Using density functional theory to study hydrogen diffusion in metals: A brief overview

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Abstract

Density functional theory (DFT) calculations have become a valuable complement to experimental methods for studying the structures and dynamics of H in metal hydrides. This article gives an overview of applications of DFT to the diffusion of H and its isotopes in metals, including pure metals, ordered alloys, and disordered alloys. Several examples are used to illustrate how DFT can be used to predict hopping rates due to activated transport and due to tunnelling using methods that can be applied to large numbers of distinct interstitial sites. The application of DFT to examples where clustering of interstitial H atoms occurs such as Sc is also described.
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1. Introduction

In recent years, first principles calculations based on density functional theory (DFT) have been applied to complement well established experimental methods for studying the diffusion of H and its isotopes in metals and other solids such as metal oxides. This trend mirrors the similar growth in influence of DFT calculations in areas such as heterogeneous catalysis [1]. Several books and reviews covering the basic theory of DFT are available [2–5]. DFT calculations have an impressive set of advantages relative to other theoretical tools: they can be applied to arbitrary configurations of atoms including all elements in the periodic table, they provide direct information on the ground state energy of these configurations, and they can be used to predict the precise mechanism of diffusion or reaction events in condensed phases. These advantages are balanced by at least two important caveats. First, the size of systems that can be treated DFT is strongly limited by the considerable computational effort involved. Second, DFT calculations are not exact because they involve approximations for electron

exchange-correlation effects [6]. It is, therefore, important to establish what level of accuracy can be expected from these calculations.

The aim of this paper is to give an overview of recent applications of DFT to the diffusion of H in metals. As described in Section 2, much of this work has concentrated on dilute concentrations of H under conditions where H diffuses by activated hopping. This section describes calculations for three types of materials in order of increasing structural complexity: pure metals, binary intermetallics, and disordered alloys. Section 3 describes how DFT has been applied to describe tunnelling contributions to diffusion and to situations where short-range pairing of H or the creation and clustering of vacancies can occur. Section 4 suggests several directions where DFT calculations should be able to make useful contributions to other regimes of H diffusion that are of technological interest.

2. Activated hopping at dilute H concentrations

Diffusion of H between interstitial sites in metals under many conditions of technological interest occurs via thermally activated hops. In this situation, the hopping rates between adjacent sites are well described by transition state theory (TST). The calculations described below for diffusion of H at dilute concentrations all made the assumption that H vibrations are decoupled

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from phonons of the solid. The temperature dependent hopping rate out of a site, k, can then be expressed as [7]

$$k = \Gamma \exp\left(\frac{-E_a}{kT}\right), \tag{1}$$

where

$$\Gamma = \frac{\prod_{i=1}^{3} \nu_i f(h\nu_i/2kT)}{\prod_{j=1}^{2} \nu_{TS,j} f(h\nu_{TS,j}/2kT)}. \tag{2}$$

In these expressions, $f(x) = \sinh x/x$, $\nu_i(\nu_{TS,i})$ are the H vibrational frequencies at the interstitial site (diffusion transition state), and E_a is the classical activation barrier, defined by the energy difference between the interstitial site and the transition state. Eq. (2) includes the effects of multiple quantized vibrational energy levels for H. At temperatures low enough that only the ground state vibrational level is populated (but not so low that diffusion does not occur via activated hopping), the temperature dependence of Eq. (1) simplifies considerably to

$$k \sim \exp\left(\frac{-[E_a - E_{ZP} + E_{ZP}^{TS}]}{kT}\right), \tag{3}$$

where $E_{ZP}(E_{ZP}^{TS})$ is the zero point energy of H at the interstitial site (transition state).

To predict hopping rates from DFT calculations using the formalism above, it is necessary to optimize the geometry of H in an interstitial site and a transition state, including the effects of lattice relaxation, and to compute the vibrational frequencies of H in these two locations. To assess anharmonic corrections to the harmonic version of TST presented above requires a larger number of calculations to describe the full potential energy surface for H in the vicinity of the interstitial site. These calculations are feasible for specific examples where high precision information is desired [8], but it is not practical to apply this approach to materials where large numbers of distinct sites need to be characterized.

