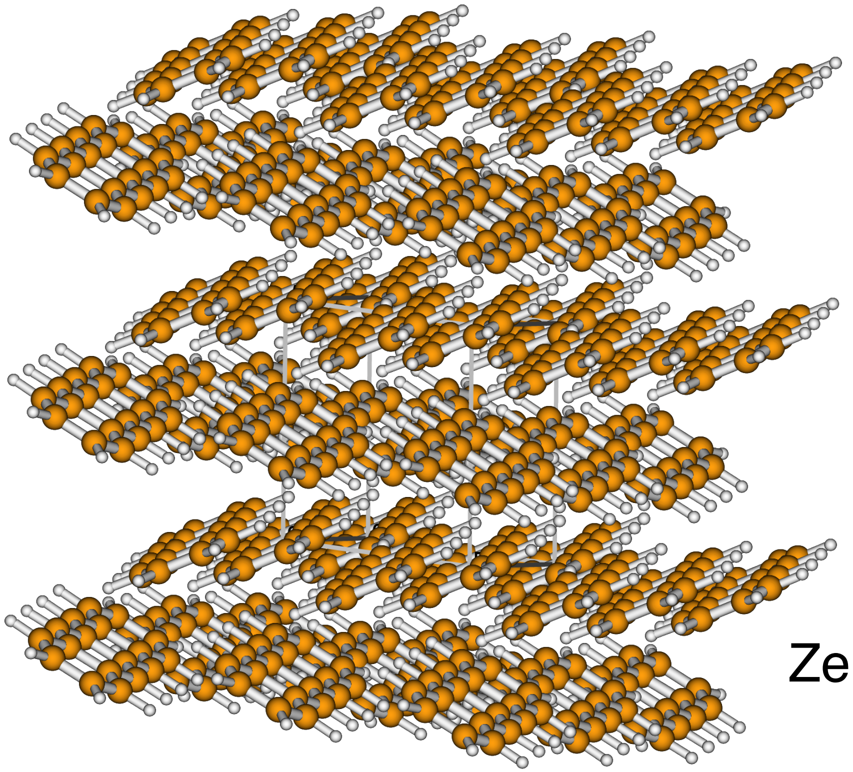
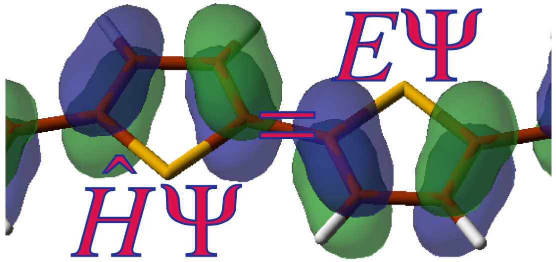
Opening New Frontiers in Singlet Fission Research





$$\hat{H}\Psi = E\Psi$$

Remco W. A. Havenith

Stratingh Institute for Chemistry,
Zernike Institute for Advanced Materials,
University of Groningen,
The Netherlands

Ghent Quantum Chemistry Group, Ghent University, Belgium

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

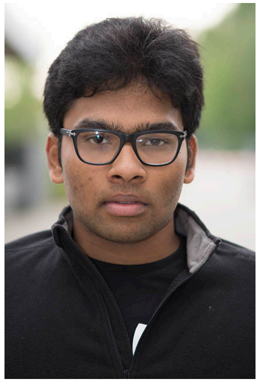
Who contributed

university of groningen

FOM

Ria Broer

Luis Enrique



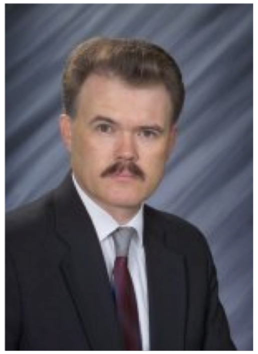
Kathir

university of groningen

icrea
Institució Catalana de Recerca i Estudis Avançats

Universitat Rovira i Virgili

Coen de Graaf



OAK RIDGE National Laboratory | OAK RIDGE LEADERSHIP COMPUTING FACILITY

Tjerk Straatsma

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

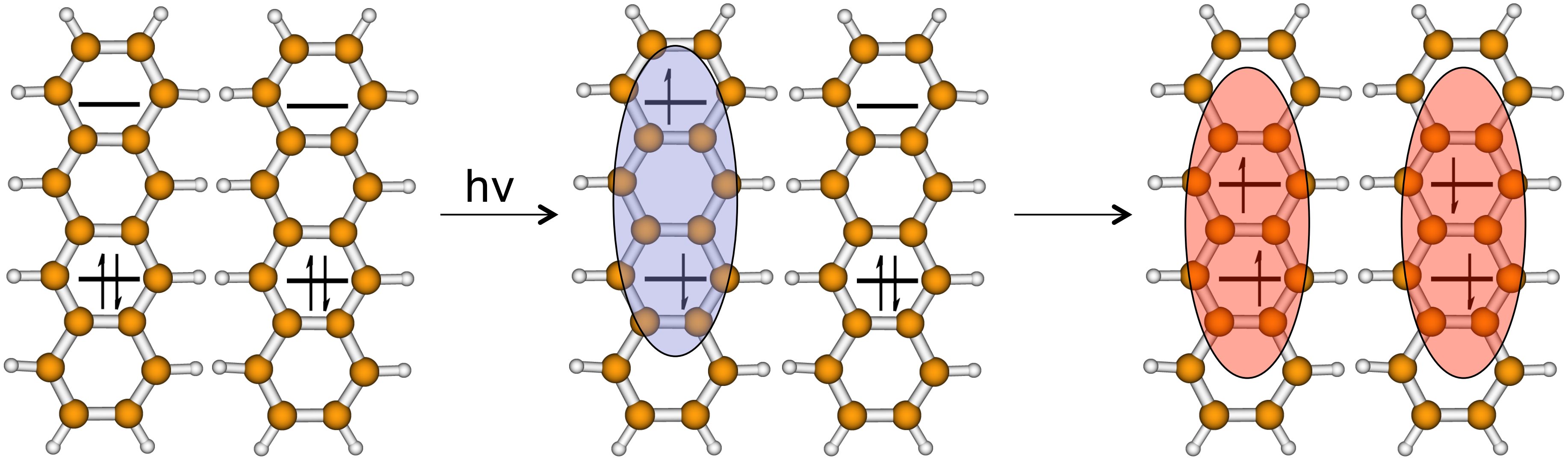
FOM Focus Group Groningen 'Next Generation Organic Photovoltaics'

