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# Inter(Intra) Molecular Singlet Fission Study Using the GronOR Non-Orthogonal Configuration Interaction Method

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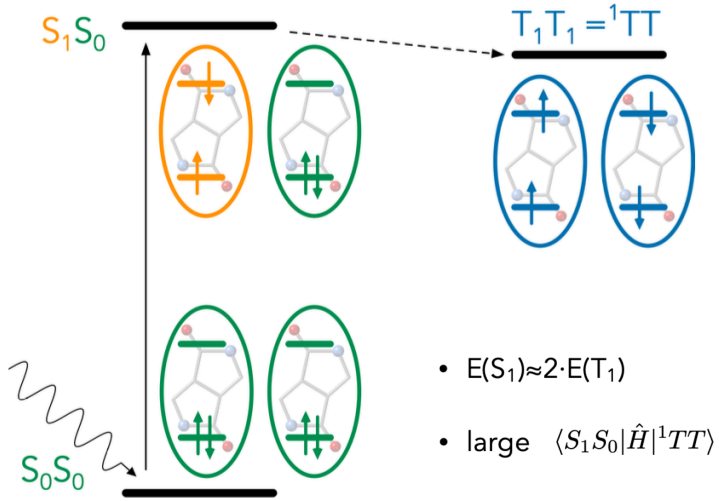
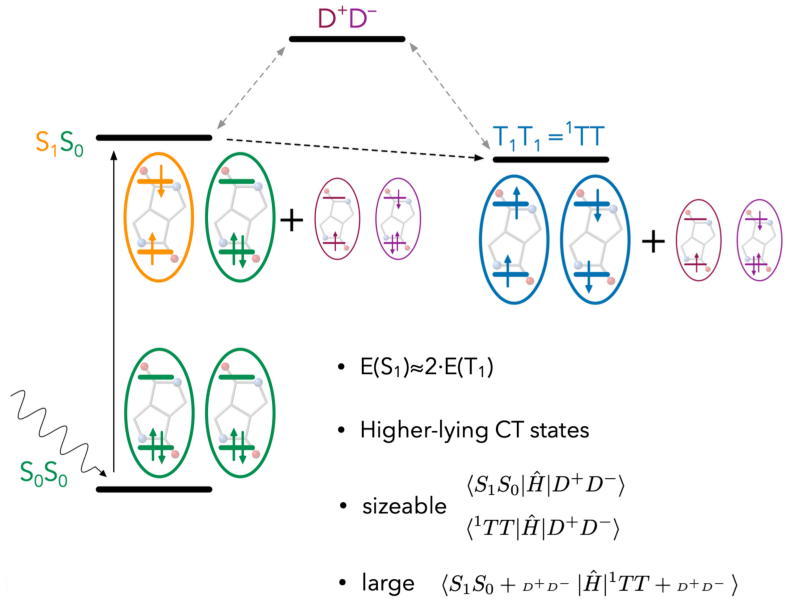
# Introduction

- Energy transfer and charge transfer are two important processes within photochemistry reactions.
- Applications: Singlet fission (one photon $\rightarrow$ four charge carriers)
- Focus on singlet fission process, exciton dispersion and triplet separation in trimers.




