

## **Understanding and reducing errors in density functional calculations**

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## I. TWO ELECTRON SYSTEMS

To make Fig. 1, we carefully interpolated accurate QMC energies<sup>1,2</sup> from  $Z^{-1} = 1$  to 0, and repeated this procedure applying PBE to the exact densities to find  $\Delta E_F(Z)$ . We also used Turbomole<sup>3</sup> to solve for self-consistent PBE energies and the eigenvalue. For  $Z \leq Z_c$ , the eigenvalue is pinned to 0, and an increasing fraction of an electron escapes. To achieve self consistency, we decreased the occupation of the orbital from 2 until we find an occupation at which the total energy converges and the eigenvalue vanishes.

## II. HO·H<sub>2</sub>O COMPLEX

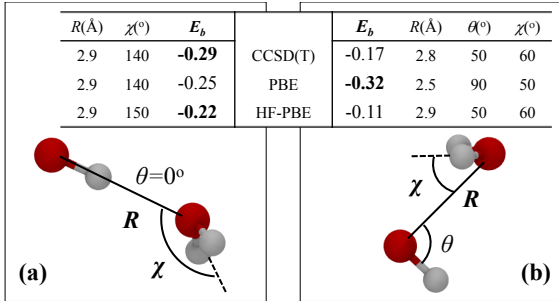


FIG. S1. Binding energies in eV of HO·H<sub>2</sub>O calculated with various methods for (a) hydrogen-bonding structure and (b) hemi-bonding structure.

PES scan results for HO·H<sub>2</sub>O complex are shown in Fig. S1. Self-consistent PBE greatly overstabilizes the hemi bond, resulting in a strong, unphysical hemi-bonding minimum,  $\Delta\epsilon_g^{\text{PBE}}$  is less than 1 eV. CCSD(T) and HF-PBE, on the other hand, give the hydrogen-bonding geometry as the global minimum.

### III. $\text{H}_2^+$ DISSOCIATION

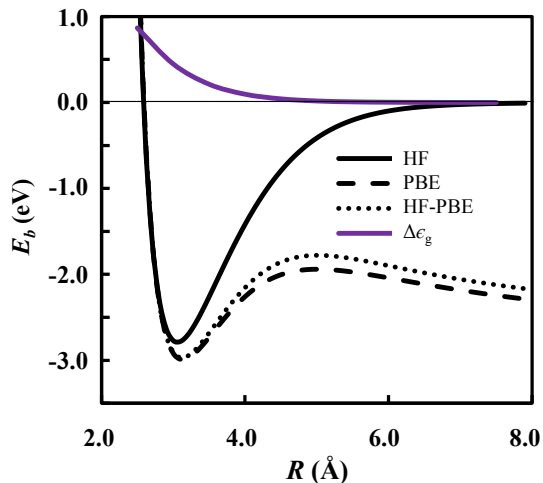


FIG. S2. Binding energy of  $\text{H}_2^+$  as a function of separation in several calculations, and the PBE HOMO-LUMO gap.

Dissociation of  $\text{H}_2^+$  with a standard functional is shown in Fig. S2. We compare self-consistent calculations with the HF-DFT method and HF method. The HOMO-LUMO gap ( $\Delta\epsilon_g$ ) is also shown in the figure.

### IV. CALCULATION DETAILS

Self-consistent PBE calculation for two electron systems were performed with an aug-cc-pV6Z basis set<sup>5</sup>. For all other calculations (e.g. NaCl dissociation, OH radical complexes,  $\text{H}_2^+$  dissociation), self-consistent PBE and HF-PBE calculations were performed with an aug-cc-pVTZ<sup>6-8</sup> basis. All calculations mentioned above were performed with the Turbomole<sup>3</sup> program. SCF convergence and density convergence criteria of  $10^{-8}$  were used, and grid size of 6 were used for PBE calculations.

### REFERENCES

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