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[1,2] 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[3] 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_2O COMPLEX

R(Å)	χ(°)	E_b
2.9	140	**-0.29**
2.9	140	-0.25
2.9	150	**-0.22**

	E_b	R(Å)	θ(°)	χ(°)
CCSD(T)	-0.17	2.8	50	60
PBE	**-0.32**	2.5	90	50
HF-PBE	-0.11	2.9	50	60

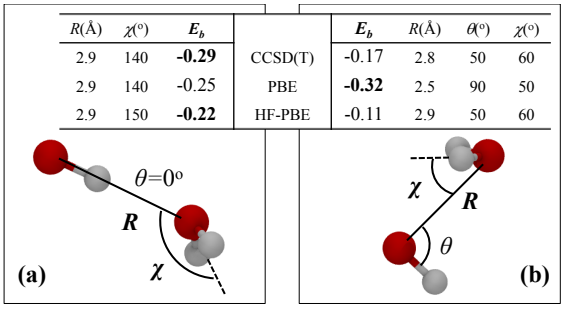

FIG. S1. Binding energies in eV of HO·H_2O calculated with various methods for (a) hydrogen-bonding structure and (b) hemi-bonding structure.

PES scan results for HO·H_2O complex are shown in Fig. S1. Self-consistent PBE greatly overstabilizes the hemi bond, resulting in a strong, unphysical hemi-bonding minimum, $\Delta\epsilon_g^{\rm PBE}$ is less than 1 eV. CCSD(T) and HF-PBE, on the other hand, give the hydrogen-bonding geometry as the global minimum.

III. H_2^+ DISSOCIATION

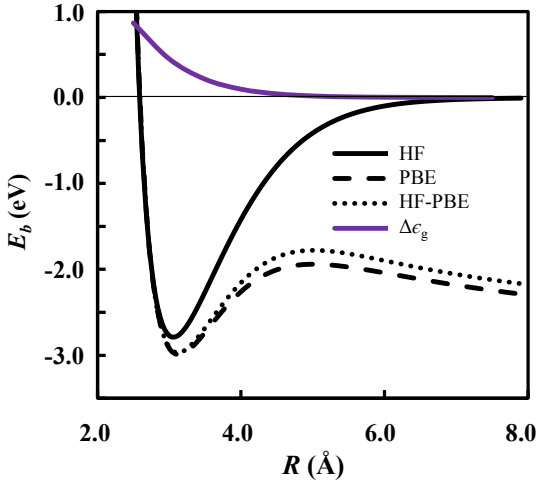

FIG. S2. Binding energy of H_2^+ as a function of separation in several calculations, and the PBE HOMO-LUMO gap.

Dissociation of 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[5]. For all other calculations (e.g. NaCl dissociation, OH radical complexes, H_2^+ dissociation), self-consistent PBE and HF-PBE calculations were performed with an aug-cc-pVTZ[6–8] basis. All calculations mentioned above were performed with the Turbomole[3] program. SCF convergence and density convergence criteria of 10^{-8} were used, and grid size of 6 were used for PBE calculations.

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