Energy Component Analysis for Electronically Excited States of Molecules: Why the Lowest Excited State Is Not Always the HOMO/ LUMO Transition

Kimber, P., & Plasser, F., *J. Chem. Theory Comput. 19*.8 (2024), 2340-2352.

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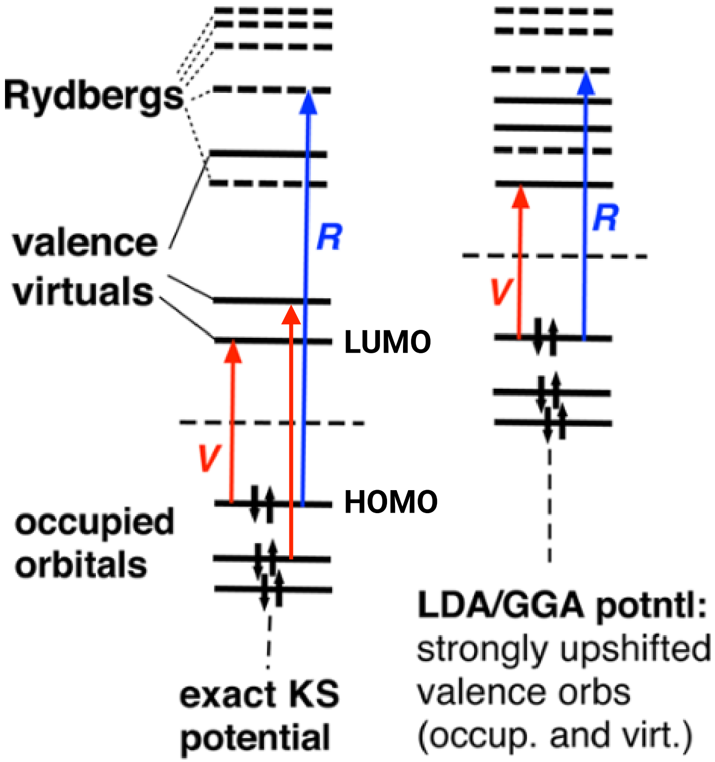
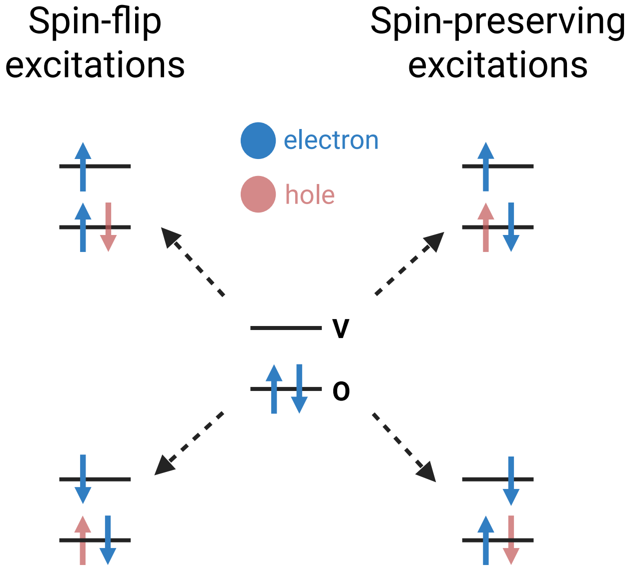
INTRODUCTION: Molecular orbital



Two-orbital two-electron model (TOTEM)



- The HOMO and LUMO energies can be strongly method dependent. → NOT good for analysis!
- Need to solve many-electron wavefunction. → Too complicated!

- Uses transition density matrix (TDM) → **focuses on electron excitation between two orbitals.**
- Reduce to be a two-body wavefunction (electron and hole quasiparticles) → can **captures correlation effects.**

Casida, M. E., & Huix-Rotllant, M. (2012). Progress in time-dependent density-functional theory. *Annual review of physical chemistry*, *63*(1), 287-323.

Van Meer, R., Gritsenko, O. V., & Baerends, E. J. (2014). Physical meaning of virtual Kohn–Sham orbitals and orbital energies: an ideal basis for the description of molecular excitations. *Journal of chemical theory and computation*, *10* (10), 4432-4441.

INTRODUCTION: Visualization methods

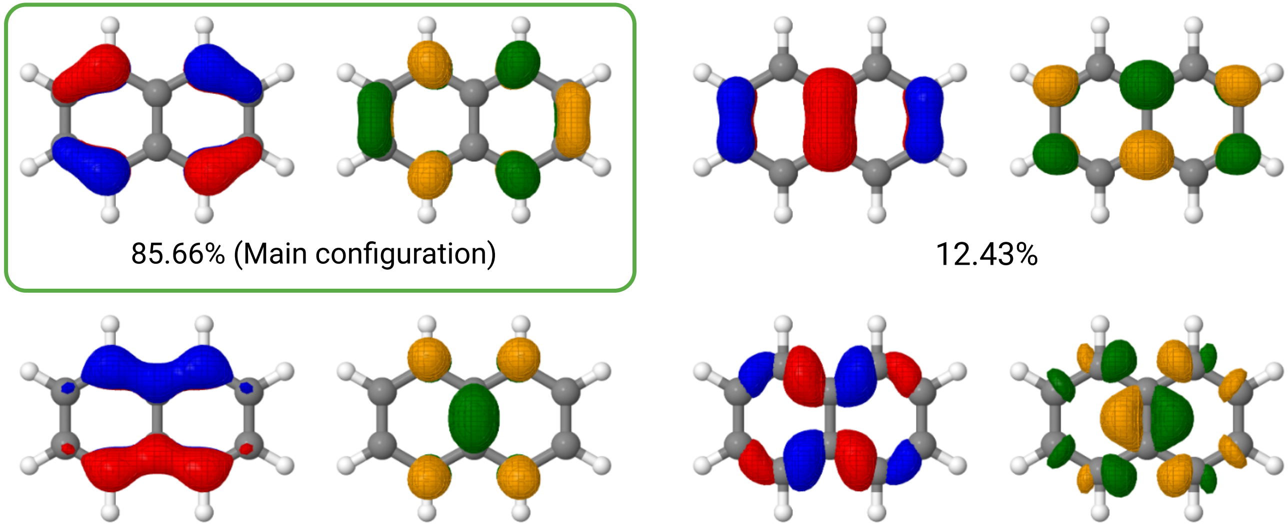
- Individual orbital do not have physical meaning.
- Each excited state is NOT defined by just one pair of orbital.

Optimal representation by natural transition orbitals (NTOs)

The compact orbital obtained from TDM.

- Compact (few orbital pairs).
- Clear hole–electron picture.

S_2 state



Hole NTO Electron NTO Hole NTO Electron NTO

85.66% (Main configuration)

12.43%

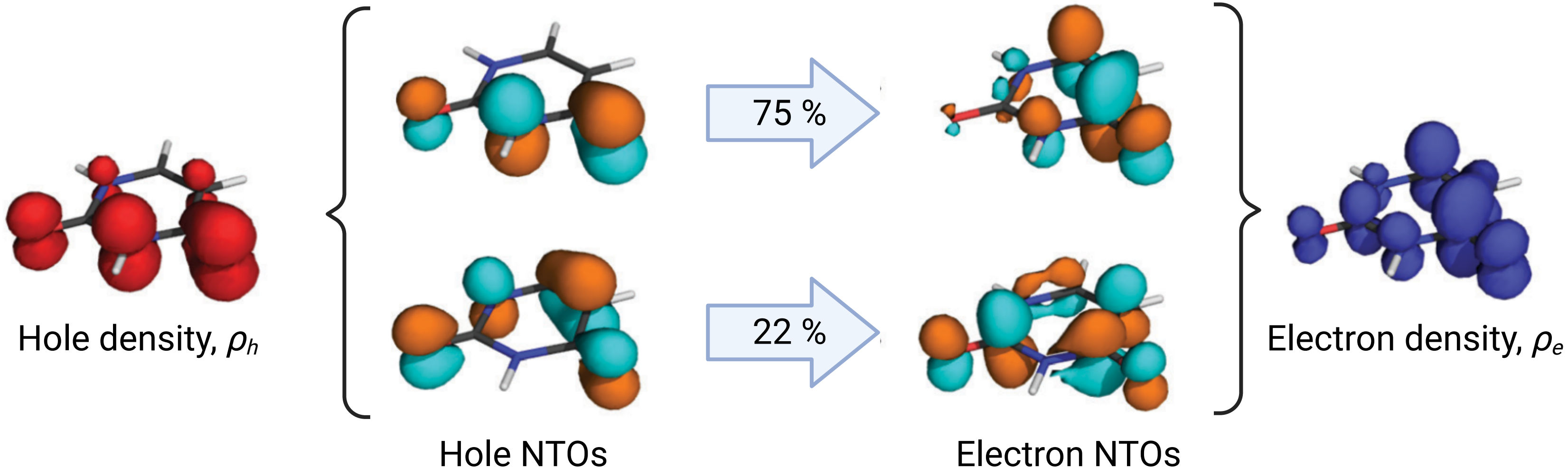
0.43%

0.35%

INTRODUCTION: Visualization methods

Multiple NTO pairs may be needed to fully describe an excited state.

