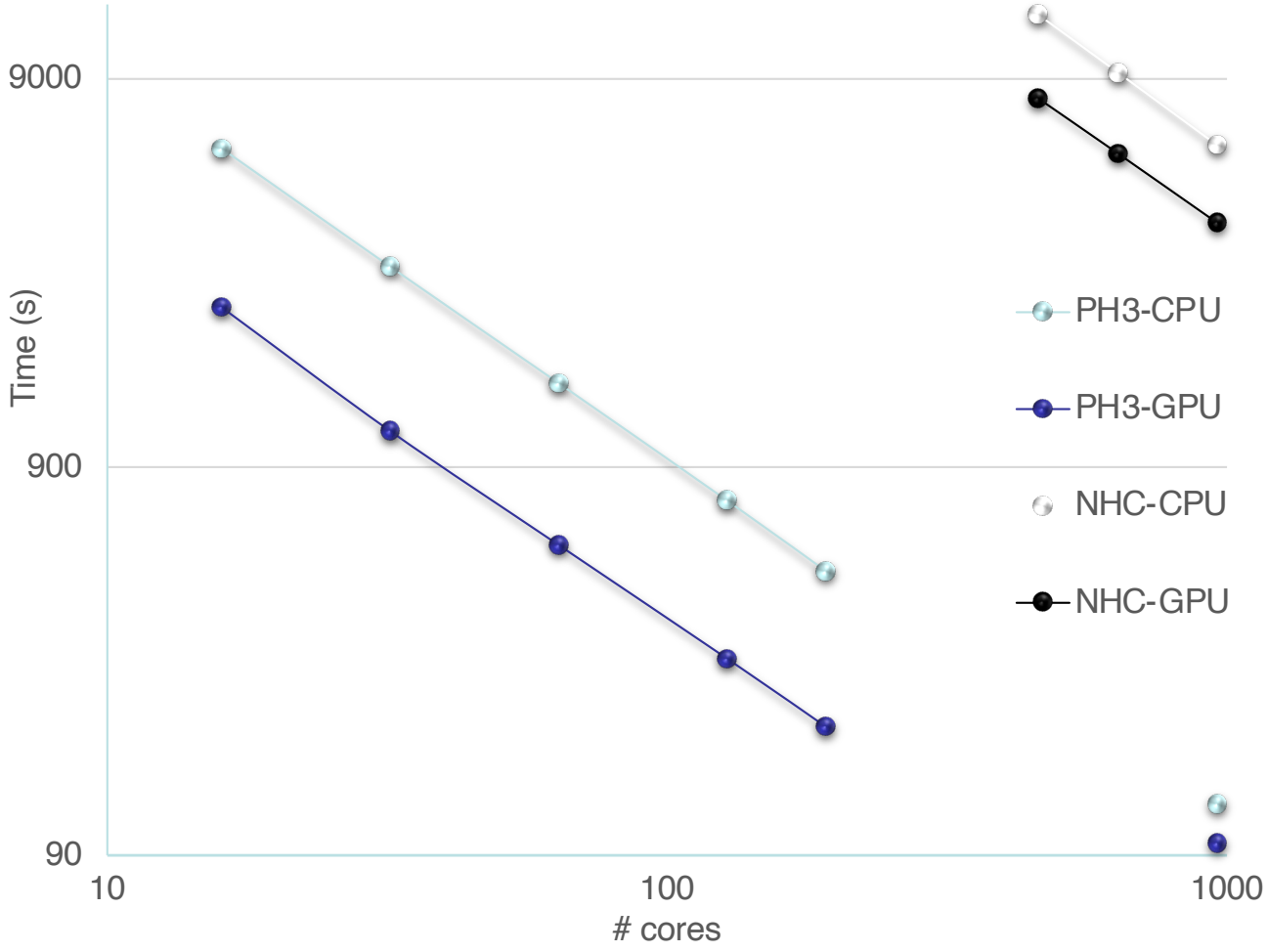
- Energy decomposition

Fragment 1	Fragment 2	ΔE_{orb} (kcal/mol)
^{3}(CO)	^{5}(Au)	-609.71
^{1}(CO)	^{1}(Au)	-108.70

