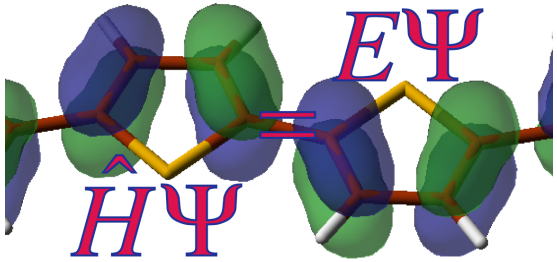
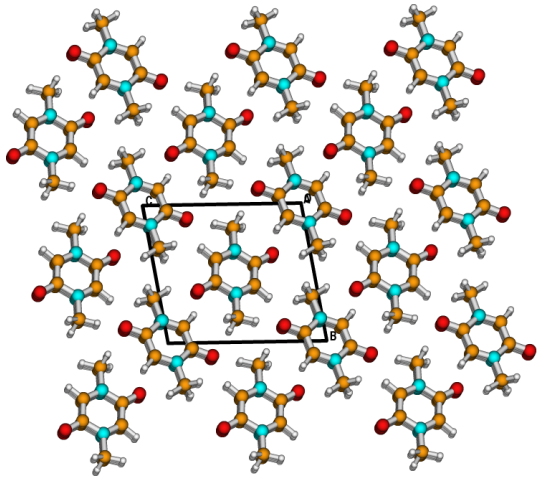
Non orthogonal configuration interaction on the next generation of supercomputers



Remco W. A. Havenith



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Theoretical Chemistry Group

Mission:

Provide independent knowledge on structures, properties and their relation, with interpretation in terms of chemical concepts

- Emphasis on
  - Molecular properties
    - Photo-physical properties
      - Spectra and excited states
    - Magnetic and electric properties
  - Non-orthogonal methods

- Application driven method development
- Computational experiments

Non Orthogonal Configuration Interaction

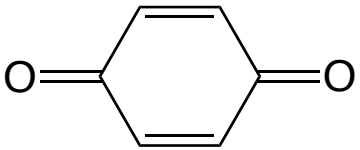
- Wavefunction expanded as: $\Psi = \sum_{i=1}^{N} c_i \Phi_i$ with Φ_i a many-electron basis function (Slater determinant, or combination thereof)
- A Slater determinant is an antisymmetrised product of orbitals:

$$\Phi_i = A \prod_j \varphi_j$$

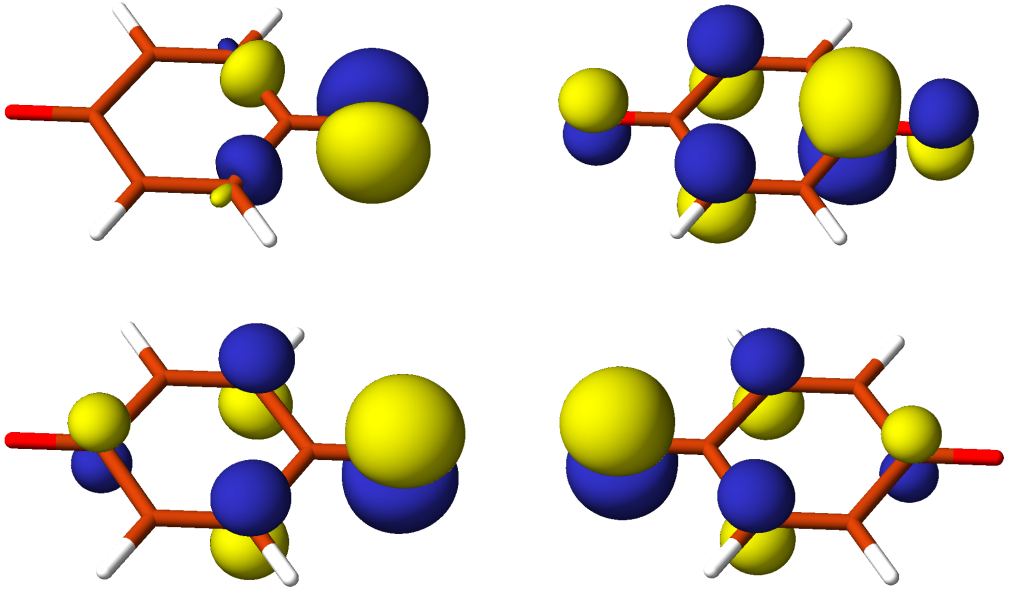
- The orbitals ϕ_j are not orthogonal, making the many-electron Φ_i's also not orthogonal: $\langle \Phi_i | \Phi_j \rangle = S_{ij}$
- The non orthogonality of the orbitals complicates the calculation of the required Hamiltonian matrix elements $\langle \Phi_i | H | \Phi_j \rangle$
- Solve $(\mathbf{H} - E\mathbf{S})(\mathbf{c}) = 0$ to get energies and Ψ (c_i's)

