Supporting information on:

NCI orbital decomposition and critical comparison to local correlation schemes

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1 Orbital density plots

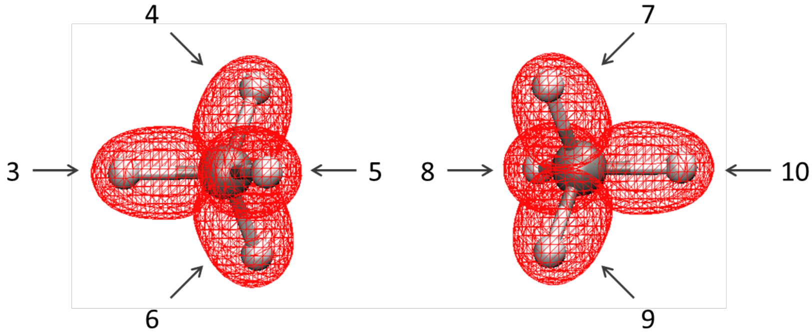


Fig. S1: Orbital densities for the methane dimer, together with their associated orbital labels. Isocontour values of 0.1 were used for isosurface representations.

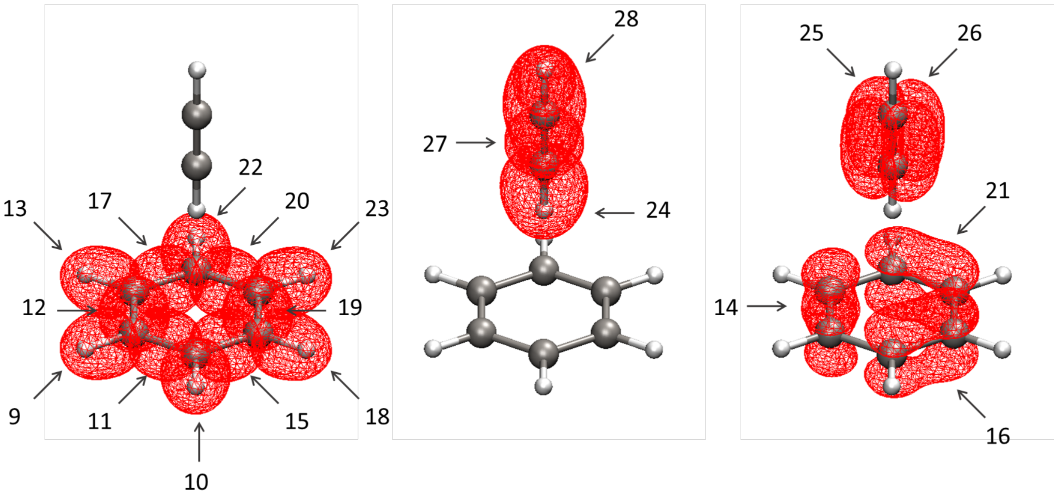


Fig. S2: Orbital densities for the benzene-acetylene, together with their associated orbital labels. Isocontour values of 0.025 were used for isosurface representations.

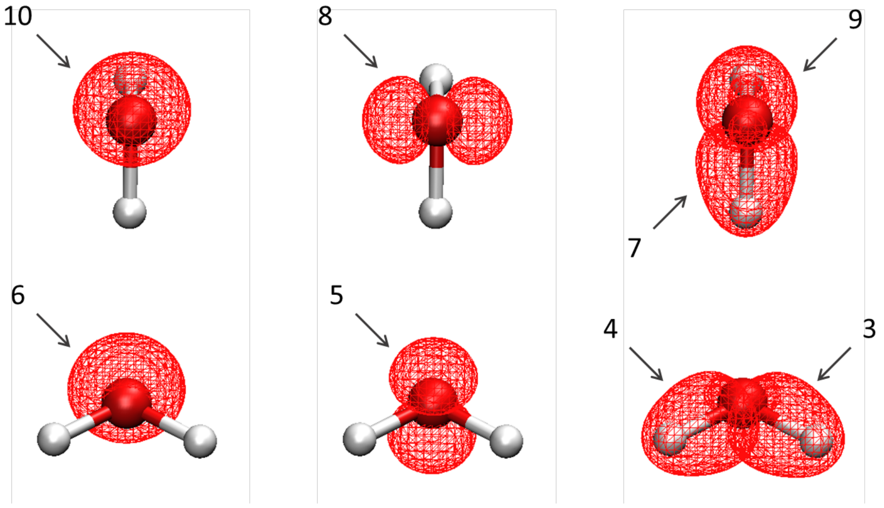


Fig. S3: Orbital densities for the water dimer, together with their associated orbital labels. Isocontour values of 0.1 were used for isosurface representations.

