Activation Energies for Quantum Diffusion of Hydrogen in Metals and on Metal Surfaces using Delocalized Nuclei within the Density-Functional Theory

Per G. Sundell* and Göran Wahnström†
Department of Applied Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden
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Hydrogen diffusion on the Cu(001) surface and in bulk Nb and Ta is studied in the quantum regime using first-principles electronic-structure calculations. We present, for the first time, a direct density-functional calculation of the activation energy required to establish the quantum-mechanically delocalized hydrogen coincidence configuration and of the corresponding tunneling matrix element. For the two bulk systems a direct comparison can be made with nuclear magnetic resonance data, and we find excellent agreement for both the coincidence energy and the tunneling matrix element.

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Hydrogen transfer and diffusion in condensed matter are of fundamental importance in areas ranging from materials to life sciences. Since hydrogen is the lightest element, great interest has been directed to the quantum nature of its motion. Diffusion of hydrogen in metals and on metal surfaces are well-studied phenomena, both experimentally and theoretically [1–4], and are of considerable importance for a large number of technological applications.

In the classical regime, the transfer rate for hydrogen between two neighboring potential wells is given by an Arrhenius expression $\nu = \nu_{\mathrm{H}} \exp[-V_{\mathrm{m}}/k_{\mathrm{B}}T]$, where the activation energy V_{m} is the energy required for the hydrogen to surmount the potential barrier separating the initial and final configurations, and the prefactor ν_{H} is equal to a hydrogen vibrational frequency. However, also when the transfer is controlled by quantum-mechanical tunneling the rate can be given by a similar expression. Flynn and Stoneham [5] showed that the rate of incoherent hopping between self-trapped ground states localized in neighboring potential wells for H in metals is given by an Arrhenius expression if the phonon excitations of the surroundings can be treated classically. In this case, however, the activation energy is not the classical barrier height but the energy required to establish a so-called coincidence configuration, where the hydrogen is quantum-mechanically delocalized over neighboring wells.

Indeed, experimentally one has found a change of the activation energy around 200 K for hydrogen diffusion in the bcc metals Nb and Ta, using both Gorsky effect [6] and nuclear magnetic resonance (NMR) [7] measurements. More recently, the same qualitative behavior has been observed for H on Cu(001) [8] and CO on Cu(111) [9] using scanning tunneling microscopy, but in these cases the transition is at lower temperatures (60 and 6 K, respectively) and much more abrupt with a nearly temperature independent diffusion at low temperatures.

The development of accurate and efficient first-principles computational schemes based on the density-functional theory (DFT) has greatly increased our understanding of hydrogen/metal systems. They avoid the bias introduced when using various types of empirical model potentials. In standard implementations of the DFT, all nuclei are treated as classical point particles. This makes it impossible to directly calculate quantities related to light nuclei being quantum-mechanically delocalized. The *ab initio* path-integral approach has been used in combination with a path-centroid description for the transfer rate [10], but it is difficult to get a reliable estimate of the rate at low temperatures and to obtain the corresponding tunneling splitting with that method [11]. Several authors have considered the quantum motion of hydrogen on potential energy surfaces (PESs) constructed from repeated DFT calculations, both in the bulk [12] and on surfaces [13–16]. However, in all these studies the nuclei are treated as classical point particles in the DFT calculations and the quantum motion is only obtained on the constructed rigid three-dimensional PESs, thus precluding the possibility to evaluate parameters of the Flynn-Stoneham model [5].

Here we introduce a method to determine the relevant activation energies and prefactors solely based on accurate first-principles electronic-structure techniques. Previous attempts have been based on parametrizations or model potentials [17–19]. We present, for the first time, a direct density-functional calculation of the energy required to establish a hydrogen coincidence configuration and of the corresponding tunneling matrix element for the two most frequently investigated H/bulk-metal systems, H/Nb and H/Ta, and for the quite recently investigated H/metal-surface system, H/Cu(001). For the two bulk systems, a direct comparison can be made with experimental data, and we find excellent agreement for both the coincidence energy and the tunneling matrix element.