Advantages of NOCI

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



$n \rightarrow \pi^*$



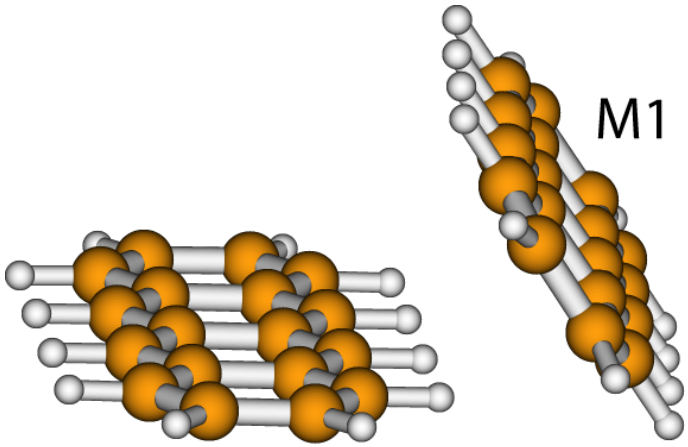
$\pi \rightarrow \pi^*$

Our Application of NOCI

- Describe wavefunctions of a cluster of molecules in terms of (localised) molecular base states
  - Φ_i's are antisymmetrised products of monomer wavefunctions:

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

  - Monomer wavefunction can be any multiconfigurational wavefunction



$\Psi^{(0)}$: Ground state

$\Psi^{(1)}$: Singlet excited state

$\Psi^{(T)}$: Triplet excited state

$$\Phi_{AB}^{[(0)\otimes(0)]} = A(\Psi_{\mathrm{M1}}^{(0)} \otimes \Psi_{\mathrm{M2}}^{(0)})$$

$$\Phi_{AB}^{[(1)\otimes(0)]} = A(\Psi_{\mathrm{M1}}^{(1)} \otimes \Psi_{\mathrm{M2}}^{(0)})$$

$$\Phi_{AB}^{[(0)\otimes(1)]} = A(\Psi_{\mathrm{M1}}^{(0)} \otimes \Psi_{\mathrm{M2}}^{(1)})$$

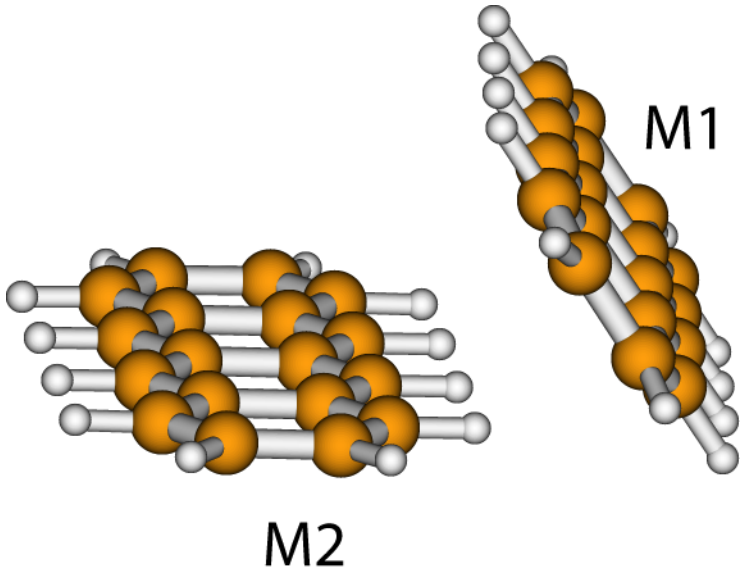
$$\Phi_{AB}^{[(T)\otimes(T)]} = A(\Psi_{\mathrm{M1}}^{(T)} \otimes \Psi_{\mathrm{M2}}^{(T)})$$

