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Abstract

We have computed the energies of adsorption of molecular hydrogen on a number of molecular linkers in metal–organic framework solid materials using density functional theory (DFT) and *ab initio* molecular orbital methods. We find that the hybrid B3LYP (Becke three-parameter Lee–Yang–Parr) DFT method gives a qualitatively incorrect prediction of the hydrogen binding with benzenoid molecular linkers. Both local-density approximation (LDA) and generalized gradient approximation (GGA) DFT methods are inaccurate in predicting the values of hydrogen binding energies, but can give a qualitatively correct prediction of the hydrogen binding. When compared to the more accurate binding-energy results based on the *ab initio* Møller–Plesset second-order perturbation (MP2) method, the LDA results may be viewed as an upper limit while the GGA results may be viewed as a lower limit. Since the MP2 calculation is impractical for realistic metal–organic framework systems, the combined LDA and GGA calculations provide a cost-effective way to assess the hydrogen binding capability of these systems.

Exploration of new hydrogen storage materials with high hydrogen uptake at ambient temperature is crucial for developing the hydrogen economy. The US Department of Energy (DOE) has set a hydrogen storage gravimetric capacity of 6.0 wt% and volumetric density of 45 kg m^{-3} for on-board vehicles as the targets for the year 2010, and 9.0 wt% and 81 kg m^{-3} as the targets for 2015 (US DOE 2004). Although a number of metal hydrides such as $NaAlH_4$ and $LiBH_4$ can meet the 6.0 wt% gravimetric capacity target, their relatively high stabilities require elevated temperature and pressure for re-forming the materials and releasing the hydrogen (Lee *et al.* 2005, Schlapbach and Züttel 2005). Recently, a new class of metal–organic framework solid materials has attracted considerable attention due to their relatively high hydrogen uptake at 77 K (Eddaoudi *et al.* 2002). For example,

isoreticular metal–organic framework-1 (IRMOF-1) can store 1.3 wt% hydrogen and iso-reticular metal–organic framework-11 (IRMOF-11) can store 1.6 wt% hydrogen at 77 K (Rowsell *et al.* 2004). At room temperature and pressure of 10 bar, hydrogen uptake of 2 wt% has been observed for isoreticular metal–organic framework-8 (IRMOF-8) (Rosi *et al.* 2003). It has also been reported that metal–organic framework-5 (MOF-5) can adsorb up to 4.5 wt% hydrogen at 78 K but only 1 wt% at room temperature and 20 bar. A recent experiment demonstrates that the adsorption of hydrogen in MOF-177 and IRMOF-20 saturates between 70 and 80 bar; within these, H_2 uptakes can be as high as 7.5 and 6.7 wt% at 77 K, respectively (Wong-Foy *et al.* 2006). Meanwhile, Dincă *et al.* (2006) reported a new metal–organic framework material with previously unknown cubic topology and with exposed Mn^{2+} coordination sites. This new metal–organic framework material gives rise to an H_2 uptake of 6.9 wt% at 77 K and 90 bar.

