Active Spaces and Non-Orthogonal Configuration Interaction for Molecules on Metal Surfaces

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We test a simple configuration-interaction approach for calculating the ground state electron population for an Anderson-Holstein model of a molecule on a metal surface. The relevant configuration interaction Hamiltonian contains both a relaxed closed-shell (RCS) state as well as a handful of non-orthogonal constrained Hartree-Fock states. We test both the strong and weak metal-molecule hybridization (Γ) limits compared with electron-electron repulsion (U). We obtain very accurate results as compared with exact numerical renormalization group (NRG) theory, recovering charge transfer states where appropriate. The current framework should open a straightforward path to run molecular non-adiabatic dynamics on metal surfaces.