$$\vdots$$

$$\Psi = c_1\Phi_{AB}^{[(0)\otimes(0)]} + c_2\Phi_{AB}^{[(1)\otimes(0)]} + c_3\Phi_{AB}^{[(0)\otimes(1)]} + c_4\Phi_{AB}^{[(T)\otimes(T)]} + \ldots$$

Diabatic representation: non-orthogonal CI

- Molecular base states:



$$\Psi(\mathrm{S}_1) = c_1\left(\Psi^{(0)}_{(M1)} \times \Psi^{(1)}_{(M2)}\right) + c_2\left(\Psi^{(1)}_{(M1)} \times \Psi^{(0)}_{(M2)}\right)$$

$$\Psi({}^1\mathrm{TT}) = \left(\Psi^{(T)}_{(M1)} \times \Psi^{(T)}_{(M2)}\right)$$

$\Psi^{(0)}$: Ground state

$\Psi^{(1)}$: Singlet excited state

$\Psi^{(T)}$: Triplet excited state

- Chemical interpretation in terms of molecular base states
- Electronic coupling between states

$$\left\langle \Psi(\mathrm{S}_1) \middle| H \middle| \Psi({}^1\mathrm{TT}) \right\rangle$$

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 transfer rates

Electron transfer rate

- Fermi Golden rule in diabatic representation (Marcus theory)

$$k_{ET} \propto \left| \left\langle \Psi_f \middle| H \middle| \Psi_i \right\rangle \right|^2$$

  – Electronic coupling between diabatic states

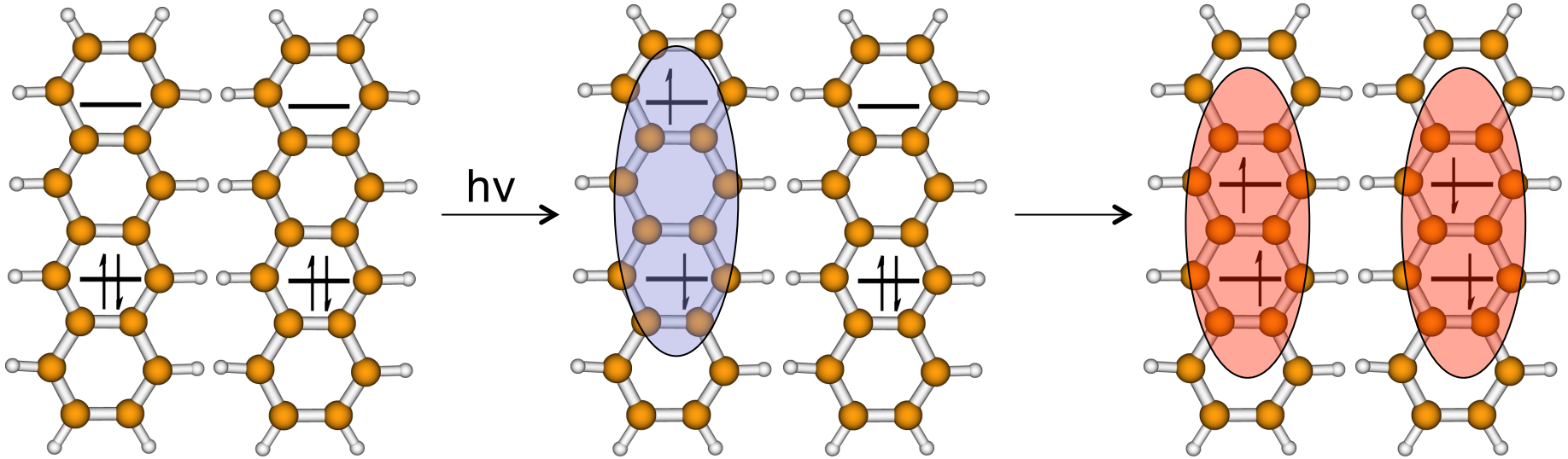
- Adiabatic representation: Non-adiabatic couplings (Landau-Zener model)

