

# Hydrogen dissociation on Mg(0001) studied via quantum Monte Carlo calculations

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We have used diffusion Monte Carlo (DMC) simulations to calculate the energy barrier for H<sub>2</sub> dissociation on the Mg(0001) surface. The calculations employ pseudopotentials and systematically improvable *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 550 atoms, show that all these errors together can be reduced to  $\sim 0.03$  eV. The DMC dissociation barrier is calculated to be  $1.18 \pm 0.03$  eV and is compared to those obtained with density-functional theory using various exchange-correlation functionals, with values ranging between 0.44 and 1.07 eV.

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## I. INTRODUCTION

The ability of calculating accurately the energetics of metal hydrides is a key issue in the design of materials, which might turn out to be useful in the current search for suitable hydrogen storage (HS) media. In particular, the kinetics of hydrogen absorption is one of the main questions which determine the functionality of a candidate HS material.

Magnesium is an interesting hydrogen absorbant because the hydride (MgH<sub>2</sub>) formed after exposure to H<sub>2</sub> can store a large amount of H (7.6% by weight), which can be later released by heating the material above  $\sim 300$  °C,<sup>1</sup> the reaction being endothermic with an enthalpy of decomposition of 76 kJ/mole.<sup>2</sup> The kinetics of hydrogen intake by Mg is quite slow because of a relatively large energy barrier that the H<sub>2</sub> molecule needs to overcome in order to dissociate before adsorption. However, it is possible to modify this material to improve its properties, for example, by doping it with traces of transition metals,<sup>3–11</sup> which have been shown to be very effective at reducing the activation energy for hydrogen dissociation<sup>12–15</sup> and also to somewhat reduce the decomposition temperature of the hydride.<sup>7</sup>

So far, the only high level quantum mechanics calculations available for the interaction of hydrogen with Mg surfaces are based on density-functional theory (DFT), which has been shown to be quite successful for investigating the relative energetics of the interaction of H<sub>2</sub> with pure and transition-metal-doped Mg surfaces.<sup>12–15</sup> However, the absolute accuracy of DFT has often been called into question. For example, we recently showed that the DFT calculated value for the enthalpy of formation of MgH<sub>2</sub> from Mg bulk and H<sub>2</sub>, a quantity obviously related to the interaction between H and Mg, strongly depends on the functional employed, with values ranging from 0.29 [with RPBE (Ref. 24)] to 0.82 eV [with local-density approximation (LDA)].<sup>16</sup>

Quantum Monte Carlo (QMC) methods<sup>17,18</sup> are becoming promising techniques to improve beyond DFT, with their increased utilization favored by the availability of faster and faster computers. Recently, diffusion Monte Carlo (DMC)

calculations on Mg and MgH<sub>2</sub> bulks showed very good accuracy in both structural parameters, cohesive energies, and enthalpy of formation of the MgH<sub>2</sub> crystal.<sup>16</sup>

Here we have coupled DMC to climbing image nudged elastic band (NEB) DFT calculations to compute the energy barrier for the dissociation of H<sub>2</sub> on the Mg(0001) surface. Since DMC forces are not yet readily available, the strategy has been to first perform DFT calculations to determine the geometries of the problem: (i) the initial state (IS) with the H<sub>2</sub> molecule in vacuum plus the clean Mg(0001) surface, (ii) the final state (FS) with the two H atoms adsorbed on two nearby hollow sites, and (iii) the transition state (TS) determined with the NEB method (see Fig. 1); then, we have used these DFT geometries to compute highly accurate DMC energies.