Hole and electron densities represent the overall distribution of hole and electron.



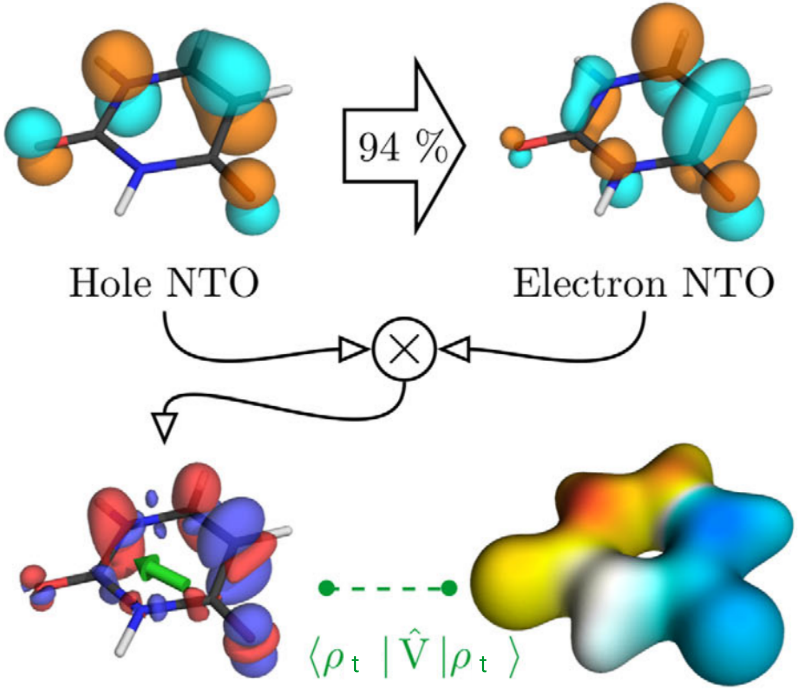
- The NTO pairs can be combined (weighted and summed) to give overall hole and electron densities.
- Represents the area where excited electron come from (ρ_h) and where its goes to (ρ_e).
- Can be used to represents the **screened coulomb interaction K_2.**

Kimber, P., & Plasser, F. (2020). Toward an understanding of electronic excitation energies beyond the molecular orbital picture. *Physical Chemistry Chemical Physics*, *22*(11), 6058-6080.

INTRODUCTION: Visualization methods

Alternative option: transition density represents the overlap between hole and electron NTOs.

😞 Shape of the transition density is more difficult to interpret.



Transition dipole moment

$$\vec{\mu}_t = \int \rho_t(r)\vec{x}\mathrm{d}r$$

Oscillator strength

$$f = \frac{2\Delta E}{3}|\vec{\mu}_t|^2$$

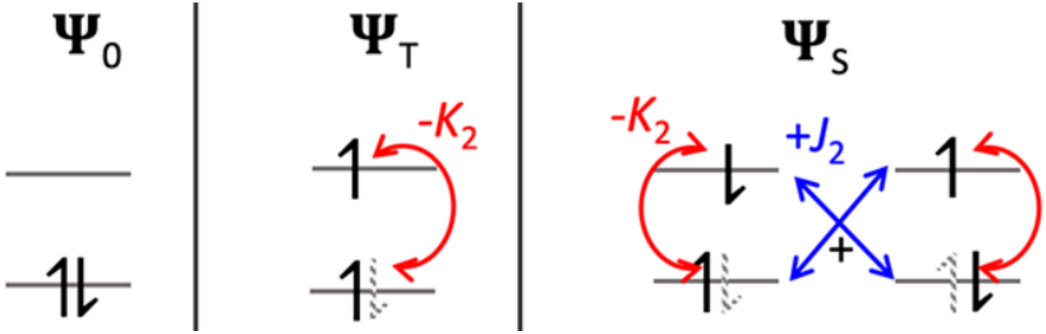
- Indicates how strongly an electronic transition interacts with light, measured by its transition dipole moment $\vec{\mu}_t$ and oscillator strength f.
- Represents the **transition density repulsion , J_2,** which is overlap between ρ_t and their ESPs.

Plasser, F., Krylov, A. I., & Dreuw, A. (2022). libwfa: Wavefunction analysis tools for excited and open-shell electronic states. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, *12*(4), e1595.

THEORY: Practical interpretation

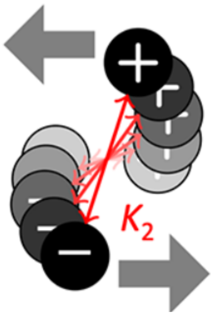
Spin-flip excitations
Triplet state

Spin-preserving excitations
Singlet state



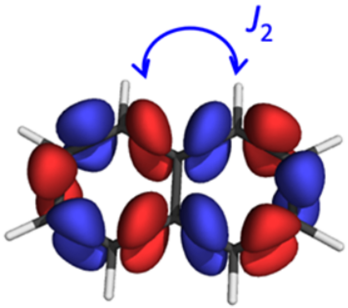
K_2

- Excited electron is attracted by the hole it left behind.
- Applies to both triplet and single states.
- Negative value (stabilize)
- Screened Coulomb interaction between electron and hole.



J_2

- Exchange interaction between excited electron and hole.
- Only applies to singlet state.
- Positive value (destabilize)
- Responsible for the $S-T$ energy splitting.
- Transition density repulsion.



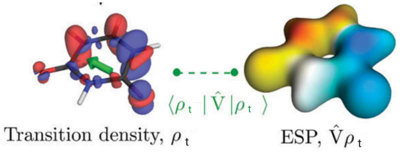
THEORY: Excited-state energy decomposition

Excitation energies can be calculated as:

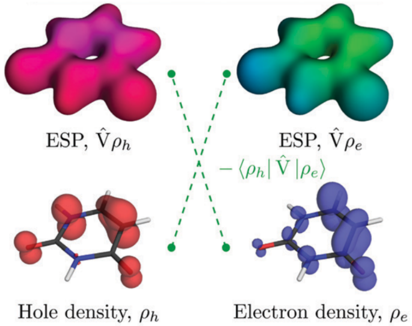
$$\Delta E = \underbrace{\sum_{ia} |C_{ia}|^2(\epsilon_a - \epsilon_i)}_{h'} + J_2 + K_2 + XC_2$$

where,

$$J_2 = \iint \frac{\rho_t(r_1)\rho_t(r_2)}{r_{12}} dr_1 dr_2 = \langle \rho_t | \hat{V} | \rho_t \rangle$$



