Joop van Lenthe

```
    t                         t           l
    t                         t           l
 tttt     u   u   rrrrr    tttt           l              eee
    t     u   u   r    r      t           l            eeeee
    t   t u   u   r           t    t      l    l         e
     ttt     uu      r          ttt         lll         eee
```
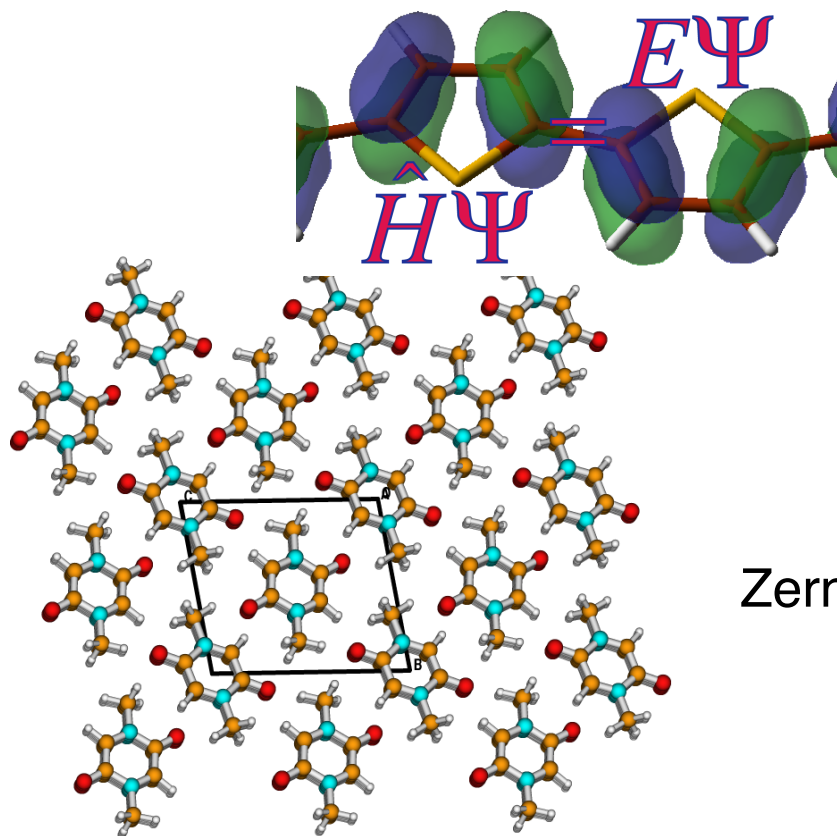
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                                          ( )_( )_( )_( )_( )
    ----       ----       ----             //  //   //  //
```

Non orthogonal configuration interaction

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

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TCCM

MARIE CURIE ACTIONS

FOM

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*icrea
Institució Catalana de Recerca i Estudis Avançats
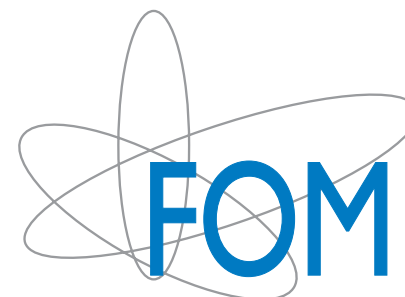
UNIVERSITAT
ROVIRA I VIRGILI

OAK RIDGE
National Laboratory | OAK RIDGE LEADERSHIP COMPUTING FACILITY
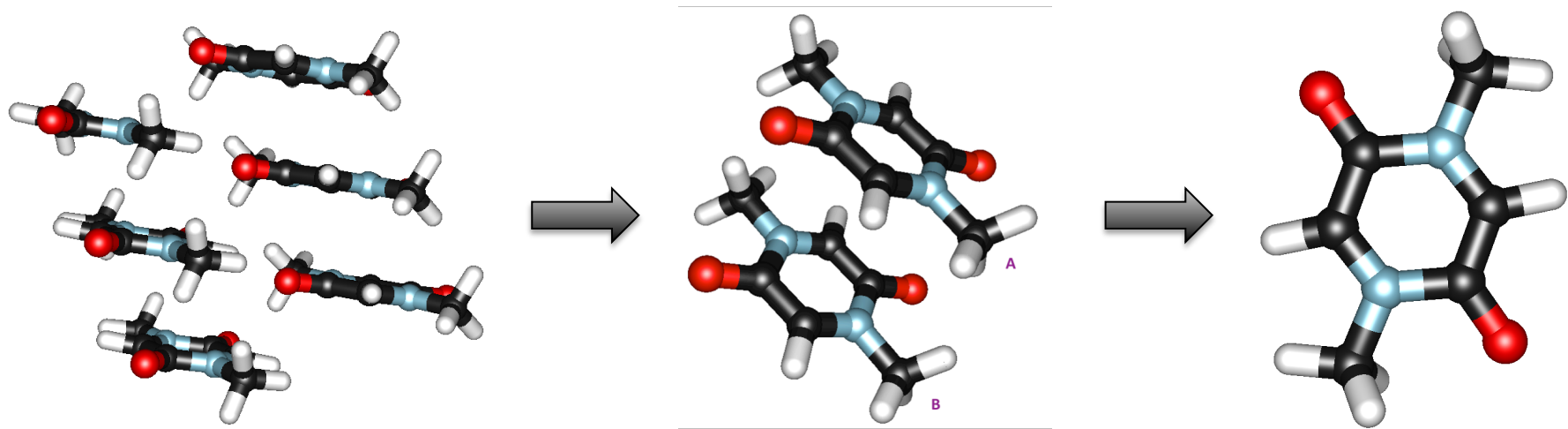
Coen de Graaf

Tjerk Straatsma

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Theoretical Chemistry

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
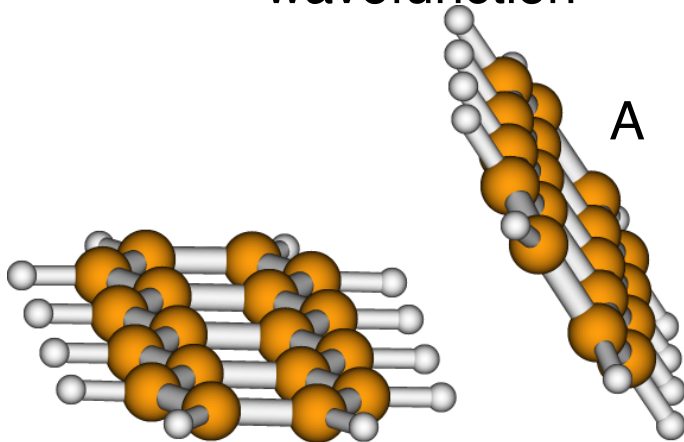
