

## UNRAVELLING OPTICAL PROPERTIES OF EXTENDED CORE CONJUGATED CHROMOPHORES WITH COMPUTATIONAL STRATEGIES: FROM SINGLE MOLECULE TO AGGREGATES



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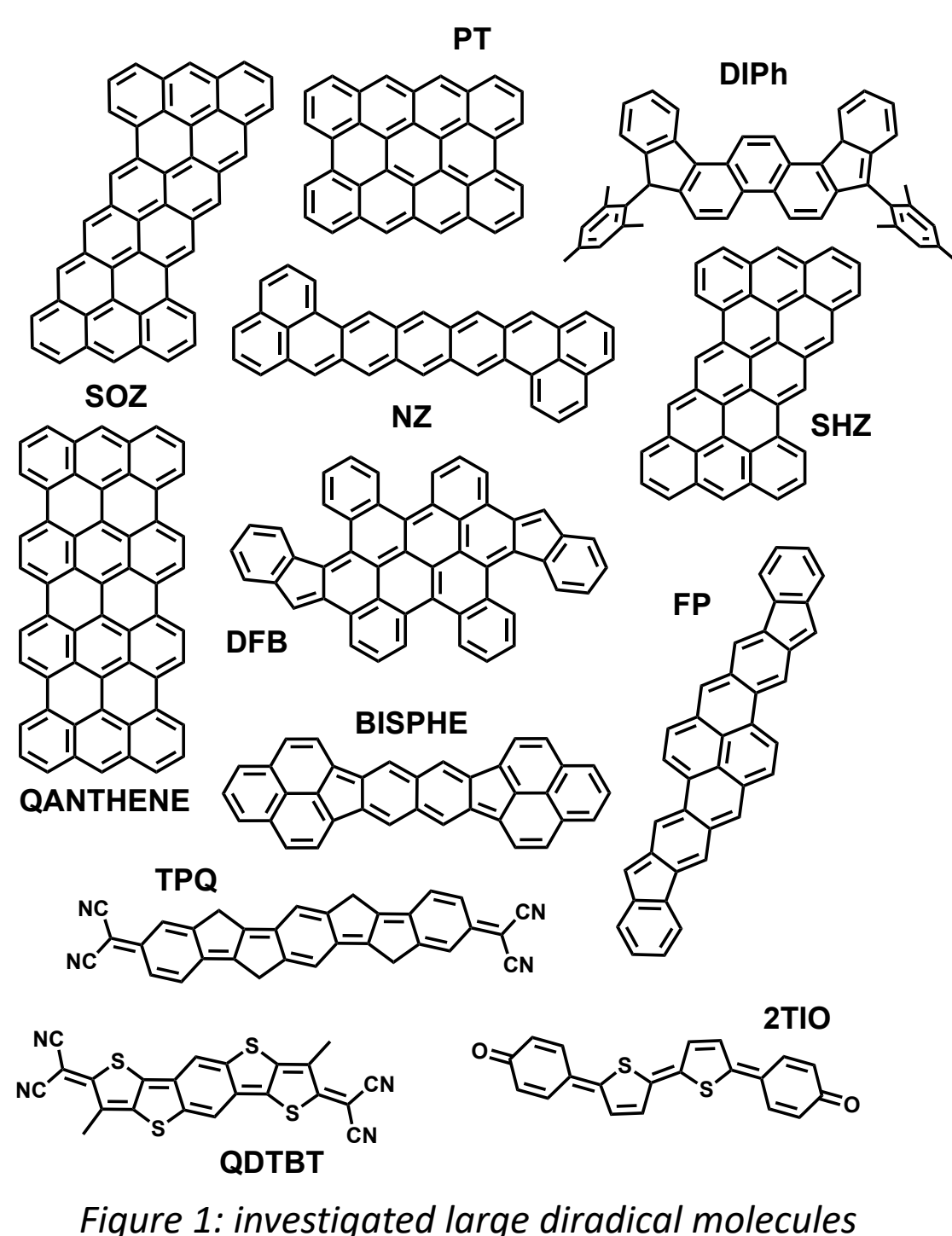
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### GENERAL INTRODUCTION

In recent years, polycyclic aromatic hydrocarbons (PAHs), especially those possessing diradical character have undergone a strong resurgence of interest due to their potential applications in optoelectronic devices [1]. Beside small HOMO-LUMO gap and small singlet-triplet gap, one distinctive character of their optical properties is the presence of a **low-lying double-exciton (DE) state** dominated by the H,H→L,L configuration [2] which may influence photophysical properties such as two-photon absorption efficiency and quenching of the fluorescence. In real optoelectronic devices, molecules are in condensed phase, intermolecular interactions play a relevant role. Generally, optical properties of **molecular aggregates** are different from those of isolated molecules [3]. Understanding optical properties of isolated molecules and how these are tuned in molecular aggregates is therefore useful for e.g. the design of devices.