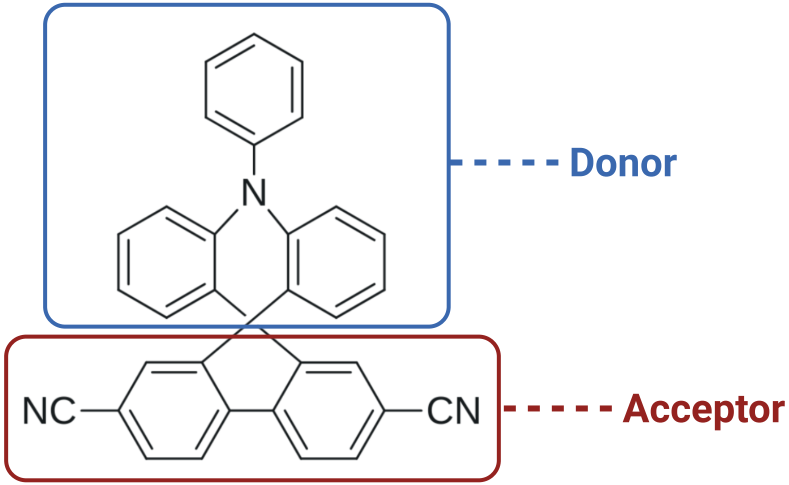
$$K_2 \approx -\iint \rho_h(r_h)\rho_e(r_e) \frac{s(r_{he})}{r_{he}} dr_h dr_e = \langle \rho_h | \hat{V} | \rho_e \rangle$$

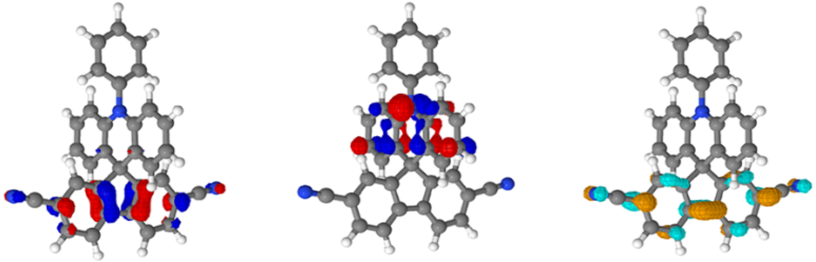


- h' is weighted sum of orbital energy differences.
- J_2 is the overlap of the transition density with its own electrostatic potential (ESP).
- K_2 is the overlap of the hole density with the ESP from electron density, or *vice versa.*
- XC_2 is the remaining part that does not come from the orbital gap, Coulomb attraction, or exchange repulsion (usually small).

RESULT: ACRFLCN & naphthalene

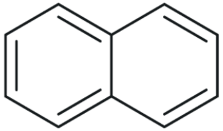
ACRFLCN: locally excited (LE) VS charge transfer (CT)

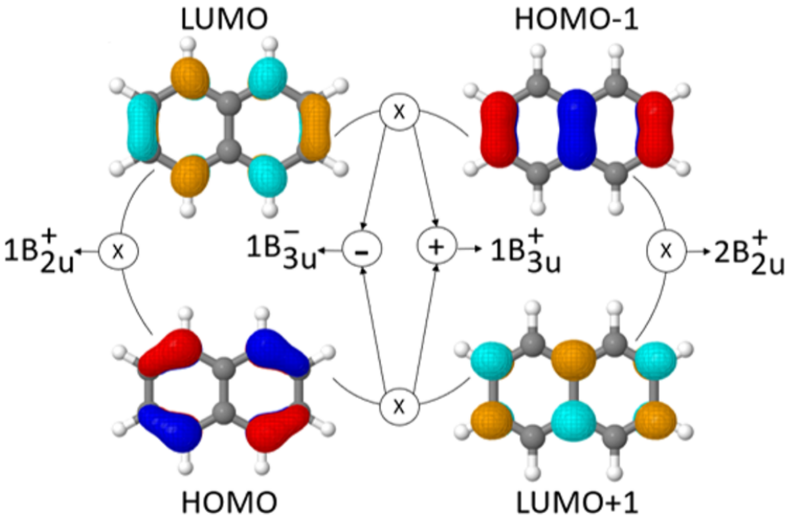




- Contains a separate donor-acceptor system.
- Charge transfer (HOMO → LUMO) VS locally excited (HOMO-1 → LUMO).

Naphthalene: ionic "+" VS covalent "−" states

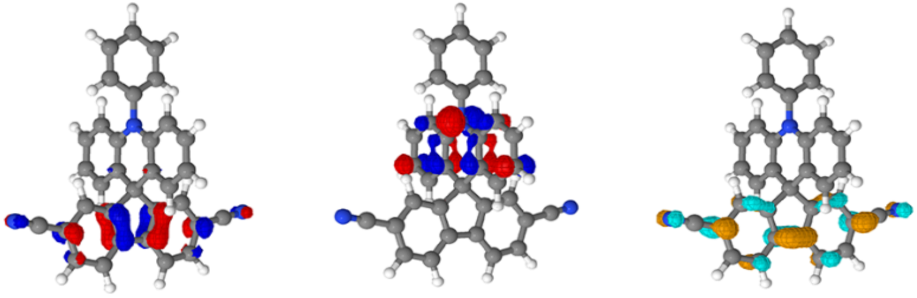




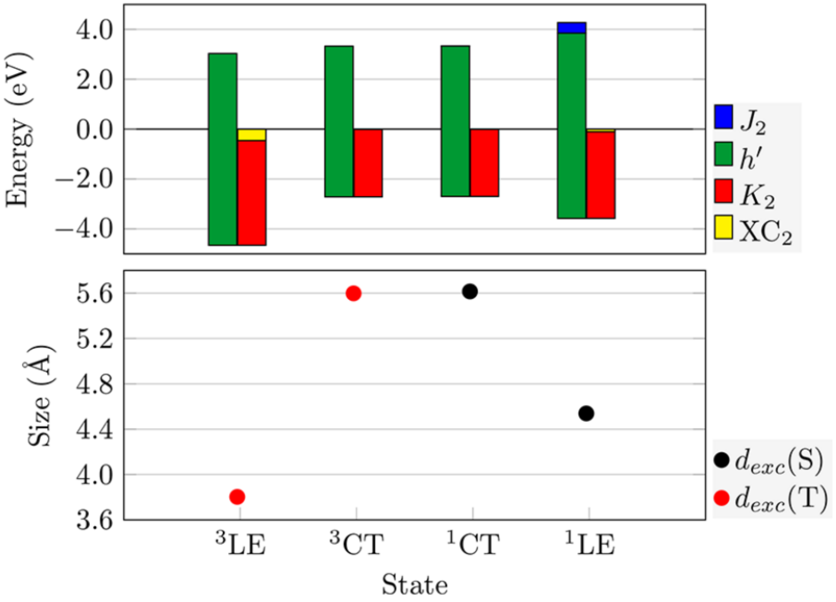
- All low-lying excited state are constructed from the same set of MOs → need additional perspectives to characterize.
- Interactions between configurations affect the oscillator strengths.
- "+" → ionic → bright state → large *f*.
- "−" → covelent → dark state → small or zero *f*.

