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Sørensen, Bent Erik

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# Absorption of hydrogen in Mg lattice

Bent Sørensen\*

Department of Mathematics and Physics, Roskilde University, Universitetsvej 1, 4000  
Roskilde, Denmark

\* Correspondence: E-mail: [boson@ruc.dk](mailto:boson@ruc.dk) tel: +45 4674 2028, fax: +45 4674 3020

## Abstract

Metal hydrides are under study as possible candidates for small-scale hydrogen storage, e.g. in connection with building-integrated fuel cells. I present a quantum chemical model calculation of the potential energy surface allowing hydrogen to enter a magnesium lattice and occupy interstitial sites, by use of a density functional method with periodic boundary conditions.

**Keywords:** Metal hydride storage, quantum chemistry, density functional theory

## 1. Introduction

Metal hydrides offer hydrogen storage at near-ambient pressures (0.06–6 MPa), with high round-trip efficiencies and with high safety in operation. Hydrogen transfer is accomplished by adding or withdrawing modest amounts of heat. Among single-metal hydrides, MgH<sub>2</sub> with a hydrogen fraction of 7.6% by mass is of interest, despite the fairly high desorption temperature of about 330°C. The enthalpy of the exothermal transfer of

hydrogen into the metal lattice at this temperature is  $-74.5 \text{ kJ mol}^{-1}$  and quantum chemical calculations have been used to study the swelling of the metal lattice when incorporating hydrogen [1, 2]. That suitability for hydrogen storage is not granted all metals is illustrated by the potential energy surface for two hydrogen atoms near a nickel surface shown in Fig. 1, using the B3LYP parametrization of the density functional method [3]. The dissociation of the hydrogen molecule into two atoms takes place outside the Ni surface, as reproduced by several previous calculations [4]. An additional potential energy minimum is found within the Ni surface, midway between the first two layers, but a quite high barrier (about 4 eV) has to be tunneled through for the H-atom to get there, and the minimum is some 2 eV higher than that of separated H-atoms outside the surface, so that spontaneous transfer is not encouraged except for a tail of the thermal distribution. In the following, I look at hydrogen near a Mg surface, in order to see if the calculated conditions are more favorable for group-II metals.

## 2. Quantum chemical approach

The calculation for  $\text{MgH}_2$  is carried out using density functional theory with periodic boundary conditions and fast multipole techniques [5, 6], rather than explicitly treating the periodic lattice as a single large molecule similar to the calculation for NiH in Fig. 1. In this way, the computing time is reduced by nearly two orders of magnitude. The SV basis set [7] is used with automatic optimization, as implemented in the Gaussian software package [8], and the PBE/PBE parametrization of the density functional exchange and correlation parts [9]. The periodicity is allowed to prevail for about 1.6 nm in directions along the Mg-

surface and into the material, which was verified to be enough to ensure stability of calculated energies.

Figure 2 (top) shows the structure of  $\text{MgH}_2$  resulting from optimization, with H atoms occupying the positions within the lattice leading to minimum potential energy. In order to compare this energy to that of the same system but with hydrogen atoms partially or fully outside the Mg lattice, a sequence of calculations were made, pulling the hydrogen atoms out of the lattice but preserving their relative positions among themselves. This allows the periodic boundary condition method to be used. Figure 2 (bottom) shows a situation with the hydrogen set pulled out 0.5 nm from the equilibrium position. Figure 3 shows the calculated map of the potential energy surface, as function of  $x$ , the pull direction perpendicular to the Mg lattice surface, and  $y$ , the coordinate describing displacements parallel to the Mg surface. Figure 4 shows the potential energy curve along the  $y = 0$  line of displacement (i.e. the potential minimum for fixed  $x$  as a function of  $y$ , as derived from Fig. 3). For completeness, also the potential energy in the case of fully separated hydrogen atoms (calculated as the energy of the Mg lattice alone, plus the energy of the hydrogen atoms alone) is indicated in Fig. 4. All potential energies are given per unit cell of two Mg-atoms and four H-atoms, with arbitrary but identical origin for all displacement calculations.

### 3. Conclusions

The first conclusion is that the  $\text{MgH}_2$  metal hydride indeed has a potential energy which is 3.5 eV (per unit cell) lower than that of the Mg and H atoms separated, thereby

providing theoretical confirmation of the ability of the Mg lattice to absorb hydrogen without energy being added externally. On their way in, the hydrogen atoms make the potential energy oscillate in concord with their positions relative to the Mg atomic centers, with an excursion range of 3 eV but at any time more than 2 eV higher than the final hydride energy (Fig. 4). The  $y = 0$  path into the Mg lattice allows the most free passage, as seen from the effect of varying  $y$  (Fig. 3), which is to rapidly increase the potential energy. The calculation finds the enthalpy of formation at standard temperature and pressure as  $-71.93 \text{ kJ mol}^{-1}$ . The experimental value vary from  $-74.5$  to  $-75.2 \text{ kJ/mol}$  between 330 and  $435^\circ\text{C}$ , respectively [10, 11]. The “sizes” of the calculated electron wavefunction parts surrounding Mg and H atoms (as estimated in terms of the density surface for which the squared density has fallen to 0.05) are very similar, denouncing the common explanation of hydrogen absorption in metal lattices based on hydrogen being “a very small atom” [12].

