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Structural properties and enthalpy of formation of magnesium hydride from quantum Monte Carlo calculations

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We have used diffusion Monte Carlo (DMC) calculations to study the structural properties of magnesium hydride (MgH_2), including the pressure-volume equation of state, the cohesive energy, and the enthalpy of formation from magnesium bulk and hydrogen gas. The calculations employ pseudopotentials and B-spline basis sets to expand the single particle orbitals used to construct the trial wave functions. Extensive tests on system size, time step, and other sources of errors, performed on periodically repeated systems of up to 1050 atoms, show that all these errors together can be reduced to below 10 meV/f.u.. We find excellent agreement with the experiments for the equilibrium volume of both the Mg and the MgH_2 crystals. The cohesive energy of the Mg crystal is found to be 1.51(1) eV and agrees perfectly with the experimental value of 1.51 eV. The enthalpy of formation of MgH_2 from Mg bulk and H_2 gas is found to be 0.85 ± 0.01 eV/f.u., or 82 ± 1 kJ/mole, which is off the experimental one of 76.1 ± 1 kJ/mole only by 6 kJ/mole. This shows that DMC can almost achieve chemical accuracy (1 kcal/mole) on this system. Density functional theory errors are shown to be much larger and depend strongly on the functional employed.

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I. INTRODUCTION

The energetics of metal hydrides has recently become an issue of large scientific and technological interest, mainly because of the revived interest in these materials as potential hydrogen storage media.[1] Magnesium hydride (MgH_2) is a particularly interesting material, as it can store up to 7.6% of hydrogen by weight, which is believed to be a large enough quantity for mobile applications, provided that all the hydrogen in the material can be made available when requested, of course. When heated above ~300 °C,[2] MgH_2 decomposes into Mg bulk and H_2 gas, the reaction being endothermic with an enthalpy of decomposition of 76 kJ/mole.[3] Conversely, MgH_2 can be synthesized by combining Mg bulk (usually in form of a powder of micrometer sized grains) and H_2 gas. The charging process can take many hours because of a large energy barrier to dissociate the H_2 molecule on the surface of magnesium.[4] As it stands, MgH_2 is not considered to be useful for hydrogen storage purposes because of the high decomposition temperature (ideal decomposition temperature should be in the range 20–100 °C) and the slow kinetics of hydrogen intake. A number of attempts are being made to modify this material to improve its properties, including doping it with traces of transition metals,[5–7] which have been shown to be very effective at reducing the activation energy for hydrogen dissociation,[8–11] and also somewhat reduce the decomposition temperature of the hydride.[6]

A number of theoretical calculations have been performed on magnesium hydride and related systems (see, for example, Ref. 12 and references therein; see also Refs. 6, 8–11, and 13–16), the most recent ones based on the implementation of quantum mechanics known as density functional theory (DFT).[17,18] Although DFT can often be reliable at predicting trends in the energetics of materials, it can be sometime in error when used to obtain absolute energies. In particular, as we show below, when applied to the calculation of the enthalpy of formation of MgH_2, the results are off by as much as 0.3 eV/f.u., depending on the functional employed, and cohesive energies can be wrong by over 0.5 eV.

Quantum Monte Carlo (QMC) techniques[19,20] are believed to be one possible way to improve beyond density functional theory. Since they are many order of magnitudes more computationally demanding, the current database of properties of materials calculated with QMC is still rather small; however, the increase in computer power in the past few years is making now possible to perform increasingly more numerous calculations on real systems, and experience is being accumulated on the predictive power of this technique.

Here, we have used QMC to calculate the structural properties of the Mg and MgH_2 crystals, together with their cohesive energies and the enthalpy of formation of MgH_2 from Mg bulk and H_2 gas. We find excellent agreement with experiments for the structural properties of the two solids, as well as the cohesive energy of the Mg solid. The enthalpy of formation of MgH_2 is slightly overestimated, but the error is of the order of 1 kcal/mole, showing that QMC on this system can almost achieve chemical accuracy.