RESULT: ACRFLCN

Frontier orbitals



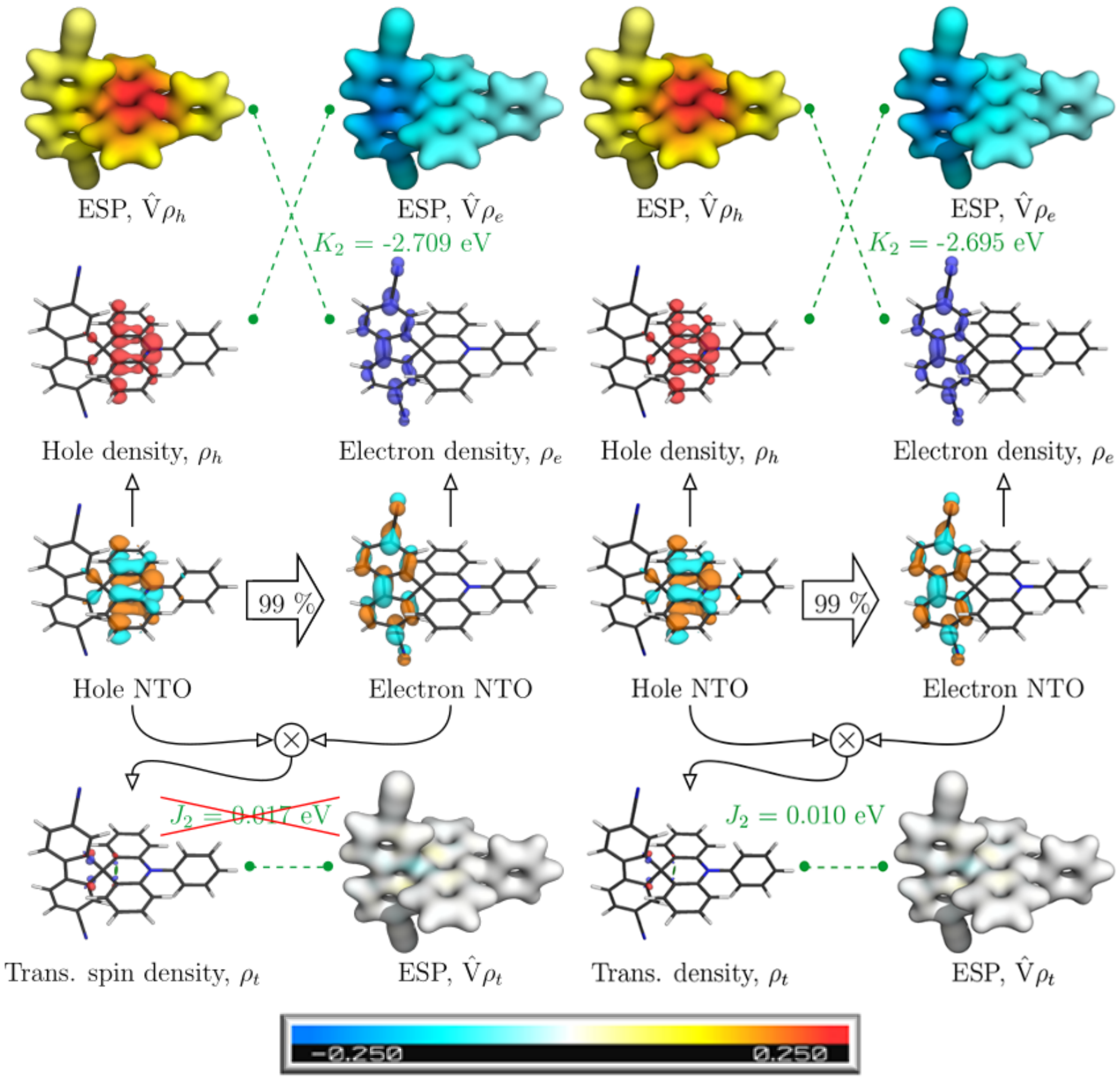
HOMO-1 (H-1) HOMO (H) LUMO (L)



Excited energy components	**Main Configuration**
T_1 (^{3}LE) = 3.03 eV = 7.69 + (-4.20) + (-0.46)	H-1 → L
T_2 (^{3}CT) = 3.32 eV = 6.04 + (-2.71) + (-0.01)	H → L
S_1 (^{1}CT) = 3.34 eV = 6.03 + 0.01 + (-2.69) + (-0.01)	H → L
S_2 (^{1}LE) = 4.26 eV = 7.43 + 0.43 + (-3.48) + (-0.10)	H-1 → L

- h' directly depends on the MO energies.
- K_2 term in LE is significantly larger than CT state (more overlap).
- J_2 almost vanishes for a state that is completely CT.
- LE vs CT: Exciton size (d_{exc}) reflects their difference.

RESULT: ACRFLCN

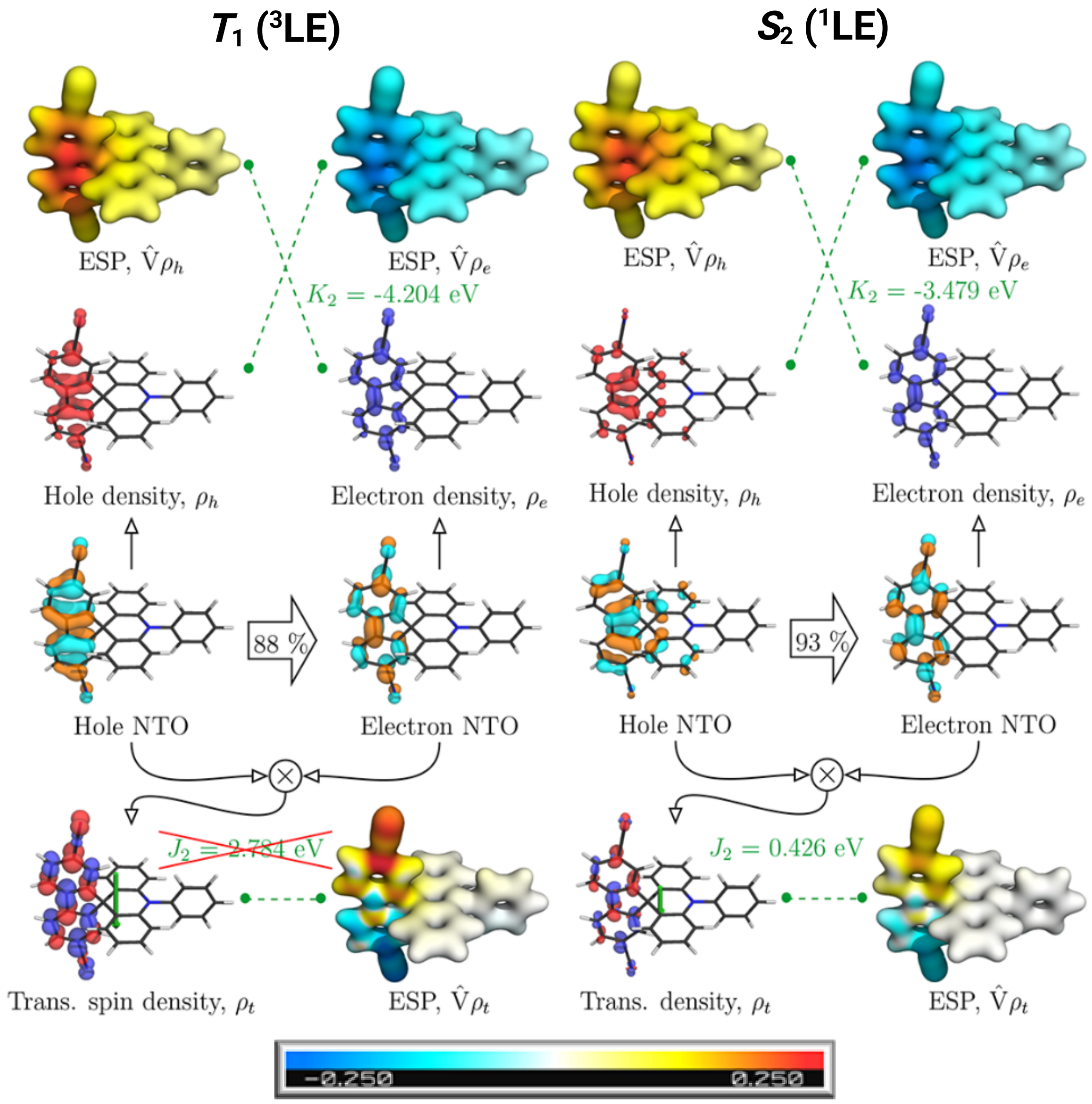


T_2 (^{3}CT)

S_1 (^{1}CT)

- Similar energy contributions and exciton size.
- Only one NTO pair dominates each state → the densities closely match the NTOs.
- HOMO → LUMO (CT)
- ρ_e locates in a region of weaker hole ESP → small K_2 term
- The product between hole and electron NTOs → transition density.
- Transition densities and their ESP almost vanish → very small J_2

