# -Supplementary Material-Correlation vs. exchange competition drive the singlet-triplet excited-state inversion in non-alternant hydrocarbons

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Basis set dependence of the  $S_1 \leftarrow S_0$  and  $T_1 \leftarrow S_0$ excitation energies for compounds 1 and 2 at the RAS[6,6]-SF level



Figure S1: Evolution with the basis set size of the lowest-singlet and lowest-triplet excitation energies of molecule  $\mathbf{1}$ , calculated with the RAS[6,6]-SF method.

## Results at the TD-DFT, (SCS-)CC2 and (SCS-)ADC(2)levels for azulene

		Azulene	
Method	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	$\Delta E_{ST}$
PBEx	2.367	1.969	398
PBE	2.369	1.973	396
PBEh	2.412	1.991	421
PBE0	2.471	2.013	458
PBE0-1/3	2.501	2.023	478
PBEHH	2.554	2.036_	518
LC-PBE	2.589	2.077	512
$LC-\omega PBE$	2.632	2.129	503
CAM-B3LYP	2.450	1.748	702
$\omega$ B97XD	2.444	1.711_	733
PBE0-DH	2.431	2.085	346
$r^2$ SCAN0-DH	2.489	2.181	308
PBE-QIDH	2.344	2.279	65
$r^2$ SCAN-QIDH	2.362	2.268	94
PBE0-2	2.251	2.388	-87
r <sup>2</sup> SCAN0-2	2.269	2.323_	54
ADC(2)	2.292	2.301	-9
SCS-ADC(2)	2.261	2.364	-103
CC2	2.346	2.374	-28
SCS-ADC(2)	2.261	2.364	-103
EOM-CCSD	2.323	2.272_	51
$CC3^{a}$	2.171	2.211	-40
$ADC(3)^{b}$	2.020	1.908	112
Exp. <sup>c</sup>	1.771	1.722	49

Table S1: Vertical excitation energies for azulene and associated  $\Delta E_{ST}$  energy difference (all in eV) calculated with different wavefunction methods and

<sup>a</sup> Taken from Ref. [2]

<sup>b</sup> Done here with the def2-SVP basis set. <sup>c</sup> Taken from Ref. [3]

Evolution of the excitation energies for azulene at all the RAS-based levels of theory as a function of the active space size



Figure S2: Evolution of the excitation energies for azulene at all the RASbased levels of theory as a function of the active space size.

### Information about the calculation of Tozer's index

The spatial overlap of a given excitation is obtained by using the Tozer's expression:

$$\Lambda = \frac{\sum_{i,a} \kappa_{ia}^2 O_{ia}}{\kappa_{ia}^2},\tag{1}$$

which takes the value  $0 \leq \Lambda \leq 1$ ; a small (large) value of Ameans a longrange(short-range) excitation.  $O_{ia}$  is equal to  $\langle |\phi_i| |\phi_a| \rangle = \int |\phi_i(\mathbf{r})| |\phi_a(\mathbf{r})| d\mathbf{r}$ , which is the inner product of the moduli of the two orbitals  $\phi_i$  and  $\phi_a$ , and  $\kappa_{ia}$  the contribution of each *ia* pair to the given excitation. This index is calculated here with the Multiwfn package.

# Detailed information about the derivation of the mSCS-CC2 method

The Spin Component Scaling scheme was historically introduced by Grimme *et al.* to heal the unbalanced description of the opposite- (OS) and same spin- (SS) electronic interactions by post-HF methods based on a perturbative treatment. In the SCS-CC2 formalism, the two interactions are weighted by two parameters, namely  $C_{OS}$  and  $C_{SS}$ , whose values were set to 6/5 and 1/3, respectively, to scale-up the Coulomb correlation arising from the OS interaction and scale-down the Fermi correlation arising from the SS interaction. However, these two values were set through a benchmark study carried out on a series of reaction energy barriers, thus specifically tuned for ground state properties. It is reasonable to assume that these values are not fully appropriate for describing the excited states of the molecules in the current study, for which the correct description of both correlation effects is crucial to achieve a decent value of  $\Delta E_{ST}$ .

A first screening was carried out for the three compounds with  $C_{OS} = 0.6 - 1.2$  and  $C_{SS} = 0.2 - 0.5$ , with a step of 0.1 for both parameters. Then, a second screening with  $C_{OS} = 0.70 - 0.80$  ( $C_{OS} = 0.80 - 0.90$ ) and  $C_{SS} = 0.1 - 0.5$  was carried out for **1** and **2** (azulene) with step of 0.05 for both parameters. As it can be seen from Figure S3, an increase of the  $C_{OS}$  and  $C_{SS}$  value leads to a decrease of the gap between  $S_1$  and  $T_1$ . In particular, for compound **1**, the  $\Delta E_{ST}$  is always positive (negative) for  $C_{OS} = 0.70$  (0.80), while the sign of  $\Delta E_{ST}$  is modulated according to the  $C_{SS}$  value for  $C_{OS} = 0.75$ . At  $C_{OS} = 0.75$  and  $C_{SS} = 0.40$ , the  $\Delta E_{ST}$  computed at mSCS-CC2 is -24 meV, in good agreement with the one obtained at EOM-CCSD. For compound **2**, the  $\Delta E_{ST}$  is always positive and at  $C_{OS} = 0.80$  and  $C_{SS} = 0.50$  it is 24 meV, close to the EOM-CCSD result. Analogously, for azulene, a  $\Delta E_{ST}$  value close to EOM-CCSD and the experimental value is obtained by setting  $C_{OS} = 0.90$  and  $C_{SS} = 0.10$  (see Figure S4), resulting in a positive  $\Delta E_{ST}$  of 47 meV in contrast with the pristine CC2 and the standard SCS-CC2 results.