2.1. Dilute H in pure metals

Kamakoti and Sholl used the formulation above to predict the diffusivity of H in pure Pd using DFT [9,10]. This is a useful example for examining the accuracy of DFT for H diffusion in metals because a large collection of experimental measurements are available that show excellent consistency [11,12]. The calculations confirm the well established facts that interstitial H in Pd prefers O sites rather than T sites, and that diffusion of H occurs by a hop from an O site into a metastable T site followed by a hop from the T site into another O site. The barrier for the latter hop is much smaller than the O to T hop, so it is the O to T barrier that is observed experimentally. The DFT-predicted classical barrier for O to T hops is 0.16 eV. After including zero point effects as in Eq. (3), the DFT-predicted barrier increases to 0.24 eV. This result is in excellent agreement with the exper-

imentally determined value of 0.23 eV. Once the parameters in Eq. (3) are known for H, it is straightforward to predict the hopping rates for D or T. The DFT predictions for the activation energies of D and T diffusion in pure Pd are 0.22 and 0.21 eV, respectively. Again, these are in very good agreement with the experimental observations of 0.21 and 0.19 eV.

A more careful comparison between DFT and experiment can be made by using Eqs. (1) and (2) to predict the temperature dependent hopping rates for O to T and T to O hops and directly computing the resulting diffusivity of H [10]. Fitting these diffusivities to the simple Arrhenius form $D = D_0 \exp(-E_d/kT)$ for $400 < T < 700$ K gave $D_0 = 3.1 \times 10^{-7}$ m^2 s^{-1} and $E_d = 0.21$ eV. Volkl and Alefield [11] used the same fitting procedure for a compilation of low and moderate temperature data and obtained $D_0 = 2.9 \times 10^{-7}$ m^2 s^{-1} and $E_d = 0.24$ eV.

Similar DFT calculations for diffusion of H in bcc Fe have been performed by Jiang and Carter [13]. These calculations showed that H in bcc Fe hops directly between adjacent T sites. An alternative mechanism involving hopping through O sites is less favorable. Jiang and Carter calculated the classical activation energy for T to T hops to be 0.088 eV, and this value is reduced to 0.042 eV after including zero point corrections as in Eq. (3). The extant experimental data for H diffusion in Fe is less precise than for Pd, but Jiang and Carter's results are entirely consistent with the experimentally observed diffusivities. It is useful to note from the results of pure Pd and Fe that the effect of zero point corrections in Eq. (3) can either increase or decrease the hopping activation energy, depending on the details of the material.

2.2. Dilute H in binary intermetallics

The mechanisms of H diffusion in ordered metal alloys, e.g., bcc CuPd, or intermetallics, e.g., Laves phase materials, can be considerably more involved than in pure metals. Interpreting experimental measurements of diffusion in these materials is often challenging because multiple distinct local processes contribute to net diffusion. DFT calculations can play a useful role in understanding these materials because they can be used to directly predict the site energies for each relevant interstitial site and the hopping rates for each type of local hop. Once these quantities are available, exact expressions are available to predict net diffusion coefficients, even for materials with complex unit cells [14].

The first application of DFT to H diffusion in Laves phase materials was a series of calculations by Bhatia, Luo, Sholl, and Sholl for C15 HfTi$_2$H$_x$ with $x \sim 4$ [15]. This example was chosen because of the availability of experimental data for both H diffusivities and nuclear spin relaxation rates. The DFT calculations correctly reproduced the experimental observation that the C15 crystal structure is not stable for HfTi$_2$ but becomes stabilized by the presence of interstitial H. Interstitial H in the C15 structure can exist in two distinct sites, e and g, with the e site being preferred in HfTi$_2$H$_x$. A third class of interstitial sites, d sites, also exists in this structure, but occupation of these sites by H is highly unfavorable [15]. Five distinct local hops can occur in this crystal structure: e to e, e to g, g to e, and two distinct g to g hops.