RESULT: ACRFLCN



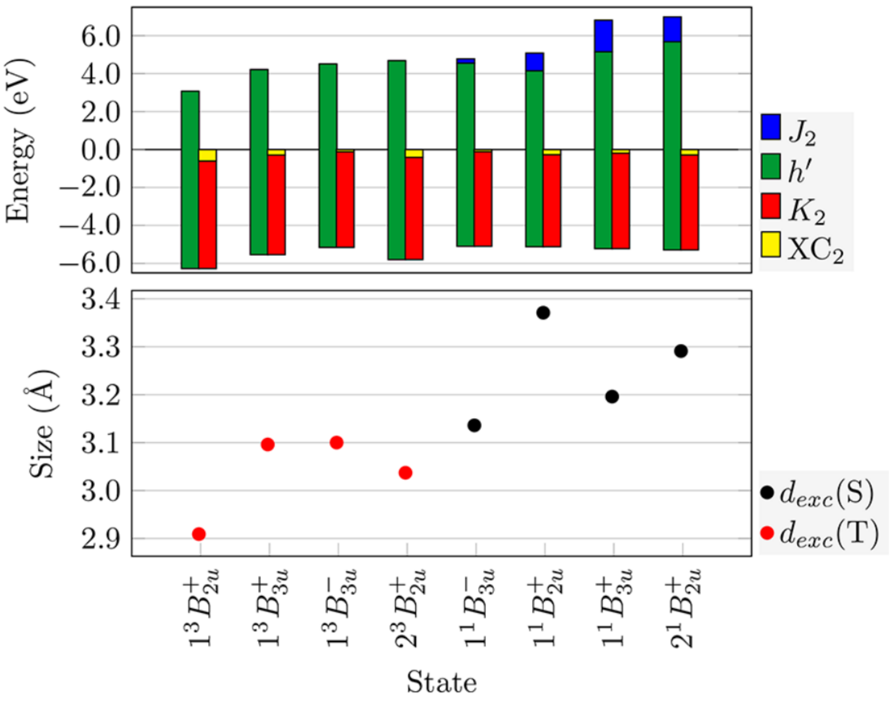
!

"formal" J_2 for the singlet using the triplet wave functions = 2.78 eV, whereas actual J_2 is only 0.43 eV. → they have different wave functions!

S_2 wave functions attempt to lower their energy by minimizing the J_2 → interacts more strongly with other electronic configurations in donor part.

- d_{exc} increase (3.8 → 4.54 Å)
- K_2 decrease (-4.20 → -3.48 eV)

RESULT: Naphthalene

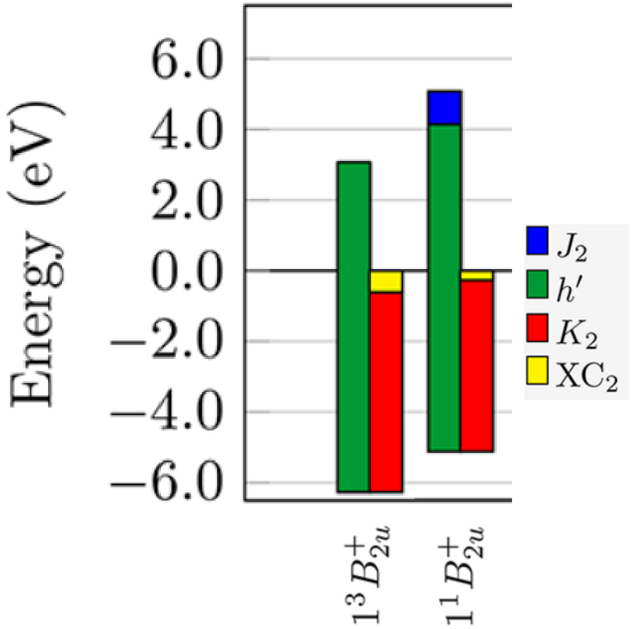


State	**Main Configuration**
T_1 ($1^3B^+_{2u}$)	H → L
T_2 ($1^3B^+_{3u}$)	$\lvert$H-1 → L$\rvert$ + $\lvert$H → L+1$\rvert$
T_3 ($1^3B^-_{3u}$)	$\lvert$H → L+1$\rvert$ - $\lvert$H-1 → L$\rvert$
T_4 ($2^3B^+_{2u}$)	H-1 → L+1
S_1 ($1^1B^-_{3u}$)	$\lvert$H → L+1$\rvert$ - $\lvert$H-1 → L$\rvert$
S_2 ($1^1B^+_{2u}$)	H → L
S_3 ($1^1B^+_{3u}$)	$\lvert$H-1 → L$\rvert$ + $\lvert$H → L+1$\rvert$
S_4 ($2^1B^+_{2u}$)	H-1 → L+1

- One NTO pair dominates in T_1, T_4, S_2, and S_4 states.
- Strong mixing of H → L+1 and H−1 → L transitions forms two states (B^+_{3u} and B^-_{3u}), differing only the sign of their linear combination.
- All excited states are LE ($d_{exc} < 3.5$ Å) → similar K_2.
- The H-1 → L+1 dominated state is the highest state in both triplet and singlet states (T_4, and S_4).
- S_1 is almost identical to T_3, differing mainly by a presence of J_2 term (0.234 eV).

RESULT: Naphthalene

T_1 ($1^3B^+_{2u}$) VS S_2 ($1^1B^+_{2u}$)



!

Same as ACRFLCN, the "formal" J_2 for H → L singlet state using T_1 wave function is 4.20 eV, while the actual J_2 is 0.94 eV.

S_2 attempt to lower its energy by minimizing the J_2 at the cost of decrease K_2 and XC_2.

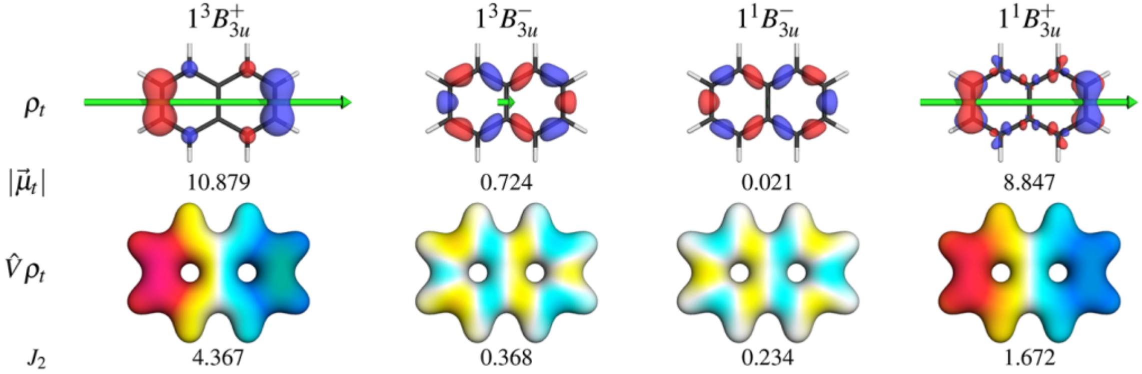
Excited energy components

T_1 ($1^3B^+_{2u}$) = 3.07 eV = 9.35 + (-5.67) + (-0.61)

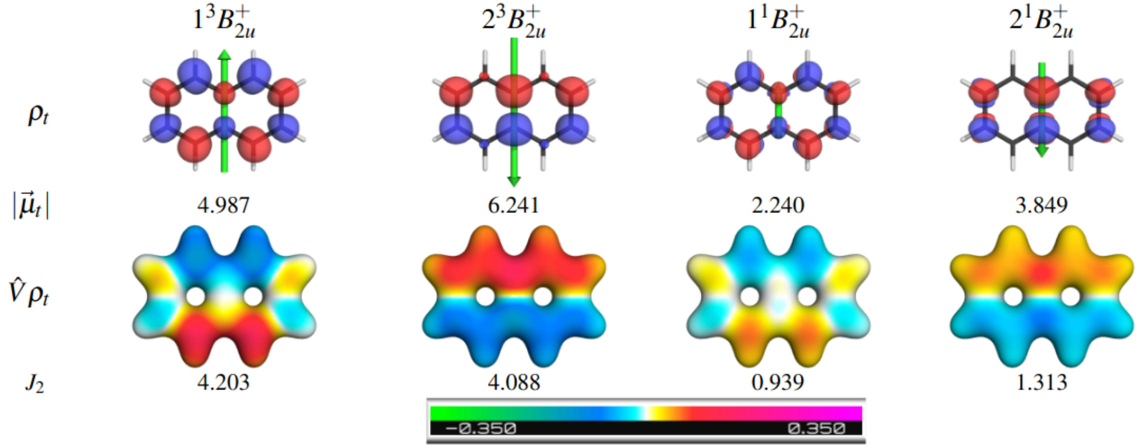
S_2 ($1^1B^+_{2u}$) = 5.09 eV = 9.27 + 0.94 + (-4.85) + (-0.27)

RESULT: Naphthalene

B_{3u} states(mainly mixtures of H-1 → L and H → L+1)



B_{2u} states(mainly H → L or H-1 → L+1)



The transition densities of all "+" states are concentrated on the atoms, while in "−" states they are located on the bonds.