In recent years, we have been interested in modelling the **optical properties** of large conjugated systems, focusing not only on isolated molecules but also considering aggregation effects. The goal of this contribution is therefore twofold. On one side, we report our recent results on the investigation of the DE state of conjugated diradicals with cost-effective computational methods such as **TDUDFT**, **SF-TDDFT** [4] and **DFT/MRCI** [5]. On the other hand, we present an investigation on the modulation of exciton states in aggregates of perylene di-imide (PBI), a well-known example of n-type organic semiconductor. In this regard we discuss the role of charge-transfer (CT) state *via* a **diabatization** procedure and a dimer-based **model-Hamiltonian (mH)** approach [6].

### Conjugated system: isolated molecules



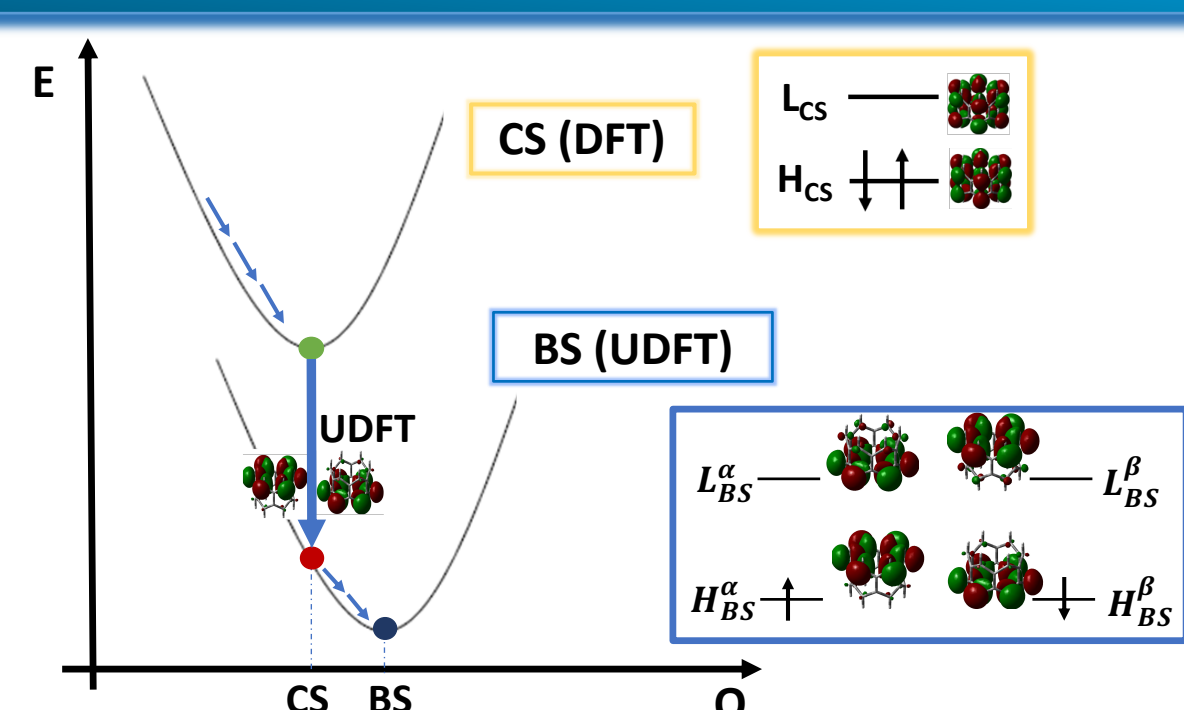
#### Diradical character

- Diradical character descriptor:  $y_0$  ( $0 \leq y_0 \leq 1$ )