- VB wavefunction



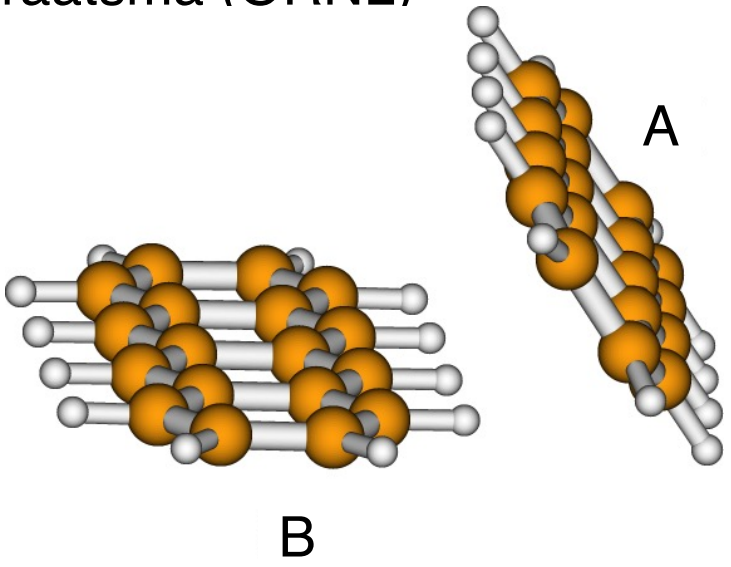
Timings



- Linear scaling with cores
- GPU version ~2x faster
- More optimization needed

GronOR

- Non orthogonal CI program, geared towards the description of molecular clusters in terms of molecular states
- Developed in collaboration with T.P. Straatsma (ORNL)
- MPI+openMP parallelization
- Accelerated using openACC



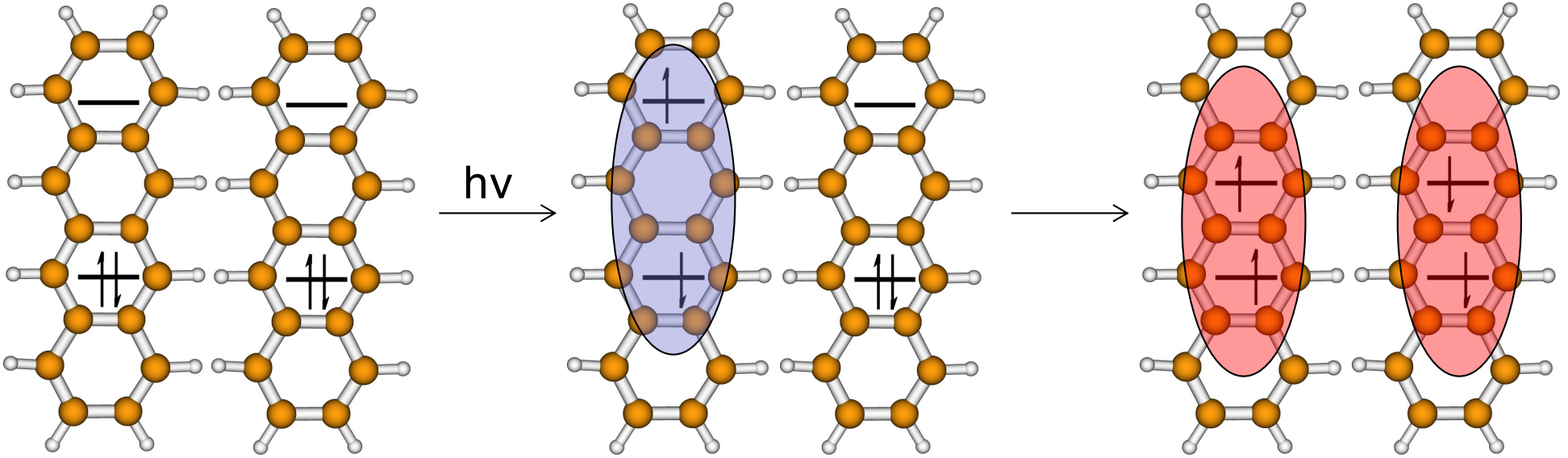
$$\Psi = c_1\Phi_{AB}^{00} + c_2\Phi_{AB}^{10} + c_3\Phi_{AB}^{01} + c_4\Phi_{AB}^{TT} + \ldots$$

