# letters to nature

## Universal alignment of hydrogen levels in semiconductors, insulators and solutions

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**Hydrogen strongly affects the electronic and structural properties of many materials. It can bind to defects or to other impurities, often eliminating their electrical activity: this effect of defect passivation is crucial to the performance of many photovoltaic and electronic devices[1,2]. A fuller understanding of hydrogen in solids is required to support development of improved hydrogen-storage systems[3], proton-exchange membranes for fuel cells, and high-permittivity dielectrics for integrated circuits. In chemistry and in biological systems, there have also been many efforts to correlate proton affinity and deprotonation with host properties[4]. Here we report a systematic theoretical study (based on *ab initio* methods) of hydrogen in a wide range of hosts, which reveals the existence of a universal alignment for the electronic transition level of hydrogen in semiconductors, insulators and even aqueous solutions. This alignment allows the prediction of the electrical activity of hydrogen in any host material once some basic information about the band structure of that host is known. We present a physical explanation that connects the behaviour of hydrogen to the line-up of electronic band structures at heterojunctions.**

Hydrogen exhibits qualitatively different behaviour depending on the host into which it is introduced. As an isolated interstitial impurity, hydrogen can occupy a number of different lattice sites and significantly modify the host structure, to the point of breaking host-atom bonds. It can act as either a donor ($H^+$) or an acceptor ($H^-$)—that is, it is amphoteric—and has mostly been found to counteract the conductivity caused by extrinsic dopants[1,5]. In some cases, however, hydrogen has been found to act as a source of conductivity[6–8]. This highly host-dependent behaviour raises questions about the underlying physical mechanisms. Some experimental information about interstitial hydrogen is available[1,5,7], but to investigate the trends that are the subject of the present study we have relied on *ab initio* methods, which allow us to screen systematically a large range of systems and properties to identify underlying relations and hidden rules. Our calculations for a representative set of semiconductors and insulators allow us to establish a connection between hydrogen's electrical characteristics

and the line-up of band structures of the host materials on an absolute energy scale. This line-up is a physics problem in its own right, with important technological applications[9]. We will demonstrate that the alignment of the hydrogen level extends to aqueous solutions, highlighting its true universality.

Our approach is based on density-functional theory (DFT) within the local density approximation (LDA) and the pseudopotential-plane-wave method[10,11]. The key quantities that determine the properties of hydrogen are (1) the formation energy, that is, the energy needed to incorporate H in the host, and (2) the electronic transition level, which defines the electrical behaviour. We obtain the formation energy of interstitial H in charge state $q$ (where $q = -1$, 0 or $+1$) by placing H in a volume of host material (a periodically repeated supercell), calculating the total energy $E_{tot}(H^q)$ of this structure, and subtracting the energy $E_{tot}(bulk)$ of a corresponding volume of pure host material:

$$E^f(H^q) = E_{tot}(H^q) - E_{tot}(bulk) - 1/2E_{tot}(H_2) + qE_F \quad (1)$$

Here the reference for the hydrogen energy is given by an $H_2$ molecule at temperature $T = 0$. The last term in the formation energy accounts for the fact that $H^+$ donates an electron, and $H^-$ accepts an electron; the energy of the reservoir with which these electrons are exchanged is the electron chemical potential or Fermi level, $E_F$. The transition level $\varepsilon(q + 1/q)$ between charge states $q + 1$ and $q$ is defined as the Fermi-level position for which the formation energies of these charge states are equal.

Figure 1a illustrates these concepts with the example of H in GaN. $H^0$ is never the lowest-energy state (characteristic of a 'negative-U' system[5]), causing the donor level $\varepsilon(+/0)$ to lie above the acceptor level $\varepsilon(0/-)$. When $E_F$ moves through the bandgap, the stable charge state thus changes directly from positive (for $E_F$ below 2.4 eV) to negative (for $E_F$ above 2.4 eV). This implies that in p-type GaN ($E_F$ close to the valence-band maximum, VBM) $H^+$ is favoured, whereas in n-type GaN ($E_F$ close to the conduction-band minimum, CBM) $H^-$ is stable, providing the basis for hydrogen's tendency to counteract the prevailing conductivity. The Fermi-level position where the positive and negative charge states are equal in energy is labelled $\varepsilon(+/-)$, and plays a crucial role in our theory. This behaviour of hydrogen in GaN is qualitatively very similar to what has been observed or calculated for other materials[1,5], although quantitatively the values of formation energies and transition levels vary over a large range.