Direct




Charge transfer enhanced

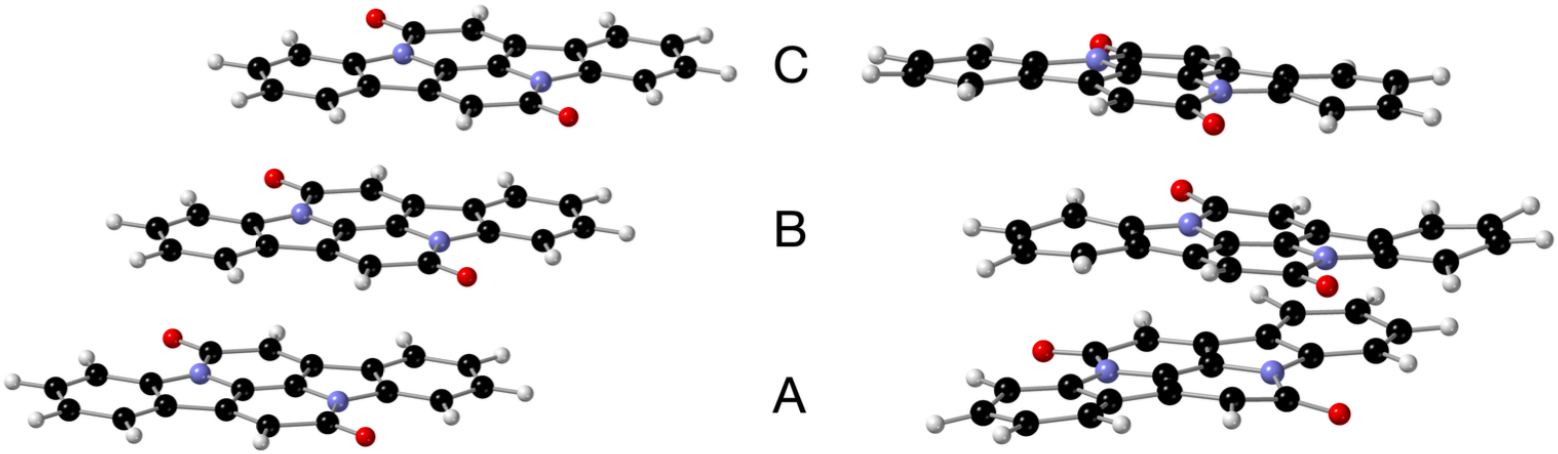
D. Casanova, Chemical Reviews 2018, 118, 7164

# Introduction

- Why indolonaphthyridine? Fallon utilizes the excited state aromatic features to adjust S-T energy gap and stability.

$$E(S_1) \approx 2 \cdot E(T_1)$$

| | $S_0$ | $S_1$ | $T_1$ | $D^+$ | $D^-$ | $2T_1$-$S_1$ |
|---|---|---|---|---|---|---|
| CASSCF (8,8) | 0.0 | 4.16 | 2.25 | 7.27 | -0.53 | 0.33 |
| CASPT2 | 0.0 | 1.83 | 0.81 | 7.10 | -1.90 | -0.20 |




Snapshot from MD simulations

Fallon et al, Journal of the American Chemical Society 2019, 141, 13867

# Methodology
## NOCI-F Algorithm

Each fragment's states expressed in CASSCF:

$$\Psi_\alpha = c_{\alpha 1}\psi_1 + c_{\alpha 2}\psi_2 + c_{\alpha 3}\psi_3 + \cdots + c_{\alpha N}\psi_N$$
$$\Psi_\beta = c_{\beta 1}\gamma_1 + c_{\beta 2}\gamma_2 + c_{\beta 3}\gamma_3 + \cdots + c_{\beta N}\gamma_N$$

Building the spin-adapted linear combinations of antisymmetrized products using fragment wavefunctions:

$$\langle \Psi_\alpha | \hat{H} | \Psi_\beta \rangle = c_{\alpha 1} c_{\beta 1} \langle \psi_1 | \hat{H} | \gamma_1 \rangle + c_{\alpha 1} c_{\beta 2} \langle \psi_1 | \hat{H} | \gamma_2 \rangle + \ldots + c_{\alpha N} c_{\beta M} \langle \psi_N | \hat{H} | \gamma_M \rangle$$

Determinant pairs contained $\Psi_\alpha$ and $\Psi_\beta$ are independent contributions, parallel implementation