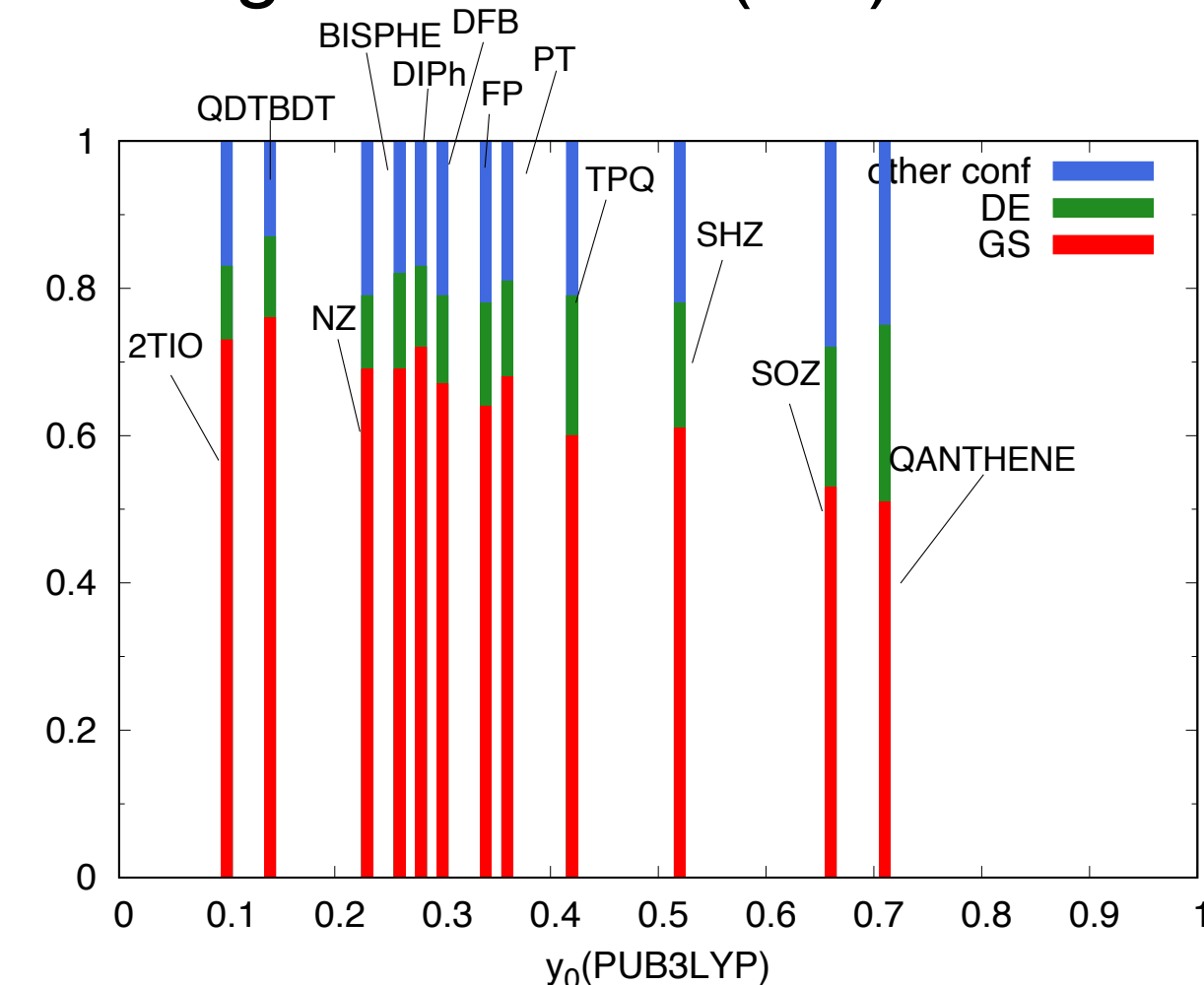
$$y_0^{PUnrestricted} = 1 - \frac{2T_0}{1 + T_0^2} \quad \text{with} \quad T_0 = \frac{n_{HOMO} - n_{LUMO}}{2}$$

$n$  = occupation number of frontier natural orbitals

#### GROUND STATE (GS) of diradicals



- For molecules exhibiting remarkable **diradical character**: the open-shell ground state (BS) is more stable.



