РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

Multireference Computational Methods for Organic Electronics

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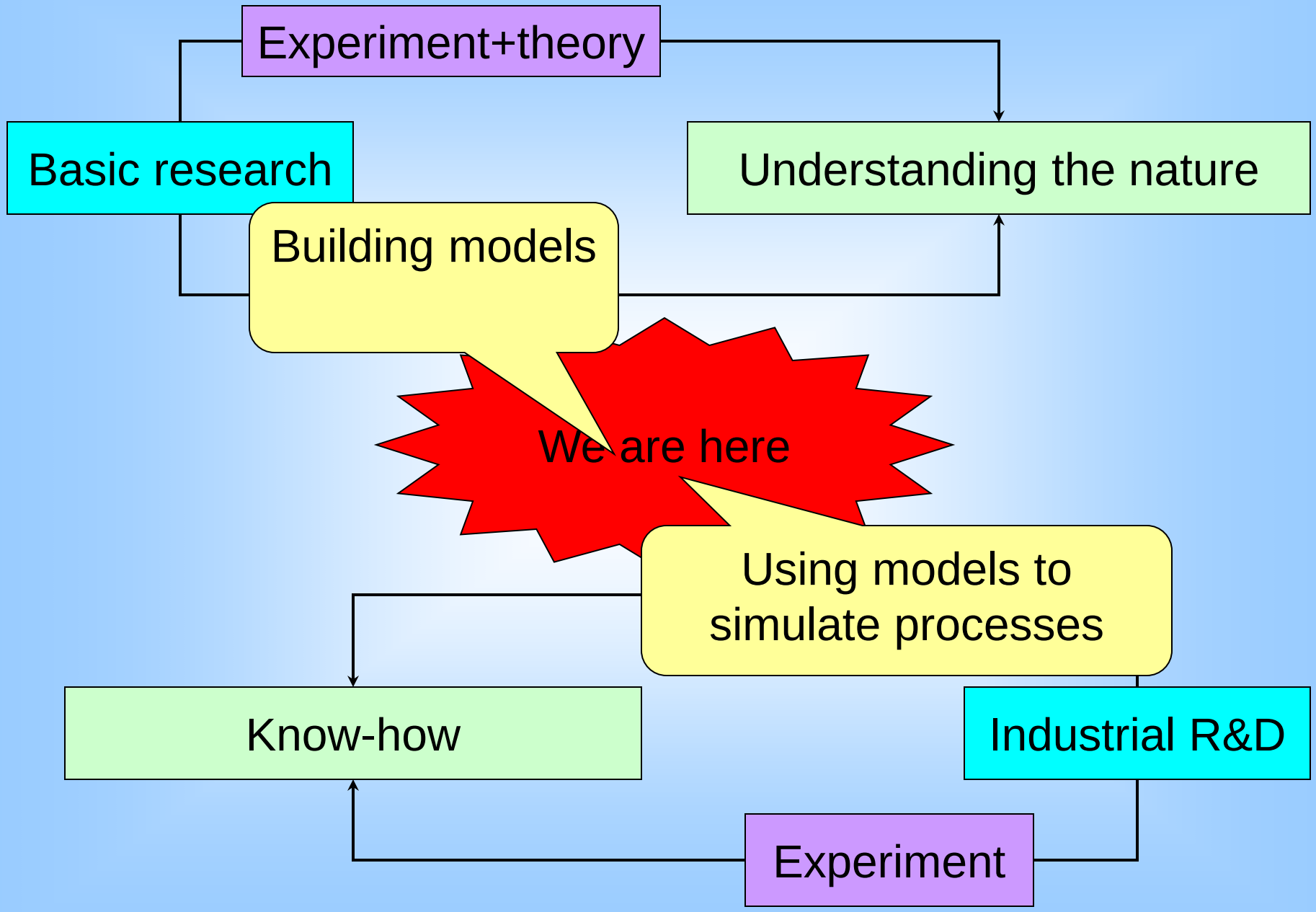

Experiment+theory
Basic research
Understanding the nature
Building models
We are here
Using models to simulate processes
Know-how
Industrial R&D
Experiment

Organic Electronic Devices

- Photovoltaics
  - Light sensors (e.g., in photo cameras)
  - Solar cells
- Light-emitting devices
- Field-effect transistors
- Chemical sensors

Problem of efficiency and chemical stability

Processes in Organic Electronics

- Light absorption
- Light emission
- Exciton recombination
- Charge separation
- Exciton transport
- Charge transport
- Chemical reactions
  - Intermolecular complexes in chemical sensors
  - Chemical degradation in excited or charged states

