

Supporting Information to
‘Outer-valence electron spectra of prototypical aromatic
heterocycles from an optimally-tuned range-separated
hybrid functional’

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This supplementary information file contains detailed information on the role and possibility of tuning the short-range Fock-exchange fraction, α .

1. The effect of α on orbital energies

As discussed in the main text, for each preset value of the short-range (SR) Fock-exchange parameter α , we can obtain the optimal range-separation parameter, γ^{opt} , by minimizing the target function J , defined by the equation:

$$J^2 = \sum_i (IP^\gamma(N+i) + \varepsilon_{\text{HOMO}(N+i)}^\gamma)^2. \quad (1)$$

Here, the ionization potential, IP , is obtained as

$$IP^\gamma(N+i) = E^\gamma(N+i-1) - E^\gamma(N+i), \quad (2)$$

a relation valid for any integer i . In the main text we have investigated the dependence of the orbital energies on α for the 3N-thiol and CuPc molecules. Here, we examine the same for the small aromatic rings benzene, pyridine, and pyrimidine. Fig. S1 shows that for these systems, increasing α from 0 to 0.3 indeed somewhat impacts the orbital energies. Interestingly, it is found that for benzene the σ orbitals are varied more significantly (i.e., stabilized in energy) with changing α , whereas for pyridine and pyrimidine increasing α more clearly changes (i.e., destabilizes in energy) the π states. Concomitantly, benzene displays a π -HOMO, whereas pyridine (for $\alpha < 0.30$) and pyrimidine exhibit a σ -HOMO (see Fig. S1). Clearly, the symmetry of the HOMO entering the minimization procedure through Eq. 1 directly influences the response of orbitals with different symmetries on increasing α . We note that the overall effect of α in this range on the eigenvalue spectrum is rather minor for these systems, both in view of the large energy spacing typical for the ionization spectrum of these molecules and compared to the effect that α has on the orbital energies of the more complex systems (see discussion in the main text). For the latter, namely 3N-thiol and CuPc, the effect of changing α from 0 to 0.2 in fact qualitatively changes the resulting spectra as, e.g., the orbital ordering in close proximity to the HOMO is altered. Hence, a specific value of α has to be chosen, as discussed in the main text and further elaborated below.

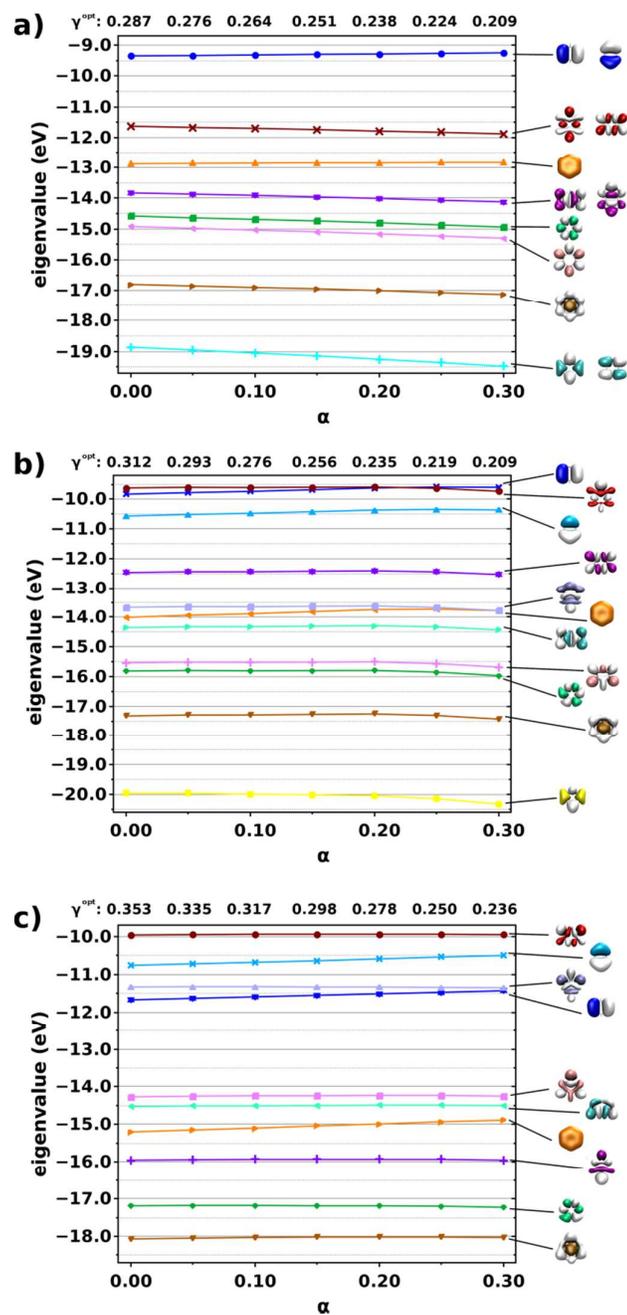


FIGURE S1: Orbital energies of benzene (a), pyridine (b), and pyrimidine (c), as calculated with the OT-RSH method using different values of the short-range Fock-exchange fraction, α .