#### Composition of the GS wavefunction

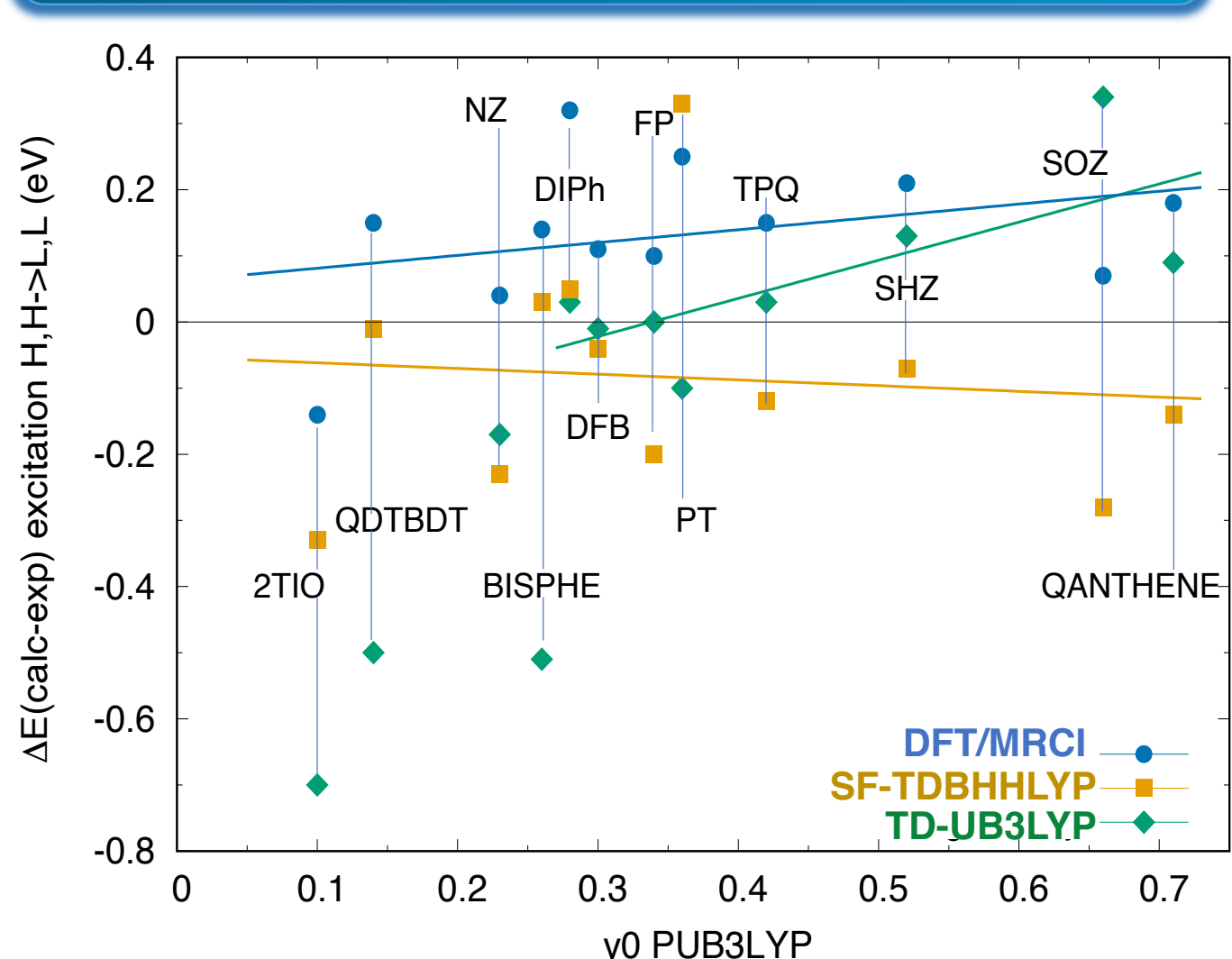
- Within single reference methods, the **unrestricted approach** is necessary (here UB3LYP)

### DOUBLE-EXCITON (DE) state of diradicals

#### Composition of the DE state wavefunction

- TDDFT is not suitable
- Within single reference methods, we can use TD-UDFT and SF-TDDFT;
- Among multireference methods, DFT/MRCI is a cost-effective alternative