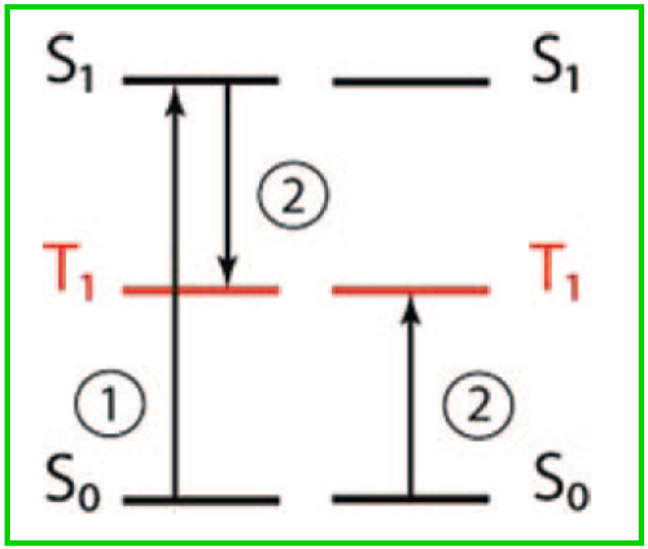
$$\left\langle \Psi_f \middle| \frac{\partial}{\partial Q} \middle| \Psi_i \right\rangle$$

  – 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

Singlet fission





- Spin allowed
- Radiationless process

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

Computational Aspects of our NOCI approach

- Typical number of $\left|\Phi_{AB}^{KL}\right\rangle \sim 20$
  - H/S matrices contain ~ 210 elements of the type $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle$ and $\left\langle \Phi_{AB}^{KL} \middle| \Phi_{AB}^{K'L'} \right\rangle$
- $\left|\Phi_{A}^{K}\right\rangle$ contains ~ 500 determinants, thus $\left|\Phi_{A}^{K}\right\rangle \otimes \left|\Phi_{B}^{L}\right\rangle = \left|\Phi_{AB}^{KL}\right\rangle \sim 2.5 \bullet 10^{5}$
- $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle = \sum_{i} \sum_{j} c_i c_j \left\langle \Delta_i \middle| H \middle| \Delta_j \right\rangle$
- Approximately $6 \bullet 10^{10}$ elements $\left\langle \Delta_i \middle| H \middle| \Delta_j \right\rangle$ have to be calculated for one matrix element $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle$!
- Only feasible when high level of parallelism is achieved.
- Fortunately, $\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle$ are independent

