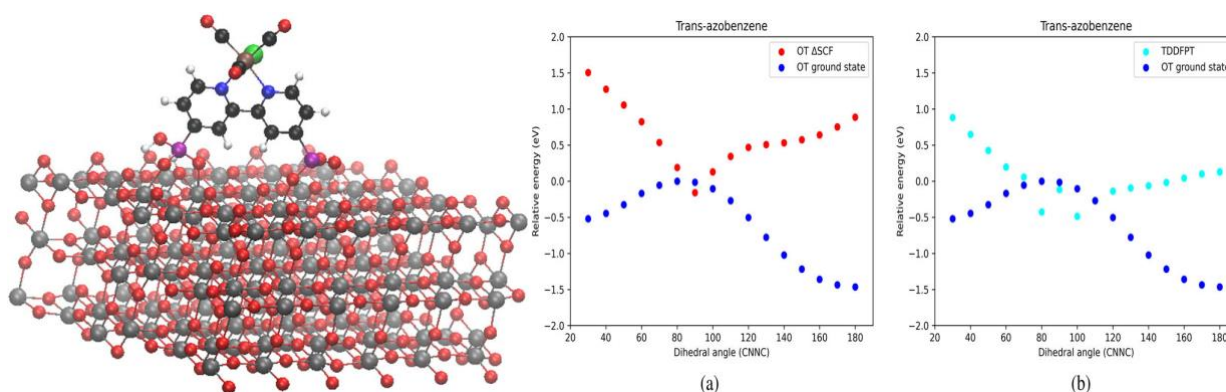


Robust Δ SCF excited state calculations for molecules and materials

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The direct energy functional minimization method using the orbital transformation (OT) scheme [1] in the program package CP2K has been explored for Δ self-consistent field (Δ SCF) calculations with fractional occupations. This allows to exploit the Δ SCF method for various kinds of molecules and periodic systems [2]. Vertical excitation energies of molecular heteroaromatic systems and condensed phase systems, such as solvated ethylene and solvated uracil obeying periodic boundary conditions, are reported using the Δ SCF method. The first singlet excitation energy profile of trans-azobenzene is investigated along the C-N-N-C dihedral angle to show the robustness for excitation energy calculation near conical interaction region. Additionally, we have implemented a recently proposed State-Targeted Energy Projection (STEP) algorithm [3] for diagonalization based SCF in CP2K. It is found that the OT scheme for fractional-occupation Δ SCF provides a smooth and robust SCF convergence for all investigated excitation energies and (non-)periodic systems.



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