DFT calculations similar to those described above for pure Pd were used to predict the rate of each of these hops. The activation energies predicted by these calculations were used as the starting point to simultaneously fit the available diffusion and spin relaxation experimental data to a model that included all possible types of hops. This approach illustrates what may be one of the most useful applications of DFT to studying H diffusion in ordered materials, namely, using DFT to provide quantitative information on local processes to constrain modeling of experimental data in complex materials.

A useful feature of DFT calculations is that once a material with a particular crystal structure has been studied, it is relatively straightforward to perform similar calculations for other materials with the same crystal structure. As an example of this approach, Bhatia and Sholl examined a series of C15 AB_2 intermetallics, namely, ZrX_2 with X = V, Cr, Mn, Fe, and Co [16]. All of these materials have been studied experimentally except $ZrMn_2$, which forms the C14 structure experimentally [17]. Site preferences for H in these materials had been examined in earlier DFT calculations by Hong and Fu [17]. Fig. 1 compares the DFT results with experimental data for $ZrCr_2$. This figure shows predictions made using Eqs. (1) and (2) as a dashed line, as well as a solid curve that shows results for an extended version of TST (discussed in Section 3.1) that include tunnelling contributions. It can be seen from Fig. 1 that the simplest version of TST (i.e. Eqs. (1) and (2)) slightly overestimates the activation energy of H diffusion in the upper temperature range for which experimental data is available. Also, this comparison and similar comparisons with experimental data for ZrV_2 and $HfTi_2$ suggest that DFT calculations based on TST as outlined above systematically overestimate the prefactor of H diffusion coefficients. This may occur because anharmonic contributions are important in the precise value of the prefactors for individual hopping rates for these materials, although
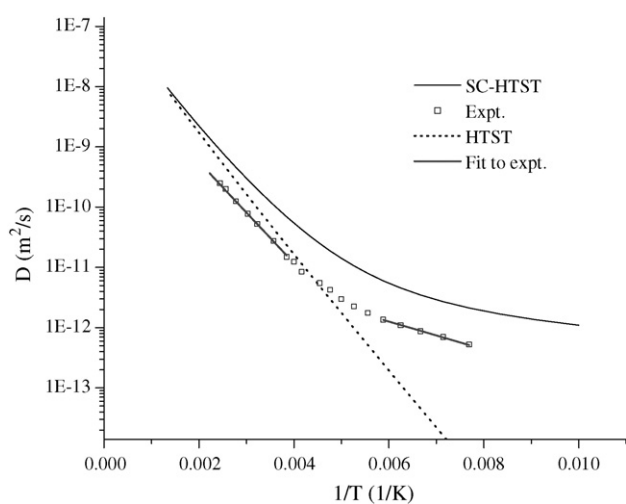
no detailed calculations have been performed to test this hypothesis.

2.3. Dilute H in disordered alloys

There are important conceptual differences between describing H diffusion in ordered materials such as the intermetallics discussed above and alloys that are disordered because of, for example, substitutional disorder. In the former case, a complete description of diffusion is possible if the hopping rates of a finite list of local events are known. For disordered materials, however, the number of distinct local events that can occur is very large, even in the idealized case in which it is obvious how to define the character of these events in terms of the identities of atoms in the vicinity of the diffusing H. H diffusion in disordered materials can be defined in terms of lattice models provided that rules for defining local hop rates for each possible site are established. Various efforts to develop models of this type based on fitting to experimental data have been made [18–23], but the large number of parameters needed to fully define even relatively simple lattice models creates significant uncertainty in this approach. DFT calculations can play a useful role in this area because they can be used to predict the hopping rates of H with complete control over the identity of atoms surrounding the diffusing H.