#### The performance & conclusion

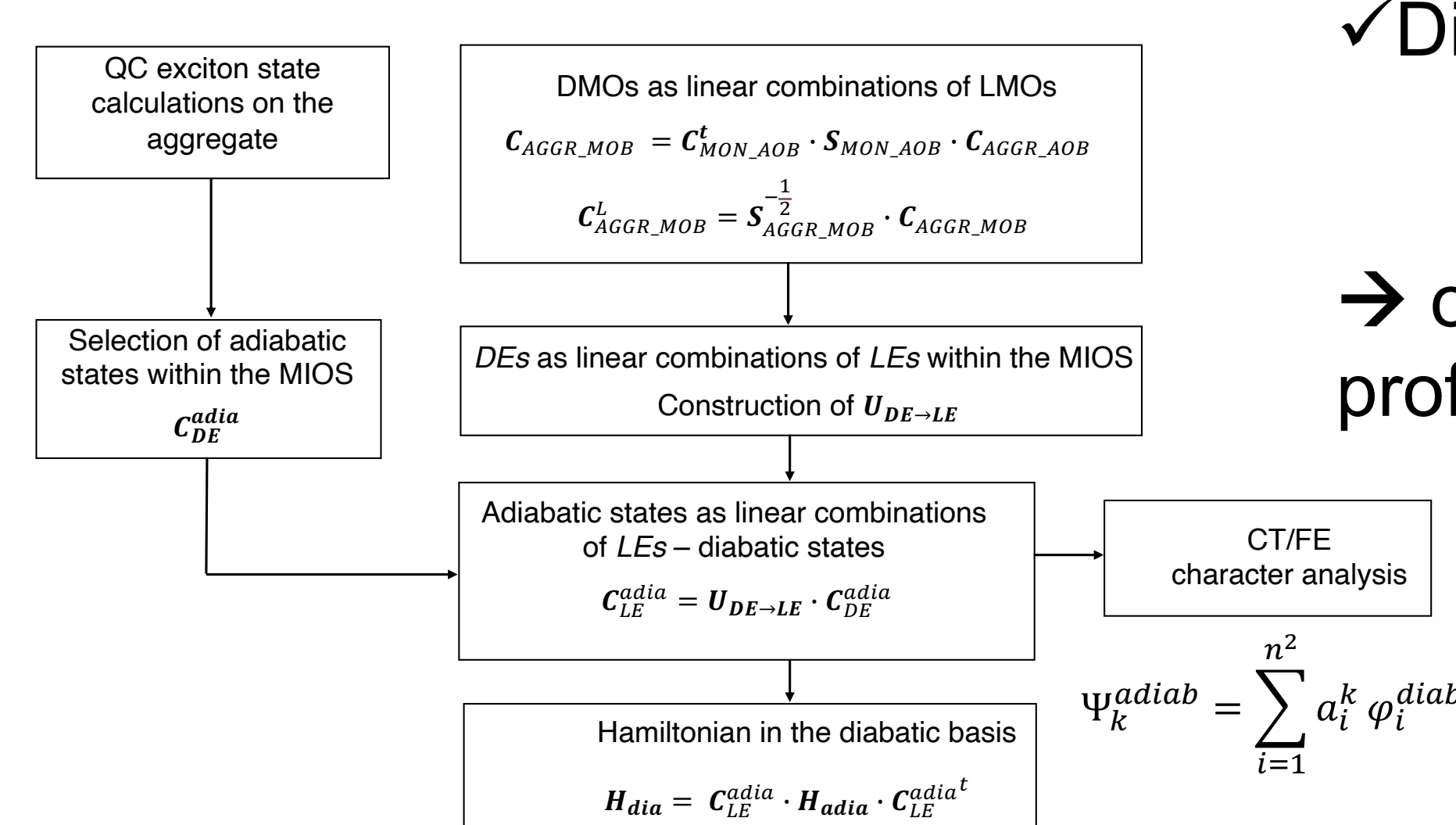


- all three methods can correctly predict the position of the DE state;
- TD-UB3LYP gives good results if  $y_0$  (PUB3LYP) > 0.3
- SF-TDBHLYP & DFTMRCI are independent from  $y_0$ , they tend to underestimate & overestimate the DE state, respectively.
- Other details can be found in ref 2.