These processes are usually simulated using density functional theory

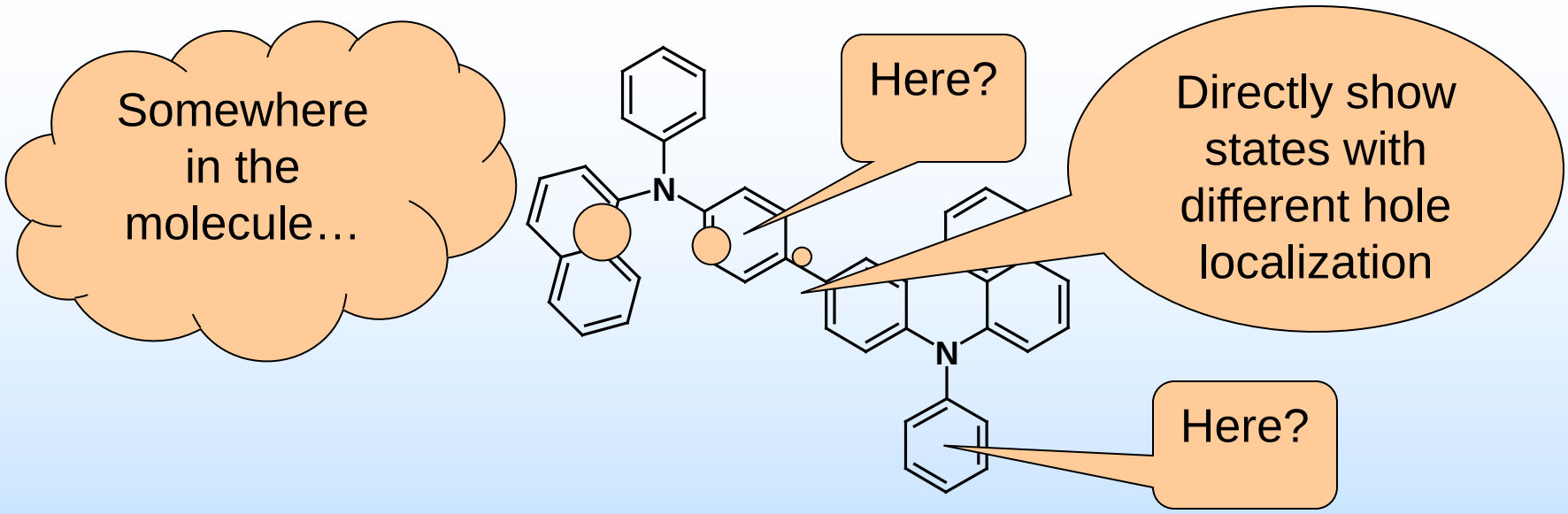
Density Functional vs. Multireference Methods

- Cheap and relatively fast
- Allows for large-scale calculations
- Allows for calculations of large molecules
- Easily automated and good for screening

- Relatively slow and expensive
- Requires focusing on only few molecules
- Moderate-size molecules can be calculated
- Unique custom calculations

So why multireference methods should be used in organic electronics?

Density Functional vs. Multireference Methods



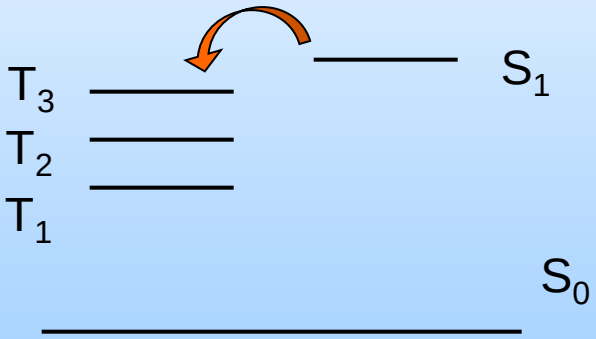
Where is the hole?

Why it is important?