## II. TECHNICAL DETAILS

DFT calculations have been performed with the VASP code<sup>19</sup> using the projector augmented wave (PAW) method

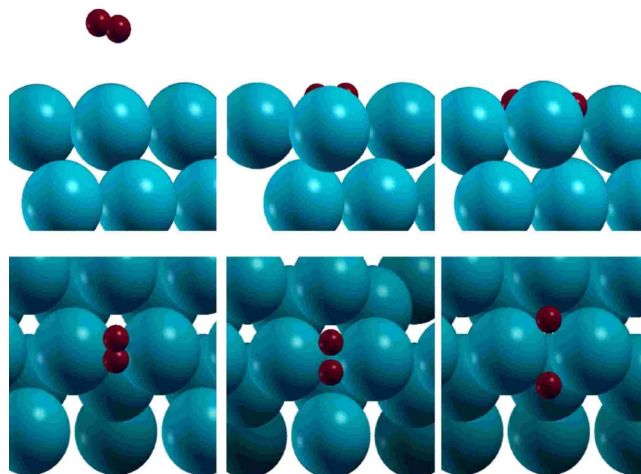


FIG. 1. (Color online) Initial-state (left), transition state (center), and final-state (right) geometries for the H<sub>2</sub> dissociation reaction on the Mg(0001) surface. Top and bottom panels show side and top views, respectively.

(Refs. 20 and 21) with the generalized gradient approximations known as PBE,<sup>22</sup> PW91,<sup>23</sup> RPBE,<sup>24</sup> or the LDA. An efficient charge-density extrapolation was used to speed up the calculations.<sup>25</sup> The plane-wave (PW) energy cutoff was 270 eV, which guarantees convergence of adsorption energies within 1 meV.<sup>14</sup> Surfaces were modeled using periodic slabs, with five atomic layers and a vacuum thickness of 10 Å. The topmost three atomic layers were allowed to relax, while the bottom two were held fixed to the positions of bulk Mg. The  $c/a$  ratio and the lattice parameter were fixed at 1.621 and 3.2 Å, respectively, which are close to the calculated PBE values at zero pressure and zero temperature.<sup>14</sup> We used  $2 \times 2$  surface unit cells (22 atoms), with  $9 \times 9 \times 1$   $\mathbf{k}$ -point grids. These settings were extensively tested (repeating calculations on  $3 \times 3$  surface unit cells and, separately, denser  $\mathbf{k}$ -point grids) and guarantee convergence of activation energies to better than 0.02 eV.<sup>14,26</sup> Activation energies have been calculated with the NEB method<sup>27</sup> using nine replicas and have been tested with calculations using 17 replicas; nine replicas proved to be sufficient to reach convergence of activation energies to better than 0.01 eV and display all the main features of the minimum-energy path.

DMC calculations have been performed using the CASINO code,<sup>28</sup> employing trial wave functions of the Slater-Jastrow type:  $\Psi_T(\mathbf{R}) = D^\dagger D^\downarrow e^J$ , where  $D^\dagger$  and  $D^\downarrow$  are Slater determinants of up- and down-spin single-electron orbitals. The Jastrow factor  $e^J$  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.<sup>29</sup> We extensively tested time step errors in our previous work on  $\text{MgH}_2$  (Ref. 16) and used here a time step of 0.05 a.u., which results in essentially negligible energy biases. We used Dirac-Fock pseudopotentials (PP) for Mg and H.<sup>30</sup> The Mg PP has a frozen Ne core and a core radius of 1.43 Å; the H PP has a core radius of 0.26 Å. The single-particle orbitals have been obtained by DFT-PW calculations with the LDA and a PW cutoff of 3400 eV, using the PWSCF package,<sup>31</sup> and re-expanded in terms of  $B$  splines,<sup>32,33</sup> using the natural  $B$ -spline grid spacing given by  $a = \pi/G_{\max}$ , where  $G_{\max}$  is the length of the largest PW. The DMC calculations were performed using the Ewald technique to model electron-electron interactions. The number of walkers in the DMC simulations varied between 2560 and 10 240, depending on the size of the system.