Non orthogonal configuration interaction

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

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

  - Molecular wavefunction can be any multiconfigurational wavefunction

A

B

Ψ^0 : Ground state

Ψ^1 : Singlet excited state

Ψ^T : Triplet excited state

$$\Phi_{AB}^{0\times0} = A(\Psi_A^0 \times \Psi_B^0)$$

$$\Phi_{AB}^{1\times0} = A(\Psi_A^1 \times \Psi_B^0)$$

$$\Phi_{AB}^{0\times1} = A(\Psi_A^0 \times \Psi_B^1)$$

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

$$\vdots$$

$$\Psi = c_1\Phi_{AB}^{0\times0} + c_2\Phi_{AB}^{1\times0} + c_3\Phi_{AB}^{0\times1} + c_4\Phi_{AB}^{T\times T} + \dots$$

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 χ_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
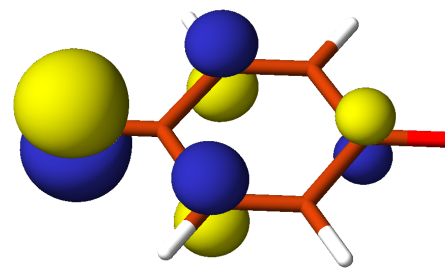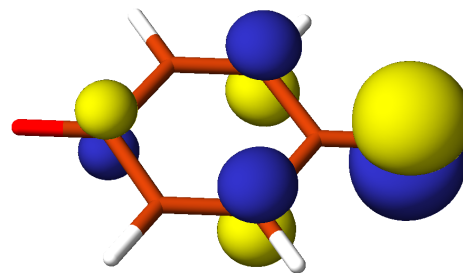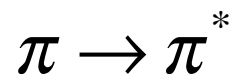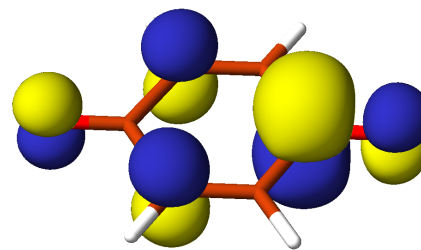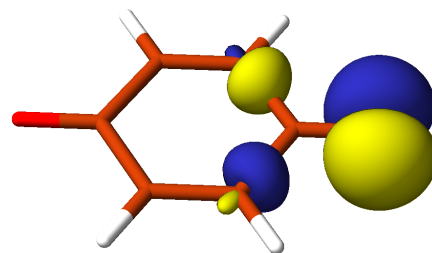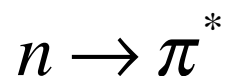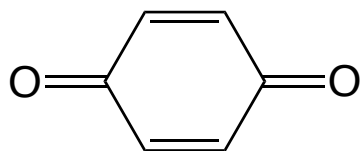
$$n \rightarrow \pi^*$$

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

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 $\left\langle\Phi_{AB}^{KL}\middle|\Phi_{AB}^{K'L'}\right\rangle$

