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Perspective

Atomistic DFT simulations are promising techniques for the discovery of hydrogen storage materials

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ABSTRACT

Efficient hydrogen storage for automobiles necessitates materials with high storage capacities, moderate dehydrogenation temperatures, and rapid kinetics for desorption and absorption. However, there are presently no known materials that exhibit all of these qualities and can be reversed. In this presentation, we provide a summary of our recent endeavours focused on creating a fundamental computational method for identifying new hydrogen storage materials. To ensure effectiveness, this technique necessitates the following essential capabilities: (i) precise forecasting of thermodynamics related to decomposition, (ii) anticipation of crystal structures for hydrides that are not yet identified, and (iii) prediction of preferred decomposition and dehydrogenation temperatures. This study demonstrates the capability of atomistic DFT modelling in identifying new materials suitable for hydrogen storage applications.

Keywords: Atomistic DFT simulations; Hydrogen Storage; Dehydrogenation Kinetics; Crystal Structure Identifications; Database Searching; Lattice Algebra Enumeration

1. Introduction

Hydrogen-powered vehicles require an effective method of storing hydrogen within the vehicle [1]. Presently, the existing technologies are well below the desired storage capacities, both in terms of space and weight [2],[3]. In addition to density, the thermodynamical characteristics of hydrogen insertion and release from its storing media are also of utmost importance. These thermodynamics determine the boundaries for the temperatures and pressures at which the refuelling events may take place. The realistic operational parameters of hydrogen-storing facilities for onboard vehicle applications determine the limits for the kinetics and thermodynamics that are appropriate. Currently, there is a worldwide endeavour to create a substance that can hold hydrogen with a high density in terms of weight and volume [4]. This substance should also enable fast and energy-efficient processes for adding or removing hydrogen at settings that are near room temperature.

The use of solely experimental techniques to find new materials for storing hydrogen through characterization and synthesis is both time-consuming and expensive. This is mostly owing to the large number of potential reaction routes, typically sluggish reaction rates, and the sheer volume of prospective novel compositions. An alternative method to enhance this solely empirical search would involve utilizing a precise, physics-based modelling technique that provides the thermodynamic properties of the substances involved in the process, therefore determining the enthalpies of hydrogen desorption. Here, we outline the methodology we employ. Computational screening of this kind helps expedite the identification of new crystal structures, chemical routes, and material compositions that enhance storage performance [5].

Discovering novel hydrogen storage materials using computational methods presents many substantial challenges: First, predicting the crystal structures of hydrides is another difficult task.

Second, the calculations must accurately determine the reaction energies of (de)hydriding processes quantitatively. This is necessary to obtain a precise understanding of the thermodynamics of these reactions, allowing for the confident identification of promising reactions and the elimination of thermodynamic 'dead ends'. Third, forecasting the paths of hydride decomposition and dehydrogenation temperatures: this frequently disregarded difficulty is equally crucial. The novel hydride material has the potential to solely provide the materials for a new-fangled hydrogen storage process. However, identifying the most thermodynamically favourable materials for releasing hydrogen in new storage reactions may be a challenging task. According to the target of US-DOE for 2025, the hydrides which have 5.5 gravimetric storage capacity, 40 gH_2/l volumetric storage capacity and the dehydrogenation temperature ranging from 233 to 333 K can be utilized for practical applications [3, 5].

This article presents a computational method that uses first-principles DFT simulations to find new materials for storing hydrogen. In the present article, we outline our strategies for addressing the three main obstacles in developing this technique and showcase the utility of DFT computations in the field of materials research.