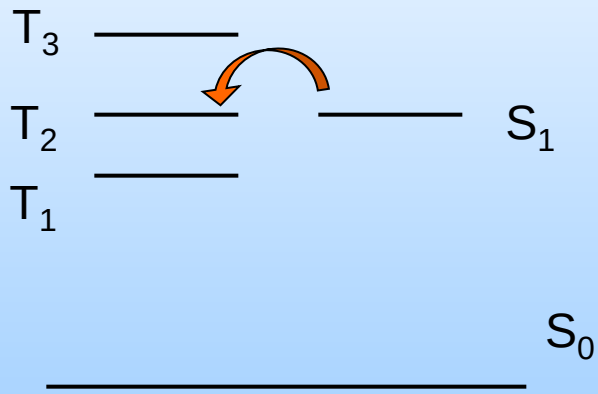
Charge localization in the molecule influences charge mobility and chemical stability of the material

Density Functional *vs*. Multireference Methods

- Overestimate the extent of charge or exciton delocalization
- Known issue with excited charge-transfer singlet states
- Underestimate triplet state energies wrt. excited singlets



- Correctly predict charge and exciton localization
- Correctly predict relative positions of excited states
- Accurate excited state energies



Why it is important?

For predicting energy transfer pathways, emission efficiency, and chemical stability of the material

What is Multireference Method?

Single-reference molecular wavefunction Ψ is single Slater determinant Φ_0 (+ possible minor corrections)

$$\Psi = \mathbf{C_0\Phi_0} + \Sigma_i C_i \Phi_i$$

Minor correction

HF, MP2, DFT, CC

Multireference molecular wavefunction Ψ is linear combination of Slater determinants Φ_i with comparable weights (+ possible minor corrections)

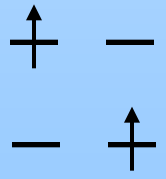
$$\Psi = \Sigma_i \mathbf{C_i\Phi_i} + \Sigma_j C_j \Phi_j$$

Minor correction

MCSCF, MRMP, MRCC

Examples

Partially filled *f* shell of lanthanides or *d* shell of transition metals



Charge hopping between similar fragments

Advantages of Multireference Methods

- Account for static correlation effects in (quasi)degenerate states
- Treats equally important states on equal grounds
- Not limited to single excitations

But

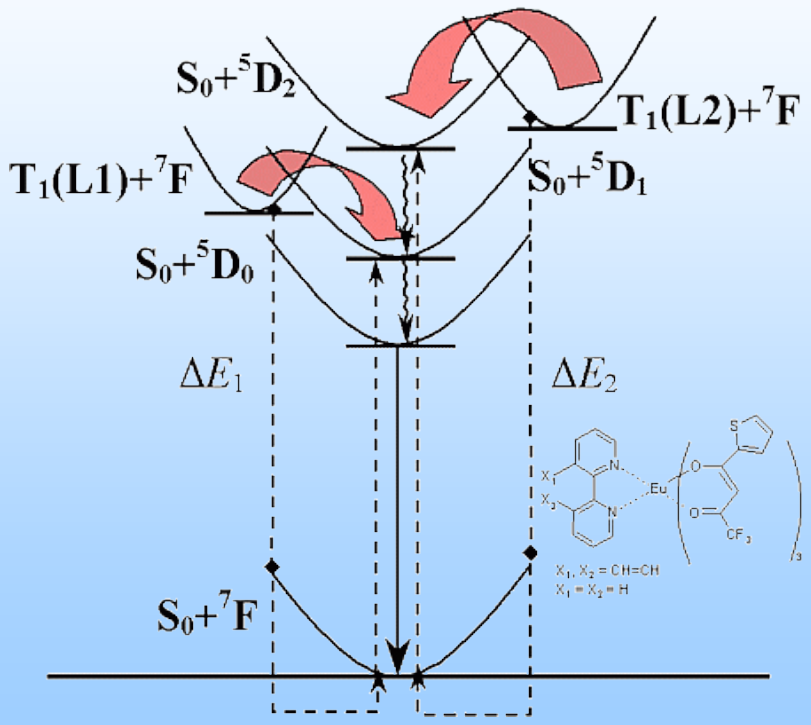
- Not a black-box method
- Requires experience and professional skills

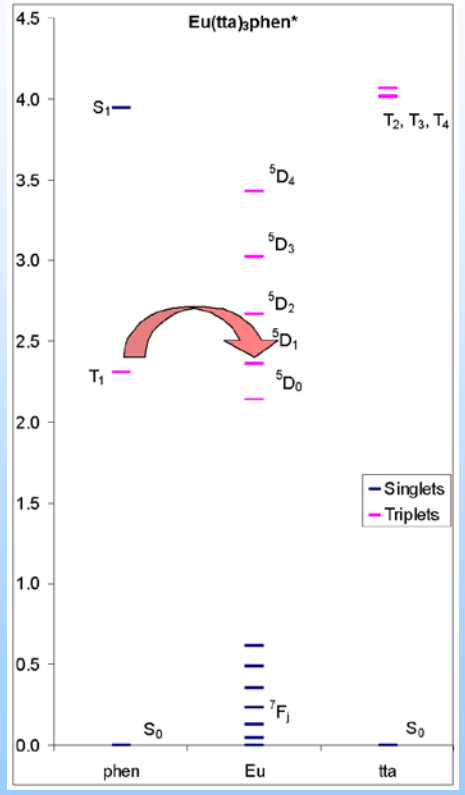
When Multireference Methods Should Be Used?