Figure S3:  $\Delta E_{ST}$  values computed at mSCS-CC2/6-311G<sup>\*</sup> level ( $C_{OS} = 0.70 - 0.80$  and  $C_{SS} = 0.1 - 0.5$ ) for compounds **1** (a) and **2** (b). The dashed lines indicate the  $\Delta E_{ST}$  obtained at EOM-CCSD level.



Figure S4:  $\Delta E_{ST}$  values computed at mSCS-CC2/6-311G\* level: a)  $C_{OS} = 0.6 - 1.2$  and  $C_{SS} = 0.2 - 0.5$ ; b)  $C_{OS} = 0.80 - 0.90$  and  $C_{SS} = 0.1 - 0.5$  for azulene.

We also evaluate the behaviour of the excited state energies as a function of the two SCS parameters to further understand the evolution of  $\Delta E_{ST}$ . Not surprisingly, the  $S_1$  excitation energy is more sensitive to the  $C_{OS}$  (and thus to Coulomb correlation effect) than  $T_1$  (see Figure S5 for 1 and 2 and Figure S6 for azulene) due to the dominant opposite-spin configuration of its wavefunctions. The reduction of  $C_{OS}$  is thus a direct way to decrease the magnitude of the Coulomb correlation, which is obviously overestimated with the SCS-CC2 method. Interestingly,  $S_1$  undergoes a slightly stronger stabilization than  $T_1$  by increasing  $C_{SS}$ , explaining the reduction of the  $\Delta E_{ST}$  observed by increasing this parameter (see Figure S3). Possibly, this could arise from the fact that the cluster operator is acting on the Hartree-Fock wavefunction which in the case of a singlet excited state leads to a higher probability density for the electrons to be in closer spatial proximity than in the triplet. Increasing  $C_{SS}$  (and thus potentially increasing the magnitude of the repulsive exchange interaction) might decrease the probability density of such electron configurations. This can be observed by fitting the  $S_1$  and  $T_1$  excitation energies through a linear function: the slope associated with the former is always larger than the latter.

In addition, a further assessment on the effect of the same-spin interaction on  $S_1$  and  $T_1$  can be done by evaluating the excitation energy variation moving from OS-CC2 ( $C_{OS} = 1.0$  and  $C_{SS} = 0.0$ ) to CC2 ( $C_{OS} = 1.0$  and  $C_{SS} = 1.0$ ), the former accounting only for opposite-spin interaction. For compound **1**, the excitation energy difference E(CC2)E(OS - CC2) for  $S_1$ is -132 meV, while for  $T_1$  is -106 meV, confirming that taking into account the same-spin interaction has a stronger impact on  $S_1$  than  $T_1$ . Analogously, one can assess the effect of neglecting the opposite-spin interaction by calculating the excitation energy variation between SS-CC2 ( $C_{OS} = 0.0$  and  $C_{SS} = 1.0$ ) and CC2, the former accounting only for same-spin interactions. As expected, the excitation energy difference E(CC2)E(SS - CC2) is larger for  $S_1$  (-499 meV) than for  $T_1$  (-96 meV).

This analysis demonstrates the limitations associated with the original values set for the SCS scheme in describing the singlet-triplet excitation energy gap for these particular compounds. Concomitantly, the facility of the  $C_{OS}$  and  $C_{SS}$  tuning suggests that the SCS-CC2 can be easily modified to provide results in agreement with more sophisticated wavefunction-based methods (in terms of both excitation energy and excited state nature) at a more affordable computational cost.

![](_page_8_Figure_2.jpeg)

Figure S5:  $S_1$  (solid lines) and  $T_1$  (dashed lines) excitation energies computed at mSCS-CC2/6-311G\* level ( $C_{OS} = 0.70 - 0.80$  and  $C_{SS} = 0.1 - 0.5$ ) for compounds **1** (a) and **2** (b).

![](_page_9_Figure_0.jpeg)

Figure S6:  $S_1$  (solid lines) and  $T_1$  (dashed lines) excitation energies computed at mSCS-CC2/6-311G\* level ( $C_{OS} = 0.80 - 0.90$  and  $C_{SS} = 0.1 - 0.5$ ) for azulene.