Parallel implementation

- Controller/worker model
  - Controller distributes to group of workers matrix elements to calculate
  - Group of workers can run on GPU or CPU
  - CPU workers run in parallel using openMP

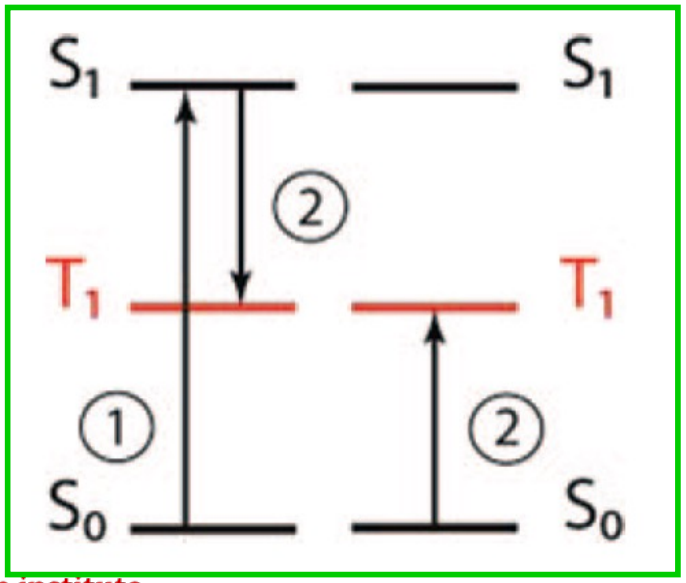
- Fault resiliency:
  - Controller
    - keeps track of which batches have been calculated
    - continues to distribute batches until all have been returned, also the ones that had been sent out before