II. TECHNIQUES

A. Density functional theory calculations

Density functional theory calculations have been performed with the VASP code.[21] The interactions between the electrons and the ionic cores were described using the projector augmented method[22,23] (PAW) with the generalized gradient approximations known as PBE,[24] PW91,[25] or the local density approximation (LDA). The Mg PAW potential has a frozen Ne core and an outermost cutoff radius for the valence orbitals of 1.06 Å. The H PAW potential has a cutoff radius of 0.58 Å. Single particle orbitals were expanded in plane waves with a plane-wave cutoff of 270 eV, and a cutoff of 1600 eV was used for the charge density. Such a large cutoff in the charge density (four times larger than the typical one used by default) is necessary to obtain very accurate forces which are used to calculate the vibrational properties of the crystals. Calculations were performed by requiring a self-consistency convergence on the total energy of 10^{-8} eV per simulation cell. With these prescriptions, convergence on the forces was at worse equal to 0.2 meV/Å and 1 or 2 orders of magnitudes smaller for most atoms in the simulation cell. Brillouin zone integration was performed using **k**-point sampling, with $18\times18\times12$ and $10\times10\times15$ Monkhorst-Pack[26] grids on the Mg and MgH_2 primitive cells, respectively. With these densities of **k** points, the structural parameters are converged to better than 0.1% and the total energies to better than 1 meV/primitive cell.

B. Quantum Monte Carlo calculations

Quantum Monte Carlo techniques have been extensively described elsewhere,[19,20] so here we only report the main technical details used in this work. Calculations have been performed using the CASINO code[43]. Diffusion Monte Carlo calculations have been performed using trial wave functions of the Slater-Jatrow type:

$$\Psi_T(\mathbf{R}) = D^{\uparrow}D^{\downarrow}e^{J}, \tag{1}$$

where $D^{\uparrow}$ and $D^{\downarrow}$ are Slater determinants of up- and down-spin single-electron orbitals and e^J is the so-called Jastrow factor, which is the exponential of a sum of one-body (electron-nucleus), two-body (electron-electron), and three-body (electron-electron-nucleus) terms, which are parametrized functions of electron-nucleus, electron-electron, and electron-electron-nucleus separations and are designed to satisfy the cusp conditions. The parameters in the Jastrow factor are varied to minimize the variance of the local energy $E_L(\mathbf{R}) \equiv \Psi_T^{-1}(\mathbf{R})\hat{H}\Psi_T(\mathbf{R})$.

Imaginary time evolution of the Schrödinger equation has been performed with the usual short time approximation and the locality approximation.[27] Time step errors have been carefully analyzed later in the paper. Since the locality approximation introduces an uncontrollable error with respect to which the DMC energy is nonvariational, we also tested the scheme of Casula[28] which treats the nonlocal part of the pseudopotential in a consistent variational scheme. We found that the zero time step extrapolation of the energies in the two schemes differed very little, which suggests that the errors in either case are rather small.[29] However, we also found that the time step error is much smaller in the locality approximation in this particular case (this may not be true in general for other systems), and therefore we decided to use the locality approximation throughout the work which allowed us to work with a larger time step.

We used Dirac-Fock pseudopotentials (PPs) for Mg and H.[30] The Mg PP has a frozen Ne core and a core radius of 1.43 Å, and the H PP has a core radius of 0.26 Å. The single particle orbitals have been obtained by DFT plane-wave (PW) calculations using the LDA and a PW cutoff of 3400 eV using the PWSCF package.[31] Such a large PW cutoff is due to the very small H PP core radius and was found to be necessary to reduce the variance of the local energy as much as possible. We then exploited the approximate equivalence between PW and B-splines[32] to expand the single particle orbitals in a basis of B-spline, as described in Ref. 33, using the natural B-spline grid spacing given by $a=\pi/G_{\max}$, where $G_{\max}$ is the length of the largest vector employed in the PW calculations.