2 Pair orbital analysis in o-DID

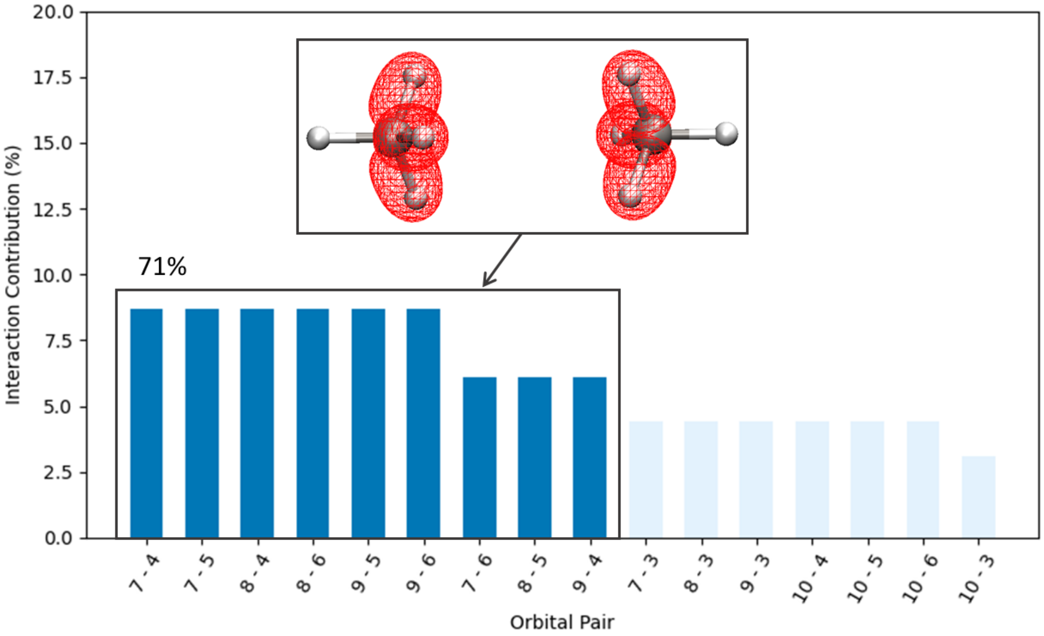


Fig. S4: Pair orbital analysis of the methane dimer. For ease of visualization, orbital densities are chosen as representation. Individual orbital labels are provided in Figure S1. Isocontour values of 0.1 were used for the isosurface representations.

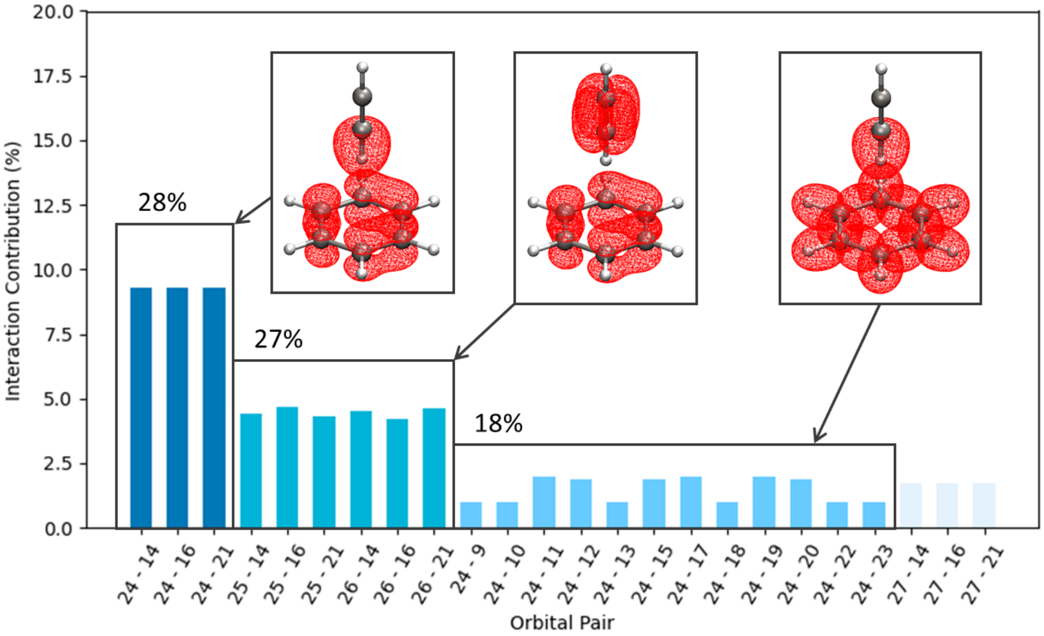


Fig. S5: Pair orbital analysis of the benzene-acetylene. Contributions below 1% were omitted for clarity. For ease of visualization, orbital densities are chosen as representation. Individual orbital labels are provided in Figure S2. Isocontour values of 0.025 were used for isosurface representations.

