



# Electronic structure properties of hydrazine borane for hydrogen storage applications

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**Abstract**— The hydrazine borane has been investigated with respect to the crystal structure, electronic properties and chemical bonding for hydrogen storage applications, using first-principle methods based on density functional theory with generalized gradient approximation.

The optimized structures and atomic coordinates are in good agreement with the experimental data. The calculated band gap indicates that Hydrazine Borane is a wide band-gap insulator. The calculated total and partial density of states of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> show that near the Fermi level is mainly dominated by the B p-states, H (B) s-states, and the end N p-states. However, in the region below -2 eV, is mainly dominated by the N p-states and the hydrogen atoms connected to the two N atoms (H<sub>4</sub>, H<sub>5</sub>, H<sub>6</sub> and H<sub>7</sub>). This strong sp hybridization in the valence band leads to the strong bonding occurring between B and H (B) and between N and H (N), which indicates that the chemical bonding in NH<sub>2</sub> and BH<sub>3</sub> are covalent.

**Keywords**— Hydrogen storage; electronic structure; hydrazine Borane.

## I. INTRODUCTION

In the search for alternative fuels, hydrogen is the ideal candidate as a clean energy carrier for both transportation and stationary applications [1]. However, the widespread use of hydrogen as fuel requires the development of a safe, reliable and cheap method for its transportation. The storage of hydrogen-based material hydride, also known as storage in solid form, is very safe. It also offers significant improvements in terms of weight and costs for applications related to the transport [1]. These new materials have a significant impact on the marketing of cars with fuel-cells to achieve the goals set by the automotive sector.

However, the challenge for success is developing competent hydrogen storage materials with good hydrogen sorption properties at ambient conditions [2]. Among many criteria for ideal solid hydrogen storage medium, excellent hydrogen sorption kinetics and light weight has always been the biggest difficulties to overcome. Some boron- and nitrogen-containing materials are attractive hydrogen-dense compounds because they can satisfy the above criteria (sorption kinetics and light weight). Among them, Ammonia borane, NH<sub>3</sub>BH<sub>3</sub>, which

has a hydrogen capacity of 19.6 wt%, exceeding that of gasoline, has made itself an attractive candidate for chemical hydrogen storage applications [3], but the hydrogen release from solid Ammonia borane is not fast enough and includes the reaction byproduct borazine, which can damage a fuel cell. Another candidate is N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> (hydrazine borane, HB) solid with 15.4 wt% hydrogen capacity, which can release 5.8 wt% H<sub>2</sub> at 140 C in 12 min [4] and can yield 11 wt% H<sub>2</sub> at 150 C in less than an hour after mixing with LiH, has attracted more attention and has been experimentally studied as one novel B-N-based material for hydrogen storage through different routes, such as thermal decomposition, hydrolysis, etc. [5-9]. This material can be easily prepared from a reaction of dihydrazine sulfate with sodium borohydride [4].

Hydrazine borane was discovered in the 1960s [10] but was thereafter little studied [11]. It gained new interest in the recent years [12]. In 2009, Hügle et al. [4] showed that an equimolar mixture of lithium hydride LiH and HB, with a balanced number of protic and hydridic hydrogen atoms (4 H<sup>+</sup> vs. 4 H<sup>-</sup>), is able to dehydrogenate in suitable conditions. In 2012, Moury et al. [7] confirmed the unsuitability of hydrazine borane in pristine state for solid-state chemical hydrogen storage whereas in 2011 Hannauer et al. [8] showed a real potential for liquid-state chemical hydrogen storage (i.e. catalytic dehydrogenation in hydrolysis conditions). However, HB has not been eliminated as a candidate solid-state chemical hydrogen storage material by the fact that like ammonia borane it can be chemically modified towards formation of derivatives [11].

In this work the hydrazine borane has been investigated with respect to the crystal structure, electronic and chemical bonding properties using first-principle methods based on density functional theory with generalized gradient approximation.

## II. COMPUTATIONAL METHODS

In this study, all the computations have been done using the ABINIT code [13] based on pseudopotentials and planewaves in density functional theory (DFT) [14]. It relies on an efficient fast Fourier transform algorithm [15] for the



conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate-gradient method [16] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [17]. We performed generalized gradient approximation (GGA-PBE) to DFT [18]. Fritz–Haber–Institute GGA pseudopotentials [19] are used to represent atomic cores.

We carefully tested the convergence of our calculations with respect to the plane-wave cut-off and k-point mesh. An energy cut-off of 50 Hartree and a 8x8x8 grid for k-point were used.

