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Accuracy of density functional theory methods for weakly bonded systems: The case of dihydrogen binding on metal centers

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Accurately calculating nonclassical metal-H_2 (dihydrogen) binding is crucial to the modeling of hydrogen sorbents as an important part of the hydrogen-based vehicle programs. We have performed highly accurate calculations using the Møller-Plesset second-order perturbation theory and coupled cluster theory with single, double, and perturbative triple excitations for the dihydrogen binding on four representative systems that cover a wide range of sorbent materials previously proposed for high-capacity room-temperature storage. Comparison with nine widely used density functional theory exchange-correlation functionals reveals that the Perdew-Burke-Ernzerhof and PW91 results are accurate to within a few hundredths of an eV/H_2. This validates the predictions using these methods.

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I. INTRODUCTION

Density functional theory (DFT) has been widely used for predicting materials properties with great success when the systems are made of strong chemical bonds. For example, the calculated cohesive energies for semiconductors such as Si and GaAs,[1] simple and transition metals such as Al,[1] Sc, and Ti,[2] can be accurate to within 0.2 eV per atom (or 5%). When the systems involve primarily weak van der Waals (vdW) interactions, however, the accuracy of the DFT calculations deteriorates due to the small magnitude of the interaction energy (which can be as small as 0.05 eV per atom).[3] The DFT typically overestimates the vdW interactions in the local density approximation (LDA) (Ref. 4) but underestimates or even gives no binding in the generalized gradient approximations (GGA).[5] Question arises for systems with *intermediate* binding strength: Can DFT still produce quantitative results that are within an acceptable range of accuracy? An important example for such systems is the metal-containing hydrogen sorbent materials on which hydrogen binds to the metal sites as an H_2 molecule (or dihydrogen). Here, the interaction between the metal center and H_2 is via a nonclassical chemical binding through electron donation and back donation (sometimes such an interaction is also termed Kubas interaction).[6] Other well-known examples of the weakly bonded systems, other than the vdW systems, include hydrogen-bonded[7] and dihydrogen-bonded systems.[8,9]

In the past several years, the metal-functionalized nanomaterials and organic frameworks have been proposed for high-capacity room-temperature hydrogen storage,[10–18] where the theoretically calculated dihydrogen binding energies on the metal sites range from about 0.15–0.25 eV for alkali and alkaline earth metals to about 0.25–0.50 eV for transition metals. Recently, Cha *et al.*[19] reported that for calcium-based systems all the DFT binding energies are seriously overestimated when compared with the Møller-Plesset second-order perturbation theory (MP2) calculations. Okamoto[20] also reported a similar overbinding for the Ti_2-C_2H_4 system. It is generally accepted that the high-level quantum-chemistry approaches, such as the MP2 (Ref. 21) and the coupled-cluster method,[22] are able to yield reliable binding energies. These recent reports thus raise a serious question whether the previous predictions of the hydrogen sorbent materials (based on the DFT calculations) are conceptually wrong. At this juncture, an accurate determination of the nonclassical metal-H_2 interaction for the hydrogen sorbent materials is so crucial that can profoundly impact the future directions of hydrogen-based vehicle programs in the U.S. and elsewhere.

In this work, we select four representative systems for high-capacity room-temperature storage (Ti, Sc, Ca, and Li) with a total of ten distinct configurations and performed the MP2 and CCSD(T) (coupled cluster theory with single, double, and perturbative triple excitations) calculations. Note that the aforementioned MP2 calculations used small basis sets (either 6-311++G** or 6-31G**). Here, we used instead larger correlation-consistent basis sets from which the complete basis set (CBS) results were derived. The results show that LDA severely overestimates the H_2 binding and hence should always be avoided. The GGA functionals tend to *underestimate* the H_2 binding, except for Perdew-Burke-Ernzerhof (PBE), Perdew-Wang (PW91), and M05–2X. Over the ten configurations, the PBE and PW91 yield accuracy to within 0.03 and 0.04 eV/H_2, respectively. The M05–2X yields even better accuracy to within 0.01 eV/H_2 but at the expense of a much higher computational cost. Thus, overall PBE or PW91 is still the most effective approach to date that combines accuracy with computational efficiency.

