Computational tools for the electronic structure study of singlet fission

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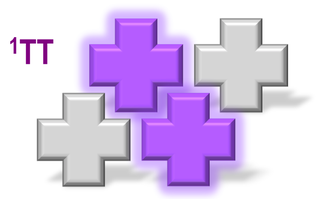
Multi-Exciton state



SF precursor

Multi-excitonic singlet as two coupled triplets ^{1}**ME** ~ ^{1}TT

$$^1TT = \left[\uparrow\downarrow\ \ \uparrow\downarrow\right] + \left[\uparrow\downarrow\ \ \uparrow\downarrow\right] + {}^1/_2 \left[\uparrow\downarrow\ \ \uparrow\downarrow + \uparrow\downarrow\ \ \uparrow\downarrow + \uparrow\downarrow\ \ \uparrow\downarrow + \uparrow\downarrow\ \ \uparrow\downarrow\right]$$

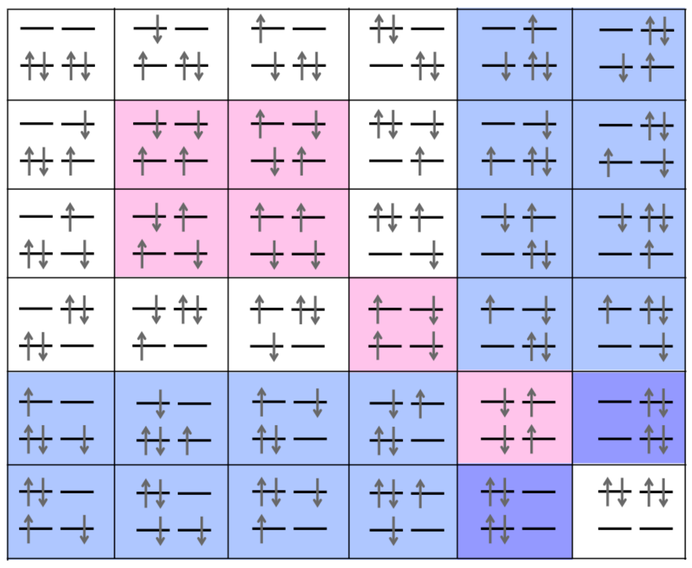
T_1T_{-1} $T_{-1}T_1$ T_0T_0

- ^{1}TT states require multiple configurations
- Other configurations might be important for the adiabatic (^{1}ME) SF precursor

RAS-2SF wavefunction

Casanova, Head-Gordon, *PCCP* **2009** *11* 9779

reference configuration ^{5}TT $\hat{R}^{2SF}$



$\hat{R}^{2SF}$ Double spin-flip excitation operator

^{1}TT configurations

Charge transfer

The RAS-2SF structure contains single-exciton, multi-exciton and charge transfer configurations

Single-Exciton states

States

- Exciton resonances
- Charge resonances
- Charge transfer
- Excimers / Trap states

Time-Dependent Density Functional Theory **TDDFT**

- Long-range corrected for charge separation (TDDFT)
- Dispersion corrections for weak interactions (DFT/TDDFT)

Constrain Density Functional Theory **C-DFT**

- DFT calculations with spin/charge constrains
- Energy of CT (diabatic) states

Fission ^{1}ME ⟶ $T_1 + T_1$

Indicators availability of the fission channel

Energy gap $\Delta E_F = E[^5ME] - E[^1ME] \rightarrow 0$ ✓

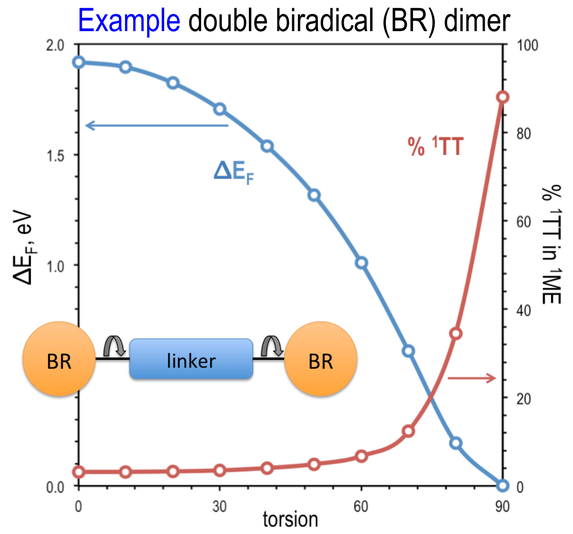
% ^{1}TT

Contribution of ^{1}TT in the overall ^{1}ME wavefunction $\frac{[^1TT]}{[^1ME]} \rightarrow 100\%$ ✓