### III. RESULTS

DFT energy barriers were calculated using four different functionals: LDA, PW91, PBE, and RPBE. The energy profiles along the minimum-energy paths are displayed in Fig. 2. We also calculated the LDA, PW91, and RPBE energies at the PBE IS, TS, and FS. In all cases the differences between

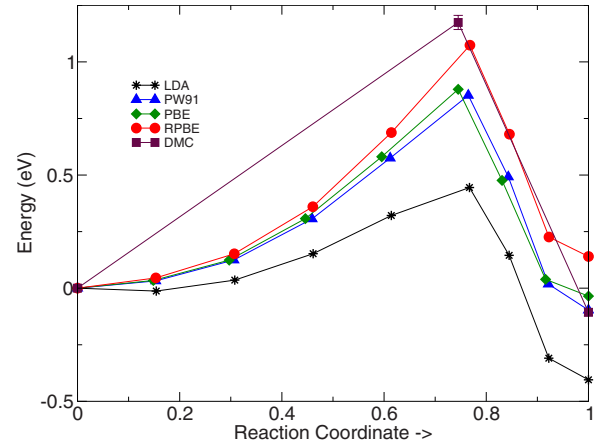


FIG. 2. (Color online) Minimum-energy profiles for the  $\text{H}_2$  dissociation reaction on the  $\text{Mg}(0001)$  surface calculated with various DFT functionals: LDA (black stars), PW91 (blue triangles), PBE (green diamonds), and RPBE (red circles). Also shown are the DMC energies (maroon squares) at the TS and the FS. Lines are guides for the eyes.

these energies and the corresponding energies obtained in the LDA, PW91, and RPBE IS, TS, and FS are between 1 and 2 meV. This also indicates that the geometries obtained with the four different functionals are very similar, and indeed this is confirmed by looking at the distances of the hydrogen atoms from the surface at the TS and at the FS (see Table I). In Table I we also report the energy barriers and the energy differences between the FS and the IS calculated with the four functionals and with the DMC (see below). Our DFT-RPBE activation energies compare well with the results of Du *et al.*<sup>13</sup> and Vegge.<sup>12</sup>

DMC calculations were performed using the PBE geometries for the IS, the TS, and the FS, as shown in Fig. 1. We used  $2 \times 2$  (88 atoms),  $3 \times 3$  (198 atoms),  $4 \times 4$  (352 atoms), and  $5 \times 5$  (550 atoms) periodically repeated supercells of the 22 atom cells used to perform the DFT calculations. These large calculations were performed to investigate DMC finite-size errors. Raw DMC energies were corrected using the

TABLE I. Average distances of molecular hydrogen from the first surface layer at the transition state ( $\bar{d}_{\text{H-surf}}^{\text{TS}}$ ) and final state ( $\bar{d}_{\text{H-surf}}^{\text{FS}}$ ) of the minimum-energy paths calculated with various exchange-correlation functionals. Also reported are the distances between the hydrogens at the transition state ( $d_{\text{H-H}}^{\text{TS}}$ ) and the activation barrier for  $\text{H}_2$  dissociation ( $E_{\text{TS-IS}}$ ) and the energy difference between the final and initial state ( $E_{\text{FS-IS}}$ ) obtained with the four DFT functionals and with DMC.

PP	$\bar{d}_{\text{H-surf}}^{\text{TS}}$ (Å)	$d_{\text{H-H}}^{\text{TS}}$ (Å)	$\bar{d}_{\text{H-surf}}^{\text{FS}}$ (Å)	$E_{\text{TS-IS}}$ (eV)	$E_{\text{FS-IS}}$ (eV)
LDA	1.09	1.02	0.74	0.44	-0.40
PW91	1.07	1.07	0.79	0.85	-0.10
PBE	1.07	1.08	0.81	0.88	-0.03
RPBE	1.07	1.0	0.81	1.07	0.14
DMC			$1.18 \pm 0.03$	$-0.11 \pm 0.02$	

