

On the vacancy formation energy for noble metals and metallic hydrogen

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ABSTRACT. We have used density functional theory and the approach given by Fumi in order to calculate the vacancy formation energy of noble metals and metallic hydrogen. We obtained a good agreement of our calculations for noble metals with experimental results and made a prediction of the value of the vacancy formation energy for metallic hydrogen.

RESUMEN. Hemos utilizado el formalismo de funcionales de densidad y el enfoque de Fumi para calcular la energía de formación de vacancia de los metales nobles y de hidrógeno metálico. Obtuvimos una buena concordancia entre nuestros cálculos para los metales nobles y los resultados experimentales e hicimos una predicción para el valor de la energía de formación de una vacancia para hidrógeno metálico.

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1. INTRODUCTION

The formation of a vacancy can be seen in a simple way as the removal of an atom from its position in the bulk of the crystal to be placed on the surface. Because of interionic forces the system relaxes. The vacancy formation energy is defined as the difference between the energies of the corresponding configurations: the crystal with the defect and the perfect crystal.

The calculation of the vacancy formation energy turns out to be quite complex, even for zero temperature. This happens because of the role of the conduction electrons in the process. There are, basically, two methods to calculate this quantity. The first one is based on the jellium model and focuses on the change of electronic densities near the vacancy [1]. This includes calculations with proper self consistent treatment of the jellium model [2,3]. This model has had some success in predicting the vacancy formation energy, for noble metals and a little bit less for the alkalis [1,2,4]. The second approach is with pseudopotential theory [5,6]. In this approach the pair potential describing the interactions between ions is an important ingredient and is obtained with perturbation and pseudopotential theory. This has not been very successful for the alkalis nor the noble metals, in predicting the vacancy formation energy [6].

The vacancy formation energy can be written as the sum of several terms [2,4]:

$$E^f = \Delta T + \Delta E_{xc} + \Delta E_c + \Delta E_r, \quad (1)$$

where ΔT is the change in kinetic energy, ΔE_{xc} is the change in exchange and correlation energy, ΔE_c is the change in electrostatic energy and ΔE_r is the change in energy because of lattice relaxation. All these changes happen when the vacancy is formed. The last three terms in Eq. (1) are small with respect to the first, specially for noble and alkali metals [2]. It is necessary to mention that in the calculation of ΔT we also have terms involving exchange and correlation energies [2]. As a first approximation E^f can be written as [1]

$$E^f = \Delta E_{\text{eigen}} - \frac{2}{5} E_F, \quad (2)$$

where ΔE_{eigen} is the change in the energy eigenvalues of the electrons and E_F is the Fermi energy of the metal. The expression for ΔE_{eigen} is [1,19]

$$\Delta E_{\text{eigen}} = -\frac{2}{\pi} \sum_{l=0} (2l+1) \int_0^{k_F} dk k \eta_l(k), \quad (3)$$

where k_F is the Fermi wave vector, $\eta_l(k)$ is the corresponding phase shift of wave vector k and angular momentum l produced by scattering from the vacancy.

In this work we are interested in the prediction of the vacancy formation energy for metallic hydrogen and the noble metals, using the method proposed by Fumi [1], with some modifications to make it more precise. More specifically, we use density functional theory to calculate ΔE_{eigen} with Eq. (3) and then we use Eq. (2) to obtain the vacancy formation energy.

On the other hand, metallic hydrogen is a material which has attracted attention in research for a number of years and several of its properties have been calculated. Among these, the superconductive transition temperature, specific heat, elastic constants and Knight shift [7-15].

The results we obtained for noble metals in this work are in good agreement with experiment. There are not experimental results for the vacancy formation energy of metallic hydrogen, and we could not find any previous calculation of this property for this material.

In Sect. 2 we describe, briefly, the equations from density functional formalism which we solved to calculate self consistently the phase shifts necessary to obtain the vacancy formation energy. In Sect. 3 we show our results and compare them with experiment and with calculations by other authors.

2. ELECTRONIC DENSITIES AROUND VACANCIES

The electronic densities and the corresponding phase shifts (which are necessary to calculate ΔE_{eigen}) are obtained using the density functional formalism of Hohenberg, Kohn and Sham [10, 11]. We have used this formalism in previous works for the calculation of properties of materials from first principles (see for example Refs. [12] to [15], where we give numerical details of the solution of the corresponding equations. Here we only give a brief description of the formalism.

The central result of the density functional theory states that there exists a one body local potential, $V_{\text{eff}}(r)$, which through the one body Schrödinger equation:

$$\left[\frac{1}{2}\nabla^2 + V_{\text{eff}}(r)\right]\varphi_i(r) = \epsilon_i\varphi_i(r),$$

generates the set of wave functions $\varphi_i(r_i)$ and the exact ground state density of the system through the independent particle density expression:

$$n(r) = \sum_{\epsilon_i < \epsilon_f} [\varphi_i(r)]^2,$$

where the sum extends up to the Fermi energy.

The effective potential is

$$V_{\text{eff}}(r) = -\Phi(r) + \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)}, \quad (4)$$

where $\Phi(r)$ is the total electrostatic potential of the system, and $E_{\text{xc}}[n(r)]$ is the exchange-correlation energy of the system.