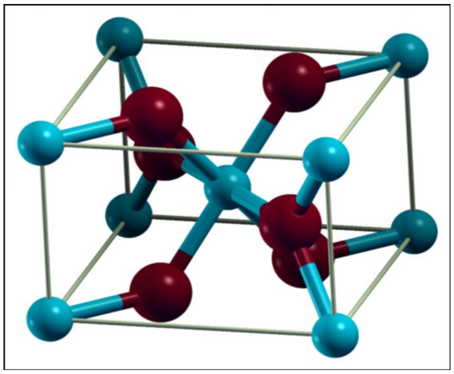

FIG. 1. (Color online) Crystal structure of MgH_2 (see also text). The Mg and H atoms are represented, respectively, by light blue and dark red colors.

We used a diffusion Monte Carlo time step of 0.05 a.u., which was found to result in errors of about 2 meV/f.u. (see below). With this time step, the acceptance ratios were 99.2% and 99.7% for the MgH_2 and Mg crystals, respectively. Total energies in the solids were obtained by correcting the raw DMC data with DFT-LDA calculations performed on the same cell size but a fully converged Brillouin zone sampling and then extrapolating these corrected DMC data to infinite size (see below). The DMC calculations were performed using the Ewald interaction to model electron-electron interactions. The number of walkers in the DMC simulations varied with the size of the systems and was never less than 1280.

III. RESULTS

Mg bulk has the hexagonal close packed structure, which is specified by a lattice parameter a and the ratio c/a of the vertical axis to one of the horizontal ones. The primitive cell contains two atoms, one at the origin and the other at $(1/3,2/3,0.5)$ in lattice vectors units. The MgH_2 solid has a tetragonal structure of rutile type (see Fig. 1), specified by a lattice parameter a and the c/a ratio. The primitive cell has two Mg atoms, one at the origin and the other in the center of the cell at $(1/2,1/2,1/2)$ plus four hydrogen atoms at $(\pm x,\pm x,0)$ and $(1/2\pm x,1/2\mp x,1/2)$. The exact values of c/a and x depend on pressure and, at ambient conditions, are found to be $c/a=0.6687$ and $x=0.304$.[34]

A. Zero point energies and high temperature vibrational effects

In order to compare the calculated structural parameters and cohesive energies with the experimental ones, we need to study the vibrational properties of the crystals. This is because the experimental parameters are usually determined at ambient conditions, and room temperature thermal expansion for the Mg and MgH_2 solids is likely to be significant.

We studied these vibrational properties within the quasiharmonic approximation, which, far from the melting temperatures, provides accurate enough results for the thermal expansion of solids. This is certainly the case for the Mg and MgH_2 solids at room temperature.

Phonons have been calculated using the PHON code,[35] which implements the small displacement method[36,37] to obtain the force constant matrix in crystals. The methods exploit the linearity relation between the displacement of the atoms from their equilibrium positions and the forces induced on all the atoms in the crystal, which holds in the harmonic approximation for small enough displacements. The method is applied by constructing a supercell which is a multiple of the primitive cell in the three spatial directions, then the atoms in the primitive cell are displaced by small amounts along three linearly independent directions, and the forces induced on all the atoms in the supercell are used to construct the force constant matrix. Symmetries can usually be used to reduce the total number of displacements needed and also to symmetrize the force constant matrix.[36] For bulk Mg, which has the hexagonal closed packed crystal structure, only two displacements are needed, one in the basal plane and one orthogonal to it (in fact, one single off symmetry displacements would be sufficient, although this would break the symmetry of the supercell and require a larger number of **k** points in the DFT calculation of forces). MgH_2 has the tetragonal structure of rutile TiO_2, with two Mg and four H atoms in the primitive cell, and the total number of displacements needed in this case is 4 (one could reduce the total number of displacements to 2 by sacrificing symmetries). If the supercell is large enough so that the forces on the atoms sitting near the edges are small, then the calculated force constant matrix becomes a good approximation of the exact one. Magnesium bulk is a metal, and convergence of the force constant matrix with the size of the supercell is readily achieved: We found that with cells containing 36 atoms ($3\times3\times2$), the zero point energy (ZPE) is converged to within 0.1 meV/atom (tested using supercells containing up to 150 atoms). However, MgH_2 is an insulator, and long range Coulomb interactions make convergence slower. Nevertheless, we found that already by using a cell containing 72 atoms ($2\times2\times3$ supercell), the ZPE can be calculated with an accuracy of 0.5 meV/f.u. (tests used supercells containing up to 576 atoms). All calculations were performed with DFT-PBE.