II. BENCHMARK SYSTEMS

The four systems are (1) Ti(Et), (2) Sc(Cp), (3) Ca(TPA), and (4) Li(TPA), where Et=ethylene, Cp=cyclopentadienyl, and TPA=terephthalic acid. (1) The Ti(Et) complex is the

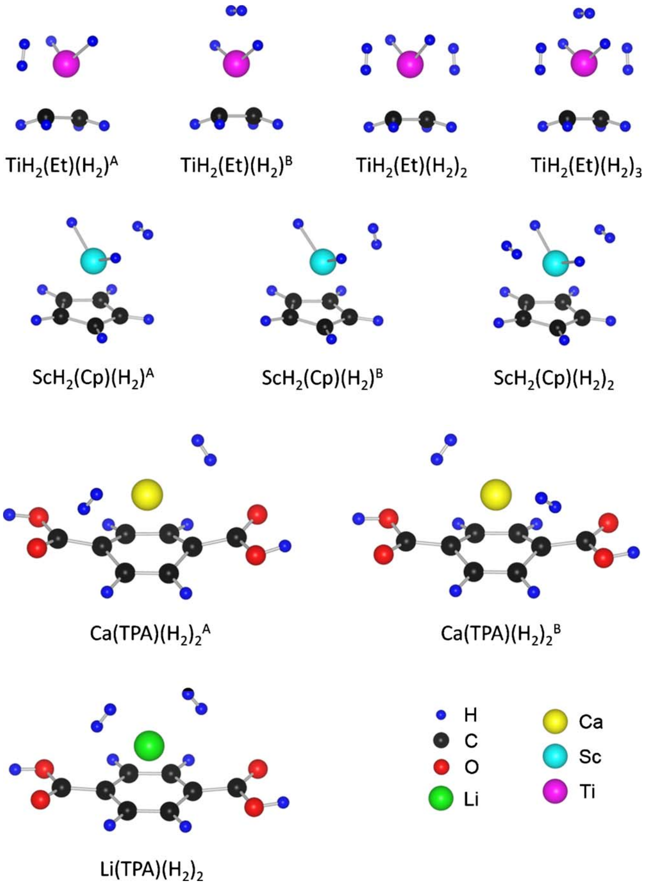

FIG. 1. (Color online) Four prototypical sorbent systems with ten distinct configurations, where Et=ethylene, Cp =cyclopentadienyl, and TPA=terephthalic acid. Superscripts *A* and *B* denote two different H_2 positions or orientations. For Ca(TPA) and Li(TPA), we considered the C_2-symmetry cases with two H_2. In our naming scheme, H_2 outside the parentheses forms hydrides, instead of dihydrogen.

smallest olefinic H_2 sorbents[13] and it represents other larger olefinic sorbents as well, such as the various 3*d* transition-metal- (TM-) decorated polymers.[12] (2) The Sc(Cp) complex represents the aromatic H_2 sorbents, such as the various TM-decorated fullerenes and nanotubes.[10,11] The (3) Ca- and (4) Li-based sorbents are variations in the aromatic systems in (2) where, instead of involving a transition metal, the main group elements Ca and Li are used. These complexes have recently been suggested for H_2 storage[14–18] because of their weaker (or lack of) metal clustering tendency.[23] The Ca(TPA) and Li(TPA) can either be the H_2 sorbents by themselves or be part of a larger framework such as the Ca- or Li-decorated metal-organic frameworks.[16,18] Within the four systems, we considered ten atomic configurations to account for the different number of H_2, different H_2 positions and orientations as shown in Fig. 1.

In this work, the H_2 binding energy is defined as $E_b=[E(\text{sorbent})+n\times E(H_2)-E(nH_2@\text{sorbent})]/n$, where $E(\text{sorbent})$ is the total energy of the sorbent system without the adsorbed H_2, $E(H_2)$ is that of H_2 molecule in vacuum, and $E(nH_2@\text{sorbent})$ is that of the sorbent system with n adsorbed H_2.

