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Quantum Monte Carlo Simulation of Nanoscale MgH_2 Cluster Thermodynamics

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One of the greatest challenges in realizing a hydrogen economy lies in storing hydrogen in a compact and lightweight form. This is particularly true for the automobile industry, where storage under high pressure or in the liquid phase poses serious hazards. A promising alternative approach is chemical storage, in which hydrogen is reversibly bound to another material. Light-metal hydrides, such as MgH_2, AlH_3, and $LiBH_4$, are among the most attractive storage materials,[1] but they are either too stable or too unstable, leading to too high or too low desorption temperatures T_d [at which pressure $p(H_2) = 1$ bar]. For example, the desorption energy (ΔE_d) of MgH_2 is 75 kJ mol^{-1} ($T_d \approx 300$ °C),[3] while ΔE_d of 20−50 kJ mol^{-1} ($T_d \approx 20-100$ °C) is desirable.

Recent theoretical[4] and experimental[5,6] work suggests that H_2 desorption thermodynamics can be tuned by decreasing the particle size to the nanoscale, due to different destabilization energies associated with metal clusters and their metal−hydride counterparts. This effect is predicted to be significant only in very small clusters, e.g., MgH_2 crystallite sizes of less than 1.0 nm.[4] However, there is evidence that colloidal MgH_2 particles as large as 5 nm are destabilized.[5] Thus, there is a critical need for *accurate* calculations to verify these findings and determine the nanoparticle size with the most desirable T_d.

By far the most widely used method for investigating H-storage materials is single-particle density functional theory (DFT), but it is challenging for DFT to predict ΔE_d with chemical accuracy (~4 kJ mol^{-1}) due to the approximate exchange-correlation (XC) energy. Numerous XC functionals, including the local density approximation (LDA), generalized-gradient approximations (GGAs), hybrid GGAs, and meta-GGAs, are currently in use, and their accuracy in predicting ΔE_d is yet to be determined for metal nanoclusters. Wide discrepancies between these approaches for other materials and properties have been reported. On the other hand, many-body quantum chemistry methods (e.g., coupled cluster: CC) can provide the most accurate results for small molecules, but their computational scaling (N^{5-7}_{el}; N_{el} = number of electrons) severely limits application to larger systems.

The quantum Monte Carlo (QMC) method solves the full many-body Shrödinger equation stochastically, scales as N^3_{el}, and provides chemical accuracy for broad classes of materials and properties. Therefore, QMC can provide both quantitative descriptions and much-needed benchmarks for nanoparticle simulations. Indeed, our QMC results reported here show that *none* of the XC functionals examined maintains the desired accuracy across the thermodynamically tunable range for MgH_2. Moreover, the DFT error depends strongly on cluster size.

Our QMC simulations are performed using the fixed-node diffusion Monte Carlo[7] (DMC) method with the QWalk code.[8] The antisymmetric fermionic nodes are determined by Slater−Jastrow trial wave functions, and DFT-GGA single-particle orbitals are used for constructing the Slater determinant. The DMC time step is 0.01 au. Our LDA and PBE[9]-GGA DFT calculations are carried out using the SIESTA code[10] with triple-ζ polarization atomic-orbital basis sets, while other DFT calculations with GGAs (PW91,[11] OLYP[12]), hybrid GGAs (PBE0,[13] B3LYP[14]), and meta-GGA (M06[15]) functionals are carried out using the GAMESS program[16] with cc-pVTZ basis sets.[17] Our CCSD(T) calculations are also performed with the GAMESS program, using up to the cc-pV5Z basis sets to obtain well converged results. To evaluate ΔE_d, the zero-point vibrational energy (ZPE)[4,18] is added to the electronic ground-state energy (E_{el}): $\Delta E_d = E(H_2) + [E(Mg_N) - E(Mg_NH_{2N})]/N$, where $E = E_{el} + \text{ZPE}$ and N is the number of Mg atoms in clusters.

Figure 1 shows that ΔE_d varies strongly with size for small clusters ($N < 20$) and converges to the bulk value for $N > 20$. Qualitatively, DFT with all of these functionals agrees with DMC, in that ΔE_d of MgH_2 clusters is even *larger* than that of the bulk, except for very small clusters with $N < 6$. Yet quantitatively, none of these functionals agrees with the DMC results within chemical accuracy across the entire range of cluster sizes.

Because of the very small energy scales under consideration, we validated the accuracy of our DMC results in three separate ways: (1) comparing with CCSD(T) results for the smallest two clusters with $N = 1$ and 2 (ΔE_d differs only by ~1−2 kJ mol^{-1}); (2) comparing with experimental data for the bulk (ΔE_d differs by ~2−3 kJ mol^{-1}); and (3) showing that the fixed-node approximation used in DMC causes a negligible variation of less than 1 kJ mol^{-1} (see details in the Supporting Information) for ΔE_d, using trial wave functions constructed from DFT with various XC functionals. Compared with DMC, the DFT errors for ΔE_d can be as large as 20−50 kJ mol^{-1} for some XC functionals, of the same order of magnitude of the tunability of ΔE_d in MgH_2 clusters, or within the required range of ΔE_d for hydrogen storage.