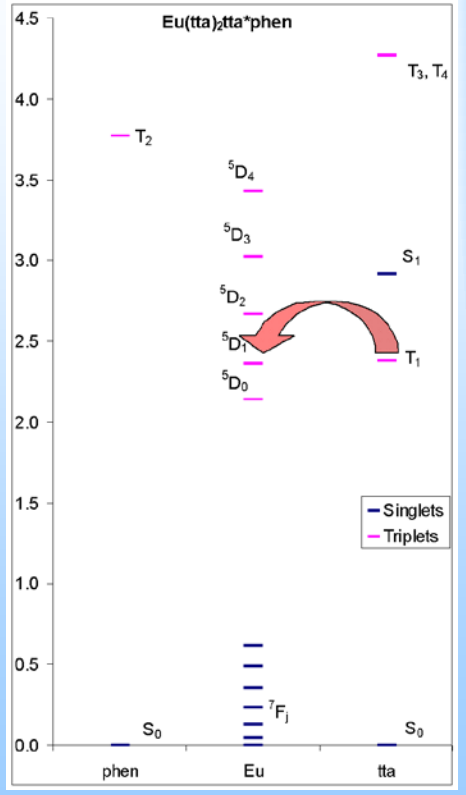
- In the case of strict or quasi-degeneration of states
- In studying potential energy surfaces where (quasi)degeneration is expected
  - Many chemical and photochemical reactions fall within this case
- When DFT gives definitely wrong results, and Coupled-Cluster methods are too expensive

