

## Inaccuracy of Density Functional Theory Calculations for Dihydrogen Binding Energetics onto Ca Cation Centers

Janghwan Cha,<sup>1</sup> Seokho Lim,<sup>1</sup> Cheol Ho Choi,<sup>2</sup> Moon-Hyun Cha,<sup>3</sup> and Noejung Park<sup>1,\*</sup>

<sup>1</sup>Department of Applied Physics, Dankook University, Yongin-si, 448-701, Korea

<sup>2</sup>Department of Chemistry, Kyungpook National University Taegu, 702-701, Korea

<sup>3</sup>Department of Physics and Astronomy, FPRD, and Center for Theoretical Physics, Seoul National University, Seoul 151-747, Korea

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We investigate the mechanism of dihydrogen adsorption onto Ca cation centers, which has been the significant focus of recent research for hydrogen storage. We particularly concentrate on reliability of commonly used density-functional theories, in comparison with correlated wave function theories. It is shown that, irrespective of the chosen exchange-correlation potentials, density-functional theories result in unphysical binding of H<sub>2</sub> molecules onto Ca<sup>1+</sup> system. This suggests that several previous publications could contain a serious overestimation of storage capacity at least in part of their results.

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One of the greatest challenges of scientific communities worldwide is a pollution-free and renewable energy source. Hydrogen storage with high enough volumetric and gravimetric density is particularly important as an energy carrier for a mobile system [1,2]. It has been discussed that, in order for the storage and discharge to be cycled near room temperature, hydrogen adsorbents need to have a binding affinity with the hydrogen molecule of a few tens of kJ/mol [3,4]. Through a very particular chemistry between the open *d* shell of metal atoms and H<sub>2</sub> molecular orbitals, an optimal strength of hydrogen adsorption can be achieved [5,6]. In order to realize such a chemistry in the form of a practical hydrogen storage system, numerous previous theory articles investigated nanostructures with dispersed transition metal (TM) atoms [3,7–9]. However, experimental trials to synthesize an open-TM-based hydrogen storage system have been unsuccessful for various reasons. The most prominent barrier is the strong tendency of aggregation of TM atoms which renders the suggested models of dispersed TMs rather hypothetical [10]. As an alternative, numerous research groups are now focused toward the alkaline-earth metals (AEMs) which have less tendency of aggregation and are believed to have similar binding affinity with dihydrogen adsorbates as TMs [11–15]. In particular, the systems of dispersed Ca atoms have been suggested as possessing the most salient properties.

In the series of computational searches for hydrogen storage materials, the density-functional theory (DFT) has been used most widely, mainly because of its practicality [16]. However, common implementations of DFT involve approximations in the exchange-correlation potential, and thus the accuracy of DFTs could not be perfectly trusted. In this regard, it is very pertinent to investigate the capability of common forms of DFT for hydrogen adsorption onto AEMs. We show that DFTs deviate significantly from the correlated wave function theories in the description of the dihydrogen adsorption onto the Ca<sup>1+</sup> system. We discuss that the valence configuration of the Ca cation

can be sharply switched between 4*s* and 3*d* upon hydrogen adsorption [17]. This sort of interaction is not widely noticed, and the reliability of DFTs for that is intriguing in the context of hydrogen storage as well as pure theory of electronic structure.

For computations, we used the GAUSSIAN 03 package (G03), NWCHEM package of version 5.1, and the Vienna *ab initio* simulation package (VASP) [18–21]. The DFT calculations were performed with the local density approximation (SVWN), the gradient-corrected approximation (BLYP), and the hybrid functional (B3LYP), as implemented in G03 and NWCHEM. In order to have a more accurate evaluation of binding energies, we carried out the correlated wave function theories with the Møller-Plesset second order perturbation (MP2) and the coupled clusters of singles, doubles, with perturbative triples corrections (CCSD(T)) [22]. Pople type Cartesian basis set and Dunning's correlation-consistent basis set are used, as implemented in those packages. The intermolecular binding energy is calculated with the counterpoise correction of the intermolecular and intramolecular basis set superposition errors (BSSEs) [25–27]. For a faster DFT calculation without BSSE, we used the plane-wave basis set with the projector-augmented-wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) version of gradient-corrected exchange-correlation functional, as implemented in the VASP.