### Conjugated system: PBI aggregates

#### Computational Approaches

##### Diabatization ( $H_{dia}$ )



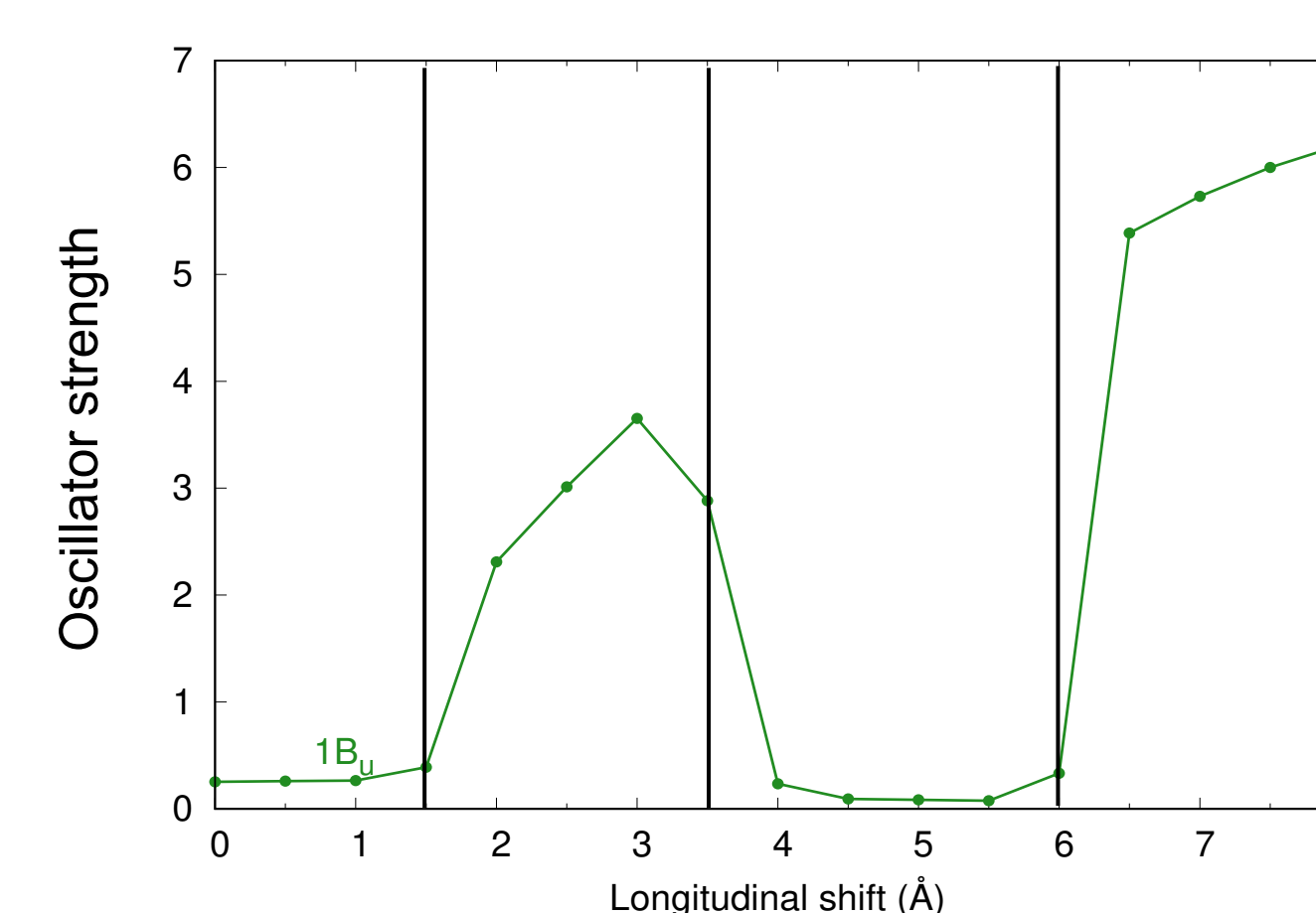
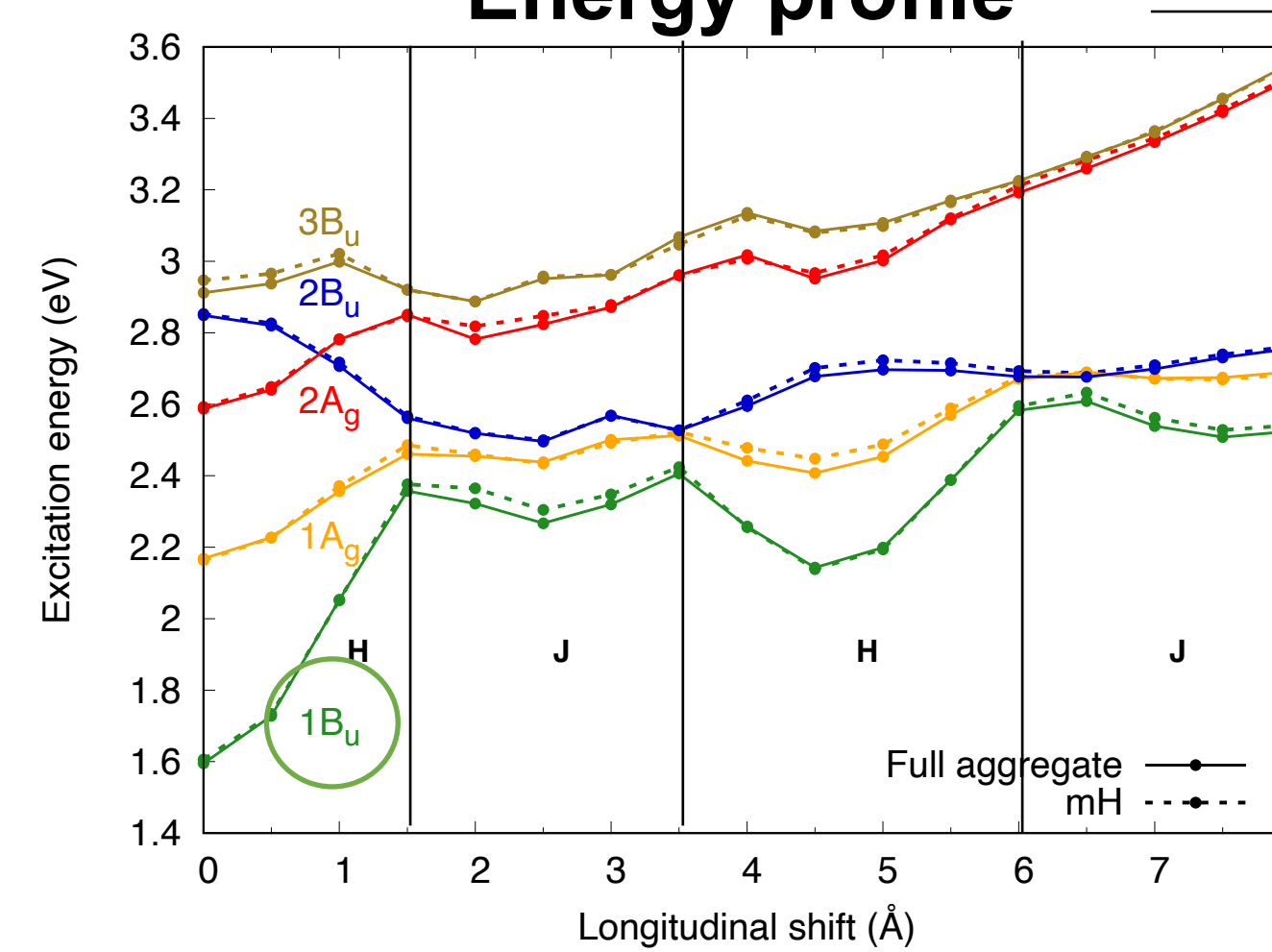
##### Model Hamiltonian (mH)