In some materials, however, hydrogen exhibits completely different behaviour: Fig. 1b shows that in ZnO, $H^0$ and $H^-$ are always higher in energy than $H^+$, for any Fermi-level position[6]. The fact that only $H^+$ is stable implies that hydrogen acts as a shallow donor, that is, as a source of conductivity. In this case, $\varepsilon(+/-)$ does not lie in the bandgap, but above the CBM. The crucial question that we want to address here is why hydrogen can exhibit such qualitatively different behaviour. A detailed analysis showed no correlation of the
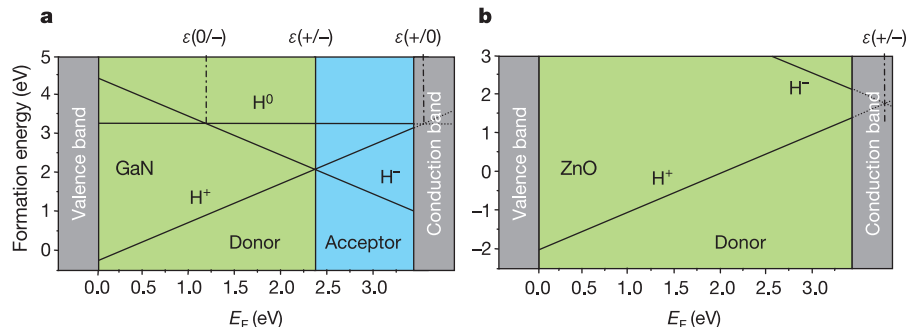


**Figure 1** Formation energy of interstitial hydrogen as a function of Fermi level in two different semiconductors, illustrating the qualitatively different position of the $\varepsilon(+/-)$ level. In GaN (**a**), $\varepsilon(+/-)$ lies within the bandgap, whereas in ZnO (**b**), $\varepsilon(+/-)$ lies above

the CBM. Energies are obtained from DFT-LDA calculations, and the range of $E_F$ corresponds to the bandgap, with $E_F = 0$ at the VBM.

position of the charge transfer level with ionicity, bandgap, cohesive energy, or hydrogen formation energy. However, we discovered a direct link with the position of the band structure on an absolute energy scale. We illustrate this concept with the examples of GaN and ZnO. Both materials have a similar bandgap (~3.4 eV), but when we connect them at an interface the band edges are significantly shifted with respect to one another. This shift is expressed by the valence-band offset, $\Delta E_v$, for which our calculations yield a value of 1.3 eV. Assuming that the hydrogen $\varepsilon(+/-)$ level occurs at the same 'absolute' energy for these two semiconductors, its position at $E_v + 2.4$ eV in GaN would place it at $E_v + 2.4 + 1.3 = E_v + 3.7$ eV in ZnO, that is, well above the ZnO CBM—consistent with explicit first-principles results for hydrogen in ZnO (ref. 6).

Figure 2 shows our results for a large number of semiconductors and insulators. The bands in Fig. 2 have been aligned using calculated valence-band offsets[9,12–14], which agree well with experimental data where available[13,15]. Effects of strain or dipoles at realistic interfaces can be included using the formalism described in ref. 13, but for our present purposes we are interested in the 'natural' band line-ups between unstrained materials. Figure 2 also displays our calculated position of the $\varepsilon(+/-)$ level with respect to the VBM for selected materials. We observe that the $\varepsilon(+/-)$ values exhibit remarkable consistency in terms of their absolute energy across a range of materials. The spread in the values is less than 0.5 eV—a very narrow range, given that the band edges span a range of almost 10 eV. Note that for ZnO the $\varepsilon(+/-)$ level lies above the CBM. Also note that the alignment is quite accurate even in the case of $SiO_2$, an insulator with a bandgap of 9 eV.

We have carried out a number of checks to test the reliability and predictive power of this universal alignment; only a few examples are mentioned here. Figure 2 shows that the expected $\varepsilon(+/-)$ value in InN lies well above the CBM. On the basis of this prediction, explicit first-principles calculations were carried out[8], confirming that only $H^+$ is stable in InN, a result that has profound consequences for growth and doping of this technologically important compound[16]. Figure 2 has also correctly predicted the donor character of H in InGaAsN alloys, in which large bandgap bowing pushes the CBM down below the $\varepsilon(+/-)$ level[17]. Predictions are also possible for H

acting as a shallow acceptor, rather than a shallow donor. The band alignment picture indicates that $\varepsilon(+/-)$ in Ge lies close to the VBM, causing H to act as a shallow acceptor in Ge. $\varepsilon(+/-)$ lies even deeper below the VBM in GaSb, which is known to systematically exhibit unintentional p-type conductivity; the alignment picture suggests that hydrogen could be a source of this conductivity.