Application: Singlet fission



SF: spin allowed radiationless process

M. B. Smith, J. Michl, *Chem. Rev.* **110** (2010), 6891

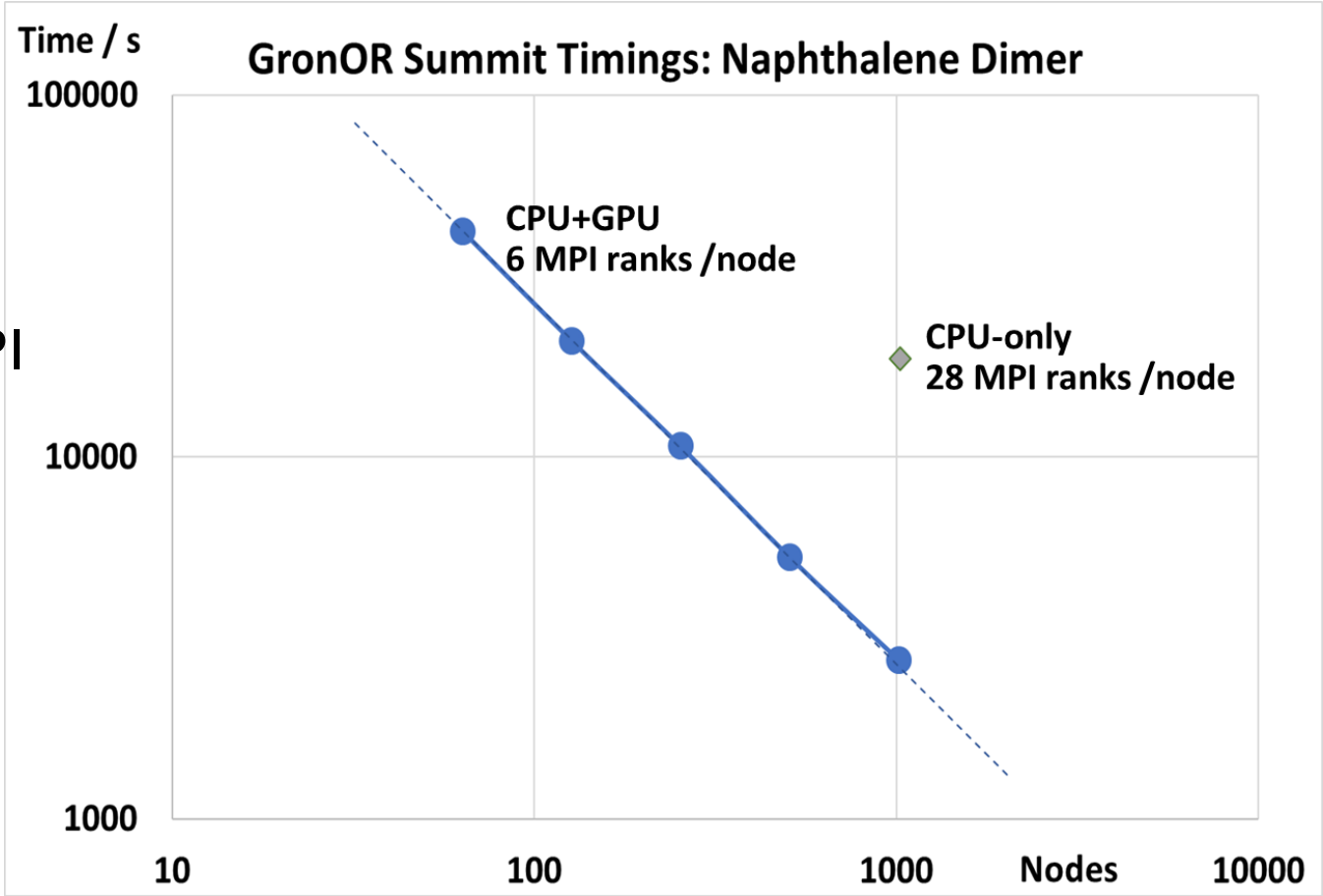


$$k_{SF} \propto \left|\left\langle \Psi_f \middle| H \middle| \Psi_i \right\rangle\right|^2 = \left|\left\langle S_0 S_1 \middle| H \middle| {}^1TT \right\rangle\right|^2$$

Performance of GronOR

Benchmark run on Summit, requiring 112,867,800 matrix element evaluations

- Each node with 6 MPI ranks
- 1 GPU per rank
- Good scalability with number of nodes
- Performance improvement from GPU is **6.8x**



Reduction of required 2-e⁻ integrals

- The MOs in the CASSCF wavefunction are expressed in *N* AOs
  - # 2-e⁻ integrals ~ $N^4/8$

- The *n* inactive + active MOs of all states of a molecule form a basis as well:

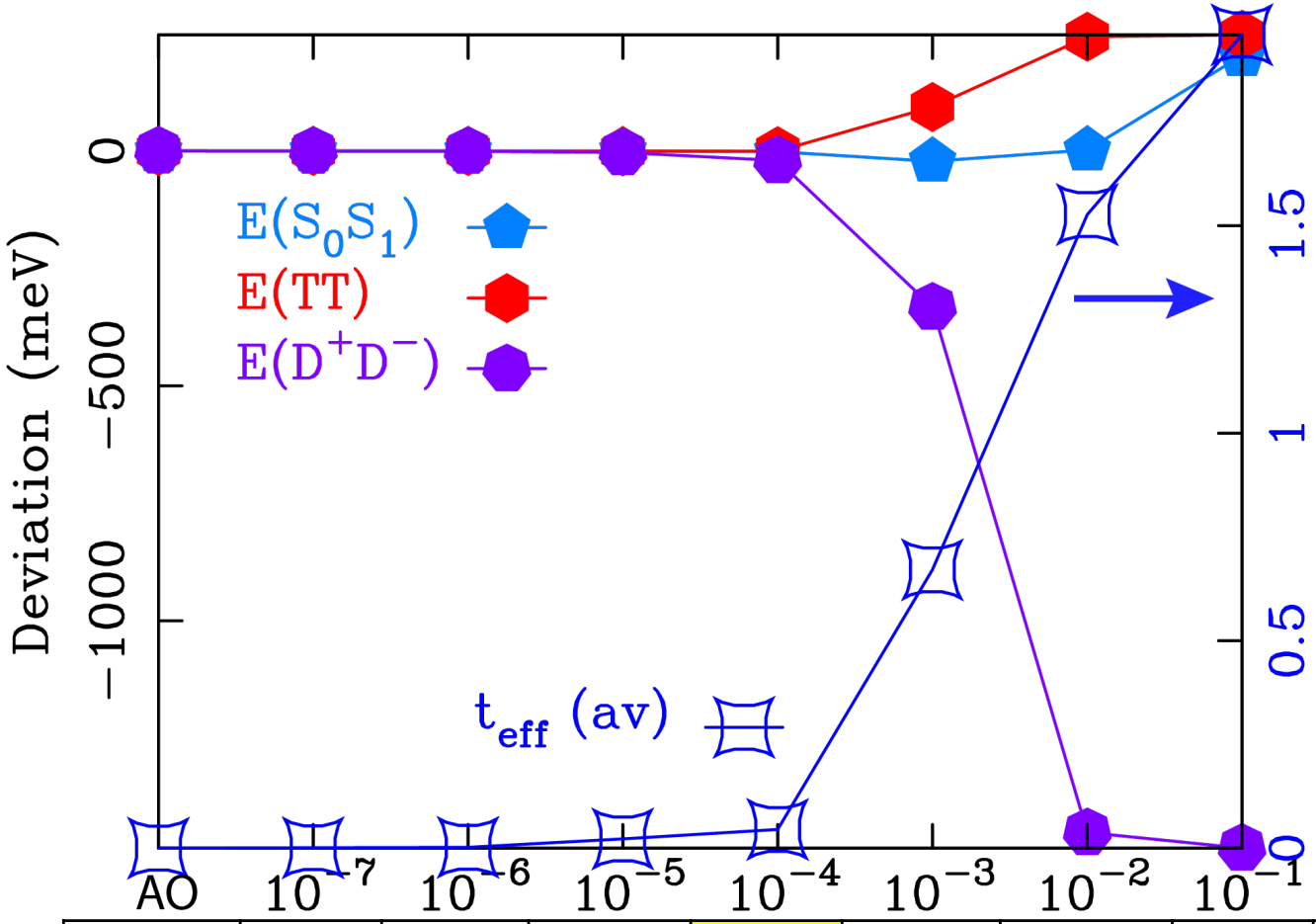
$$\left\{\phi_1^{S_0},\ldots,\phi_n^{S_0},\phi_1^{S_1},\ldots,\phi_n^{S_1}\right\}$$

- Redundant basis, eliminate linear dependencies, based on threshold ε, and transform MOs and 2-e⁻ integrals to new basis

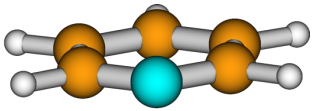
- Dimension of new basis $m << N$

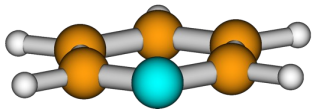
R.K. Kathir, C. de Graaf, R. Broer, R.W.A. Havenith, *J. Chem. Theory Comput.*, **16** (2020), 2941