↓

The "+" states show significantly larger transition moments and ESPs than the "−" states.

↓

The positive correlation between J_2 and transition moments → brighter singlet states are shifted to higher energy.

CONCLUSION

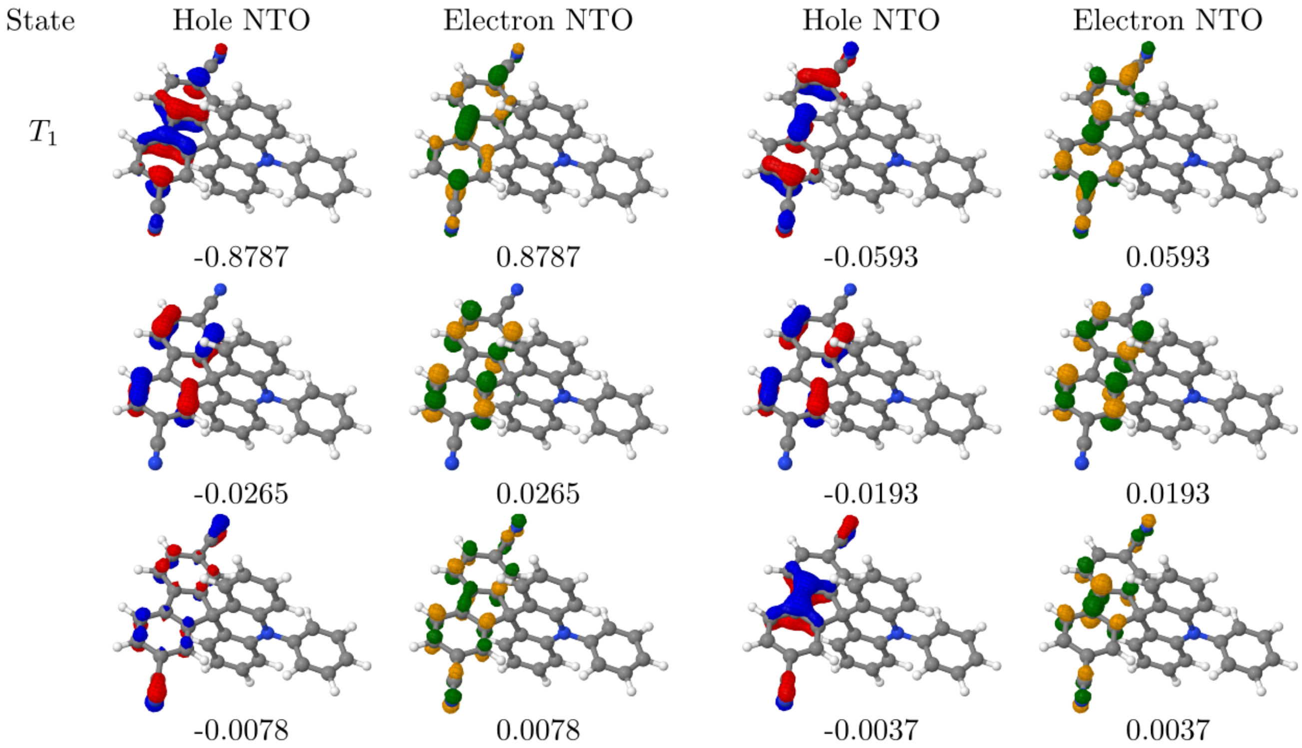
Why the lowest excited state is not always the H → L Transition?

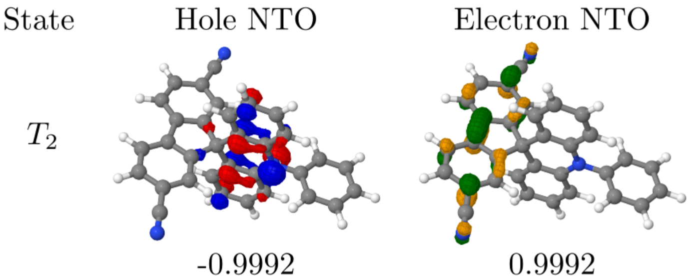
- The Coulomb attraction (K_2) stabilizes locally excited states, especially triplets, while the exchange repulsion (J_2) destabilizes locally excited singlet states.

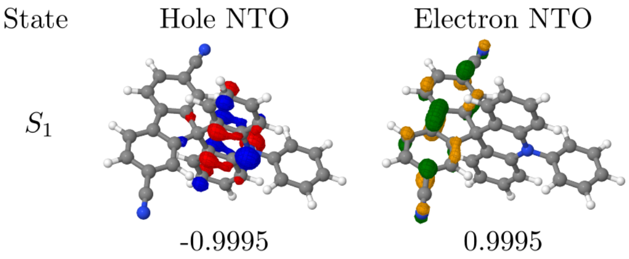
- In **ACRFLCN**, the lowest triplet state, T_1, originates from the H-1 → L transition because the stronger K_2 stabilizes this configuration below the H → L transition.

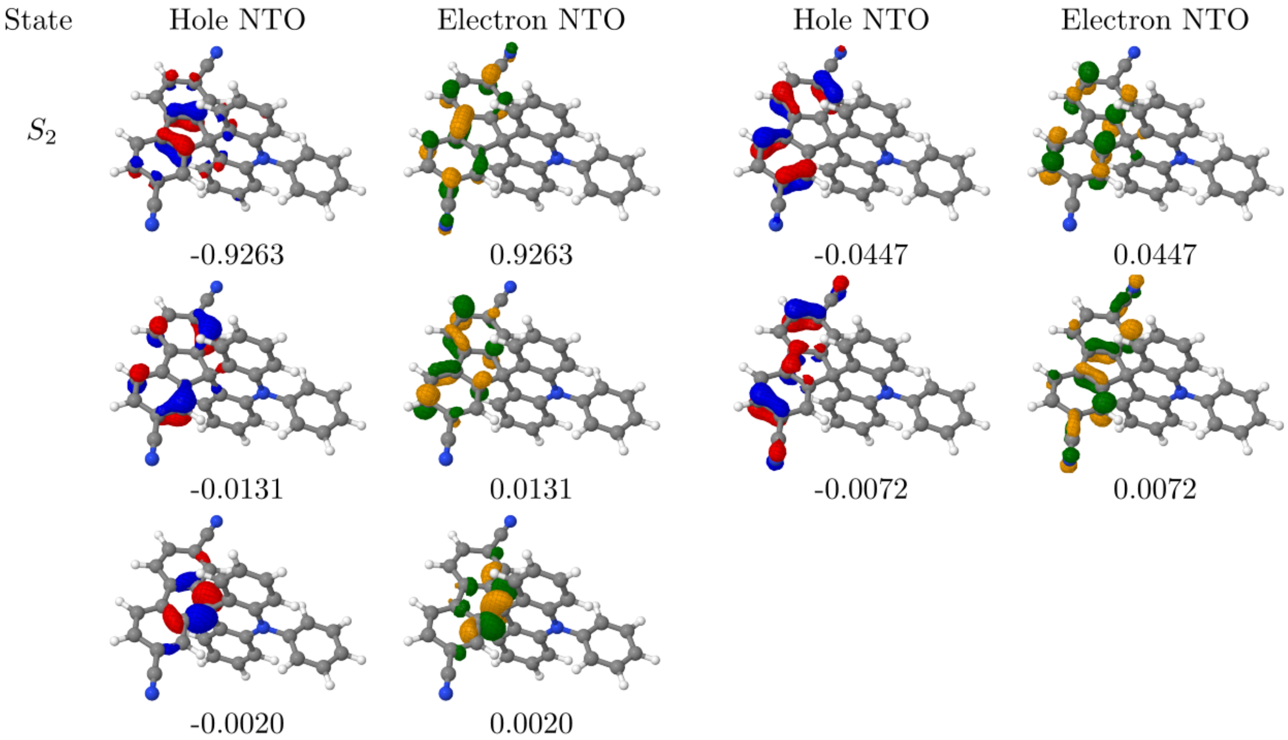
- For **naphthalene**, the lowest S_1 arises from a linear combination of H−1 → L and H → L+1 transitions because J_2 destabilize the H → L state and shifts it to higher energy.