# Results
## Intermolecular Singlet Fission

Table 1: Total SF electronic couplings (in meV) for a regular and a thermally disordered trimer of indolonaphthyridines

| | Regular | | | Distorted | | |
|---|---|---|---|---|---|---|
| | $S_1S_0S_0$ | $S_0S_1S_0$ | $S_0S_0S_1$ | $S_1S_0S_0$ | $S_0S_1S_0$ | $S_0S_0S_1$ |
| $T_1T_1S_0$ | 12.58 | 11.68 | 0.03 | 38.92 | 17.89 | 3.85 |
| $S_0T_1T_1$ | 0.03 | 11.68 | 12.58 | 2.66 | 20.19 | 1.42 |
| $T_1S_0T_1$ | 0.04 | $< 0.01$ | 0.04 | 0.30 | 0.05 | 2.13 |

Table 2: Total triplet separation and double triplet diffusion couplings (in meV) for a regular and a thermally disordered trimer of indolonaphthyridines

| | Regular | | Distorted | |
|---|---|---|---|---|
| | $T_1T_1S_0$ | $S_0T_1T_1$ | $T_1T_1S_0$ | $S_0T_1T_1$ |
| $S_0T_1T_1$ | 0.11 | | 0.04 | |
| $T_1S_0T_1$ | 3.13 | 3.13 | 1.32 | 0.98 |

Sousa et al, Journal of the Physical Chemical C 2025, 129(8), 4290-4302

# Results
## Intermolecular Singlet Fission

Table 3: Total singlet exciton diffusion couplings (in meV) for a regular and a thermally disordered trimer of indolonaphthyridines

| | Regular | | Distorted | |
|---|---|---|---|---|
| | $S_1S_0S_0$ | $S_0S_1S_0$ | $S_1S_0S_0$ | $S_0S_1S_0$ |
| $S_0S_1S_0$ | 78.02 | | 46.97 | |
| $S_0S_0S_1$ | 11.65 | 78.02 | 2.04 | 12.34 |

Table 4: Total triplet exciton diffusion couplings (in meV) for a regular and a thermally disordered trimer of indolonaphthyridines

| | Regular | | Distorted | |
|---|---|---|---|---|
| | $T_1S_0S_0$ | $S_0T_1S_0$ | $T_1S_0S_0$ | $S_0T_1S_0$ |
| $S_0T_1S_0$ | 0.70 | | 0.85 | |
| $S_0S_0T_1$ | $<$0.01 | 0.70 | 0.01 | 0.53 |

# Results
## Intermolecular Singlet Fission

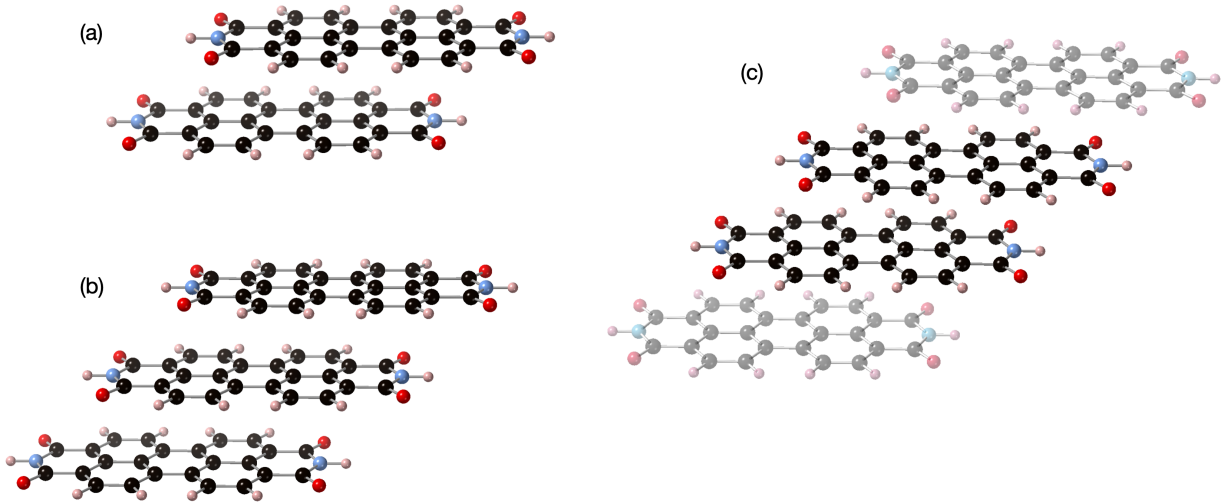



Table 5: Direct and total SF electronic couplings $\gamma$ (in meV) for dimers and trimers of various PDI derivatives.

