

Subsystem Density-Functional Theory for Interacting Open-Shell Systems: Spin Densities and Magnetic Exchange Couplings – Supporting Information–

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Date: May 15, 2020

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S1 Verdazyl Dimer

S1.1 Potential Energy Surface of the Verdazyl Dimer

Fig. S-1 shows the potential energy surface for the BS, triplet and closed-shell state calculated with KS-DFT and sDFT. The equilibrium distance between the monomers is at about 3.0 Å for the triplet and BS spin state with sDFT and at about 3.6 Å with broken-symmetry KS-DFT. The closed-shell state calculated with KS-DFT has an equilibrium distance of about 3.0 Å.

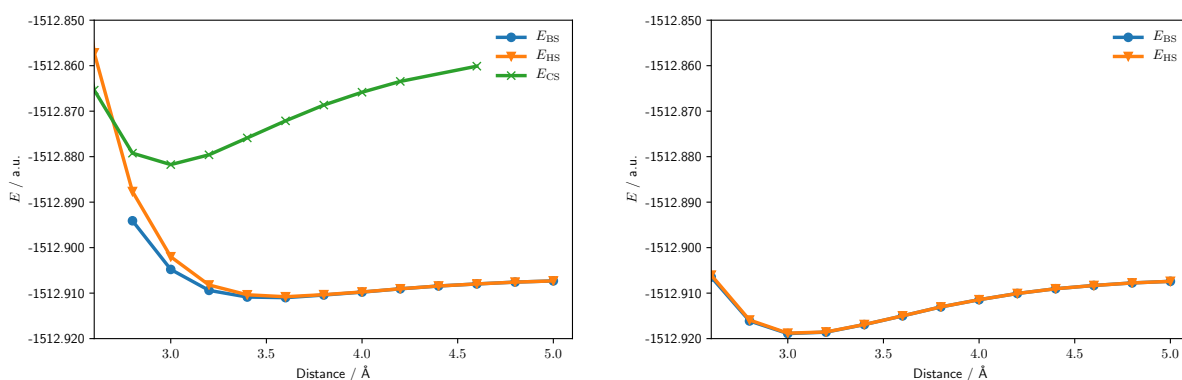


Figure S-1: Potential energy surface for the BS, triplet (HS) and closed-shell (CS) state for the verdazyl dimer shown in Fig. 1 in the Manuscript, calculated with BS/KS-DFT (PBE0) (left) and sDFT (FAT PW91k PBE0/PBE in supersystem basis) (right).

S1.2 Spin Density of the Verdazyl Dimer

Fig. S-2 shows the HS spin density calculated with KS-DFT for selected distances.