### References and Notes

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Figure 1. Potential energy surface in eV for two hydrogen atoms near a nickel surface: the variational coordinates are distance between hydrogen atoms and height of the center of mass of the two H atoms over the (1,1,1) surface of the Ni-layer below the top layer. The energy scale has an arbitrarily chosen origin.

Figure 2. Two configurations of the Mg-2H periodic structure used in the potential energy calculations performed. The situation on top corresponds to the MgH<sub>2</sub> hydride equilibrium configuration found by optimization, while the H atoms in the lower figure have been moved 0.5 nm out of the Mg lattice, along what is used as the negative x-axis in Figs. 3 and 4, and perpendicular to one of the lattice surface planes.

Figure 3. Potential energy plot of Mg-2H system as a function of the displacement of the H atoms in two directions relative to the equilibrium position within the hydride shown in Fig. 2 (top).

Figure 4. Potential energy plot for Mg-2H system as a function of x-displacement (as in Fig. 3 but with y fixed at zero).



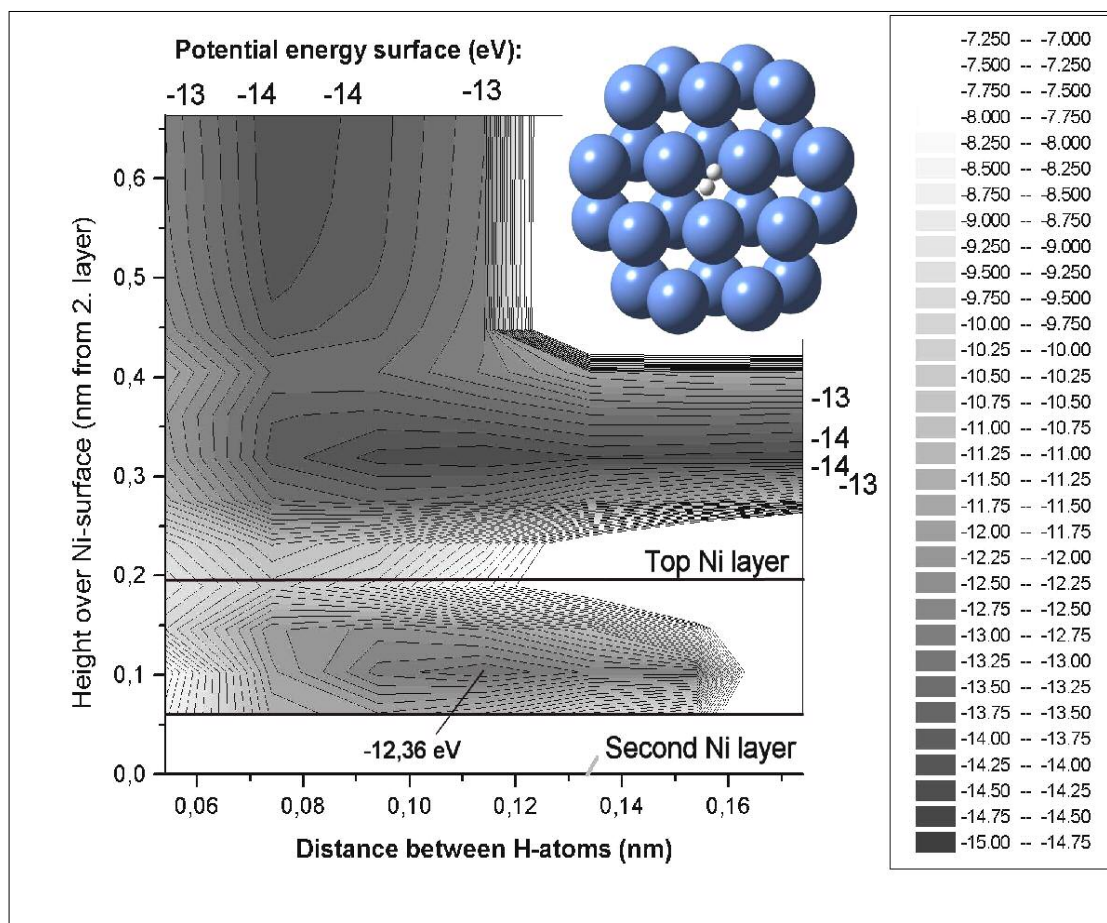


Fig. 1

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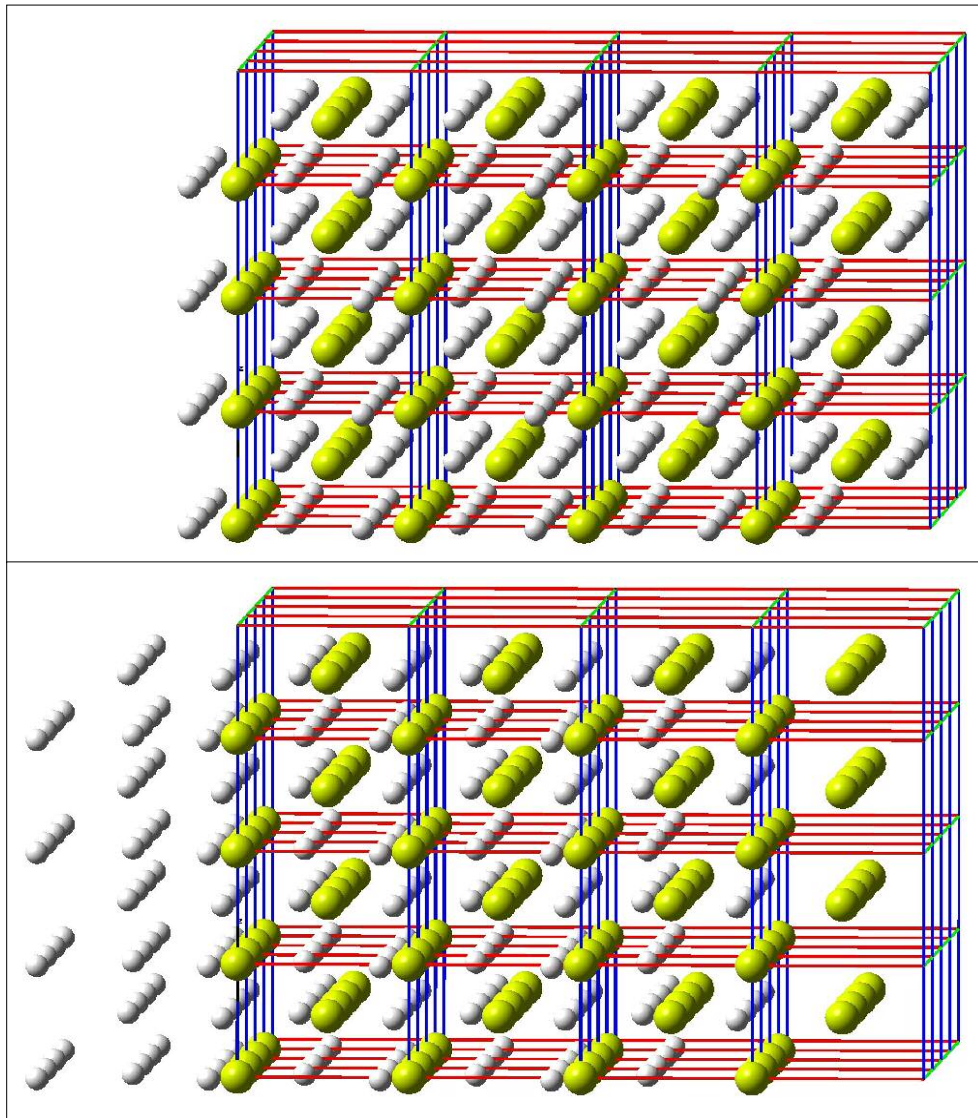