2. First-principles calculations

First-principles DFT calculations are fundamental in the fields of computational materials science and quantum chemistry. They leverage the core principles of quantum mechanics to offer insights into the characteristics of materials as shown in Figure 1. The use of a plane wave basis set is a feature of these calculations providing a powerful framework for representing electronic wave functions. By expressing wave functions in terms of plane waves this method enables a precise description of the electronic structure. Additionally, pseudopotentials play a role by defining how valence electrons interact with cores simplifying computations by replacing core electrons with an effective potential. This targeted approach towards electrons enhances both computational efficiency and accuracy. While these techniques have significantly improved our understanding of materials and molecules ongoing research focuses on refining pseudopotential and basis set selections to enhance the accuracy of exchange-correlation functionals. Nonetheless, first-principles DFT calculations remain essential, for analyzing and predicting the behaviours of materials contributing significantly to technological advancements and discovery of innovative materials. The field of chemistry and materials science benefits, from a variety of DFT-based software tools as shown in Figure 2, each known for its specific strengths and applications. For example, Quantum ESPRESSO is widely recognized for its efficiency in performing structure calculations for systems [6],[7],[8],[9]. CASTEP is highly regarded for its accuracy and versatility in analyzing state and physical properties [5],[10]. Wien2k excels at modeling the structures of solids especially when studying spectroscopic properties. VASP is well respected for its ability to handle large-scale DFT calculations in the realm of materials science. These software programs along, with Gaussian, NWChem, CP2K and ADF form a collection of tools that enable researchers to explore molecular and materials systems deeply and accurately.

3. Predicting the structure of the hydrides

Predicting the energetics of the dissociation of H_2 storage compounds requires prior knowledge of the energy and crystalline structures. In the case of compounds that have not been created yet, their crystal structures cannot be determined by experimentation. Therefore, a crucial capacity of any atomistic computational method is capable of predicting the crystal structures of the compounds at the ground state energies. We provide two distinct methodologies for addressing the issue of the prediction of the crystal structures.

1. Database searching methods
2. Lattice algebra enumeration

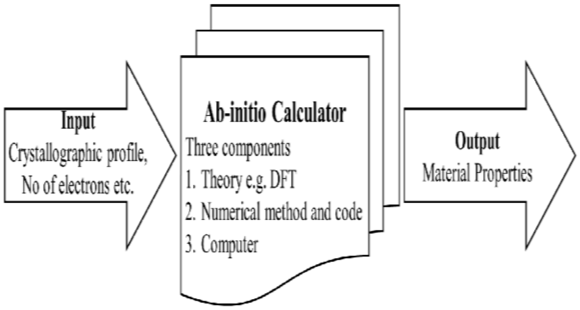

Figure 1: *A Schematic illustration of First-principles calculations using various computational codes*

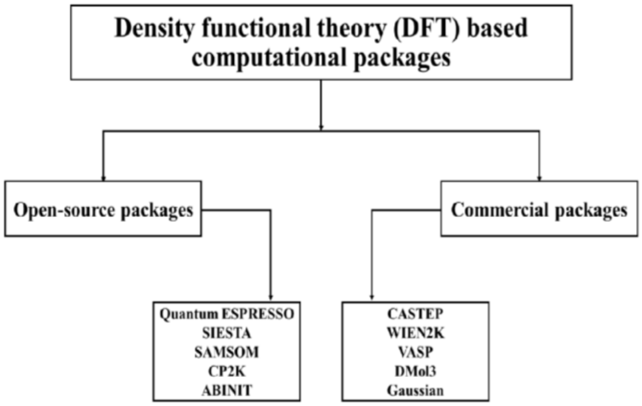

Figure 2: *Some DFT-based computational codes*

3.1. Database searching methods

This method includes looking for similar structural candidates in crystallography databases, like Materials Projects (MP), Automatic Flow for Materials Discovery (AFLOW), Crystallography Open Database (COD), Materials Cloud and Computational 2D Materials Database (C2DB) as presented in Figure 3. This is the first strategy. To begin, one generates a list of potential structures of the required compound from the MP (or another) database by making use of the structures of chemically comparable substances. This is a basic concept. In the following step, DFT computations are carried out on all possible structures to determine which structure has the lowest energy. This is followed by the computation of phonons and the verification of the structure's dynamical stability for the structure or structures with the lowest energy [11],[12]. If the compound is unstable dynamically, one has two options: either one may re-relax by moving atoms across the unstable mode(s) or one can do molecular dynamics (MD) simulations based on DFT to look for lower energy patterns. When dealing with stoichiometries that have pretty common and straightforward chemistries, it is frequently possible to discover a pretty large collection of candidate structures. This gives a substantial pool from which to sample the possible configurations of crystalline structure types. The first approach that has lately gained a lot of popularity in the field of hydride crystal structure research is the database searching strategy.