### III. RESULTS AND DISCUSSIONS

#### A. Crystal structure

The crystal structure of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> has an orthorhombic structure with the space group Pbcn, No 60) [20]. Moreover, it has 80 atoms (Fig. 1) and contains one occupation sites of each atom (8d) (we have 8 molecule of HB in the unit cell). As shown in Fig. 1, each hydrazine unit N<sub>2</sub>H<sub>4</sub> connected terminally to one BH<sub>3</sub> group to generate one hydrazine borane (HB) molecule, with the BH<sub>3</sub> groups locating in one side of

the N-N bond. It can be considered as a derivative of ammonia borane where the NH<sub>3</sub> moiety is substituted by N<sub>2</sub>H<sub>4</sub>.

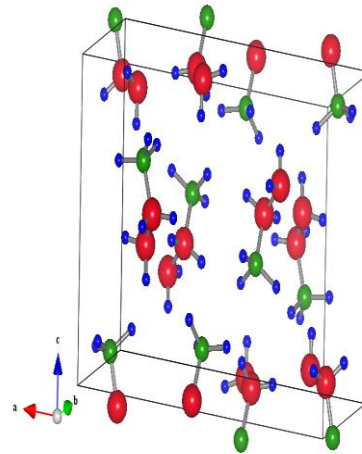


Fig. 1 The unit cell of solid Hydrazine Borane. B is shown as green and medium spheres, N in red and big spheres, and H in blue and small spheres.

TABLE 1 :

CALCULATED LATTICE PARAMETERS AND ATOMIC POSITION OF HYDRAZINE BORANE COMPARED TO THE EXPERIMENT AND OTHER THEORETICAL WORK

	Lattice parameters (Å°)			Atomic position				
	a	b	c	Atom	Site	x	y	z
Exp a:	13.1227	5.100	9.5807			0.6048	0.3628	0.6017
This work:						0.6064(1) a	0.3589(6) a	0.6045(3) a
Other works	13.2202	5.137	9.6519					
b:	12.3400	5.260	9.6600	B1	8d			
				N1	8d	0.6401	0.3809	0.4448
						0.6412(1) a	0.3777(6) a	0.4456(3) a
				N2	8d	0.6598	0.1281	0.3845
						0.6609(1) a	0.1208(6) a	0.3844(3) a
				H1	8d	0.52971	0.2248	0.6039
						0.5309 a	0.2174 a	0.6079 a
				H2	8d	0.6729	0.2689	0.6692
						0.6759 a	0.2654 a	0.6724 a
				H3	8d	0.5849	0.5841	0.6379
						0.5857 a	0.5827 a	0.6413 a
				H4	8d	0.7074	0.4847	0.4345
						0.7099 a	0.4823 a	0.4341 a
				H5	8d	0.5855	0.4762	0.3886
						0.5855 a	0.4742 a	0.3886 a
				H6	8d	0.5986	0.0156	0.4082
						0.5981 a	0.0078 a	0.4078 a
				H7	8d	0.6605	0.1487	0.2793
						0.6617 a	0.1428 a	0.2773 a

<sup>a</sup> ref 20, <sup>b</sup> ref 2

We did a crystal geometry optimization and we relaxed the atomic positions; this relaxation lowered the total energy. The final structure obtained within the PBE GGA approximations

is given in Table 1. The deviation from the experiment [20] is less than 0.75%. Also our results are more accurate than the theoretical calculations of quin et al [2] using the projector



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augmented wave (PAW) with the generalized gradient approximation (GGA) [2]

### B. Electronic structure

The electronic structure is calculated to understand the bonding characteristics of hydrides, and further reveal the mechanism about structural stability. We have calculated the band structure along high symmetry lines as shown in the Fig. 2. In addition, we also plot the total and the decomposed partial density of states (PDOS) of each atom in Fig. 3 and fig. 4.

Fig 2 shows the calculated band structures along the high symmetry point: Z (0,0,1/2), Gamma (0,0,0), X (1/2,0,0), S(1/2,1/2,0), R(1/2,1/2,1/2), Y(0,1/2,0) and T(0,1/2,1/2). The calculated band structures indicated that N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> has a direct wide band gap at Gamma point with a value equal to 5.78 eV little greater than the calculated gap reported by quian et al. [2] the calculated band gap obtained is always equal or smaller than the actual gap, due to the well-known band-gap underestimation in density functional theory calculations [1], so the N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> can be considered as an insulator. In our best of knowledge there are no previous experimental (or theoretical) works on the band structures of this compound.