| | dimer | | trimer | |
|---|---|---|---|---|
| | $\gamma$ direct | $\gamma$ total | $\gamma$ direct | $\gamma$ total |
| EP | 2.24 | 25.68 | 2.28 | 27.60 |
| C3-I | 1.16 | 34.43 | 1.20 | 33.11 |
| C7 | 4.14 | 33.47 | 4.13 | 30.68 |
| C8 | 7.74 | 17.54 | 7.72 | 26.78 |

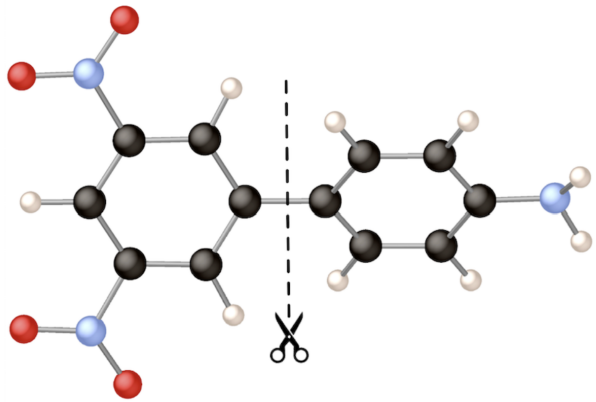
R1: ethylphenyl (EP)

propyl (C3–I)

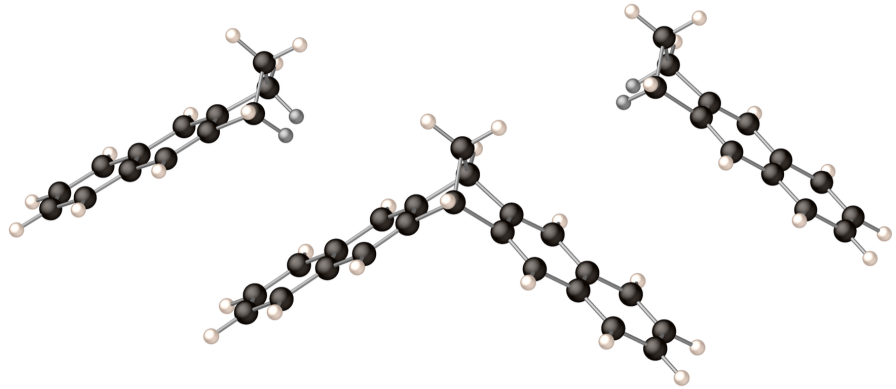
heptyl (C7)

octyl (C8)

# Results
## Intramolecular Singlet Fission



Overlap Fragment Method



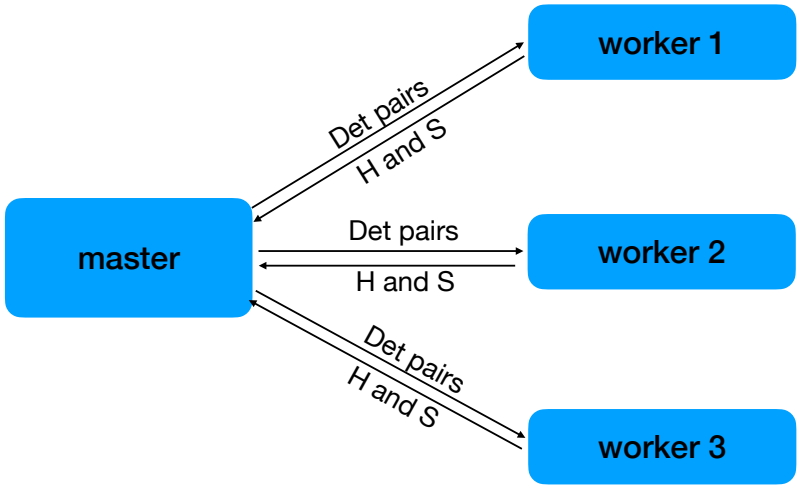
Norbornyl-bridged naphthalene dimer

Table 6: CASSCF(6,6) and CASPT2 relative energies of the fragment states and NOCI-F relative energies of the MEBFs with correlation correction. All energies in eV.