Figure 3: *Some important databases for the discovery of materials*

3.2. Lattice algebra enumeration

The aforementioned database searching strategy has proven to be highly efficient in several applications. However, it is limited in its ability to accurately anticipate entirely novel crystal structure types that have not been previously observed. Here, we provide a method called lattice algebra enumeration that overcomes this limitation. We demonstrate the application of this technique in the investigation of the composition of Li_2NH, a substance used for hydrogen storage. This approach is feasible because we can observe that the ordering problem can be converted into a binary alloy problem. This enables us to apply proven lattice algebra methods that have been developed in the alloy theory. We examine input architectures with tiny unit cells, where all N-H dimers are arranged in either antiparallel or parallel configurations along certain principal orientations. The task of enumerating various configurations of N–H dimers, given a specific orientational axis, may be conceptually equated to the binary alloy problem on a predetermined fcc lattice. This equivalence arises from the placement of N and Li atoms in a cubic fluorite structural location, resulting in the formation of a fcc sublattice by N. We categorize parallel N–H alignments as 'atoms' of type A and classify antiparallel H–N alignments as atoms of type B. By employing lattice algebra techniques derived from alloy theory, we may systematically list all conceivable organized configurations according to this lattice structure, within a predetermined cell dimension. Through a systematic examination of several organized configurations, we have discovered a stable arrangement of Li_2NH with a low energy level. This arrangement exhibits orthorhombic Pnma symmetry at a temperature of 0 K.

4. Precision of DFT computations in predicting hydrogenation enthalpies

The implementation of DFT has turned into a well-accepted and commonly used method for calculating the binding energies of complex crystals. Because the release of hydrogen reactions results in the production of H_2, and the majority of existing DFT functionals are recognized to have lower accuracy when applied to molecules and atoms compared to larger systems, it is reasonable to question the reliability of the determined DFT formation energies for screening potential hydrogen storage materials. To assess the effectiveness of using DFT for forecasting the thermodynamics of metal hydride hydrogen storage, it is necessary to have a precise grasp of the quantitative accuracy of DFT predictions.

Before that, we conducted a comprehensive investigation on ABH_3 hydride compounds containing Li and Cu [13],[14]. Figure 4 illustrates the dehydrogenation and regeneration reactions for ABH_3 hydrides. In our research, we determined the enthalpies of hydrogen release by employing the generalised gradient approximation (GGA) for the exchange-correlation function. For Cu-based hydrides, we observed that the local-density approximations (LDA) consistently produced larger hydrogenation enthalpies compared to the GGA [13]. We ascribed this difference to how the GGA and LDA models describe the H_2 molecule. Lately, we have employed this method to calculate the thermodynamics of storage reactions for a broad spectrum of hydrides. The utilization of a first-principles approach has led to the derivation of thermodynamic characteristics through calculations that exhibit a strong agreement with actual results. Additionally, we acknowledge recent research in the provided reference that examines the precision of DFT for perovskites [10]. The purpose of this research is to showcase the precision of DFT in predicting the thermodynamic parameters of dehydrogenation processes involving basic binary hydrides of alkaline earth, alkali, and early transition metals, which are generally referred to as M. Although these reactions have little practical utility for hydrogen storage, it is important to thoroughly assess the enthalpies and entropies of these reactions to verify the precision of the existing first-principles electron structure approaches. The metal hydrides undergo decomposition using a subsequent general reaction.

$$MH_p \rightarrow M + \frac{p}{2}H_2 \qquad (1)$$

A possible expression for the enthalpy (ΔH) that corresponds to equation (1) is as follows:

$$\Delta H = \frac{p}{2}\left[E_{H_2}^{tot} + E_{H_2}^{vib} + \frac{7}{2}\kappa_b T\right] + E_M^{tot} + E_M^{vib} - E_{MH_p}^{tot} - E_{MH_p}^{vib} \qquad (2)$$

Here, E^{tot} is total energy whereas E^{vib} is the vibrational energy, which is obtained from the phonon calculations. Wolverton et al [1] have utilized equation (2) for different compounds and they reported that the inclusion of vibrations enhances the accuracy of the predicted ΔH values, which are computed with PBE-GGA functionals. Furthermore, they suggested that the vibrations should be incorporated into the discovery of novel materials for hydrogen storage.