Furthermore, our calculations show that the magnitude of this DFT error varies with cluster size, and the variation is particularly significant for clusters with $N < 11$, the most interesting region where ΔE_d increases with N (Figure 1). In general, the magnitude of the error increases with N, except for M06 (decreases with N) and LDA (increases with N up to $N \approx 20$ and then decreases). The PBE, PBE0, PW91, and OLYP functionals have similar trends of errors in that their magnitudes increase dramatically with N until ΔE_d peaks, while the error of B3LYP barely changes for $N < 15$

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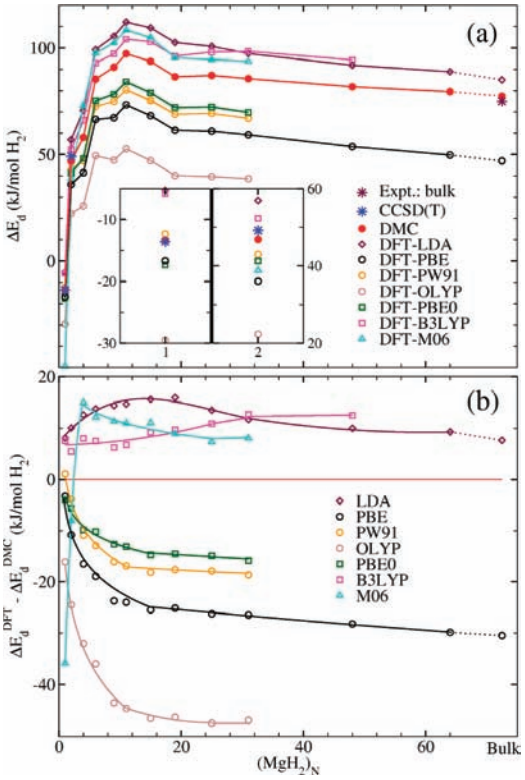

Figure 1. (a) Calculated desorption energy ΔE_d (kJ/mol H_2) of MgH_2 clusters as functions of the size with the DMC, DFT, and CCSD(T) methods. The XC approximations used in DFT include LDA, GGAs (PBE, PW91, and OLYP), hybrid GGAs (PBE0 and B3LYP), and meta-GGAs (M06). The statistical errors (not shown) of DMC results are less than 0.5 kJ/mol. The inset zooms in the small-cluster region. (b) Differences of ΔE_d calculated between the DFT and the DMC methods. Here the symbols are data, while the solid lines are the guide to the eye.

and then increases slightly until $N \approx 31$. These size-dependent, nonsystematic errors raise concerns regarding the ability of DFT to accurately predict ΔE_d, and it is clear that no single correction can be applied uniformly for clusters with different sizes.

This error dependence on size for ΔE_d is mainly due to the fact that DFT relies heavily on error cancellation to predict the correct E_{el}, and this cancellation cannot be applied equally for different clusters. For example, as summarized in Table 1, both LDA and PBE predict rather inaccurate cohesive energies E_{coh} for bulk Mg and MgH_2, with errors > 0.5 eV for MgH_2, whereas the errors of ΔE_d are 0.10 and 0.29 eV, respectively. Although PBE significantly improves E_{coh} (Mg) over LDA, it predicts ΔE_d much less accurately than LDA simply because of a smaller error cancellation. Furthermore, for a given XC functional, DFT has similar errors for similar systems. Consequently, the errors for the molecule-like small Mg and MgH_2 clusters are closer to that for the H_2 molecule than large clusters, so that the error cancellation is expected to be better for small clusters than for large ones. As a result, the error of ΔE_d increases with the cluster size, as seen in Figure 1 for most of the XC functionals considered.

Comparing these XC approximations, we find that, in general, hybrid GGAs (PBE0 and B3LYP) are more accurate than standard GGAs (PBE, PW91, and OLYP), while the meta-GGA functional (M06) has mixed performance across the cluster sizes. We are now extending QMC to other metals and metal hydrides to determine how broadly applicable these conclusions based on MgH_2 are. Nevertheless, these results strongly suggest that when modeling nanoscale effects on metal hydrides it is crucial to apply highly accurate methods to benchmark DFT; DMC can be an important standard in this role.

Table 1. Calculated Cohesive Energies (E_{coh}) of Bulk Mg and MgH_2, the Binding Energy (E_b) of the H_2 Molecule, and the Desorption Energy (ΔE_d) using DFT (LDA, PBE) and DMC Methods, Compared with Experimental Data[a]

	LDA	PBE	DMC	Expt
E_{coh} (MgH_2)	7.294	6.214	6.808 (4)	6.77[a]
E_{coh} (Mg)	1.761	1.459	1.516 (3)	1.51[b]
E_b (H_2)	4.649	4.264	4.489 (1)	4.48[c]
ΔH_d	0.884	0.491	0.803 (5)	0.78[a]

[a] Reference 2. [b] Reference 19. [c] Reference 20. [a] Energies are in units of eV. Note that $E_d = E_{coh}(MgH_2) - E_{coh}(Mg) - E_b(H_2)$.

A second, more preliminary, conclusion is that cluster size alone is insufficient to explain experimentally observed nanoscale effects in metal hydrides. While QMC predicts MgH_2 destabilization only for subnanometer particles, accelerated H_2 desorption kinetics are reported for MgH_2,[5] $NaAlH_4$,[6] $LiBH_4$,[21] and NH_3BH_3[22] particles as large as 5 nm on various supports. This suggests that the specific chemical environment of the nanoparticle plays an important role in destabilization, a factor that should be addressed in future modeling of these systems.

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Supporting Information Available: DMC results of ΔE_d for the smallest MgH_2 cluster using various Slater determinants, and desorption energy data and cluster geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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