- Aim:
  - Deliver the science for highly efficient, long-lived, and low-cost organic photovoltaic devices
- Challenge:
  - Charge separation at the donor/acceptor interface
- Approach:
  - Multi-disciplinary:
    - Material development
    - Physical characterisation (OPV device physics)
    - *Theoretical modelling*

Theoretical challenges

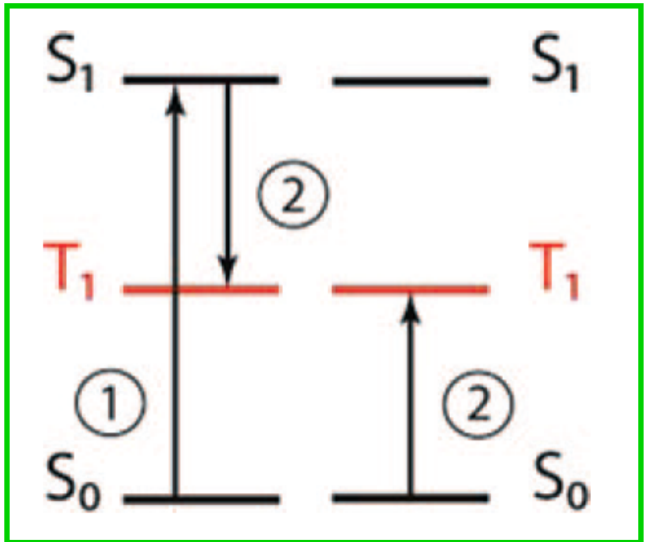
- Predict molecular properties that determine the dielectric properties of the interface
  - Dipole moments
  - Polarisability
- Modelling of the donor/acceptor interface
  - Molecular Dynamics simulations
    - Time scales of molecular motion
- Calculation of the excited states
  - Theoretical methods
  - Influence of molecular structure
  - Influence of the embedding using multiscale modelling
- Approximation of the electron/energy transfer rates

Singlet fission



SF: spin allowed radiationless process

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



It is attractive to build the wavefunctions of the solid from state-specific molecular wavefunctions

Singlet fission rate

- Fermi Golden rule in diabatic representation (Marcus theory)

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

  - Electronic coupling between diabatic states
    - Directly accessible with our non orthogonal CI approach

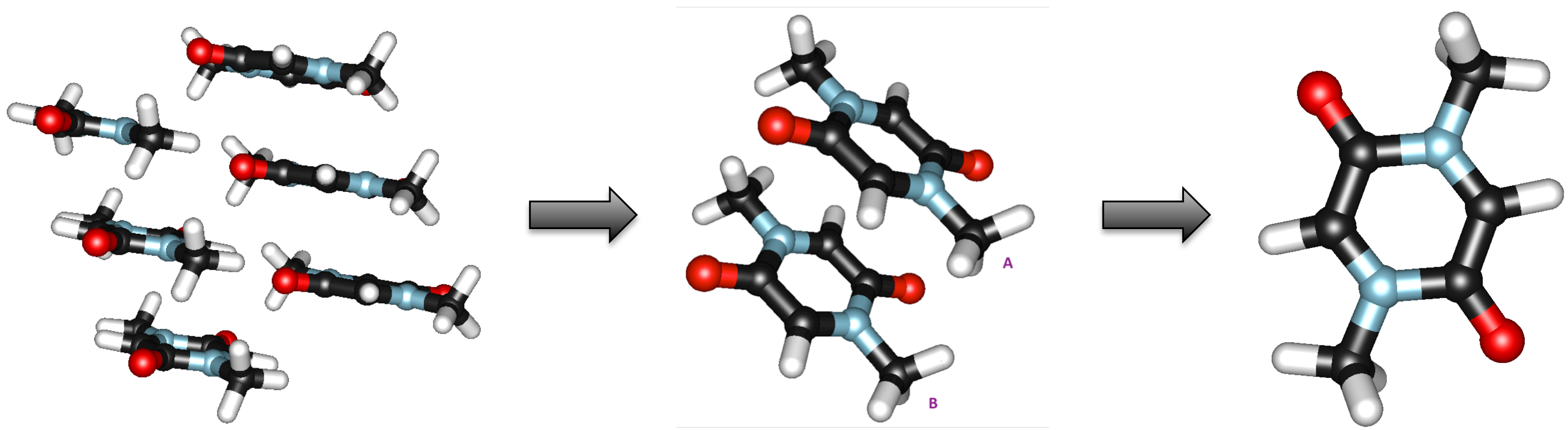
- Adiabatic representation: Non-adiabatic couplings (Landau-Zener model)

$$\langle \Psi_f | \frac{\partial}{\partial Q} | \Psi_i \rangle$$

  - Potential energy surfaces and conical intersections/ crossings

P.F. Barbara, T.J. Meyer, M.A. Ratner, *J. Phys. Chem.* **100** (1996), 13148
F. Bernardi, M. Olivucci, and M.A. Robb, *Chem. Soc. Rev.* **25** (1996), 321

Cluster approximation for solids



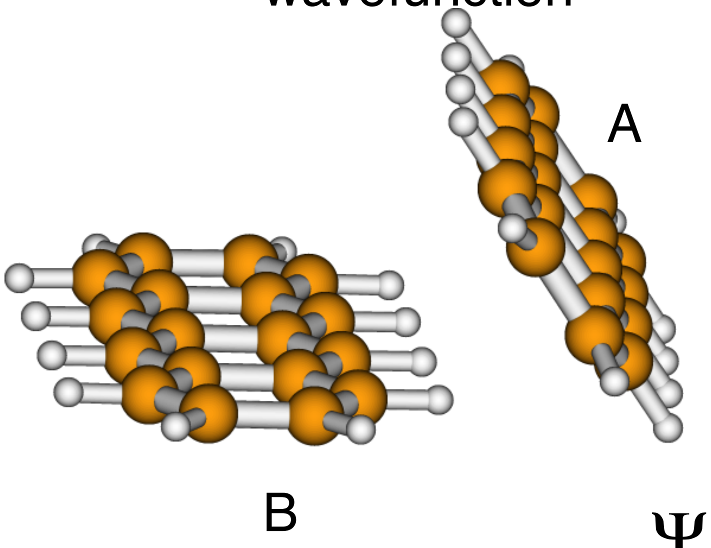
- Describe solid in terms of molecular wavefunctions
- Compute wavefunctions of each molecule for specific states (CASSCF)
- Form many-electron basis functions (S_0S_0, S_0S_1, ^1TT, CT), each describing a particular combination of molecular states