Kamakoti and Sholl have used DFT calculations to derive lattice models for the diffusion in H in Pd-rich CuPd alloys [10,24]. At most compositions and temperatures, these alloys form a substitutionally disordered fcc crystal [25]. DFT calculations were used to calculate the energy of H in 27 distinct O sites, 54 distinct T sites, and 10 representative diffusion transition states in each of $Cu_{48}Pd_{52}$ and $Cu_{26}Pd_{74}$. These results, together with DFT results for pure Pd, were used to fit the parameters in a lattice model that defined the binding energy of H in arbitrary O and T sites and the transition states separating these sites as functions of the local arrangement of Pd and Cu atoms on the fcc lattice and the alloy lattice constant. Once this lattice model was defined, Monte Carlo simulations were used to predict net diffusion coefficients in the disordered alloy as a function of temperature and alloy composition. The predicted diffusion coefficients from this model for fcc CuPd alloys are shown in Fig. 2.

Because the lattice model mentioned above defines the energies of H in each interstitial site, it can also be used to directly predict the solubility of H in the alloy [24]. By predicting both the H diffusivity and solubility from a DFT-based model, the permeability of H through an alloy membrane in the limit that transport through the membrane is limited by bulk transport of interstitial H is obtained. It is noteworthy that this prediction requires no experimental data apart from identification of the crystal structure of the alloy. Comparisons of first-principles predictions of membrane permeability with experimental measurements using alloy foils for CuPd alloys indicate that this theoretical approach accurately captures the variations in permeability observed experimentally with temperature and alloy composition [24]. This comparison involved both CuPd alloys in an fcc structure and the partially ordered bcc CuPd alloy that forms for a limited range of compositions and temperatures.

Fig. 1. Theoretical and experimental results for the diffusivity of H in $ZrCr_2$. Experimental data is from Renz et al. [65] with fits from Majer [66] The dashed line is the result of harmonic TST as determined from DFT calculations, while the upper solid curve shows semi-classical harmonic TST results. Reproduced by permission from Bhatia and Sholl [16] (copyright 2005 by the American Physical Society).
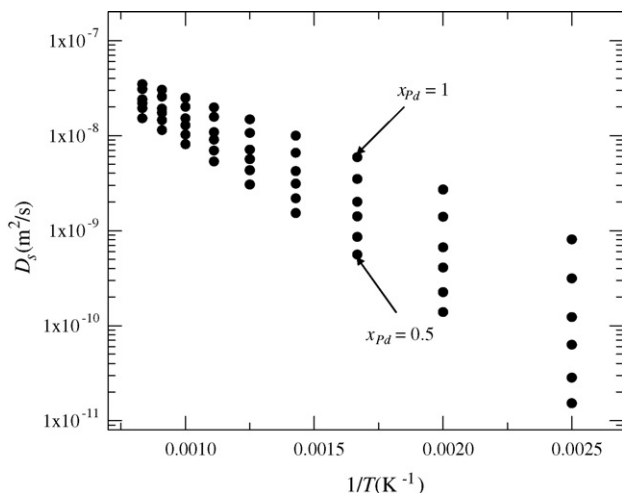
Fig. 2. Diffusion coefficients of H in fcc CuPd alloys predicted using a DFT-based lattice model, with x_{Pd} denoting the fractional content of Pd in the alloy. Results are shown (in descending order at each temperature) for pure Pd, and $x_{Pd} = 0.9$, 0.8, 0.7, 0.6, and 0.5. Reproduced by permission from Kamakoti and Sholl [10] (copyright 2005 by the American Physical Society).

The good agreement between first-principles predictions for CuPd alloys and experimental tests with alloy membranes suggest that these theoretical tools may be useful for screening ternary alloys for membrane applications prior to experimental studies. Initial work in this direction has been done by Kamakoti and Sholl, who extended their DFT-based lattice modeling of fcc CuPd alloys to ternary alloys containing small amounts of a third metal [26]. Two complications that already exist for binary alloys and that becomes more acute for ternary alloys are to define lattice models that capture the relevant physical parameters that determine local hopping rates and to demonstrate that a sufficient set of DFT results are available to fit these parameters with reasonable statistical certainty. In the work mentioned above, this problem was handled in a somewhat *ad hoc* manner by considering a small number of possible models. A more rigorous approach to this problem would be to adapt the cluster expansion method that is well developed for studying ordering of metal atoms within alloys [27,28]. This method can be used to rapidly select the best models from very large classes of possible models and to then indicate if additional DFT calculations are needed to improve the reliability of the DFT data set used in fitting the final model.