2. Minimization of fractional-charge energy curvatures compared with minimization of the target function J : PTCDA and NTCDA

In former work¹ we have shown that for 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA), the optimal value of α can be tuned from first-principles using a *triple-tuning* procedure, where the i values of Eq. (1) are taken to be 1,0 and -1. The α tuning is then performed by examining the linearity of the total energy as a function of the fractional charge in the double-cation to single anion range via the root mean square d of the associated curvatures, which serves as a measure for the overall curvature of the three segments (see supplementary information of ref.1). As discussed in the main text, an equivalent tuning condition is realized by minimizing the target function J , which is a measure for the remaining curvature, as suggested and discussed by Stein et al.² In light of this equivalence, we can use the minimal value of J obtained for each α (with the associated tuned γ^{opt}) as a measurement of the remaining curvature, and choose the optimal value of α for which J is minimal. Curves of the minimal value of d and J for each α for the PTCDA and NTCDA molecules are given in Figs. S2a and S2b. The results confirm the equivalence of J and d as tuning criteria.

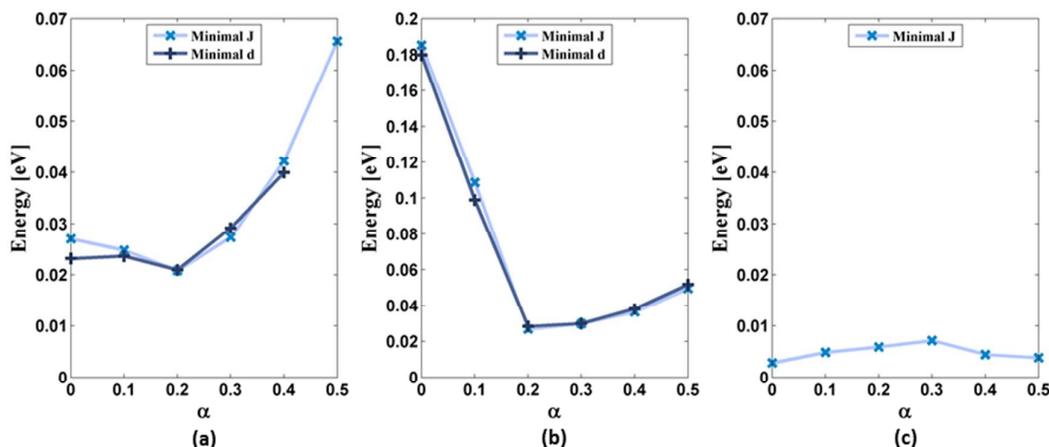


FIGURE S2: Minimal values of the target function, J , and the energy curvatures RMS, d (as defined in the text) as a function of the short-range Fock-exchange fraction, α , for (a) PTCDA and (b) NTCDA, and minimal values of the target function, J , for CuPc (c). For each α , the range-separation parameter γ was tuned to minimize J from the triple-tuning procedure discussed in the text, and J and d were then computed using this optimal γ^{opt} value.

3. Minimization of the target function J : 3N-thiol and CuPc

The above-suggested tuning procedure of α using the minimal value of J for $i=1,0,-1$, was not successful for the complex molecules we examined in this work, 3N-thiol and CuPc, for different reasons. Within the above-discussed triple-tuning procedure, we examine the system under the extraction of one and two electrons, and the addition of one electron. In the case of 3N-thiol, while the first electron is being extracted from a π -type HOMO orbital, the orbital ordering of the cation changes and displays a σ -type HOMO, from which the second electron is extracted. However, the second cation of 3N-thiol shows a π -orbital as the LUMO in both spin channels, and therefore the “hole density” of the cation does not correspond to its HOMO. Similarly to the strategy discussed in the main text for pyridine, also for 3N-thiol we performed several additional tests and prepared an alternative starting configuration for the cationic ground-state. However, differently from the case of pyridine, this strategy did not result in a new converged ground-state orbital configuration, i.e., the HOMO of the cation nevertheless remained a σ -orbital. As discussed in the main text, such a situation complicates the use of the IP theorem and the minimization through Eq. (1), which we therefore could not apply successfully for the cation of 3N-thiol.

For the CuPc molecule, we did not encounter the above issue, as the orbital ordering in the cation was conserved, and the second electron was extracted from the same orbital as the first one. However, in this case the triple-tuning procedure worked very well, so that for the range of $\alpha=0-0.5$ the minimal value of the target function J was smaller than the numerical error, as shown in Fig. S2c. For this reason we could not use this method to choose an optimal value for the short-range fraction, α .

It seems that while PTCDA and NTCDA served as good test-cases, the suggested method for first-principles α -tuning is harder to apply for the more complex systems studied here. Therefore, in the main text we suggested other possibilities for choosing α . However, we still learn from the cases of PTCDA and NTCDA, where the α -tuning is possible, that it is important to incorporate short-range Fock-exchange to achieve accuracy in the description of the outer-valence spectra, with the preferable fraction of $\alpha=0.2$. Indeed, as shown in the main text, for all the cases studied in this work, such a short-range fraction greatly improves the resulting spectra when compared to GW and to experiment.

- (1) Refaely-Abramson, S.; Sharifzadeh, S.; Govind, N.; Autschbach, J.; Neaton, J. B.; Baer, R.; Kronik, L. *Phys. Rev. Lett.* **2012**, *109*, 226405.
- (2) Stein, T.; Autschbach, J.; Govind, N.; Kronik, L.; Baer, R. *J. Phys. Chem. Lett.* **2012**, *3*, 3740–3744.