Non orthogonal configuration interaction

- Describe wavefunctions of a cluster of molecules in terms of (localised) molecular many-electron basis functions (MEBF)
  - MEBFs are spin-adapted antisymmetrised products of molecular wavefunctions:

$$\Phi_{AB}^{KL} = A(\Phi_A^K \times \Phi_B^L)$$

  - Molecular wavefunction can be any multiconfigurational wavefunction



Ψ^0 : Ground state

Ψ^1 : Singlet excited state

Ψ^T : Triplet excited state

$$\Phi_{AB}^{00} = A(\Psi_A^0 \times \Psi_B^0)$$

$$\Phi_{AB}^{10} = A(\Psi_A^1 \times \Psi_B^0)$$

$$\Phi_{AB}^{01} = A(\Psi_A^0 \times \Psi_B^1)$$

$$\Phi_{AB}^{TT} = A(\Psi_A^T \times \Psi_B^T)$$

$$\vdots$$

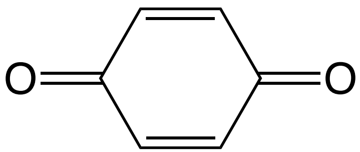
$$\Psi = c_1\Phi_{AB}^{00} + c_2\Phi_{AB}^{10} + c_3\Phi_{AB}^{01} + c_4\Phi_{AB}^{TT} + \ldots$$

Non Orthogonal Configuration Interaction

- Wavefunction expanded as: $\Psi = \sum_{i=1}^{N} C_i \Phi_i$ with Φ_i a many-electron basis function ((MEBF) Slater determinant, or combination thereof)
- The orbitals ϕ_j in a MEBF are not orthogonal, making the many-electron MEBFs also not orthogonal: $\left\langle \Phi_i \middle| \Phi_j \right\rangle = S_{ij}$
- The non orthogonality of the orbitals within one MEBF and of the orbitals in a different MEBF complicates the calculation of the required Hamiltonian matrix elements $\left\langle \Phi_i \middle| H \middle| \Phi_j \right\rangle$
- Solve $(\mathbf{H} - E\mathbf{S})(\mathbf{C}) = 0$ to get energies and Ψ (C_i's)

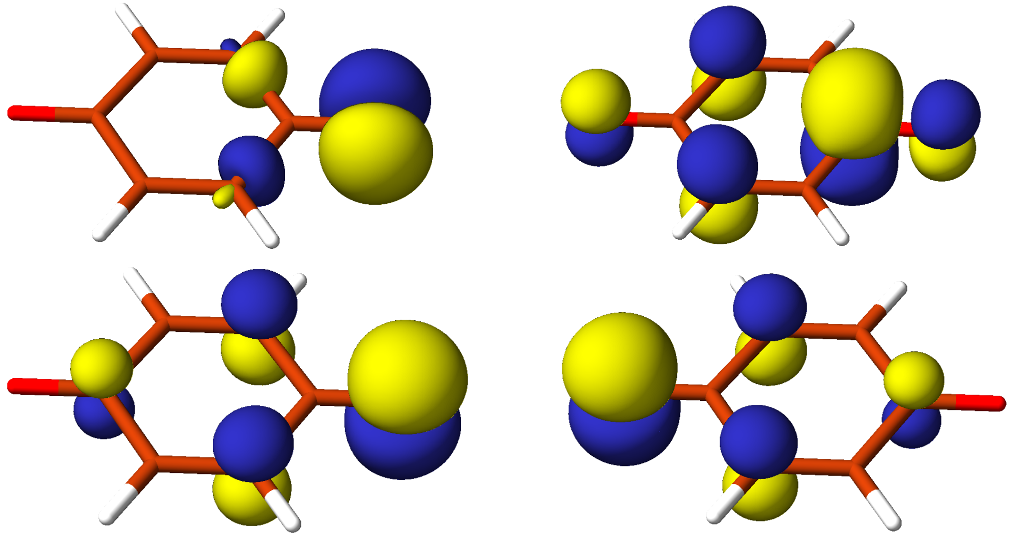
Advantages of this NOCI

- Inclusion of orbital relaxation effects
- Inclusion of (static) correlation effects
- Short wavefunction expansions
- Chemical interpretability
  - Description of system in terms of predefined states



$$n \rightarrow \pi^*$$

$$\pi \rightarrow \pi^*$$



- ***Con***: no simple Slater rules for the computation of matrix elements of the Hamilton operator in the MEBF basis

Computational Aspects of our NOCI approach

- Typical number of $\left|\Phi_{AB}^{KL}\right\rangle$ ~ 20
  - H/S matrices contain ~ 210 elements of the type $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle$ and $\left\langle \Phi_{AB}^{KL} \middle| \Phi_{AB}^{K'L'} \right\rangle$
- If $\left|\Phi_{A}^{K}\right\rangle$ contains ~ 500 determinants, then $\left|\Phi_{A}^{K}\right\rangle \times \left|\Phi_{B}^{L}\right\rangle = \left|\Phi_{AB}^{KL}\right\rangle \sim 2.5 \bullet 10^{5}$
- $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle = \sum_i \sum_j c_i c_j \left\langle \Delta_i \middle| H \middle| \Delta_j \right\rangle$
- Approximately 10^{7} elements $\left\langle \Delta_i \middle| H \middle| \Delta_j \right\rangle$ have to be calculated for one matrix element $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle$
- Aim for high level of parallelism
- Easy to parallelize