When we omit gradient correction it is possible to obtain

$$\frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)} = \frac{d}{dn} [n(r)\epsilon_{\text{xc}}(r)], \quad (5)$$

where $\epsilon_{\text{xc}}[n(r)]$ is the exchange-correlation energy per particle in a homogeneous electron gas of density $n(r)$.

For the exchange-correlation contribution to the effective potential [Eq. (6)], we use the expression given by Gunnarson and Lundquist (18) in double Rydbergs (1 Rydberg = 13.6 eV):

$$\begin{aligned} V_{\text{xc}}(r) &= \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)} \\ &= -0.619 \times \left[\frac{1}{r_s} + 0.0585 \ln \left(1 + \frac{11.4}{r_s} \right) \right], \end{aligned} \quad (6)$$

where

$$\frac{4}{3}\pi r^3 = \frac{1}{n(r)}.$$

In order to have $V_{\text{eff}}(r)$ vanishing at large r , the exchange-correlation part is rescaled to

$$V_{\text{xc}}(r) \Rightarrow V_{\text{xc}}[n(r)] - V_{\text{xc}}[n_0], \quad (7)$$

where n_0 is the equilibrium density.

TABLE I. Phase shifts at the Fermi level $\eta_l(K_F)$ for H, Cu, Ag and Au.

		Phase Shifts							
H		η_0	η_1	η_2	η_3	η_4	η_5	η_6	η_7
$r_s = 1.0$		-0.3649	-0.1764	-0.0690	-0.0254	-0.0093	-0.0035	-0.0013	-0.0005
Cu		η_0	η_1	η_2	η_3	η_4	η_5		
$r_s = 2.67$		-0.6135	-0.2181	-0.0493	-0.0043	-0.0008	-0.0000		
Ag		η_0	η_1	η_2	η_3	η_4	η_5		
$r_s = 3.01$		-0.6497	-0.2209	-0.0445	-0.0047	-0.0001	-0.0000		
Au		η_0	η_1	η_2	η_3	η_4	η_5		
$r_s = 3.02$		-0.6508	-0.2210	-0.0444	-0.0046	-0.0001	-0.0000		

TABLE II. Calculated values of ΔE_{eigen} , in electron volts, for Cu, Ag, Au and H.

	Cu	Ag	Au	H
ΔE_{eigen}	4.1939	3.2413	3.2201	31.767

The electrostatic potential obeys Poisson’s equation:

$$\nabla^2 \Phi = -4\pi D(r), \tag{8}$$

where $D(r)$ is the total charge density.

For this case, $D(r)$ corresponds to a vacancy in jellium, *i.e.*:

$$D(r) = n_0 \theta(r - R_{\text{WS}}) - n(r), \tag{9}$$

where $\theta(x)$ is the step function and R_{WS} is the Wigner-Seitz radius.

The phase shifts used in the calculation of ΔE_{eigen} are a subproduct of the selfconsistent calculation of the electron densities. They are produced by the scattering of the electrons by $V_{\text{eff}}(r)$.

3. RESULTS AND DISCUSSION

We solved selfconsistently the corresponding equations of density functional theory of Sect. 2 with values of the density parameter r_s equal to the values for which we have experimental results of E^f . For metallic hydrogen we took the expected value [12] of $r_s = 1.0$ (a.u.).

The phase shifts produced by the scattering of the electrons by $V_{\text{eff}}(r)$, which came out from the selfconsistent calculation of the electronic densities, are given in Table I at the Fermi level, K_F . The calculations of $\eta_l(k)$ were performed at values of k corresponding to a 24 points Gaussian integration to obtain ΔE_{eigen} . The values for ΔE_{eigen} for each material are shown in Table II in electron-volts. In Table III we show the experimental

TABLE III. Experimental and calculated values of the vacancy formation energies, in electronvolts, of Cu, Ag, Au and H with the corresponding values of r_s , for which the measurements were taken and the calculations performed. Experimental results are from Ref. [20]. We could not find any more calculations for noble metals, except for copper Ref. [21].

	Cu	Ag	Au	H
r_s	2.67	3.01	3.02	1.0
E_{exp}^f	1.29 ± 0.02	1.16 ± 0.02	0.97 ± 0.01	—
E_{calc}^f	1.38	1.03	1.02	11.72
$E_{\text{Ref. [1]}}^f$	1.17	0.92	0.91	8.35
$E_{\text{Ref. [21]}}^f$	1.29	—	—	—

and calculated values of E^f , with the corresponding values of r_s , for each material. The expression given by Fumi [1] for the vacancy formation energy is $E^f = \frac{1}{6}E_F$. We also give the values predicted by Fumi. We can see a better agreement of our calculations with experiment for noble metals, than those given by Fumi [1]. This means that, for the noble metals, the sum of the last three terms in Eq. (1) makes a very small contribution to E^f . Notice that the predicted value of E^f for metallic hydrogen is about one order of magnitude larger than the values for noble metals. We could not find any other calculation of E^f for metallic hydrogen in order to compare with our prediction. We could not find any more calculations for noble metals except for copper, Ref. [21], where a phenomenological pseudopotential is used.

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