Current program

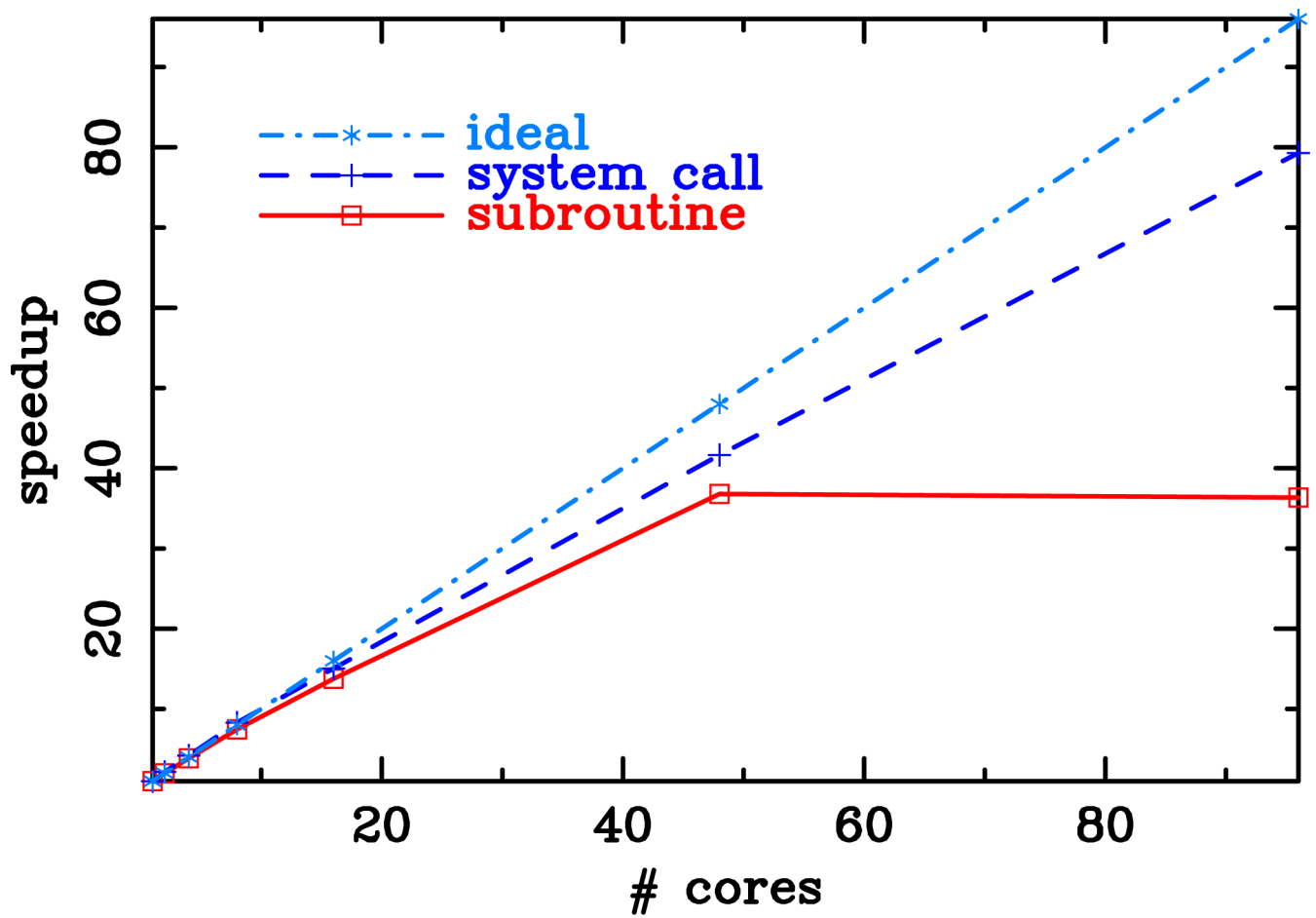
- Based on existing GNOME code for evaluation of $\langle \Delta_i | H | \Delta_j \rangle$
- First, remove all *i,j* combinations for which $|c_i c_j| < threshold$
- Parallelized using MPI and OpenMP
- Evaluation of $\langle \Delta_i | H | \Delta_j \rangle$ in parallel
  - All elements are divided over the nodes, then divided over the cores

```
!$OMP DO SCHEDULE(DYNAMIC) REDUCTION(+:hmat)
do ij=ijstart,ijend
    i=iloop(ij,1)
    j=iloop(ij,2)
    call gnome(hh,gnome)
    hmat=hmat+hh
enddo
!$OMP END PARALLEL
```

```
gnome(hh,gnome)>gnome.out) \ call gethfo(hh)
```

Performance

- Test case I: 52 determinants, 1378 matrix elements $\langle \Delta_i | H | \Delta_j \rangle$