Technical Aspects

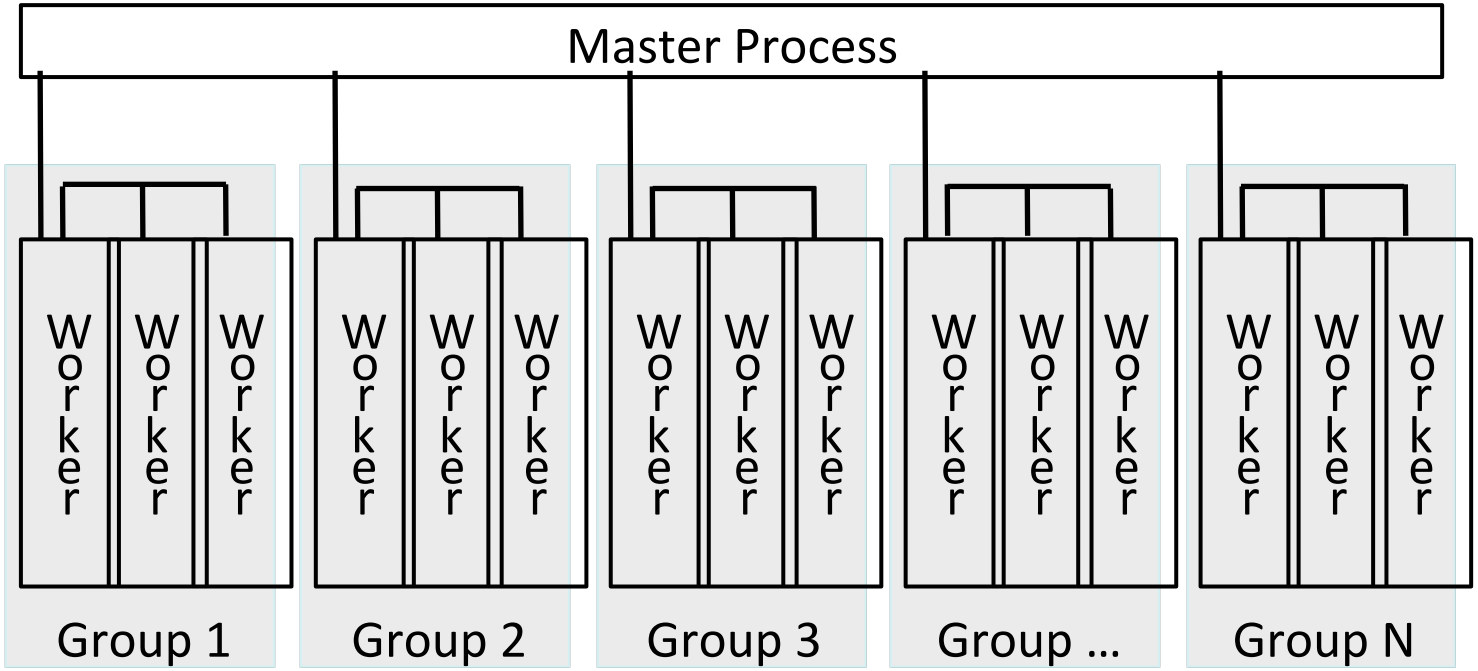
- Evaluation of $\langle \Delta_i | H | \Delta_j \rangle$ with non orthogonal orbitals
  - $H_{ij} = \sum_{i,j} h_{ij} S^{(i,j)} + \sum_{i<k} \sum_{j<l} [(ij \mid kl) - (ik \mid jl)] S^{(i,j,k,l)}$
  - First and second order co-factors needed
- With corresponding orbitals, then $\langle c_i | d_j \rangle = \lambda_i \delta_{ij}$

  and $S^{(i,i)} = \prod_{m \neq i} \lambda_m \quad (S^{(i,j)} = 0 \text{ for } i \neq j)$
- No 4-index, but transform co-factors to common basis in which the corresponding orbitals c_i and d_i are expressed
- SVD and matrix multiplications
- Use GPUs

The GronOR code

- In collaboration with OLCF, based on the GNOME code
  - OpenACC for GPU off-loading
  - Master-worker model with task based load balancing
  - MPI parallelization with point-to-point non-blocking communication
  - Avoid global synchronization and global reduction operations
  - Fault resilient implementation

GronOR Master-Worker Process Layout

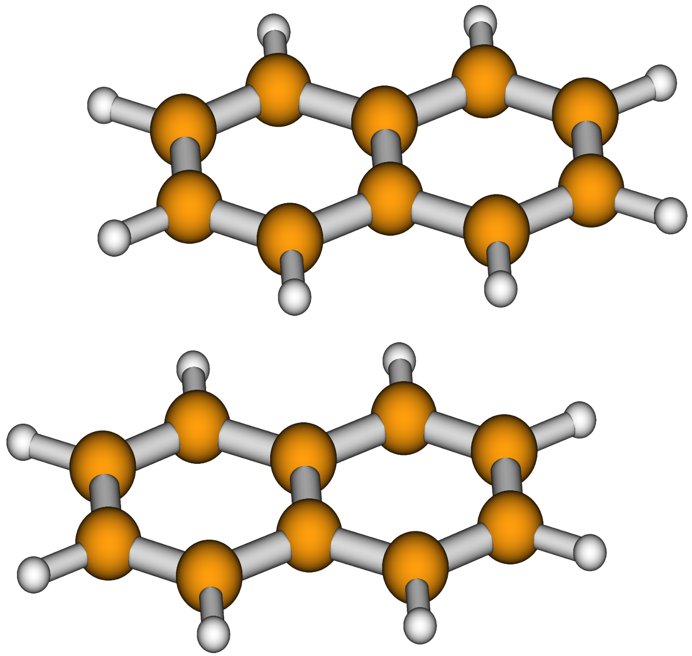


Each process group has the same number of worker processes
Each process group should have sufficient aggregate memory to hold all integrals: One-electron integrals are duplicated
Two-electron integrals are distributed

Consequences of Node Faults: All processes on a failing node fail
If a worker process fails, the entire group to which it belongs will fail

Case study I - Naphthalene dimer

Anti-symmetrised products of CAS(4,4) wavefunctions



			E (eV)
Ψ^0_A	$\times$	Ψ^0_B	0.00
Ψ^1_A	$\times$	Ψ^0_B	6.54
Ψ^0_A	$\times$	Ψ^1_B	6.54
Ψ^T_A	$\times$	Ψ^T_B	8.64