90 Th Thorium	7 N Nitrogen	19 K Potassium
39 Y Yttrium	8 O Oxygen	92 U Uranium


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
T_1
-0.8787
0.8787
-0.0593
0.0593
-0.0265
0.0265
-0.0193
0.0193
-0.0078
0.0078
-0.0037
0.0037


State
Hole NTO
Electron NTO
T_2
-0.9992
0.9992


State
Hole NTO
Electron NTO
S_1
-0.9995
0.9995


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
S_2
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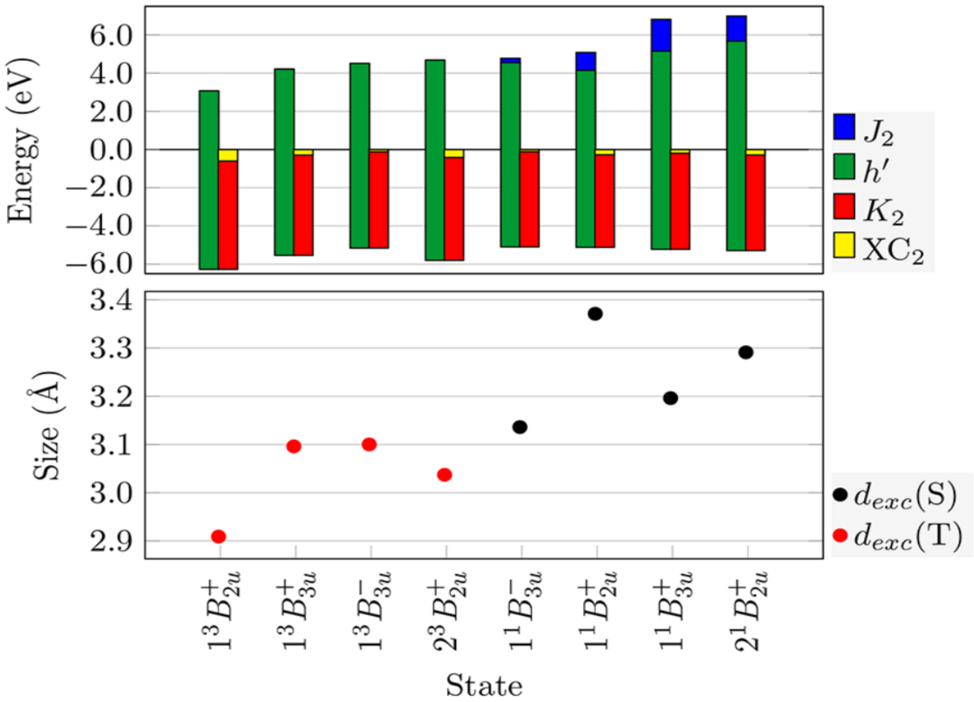
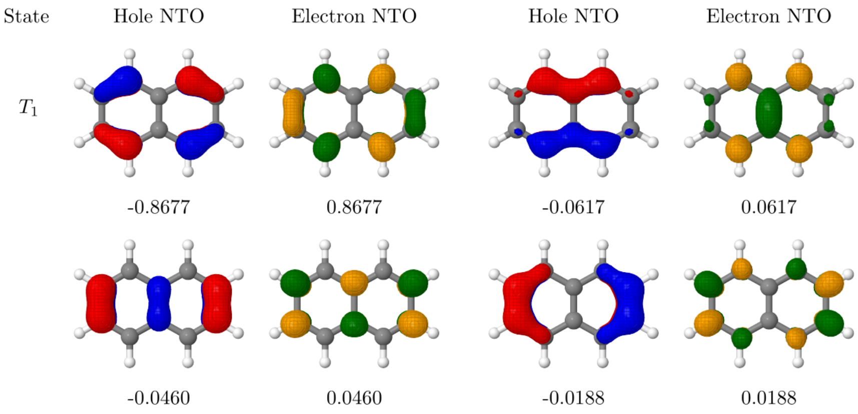
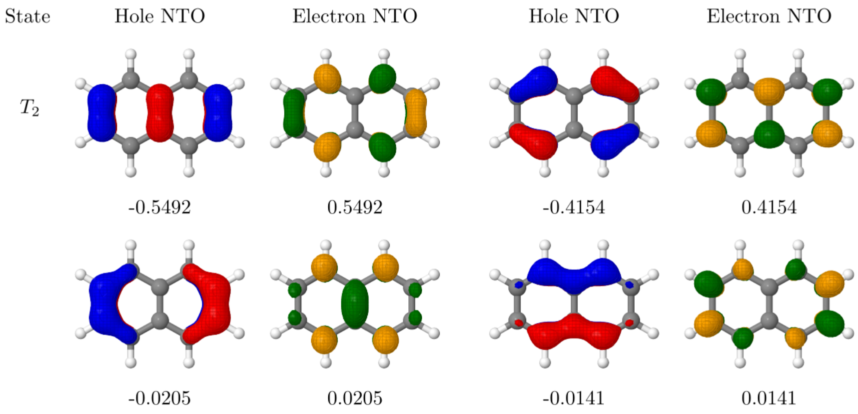
0.0447
-0.0131
0.0131
-0.0072
0.0072
-0.0020
0.0020



Excited energy components	**Main Configuration**
T_1 ($1^3B^+_{2u}$) = 3.07 eV = 9.35 + (-5.67) + (-0.61)	H → L
T_2 ($1^3B^+_{3u}$) = 4.21 eV = 9.76 + (-5.26) + (-0.29)	$\vert$H-1 → L$\vert$ + $\vert$H → L+1$\vert$
T_3 ($1^3B^-_{3u}$) = 4.51 eV = 9.67 + (-5.05) + (-0.11)	$\vert$H → L+1$\vert$ - $\vert$H-1 → L$\vert$
T_4 ($2^3B^+_{2u}$) = 4.68 eV = 10.48 + (-5.39) + (-0.41)	H-1 → L+1
S_1 ($1^1B^-_{3u}$) = 4.78 eV = 9.65 + 0.23 + (-4.99) + (-0.11)	$\vert$H → L+1$\vert$ - $\vert$H-1 → L$\vert$
S_2 ($1^1B^+_{2u}$) = 5.09 eV = 9.27 + 0.94 + (-4.85) + (-0.27)	H → L
S_3 ($1^1B^+_{3u}$) = 6.82 eV = 10.37 + 1.67 + (-5.03) + (-0.19)	$\vert$H-1 → L$\vert$ + $\vert$H → L+1$\vert$
S_4 ($2^1B^+_{2u}$) = 6.99 eV = 10.97 + 1.31 + (-5.01) + (-0.28)	H-1 → L+1


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
T_1
-0.8677
0.8677
-0.0617
0.0617
-0.0460
0.0460
-0.0188
0.0188


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
T_2
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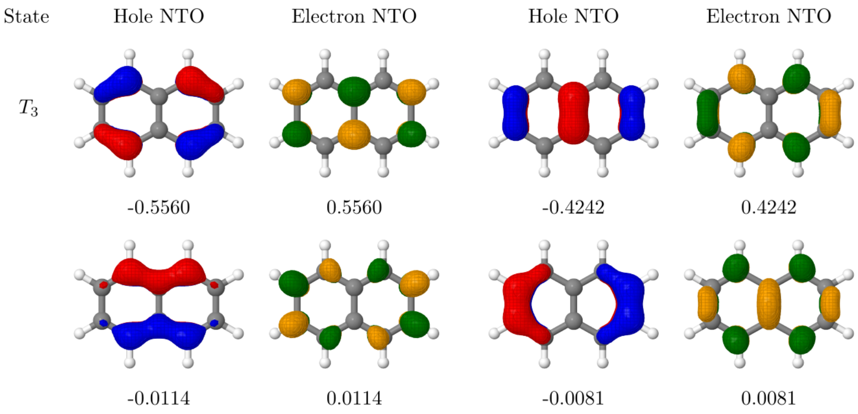
0.5492
-0.4154
0.4154
-0.0205
0.0205
-0.0141
0.0141