- ✓ Dimer-based

→ output: Exciton states energy profile + character

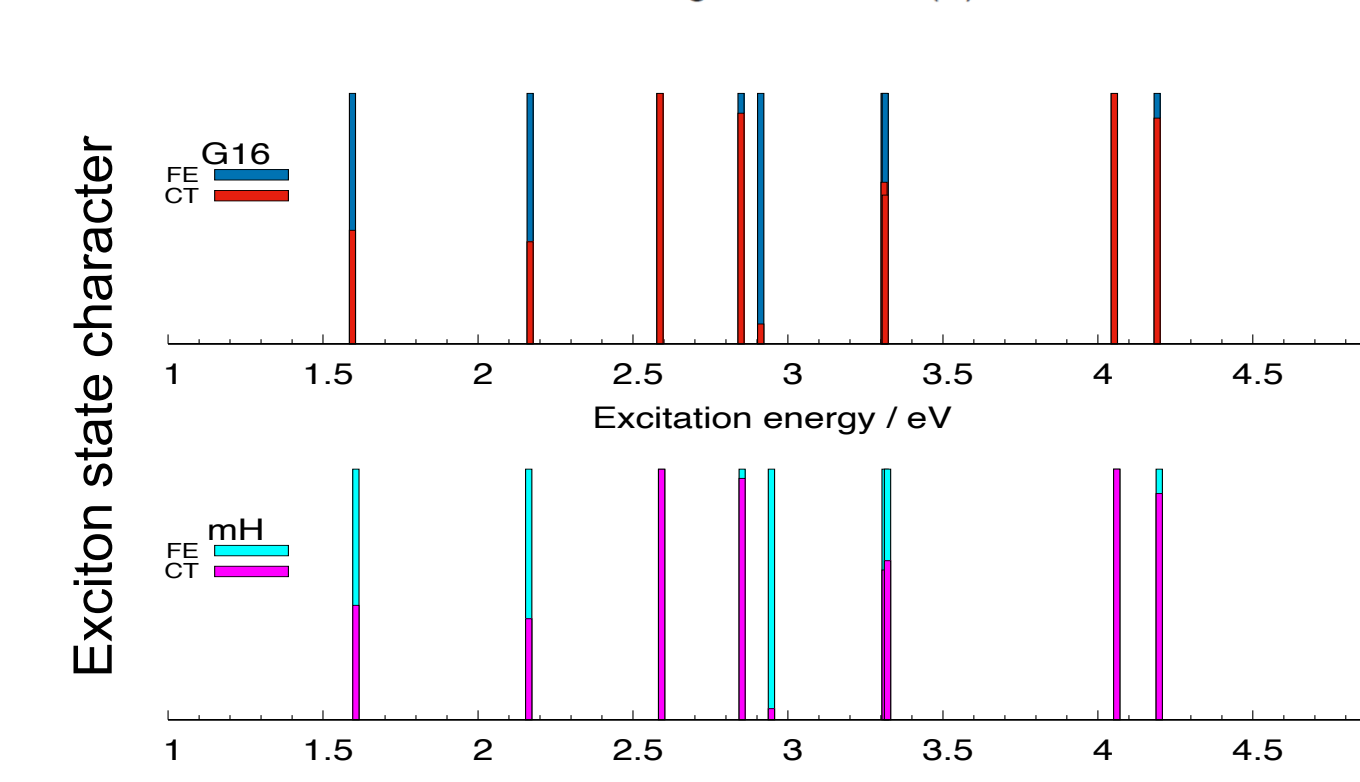
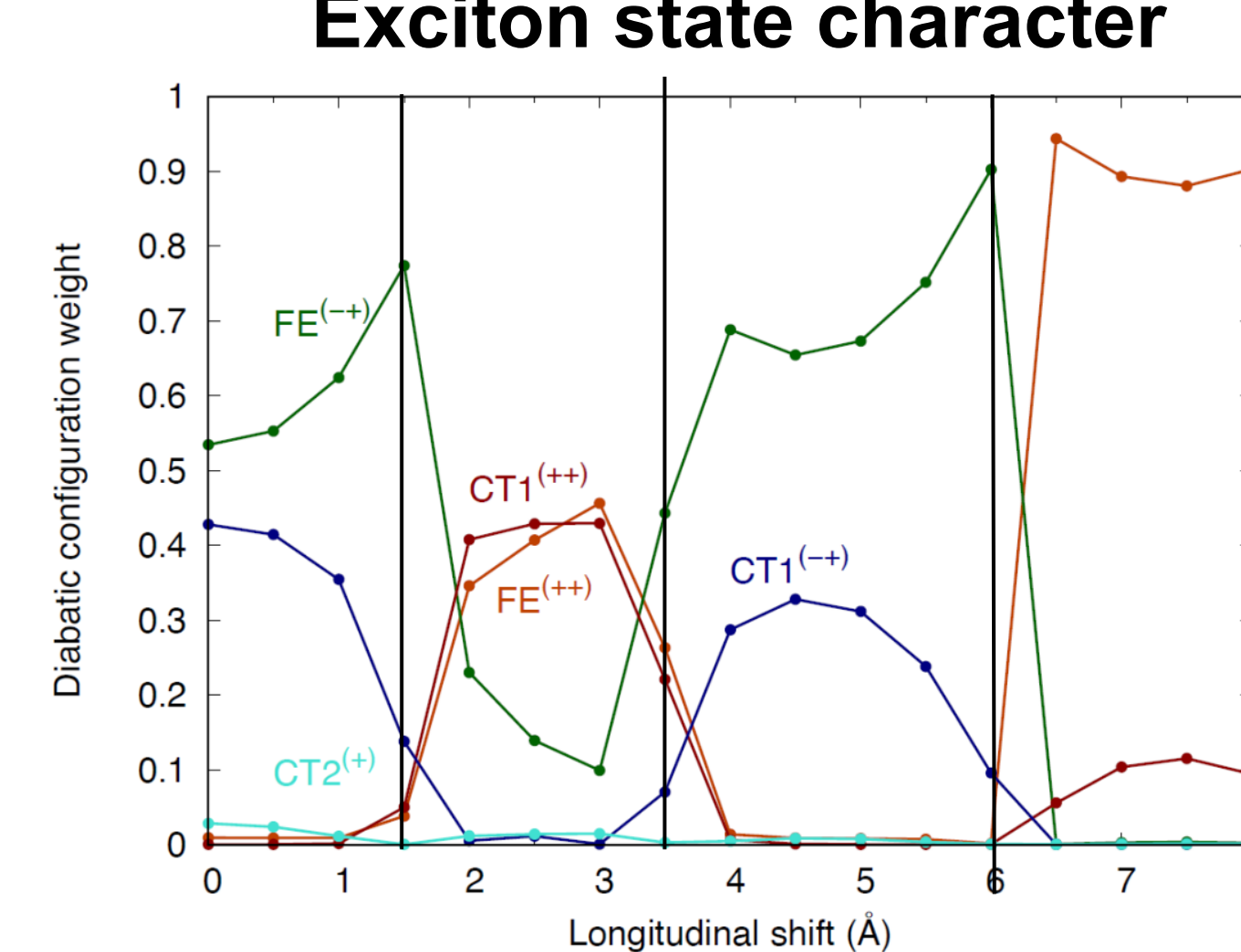
#### Trimer of PBI

#### Energy profile



\* Full aggregate = TD-ωB97XD/6-31G\*

#### Exciton state character



### Conclusion

- Unconventional CT-mediated aggregation is rationalized in terms of CT & FE interactions
- mH reproduces well full-aggregate calculations

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