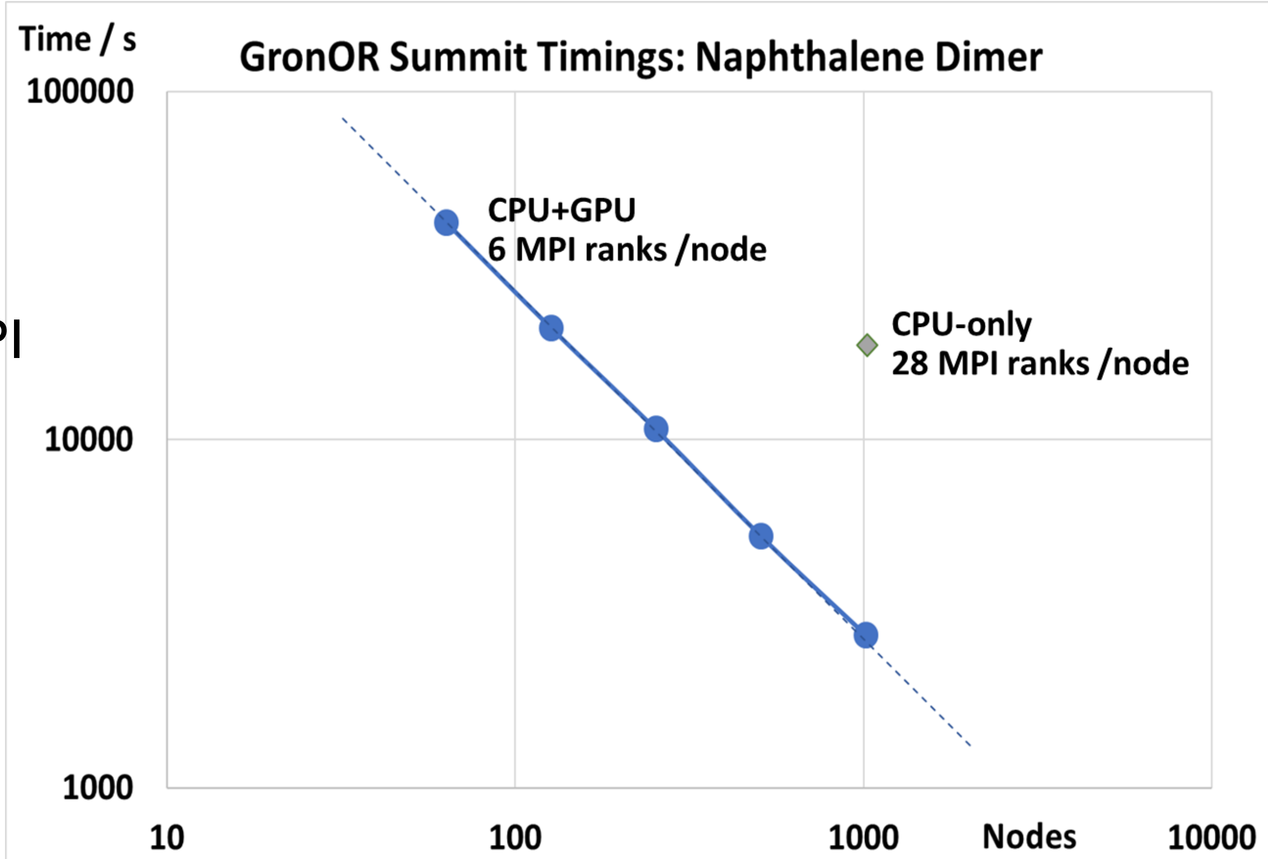
B

- Neglect of dynamical correlation (S_1 too high)
- Endoergic

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 ~ $N^4/8$

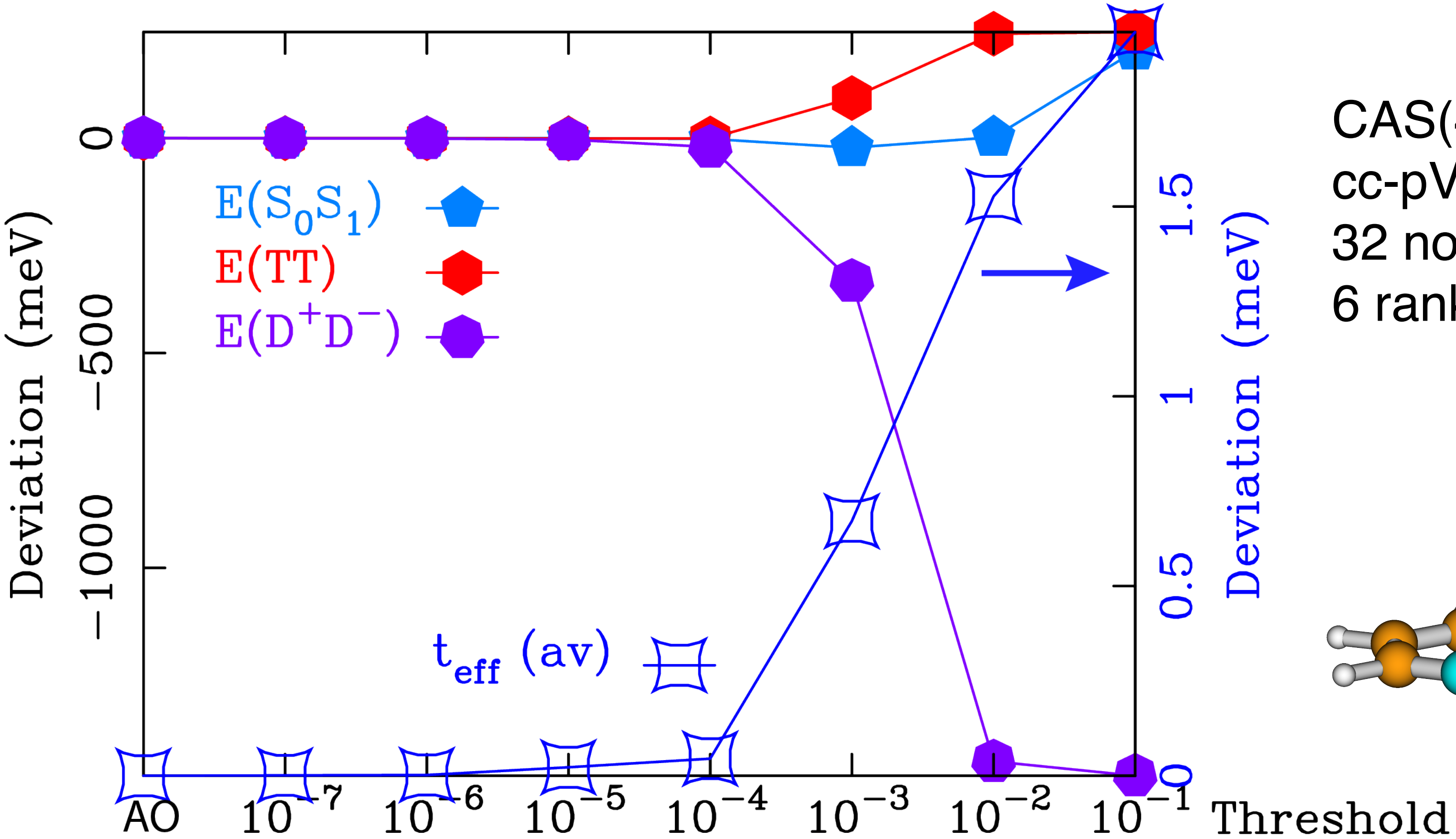
- The *n* inactive + active MOs of all states of a molecule form a basis as well:

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

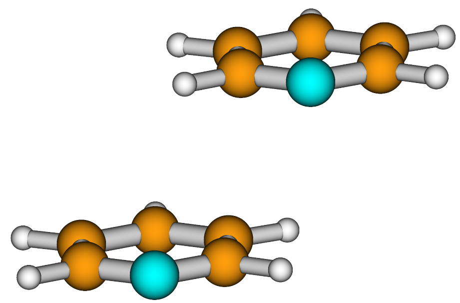
- Redundant basis, eliminate linear dependencies, based on threshold ε, and transform MOs and 2-e$^-$ integrals to new basis