Phonons calculated with the direct method described above may suffer from inaccuracies due to the size of the displacements and/or numerical noise in the calculated forces. To reduce the latter, one would like to maximize the size of the displacements, but too large displacements would cause departure from the harmonic regime. A compromise between these two opposite requirements then needs to be found, and this is usually achieved with displacement sizes of the order of a fraction of a percent of the interatomic distances. In order to test the size of the displacements, we repeated the calculations using displacements of 0.067, 0.04, 0.02, and 0.01 Å, and we found that even with the largest displacement, the ZPE is converged to less than 0.2 meV/atom in Mg and 1 meV/f.u. in MgH_2. We then decided to use displacements of 0.04 Å.

The fundamental vibrational frequency of the H_2 molecule has been obtained by calculating the total energy of the H_2 molecule in a large cubic box of size 13.5 Å for five different values of the H-H distance, ranging from $R_0 - 0.0135$ Å to $R_0 + 0.0135$ Å, where $R_0 = 0.75$ Å is the calculated equilibrium distance with DFT-PBE. The five energies have been fitted to a parabola, providing a force constant of 33.35 eV/Å^2, which corresponds to a stretching vibrational frequency of 127 THz [only slightly lower that the experimental value of 131.8 THz (Ref. 38)], giving a ZPE of 0.263 eV.

B. Density functional theory results

Initially, we performed DFT calculations on the crystals with PBE, PW91, and LDA. Energy versus volume curves were fitted to a Birch-Murnaghan equation of state,[39] which provided equilibrium volumes and bulk moduli. In the range of volumes considered, c/a's do not change very much from their zero pressure values, and the structural parameters are essentially unchanged if c/a is kept fixed. Therefore, for simplicity, we decided to fix c/a to their calculated zero pressure values of 1.621 and 0.6682 for Mg and MgH_2, respectively. The MgH_2 crystal has an additional degree of freedom, which defines the position of the H atoms in the lattice. This has also been optimized by fully relaxing the crystal at each different volume. These relaxations are essential in the calculation of phonons, because if the crystal is not in its ground state, imaginary phonon frequencies appear. However, as far as the energy is concerned, the differences from calculations in which the H positions are kept at their zero pressure equilibrium values are undetectable.

In Table I, we report the structural parameters of Mg and MgH_2 calculated with the three density functionals, and we report the results both at zero temperature (with and without ZPE) and at room temperature. Both Mg and MgH_2 are fairly soft materials, with bulk moduli of the order of 40 and 50 GPa. Room temperature thermal pressures are about 1 and 1.8 GPa for Mg and MgH_2, respectively, which means that volume thermal expansion is about 2% and 3.5% for the two solids. This is significant and cannot be ignored in a fair comparison with the experimental data. We also report in the same table the cohesive energies of the two solids. The experimental cohesive energy of MgH_2 can be estimated by combining the cohesive energy of the Mg crystal (1.51 eV/atom), the dissociation energy of the hydrogen molecule (4.48 eV/molecule), and the enthalpy of formation of MgH_2 from Mg and H_2, whose value extrapolated at zero temperature is 0.79 ± 0.01 eV/f.u.,[3] which therefore give a result of 6.78 ± 0.01 eV/f.u. By comparing the calculated cohesive

TABLE I. Bulk properties (volume/f.u. V_0 in Å^3, and bulk modulus k_0 in GPa) and cohesive energies (E_{coh}, in eV) of Mg and MgH$_2$. Calculated properties are reported at zero temperature with and without zero point energies (ZPEs) and at the temperatures at which the experimental data have been taken. Also reported is the binding energy of the H_2 molecule.