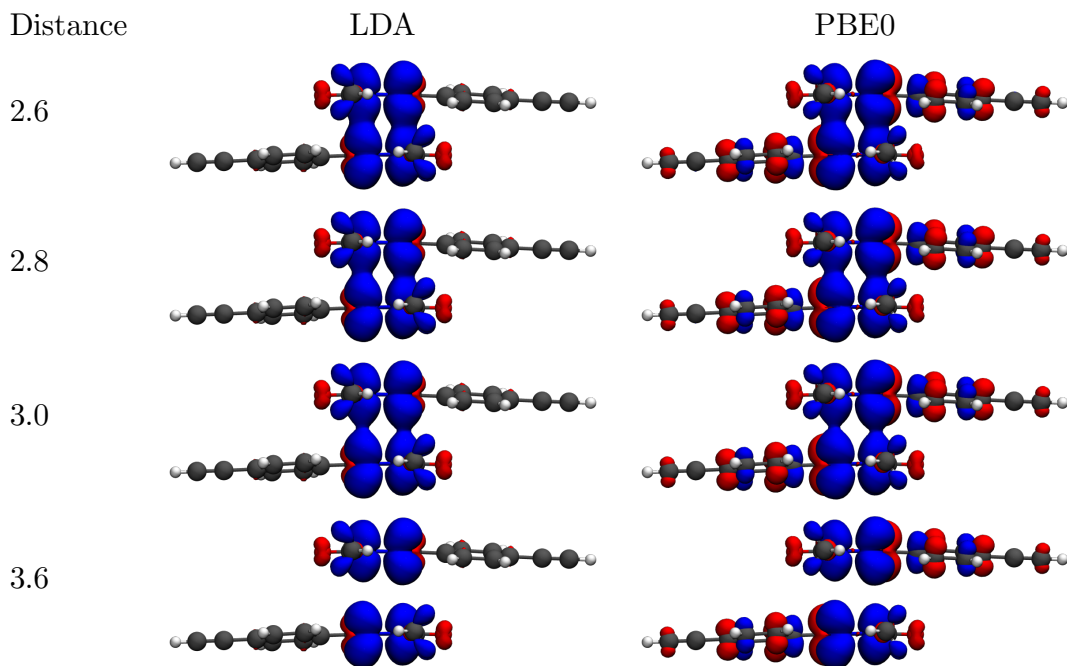


Figure S-2: KS-DFT spin densities of the HS state of the verdazyl dimer shown in Fig. 1 in the manuscript for selected distances. An isovalue of 0.001 a.u. was applied.

S2 TTTA Crystal Structure

Fig. S-3 shows the spin density of the HS state ($S = 13$) for the cut out of the crystal structure shown in Fig. 10 in the manuscript. On the right side the spin density as a sum-of-isolated monomers densities and on the left side the converged sDFT density are shown. The spin density difference between these is shown in Fig. S-4. The spin density of the $S=0$ BS state as a sum-of-isolated monomers contributions (left) and the converged sDFT spin-density (right) is shown in Fig. S-5. Fig. S-6 shows the corresponding spin density difference. For the $S=2$ BS state the sDFT spin density is shown in Fig. S-7.

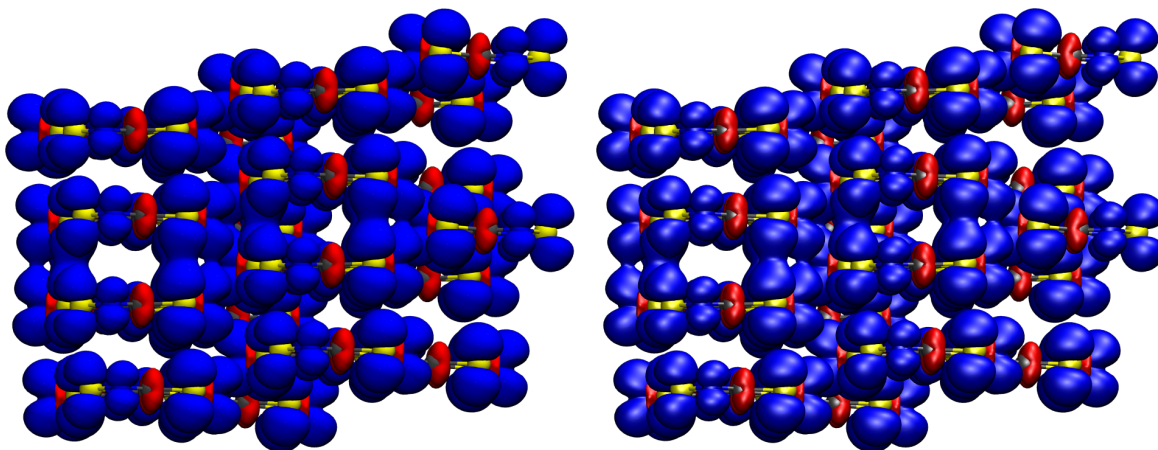


Figure S-3: Spin density of the high-spin state of the crystal structure cut-out of TTTA. Left: The spin-density of the isolated subsystems, calculated with PBE. Right: sDFT PBE/PBE/PW91k spin-density. An isovalue of 0.001 a.u. was applied.