Examples of Application of Multireference Methods

Energy transfer pathways in lanthanide complexes



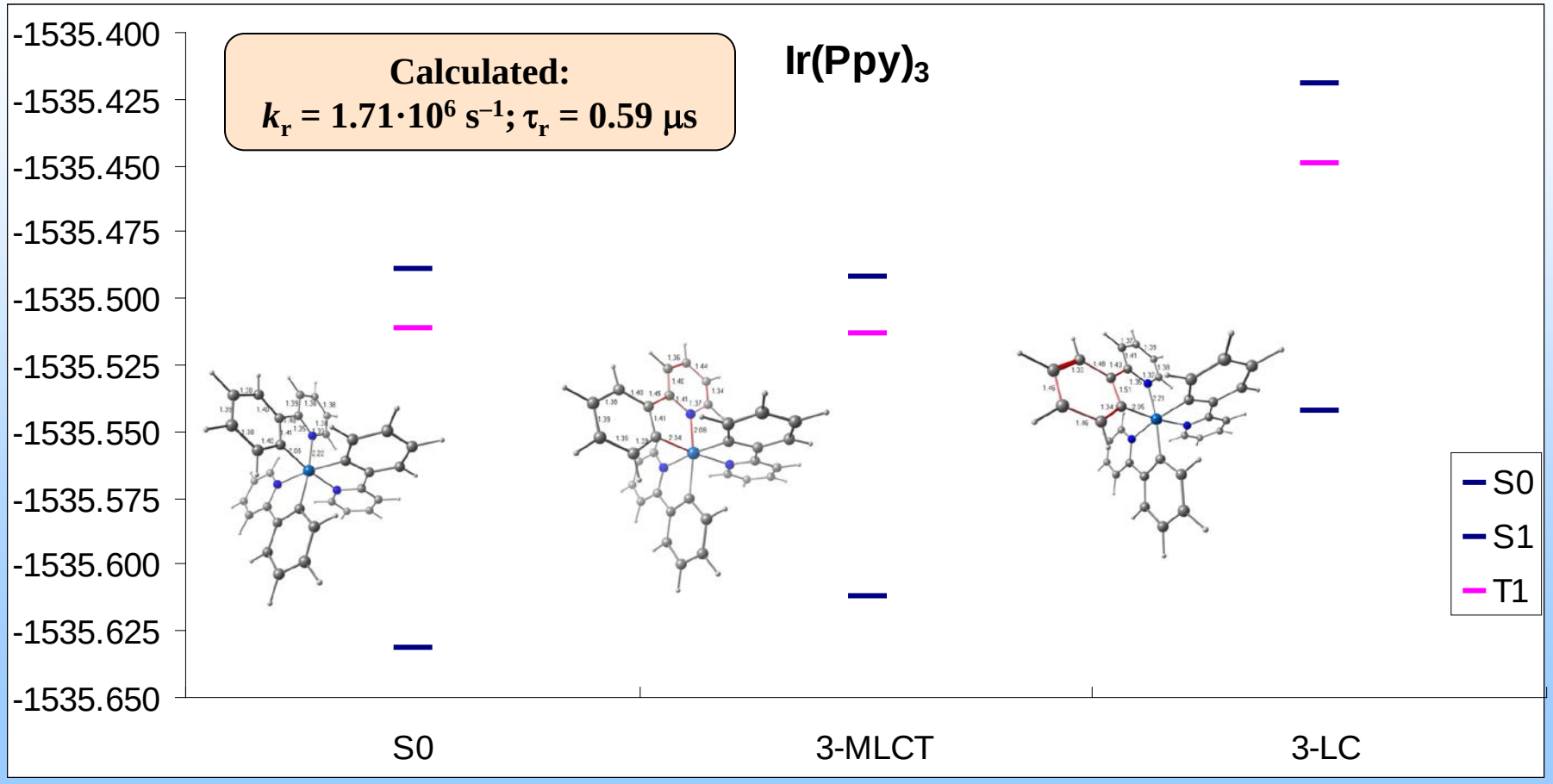




Accurate calculation of ligand-localized triplet states helps one to find the best antenna ligands

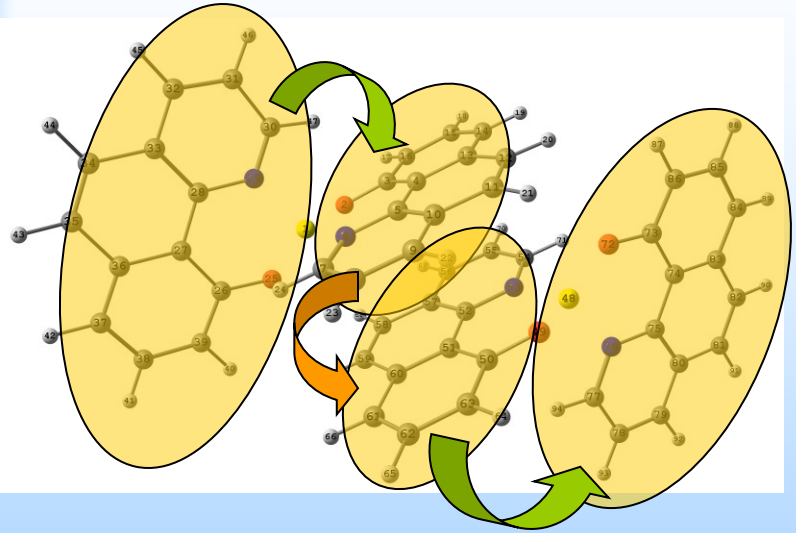
Examples of Application of Multireference Methods

Phosphorescence rate constant in iridium complexes



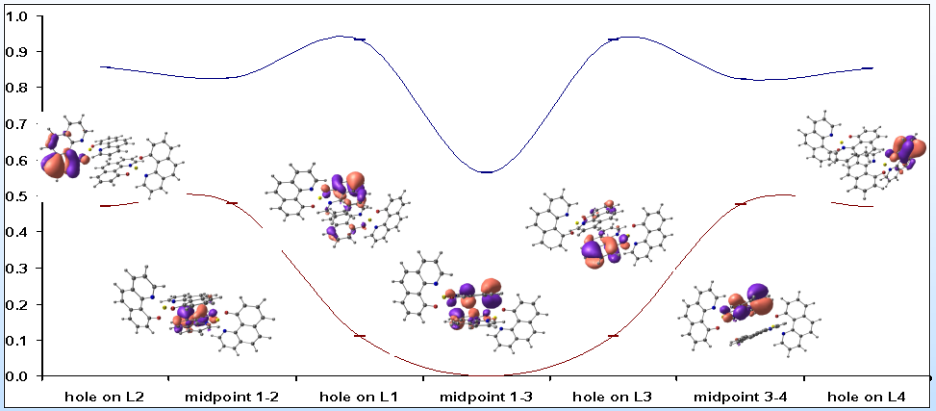
Examples of Application of Multireference Methods