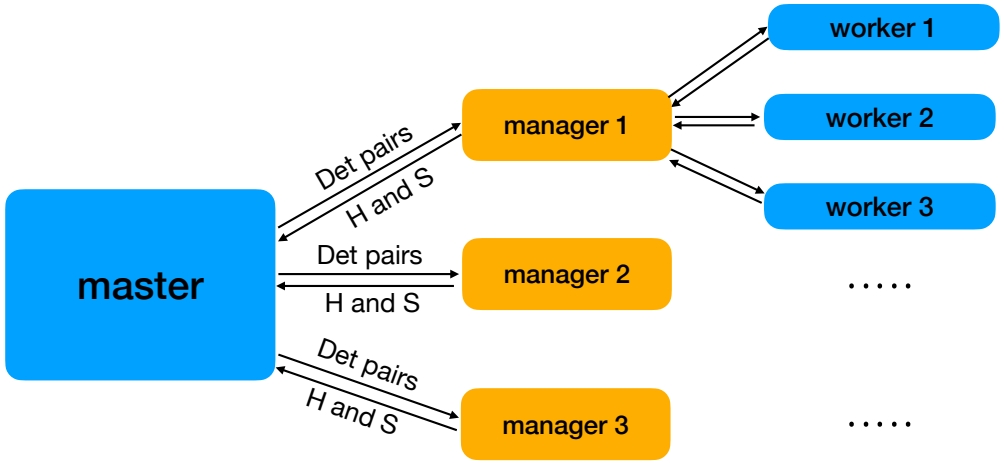
| State | CASSCF | CASPT2 | ref. weight | MEBF | NOCI-F |
|---|---|---|---|---|---|
| $S_0$ | 0.00 | 0.00 | 0.620 | $S_0S_0$ | 0.00 |
| $S_1$ | 5.64 | 4.63 | 0.613 | $S_1S_0$, $S_0S_1$ | 4.51 |
| $T_1$ | 3.60 | 3.25 | 0.603 | $T_1T_1$ | 6.27 |
| $D^+$ | 7.17 | 7.71 | 0.620 | $D^+D^-$, $D^-D^+$ | 5.42 |
| $D^-$ | 2.41 | 1.06 | 0.610 | | |