In Fig. 1(a), we plot our results of MP2 calculations for the potential energy curve of the dihydrogen adsorption onto Ca<sup>1+</sup>. The distance between Ca and the center of H<sub>2</sub> is denoted by *Z* in the inset of Fig. 1(a). At each point of *Z*, the H-H distance is allowed to relax. It has been discussed that the MP2 result for the intermolecular binding energy increases with the basis set size [28]. The similarity between the results of three different basis sets, as shown in Fig. 1(a), shows that the MP2 result for this system is almost converged: calculations with a larger basis set may not deviate much from that shown in Fig. 1(a). The same

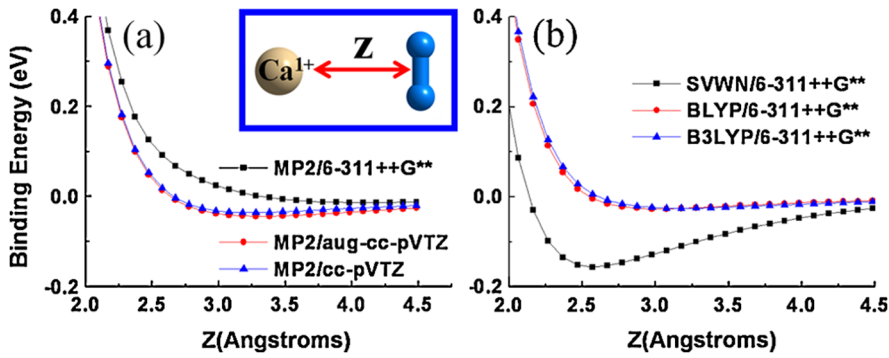


FIG. 1 (color online). The binding energy curve between  $\text{Ca}^{1+}$  and  $\text{H}_2$  calculated by (a) MP2 and (b) DFTs. The distance between Ca and the center of  $\text{H}_2$  is denoted by  $Z$ , as shown in the inset of (a). The employed basis sets and the exchange-correlation potentials are denoted in the picture. The red solid circles in (a) are calculated with the cc-pVTZ for Ca atom and the aug-cc-pVTZ for H atoms. Spin doublet is assumed throughout these calculations.

calculations were performed with the DFTs with three different forms of the exchange-correlation potentials: the local density approximation (SVWN), the gradient-corrected approximation (BLYP), and the hybrid functional (B3LYP), as shown in Fig. 1(b). We found that even though the difference in the binding energy between the local-density-approximated DFT and gradient-corrected ones are significant [29], the overall electronic structures are consistent throughout the computation method.

More striking problems arise in the cases of more  $\text{H}_2$  molecules adsorption. In Fig. 2(a), we placed four  $\text{H}_2$  molecules with the same distance, as denoted by  $Z$  in the figure, from the  $\text{Ca}^{1+}$  center. This system reflects features of hydrogen adsorption onto the Ca atoms dispersed over graphene [12]. In this calculation, all degrees of freedoms except the Ca- $\text{H}_2$  distances were allowed to relax [30]. As the four  $\text{H}_2$  molecules approach the  $\text{Ca}^{1+}$  center, they tend to remain in the plane, as depicted in Fig. 2(a). The BSSE-corrected binding energies are plotted in Fig. 2(b) along the Ca- $\text{H}_2$  distance ( $Z$ ). Figure 2(c) shows the same data as Fig. 2(b) in a narrower range of the Ca- $\text{H}_2$  distance and a narrower energy window. Figure 2(d) shows the variation

of the bond length of  $\text{H}_2$  molecules along the Ca- $\text{H}_2$  distance [30].