Charge hopping profiles in Bebq2 dimers

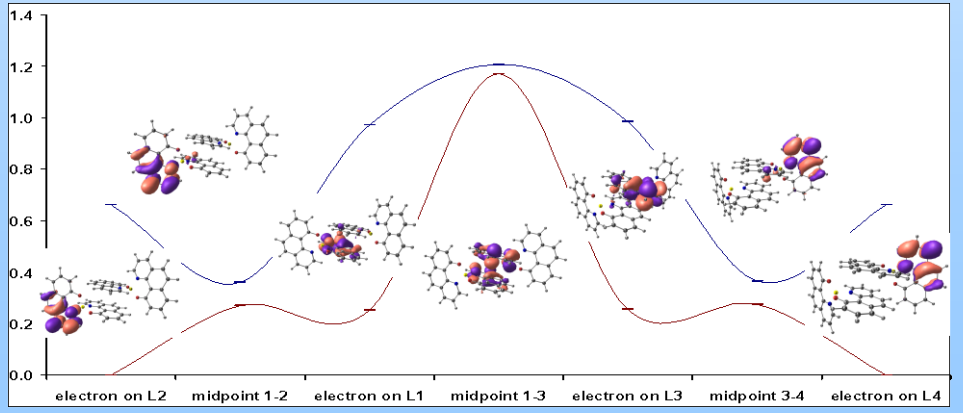


Understanding charge transfer mechanism in Bebq2 helps one to understand the same mechanisms in similar complexes, such as AlQ3

Hole hopping



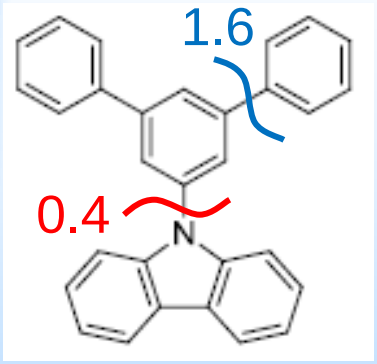
Electron hopping



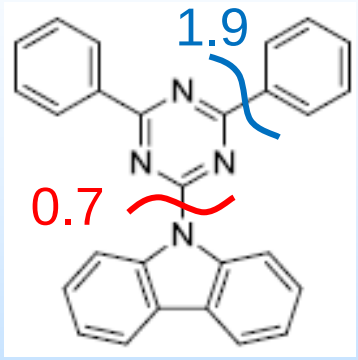
Examples of Application of Multireference Methods

Chemical stability in a series of OLED hosts

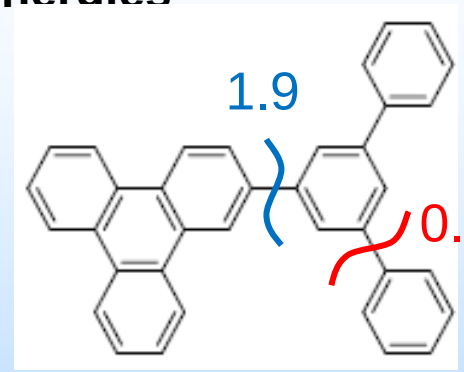
Excited state dissociation energies



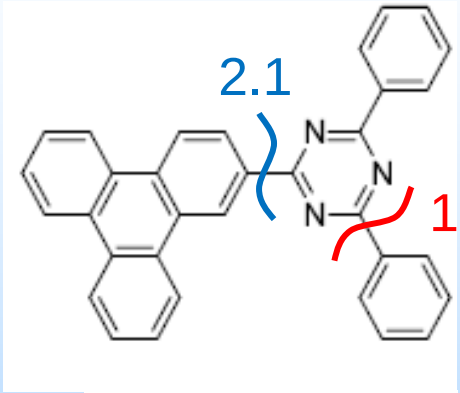
TerphCarb



DPTZCarb



TerphTriphen



DPTZTriphen

Carbazolyl detachment is more probable

Phenyl detachment is more probable

More stable

In all these cases single-reference methods (DFT or HF+MP2) fail

Conclusions

- Multireference methods are not suitable for screening
- However, they provide better values of important physical parameters
- And deeper insight into mechanisms of charge and energy transfer and chemical processes in organic electronics

Thank you for your attention!

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