Sousa et al, Physical Chemistry Chemical Physics 2025

# Parallel Implementations of GronOR




(a) Worker-Master Execution Model




(b) Worker-Manager-Master Execution Model

# Results
## Performance-Related (Frontier)

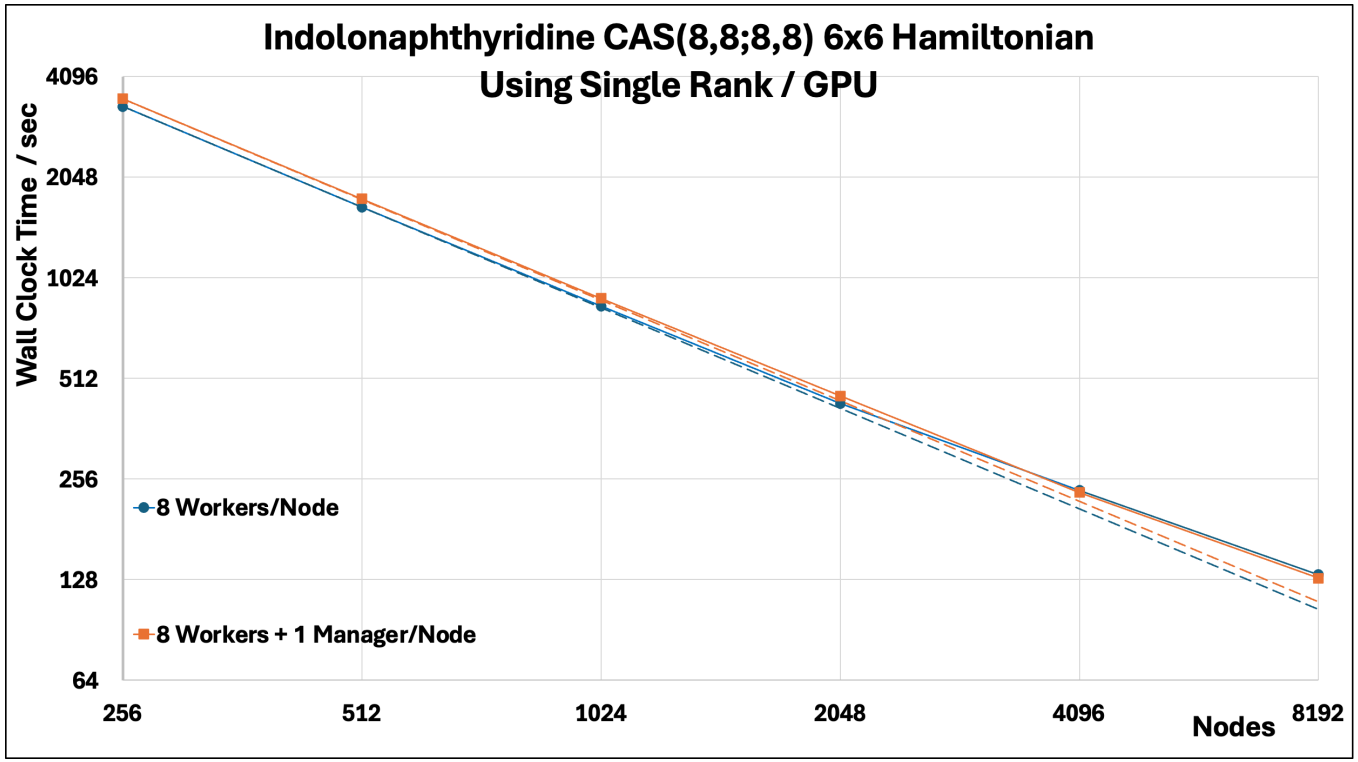



Figure 1: Scalability of indolonaphthyridine dimer calculations on Frontier, using the master-worker execution model with eight ranks per node and the master-manager-worker execution model with eight worker ranks and one manager ranks per node. The dashed line indicates linear scaling. Maximum running ranks reach 65536.

# Conclusions

- Chemistry-related
  - GronOR provides an efficient way to study the intermolecular singlet fission of indolonaphthyridine trimer, PDI dimer and PDI trimer using NOCI-F method.
  - Overlap fragment method is proposed to explore intramolecular singlet fission with NOCI-F method.
- Performance-related
  - Worker-manager-master execution model resolves intermittent MPI failure on Frontier and obvious advantage starts to show on high node-counts.
  - New SVD algorithm is implemented in ROCSOLVER and allows GronOR to take full advantages of GPUs on Frontier.
- Future Plan

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- Jordi Ribas[6]
- Ionut Octavian Stan[3]
- Spancer Dong[1]

GronOR:

- Gitlab: https://gitlab.com/gronor/gronor.git
- Open source, updated frequently
- International Collaborations

1). Oak Ridge National Laboratory, Oak Ridge, TN, USA. 2). University of Alabama, Tuscaloosa, AB. 3). Universitat Rovira i Virgili, Tarragona, Spain 4). ICREA,Barecelona, Spain. 5). University of Groningen, Groningen, the Netherlands. 6). Universitat de Barcelona, Barcelona, Spain

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