Regarding Fig. 2, we summarize three main findings and their implications as follows. First, binding energy curves show a hump at around  $Z = 2.7$  Å, as shown in Fig. 2(b). The bond lengths of  $\text{H}_2$  increase substantially as the four hydrogen molecules pass through the point of  $Z = 2.7$  Å, as shown in Fig. 2(d). When  $Z$  is smaller than 2.7 Å, the four  $\text{H}_2$  molecules constitute the Kubas complex with Ca's  $3d$  orbital, resulting in the increased H-H bond length [5]. Details will be explained in the next paragraph. Second, the adsorption geometry of the four  $\text{H}_2$  molecules are stable at around  $Z = 2.3$  Å. However, of particular notice is that the energetics of DFTs in Fig. 2(b) are very different from those of MP2 and CCSD(T). All DFT results show that the configuration of the four  $\text{H}_2$  adsorbates at around  $Z = 2.3$  Å is the global energy minimum. Meanwhile, the MP2 and CCSD(T) indicate that such a configuration is only locally stable, and the energy is higher than the fully detached four  $\text{H}_2$  molecules from the  $\text{Ca}^{1+}$  center. Even though the quantitative accuracy of DFTs may vary depending on the choice of the exchange-correlation poten-

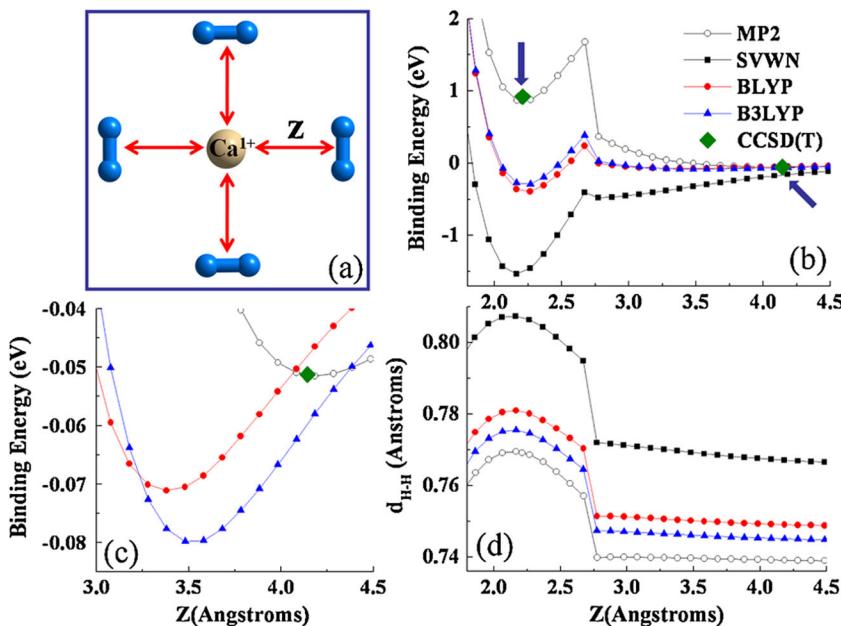


FIG. 2 (color online). (a) The geometry and reaction coordinate for the adsorption of four  $\text{H}_2$  molecules onto a  $\text{Ca}^{1+}$  cation center.  $Z$  denotes the distance between the Ca atom and the center of each  $\text{H}_2$  molecule. (b) The binding energy between the four  $\text{H}_2$  molecules and the  $\text{Ca}^{1+}$  calculated by the DFTs (SVWN, BLYP, B3LYP), MP2, and CCSD(T). (c) The same as (b) in a narrower window. (d) The bond length of  $\text{H}_2$  along the reaction path. The CCSD(T) results, indicated by arrows in (b), were calculated after the geometry optimization with the CCSD. The employed basis sets in these calculations is the 6-311++G\*\*.

tial and the character of the system to be studied [31,32], it has been believed that DFTs could provide a broadly correct physics. However, it is noteworthy that the DFT energetics shown in Fig. 2(b) are qualitatively different from the correlated wave function theories. Third, in the medium or long range interaction at around  $Z = 3.0\text{--}4.5 \text{ \AA}$ , as shown in Fig. 2(c), the DFT energetics show deeper potential wells, in contrast to the cases between two neutral molecules [33–35].