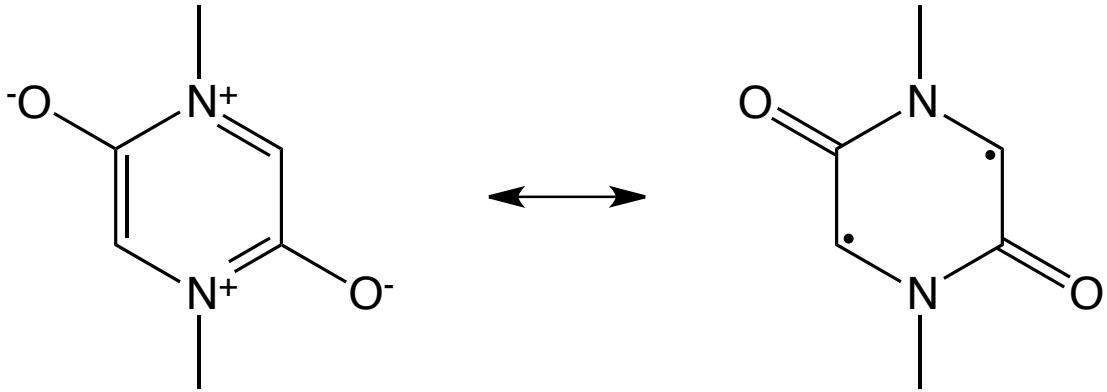
More parallelism needed

- 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 $S^{(i,i)} = \prod_{m \neq i} \lambda_m \quad (S^{(i,j)} = 0 \text{ for } i \neq j)$
- Transform co-factors to common AO basis in which the corresponding orbitals c_i and d_i are expressed
- SVD and matrix multiplications
- Use GPUs?

Potential applications: The biradicaloid

- Promising candidate for singlet fission



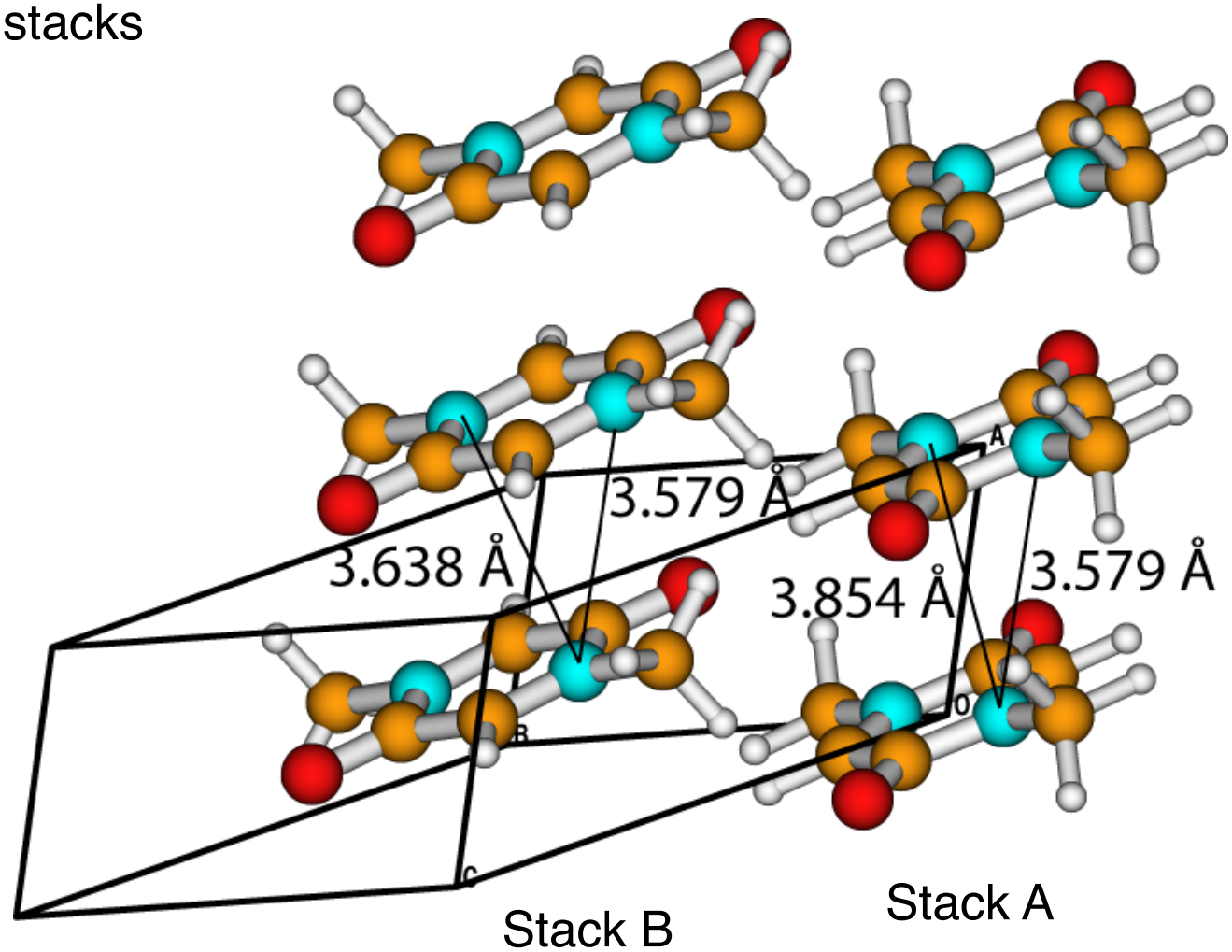
- 2 x $E(T_1) < E(S_1)$
- No crystal data available