		$T=0$ K			T^{a}
		V_0, k_0 (no ZPE)	V_0, k_0 (with ZPE)	E_{coh} (with ZPE)	V_0, k_0
Mg					
	LDA	21.59, 40.6	21.80, 39.3	−1.74	22.14, 36.4
	PBE	22.86, 36.5	23.08, 35.9	−1.47	23.47, 34.0
	PW91	22.86, 36.4	23.10, 35.2	−1.45	23.50, 32.6
	Expt.			−1.51[b]	23.24,[c] 36.8 ± 3.0,[d]
	DMC	22.96 ± 0.05, 35.5 ± 1.2	23.19 ± 0.05, 34.4 ± 1.4	−1.51 ± 0.01	23.61 ± 0.04, 31.2 ± 2.4
MgH_2					
	LDA	29.36, 55.5	30.32, 51.4	−7.16	30.36, 49.9
	PBE	30.84, 51.1	31.92, 45.8	−6.17	32.03, 43.5
	PW91	30.72, 51.5	31.79, 46.4	−6.27	31.89, 43.9
	Expt.			−6.78 ± 0.01[e]	30.49,[f] —
	DMC	29.48 ± 0.03, 58.6 ± 3.6	30.53 ± 0.05, 42.0 ± 1.5	−6.84 ± 0.01	30.58 ± 0.06, 39.5 ± 1.7
H_2					
	LDA			−4.59	
	PBE			−4.23	
	PW91			−4.25	
	Expt.			−4.48[g]	
	DMC			−4.484 ± 0.002	

[a] $T=298$ K for Mg, $T=260$ K for MgH$_2$.

[b] Reference 40.

[c] Reference 41.

[d] Reference 42.

[e] Reference 3.

[f] Reference 34.

[g] Reference 38.

energies with the experimental ones, it is clear that the three functionals provide quite scattered results, with the LDA doing better on MgH$_2$ and PBE doing better on Mg. It is also apparent that errors can be significant, of up 0.6 eV for PBE. This error is well over ten times a kcal/mole, which is the typical quantity quoted as *chemical accuracy*.

C. Diffusion Monte Carlo results

1. Time step tests

The dependence of the DMC energy on time step in the MgH$_2$ crystal was studied by repeating simulations with a $2\times2\times3$ supercell (72 atoms) at time steps ranging from 0.005 to 0.15 a.u. Calculations were performed at the volume of 30.835 Å^3/f.u. and using the *A* point (0.5,0.5,0.5), which is at one corner of the Brillouin zone. For the Mg crystal, we used a $3\times3\times2$ supercell (36 atoms), a volume of 22.785 Å^3/atom, and the H point (0.5,0.5,0.5), also at one corner of the Brillouin zone.

Results of total energy/fu for MgH$_2$ and total energy/atom for Mg are displayed in Fig. 2, from which it is evident that using a time step of 0.05 a.u., time step errors are well below 5 meV/f.u. In Fig. 2, we also display the results obtained with the scheme proposed by Casula,[28] and we observe that for short enough time steps, the two sets of energies are very close and extrapolate to roughly the same value in the limit of zero time step (to less than 5 meV/f.u.). As mentioned earlier, this suggests that the error introduced with either scheme is very small. However, the locality approximation results in a much weaker dependence of the DMC energy on time step, and this is what we used because it allowed us to work with much larger time steps. We note that for the Mg crystal, the time step error is much smaller, which, in principle, would allow us to work with larger time steps; however, for consistency, we used the same time step of 0.05 a.u. also for the Mg crystal.

To calculate the total energies of the Mg atom and the H$_2$ molecule, we used trial wave functions obtained from plane-wave calculations in which the Mg atom or the H$_2$ molecule was placed at the center of a large cubic box with a side of 13.5 Å. The DMC calculations were then performed using B-splines and no periodically boundary conditions. We dis-