### Results of NICS values at various DFT levels for $S_0$ and $T_1$ excited states of compounds 1 and 2

We also calculated NICS values of the  $S_0$  and  $T_1$  electronic states of molecules **1** and **2** at the HF, CAM-B3LYP, LC-PBE, B97X-D, PBE0, PBE and PBEh levels, employing the GIAO method with the Gaussian program package. At the  $S_0$ , both molecules exhibit local aromaticity while, as predicted by the Bairds rule, for the  $T_1$  state the NICS values indicate the local antiaromaticity of each ring in both molecules. Establishing a correlation between the energy gap and the aromaticity of  $T_1$  or  $S_0$  does not seem possible with the present results as shown in the following figures:

![](_page_10_Figure_2.jpeg)

Figure S7: NICS values for 5- and 7-membered rings of  $S_0$  (top) and  $T_1$  (bottom) of molecules **1** and **2**.

# Optimized cartesian coordinates of the compounds

Table lene.	S2: Cartes	ian coordin	ates of azu-
$\mathbf{C}$	-0.74454	0.00000	0.55197
$\mathbf{C}$	-1.58484	0.00000	-0.54767
$\mathbf{C}$	-1.25820	0.00000	-1.89659
$\mathbf{C}$	-0.00000	0.00000	-2.48367
$\mathbf{C}$	1.25820	0.00000	-1.89659
$\mathbf{C}$	1.58484	0.00000	-0.54767
$\mathbf{C}$	-1.14300	0.00000	1.89096
$\mathbf{C}$	0.74454	0.00000	0.55197
Н	-2.64688	0.00000	-0.31766
Н	-2.09729	0.00000	-2.58271
Н	-0.00000	0.00000	-3.56913
Н	2.09729	0.00000	-2.58271
Н	-2.16614	0.00000	2.23604
$\mathbf{C}$	-0.00000	0.00000	2.69074
$\mathbf{C}$	1.14300	0.00000	1.89096
Н	2.64688	0.00000	-0.31766
Н	0.00000	0.00000	3.77195
н	2.16614	0.00000	2.23604

Table	e S3: Cartesi	an coordina	tes of 1.
$\mathbf{C}$	-1.14781	-1.34627	0.00000
$\mathbf{C}$	-2.51824	-1.64827	0.00000
$\mathbf{C}$	-3.52776	-0.71084	0.00000
$\mathbf{C}$	-3.52776	0.71085	0.00000
$\mathbf{C}$	-2.51824	1.64827	0.00000
$\mathbf{C}$	-1.14781	1.34625	0.00000
$\mathbf{C}$	-0.00001	-2.17496	0.00000
$\mathbf{C}$	-0.67496	0.00000	0.00000
Н	-2.81611	-2.69146	0.00000
Н	-4.52867	-1.13063	0.00000
Н	-4.52867	1.13064	0.00000
Н	-2.81609	2.69147	0.00000
Н	0.00001	-3.25480	0.00000
$\mathbf{C}$	0.00001	2.17496	0.00000
$\mathbf{C}$	1.14781	-1.34625	0.00000
$\mathbf{C}$	0.67496	-0.00000	0.00000
$\mathbf{C}$	1.14781	1.34627	0.00000
Н	-0.00001	3.25480	0.00000
$\mathbf{C}$	2.51824	-1.64827	0.00000
$\mathbf{C}$	2.51824	1.64827	0.00000
$\mathbf{C}$	3.52776	-0.71085	0.00000
Н	2.81609	-2.69147	0.00000
$\mathbf{C}$	3.52776	0.71084	0.00000
Н	2.81611	2.69146	0.00000
Н	4.52867	-1.13064	0.00000
Н	4.52867	1.13063	0.00000

Table	e S4: Cartesi	an coordina	tes of 2.
$\mathbf{C}$	-3.12965	0.00000	0.00000
$\mathbf{C}$	-2.51508	-1.24040	0.00000
$\mathbf{C}$	-1.16659	-1.56090	0.00000
$\mathbf{C}$	-2.51508	1.24040	0.00000
$\mathbf{C}$	-0.00000	-0.68630	0.00000
$\mathbf{C}$	-1.16659	1.56090	0.00000
$\mathbf{C}$	0.00000	0.68630	0.00000
Н	-4.21301	0.00000	0.00000
Н	-3.18089	-2.09868	0.00000
Н	-3.18089	2.09868	0.00000
$\mathbf{C}$	-0.68255	-2.89608	0.00000
Н	-1.31948	-3.76916	0.00000
$\mathbf{C}$	1.16659	-1.56090	0.00000
$\mathbf{C}$	0.68255	-2.89608	0.00000
Н	1.31948	-3.76916	0.00000
$\mathbf{C}$	-0.68255	2.89608	0.00000
Н	-1.31948	3.76916	0.00000
$\mathbf{C}$	1.16659	1.56090	0.00000
$\mathbf{C}$	0.68255	2.89608	0.00000
Н	1.31948	3.76916	0.00000
$\mathbf{C}$	2.51508	1.24040	0.00000
$\mathbf{C}$	2.51508	-1.24040	0.00000
$\mathbf{C}$	3.12965	-0.00000	0.00000
Н	3.18089	2.09868	0.00000
Н	3.18089	-2.09868	0.00000
Н	4.21301	-0.00000	0.00000

#### References

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