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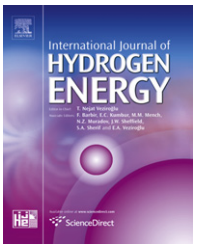

# Characterization of hydrogen in metallic alloys suitable for electrolysis

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ABSTRACT

In this work we determine some fundamental microscopic and macroscopic properties of metals and metallic alloys–hydrogen systems. We deal with simple hydride such as LiH, NaH e $CaH_2$, which react with water producing hydrogen.

Using a calculus program based on the density functional formalism, we obtain values of important properties in the determination of the behaviour of the system, such as the variation of the electronic density and of the induced density of states due to the presence of hydrogen in the matrix.

The general features of these methods are discussed and the corresponding results are compared with experimental data.



## 1. Introduction

There is a persistent interest in the behaviour of hydrogen in different metallic systems due to their technological relevance (mainly because of the embrittling of metals in hydrogen–assisted cracking and as an energy storage media) as well as the exemplarity of the problem from the point of view of basic research.

Hydrides can provide large amounts of energy when burned. They can be used as fuel. They are less flammable and less volatile than hydrocarbon fuels. Also, they are relatively environmentally friendly because they degrade quickly in the environment.

Some of these hydrides, such LiH, NaH and $CaH_2$ react with water in order to produce hydrogen.

These systems have been object of several experimental studies, as heat of solution, diffusion properties and interaction with defects [1,2]. From a theoretical point of view, the progress has been slower. The reason is that a complete theory must take into account the local nature of the strong interactions with the nearest neighbours as well as the extended nature of the electronic states in the conduction band of the metal, and this must be done in a self-consistent way. Until now, the existing numerical calculations have emphasized one of these two aspects separately [3–5].

In this work we select one of the systems that can be used in electrolysis process:

$$2LiH + H_2O \rightarrow Li_2O + 2H_2$$

The Lithium Hydride is frequently used as a hydrogen source or reducing agent to prepare other hydrides amides and 2H isotopic compound, as a shielding material for thermal neutrons. With hydrogen content three times that of NaH, LiH has the highest hydrogen content of any hydride.

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LiH is periodically of interest for hydrogen storage, but applications have been precluded by the high instability of this material. Thus removal of $H_2$ requires high temperatures, well above the 700 °C used for its synthesis. We study in detail this hydride due to it is a precursor to complex stable metal hydrides.

## 2. Theoretical model

The need to rationalize the observed trends and predict the behaviour of the stability of metal hydrides, is particularly interesting from a technological point of view.

The electronic structure of impurities in metals is an important problem in the theory of alloys because in many cases the linear response theory is inadequate. The present is an example where the nonlinear screening is important. Band structure and cluster calculations have been developed to investigate particular aspects of the electronic structure of point defects in metals [6–10].

One of the most important quantities of metal-hydrogen systems is the induced screening charge density, $n$, which is fundamental for determining properties such as the volume of dissolution of hydrogen in metals, heat of solutions, activation energies, diffusion properties and values of chemical potentials, among others.

For this calculation we use a calculus program based on the Density Functional Formalism [6,7]. The material is modelled by the so-called jellium model [8], in which the metal can be replaced by a uniform electron gas with a background of positive charge of the same average density as the gas, in order to maintain the neutrality of the metal [9]: $n_0^{-1} = (4/3)\pi r_s^3$. (Atomic units are used throughout).

The former equation defines a value of $r_s$, characteristic of this model, as the radius of the sphere occupied by one electron in the jellium.

In a previous work [10] we have adopted as $r_s$ for each element of the Periodic Table the one obtained by the bulk modulus B that comes from the (inverse of the) compression K of the electronic density at interstitial positions. The principal contribution to this compression is due to the free electrons, and is written as [10]:

$$B = \frac{1}{K} = -V\frac{\partial P}{\partial V} \tag{1}$$

Taking these values, and using the parameterization obtained in our previous work [10], we have for the induced charge density, or equivalently, for the integrated induced density charge Q(R), the following:

$$Q(R) = 4\pi \int_0^R n(r) r^2 dr, \tag{2}$$

with the appropriate boundary conditions.

The program of calculus uses the Kohn-Sham method [6,7] within the functional density formalism to obtain the screening charge density, and the Jellium model for the lattice [10].