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
T_3
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0.5560
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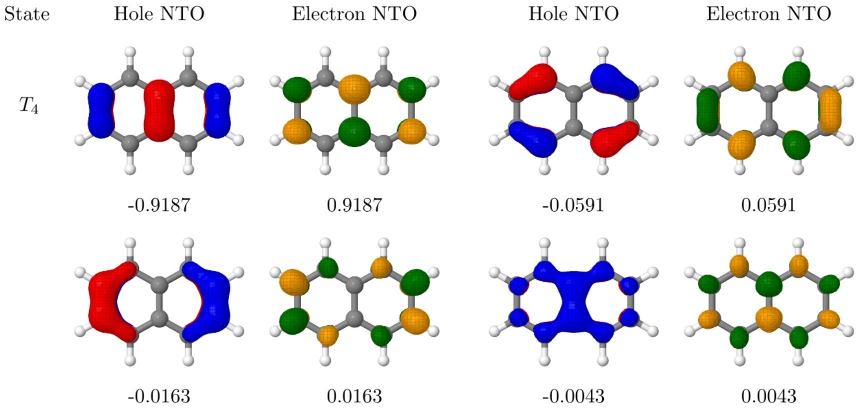
0.4242
-0.0114
0.0114
-0.0081
0.0081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Hole NTO
Electron NTO
Hole NTO
Electron NTO
T_4
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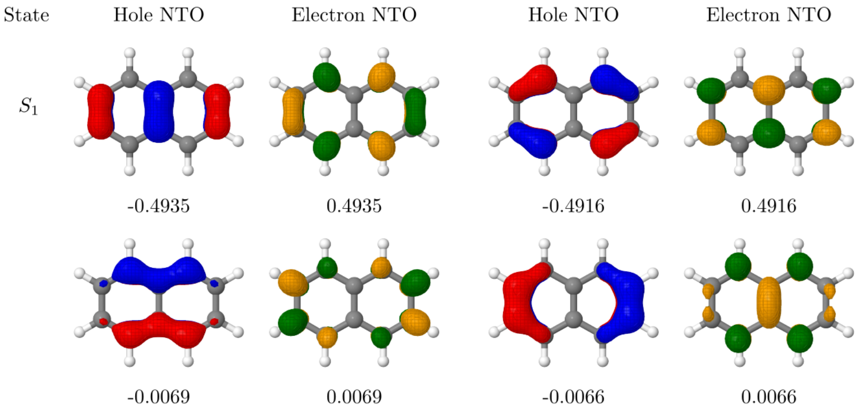
0.9187
-0.0591
0.0591
-0.0163
0.0163
-0.0043
0.0043


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
S_1
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0.4935
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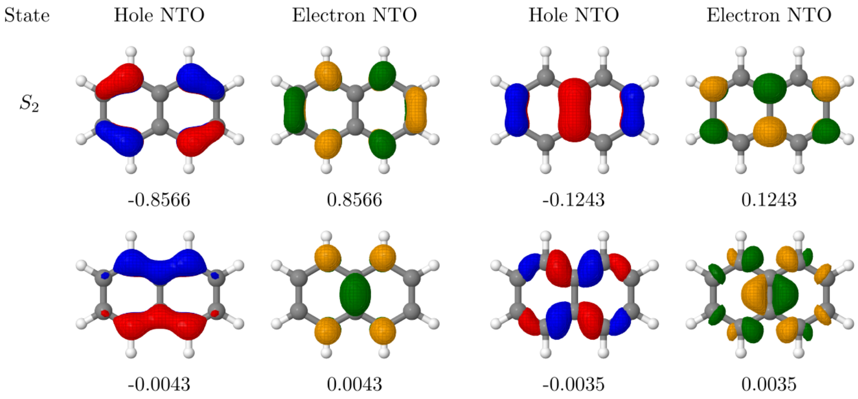
0.4916
-0.0069
0.0069
-0.0066
0.0066


State
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Electron NTO
Hole NTO
Electron NTO
S_2
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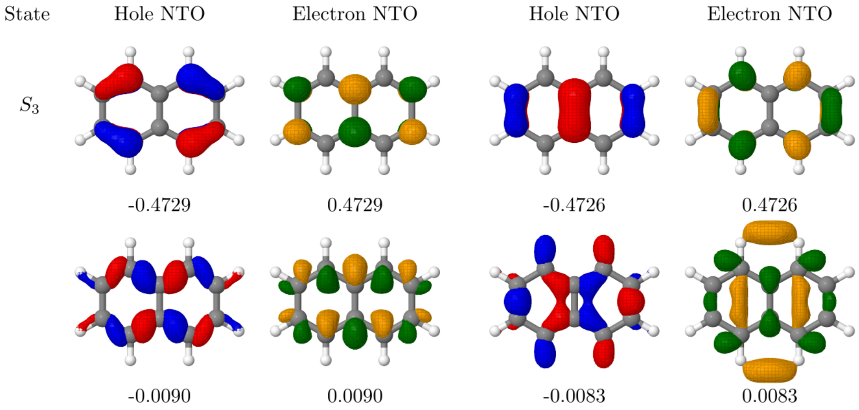
0.8566
-0.1243
0.1243
-0.0043
0.0043
-0.0035
0.0035


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
S_3
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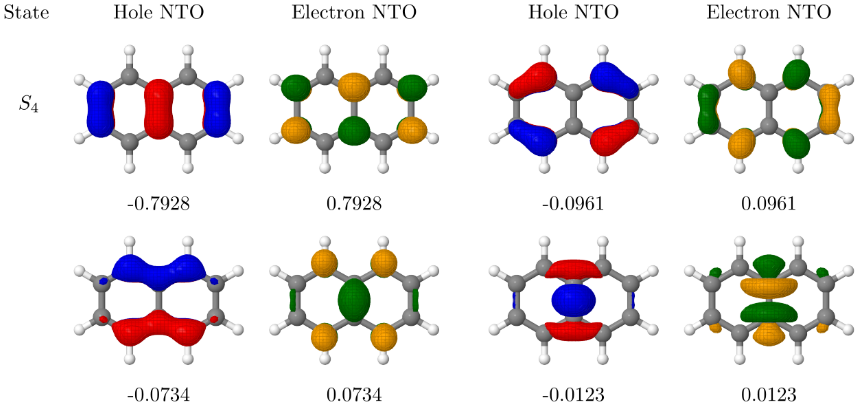
0.4729
-0.4726
0.4726
-0.0090
0.0090
-0.0083
0.0083


State
Hole NTO
Electron NTO
Hole NTO
Electron NTO
S_4
-0.7928
0.7928
-0.0961
0.0961
-0.0734
0.0734
-0.0123
0.0123

Electrostatic potential (ESP)

$$
\begin{aligned}
\iint \frac{\rho_A(r_1)\rho_B(r_2)}{r_{12}} \mathrm{d}r_1 \mathrm{d}r_2 &= \int \rho_A(r_1)\left(\int \frac{\rho_B(r_2)}{r_{12}} \mathrm{d}r_2\right) \mathrm{d}r_1 \\
&= \int \rho_A(r_1) \hat{V} \rho_B(r_1) \mathrm{d}r_1 = \langle \rho_A | \hat{V} | \rho_B \rangle .
\end{aligned}
$$

Natural transition orbital (NTO)

The 1-electron transition density matrix (1TDM) is defined as

Contributed MO

$$\gamma_{0I}(r_h, r_e) = \sum_{pq} \gamma^{0I}_{pq} \phi_p(r_h) \phi_q(r_e)$$

where,

Creation and annihilation operator of MO

$$\gamma^{0I}_{pq} = \left\langle \Psi_0 \middle| \hat{a}^{\dagger}_p \hat{a}_q \middle| \Psi_I \right\rangle$$

Applying the singular value decomposition,

Amplitude

NTOs representing the hole and electron

$$\gamma_{0I}(r_h, r_e) = \sum_{t} \sqrt{\lambda_t}\, \psi^h_t(r_h) \psi^e_t(r_e)$$