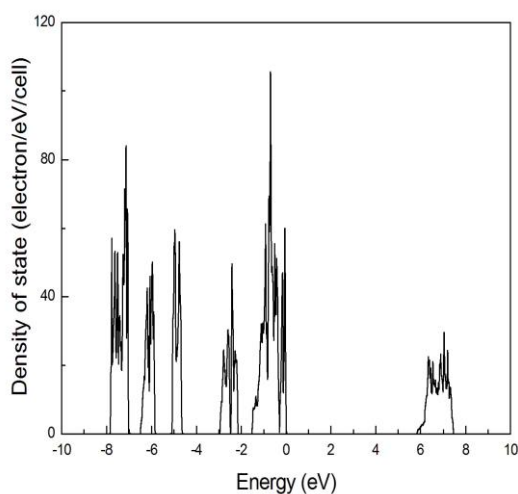


Fig.3: The calculated total electronic density of states (DOS) for Hydrazine Borane solid. The Fermi level is set at zero energy.

Fig. 3 and Fig.4 show the calculated total and partial DOS for Hydrazine Borane solid respectively. It can be seen that the total DOS of Hydrazine Borane comprises two well-separated regions: the region above 5.7 eV (conduction band) and the region below 0eV (region of valence band). This later is also separated to two regions: the region from -2 eV to 0 eV (top of the valence band) and the region below -2 eV (lower

energy region of valence band). The PDOS (fig. 4) shows that the electronic density of states near the Fermi level ( between -2 and 0 eV) is mainly contributed by the B p-states, N (especially the N2 atom) p-states and hydrogen atoms connected to B atom (H1, H2 and H3). However, in the region below -2 eV, is mainly dominated by the N p-states and the hydrogen atoms connected to the two N atoms (H4, H5, H6 and H7). This strong sp hybridization between B and H (B) and between N and H (N) in the valence band leads to the strong bonding occurring between B and H (B) and between N and H (N), which indicates that the chemical bonding in NH<sub>2</sub> and BH<sub>3</sub> are covalent.

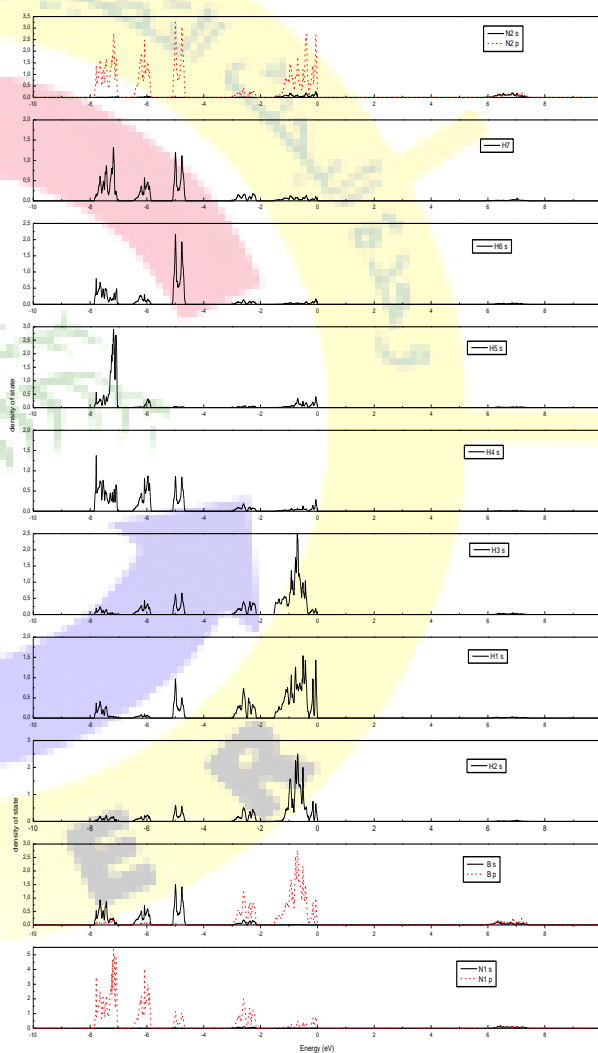


Fig. 4: The calculated partial electronic density of states (DOS) for Hydrazine Borane. The Fermi level is set at zero energy; s-state and p-state contributions are distinguished with black continue and red dashed line respectively.



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#### IV. CONCLUSION

In this paper, we have investigated the hydrazine borane with respect to the crystal structure, electronic properties and chemical bonding for hydrogen storage applications, using first-principle methods based on density functional theory with generalized gradient approximation.

The optimized structures and atomic coordinates are in good agreement with the experimental data. We have found that the calculated band gap indicates that Hydrazine Borane is a wide band-gap insulator.

The calculated total and partial density of states of  $N_2H_4BH_3$  show that near the Fermi level is mainly contributed by the B p-states, N p-states and hydrogen atoms connected to B atom. However, the region below -2 eV, is mainly dominated by the N p-states and the hydrogen atoms connected to the two N atoms. This strong sp hybridization between B and H (B) and between N and H (N) in the valence band leads to the strong bonding occurring between B and H (B) and between N and H (N), which indicates that the chemical bonding in  $NH_2$  and  $BH_3$  are covalent.

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