Density-Functional Theory-Based Embedding Approaches for Transition-Metal Complexes

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Supporting Information

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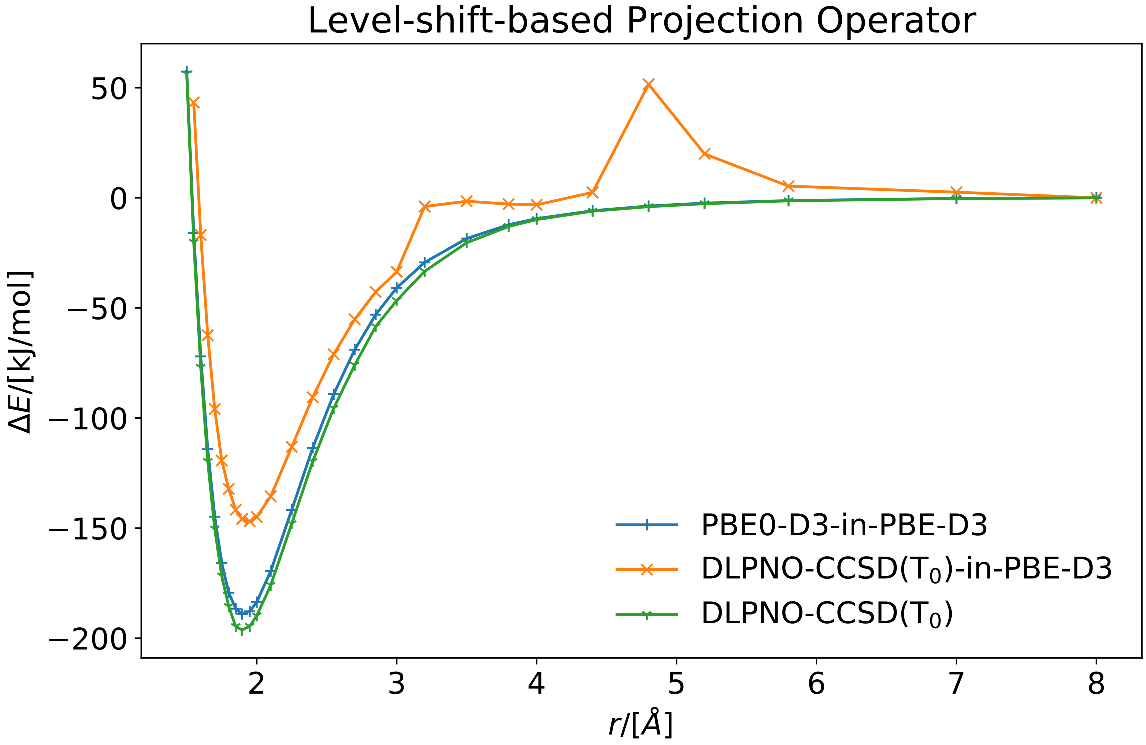

Figure S1: Full-scale figure for the potential energy surfaces for the dissociation of CO from $Cr(CO)_6$ and level-shift based embedding. This graph corresponds to Fig. (3) of the main text.

1 Full-scale Figures

The full-scale figure that corresponds to the potential energy surface for the dissociation of carbon monoxide from chromium hexacarbonyle is shown in Fig. S1. The non-full-scale figure is shown in Fig. (3) of the main text.

2 Double Hybrid Functional Embedding

The energy contributions to the correlation energy which have to be calculated with second order Møller-Plesset perturbation theory (MP2) are calculated for this double hybrid functional embedding using domain-based local pair natural orbital (DLPNO) MP2. The orbital pairs of the supersystem are divided into pure environment pairs $\left(\psi_i^B\psi_j^B\right)$, cross pairs $\left(\psi_i^A\psi_j^B\right)$ and pure active pairs $\left(\psi_i^A\psi_j^A\right)$. The local MP2 amplitude equations are solved for all orbital pairs $\left(\psi_i^B\psi_j^B\right) \cup \left(\psi_i^A\psi_j^B\right) \cup \left(\psi_i^A\psi_j^A\right)$ using the supersystem Fock operator constructed with the functional employed in the environment system. The sum of the pair energies for the respective set are evaluated

$$E_{AA}^{\mathrm{LMP2}} = \sum_{\left(\psi_i^A\psi_j^A\right)} \epsilon_{ij} \tag{1}$$

$$E_{AB}^{\mathrm{LMP2}} = \sum_{\left(\psi_i^A\psi_j^B\right)} \epsilon_{ij} \tag{2}$$

$$E_{BB}^{\mathrm{LMP2}} = \sum_{\left(\psi_i^B\psi_j^B\right)} \epsilon_{ij} \tag{3}$$

and stored. Then a second local MP2 calculation is performed using only the pure active orbital pairs and the embedded Fock operator in which the contribution from the active system is described using the functional employed in the environment. In this part of the calculation, the occupied orbitals of the environment are not removed from the virtual space in the MP2 calculation [the virtual orbital space therefore consists of the (supersystem) virtual orbitals and the occupied environemnt orbitals], which was the case for the supersystem MP2 calculation above. We will denote the energy calculated like this as $E_{AA}^{\mathrm{LMP2,Emb}}$. The energy contribution to the interaction energy originating from the double hybrid treatment of the interaction is then calculated as

$$E_{\mathrm{int}}^{\mathrm{LMP2}} = E_{AA}^{\mathrm{LMP2}} - E_{AA}^{\mathrm{LMP2,Emb}} + E_{AB}^{\mathrm{LMP2}} \tag{4}$$

and the energy contribution for the environment system is calculated as

$$E_B^{\text{LMP2}} = E_{BB}^{\text{LMP2}}. \tag{5}$$

The energy decomposition in Eq. (4) allows the recovery of the energy contributions from the presence of the occupied environment orbitals in the space of the virtual orbitals in the correlation treatment for the active system. This contribution will be close to zero for a level-shift type projection operator. This formulation of the double hybrid embedding is exact in the sense that embedding of the same double hybrid functionals into each other gives the corresponding supersystem result.