Understanding and reducing errors in density functional calculations

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(Dated: 10 June 2013)
I. TWO ELECTRON SYSTEMS

To make Fig. 1, we carefully interpolated accurate QMC energies\textsuperscript{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\textsuperscript{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$_2$O COMPLEX

\begin{table}[ht]
\centering
\begin{tabular}{ccc}
\hline
\textit{R} (Å) & $\theta$ (°) & $E_b$ (eV) \\
\hline
2.9 & 140 & -0.29 \\
2.9 & 140 & -0.25 \\
2.9 & 150 & -0.22 \\
\hline
\end{tabular}
\end{table}

FIG. S1. Binding energies in eV of HO-H$_2$O calculated with various methods for (a) hydrogen-bonding structure and (b) hemi-bonding structure.

PES scan results for HO-H$_2$O complex are shown in Fig. S1. Self-consistent PBE greatly overstabilizes the hemi bond, resulting in a strong, unphysical hemi-bonding minimum, $\Delta E_{\text{PBE}}$ is less than 1 eV. CCSD(T) and HF-PBE, on the other hand, give the hydrogen-bonding geometry as the global minimum.
III. H$_2^+$ DISSOCIATION

![Diagram showing binding energy as a function of separation in several calculations and the PBE HOMO-LUMO gap.](image)

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.

REFERENCES