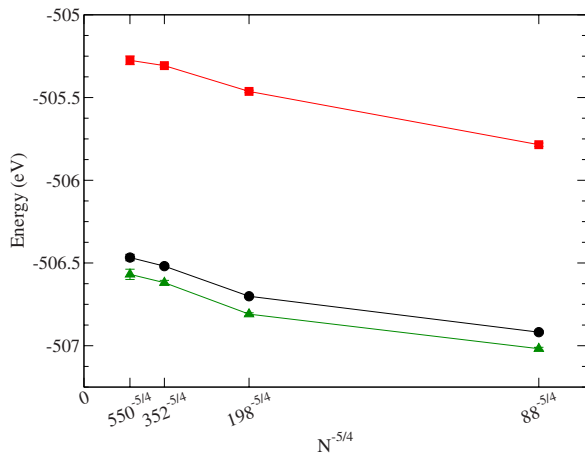


FIG. 3. (Color online) Diffusion Monte Carlo energies for the initial state (black circles), the transition state (red squares), and the final state (green triangles) for the  $H_2$  dissociation reaction on the Mg(0001) surface as a function of  $N^{-5/4}$ , with  $N$  as the number of atoms in the simulation cell.

difference between the LDA  $\mathbf{k}$ -point converged energies and the LDA energies with a  $\mathbf{k}$ -point sampling corresponding to the same simulation cell employed in the DMC calculations. These corrections make it easier to extrapolate the DMC results to infinite size.

It was shown by Drummond *et al.*<sup>34</sup> that for calculations on two-dimensional (2D) systems DMC energies obtained using the Ewald interaction should have  $N^{-5/4}$  behavior, where  $N$  is the number of atoms (or, more generally, electrons) in the system. They showed that the leading error in the kinetic energy of the 2D homogeneous electron gas falls off as  $o(N^{-5/4})$ . The system studied here is a 2D slab, and we therefore follow their recommendation of assuming an error in the total energies of the slab going as  $N^{-5/4}$ . In Fig. 3 we show the DMC energies for the IS, the TS, and the FS as a function of  $N^{-5/4}$ , and we notice that if we disregard the smallest system (88 atoms) the other three sizes fit more or less on a straight line. In fact, the behavior is not exactly linear, but the deviations appear to be similar for the IS, the TS, and the FS. In Fig. 4 we plot the energy differences between the TS and the IS, and between the FS and the IS as a function of  $N^{-5/4}$ . The finite-size dependence of these differences is much weaker and easily extrapolable to infinite size if just the smallest system (88 atoms) is not included in the fit.

The DMC extrapolated results to infinite size are plotted in Fig. 2 from which we observe that at the TS the RPBE result appears to be the nearest, while at the FS the PBE and the PW91 functionals appear to be those with the closest energy.

#### IV. DISCUSSION AND CONCLUSIONS

Before discussing our findings, we should point out once more that the present DMC results for the dissociation barrier are not the “real” DMC results for the activation barrier because we used DFT-PBE geometries for the IS, the TS,

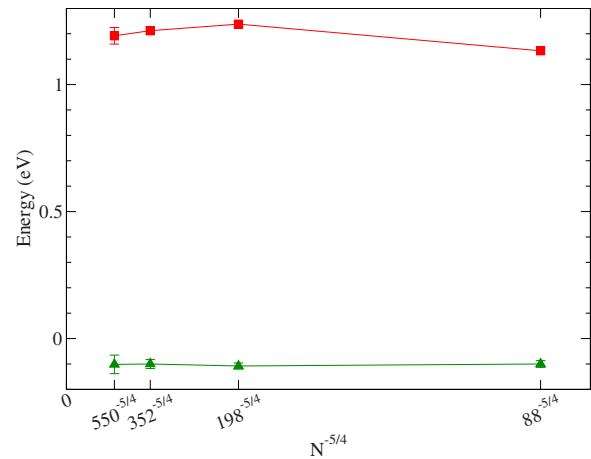


FIG. 4. (Color online) Diffusion Monte Carlo energy differences between the transition state and the initial state (red squares) and between the final state and the initial state (green triangles) for the  $H_2$  dissociation reaction on the Mg(0001) surface as a function of  $N^{-5/4}$ , with  $N$  as the number of atoms in the simulation cell.

and the FS. At present this is all we can do because we do not have easy access to DMC forces; however, we argued that the similarity of the geometries found with the four DFT functionals employed here may suggest that these geometries are indeed reliable.