The configurations in which the four  $\text{H}_2$  molecules are closer to Ca than  $Z = 2.7 \text{ \AA}$  have characteristically different electronic structure than those with far separated  $\text{H}_2$  molecules: the electronic structure changes abruptly between  $A_{1g}$  and  $B_{2g}$  states, resulting in the discontinuous part of the potential energy surface near  $Z = 2.7 \text{ \AA}$  in Fig. 2(b) [36]. In Figs. 3(a) and 3(b), we plot the Hartree-Fock molecular orbitals at  $Z = 2.3 \text{ \AA}$  and  $Z = 3.6 \text{ \AA}$ , respectively. In the case of the isolated  $\text{Ca}^{1+}$  cation or that with far separated four  $\text{H}_2$  molecules, the singly occupied HOMO is mainly made up of the Ca's  $4s$  orbital, keeping the ground state symmetry of  $A_{1g}$ . With the adsorbed four  $\text{H}_2$  molecules when the Ca- $\text{H}_2$  distance is closer than  $Z = 2.7 \text{ \AA}$ , the Ca's  $3d_{xy}$  orbital constitutes the HOMO level, as shown in Fig. 3(a). We understand that the adsorbed four  $\text{H}_2$  molecules stabilize the Ca's  $3d_{xy}$  orbital with a trace of hybridization with the  $\text{H}_2$ 's  $\sigma^*$  orbitals. This hybridization forces the four  $\text{H}_2$  molecules to remain in the plane, preserving the  $B_{2g}$  symmetry of the wave function. This particular feature of electronic structures was also obtained with the three DFTs as well. The increased H-H bond length when  $Z$  is smaller than  $2.7 \text{ \AA}$ , as observed in Fig. 2(d), should naturally be ascribed

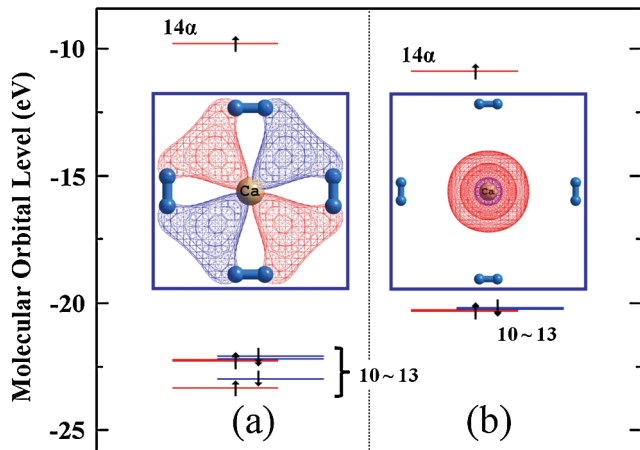


FIG. 3 (color). The Hartree-Fock molecular orbital levels at (a)  $Z = 2.3 \text{ \AA}$  and (b)  $Z = 3.6 \text{ \AA}$  of the system described in Fig. 2. A contour of the singly occupied HOMO, which is the  $14\alpha$  orbital, is depicted in the inset. The four doubly occupied orbitals, from the tenth to thirteenth, are derived from the  $\sigma$  level of four  $\text{H}_2$  molecules. The Kohn-Sham orbitals of DFTs have almost the same structures as the Hartree-Fock ones with only slight difference in the interlevel spacing (not shown).

to the formation of the Kubas complex between the downshifted  $3d_{xy}$  orbital of Ca and the four neighboring  $\text{H}_2$  molecules [5].

The results shown in previous paragraphs indicate that the energetics calculated by the approximated DFTs can be wrong for the interactions between  $\text{H}_2$  molecules and the  $\text{Ca}^{1+}$  system. This warning should also apply to previously published articles [11–15]. We investigated the Ca cation system with different charge states and found that the DFT results are particularly incorrect for the  $\text{Ca}^{1+}$  system. In this regard, we suggest that, if the Ca adatom on a surface appears to have a singly positive charge, the hydrogen binding energy onto the Ca adatom should be treated with care. For example, it was reported that the Ca atom on graphene is almost singly charged after the electron transfer from the Ca atom to graphene [12,13]. The DFT calculation showed that such a Ca atom traps four  $\text{H}_2$  molecules. Below we explicitly show that the commonly approximated DFTs should not be used for this type of system.