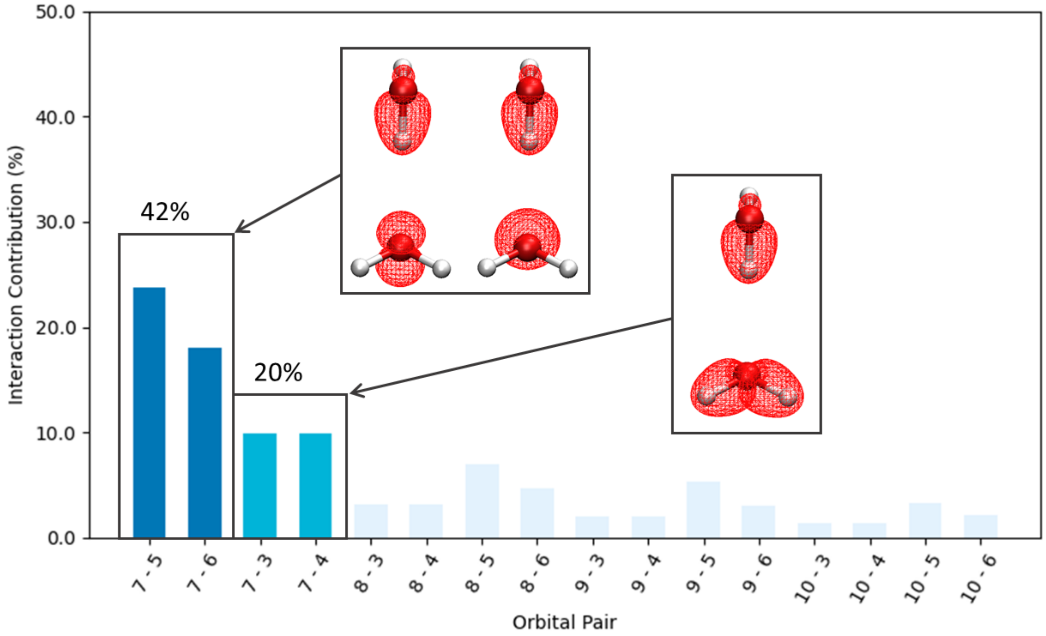


Fig. S6: Pair orbital analysis of the water dimer. For ease of visualization, orbital densities are chosen as representation. Individual orbital labels are provided in Figure S3. Isocontour values of 0.1 were used for isosurface representations.