III. HIGH-LEVEL CALCULATIONS

Here, we used the cc-*pVnZ* basis sets for all the elements except for Ca for which we found that the core-valence cc-*pwCVnZ* basis sets[40] is required for the desired accuracy of 0.01 eV/H_2. The index nZ=DZ, TZ, or QZ, which stands for double, triple, or quadruple ζ, respectively. Core orbitals (1*s* for C and O, 1*s*, 2*s*, 2*p* for Ca, Sc, and Ti) were frozen in the post-Hartree-Fock correlation calculations. To obtain accurate binding energies, we adopted the following procedure: (i) first, we fully optimized the atomic structures at the MP2 level of theory with the TZ basis set. (ii) Next, the energies of the relaxed structures from step (i) were refined at the MP2 level with the QZ basis set. (iii) Next, we used the results in (i) and (ii) to extrapolate to the results at the CBS limit using an established scheme,[24,25] where one calculates the Hartree-Fock energy $E_X^{\text{HF}}=E_{\text{CBS}}^{\text{HF}}+Ae^{-1.54X}$ and the correlation energy $E_X^{\text{cor}}=E_{\text{CBS}}^{\text{cor}}+BX^{-3}$ with either the TZ(X=3) or QZ(X=4) basis set. The values for $E_{\text{CBS}}^{\text{HF}}$ and $E_{\text{CBS}}^{\text{cor}}$ are obtained by extrapolating to $X=\infty$. (iv) Finally, we included the higher level correlation effects at the CCSD(T) level. We take the difference of the MP2 and CCSD(T) binding energies, usually termed ΔCCSD(T) obtained using the TZ basis set, and apply this ΔCCSD(T) to the CBS-MP2 results obtained in (iii). This approach has been widely used to obtain accurate binding energies in weakly interacting systems[26] for which the correlation contribution is especially important.

We used the MOLPRO program.[27] For the Li(TPA) complexes with odd number of electrons, however, spin-polarized calculation is required, which is beyond the reach of the MOLPRO program. In this case, we performed the TZ MP2 calculations plus the ΔCCSD(T) calculated with the DZ basis set using the GAUSSIAN03 program.[28] We have checked that, given the same basis set, the GAUSSIAN03 and MOLPRO programs give negligible difference in the calculated binding energy.

Table I lists the binding energies obtained at each step. The last column gives the most accurate CCSD(T)-corrected CBS-MP2 results (hereof termed “accurate”). We have estimated the errors in the “accurate” results, for example, by including diffuse Gaussian functions in the basis sets and by carrying out full CCSD(T) structural optimization[29] for the Ti(Et) complexes. We found that the errors are to within 0.01–0.02 eV/H_2.

IV. COMPARISON WITH DFT

We considered nine widely used exchange-correlation functionals, namely, LDA, PW91, PBE, BLYP, TPSS, B3LYP, B98, X3LYP, and M05–2X, where LDA is in its SVWN5 parameterization.[30] PW91,[31] PBE,[32] and BLYP (Refs. 33 and 34) are pure GGA functionals, TPSS is a meta-GGA functional,[35] B3LYP,[36] B98,[37] and X3LYP (Ref. 38) are hybrid GGA functionals, and M05–2X (Ref. 39) is a metahybrid GGA functional. Among the GGA functionals, the X3LYP and M05–2X were designed particularly for weakly bonded systems.

The first observation from our results is that LDA overestimates the binding energies significantly. For the Ti(Et),

TABLE I. H_2 binding energies (in eV) calculated at the MP2 and CCSD(T) level with different basis sets. Column 1 is obtained by MP2 with the TZ basis set. Column 2 is by MP2 with the QZ basis set. Column 3 is by CBS extrapolation (see text for details). Column 4 is by CCSD(T) with the TZ basis set. Column 5 is the difference between columns 4 and 1, except for Li for which the difference is obtained by using the DZ basis set. Column 6 is the sum of columns 3 and 5, except for Li for which the sum is between columns 1 and 5. All calculations use the structures optimized by MP2 with the TZ basis set.