As shown in Fig. 4, we investigated the binding strength of four  $\text{H}_2$  molecules onto Ca that is adsorbed on a coronene molecule. We calculated the binding energy using the DFT with the PBE-type gradient-corrected functional and the plane wave basis set [20,21]. The binding energy and the binding distance show similar patterns as the results of BLYP and B3LYP for the case of the bare  $\text{Ca}^{1+}$  system, as shown in Fig. 2(b). Note that the adsorbed Ca atom on graphene also has the feature of  $\text{Ca}^{1+}$  ion [12,13]. We calculated the binding energy between the four  $\text{H}_2$  molecules and the Ca-coronene substrate using MP2 with the 6-311++G\*\* basis set. To calculate the binding energy, the total energy of the hydrogen adsorbed Ca-coronene system at fixed  $Z$  was subtracted by the total energy of the optimized Ca-coronene structure and that of four independent hydrogen molecules in the same supercell. The BSSE-corrected MP2 binding energy for the configuration shown in Fig. 4(a) was found to be  $0.80 \text{ eV}$ , which tells us that the geometry is unstable in comparison with the configuration with far detached four  $\text{H}_2$  molecules. Note that this result is consistent with the MP2 and CCSD(T) results for the case of the four  $\text{H}_2$  molecules onto the bare  $\text{Ca}^{1+}$ , as shown in

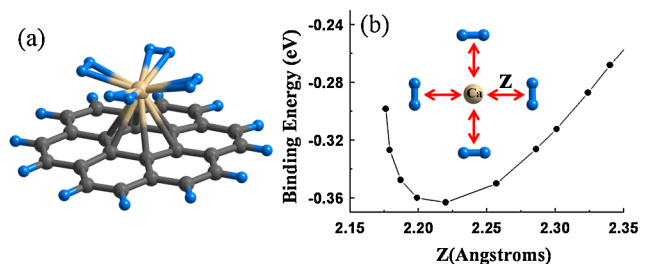


FIG. 4 (color online). (a) The optimized geometry of the four  $\text{H}_2$  molecules onto the Ca-adsorbed coronene. (b) The binding energy curve of the four  $\text{H}_2$  molecules along the distance between Ca- $\text{H}_2$ . The definition of the binding energy is given in text. Besides the Ca- $\text{H}_2$  distances, as denoted by  $Z$  in the inset of (b), all other degrees of freedoms are allowed to relax.



Fig. 2(b). Here, we emphasize again that the aforementioned fallacy of the approximated DFTs for the interaction between  $\text{Ca}^{1+}$  and  $\text{H}_2$  molecules applies not only to the gas-phase  $\text{Ca}^{1+}$  but also to the Ca-dispersed nanostructures, which have been common targets in previous research.

In conclusion, we investigated the hydrogen molecular adsorption onto Ca cation centers, using DFTs and higher correlated wave function theories: MP2 and CCSD(T). We found that the results calculated with DFTs for hydrogen adsorption geometry and binding energy are not consistent with the MP2 and CCSD(T) for the  $\text{Ca}^{1+}$  system. While the geometry of the four  $\text{H}_2$  molecules adsorbed onto  $\text{Ca}^{1+}$  is only locally stable and energetically unstable in the MP2 and CCSD(T) results, all DFTs report that the adsorption geometry of the four  $\text{H}_2$  molecules is the global energy minimum. We also showed that this inconsistency exists not only in the case of the bare  $\text{Ca}^{1+}$  system but also in the Ca-adsorbed nanostructures which were previously suggested as a potential hydrogen storage system. These indicate that previous suggestions for the Ca-based hydrogen storage system should be reinvestigated with particular care about the charge state of Ca.

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\*Corresponding author: noejung@dku.edu

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- [35] An independent in-depth study is necessary for DFT functionals in the long range interaction between molecules with monopole. However, the main focus of the present letter should be on the short range interaction, as depicted in Figs. 2(b), 3, and 4.
- [36] Since there is a sharp transition of the HOMO from the 4s to the  $3d_{xy}$  orbital, the full range of the binding energy diagram can only be properly described by multireference calculations. We performed the complete active space self-consistent field (CASSCF) calculations of full valence space. Except for the transition region near  $Z = 2.7 \text{ \AA}$ , the CASSCF showed consistent energetics as the single reference MP2 and CCSD(T). However, since either the adsorption or desorption path of the four  $\text{H}_2$  molecules does not necessarily follow the constraint of the  $D_{4h}$ , the emphasis should be given to the energetics of equilibrium points rather than the transition region.