Radical character

Number of unpaired electrons of ^{1}ME $N_U = \sum_i 1 - |1 - n_i|$ $N_U \rightarrow 4$ ✓

Example double biradical (BR) dimer



Delocalization

Dependence of transition energy with number of molecules (molecular crystal)

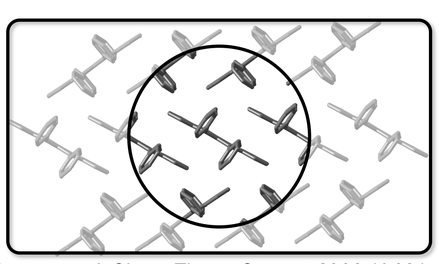
n # molecules

$E_1(\infty)$ transition crystal

A ΔE/molecule

Tc > DPT > Rub

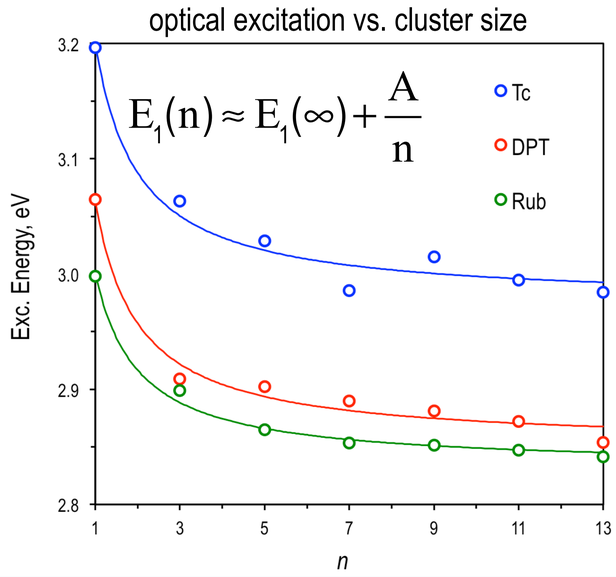
+ coupling **−**



Casanova, *J. Chem. Theory Comput.* **2014** *10* 324

optical excitation vs. cluster size

$$E_1(n) \approx E_1(\infty) + \frac{A}{n}$$



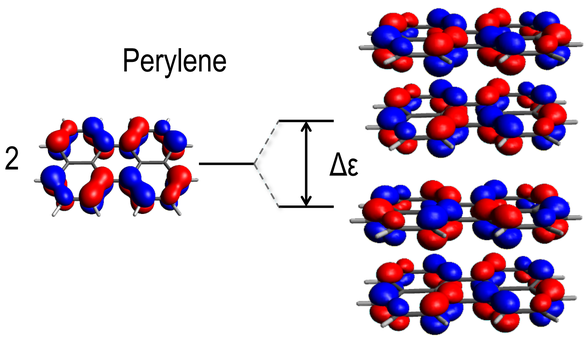
Chromophore Coupling

Orbital Splitting

$\Delta\varepsilon_H = \varepsilon_{HOMO} - \varepsilon_{HOMO-1}$

$\Delta\varepsilon_L = \varepsilon_{LUMO+1} - \varepsilon_{LUMO}$

Perylene

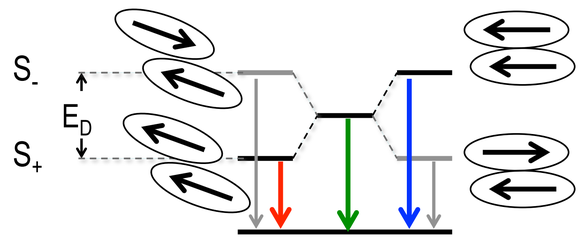


single-particle coupling

Davydov Splitting

$$S_{+/-} = \frac{1}{\sqrt{2}}\left(S_0S_1 \pm S_1S_0\right)$$

$E_D = \left|E[S_+] - E[S_-]\right|$



exciton coupling

Diabatization

First Order $\langle S_0S_1|\hat{H}|TT\rangle$

Second Order $\sum_{X \neq TT,S_0S_1} \frac{\langle S_0S_1|\hat{H}|X\rangle\langle X|\hat{H}|TT\rangle}{\Delta E_X}$