- Dimension of new basis $m \ll N$

Case study II - Pyridine

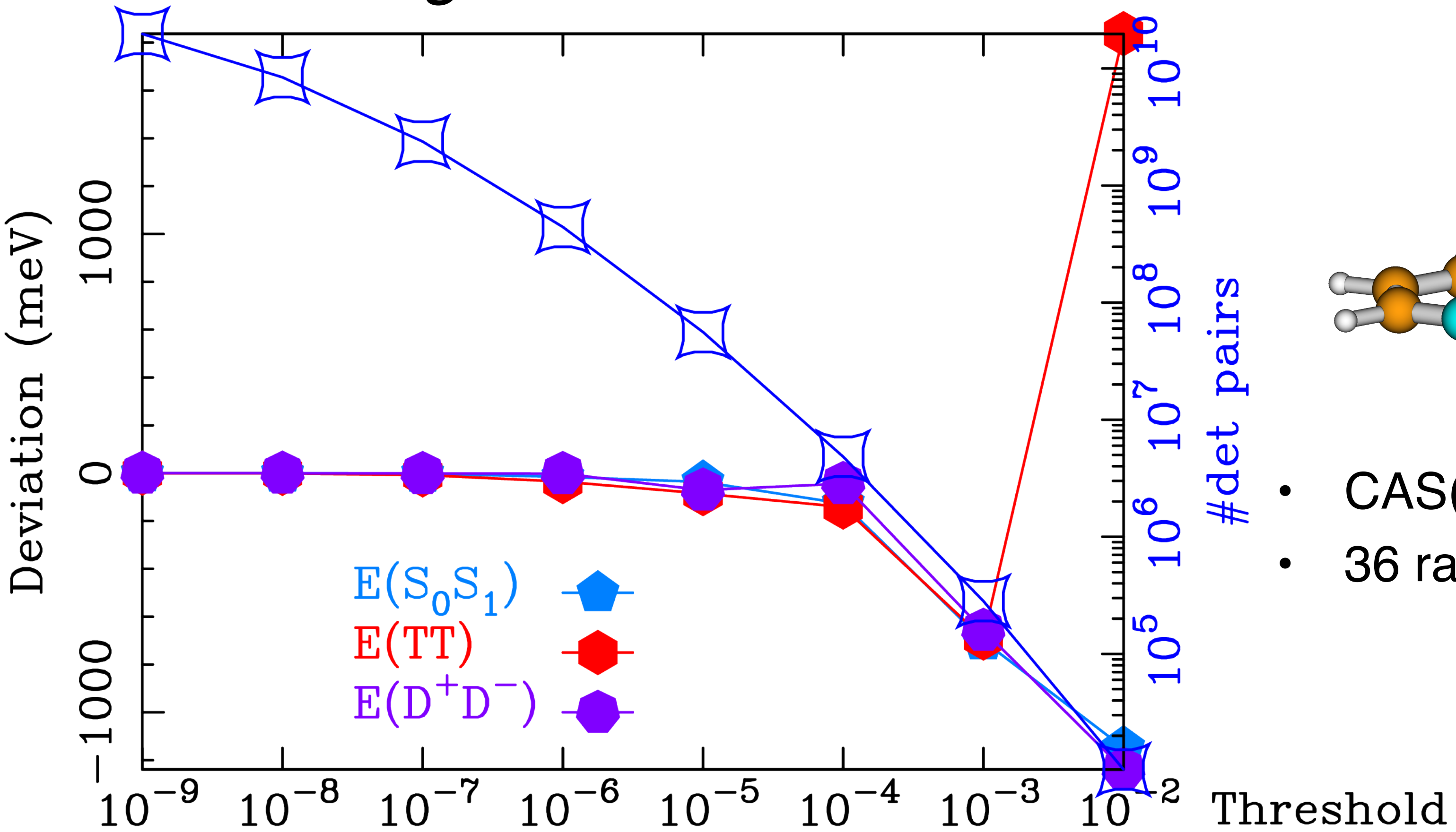


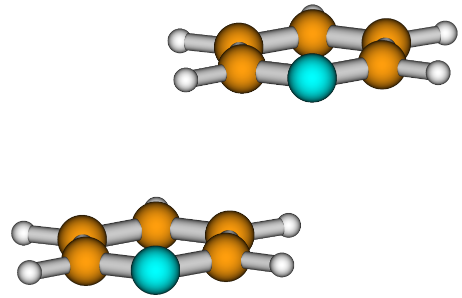
CAS(4,4)/
cc-pVTZ
32 nodes,
6 ranks/node



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)

CI threshold – remove contributions from configurations with small CI coefficients





