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# Wave functions are mapped in intermolecular potential energy surfaces of $\pi$-stacked aggregates

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$\pi-\pi$ interactions are of utmost importance for life- and material-science but their nature is still controversially debated. The existing discrepancies are raionalized by (i) Demonstrating that $\pi-\pi$ interactions reflect the wave function properties of repulsive interactions in a particularly pronounced manner (ii) Showing that the resulting fluctuations in repulsive interactions lead to the counterintuitive behavior of repulsive and attractive components in the interaction energy.
The wave function character of repulsive interactions is rationalized by partitioning the exchange-repulsion contribution to the interaction energy between two closed shell systems into molecular orbital pair contributions to the exchange (MOPCE) energy [1,2]. This reveals that the repulsion in $\pi$-stacked dimers is governed by repulsion of the $\pi$-orbitals on the respective systems. For constant interplanar distances MOPCE terms are essentially proportional to the squared overlap integral of the respective orbitals, which causes that the exchange-repulsion interactions are mapping spatial oscillations of the interacting wave functions. Our model resembles frontier orbital theory and allows to reproduce energetically favorable arrangements of $\pi$-stacked systems such as benzene- or pentacene-dimers [3] as well as donor-acceptor systems such as benzene and para-benzoquinone.
Furthermore, we explain why the importance of attractive and repulsive contributions to the interaction of two molecules frequently leads to controversal debates. Repulsive interactions commonly decrease exponentially with the distance of interacting systems while attractive interactions behave smoother e.g. as a power of the inverse distance. This causes that arrangements with reduced repulsion will give rise to a decreased equilibrium distances for which the repulsive interactions are generally increased. This repulsion paradoxon: less repulsion gives more repulsion! is shown to be relevant for various $\pi-\pi$ interactions and halogen bonding.

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