As mentioned earlier, one of the quantities to be determined is the volume of solution of hydrogen $v_H$ in the material, defined as the change in volume of the mesh to add to it an atom of hydrogen in interstitial sites. This quantity determines much of the variation of the properties of metal-hydrogen systems, such as the mechanical fragility, among others. The value of this quantity is given by the following equation (see details in [10]):

$$v_H = S/3B, \tag{3}$$

where B is the bulk modulus and S is defined, taking into account the spherical symmetry, as:

$$S = 4\cdot\pi\cdot n_0 \lim_{R\to\infty} \int_0^R [1 - Q(r)]\cdot r\cdot dr.$$

Finally, the volume of solution of hydrogen is:

$$v_H = \frac{1}{B\cdot r_S^3} \lim_{R\to\infty} \int_0^R [1 - Q(r)\cdot r\cdot] dr \tag{4}$$

Due to the relative scarcity of ab initio theoretical models describing the behaviour of hydrides, several empirical and semi empirical [11–13] models have been proposed. In particular, Griessen and Driessen [13], searching for a correlation between the standard heat of solution ($\Delta H$) of metal hydrides and the minimum number of band structure parameters of the host metal, found that the experimental values for $\Delta H$ show a trend that can be reasonably reproduced by the following semi–empirical relation:

$$\Delta H_G = n_s/2(\alpha_G \Delta E_G + \beta_G), \tag{5}$$

where $n_s$ is the number of electrons per atom in the lowest conduction band of s-metal host. $\Delta E_G$ is the difference between the Fermi energy $E_F$ and $E_s$, the energy for which the integrated density of states in the host metal is $n_s/2$ electrons per atom. For alkali metals $n_s = 1$, and $E_s$ roughly corresponds to the centre of the lowest conduction band, since this band is predominantly of character s with respect to the interstitial sites occupied by H atoms. $\alpha_G$ and $\beta_G$ are empirical constants, which for adjusting the previous expression (5) to experimental values of heat of solution of a large number (over 80) metal guests, take the values: $\alpha_G = 29.62$ kJ/mol eV H and $\beta_G = -122.0$ kJ/mol H for standard solution (at room temperature and atmospheric pressure) at infinite dilution. While the model given in ref. [11] correctly predicts the trend, it is necessary to apply the band theory to get its value. In the present work we show that $\Delta H$ can be evaluated within the jellium model, in terms of an effective radius $r_s$ of the sphere occupied by an electron in the interstitial region of the metal. This effective radius is obtained from a correlation of $r_s$ with the bulk modulus of the matrix guest. Thus, we propose a simple relationship between the heat of solution $\Delta H$ and the effective radius $r_s$ applicable throughout the periodic table and regardless of the host group.

The electronic structure is another important aspect of the interaction of hydrogen with metals, due to the strong interaction between the hydrogen 1s state located and the states of the conduction band of metal. Self-consistent calculations are often performed, including the strong nonlinearity of the shielding of the proton, and have provided values for solution energies, diffusion paths [14–17] and others. The results are presented as the spatial distribution of the screening charge, and have not been emphasized in the energy spectrum. In [18] we presented the change in the density of states $\Delta g$ induced

a hydrogen atom in a jellium model, which is expected to be a better representation of (but not only) simple metals like Al or Mg. We also give a parameterization of $\Delta g$ as a function of energy $e = k^2/2$ and the parameter of the jellium $r_s$ which allows easy handling of this amount.

The first step is to calculate the self-consistent $\Delta g$ for various values of $r_s$. We use the Kohn–Sham scheme [3] of spin–independent density functional theory. It should solve the Schrödinger equation self-consistent independent particle using an effective potential $V_{eff}[r,\eta]$.

The spherical symmetry of the potential allows a decomposition of $\Delta g$ in partial waves, resulting in the radial Schrödinger equation for radial functions $R_{kl}(r)$ leading to the total eigenfunctions being the spherical harmonic polynomials $Y_{l,m}$. For hydrogen, the asymptotic behaviour of the wave functions is:

$$R_{kl} \underset{r\to\infty}{\sim} \sin\left(kr - \frac{1}{2}l\pi + \eta_l(k)\right)$$

With the previous phase shifts $\eta(k)$, the density of states $\Delta g$ can be written as a sum of partial contributions [18]

$$\Delta g(\varepsilon) = \sum_l \Delta g_l(\varepsilon) = 2\sum_l (2l+1)\left(\sum_{s=1}^{B_l}\delta(\varepsilon - \varepsilon_{ls}) + \frac{1}{\pi}\frac{d\eta_l}{d\varepsilon}\right) \quad (6)$$

The first term corresponds to the bound states and the second to the scattering states. This phase shifts expansion are often negligible for $l > 3$.