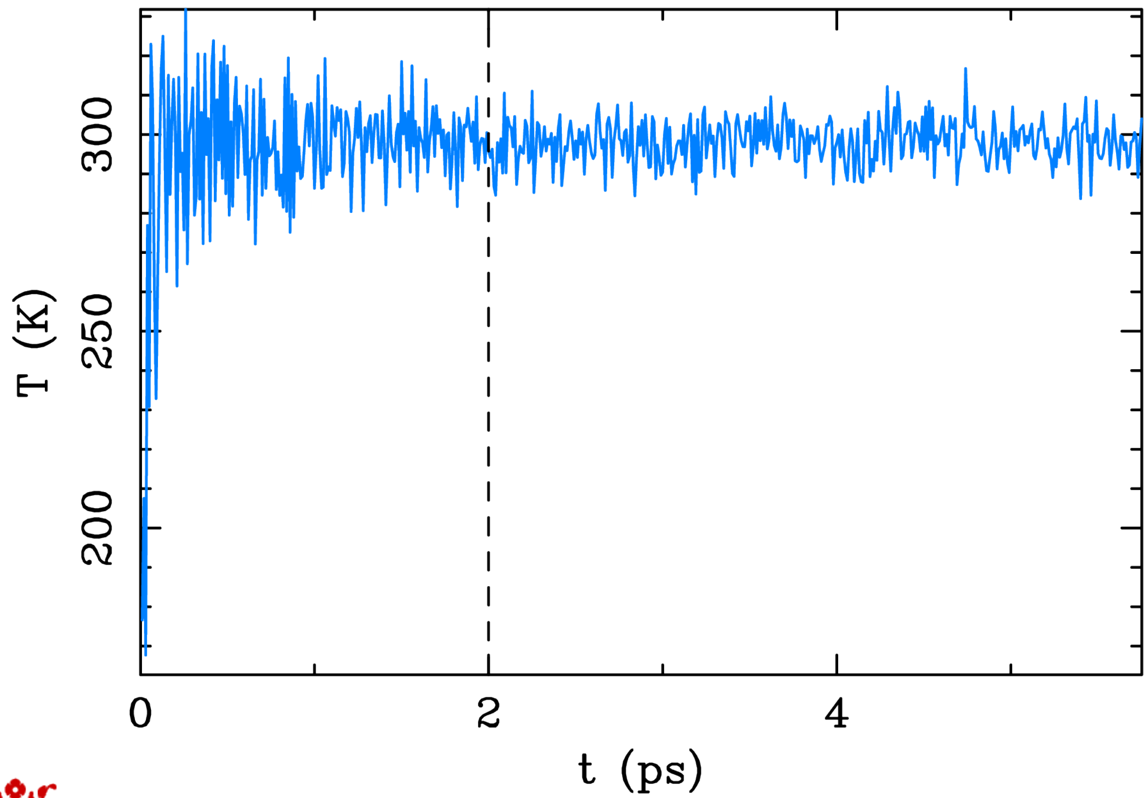
- CAS(6,6)/6-311G**
- 36 ranks/node

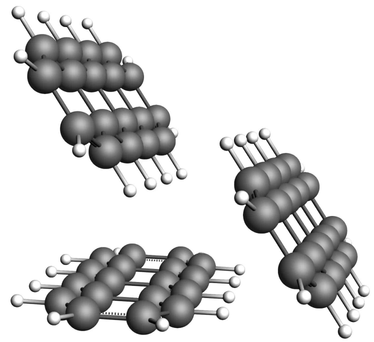
1024		1024		64	1024*			Nodes
6238		3002		406	87			Time (s)

*6 ranks/node

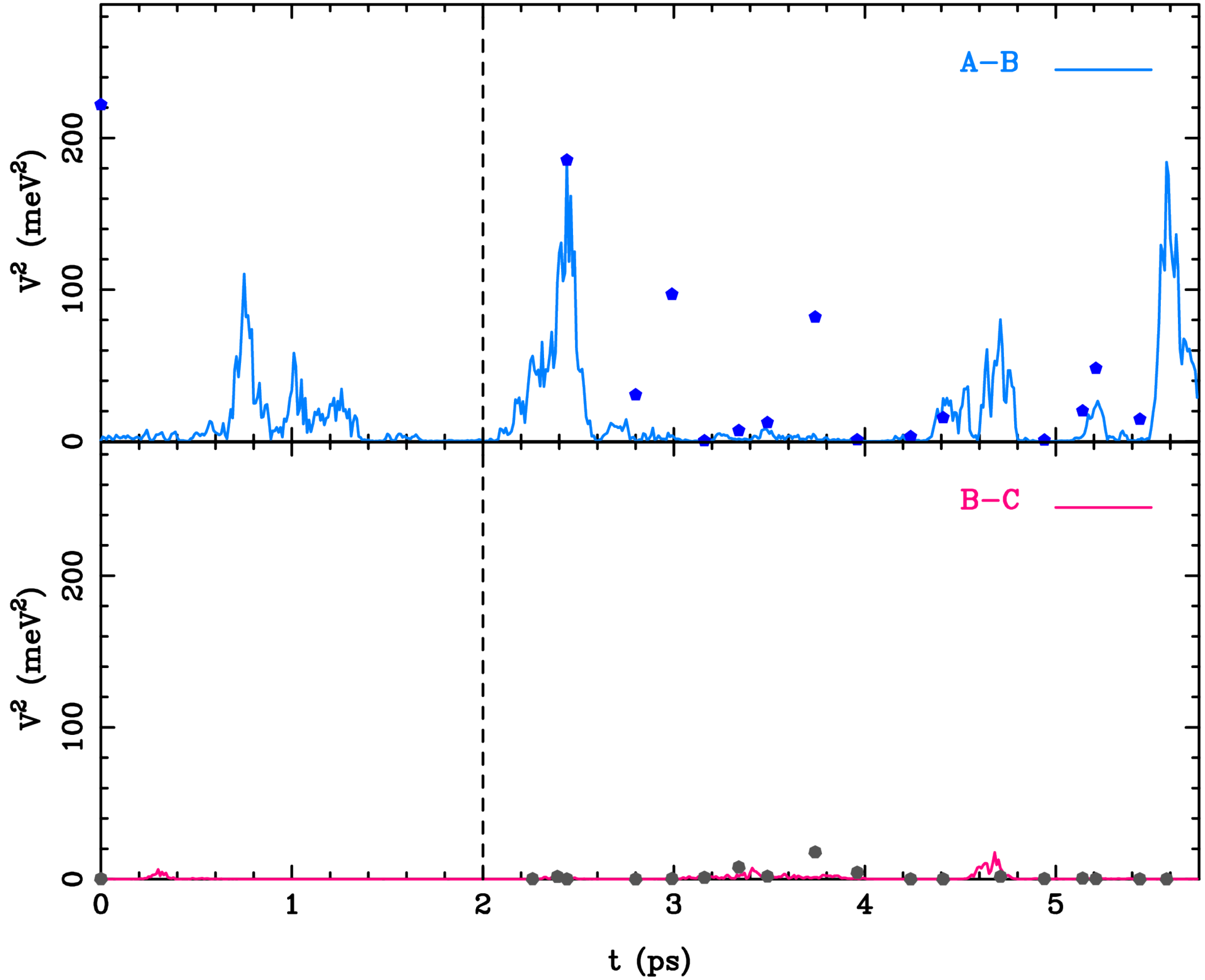
Singlet fission in tetracene

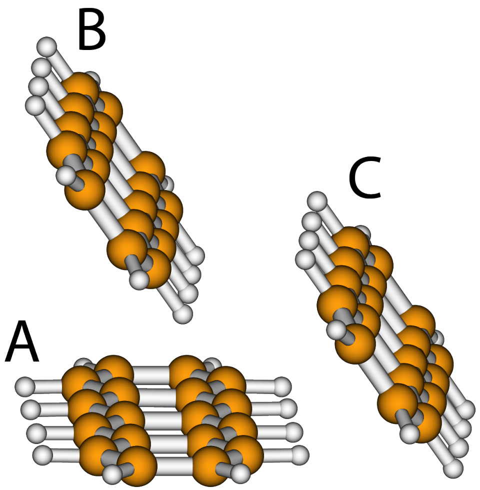
- Geometry dependence of coupling in solid
  - MD using DFTB (NVT)
  - Estimate coupling using DFT and NOCI