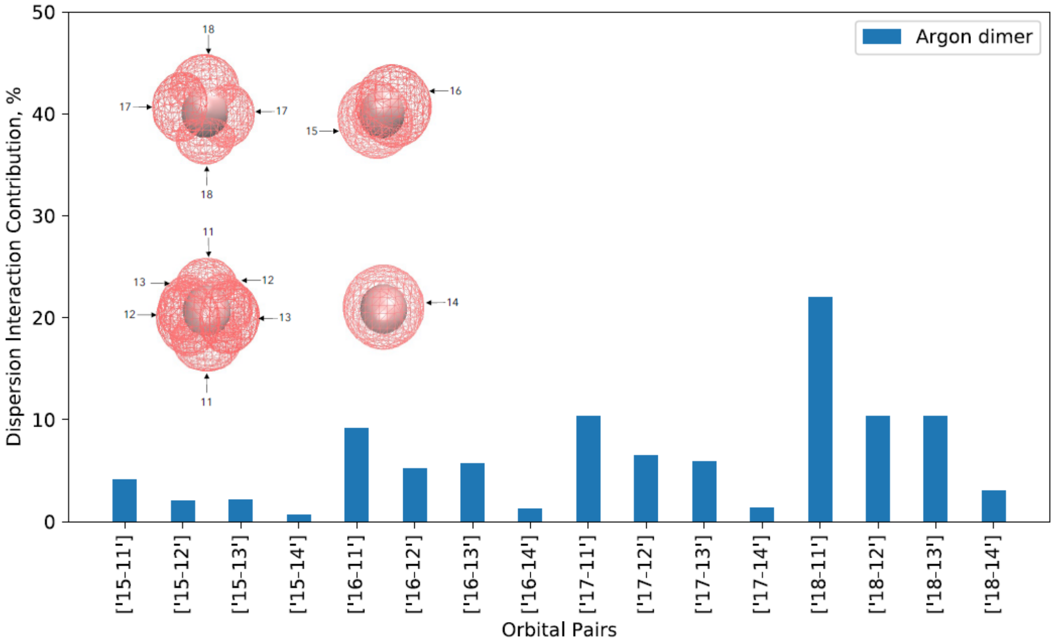
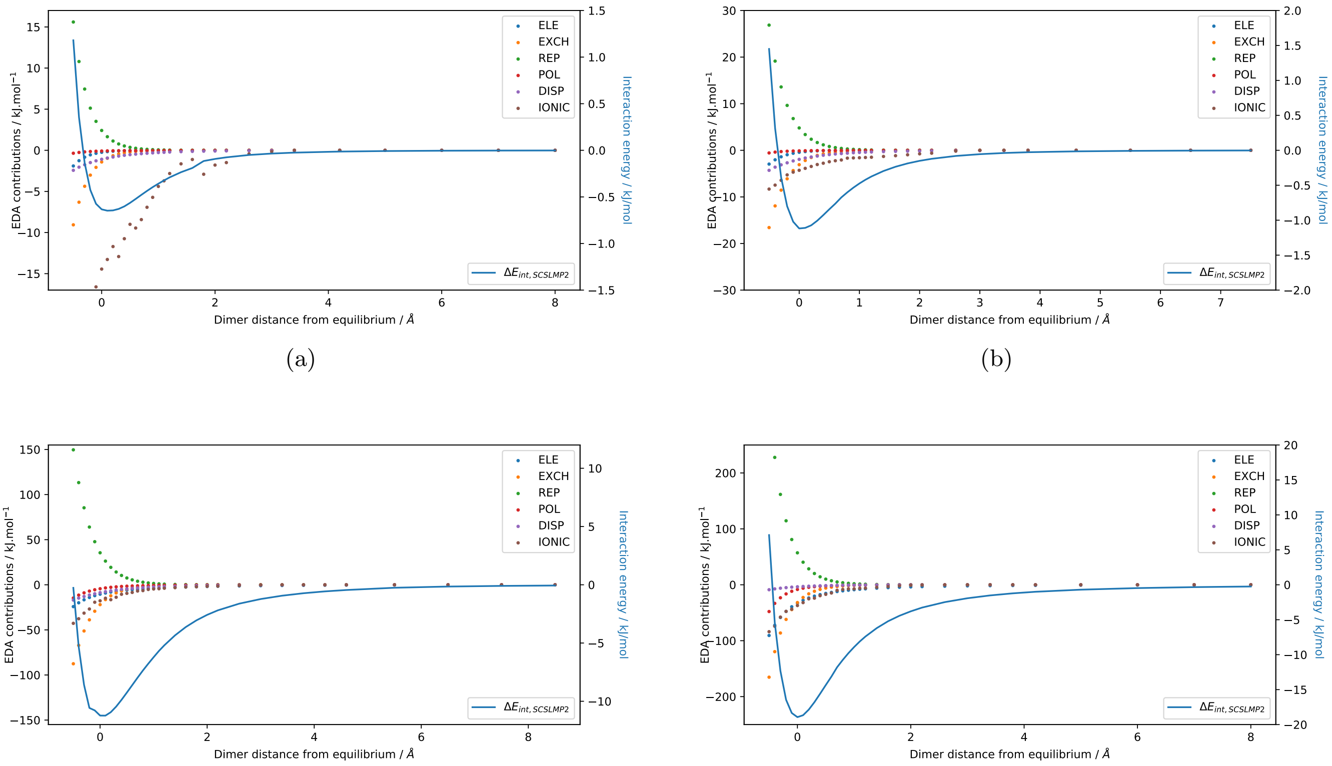


Fig. S7: Pair orbital analysis of the Argon dimer. For ease of visualization, orbital densities are chosen as representation. The numbers of the orbitals aid the interpretation of the pair interaction in the x-axis. Isocontour values of 0.05 were used for isosurface representations.

3 Wave function energy decomposition analysis



(a) (b)

(c) (d)

Fig. S8: Energy decomposition analysis of the interaction energy as dimer is moved closed to each other and upon dissociation. Zero indicates equilibrium distance of the dimers. The HF reference energy for each geometry is decomposed into electrostatics, exchange, repulsion and polarization following the Kitaura-Morokuma scheme as extended by Su and Li.[1] The correlation energy is decomposed into its components dispersion and ionic contributions using PNO-SCS-LMP2. For both methods, aug-cc-pVTZ, H = cc-pVTZ basis functions are used. The blue line is the interaction energy calculated at PNO-SCS-LMP2 level of theory (energy range is on the y-axis of the right side). Systems are as follows: (a) argon dimer, (b) methane dimer, (c) benzene-acetylene, and (d) water dimer. Oscillations in the ionic terms along the potential energy surfaces originate from numerical instabilities in the convergence of the localized (virtual) orbitals.