Despite these advances, the DOE's 2010 targets are still not met with the existing metal–organic framework materials at room temperature. It has been recognized that one possible way to enhance H_2 uptake at room temperature is to design new metal–organic framework materials that can adsorb hydrogen molecules with adsorption energies in the range of 0.15–0.25 eV or 15–25 kJ mol^{-1} (Bhatia and Myers 2006, Kim *et al.* 2006). Several *ab initio* calculations have been reported for studying the adsorption interactions between molecular hydrogen and subunits in metal–organic framework materials. Hübner *et al.* (2004) applied the RIMP2/TZVPP method to calculate the energies of binding between a hydrogen molecule and the various substituted benzenes, C_6H_6, C_6H_5F, C_6H_5OH, $C_6H_5NH_2$, $C_6H_5CH_3$ and C_6H_5CN. These substituted benzenes were treated as simplified subunits for linkers in metal– organic framework systems. The authors found that the $H_2 \cdots C_6H_5NH_2$ interaction was the strongest, with a binding energy of 4.5 kJ mol^{-1} (Hübner *et al.* 2004). Sagara *et al.* (2004) carried out MP2 calculations to evaluate the energies of binding between a hydrogen molecule and metal–oxide cluster or Li-terminated 1,4-benzenedicarboxylate (BDC). The hydrogen binding energies were estimated to be 6.9 and 5.4 kJ mol^{-1}, respectively. Moreover, the energies of hydrogen binding with isoreticular metal–organic framework (IRMOF) materials were estimated to be in the range of 4.2–5.5 kJ mol^{-1}, based on the RIMP2/QZVPP level of theory and basis sets (Sagara *et al.* 2004). Later, Sagara *et al.* (2005) found that MOF1-4NH$_2$ gave the highest hydrogen binding energy among the isoreticular metal–organic frameworks studied (including IRMOF-1, IRMOF-3, IRMOF-1-4NH$_2$, IRMOF-6, IRMOF-8, IRMOF-12, IRMOF-14, IRMOF-18 and IRMOF-993) and its binding energy was appreciably larger (>10%) than that of the polybenzoid structures, such as IRMOF-993 and IFMOF-14. Lochan and Head-Gordon (2006) calculated the energies of binding between the substituted benzenedicarboxylate groups and a hydrogen molecule to be 3–5 kJ mol^{-1}, by using the basis set superposition error (BSSE) corrected RIMP2/CBS//MP2/6-31G* method. Yang and Zhong (2006a) performed a combined grand canonical Monte Carlo simulation and density functional theory calculation of hydrogen adsorption in metal–organic framework systems with open metal sites. In another paper, Yang and Zhong (2006b) performed a molecular simulation of adsorption of carbon dioxide/methane/hydrogen mixture in metal–organic framework material. Despite these advances, much more theoretical effort is needed to accurately compute the hydrogen binding energies for the increasingly large number of metal–organic framework materials. A major obstacle for theoretical study of hydrogen adsorption in realistic metal–organic framework materials is that high level *ab initio* methods are computationally very expensive and even impractical. A cost-effective computational strategy is needed to assess the hydrogen binding capability of metal–organic framework materials.

Density functional theory (DFT) has been widely used to study interactions of molecules with surfaces (Alfè and Gillan 2006). However, DFT with conventional approxima-
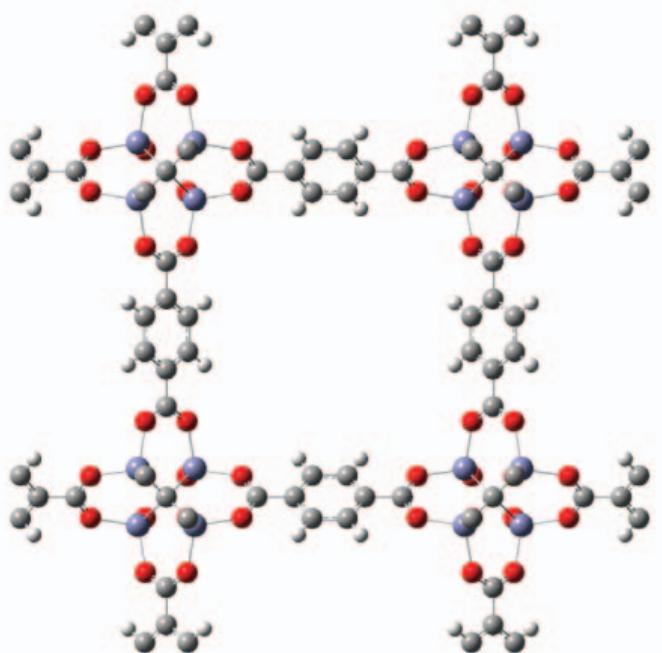
Figure 1. The unit cell of a prototype metal–organic framework (MOF-5) solid, which contains four molecular linkers. Grey: carbon atom; red (or dark): oxygen atom; white: hydrogen atom; blue (or gray spheres): zinc atom.

tions is known to be problematic for describing weak physisorption interactions largely because the dispersion forces and the van der Waals interactions are not properly accounted for. Development of DFT to properly treat weak interactions has been an active research area in the past ten years (Andersson *et al.* 1996, Kohn *et al.* 1998, Elstner *et al.* 2001, Rydberg *et al.* 2003, Lin *et al.* 2005). Jhi *et al.* (2000) performed DFT calculations within the local-density approximation (LDA) to study oxygen molecules binding with carbon nanotubes. Dag *et al.* (2003) applied the DFT method within the generalized gradient approximation (GGA) to investigate molecular and atomic oxygen adsorption on single-wall carbon nanotubes. Giannozzi *et al.* (2003) also studied oxygen adsorptions on carbon graphite and nanotubes using DFT methods. These DFT studies show that the LDA method generally gives notably higher binding energies than the GGA method (Dag *et al.* 2003). Similar conclusions have been drawn for hydrogen adsorption on graphene layers (Okamoto and Miyamoto 2001, Cabria *et al.* 2005). Agrawal *et al.* (2006) performed both LDA and GGA calculations to study CH_4 molecules binding with carbon nanotubes and nanoropes. They found that the LDA method overestimates the CH_4 binding with the carbon nanotubes while the GGA method underestimates the binding.