- Possible structure? Electronic coupling between S_1 and ^1TT?

A. Akdag, Z. Havlas, J. Michl, *J. Am. Chem. Soc.* **134** (2012), 14624-14631

A possible structure

- Two different stacks

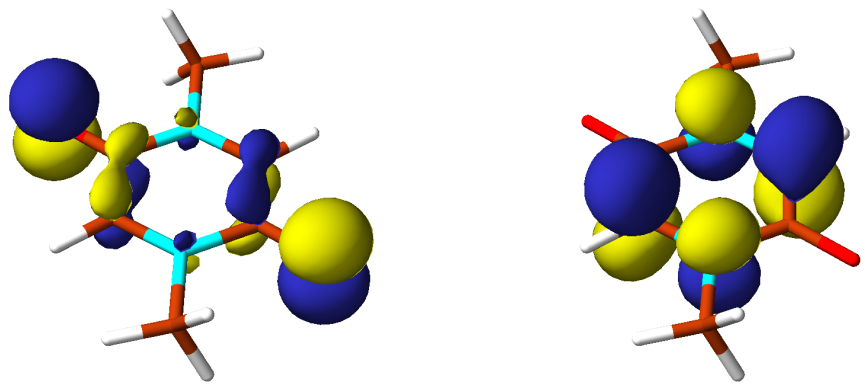


Monomer excitation energies

CASSCF(6,5)/ANO-L (energies in eV)

	CASSCF	**CASPT2**	**Lit. [1]**
S_1	2.71	2.42	2.21
T_1	0.77	1.06	1.15

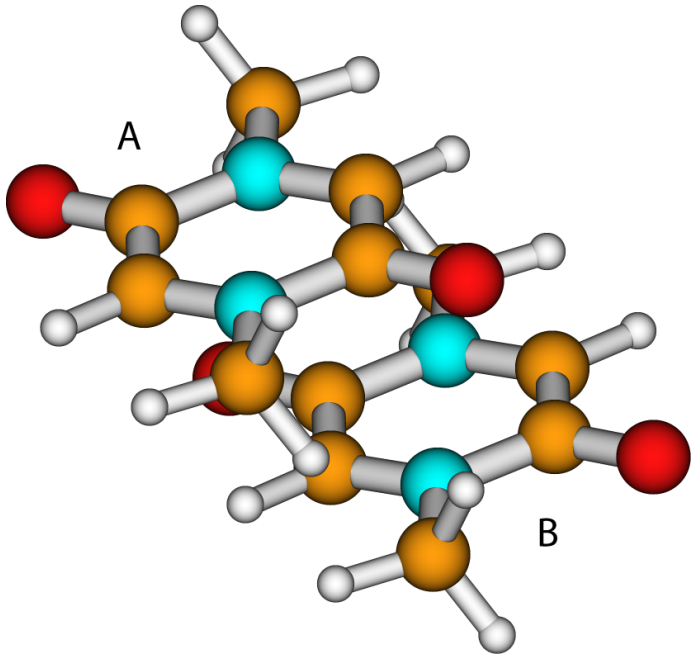
- State specific orbitals



[1] A. Akdag, Z. Havlas, J. Michl, *J. Am. Chem. Soc.* **134** (2012), 14624-14631

The molecular base states

Löwdin orthogonalise the orbitals
and perform CASCI(12,10):