Fig. 2

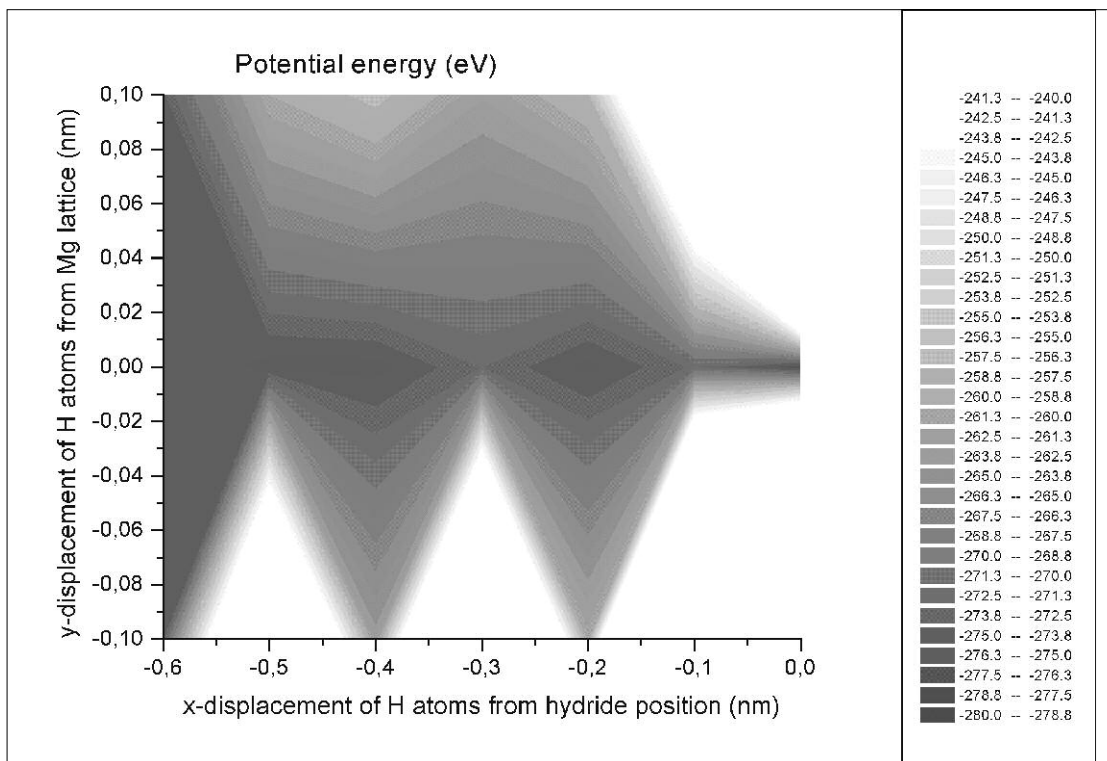


Fig. 3

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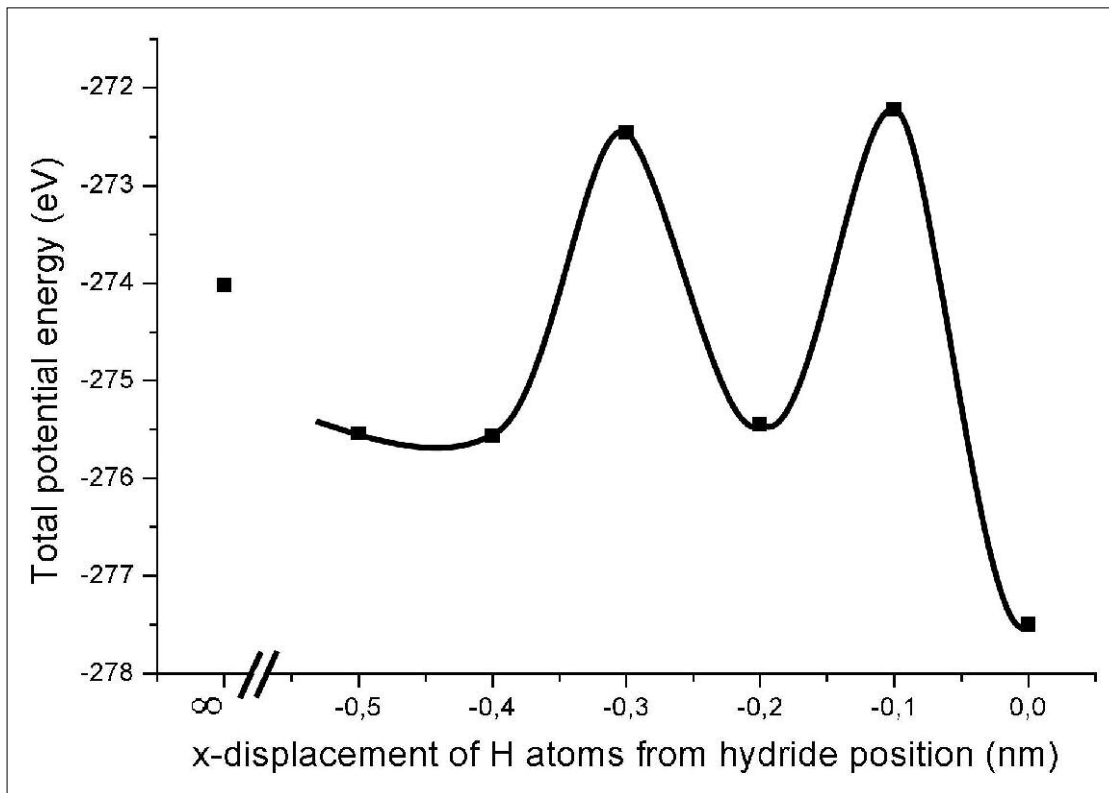


Fig. 4

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