Effective coupling, DFT and NOCI



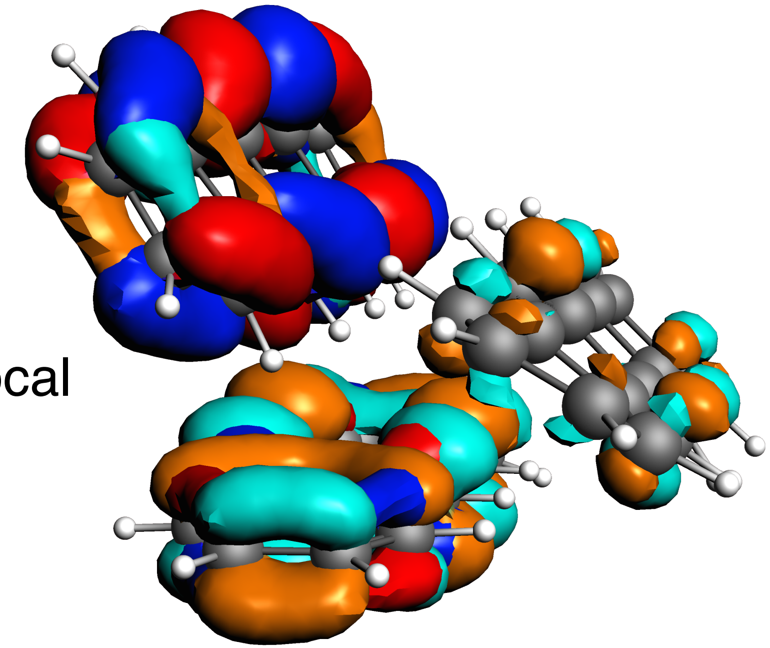


- Coupling heavily dependent on geometry
- AB/AC orientation best

Tetracene coupling

- Large electronic coupling in the AB orientation

- Molecules A and B get closer
  - Larger HOMO/HOMO and LUMO/LUMO overlap

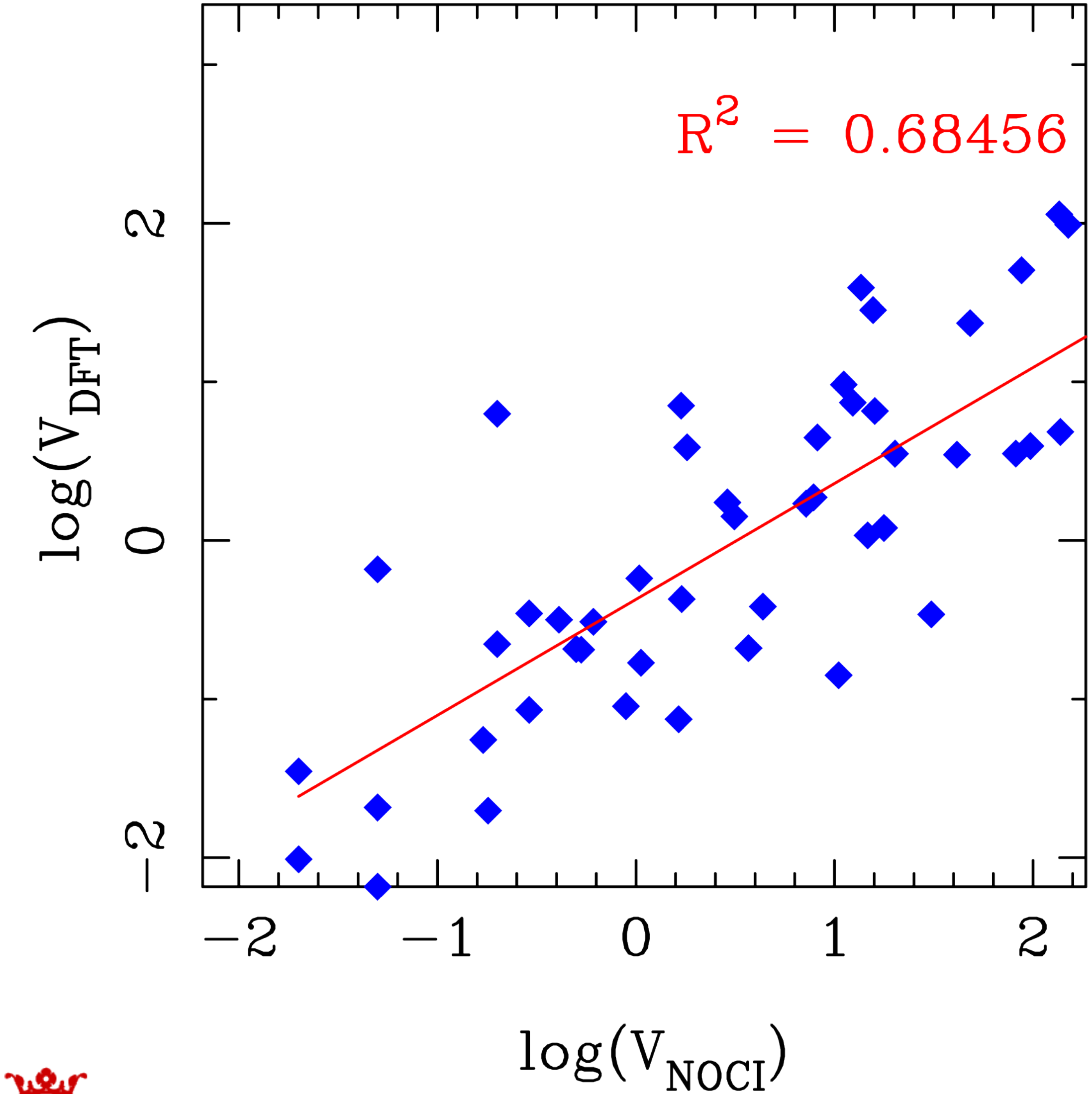


- Strong mixing of CT states (30%) in local excited state on A and in ^{1}TT state

- Direct coupling: 5 meV

- CT mediated coupling: 32 meV

Correlation NOCI vs DFT



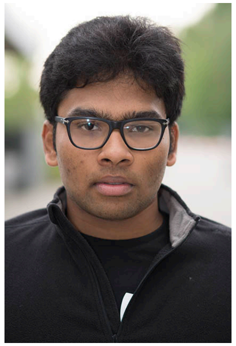
- Only weak correlation

Conclusions and outlook

- Parallel NOCI program GronOR is working and ready to be used for interesting applications
  - Further optimizations are in progress
  - Better handling of CI lists
  - Inclusion of dynamical correlation and embedding effects
- Tetracene
  - CT states enhance the coupling
  - Coupling and CT state mixing heavily dependent on geometry
  - Static picture not always sufficient for predicting singlet fission
  - Weak correlation NOCI vs DFT couplings
- Further studies:
  - Cibalackrot and other SF molecules
  - Effects of functional groups on electronic coupling

Theoretical Chemistry Group



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MARIE CURIE ACTIONS

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