## 3. Results and discussion

As lithium hydride is used in the production of a variety of reagents, such as lithium aluminium hydride and lithium borohydride and more complex hydrides, we study in detail some of its basic properties.

First of all, we study the screening charge density of hydrogen in a matrix of Li due to it is important for electrolysis process. In Fig. 1 we show two probable situations: introducing one molecule of hydrogen, and two hydrogen atoms. We observe that the screening is more important in the case of two atoms of hydrogen than for the molecule. For this reason is that we can use a linear response model for the molecule, meanwhile the treatment with atoms of hydrogen must have into account non-linear perturbation. Moreover, the volume of solution of $H_2$ in Li is 2.56Å$^3$ against 3.2Å$^3$ of 2H. The differences between the calculations with $H_2$ and two hydrogen atoms can be explained due to because the effects that are not considered here, such as those associated with the strain energy or the interaction of the core-hydrogen (Table 1).

**Table 1 – Results for ΔH, compared with other model and experiments.**

| ΔH jellium ($H_2$) | ΔH [19] | ΔH exp |
|---|---|---|
| −15.45 kJ/gr | −17.78 kJ/gr | −11.39 kJ/g |

Clearly, the jellium approximation correctly describes the properties of the component heavily dependent of free electron density, such as the heat of solution, and gives the trends observed experimentally.

With respect to the density of state (DOS) of H and $H_2$ in Li, in Fig. 2 we observe the value of $\Delta g$, for three cases: one and two atoms of H and a molecule.

The lower spectrum (zone where the wave vector is far from the Fermi wave vector) is dominated by $\Delta g$ with $l = 0$ for a general spherical potential, thus the more important contribution of single hydrogen atoms, and at the bottom of the band this is strictly the only contribution.

For high values of the wave vector, these states are mixed to give a bound state of $H_2$.

In summary, we study some important properties of LiH system obtained with a theoretical model based of functional density formalism (**jellium** model, described previously), comparing them with experimental available values of some properties of the behaviour of hydrogen in Lithium Hydride.

Studies for other hydrides, such as more complex compounds of Li with H (and D) are under way.

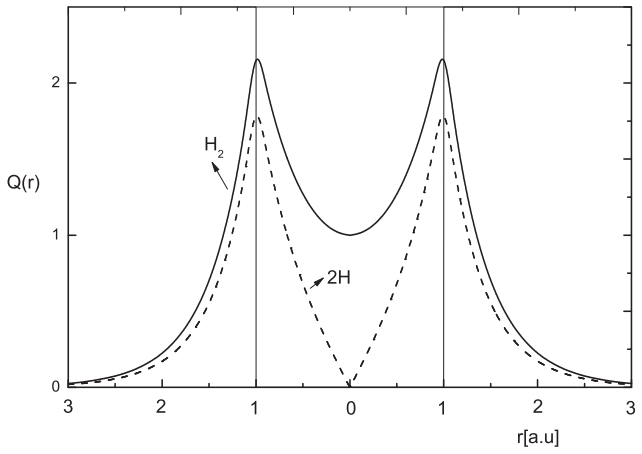


**Fig. 1 – Induced screening charge density for two hydrogen atoms and for a molecule $H_2$ as function of the distance to them, in a matrix of Li.**

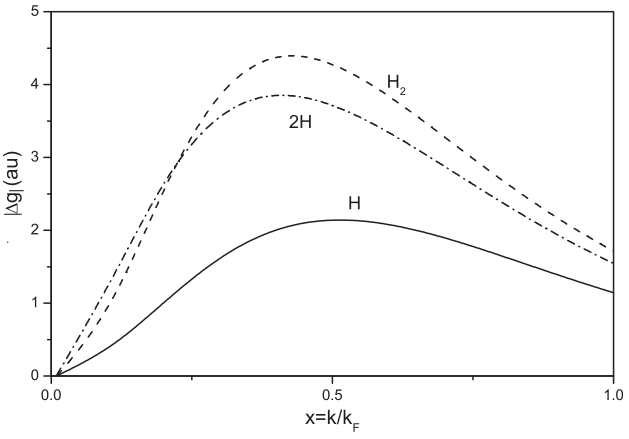


**Fig. 2 – Density of states as function of the wave vector $k$ measures with respect to Fermi wave vector $k_F$ for one hydrogen atom, two hydrogen atoms and a molecule of $H_2$.**

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