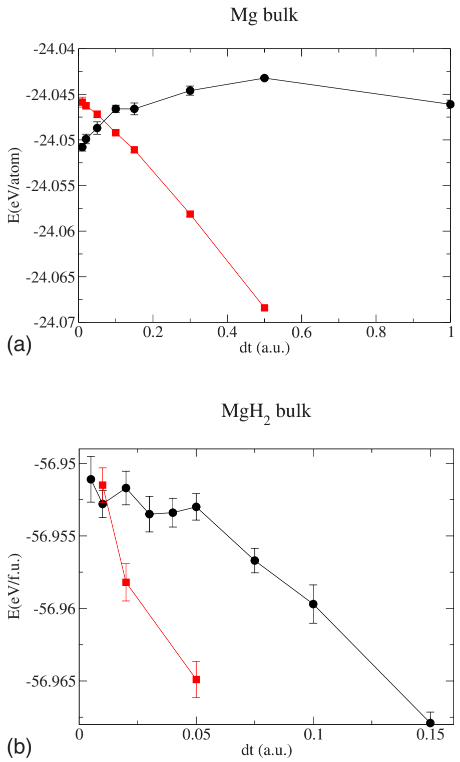

FIG. 2. (Color online) Diffusion Monte Carlo energies for Mg bulk (a) and MgH_2 bulk (b) as function of time step. Dots and squares correspond to calculations performed with the locality approximation and with the scheme proposed by Casula (Ref. 28), respectively.

play in Fig. 3 the DMC energies as function of time step, from which we can obtain very accurate zero time step values. In the case of Mg, we also performed one calculation with the scheme of Casula,[28] which gave essentially the same energy. For the H_2 molecule, we display the binding energy calculated at the equilibrium distance of 0.75 Å, obtained by subtracting from the energy of the molecule twice the energy of the H atom, which is calculated to be 13.606 35(5) eV. Both the energies of the H atom and the H molecule are in excellent agreement with the experimental data.

2. Mg crystal

In the Mg crystal, we studied the dependence of the DMC energy on the size of the simulation cell by repeating the calculations with $4\times4\times3$, $5\times5\times3$, $6\times6\times4$, $8\times8\times5$, and $9\times9\times6$ supercells, containing 96, 150, 288, 640, and 972 atoms, respectively. Results are displayed in Fig. 4, where we show the total energies/atom E_N as function of $1/N$, with N the number of atoms in the simulation cell. On the same graph, we also show the energies $E_N^c = E_N + [E_\infty^{DFT} - E_N^{DFT}]$, where E_∞^{DFT} are the DFT energies calculated with fully converged **k**-point sampling and E_N^{DFT} are the DFT energies calculated with **k**-point samplings corresponding to the N-atom cells used in the DMC calculations. It is clear that the raw DMC energies E_N are quite scattered and somewhat difficult to extrapolate to infinite size. This is due to the metallic nature of Mg. However, the DFT corrected energies E_N^c are much better behaved, with data fitting quite well onto a straight line, which makes it possible to extrapolate to infinite size. In particular, we note that with no loss of accuracy, we can also use only the calculations with the $4\times4\times3$, $5\times5\times3$, and $6\times6\times4$ supercells to extrapolate to essentially the same infinite size value.

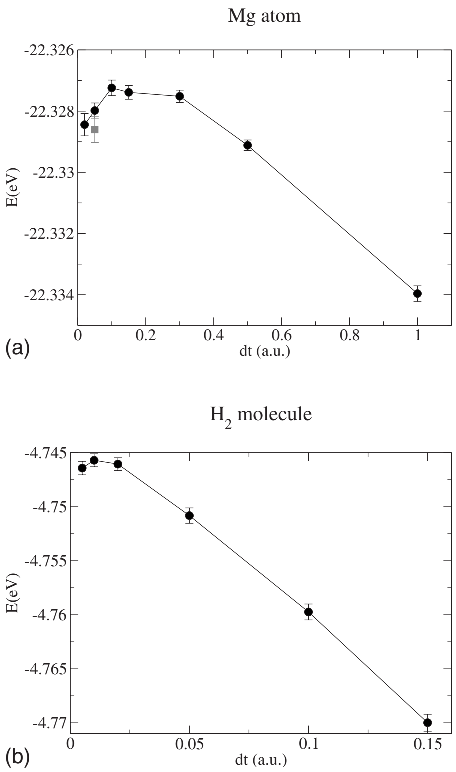

FIG. 3. Dots: diffusion Monte Carlo total energy for the Mg atom (a) and binding energy of the H_2 molecule (b) as function of time step. Calculations have been performed with the locality approximation. Square: calculation performed with the scheme proposed by Casula (Ref. 28).