3. Other aspects of H diffusion in metals

3.1. Tunnelling

The fact that quantum mechanical tunnelling of H between interstitial sites in metals can make significant contributions to H diffusion is well known [29,30]. DFT can be used to make quantitative predictions about these effects by computing the potential energy surface for interstitial H and applying a suitable theoretical formalism to this potential energy surface. The most detailed approach to this problem has been in the work of Sundell and Wahnström, who have used the

small polaron theory of phonon assisted tunnelling for H diffusion in bcc Nb and Ta [8]. Sundell and Wahnström have used similar methods to examine tunnelling effects in the diffusion of H on a Cu(1 0 0) surface [31,32]. In both examples, very good agreement between theoretical predictions and experimental observations was found. Unfortunately, applying these methods to any individual hopping process of interest is relatively time consuming, so it is difficult to envision using this approach to describe diffusion in materials such as substitutionally disordered alloys where many individual events must be characterized.

A more approximate formalism to account for tunnelling effects is the semi-classical harmonic TST (SC-HTST) approach of Fermann and Auerbach [16,33]. A key approximation in this approach is that there is no explicit coupling between the degrees of freedom of the diffusing atom and lattice phonons or conduction electrons. The important advantage of this approach is that it only requires the same information already needed to apply Eqs. (1) and (2), namely, the energy of H in the interstitial site and at the relevant transition state and the harmonic vibrational frequencies of H in each of these locations, including the imaginary frequency associated with the unstable direction on the potential energy surface at the transition state. The solid curve in Fig. 1 was computed using this SC-HTST approach [16]. At high temperatures, the SC-HTST approach agrees with the result of Eqs. (1) and (2). At lower temperatures, however, the inclusion of tunnelling causes curvature in the Arrhenius plot of the diffusion coefficient. As noted above, DFT overpredicts the diffusion prefactor for H diffusion in ZrCr$_2$. The striking feature of Fig. 1, however, is how well the temperature dependent diffusion activation energy predicted using this DFT-based approach agrees with the experimental data. The high and low temperature fits to the experimental data shown in Fig. 1 yield activation energies of 0.161 and 0.049 eV, respectively. Fitting the DFT-based results in the same range of temperatures yields activation energies of 0.167 and 0.046 eV. This SC-HTST approach also gives a simple prediction for the temperature below which tunnelling contributions become significant. For ZrCr$_2$, this crossover temperature is predicted to be ∼200 K.

Bhatia and Sholl also applied the SC-HTST approach to DFT calculations for H diffusion in bcc CuPd [16]. Experimental measurements at various temperatures have been reported for H and D diffusion in this ordered alloy [11,34,35]. The temperature dependent diffusion activation energies predicted by the DFT calculations are entirely consistent with the variation in reported experimental values, indicating that tunnelling contributions to H diffusion are important for $T < 200$ K in bcc CuPd.

It is worth reiterating that the SC-HTST formalism of Fermann and Auerbach requires no information that is not already calculated when using DFT calculations to predict H hopping rates between interstitial sites using standard harmonic TST. In other words, the SC-HTST method makes it possible to routinely estimate the importance of tunnelling contributions in any situation where DFT is applied to examine H diffusion in metals. If highly accurate information is required for cases where these contributions are found to be large, it would be appro-

priate to apply the more rigorous and time-consuming methods introduced by Sundell and Wahnström.

3.2. Pairing

All of the discussion above has been related to interstitial H at low concentrations in metals. In this regime, H diffusion can be characterized by examining motion of an isolated H atom through representative interstitial sites if cooperative effects involving multiple H atoms can be neglected. It is important to note that there are some examples where this approach is not justified. To illustrate how DFT calculations can be applied to these examples, we will briefly examine the diffusion of H at low concentrations in the hcp metals Sc, Zr, Hf, and Mg.