The starting point is to consider a system consisting of a hydrogen atom interacting with the host metal lattice atoms. The electronic degrees of freedom have been eliminated via the usual Born-Oppenheimer approximation. We also assume the light hydrogen atom to be adiabatically decoupled from the motion of the heavy metal lattice atoms and the latter are treated as classical pointlike particles. The hydrogen atom is described by a wave function $\psi(\mathbf{r};\{\mathbf{R}\})$, where $\{\mathbf{R}\}$ denotes the (classical) positions of the metal atoms and $\mathbf{r}$ the position of the hydrogen atom. In particular, we are interested in finding $\{\mathbf{R}\}$ corresponding to the self-trapped and the coincidence configurations of a hydrogen interstitial. The expectation value of the force exerted on metal atom I, when the hydrogen atom is in quantum state n, is given by

$$\mathbf{F}_I = -\langle\psi_n(\mathbf{r};\{\mathbf{R}\})|\nabla_I V(\mathbf{r},\{\mathbf{R}\})|\psi_n(\mathbf{r};\{\mathbf{R}\})\rangle, \qquad (1)$$

where the notation $V(\mathbf{r},\{\mathbf{R}\})$ is used for the interaction potential. We have performed the calculations in two steps. This is based on the fact that the effect on the lattice distortion from the *finite extension* of the hydrogen wave function in the self-trapped configuration is very small [20]. Therefore, we first treat the hydrogen nucleus as a pointlike particle when determining the relaxed self-trapped lattice configuration. Equation (1) then reduces to the usual Hellmann-Feynman forces. For the coincidence configuration, the delocalized nucleus is represented by two symmetrically displaced point particles with equal weight and localized in adjacent potential minima. In this case, the force $\mathbf{F}_I$ becomes equal to a weighted average of Hellmann-Feynman forces.

In the second step, we map out three-dimensional PESs for the hydrogen motion in these fixed lattice configurations by performing a large set of first-principles total energy calculations corresponding to different positions of the hydrogen nucleus. The energies for the ground and excited states, as well as tunneling matrix elements for the coincidence configuration, can then be obtained by solving the Schrödinger equation for the hydrogen motion [21].

Our first-principles calculations are based on the DFT together with a generalized gradient approximation for the exchange-correlation energy due to Perdew and Wang [22]. The electron-ion interaction is described by the projector augmented wave method [23], and to solve the Kohn-Sham equations we use the Vienna *ab initio* simulation package (VASP) [24,25].

The hydrogen/bulk-metal calculations were performed with a plane-wave basis set having an energy cutoff of 250 meV. A lattice constant of $a_b = 3.32$ Å was found for both Nb and Ta in their bcc structure. Atomic hydrogen was found to preferably occupy tetrahedral sites in the lattice. A cubic supercell containing 54 metal atoms and one hydrogen, sampled with a $4 \times 4 \times 4$ Monkhurst-Pack k-point mesh, was used when calculating the potential energies. However, for computational reasons the PESs for hydrogen motion were mapped out using smaller supercells. A hydrogen concentration $c = 1/16$ was found to be sufficient for reproducing most of the local distortion of the host lattice. At this concentration, first-principles data points were generated on regular grids with a grid spacing of $a_b/8$.

In the hydrogen/metal-surface calculations the energy cutoff was set to 273 meV. A lattice constant $a_s = 3.64$ Å was found for pure fcc Cu. The surface was modeled by a six-layer slab separated by 12.7 Å of vacuum. The two outermost layers were allowed to relax, and the relative change in separation was -3.3% between the first and second layer, and $+0.5\%$ between the second and the third layer. The effect of finite hydrogen coverages was investigated using $(n \times n)$ overlayers with $n = 1$, 2, and 3. Adsorption was found to preferably take place over the fourfold hollow site. In evaluating the potential energies, 1/9 of a monolayer (ML) hydrogen was used with a $4 \times 4 \times 1$ k-point mesh. The PESs were mapped out for a coverage of 1/4 ML using a grid spacing of $(a_s/\sqrt{2})/8$.

In Table I, we summarize our calculated energies describing the hydrogen-lattice coupling for the bulk and surface cases. The self-trapping energy V_{st} is defined as the potential energy gained by allowing the host metal atomic positions to relax around a hydrogen atom located at a stable interstitial site. This quantity was found to be considerably larger (nearly a factor 10) in the bulk. The distortions were also larger. The coincidence energy V_c is defined as the additional potential energy required to reach the lowest symmetric tunneling configuration from the self-trapped configuration. This quantity was found to be more similar for the bulk and surface cases. For a reference, we have also determined the classical migration energy V_m, defined as the potential energy needed to move the hydrogen classically via an adiabatic deformation of the host lattice from one site to the next. It was found to be considerably larger than the coincidence energy for both bulk and surface.