The purpose of this paper is to examine the accuracy of three popular DFT methods for calculating the hydrogen binding with molecular linkers in metal–organic framework materials. Figure 1 shows the unit cell of a prototype metal–organic framework system (MOF5) which contains four molecular linkers. We employed the LDA with the Vosko–Wilk–Nusair functional (Vosko *et al.* 1980), the GGA with the Perdew–Burke–Ernzerhof (PBE) functional (Perdew *et al.* 1996, 1997), as well as the Becke three-parameter Lee–Yang–Parr (B3LYP) hybrid functional (Becke 1988, Lee *et al.* 1988). These DFT methods were used to optimize geometric structures of metal-terminated (Li, Cu, Zn) benzenedicarboxylate (BDC) molecular linkers, with and without an adsorbed hydrogen molecule. To calculate the hydrogen binding energies, we considered that the hydrogen mole-
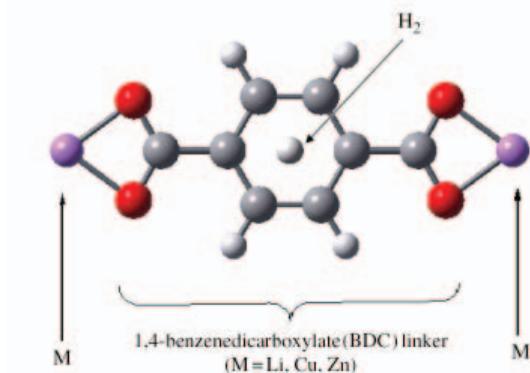
Figure 2. Hydrogen molecule binding with the M–BDC–M (M =Li, Cu, Zn) molecular linkers in a perpendicular orientation. Grey: carbon atom; red (or dark): oxygen atom; white: hydrogen atom; pink (or smaller gray spheres): metal atom.

cule was in a perpendicular orientation to the BDC plane, as shown in figure 2. Note that we did not consider hydrogen adsorption on the metal atom because our model for the metal site is highly simplified; the surrounding environment is very different to that in real metal–organic framework systems. Here, the different metal atoms were selected for the purpose of testing the metal effects on the interaction of hydrogen molecules with the benzenoid linkers. In addition to the DFT calculations, we also performed geometry optimization and calculation of hydrogen binding energies using the Møller–Plesset second-order perturbation (MP2) method, and we set the convergence threshold to be 10^{-6} Hartree. In general, the hydrogen binding energies were evaluated with the formula $\Delta E_{binding} = E(H_2 + MOF) - E(H_2) - E(MOF)$ where all the electronic energies were corrected using the full counterpoise procedure to account for the basis-set superposition error (BSSE) (Boys and Bernardi 1970). The BSSE corrections were undertaken for DFT and MP2 optimized structures, respectively. In both DFT and MP2 calculations, Dunning's correlation consistent triple-zeta basis sets (cc-pVTZ and aug-cc-pVTZ) (Woon and Dunning 1993, Kendall *et al.* 1992) were applied for the elements C, O, H and Li, while the effective-core pseudopotentials of the Stuttgart/Dresden basis sets (Stoll *et al.* 1984) were applied for Cu and Zn. All calculations were performed with the Gaussian 03 software package (Frisch *et al.* 2004).

To confirm that the perpendicular orientation of the hydrogen molecule was the most stable configuration when binding with the Li-terminated BDC molecular linker, we used the highest level of theory considered in this work, namely, MP2/aug-cc-pVTZ//MP2/cc-pVTZ. We examined eight possible adsorption configurations for the hydrogen molecule, as shown in figure 3. It is found that the perpendicular orientation is 1.71 kJ mol^{-1} lower in binding energy than the parallel orientation. The parallel orientation gives the second lowest binding energy.