All of the calculations reported below were performed using plane wave DFT calculations with the PW91 GGA functional using a supercell with 54 atoms of the hcp metal and 1 or 2 H atoms. The details of these calculations were very similar to our earlier work [15,16]. The crystal structure of hcp metals typically shows a slight contraction of the c/a ratio relative to ideal spherical packing, [36] and this effect is also seen in our DFT calculations. For example, the experimental crystal structure of Sc has $a = 3.309$ Å and $c/a = 1.594$, [36] while our calculations give $a = 3.306$ Å and $c/a = 1.544$. All DFT calculations below were performed with the DFT-optimized crystal structure of the hcp metals. All energies reported below include zero point corrections within the harmonic approximation.

Table 1 summarizes the energy difference between isolated H atoms in T and O sites of Sc, Zr, Hf, and Mg obtained from DFT, δE_{TO}. This energy is defined so that positive values imply that the T site is the energetically favored site. Results are also shown for D and T atoms. In Sc and Mg, T sites are favored over O sites for all isotopes of H. T and O sites are almost equivalent in energy for H in Hf, and in Zr the O site is favored over the T site.

Motivated by experimental observations of pairing or clustering of H at low concentrations in Sc, [37–43] we examined the energy of a pair of H atoms in all possible nearby interstitial sites in Sc. As might be expected, placing a pair of H atoms very close together, for example, in adjacent T and O sites, is energetically unfavorable compared to placing H atoms in the same sites with a large spatial separation between them. Crucially, however, there is one configuration that is energetically favorable. When H atoms are placed in T sites separated by a Sc atom along the c axis, the energy of this pair is 0.108 eV lower than having the H atoms in well separated T sites. This

Table 1
Values of δE_{TO} for isolated H, D, and T atoms in four hcp metals as computed using DFT

Metal	δE_{TO} (H)	δE_{TO} (D)	δE_{TO} (T)
Sc	0.045	0.063	0.072
Zr	−0.054	−0.029	−0.017
Hf	0.006	0.034	0.047
Mg	0.049	0.075	0.087

All energies are shown in eV.

Table 2
Values of the pairing energy, δE_{pair} for H, D, and T pairs in four hcp metals as computed using DFT

Metal	δE_{pair} (H)	δE_{pair} (D)	δE_{pair} (T)
Sc	0.108	0.108	0.108
Zr	0.078	0.083	0.085
Hf	0.047	0.051	0.053
Mg	0.012	0.012	0.012

All energies are shown in eV.

is entirely consistent with experimental studies of H in Sc [37–43].

To examine whether pairing of H atoms along the c axis will occur in the other hcp metals, DFT calculations were performed for Zr, Hf, and Mg for the same pair of interstitial sites as is favored in Sc. The results are summarized in Table 2, where the pairing energy is the energy difference between the paired state and well-separated interstitial atoms with the convention that the pairing energy is positive if pairing is energetically favored. It can be seen from these results that the tendency for pairing is strongest in Sc, but is also considerable in Hf. The predicted isotopic dependence of this effect in Sc and Hf is weak. Because O sites are favored for individual H atoms in Zr (see Table 1), it is more appropriate to compare the energies of paired H atoms in Zr with the situation when the separated atoms are in O sites. This calculation predicts that isolated O sites are weakly preferred for H, but for interstitial T in Zr the formation of paired states in adjacent T sites is favored relative to the separated O sites.

The results above indicate that the diffusion of H at low concentrations in Mg and Zr can be understood in terms of the hopping of individual H atoms. DFT calculations were performed to characterize the transition states for hops between adjacent O sites and between T and O sites in each of these metals. Including zero point corrections as in Eq. (2), these calculations predict that the dominant energy barrier to long-range diffusion in Mg is the T to O hop, with an activation energy of 0.21 eV. Hops between adjacent O sites in Mg proceed with a lower barrier of 0.14 eV. These barriers are similar to those calculated with DFT by Vegge for the diffusion of H into interstitial sites in Mg from a clean Mg(0 0 0 1) surface [44]. The activation energies for H diffusion in Zr are considerably larger. Diffusion in Zr will be dominated by the energy barriers to escape from O sites, which are 0.48 eV for hops between adjacent O sites and 0.46 for hops from an O site into an adjacent T site.