Next, we consider the kinetic parts of the energies given in Table I. The difference K_c between the zero-point energies for the self-trapped and coincidence configurations was found to be small for both the bulk and surface cases. We have also estimated the kinetic addition K_m to

TABLE I. The potential energy for the self-trapped (V_{st}) and for the coincidence (V_c) configuration, together with the classical migration energy (V_m). K_c and K_m are the kinetic contributions (zero-point energies), and $E_c \equiv V_c + K_c$ and $E_m \equiv V_m + K_m$ are the total energies. All results are in meV.

	Bulk				Surface	
	H/Nb	D/Nb	H/Ta	D/Ta	H/Cu(001)	D/Cu(001)
V_{st}	189		185		26	
V_c	19		19		11	
V_m	148		180		126	
K_c	+4.6	+3.8	+9.4	+7.1	−2.6	−1.7
K_m	−22	−17	−15	−12	+53	+43
E_c	24	23	29	26	8.6	9.5
E_m	126	131	165	168	180	170

TABLE II. The hydrogen ground states and vibrationally excited states. The ground-state energy E_0 and the excitation energies $\hbar\omega_n$ are calculated in the self-trapped configuration, whereas the corresponding bare tunneling matrix elements J_n are determined in the symmetric coincidence configuration. All results are in meV.

	Bulk				Surface	
	H/Nb	D/Nb	H/Ta	D/Ta	H/Cu(001)	D/Cu(001)
E_0	274	197	279	200	110	75
J_0	0.80	0.10	0.82	0.10	0.90×10^{-6}	0.85×10^{-9}
$\hbar\omega_1$	122	93	121	93	71	50
J_1	2.3	0.34	2.3	0.36	0.40×10^{-3}[a]	0.55×10^{-6}[a]
$\hbar\omega_2$	176	134	178	136	77	53
J_2	6.7[b]	1.4[b]	7.1[b]	1.5[b]	0.21×10^{-3}	0.16×10^{-6}

[a] Largest value of the twofold degenerated first excited state.
[b] Largest value of the twofold degenerated second excited state.

the classical migration energy. This was calculated as the difference between the zero-point energy in a two-dimensional plane separating adjacent sites for the symmetric configuration, and the zero-point energy at a relaxed stable site. We note a large (~30%) kinetic contribution to the migration barrier at the surface. For the resulting total energies, we use the notation $E_c \equiv V_c + K_c$ and $E_m \equiv V_m + K_m$, respectively.

The calculated ground and first excited hydrogen states are summarized in Table II. The vibrational frequencies for both H in the metals and on the metal surface agree well with the experimental results [3,8]. The calculated isotope dependence for J_0 in the H/bulk-metal cases is fully consistent with quench-recovery experiments at low temperatures ($T \lesssim 100$ K), where the ratio $J_0(H)/J_0(D) \approx 10$ was obtained for H in Ta [26]. In the surface case, the tunneling matrix elements are significantly smaller. This is due to the larger jump distance at the surface ($d_s = 2.57$ Å) compared to bulk ($d_b = 1.17$ Å). Our PESs for H/Ta are shown in Fig. 1 and the corresponding ground-state wave functions in Fig. 2.

For the transition rate between ground states of neighboring sites, Flynn and Stoneham [5] derived the following expression:

$$\nu = \frac{1}{\hbar}\left(\frac{\pi}{4E_c k_B T}\right)^{1/2} J_0^2 \exp[-E_c/k_B T], \tag{2}$$

where E_c is the coincidence energy and J_0 the bare tunneling matrix element. Equation (2) is valid only at low enough temperatures such that contributions from vibrationally excited states of the hydrogen can be neglected, but at high enough temperatures such that the lattice motion can be treated classically. The latter implies that $T \gtrsim T_D/2$, where T_D is the Debye temperature (equal to 275, 225, and 315 K for Nb, Ta, and Cu, respectively).