- If $\left|\Phi_A^K\right\rangle$ contains ~ 500 determinants, then $\left|\Phi_A^K\right\rangle\times\left|\Phi_B^L\right\rangle=\left|\Phi_{AB}^{KL}\right\rangle \sim 2.5\bullet10^5$

- $\left\langle\Phi_{AB}^{KL}\middle|H\middle|\Phi_{AB}^{K'L'}\right\rangle=\sum_i\sum_j c_i c_j\left\langle\Delta_i\middle|H\middle|\Delta_j\right\rangle$

- 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

Current program

- Based on existing GNOME code for evaluation of $\langle \Delta_i | H | \Delta_j \rangle$

- First, remove all i,j combinations whose occupations differ by more than two electrons, and all combinations for which $|c_i c_j| < \varepsilon$

- 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

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

Performance

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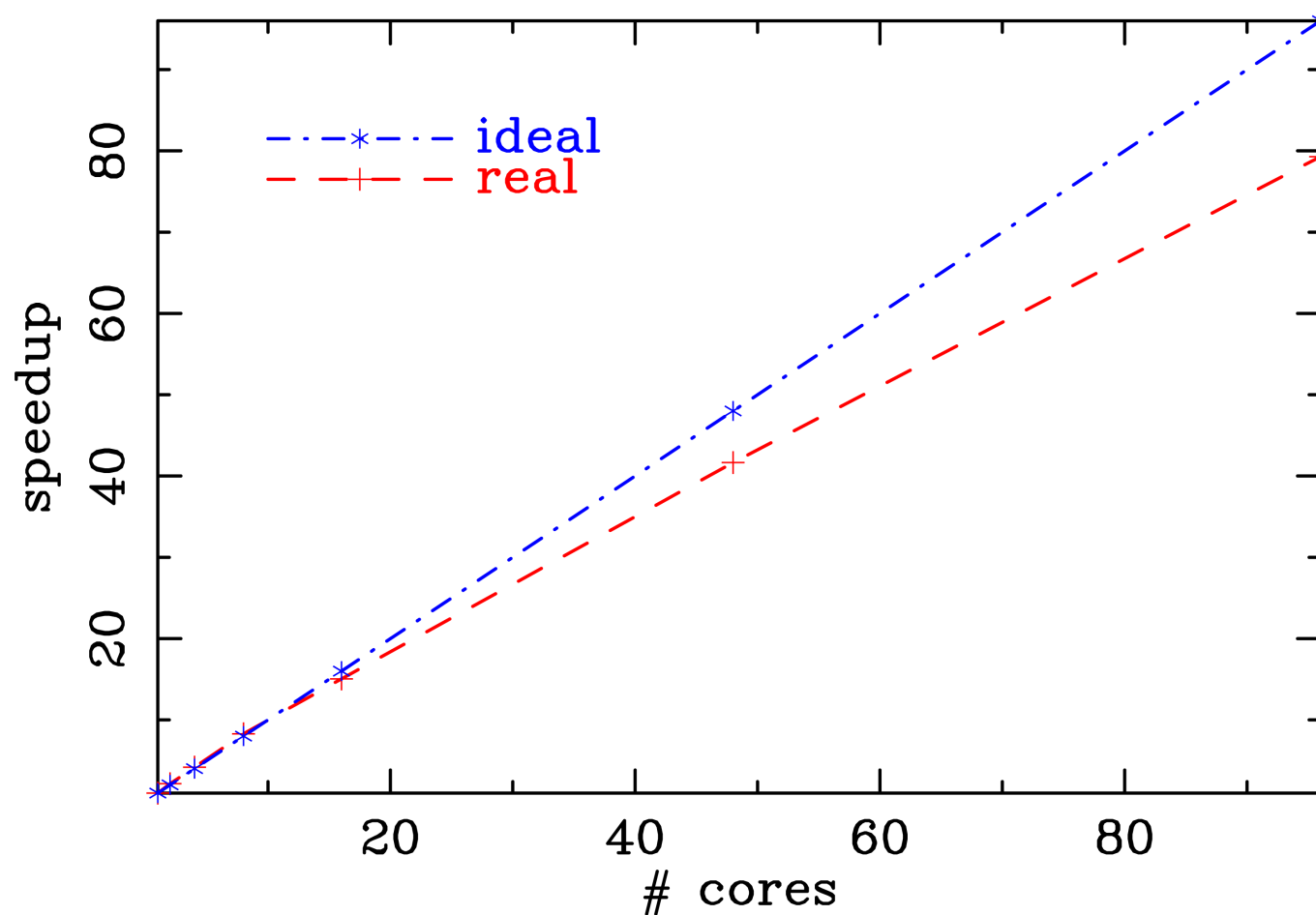
Technical Aspects

- 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 AO basis in

  which the corresponding orbitals c_i and d_i are expressed

- SVD and matrix multiplications

- Use GPUs?

- Use molecular orbitals as one-electron basis

The procedure - NOCI

OLD approach (MOLCAS)

- CASCI wavefunction as approximation to ASP