Figure 2 establishes a strong correlation between the location of the hydrogen $\varepsilon(+/-)$ level and the band structures on an absolute energy scale. We now address the physics behind this correlation. Alignment of impurity levels in accordance with band offsets has been previously reported, mainly for transition metals[18,19]. Some of the arguments that were put forward to explain these trends focused on a lack of interaction between the impurity and the surrounding semiconductor, describing the electronic levels as directly linked to the vacuum level[18]. Such arguments are clearly inappropriate in the case of hydrogen, which forms strong bonds (with highly host-dependent bond energies) with the host atoms. Other models considered strong interaction[20], but only addressed alignment between semiconductors with similar lattice constants and belonging to the same class (for example, only III–V or only II–VI compounds). We do not invoke such assumptions here.

We propose the following explanation, which is grounded in explicit first-principles calculations but which captures the essence of the physics in a simple molecular-orbital description. Without losing generality, we can take a compound semiconductor CA (where C stands for cation and A for anion) as an example. In the positive charge state H forms a strong bond with the anion[5,6,8]; this results in the creation of a dangling bond on the cation: $db_C$. Cation dangling bonds have energy levels near the CBM (or lowest unoccupied molecular orbital, LUMO); it is thus energetically most favourable to leave them unoccupied, amounting to the formation of $db_C^+$, a cation dangling bond in the positive charge state. Conversely, in the negative charge state H forms a strong bond with the cation, leading to the creation of a dangling bond on the anion. Anion dangling bonds have energy levels near the VBM (or highest occupied molecular orbital, HOMO), and those levels prefer to be fully occupied with electrons, amounting to formation of $db_A^-$. Within this picture, the formation energies of $H^+$ and $H^-$ necessarily strongly depend on the
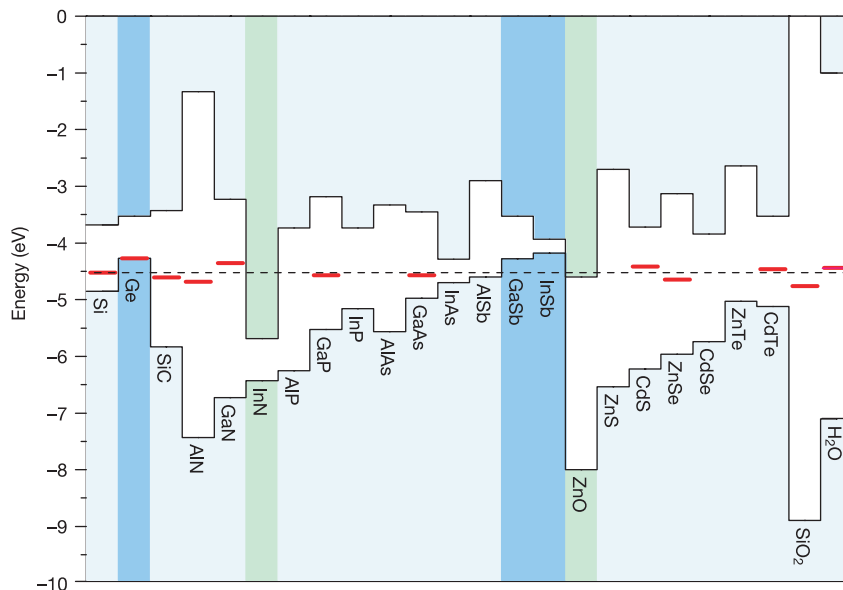


**Figure 2** Band line-ups and position of the $\varepsilon(+/-)$ level for a range of semiconductors and insulators. For each material, the lower line indicates the position of the VBM, the upper line the position of the CBM, and the thick red line the position of the $\varepsilon(+/-)$ level (calculated within DFT-LDA) with respect to the VBM. The band offsets have error bars of $\pm 0.2$ eV. We have chosen the CBM of Si to lie at a value that roughly corresponds to its electron affinity, but electron affinities in general explicitly depend on surface conditions. For $SiO_2$ $\varepsilon(+/-)$ was taken from ref. 3. For $H_2O$, the $\varepsilon(+/-)$ level shown is the potential of the SHE ($-4.44$ eV), and the band edges are the calculated HOMO and LUMO levels of the $H_2O$ molecule (in the absence of reliable information about the band structure of liquid $H_2O$ on an absolute energy scale). The dashed line at $-4.5$ eV is a fit to the available data for the level positions. Materials in which H acts exclusively as a donor (acceptor) are marked in green (blue).

host (as indeed we find from first-principles calculations). But these formation energies are related in the following fashion.