Using the NMR technique, the diffusivity of hydrogen has been determined from the spin-lattice relaxation rate between 130 and 450 K in Nb and between 120 and 450 K in Ta by Messer *et al.* [7]. The data obtained shows an Arrhenius behavior with a change of the slope around 200 K in both metals. By fitting to Eq. (2), they obtained the data given in Table III. Quite similar results have been obtained utilizing the Gorsky effect by Qi *et al.* [6]. The NMR data is viewed to be more reliable since it gives information on the characteristic time scales for the elementary jump process directly, while measurements based on the Gorsky effect are more macroscopic in nature and might be affected by defects in the material [7].

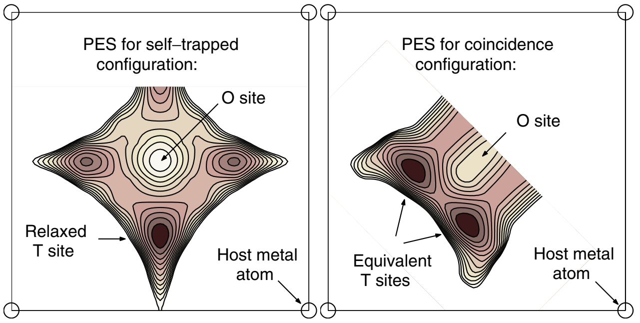

FIG. 1 (color online). Comparison of the self-trapped and coincidence PESs in a (001) plane for H/Ta. Contours differ by 50 meV.

Both our calculated coincidence energy E_c and bare tunneling matrix element J_0 agree remarkably well with the experimental results (cf. Table III). Taking the given uncertainty in the experimental data into account, the agreement can be considered excellent. We have also investigated the sensitivity of J_0 on the PES. Our PESs are determined for $c = 1/16$. At lower concentrations, the barrier heights are slightly reduced. The classical barrier height V_m is reduced by a factor $\alpha = 0.81$ ($\alpha = 0.92$) for H/Nb (H/Ta), when the concentration is reduced from $c = 1/16$ to $c = 1/54$. If the PES is scaled by the factor α, we obtain slightly larger tunneling matrix elements, $J_0 = 1.08$ meV ($J_0 = 0.92$ meV) for H/Nb (H/Ta). This gives a reasonable estimate of the uncertainty in our calculated tunneling matrix elements.

For H on Cu(001), the observed low temperature behavior ($T < 60$ K), is in a temperature range too low for Eq. (2) to be valid. No direct comparison can be made but our results with a low activation energy for the coincidence configuration, a much smaller tunneling matrix

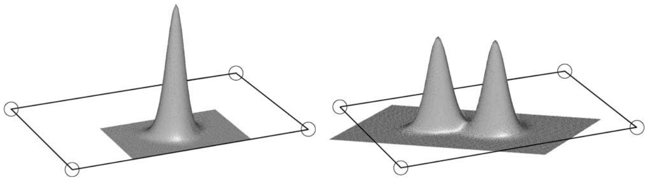

FIG. 2. Wave functions in a (001) plane for H self-trapped at a T site, and for H in the coincidence configuration between two neighboring T sites in Ta.

TABLE III. Calculated values for the coincidence energy E_c and the bare tunneling matrix element J_0, compared with experimental data [7]. All results are in meV.

	Theory		Experiments	
	H/Nb	H/Ta	H/Nb	H/Ta
E_c	24	29	27 ± 2	32 ± 8
J_0	0.80	0.82	$0.9^{+0.1}_{-0.2}$	0.7 ± 0.2

element compared with the H/bulk-metal cases, and a large isotope effect for the tunneling matrix element are all consistent with the experimental results.

In conclusion, we have for the first time presented a direct first-principles density-functional calculation of the activation energy required to establish the quantum-mechanically delocalized hydrogen coincidence configuration and of the corresponding tunneling matrix element. We have applied the method to two of the most frequently investigated H/bulk-metal systems, H/Nb and H/Ta, and to the recently investigated H/metal-surface system, H/Cu(001). For the two bulk systems, the small polaron theory of Flynn and Stoneham [5] is applicable in the temperature range $100 < T < 200$ K, and we find excellent agreement for both the coincidence energy and bare tunneling matrix element. For the surface case, our results are consistent with the experimental findings, but here a more detailed investigation of the coupling of the tunneling hydrogen to the lattice and electronic degrees of freedom is necessary.

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*Electronic address: sundell@fy.chalmers.se
†Electronic address: wahnstrom@fy.chalmers.se

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