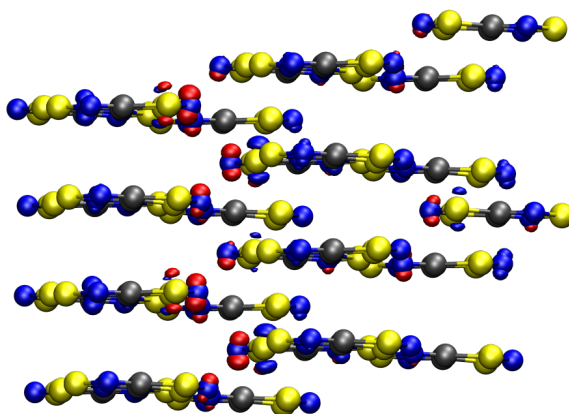


Figure S-4: Spin density difference between sDFT and the isolated monomer densities of the crystal structure cut-out of TTTA for the HS state. An isovalue of 0.001 a.u. was applied.

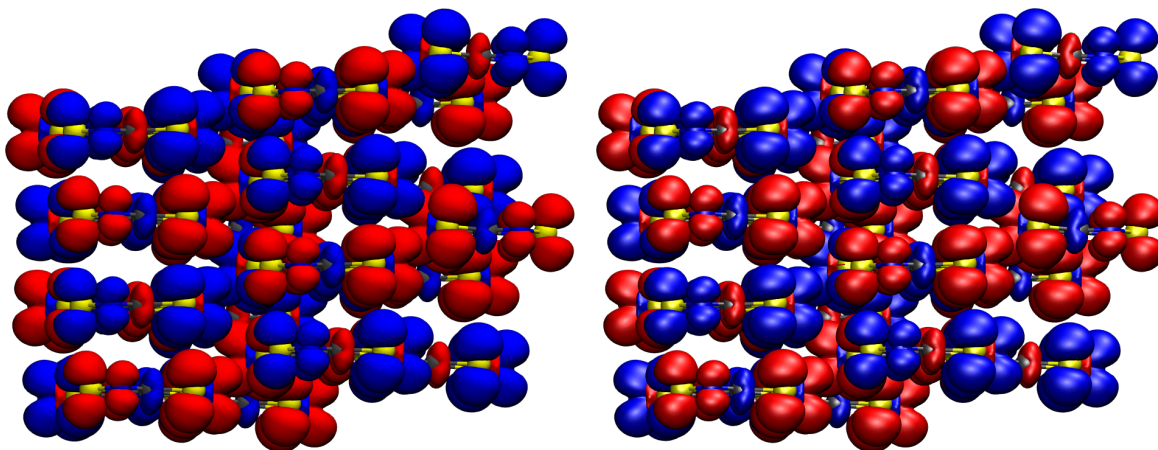


Figure S-5: Spin density of an BS state ($S = 0$) of the crystal structure cut-out of TTTA. Left: The spin-density of the isolated subsystems, calculated with PBE. Right: sDFT PBE/PBE/PW91k spin-density. An isovalue of 0.001 a.u. was applied.

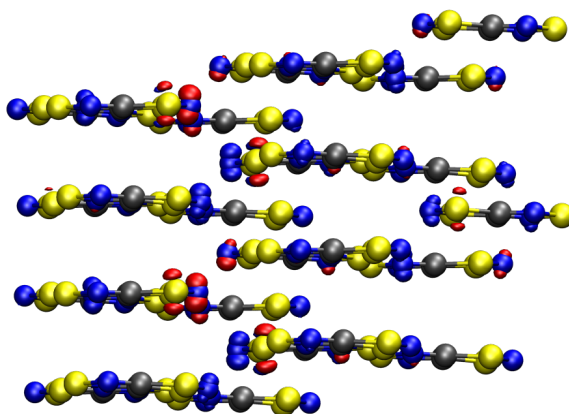


Figure S-6: Spin density difference between sDFT and the isolated monomer densities for the high-spin state. An isovalue of 0.001 a.u. was applied.

