## Non-orthogonal Configuration Interaction for the Calculation of Electronic Couplings



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## Team















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## FOM Focus Group Groningen 'Next Generation Organic Photovoltaics'

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



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## 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



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T<sub>1</sub>



## Singlet fission rate

• Fermi Golden rule in diabatic representation (Marcus theory)

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

- Electronic coupling between diabatic states
  - Directly accessible with our non orthogonal CI approach
- Adiabatic representation: Non-adiabatic couplings (Landau-Zener model)

$$\left\langle \Psi_{f} \Big| rac{\partial}{\partial Q} \Big| \Psi_{i} 
ight
angle$$

 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



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## 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<sub>0</sub>S<sub>0</sub>, S<sub>0</sub>S<sub>1</sub>, <sup>1</sup>TT, CT), each describing a particular combination of molecular states



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#### 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



Β

 $\Psi^0$ : Ground state  $\Psi^1$ : Singlet excited state  $\Psi^T$ : Triplet excited state  $\Phi_{AB}^{00} = A(\Psi_A^0 \times \Psi_B^0)$   $\Phi_{AB}^{10} = A(\Psi_A^1 \times \Psi_B^0)$   $\Phi_{AB}^{01} = A(\Psi_A^0 \times \Psi_B^1)$   $\Phi_{AB}^{TT} = A(\Psi_A^T \times \Psi_B^T)$ :

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

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## Non Orthogonal Configuration Interaction

- Wavefunction expanded as:  $\Psi = \sum_{i=1}^{N} c_i \Phi_i$  with  $\Phi_i$  a many-electron basis function ((MEBF) Slater determinant, or combination thereof)
- The orbitals  $\chi_j$  in a MEBF are not orthogonal, making the manyelectron MEBFs also not orthogonal:  $\langle \Phi_i | \Phi_j \rangle = S_{ij}$
- 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  $\langle \Phi_i | H | \Phi_j \rangle$
- Solve  $(\mathbf{H} E\mathbf{S})(\mathbf{c}) = 0$  to get energies and  $\Psi$  (c<sub>i</sub>'s)



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## 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



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



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## 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  $\langle \Phi_{AB}^{KL} | H | \Phi_{AB}^{K'L'} \rangle$  and  $\langle \Phi_{AB}^{KL} | \Phi_{AB}^{K'L'} \rangle$
- If  $|\Phi_A^K\rangle$  contains ~ 500 determinants, then  $|\Phi_A^K\rangle \times |\Phi_B^L\rangle = |\Phi_{AB}^{KL}\rangle \sim 2.5 \cdot 10^5$

• 
$$\left\langle \Phi_{AB}^{KL} \middle| H \middle| \Phi_{AB}^{K'L'} \right\rangle = \sum_{i} \sum_{j} c_{i} c_{j} \left\langle \Delta_{i} \middle| H \middle| \Delta_{j} \right\rangle$$

- Approximately  $10^7$  elements  $\langle \Delta_i | H | \Delta_j \rangle$  have to be calculated for one matrix element  $\langle \Phi_{AB}^{KL} | H | \Phi_{AB}^{K'L'} \rangle$
- Aim for high level of parallelism
- Easy to parallelize



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## 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 
$$S^{(i,i)} = \prod_{m \neq i} \lambda_m$$
  $(S^{(i,j)} = 0 \text{ for } i \neq j)$ 

- No 4-index, but transform co-factors to common AO basis in which the corresponding orbitals c<sub>i</sub> and d<sub>i</sub> are expressed
- SVD and matrix multiplications
- Use GPUs



#### Performance old code

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



## The GronOR code



- In collaboration with OLCF, based on the GNOME code
  - OpenACC for GPU off-loading
  - Master-slave 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



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## GronOR Master-Slave Process Layout



Each process group has the same (user specified) number of slave 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 slave process fails, the entire group to which it belongs will fail



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#### Test case: Naphthalene dimer

#### Anti-symmetrized products of CAS(4,4) wavefunctions



- Neglect of dynamical correlation (S<sub>1</sub> too high)
- Endoergic



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#### Electronic couplings

In meV



## Performance of GronOR





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#### Biradicaloid dimer

Anti-symmetrized products of CAS(2,2) wavefunctions



## Stack A

• The relative energies of the cluster MEBFs



MEBF	E <sub>rel</sub> (eV)	MEBF	E <sub>rel</sub> (eV)
Â[AB]	0.00	Â[A <sup>T</sup> B <sup>T</sup> ]	1.61
Â[ <mark>A</mark> SB]	3.81	Â[A+B-]	4.49
Â[A <mark>B</mark> S]	3.81	Â[ <mark>A<sup>-</sup>B</mark> +]	4.49

• The energies and weights of the diabatic states

В	MEBF	S[1]	S[2]	S'[1]	S'[2]
N N _ 2 59 Å	Â[ <mark>A</mark> SB]	0.50	0.50	0.45	0.50
N - N = 3.36  A	Â[A <mark>B</mark> <sup>S</sup> ]	0.50	0.50	0.45	0.50
N-N = 3.85 A	$\hat{A}[A^+B^-] + \hat{A}[A^-B^+]$	-	-	0.09	0.00
	Energy (eV)	3.72	3.90	3.64	3.90
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#### Electronic coupling between diabatic states (meV)

		Ψ(S[1])	Ψ(S[2])	Ψ′(S[1])	Ψ <b>′</b> (S[2])
Stack A	Ψ( <sup>1</sup> TT)	4.0	0.0	16.5	0.0
	Ψ <b>'(</b> ¹TT)	6.9	0.0	11.8	0.0
Inter- stack	Ψ( <sup>1</sup> TT)	0.4	0.1	0.2	0.3
	Ψ′( <sup>1</sup> TT)	3.3	0.0	0.1	0.2

Primed states include virtual charge-transfer states

Inclusion of virtual CT states enhances the coupling



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### Current applications



## 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 integrals and CI lists
    - Molecular orbital basis
  - Inclusion of dynamical correlation
- Biradicaloid is a suitable building block for singlet fission chromophores
- Further studies:
  - Cibalackrot and other (small) SF molecules



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