  - Mixing in contaminating CSFs
 - (Unwanted orthogonalizations)

NEW approach (GNOME)

- Proper ASP of molecular wavefunctions
  - Clear chemical interpretation of the state
  - No orthogonalizations

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Theoretical Chemistry

The many-electron basis functions

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

		E (eV)
Ψ_A^0 × Ψ_B^0		0.00
Ψ_A^1 × Ψ_B^0		2.58
Ψ_A^0 × Ψ_B^1		2.58
Ψ_A^T × Ψ_B^T		1.44
Ψ_A^+ × Ψ_B^-		3.56
Ψ_A^- × Ψ_B^+		3.56
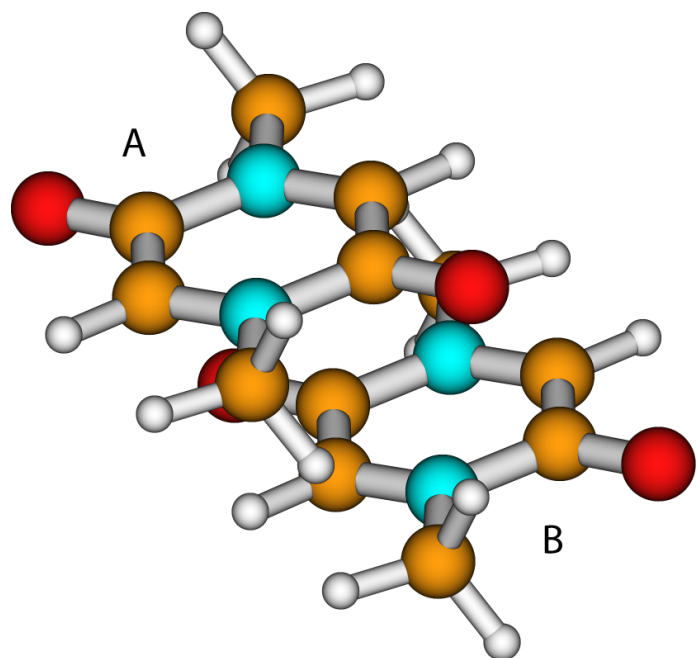
Stack A – GNOME procedure (CAS(2,2))

- The relative energies of the cluster MEBFs
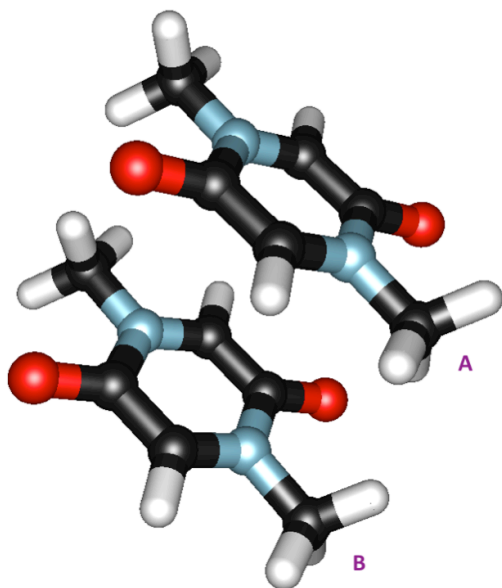
MEBF	E_{rel}(eV)	MEBF	E_{rel}(eV)
Â[AB]	0.00	Â[$A^T B^T$]	1.61
Â[A^SB]	3.81	Â[$A^+ B^-$]	4.49
Â[AB^S]	3.81	Â[$A^- B^+$]	4.49

- The energies and weights of the diabatic states

N-N = 3.579 Å

N-N = 3.854 Å

MEBF	S[1]	S[2]	S'[1]	S'[2]
Â[A^SB]	0.50	0.50	0.45	0.50
Â[AB^S]	0.50	0.50	0.45	0.50
Â[$A^+ B^-$] + Â[$A^- B^+$]	-	-	0.09	0.00
Energy (eV)	3.72	3.90	3.64	3.90

Electronic coupling between diabatic states (meV)

		$\Psi(S[1])$	$\Psi(S[2])$	$\Psi'(S[1])$	$\Psi'(S[2])$
Stack A	$\Psi(^1TT)$	356.7	0.0	353.9	0.1
	$\Psi'(^1TT)$	356.8	0.0	367.6	0.1
Inter-stack	$\Psi(^1TT)$	92.5	23.4	96.6	23.2