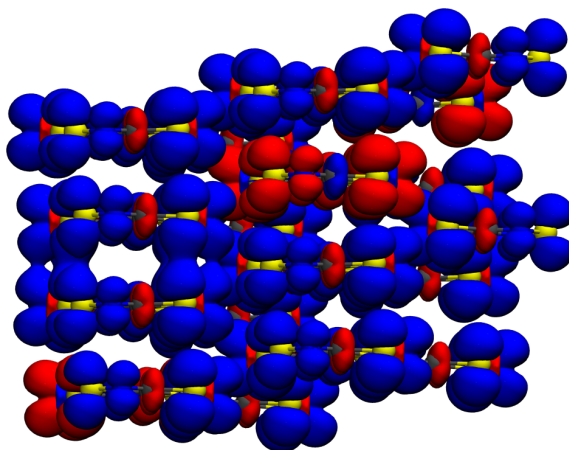


Figure S-7: Subsystem DFT (PBE/PBE/PW91k) spin density of an BS state ($S = 2$) for the crystal structure cut out. An isovalue of 0.001 a.u. was applied.

S3 Convergence of $\langle \hat{S}^2 \rangle$

The progression of the $\langle \hat{S}^2 \rangle$ value with respect to the FAT cycles of the PBE/PBE Huzinaga calculation for the SAXPOW01 TTTA dimer is shown in Fig. S-8. A slow convergence from an initial $\langle \hat{S}^2 \rangle$ value of 0.915 to 0 can be seen.

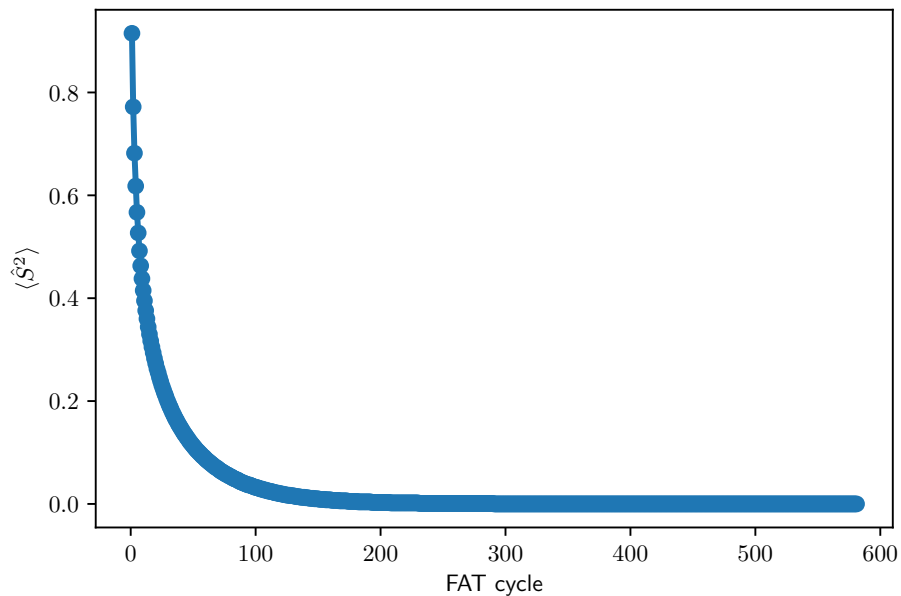


Figure S-8: The $\langle \hat{S}^2 \rangle$ value with respect to the FAT cycle for a Huzinaga PBE/PBE calculation in supersystem basis for the SAXPOW01 TTTA dimer.

S4 Magnetic Exchange Coupling Constants

In the following all calculated $\langle \hat{S}^2 \rangle_{\text{BS}}$ and magnetic exchange coupling constants for the TTTA dimers SAXPOW01, SAXPOW05 and SAXPOW06 are shown.

S4.1 SAXPOW05

Table S-I: Magnetic exchange coupling constants calculated for the SAXPOW05 dimer with broken-symmetry KS-DFT and sDFT for different XC-/(non-additive-XC-)functionals.

NAKE	LDA(/LDA)	PBE(/PBE)	PBE0(/PBE)
	J / cm^{-1}	J / cm^{-1}	J / cm^{-1}
KS-DFT			
	-328	-236	-93
sDFT, Subsystem basis			
PW91k	-6	-10	-9
sDFT, Supersystem basis			
PW91k	-43	-37	-24

Table S-II: $\langle S^2 \rangle_{\text{BS}}$ values calculated for the SAXPOW05 dimer with broken-symmetry KS-DFT and sDFT for different different XC-/(non-additive-XC-)functionals.