The calculations with these three supercell sizes were then repeated at eight different volumes, between 21 and 25 Å^3/atom. At each volume, the DFT corrected DMC re-

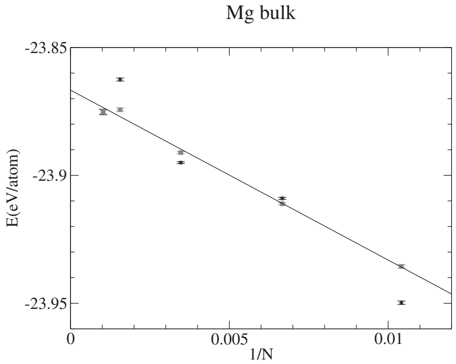

FIG. 4. Diffusion Monte Carlo total energy for the Mg crystal as function of $1/N$, where N is the number of particles in the simulation cell. Black and gray dots correspond to raw and DFT corrected (see text) results; solid line is a linear least squares fit to the DFT corrected results.

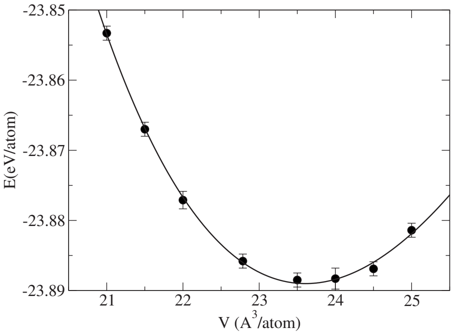

FIG. 5. Diffusion Monte Carlo free energies at 298 K for the Mg crystal as function of volume V. Dots correspond to DMC calculations extrapolated to infinite size and include vibrational free energies calculated with DFT-PBE. Solid line is a least squares fit to a Birch-Murnaghan equation of state.

sults were extrapolated to infinite size and the results were fitted to a Birch-Murnaghan equation of state to obtain the structural parameters. We performed the fit by weighting each energy point E_i point with $1/\sigma_i^2$, where σ_i is the standard error on E_i. We report in Table I the results obtained both at zero temperature (with and without zero point energy) and at room temperature. The latter are also shown in Fig. 5. The room temperature corrected DMC results slightly overestimate the equilibrium volume and also underestimate the bulk modulus, but the calculated cohesive energy is in perfect agreement with the experimental data.

3. MgH_2 *crystal*

For the MgH_2 crystal, size effects were studied using $2\times2\times3$, $3\times3\times4$, $4\times4\times6$, and $5\times5\times7$ supercells, containing 72, 216, 576, and 1050 atoms, respectively. These tests were performed at the volume of 30 Å^3/f.u. The results for the four sizes studied are displayed in Fig. 6, where we show total energies/f.u. E_N as function of $1/N$, as well as the DFT corrected energies E_N^c. In this case, the DFT corrections are much smaller, which is not surprising because of the large band gap in MgH_2. A small difference between the two sets of data can be observed for the smallest sizes, but it is clear that they both fit very well onto straight lines, which allows us to easily extrapolate the results to infinite size. In fact, in this case, the extrapolated results for the two sets only differ by 5 meV/atom.

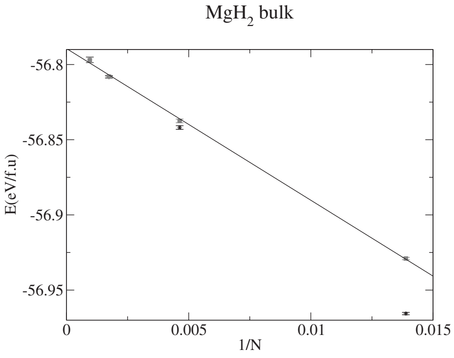

FIG. 6. Diffusion Monte Carlo total energy for the MgH_2 crystal as function of $1/N$, where N is the number of particles in the simulation cell. Black and gray dots correspond to raw and DFT corrected (see text) results; solid line is a linear least squares fit to the DFT corrected results.