The present results would suggest that RPBE is the best functional to calculate the dissociation energy barrier; however, for the reverse barrier this would not be the case. Other related quantities are also badly calculated with RPBE, such as the enthalpy of formation of  $MgH_2$  from Mg bulk and  $H_2$  that we find to be 0.29 eV (this includes zero-point energies), which is about 0.5 eV lower than the experimental value of 0.79 eV or the DMC value of 0.85 eV.<sup>16</sup> As far as this enthalpy of formation is concerned, the RPBE is the functional which has the worse agreement with DMC among LDA, PBE, PW91, and RPBE.

We found in the literature two experimental values for dissociation energy barrier. The first one reported in Ref. 35 ( $\sim 1.0$  eV) refers to the recombination barrier (which, in this particular case, is similar to the dissociation barrier) identified with the barrier for desorption from the surface. This value was not directly measured in the thermal programmed desorption (TPD) experiments of Ref. 35 because complete desorption spectra as function of temperature could not be taken due to the onset of Mg sublimation at  $\sim 450$  K, which overlaps with the temperature at which  $H_2$  desorbs. However, it was noted that the onset of  $H_2$  desorption appears at 425 K, which is similar to that of the H/Be(0001) system that has a determined desorption energy of  $\sim 1$  eV,<sup>36</sup> and so—by analogy—it was suggested that the activation energy for desorption might be the same on the H/Mg(0001) system as well.

The second, and most recent one, refers to the dissociation of  $H_2$  on a 400-Å-thick magnesium film and has a reported value for the dissociation barrier of  $0.75 \pm 0.15$  eV.<sup>37</sup> This value is in good agreement with the calculated PBE dissociation energy but is significantly lower than the present DMC dissociation energy, even if a correction of 0.08 eV is

applied to take zero-point effects into account (see Vegge<sup>12</sup>). It should be noted, however (as pointed out in Ref. 37), that the experimental situation may not be the same as the theoretical ones due to the possible presence of steps on the surface which might be more reactive sites and lower the H<sub>2</sub> dissociation barrier. We investigated possible effects due to the presence of steps, and we found that the energy barrier is hardly affected by steps on the Mg(0001) surface, so this might not be the reason for the apparent higher activity inferred from these experimental data. We speculate that a more likely reason might be the following. The experimentally inferred dissociation energy of  $0.75 \pm 0.15$  eV is based on the use of the Arrhenius relations with assumed prefactors of  $\sim 10^{12}$  Hz. As shown in Refs. 38 and 39, these values could be underestimated by more than 2 orders of magnitude because the classical prefactors do not include the enhancement due to the much larger entropy that the molecules have in vacuum. It is possible that just this prefactor enhancement could explain an activation energy up to  $\sim 0.25$  eV higher, or in other words that the correct experimental number may, in fact, be  $1.0 \pm 0.15$  eV, which would agree well with the present DMC results. It will be interesting to investigate this possibility to confirm or otherwise this suggestion, and we plan to do this in the future.

In summary, we have performed here DFT and DMC calculations for the activation energy needed to dissociate the

H<sub>2</sub> molecule on the Mg(0001) surface. We have shown that the four functionals employed—LDA, PW91, PBE, and RPBE—all give different results, with values ranging from 0.44 to 1.07 eV. Such a large variability calls into question the reliability of certain DFT functionals and makes it difficult to make choices on which functional to employ when highly accurate energy values are needed. However, we showed that the geometries of the IS, TS, and FS are predicted to be very similar by the four functionals, which therefore provides some confidence that these geometries are indeed accurate. We have then used these geometries (the PBE ones to be precise) to calculate DMC energies and obtained a value for the activation energy for H<sub>2</sub> dissociation of  $1.18 \pm 0.03$  eV, which is close to the DFT-RPBE value of 1.07 eV. The inverse barrier is calculated to be  $1.28 \pm 0.03$  eV, which is at least 0.3 eV higher than any of the results obtained with the four DFT functionals and casts doubts on the reliability of DFT adsorption energies.

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