	1 MP2 TZ	2 MP2 QZ	3 MP2 CBS	4 CCSD(T) TZ	5 ΔCCSD(T) =4−1	6 accurate =3+5
$TiH_2(Et)(H_2)^A$	0.37	0.40	0.42	0.32	−0.05	0.37
$TiH_2(Et)(H_2)^B$	0.29	0.31	0.33	0.21	−0.07	0.26
$TiH_2(Et)(H_2)_2$	0.39	0.41	0.43	0.32	−0.07	0.36
$TiH_2(Et)(H_2)_3$	0.43	0.45	0.47	0.33	−0.09	0.37
$ScH_2(Cp)(H_2)^A$	0.21	0.23	0.24	0.20	−0.01	0.23
$ScH_2(Cp)(H_2)^B$	0.19	0.20	0.21	0.18	−0.01	0.20
$ScH_2(Cp)(H_2)_2$	0.21	0.23	0.24	0.20	−0.01	0.23
$Ca(TPA)(H_2)_2^A$	0.25	0.25	0.26	0.24	−0.02	0.24
$Ca(TPA)(H_2)_2^B$	0.22	0.23	0.23	0.20	−0.02	0.21
$Li(TPA)(H_2)_2$	0.16				−0.00	0.16

Sc(Cp), Ca(TPA), and Li(TPA) systems, the overestimation (on average) is 0.53 eV/H_2 (160%), 0.37 eV/H_2 (150%), 0.24 eV/H_2 (120%), and 0.10 eV/H_2 (60%), respectively. Therefore, LDA should always be avoided in the modeling of H_2 sorbents.

Figure 2 compares the binding energies calculated from the eight GGA functionals with the accurate results. We see that the worst overall agreement is for BLYP with an average deviation from the accurate results by 0.15 eV/H_2 whereas the best agreement is for the most sophisticated M05–2X functional with an average deviation by only 0.01 eV/H_2. Even the BLYP error here appears to be smaller than that of the cohesive energy in strong chemical bond systems obtained by GGA, i.e., about 0.2 eV per atom.[1,2] This is understandable as the strength of the dihydrogen interaction is noticeably weaker.

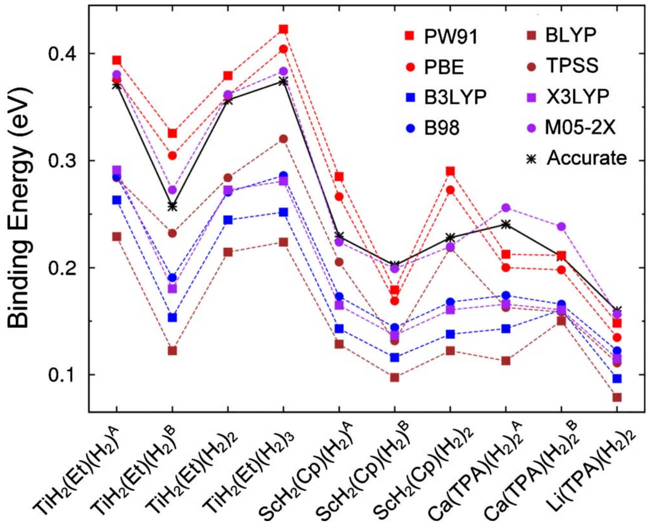

FIG. 2. (Color online) Calculated H_2 binding energies from eight different GGA functionals. They are compared with the results of an accurate calculation (see text for details).

For large-scale calculations, one would prefer the pure GGA functionals as the M05–2X hybrid functional involves Hartree-Fock-type calculations that are computationally too demanding (especially for periodic systems). Importantly, the PBE and PW91 functionals, which have already been widely used in the theoretical modeling of H_2 sorbents, also give an impressive agreement with the accurate results. The average deviations are only 0.03 and 0.04 eV/H_2 for PBE and PW91, respectively. These happen to be within the so-called *chemical accuracy*, i.e., 1 kcal/mol (or 0.043 eV/H_2) that quantum-chemistry methods usually target at.

V. SUMMARY

In summary, we have systematically studied dihydrogen binding on four representative metal centers that cover a wide range of previously proposed hydrogen sorbent materials by high-level quantum-chemistry MP2 and CCSD(T) calculations. By using these results as benchmark, we assessed the accuracy of nine DFT exchange-correlation functionals in calculating the dihydrogen binding energies. It is concluded that the previous predictions using either the PBE or the PW91 functional are valid even at the accurate quantum-chemistry level. On the other hand, previous results using the LDA functional overestimate the dihydrogen binding severely and are hence incorrect.

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