			E (eV)
$\Psi^{(0)}_{(MA)}$	$\otimes$	$\Psi^{(0)}_{(MB)}$	0.00
$\Psi^{(1)}_{(MA)}$	$\otimes$	$\Psi^{(0)}_{(MB)}$	2.58
$\Psi^{(0)}_{(MA)}$	$\otimes$	$\Psi^{(1)}_{(MB)}$	2.58
$\Psi^{(T)}_{(MA)}$	$\otimes$	$\Psi^{(T)}_{(MB)}$	1.44
$\Psi^{(+)}_{(MA)}$	$\otimes$	$\Psi^{(-)}_{(MB)}$	3.56
$\Psi^{(-)}_{(MA)}$	$\otimes$	$\Psi^{(+)}_{(MB)}$	3.56

Diabatic excited states

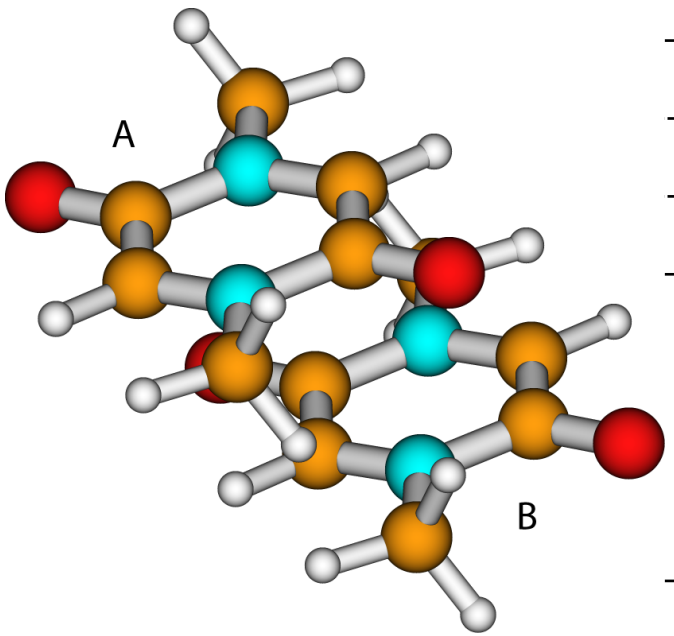
- Weights of base states

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

- Energies

Base State	**S_1**	**S_2**	**^1TT**
$A^* \times B$	***0.500***	***0.500***	0.000
$A \times B^*$	***0.500***	***0.500***	0.000
$A^t \times B^t$	0.000	0.000	***1.000***
Energy (eV)	2.37	2.82	1.44

Coupling between localised states



	$\lvert t_{ij} \rvert$		$\lvert H'_{ij} \rvert$		
	S_1	S_2	S_1	S_2	
^1TT	42.5	0.16	40.3	0.16	meV

vs.

	$\lvert t_{ij} \rvert$		$\lvert H'_{ij} \rvert$		
	S_A	S_B	S_A	S_B	
^1TT	32.9	33.1	28.5	28.8	meV

Final excited states

- Weights and energies

	Dimer states			
Basis of excited states	**Ground state**	**S_1**	**S_2**	**^1TT**
Ground state	***0.998***	0.104	0.000	0.000
S_1	0.002	***0.895***	0.000	0.000
S_2	0.000	0.000	***1.000***	0.000
^1TT	0.000	0.002	0.000	***0.999***
Energy (eV)	0.00	2.69	2.83	1.44

Concluding remarks

- Non-orthogonal CI is a suitable method for the description of excited states in molecular solids and for the calculation of the electronic coupling between molecular excited states

- Performance issues have to be solved
- More parallelism should be introduced for the calculation of the matrix elements

- The biradicaloid is potentially interesting for singlet fission

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Theoretical Chemistry

Financial support

- Zernike Institute for Advanced Materials (Dieptestrategie)
- FOM Focus Group 'Next Generation Organic Photovoltaics' (DIFFER)
- FOM/Shell
- ITN-EJD-TCCM (Horizon2020)

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DIFFER
Dutch Institute for Fundamental Energy Research

MARIE CURIE ACTIONS

Thank you for
your attention!