Our key quantity is $\varepsilon(+/-)$, the Fermi-level position where $H^+$ and $H^-$ have equal formation energy. In the model, this occurs when the Fermi level is located midway between $db_C$ and $db_A$. Indeed, to form $H^+$ we need to remove an electron from $db_C$; and to form $H^-$ we need to place an electron in $db_A$. The location of $E_F$ halfway between $db_C$ and $db_A$ corresponds to the 'charge neutrality' level that has been extensively discussed in the literature[21]. Indeed, it is well established that the charge neutrality level can be used to line up semiconductor band structures. If $\varepsilon(+/-)$ coincides with the charge neutrality level, then the alignment of $\varepsilon(+/-)$ in accordance with band line-ups follows directly from the established use of the charge neutrality level for this purpose. A crucial feature is that, within this model, the strengths of the individual H–C and H–A bonds (which are highly material dependent) do not enter into the determination of $\varepsilon(+/-)$. We note that, being a localized deep level, $db_C$ is related to conduction-band states derived from the entire Brillouin zone, and not directly tied to the position of the CBM, which reflects only a single point in the zone. Similarly the $db_A$ state is distinct from the VBM. This explains why $\varepsilon(+/-)$ can fall outside the bandgap.

We point out that the energetic position of $\varepsilon(+/-)$ on our absolute energy scale is about 4.5 eV below the vacuum level. This value is remarkably similar to an important quantity in electrochemistry, namely the chemical potential for electrons under 'standard hydrogen electrode' (SHE) conditions, which is at $-4.44$ eV referenced to the vacuum level (see Fig. 2). This is not a coincidence. The 'normal' or 'standard' hydrogen electrode refers to an $H^+(aq.)/H_2(g)$ electrode in water. In the framework of the present study, the relevant reaction is viewed as formation of $H^+$ (with $H_2$ as the reservoir) in an $H_2O$ host. The equivalent of the $\varepsilon(+/-)$ level for this system can be estimated on the basis of formation energies of hydrated $H_3O^+$ and $OH^-$ (refs 22, 23), resulting in a $\varepsilon(+/-)$ value between $-4.2$ and $-4.5$ eV (reflecting the spread in values for hydration enthalpies), in satisfactory agreement with the potential of the SHE. This alignment, included in Fig. 2, allows a direct connection to an important problem in electrochemistry, namely the prediction of band-edge positions of semiconductors and insulators in contact with water[24].

More generally, we have observed that $\varepsilon(+/-)$ levels based on proton affinities and deprotonation energies[22] for a wide range of molecules fall within a narrow range. Dielectric screening, which is implicitly present in a liquid environment and plays a central role in the charge neutrality level[21], narrows this range even further. The fact that the universality of the alignment extends to aqueous solutions highlights the commonality of driving forces for hydrogen chemistry across a wide range of systems. □

## Methods

The calculations for interstitial H were performed in supercells containing either 64 atoms for zinc blende or 96 atoms for wurtzite. Effects of semicore $d$ states (such as the $3d$ states in Ga or Zn) were included using the nonlinear core correction[11]. For H the Coulomb potential is used. Energy differences for hydrogen-containing systems are well converged at a 40-Ry plane-wave cut-off. For each charge state of H, many possible sites in the lattice were explored and the global minimum was identified. We estimate the error bar on $\varepsilon(+/-)$ due to DFT-LDA errors to be ~0.4 eV, based on comparisons between calculations with different pseudopotentials (particularly those that result in different bandgaps owing to different treatments of the semicore $d$ states). The bandgap error inherent in DFT-LDA has only minor effects on $\varepsilon(+/-)$, because the formation energies of $H^+$ and $H^-$ are not sensitive to bandgap corrections: for $H^+$, the defect-induced state is unoccupied, whereas for $H^-$, the state is related to an anion dangling bond and thus valence-band derived. Calculations for band line-ups were performed for nonpolar interfaces using the methodology of ref. 12. The line-up for Si/SiO₂ was taken from ref. 25.

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# Chaperonin-mediated stabilization and ATP-triggered release of semiconductor nanoparticles

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**Various properties of semiconductor nanoparticles, including photoluminescence and catalytic activity, make these materials attractive for a range of applications[1,2]. As nanoparticles readily coagulate and so lose their size-dependent properties, shape-persistent three-dimensional stabilizers that enfold nanoparti-**