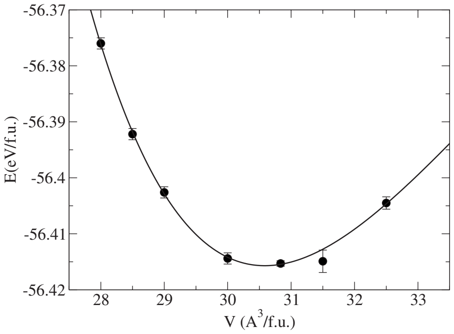

FIG. 7. Diffusion Monte Carlo free energies at 260 K for the MgH_2 crystal as function of volume V. Dots correspond to DMC calculations extrapolated to infinite size and include vibrational free energies calculated with DFT-PBE. Solid line is a least squares fit to a Birch-Murnaghan equation of state.

The calculations were repeated at seven different volumes between 28 and 32.5 Å^3/f.u., and the DFT corrected DMC results were then fitted with a Birch-Murnaghan equation of state to obtain the structural parameters. Also in this case, we used the inverse of the variances to weight each point in the fit. We report in Table I the results obtained both at zero temperature (with and without zero point energy) and at $T = 260$ K, which is the temperature at which the experimental data are reported.[34] The high temperature results are also shown in Fig. 7. It is clear that once thermal effects are added onto the calculations, the agreement with the experimental equilibrium volume is almost perfect. The cohesive energy is slightly overestimated, but the error is only 0.06 eV, i.e., of the order of chemical accuracy.

4. *Enthalpy of formation of* MgH_2

We can now calculate the enthalpy of formation of MgH_2 from Mg bulk and H_2 in the gas phase by adding the cohesive energies of the MgH_2 and Mg crystals to the binding energy of the H_2 molecule. We obtain enthalpy of formations of 0.82, 0.47, and 0.57 eV/f.u. with LDA, PBE, and PW91, respectively, and with DMC we obtain the value of 0.85 ± 0.01 eV/f.u. The LDA value is very accurate, but this is the result of large cancellations of errors in the cohesive energies of the crystals and the binding energy of the H_2 molecule. The DMC result is only 0.06 eV higher than the experimental value of 0.79 ± 0.01 eV/f.u.; however, in this case, both the cohesive energies of the crystals and the binding energy of the H_2 molecule are very accurate.

IV. CONCLUSIONS

We pointed out in this work the difficulty of using density functional theory to calculate the enthalpy of formation of MgH_2 with high accuracy. We studied the effect of three different exchange-correlation functionals, PW91, PBE, and LDA, and found that although the generalized gradient approximation (GGA) ones appear to work better on the Mg solid, the LDA gives better results on the MgH_2 solid. It turns out, therefore, that is difficult to get a good DFT value for the enthalpy of formation of MgH_2: The two GGA functionals give an enthalpy of formation in error of more than 0.2 and 0.3 eV/f.u. respectively. The LDA is the functional that does best, but for the wrong reason, because the cohesive energies of the crystals and the binding energies of the molecule are wrong by up to 0.4 eV/f.u., and the enthalpy of formation is accurate only because of large cancellation of errors.

Diffusion Monte Carlo appears to deliver much better accuracy in general. We have shown that the DMC equilibrium volume of MgH_2 agrees perfectly with the experimental one, once high temperature thermal expansion is included in the calculations, and the equilibrium volume of Mg is only slightly overestimated. The cohesive energy of Mg is also predicted in perfect agreement with the experimental data, and so is the binding energy of the H_2 molecule. A small error is present in the cohesive energy of the MgH_2 crystal, which determines the small inaccuracy in the enthalpy of formation, for which we find a DMC value of 0.85 ± 0.01 eV/f.u.. However, this is only 0.06 higher than the accepted experimental one of 0.79 ± 0.01 eV/f.u., or 76.1 ± 1 kJ/mole. This result is not very far from the LDA value, but with the important difference that now all three terms that enter the enthalpy of formation are calculated accurately, and we do not rely on fortunate cancellation of errors.

Although the DMC error is slightly larger than 1 kcal/mole, and therefore we cannot claim chemical accuracy, we are not far from it, and therefore we argue that quantum Monte Carlo techniques have useful predictive power in the search of metal hydrides with workable decomposition temperatures.

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