Improvement of algorithm



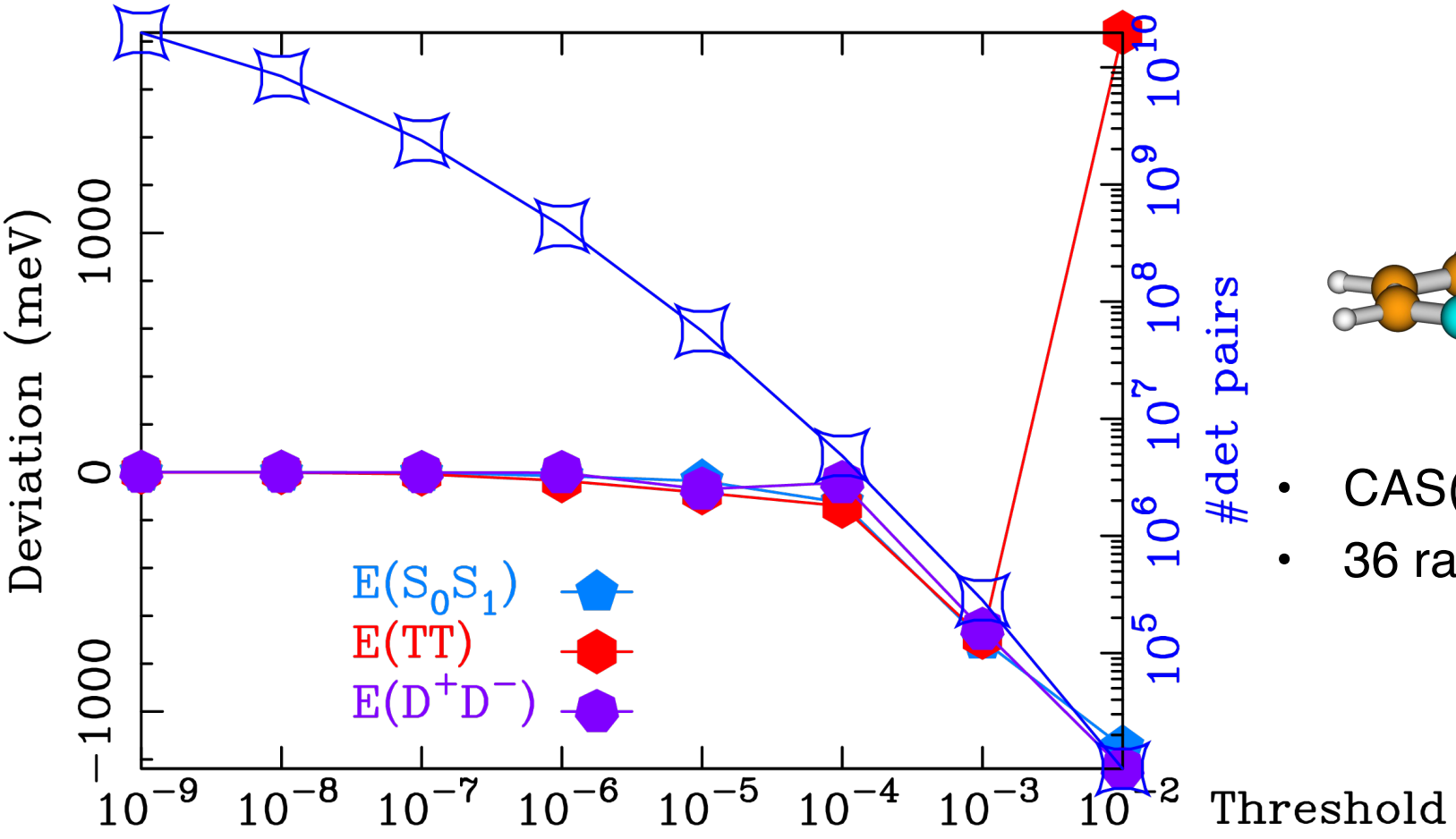
CAS(4,4)/
cc-pVTZ
32 nodes,
6 ranks/node

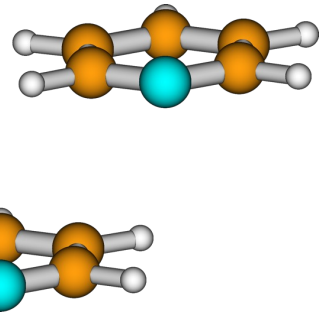




570	148	136	110	98	72	54	48	#bf
46000	841	600	257	162	47	15	9.1	Integral size (MB)
2408	253	244	226	219/ 73	210	205	204	Time (s)

Improvement of algorithm





- CAS(6,6)/6-311G**
- 36 ranks/node

1024		1024		64	1024*			Nodes
6238		3002		406	87			Time (s)

*6 ranks/node

Conclusions

- Algorithm is important
- Supercomputers and use of accelerators make large calculations possible in combination with smart algorithms
- Working on existing codes is difficult:
  - Implementation of most efficient parallelization strategy may require substantial restructuring of the code

Financial support

- OLCF for computer time on SUMMIT (ESP, DD)
- FOM Focus Group ‘Next Generation Organic Photovoltaics’ (DIFFER)
- FOM/Shell
- ITN-EJD-TCCM (Horizon2020)

DIFFER
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