The calculated energies of binding between a hydrogen molecule and the metal-terminated benzenedicarboxylate, based on three DFT and the MP2 methods, are all collected in table 1. It can be seen that the hydrogen binding energies calculated using the diffusive aug-ccpVTZ basis sets are lower than those obtained using the cc-pVTZ basis sets. First, the MP2/cc-pVTZ results are between -3.80 and -4.01 kJ mol^{-1}, while the MP2/aug-cc-pVTZ results are between -4.85 and -5.10 kJ mol^{-1}. The former values are very close to those obtained in previous theoretical studies of hydrogen binding with the benzenoid systems (Hübner *et al.*, $H_2 \cdots C_6H_6$, MP2/TVZPP: 3.91 kJ mol^{-1}; Lochan and
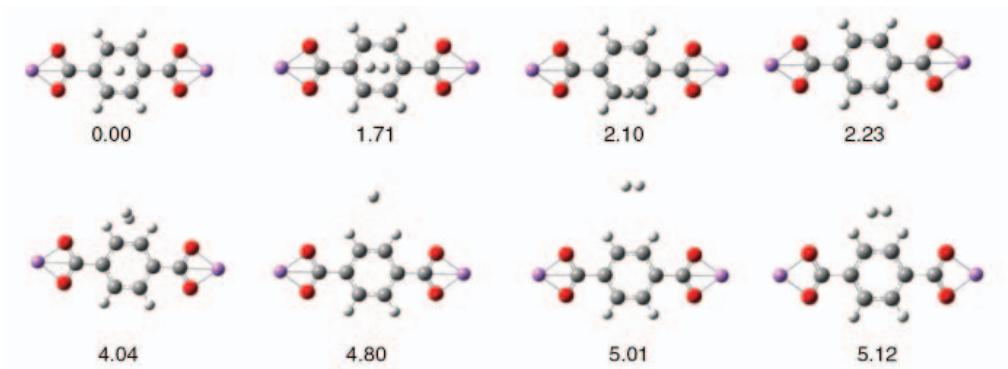
Figure 3. Relative electronic energies (kJ mol^{-1}) among eight H$_2$ adsorption configurations with the BDC–Li$_2$ molecular linker. The electronic energies were calculated at the MP2/aug-cc-pVTZ level and based on the MP2/cc-pVTZ optimized geometries. Grey: carbon atom; red (or dark): oxygen atom; white: hydrogen atom; pink (or smaller gray spheres): lithium atom.

Table 1. The calculated energies of binding (kJ mol^{-1}) between a hydrogen molecule and M– BDC–M (M = Li, Cu, Zn) linkers in metal–organic framework systems, using three DFT (LDA– VWN, GGA–PBE) and the MP2 methods together with the cc-pVTZ or aug-cc-pVTZ basis sets, respectively, for geometry optimization (with the exception of the MP2/aug-cc-pVTZ calculation for which the geometries are based on the MP2/cc-pVTZ optimization). The H$_2$ binding distances (Å) to the benzenoid surface are shown in parentheses.

	Li	Cu	Zn
LDA–VWN/cc-pVTZ	−9.74 (2.36)	−9.07 (2.40)	−8.82 (2.38)
GGA–PBE/cc-pVTZ	−1.71 (3.03)	−1.38 (3.16)	−1.25 (3.08)
MP2/cc-pVTZ	−4.01 (2.66)	−3.80 (2.67)	−3.93 (2.68)
LDA–VWN/aug-cc-pVTZ	−9.95 (2.35)	−9.24 (2.36)	−8.99 (2.37)
GGA–PBE/aug-cc-pVTZ	−1.79 (2.68)	−1.36 (2.67)	−1.34 (2.83)
MP2/aug-cc-pVTZ//MP2/cc-pVTZ	−5.10	−4.85	−5.06

Head-Gordon, H$_2$ ⋯ BDC, RIMP2/CBS//MP2/6-31G*: 4.029 kJ mol^{-1}). Our MP2 calculations indicate that large diffusive basis sets are necessary to accurately determine the physisorption energies of hydrogen with metal-terminated benzenedicarboxylate. Second, while the LDA–VWN, GGA–PBE and MP2 calculations all show that the hydrogen molecule can bind to the metal-terminated benzenedicarboxylate, the hybrid B3LYP method predicts otherwise, that is that it is energetically unfavorable for the hydrogen molecule to bind with substituted benzenedicarboxylate. As shown in figure 4, the binding energies calculated on the basis of B3LYP are positive, and decrease monotonically; no energy minimum is seen. This suggests that hybrid DFT methods may be problematic for assessing weak physisorption interaction. Third, the GGA–PBE predicts notably larger binding distance between the hydrogen molecule and the benzenoid surface than LDA–VWN or MP2. Meanwhile, the LDA–VWN method consistently gives notably higher hydrogen binding energies compared to the more accurate MP2 method, while the GGA–PBE method consistently gives lower hydrogen binding energies. This situation reflects the difficulty of using current DFT functionals to deal with the dispersion forces. The dispersion forces do not simply come from the charge overlap, which can be well accounted for by the local or semi-local DFT approximations, but from charge fluctuations, which go beyond the conventional DFT method.
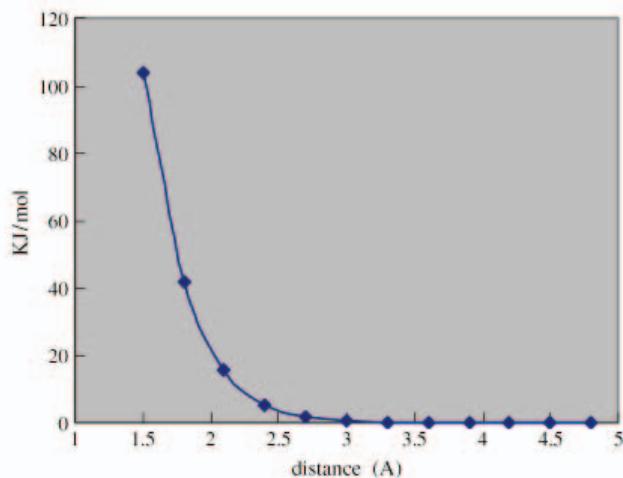
Figure 4. Calculated energy of binding between the H_2 and Li–BDC–Li versus the distance between H_2 and the plane of Li–BDC–Li, using the B3LYP/cc-pVTZ level of theory.