	$\Psi'(^1TT)$	92.7	23.9	98.4	23.1
Stack A	$\Psi(^1TT)$	4.0	0.0	16.5	0.0
	$\Psi'(^1TT)$	6.9	0.0	11.8	0.0
Inter-stack	$\Psi(^1TT)$	0.4	0.1	0.2	0.3
	$\Psi'(^1TT)$	3.3	0.0	0.1	0.2

Tetracene trimer
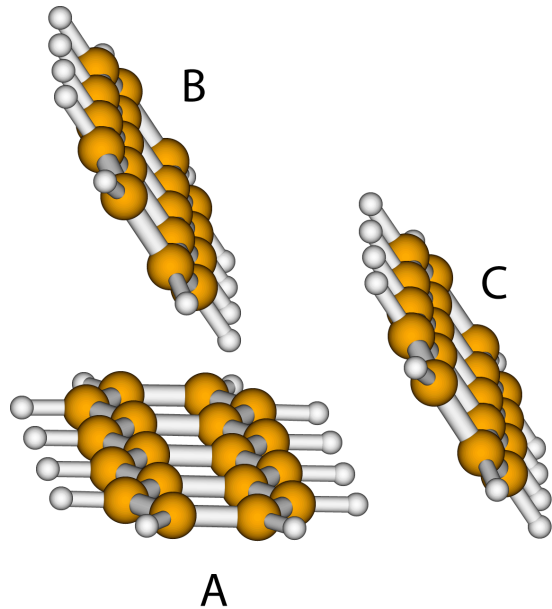
- Coupling between S_1 excited states:

- In dimer:
  - AB: 4.5 meV
  - BC: 43.8 meV

- In trimer:
  - AB: 4.0 meV
  - BC: 44.1 meV
  - AC: 11.6 meV

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- FOM Focus Group 'Next Generation Organic Photovoltaics' (DIFFER)

- FOM/Shell

- ITN-EJD-TCCM (Horizon2020)

Thank you for your attention!

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Theoretical Chemistry

$$I_1 = \langle \Delta_a | \sum_\mu \Omega_\mu | \Delta_b \rangle$$

$$I_1 = \sum_i \sum_j \langle a_i | \Omega_1 | b_j \rangle S(i,j)$$

$$I_2 = \langle \Delta_a | \sum_{\nu > \mu} \Omega_{\mu\nu} | \Delta_b \rangle$$

$$I_2 = \sum_{k>i} \sum_{l>j} \langle a_i a_k | \bar{\Omega}_{12} | b_j b_l \rangle S(ik, jl)$$

For non-singular overlap matrices S:

$$S(ik, jl) = 2(1 - p_{ik}) S(ij) S(kl)/|S|$$

For singular S a similar factorization is possible, so:

$$I_2 = \sum_{p,q,r,s} \langle \chi_p \chi_r | \Omega_{12} | \chi_q \chi_s \rangle B(pr, qs)$$

where also B can be factorized.