direct coupling mediated coupling

- physically sound and intuitive
- definition diabatic states is arbitrary

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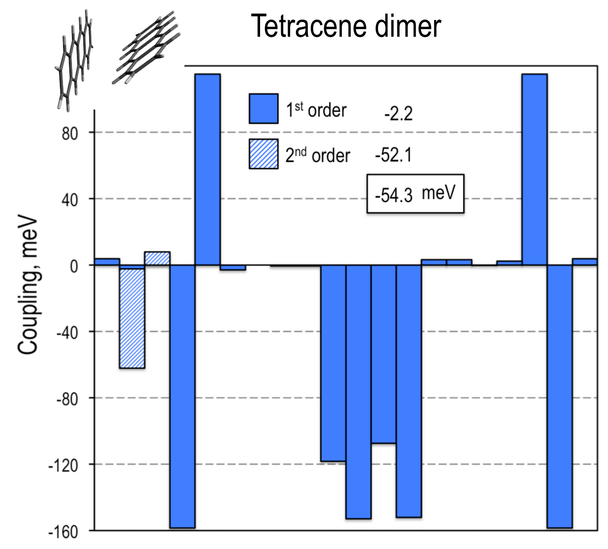
Tetracene dimer



One-Particle Transition Density Matrix

Non adiabatic coupling (NAC) $\langle S_1|\nabla_Q|^1ME\rangle$

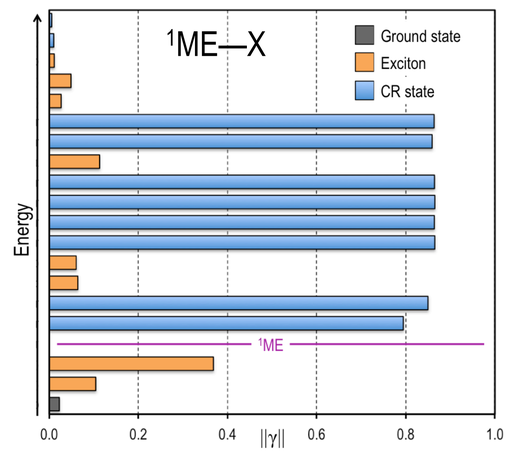
$NAC = \left|Tr\left[\gamma\nabla_Q\right]\right| \leq \|\gamma\| \cdot \|\nabla_Q\|$ $\|\gamma\|^2 = Tr\left[\gamma\gamma^+\right]$

✗ $0 \leq \|\gamma\| \leq 1$ ✓

- magnitude of one-electron transition
- approximation to the strength of NAC

Feng, Luzanov, Krylov, *J. Phys. Chem. Lett.* **20134** *4* 3845

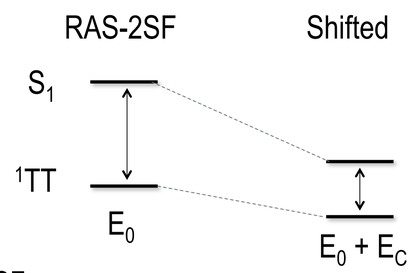
Anthracene dimer



Dynamic correlation

RAS-2SF lack of dynamic correlation ⟹ Overestimation S_1 vs. ^{1}TT

Energy shift



Approaches to **E_R**

E_0 RAS-2SF energy

E_C correction energy $E_C[S_1] = E_R[S_1] - E_0[S_1]$

E_R reference energy $E_C[^1TT] = 2\left(E_R[T_1] - E_0[T_1]\right)$

Experimental

- Correlation + environment
- Only characterized systems

Calculations

- S_1 and T_1 monomer states
- DFT and/or *ab initio*
- Known and unknown systems

Second-order perturbation theory **RAS(2)-2SF**

Correction to the RAS-2SF energies

$$E^{RAS(2)} = E^{RAS} - \sum_{k \neq H,P} \frac{\left|\langle k|\hat{H}|0\rangle\right|^2}{E_k - E_0}$$

Under development

Casanova, *J. Chem. Phys.* **2014** *140* 144111