NAKE	LDA(/LDA)	PBE(/PBE)	PBE0(/PBE)
KS-DFT			
	1.003	1.070	1.208
sDFT, Subsystem basis			
PW91k	1.094	1.120	1.217
sDFT, Supersystem basis			
PW91k	1.084	1.113	1.213

Table S-III: Magnetic exchange coupling constants calculated for the SAXPOW05 dimer from sDFT densities using the accurate T_s from supersystem orbitals.

	LDA	PBE	PBE0
	J / cm^{-1}	J / cm^{-1}	J / cm^{-1}
Subsystem basis			
LDA/LDA/PW91k	-131	-135	-123
PBE/PBE/PW91k	-113	-117	-104
PBE0/PBE/PW91k	-83	-86	-75
Supersystem basis			
LDA/LDA/PW91k	-211	-202	-140
PBE/PBE/PW91k	-172	-168	-123
PBE0/PBE/PW91k	-112	-111	-81

Table S-IV: Magnetic exchange coupling constants calculated for the SAXPOW05 dimer from the sum-of isolated monomer (spin) densities using the accurate T_s from supersystem orbitals.

	LDA	PBE	PBE0
	J / cm^{-1}	J / cm^{-1}	J / cm^{-1}
Subsystem basis			
Isolated, LDA	-126	-130	-119
Isolated, PBE	-109	-114	-103
Isolated, PBE0	-78	-82	-73
Supersystem basis			
Isolated, LDA	-153	-158	-142
Isolated, PBE	-134	-138	-123
Isolated, PBE0	-89	-93	-82

S4.2 SAXPOW06

Table S-V: Magnetic exchange coupling constants calculated for the SAXPOW06 dimer with broken-symmetry KS-DFT and sDFT for different XC-/(non-additive-XC-)functionals.

NAKE	LDA(/LDA)	PBE(/PBE)	PBE0(/PBE)
	J / cm^{-1}	J / cm^{-1}	J / cm^{-1}
KS-DFT			
	-33	-23	-7
sDFT, Subsystem basis			
PW91k	0	0	0
sDFT, Supersystem basis			
PW91k	1	1	1

Table S-VI: $\langle S^2 \rangle_{\text{BS}}$ values calculated for the SAXPOW06 dimer with broken-symmetry KS-DFT and sDFT for different XC-/(non-additive-XC-)functionals.

NAKE	LDA(/LDA)	PBE(/PBE)	PBE0(/PBE)
KS-DFT			
KS-DFT	1.097	1.127	1.235
sDFT, Subsystem basis			
PW91k	1.102	1.129	1.231
sDFT, Supersystem basis			
PW91k	1.102	1.129	1.233

Table S-VII: Magnetic exchange coupling constants calculated for the SAXPOW06 dimer from sDFT densities using the accurate T_s from supersystem orbitals.

	LDA	PBE	PBE0
	J / cm^{-1}	J / cm^{-1}	J / cm^{-1}
Subsystem basis			
LDA/LDA/PW91k	-22	-23	-9
PBE/PBE/PW91k	-17	-18	-7
PBE0/PBE/PW91k	-13	-13	-7
Supersystem basis			
LDA/LDA/PW91k	-35	-36	-14
PBE/PBE/PW91k	-24	-25	-9
PBE0/PBE/PW91k	-12	-13	-7

Table S-VIII: Magnetic exchange coupling constants calculated for the SAXPOW06 dimer from the sum-of isolated monomer (spin) densities using the accurate T_s from supersystem orbitals.

	LDA	PBE	PBE0
	J / cm^{-1}	J / cm^{-1}	J / cm^{-1}
Subsystem basis			
Isolated, LDA	-21	-21	-8
Isolated, PBE	-17	-17	-6
Isolated, PBE0	-12	-12	-7
Supersystem basis			
Isolated, LDA	-25	-25	-8
Isolated, PBE	-19	-19	-7
Isolated, PBE0	-13	-13	-7