It is known that the LDA tends to underestimate the bonding distance and overestimate the binding energy while the GGA tends to strongly underestimate the binding energy, or yield no bonding at all. Physical insights into the difference in predicted binding energies between the GGA and LDA can be understood on the basis of an electron gas with a uniform positive background (the jellium model, which is a prototype model system for evaluating effects of electron correlation). A homogeneous electron gas system can be completely specified by its density n, or the parameter r_s defined by $4\pi r_s^3/3 = 1/n$ with r_s in atomic units. It can be viewed that r_s characterizes the mean distance between electrons. Typical r_s values for elemental solids are in the range of 1–3. For example, $r_s = 3.23$ for Li and 1.31 for C (Kittel 1996). Compared to the LDA, the GGA involves additional contributions to the exchange–correlation energy, which are dependent on the gradient of the electron density $|\nabla r_s|$. Letting the exchange enhancement factor $F_x^{LDA} = 1$, it has been shown that $F_x^{GGA} = 1 + (^5/_{162})(^3/_{2\pi^3})^{^2/_3} |\nabla r_s|^2/r_s^2 +$ [higher gradient terms] (Svendsen and von Barth 1996). Thus $F_x^{GGA} \geq F_x^{LDA} = 1$. In other words, the GGA always gives rise to lower exchange energy than the LDA. The larger the density gradient is, the lower the exchange energy the GGA predicts as compared to the LDA prediction. This difference in predicted exchange energy occurs particularly in places where a molecule binds to a solid. In this case, the GGA generally leads to greater lowering of the exchange energy than in solids. Hence, the GGA tends to predict underbinding whereas the LDA tends to predict overbinding. Indeed, our GGA and LDA results are consistent with the known trends. This is also why the more accurate MP2 results are in the range between the LDA and GGA results.

In summary, three DFT and the *ab initio* MP2 methods were employed to study the hydrogen adsorption on metal-terminated benzenedicarboxylate (as linkers in metal–organic framework systems). It is found that the hybrid B3LYP method predicts qualitatively incorrect hydrogen binding energies. The LDA–VWN method tends to overestimate the hydrogen binding energies while the GGA–PBE method tends to underestimate the binding energies. The MP2 method is expected to give much more accurate binding energies than the DFT methods. Importantly, the MP2 binding energy results are consistently in between the LDA–VWN and GGA–PBE results. In other words, the LDA–VWN results may be viewed as an upper limit while the GGA–PBE results may be viewed as a

lower limit for the hydrogen binding energies. Because the LDA–VWN and GGA–PBE calculations require much less computational cost compared to the MP2 calculations, one could estimate the hydrogen binding energies in realistic metal–organic framework systems on the basis of combined LDA–VWN and GGA–PBE calculations. Our result also indicates that the hydrogen energy of binding with the Li-terminated benzenedicarboxylate is larger than that with Cu- or Zn-terminated benzenedicarboxylate. This result indicates the importance of changing metal sites for the design of new metal–organic framework materials with stronger hydrogen binding.

In closing, we can remark that the combined LDA–VWN and GGA–PBE calculations can provide a cost-effective way to assess the interaction between hydrogen molecules (adsorbent) and metal–organic frameworks (adsorbate) and thus offer a guide to experimental design of new metal–organic framework materials, with the ultimate goal of meeting the DOE's hydrogen storage targets.

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