DENSITY MATRIX CHANGES IN MOLECULAR INTERACTIONS

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When two molecules are close, their electronic densities fluctuate and deform in response to one another. Although small, these changes drive many physical, chemical, and biological phenomena, including collision-induced absorption in molecular spectra, molecular-crystal formation, and ligand–protein binding. Here, we investigate electron-density changes in selected model systems representing different van der Waals interactions, including hydrogen bonding, σ-hole bonding, atom…atom contacts, and dispersive stacking.

We use propSAPT, an innovative variant of symmetry-adapted perturbation theory developed by our group for molecular-property calculations. The method expresses interaction-induced electron-density changes as perturbative corrections in orders of the interaction operator and has previously been applied to interaction-induced properties such as dipole moments.[1] In propSAPT, density corrections naturally decompose into polarization, exchange, and dispersion contributions, analogous to the standard SAPT energy decomposition. This enables physically transparent analysis and visualization of noncovalent-interaction-induced density shifts. We compare propSAPT differential densities with supermolecular coupled-cluster results and contrast dispersion-driven density changes with those from the MBD@FCO many-body dispersion model based on quantum Drude oscillators.[2]

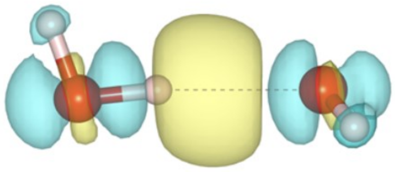

Figure 1. Electron density changed induced by dispersion interaction in water dimer

REFERENCES

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[2] A. Khabibrakhmanov, M. Gori, C. Müller, and A. Tkatchenko, J. Am. Chem. Soc. **147**(44), 40763–40775 (2025).