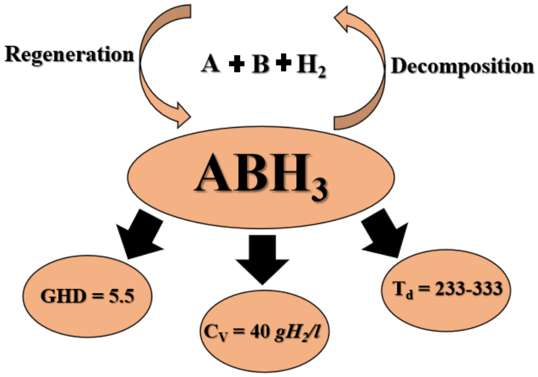

Figure 4*:* *A general representation of regeneration and decomposition reactions for ABH_3 hydrides.*

5. Decomposition and dehydrogenation temperatures

Decomposition and dehydrogenation temperatures play roles in the field of materials, particularly in relation, to how they impact hydrogen storage and release. These temperatures are indicators of the stability and hydrogen desorption properties of hydride materials significantly influencing their practical use in storing hydrogen. The decomposition temperature marks the point at which a hydride material breaks down thermally releasing hydrogen gas. On the other hand, the dehydrogenation temperature signifies when the material releases hydrogen through desorption an important factor in assessing its suitability for storing and retrieving hydrogen. These temperatures vary significantly depending on the composition, structure and inherent characteristics of the hydride material being studied. Understanding and optimizing these temperatures are steps in developing effective hydrogen storage materials. Therefore, researchers are actively seeking hydride systems, with decomposition and dehydrogenation temperatures to enhance the potential of using hydrogen as an energy source. It is interesting to note that the atomistic DFT computation gives highly accurate predictions about the decomposition and dehydrogenation temperatures of the hydrides as calculated in the previous work [3-5]. We can calculate the dehydrogenation temperatures for the hydride materials by using the following equations.

$$\Delta G = \Delta H - (T_d \times \Delta S) \qquad (3)$$

Where ΔS is the change in entropy of the system and T_d is the dehydrogenation temperature for the hydrides. By increasing temperature $\Delta G \approx 0$, So, equation (3) can be modified to equation (4) as given below [15].

$$T_d = \frac{|\Delta H|}{\Delta S} \qquad (4)$$

6. Conclusion

Atomistic DFT calculations were usually limited to theoretical physicists, and may now be widely utilized in several fields of materials research that are directly applicable to industry. Additional proof of the effectiveness of this method may be observed in our recent endeavours focused on the exploration of novel materials for storing hydrogen. Currently, no material possesses the necessary combination of high storage densities, suitable dehydrogenation temperatures and cost-effectiveness required for use in onboard applications. It is necessary to develop new hydrides that have improved characteristics. Two examples of approaches for identifying ground-state crystals of novel materials were presented: one of them is database searching whereas the other is lattice algebra enumeration. These approaches are essential because the precision of any thermodynamic forecast based on fundamental principles would be influenced by the crystalline geometry of the phases being studied. Both techniques have demonstrated efficacy in detecting low-energy phases. Further study in this field is strongly recommended, particularly in situations when the available database of potential structure prototypes is limited. Overall, these qualities make DFT computing an important tool for estimating the thermodynamics of hydrogen storage processes. Nevertheless, it is crucial to acknowledge that while having favourable thermodynamics is vital, it is not enough to ensure the creation of appropriate hydrogen storage materials. The dynamics of hydrogen absorption and release will also have a significant impact and should be taken into account in any comprehensive analysis of hydrogen storage.

Data availability statement: The whole data of this research is included in this article.

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Author contribution: Zunaira Bibi wrote the original draft, Mubashar Ali contributed to the conceptualization, writing, reviewing and editing of the original draft, Masood Yousaf contributed to reviewing and editing the original draft, Ahsan Zafar conducted a formal analysis of this work.

Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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