In the two hcp metals analyzed above where pairing of interstitial H is favored, Sc and Hf, accurately predicting the diffusivity of H will require a treatment that includes the temperature-dependent balance between paired and isolated interstitial atoms and further DFT calculations to predict the activation energies associated with hops into and out of paired states. It would be interesting to pursue this analysis as a route towards providing a microscopic description of the experimental observations that have been reported for these metals [37–43]. Another valuable future use for the types of calculations described above will be to examine the possibility that pairing or

similar phenomena occur in metals with more complex crystal structures than the hcp metals considered here.

3.3. Vacancy creation and clustering

The discussion of hcp metals in the previous section gave one example where it can be energetically favorable for H atoms to cluster together in metals. A more dramatic example of this general phenomenon occurs when the role of H on the formation and behavior of vacancies in metals is considered. The influence of H on vacancy stability and clustering in metals has been examined using DFT by Lu and Kaxiras for Al [45] and a range of fcc metals by Zhang and Alavi [46]. Lu and Kaxiras showed that many H atoms can become trapped at an isolated vacancy in Al; only when more than 12 H atoms were clustered around a vacancy does the trapping energy for H become unfavorable. A significant implication of this observation is that H can substantially reduce the formation energy of vacancies in Al. This reduction in energy can be enough to make clustering of vacancies favorable, a situation that does not occur in bulk Al. The calculations of Zhang and Alavi are complementary to those of Lu and Kaxiras because they consider the role of vacancies in fcc metals with large H concentrations. Although neither of these studies specifically considered the diffusion of H or of vacancies, there are clearly interesting opportunities to use DFT calculations to probe these issues and in doing so to complement experimental studies of vacancy formation in metal hydrides.

4. Outlook

This article has given an overview of applications of DFT calculations to the diffusion of H in metals. This overview is not intended to be exhaustive; the topics covered above are just one part of the larger impact that DFT calculations can have on understanding the properties of H in solids. H diffusion in metal oxides [47–49] and semiconductors [50–52] has also been studied using DFT. DFT calculations are also playing an important role in screening metal hydrides for H_2 storage applications, [53–56] and for examining reaction mechanisms related to reversible H_2 storage in complex hydrides [57–60]. It is, perhaps, stating the obvious to comment that these approaches will continue to be of enormous use to complement experimental studies for the foreseeable future. It is important to realize, however, that DFT calculations cannot be expected to "replace" experimental observations. It is crucial to remember that these calculations are not exact and that they have important limitations that are dictated by the computational cost of examining materials defined by more than ~100 independent atoms. The greatest opportunities for DFT (or any theoretical approach) to make a lasting impact in this field are when it is used in close conjunction with creative and careful experimental work.

I conclude by identifying several topics within the study of hydrogen–metal interactions where first-principles methods appear poised to make advances in the near future. The work described above was mainly focused on H diffusion at low concentrations. In the potential application of complex metal hydrides to reversible H_2 storage, it is of course desirable to cycle a material over a wide range of H concentration. It would be useful to develop detailed descriptions of the diffusion (and other potentially rate-controlling processes) of H over the full composition history required for these processes. There are also considerable opportunities in using DFT to examine potential routes to enhancing the properties of metal membranes for H_2 purification of metal hydrides for H_2 storage via the substitution of small concentrations of metals in alloys or hydrides with known properties. DFT and related atomically detailed calculations can also potentially be used to test the viability of enhancing cycling kinetics in metal hydrides by using nano-sized particles [61,62]. Finally, there have been successful examples of using DFT to "design" metal catalysts with improved properties relative to known materials, [63,64] and it is clearly possible to contemplate using similar strategies in the search for effective catalysts to enhance the reaction kinetics of complex hydrides.

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