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# Hydrogen tunneling on a metal surface: A density-functional study of H and D atoms on Cu(0 0 1)

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## Abstract

Using density-functional calculations, we present a theoretical investigation of the adsorption, self-trapping and diffusion of atomic hydrogen on Cu(0 0 1). The hydrogen motion is treated quantum-mechanically, by mapping out three-dimensional potential energy surfaces and solving a Schrödinger equation for H and D numerically. The ground-state energy levels and tunneling matrix elements are used to calculate the hop rate of hydrogen over a wide range of temperatures. We demonstrate how to include couplings of a tunneling adsorbate to the electronic and lattice degrees of freedom of the substrate on a first-principles basis. The results agree well with scanning tunneling microscopy data by Lauhon and Ho.

*Keywords:* Density-functional calculations; Surface diffusion; Quantum effects; Tunneling; Vibrations of adsorbed molecules; Surface defects

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## 1. Introduction

Hydrogen diffusion on metals is a phenomenon of great fundamental and technological importance [1,2]. Due to the small adsorbate mass, quantum-mechanical tunneling through the classical migration barriers becomes the dominating diffusion mechanism at sufficiently low temperatures. Frequently, this is displayed as some deviation from a simple Arrhenius behavior for the diffusion rate. Such deviations have been observed both by field emission microscopy (FEM) for hydrogen isotopes on W [3–6] and Ni [7] surfaces, and by various optical techniques on Ni [8–10] surfaces. A major problem, however, has been a qualitative disagreement between the results obtained from different experimental methods [7,10]. Also, the diffusion rates for hydrogen isotopes of different mass have been found to remain unexpectedly similar even at the lowest investigated temperatures.

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The existence of a low-temperature regime dominated by quantum tunneling motion has been demonstrated in theoretical works based on model potentials for diffusion of hydrogen isotopes on various metals [11–17]. Unfortunately, direct comparisons between theory and experiments are often rather difficult due to inherent uncertainties regarding adsorbate–adsorbate interactions and the presence of surface defects.

Recent advances in scanning tunneling microscopy (STM) have made it possible to track the motion of individual atoms and molecules on a surface [18]. This allows for an accurate investigation of the intrinsic properties of the adsorbed species, that might be difficult to accesses in a more macroscopic experiment. Since a real space image of the surface is obtained, it is even possible to determine the influence of the local environment on the behavior of a single adsorbate. In particular, any effects due to impurities or other defects can often be avoided, so that measurements are performed on extremely well-characterized systems. Data from STM experiments then constitute an excellent test ground for theoretical work, and can provide new insights regarding the quantum-mechanical nature of nanoscale chemistry [19,20].

A beautiful illustration of the technique is the pioneering study on the diffusion of hydrogen isotopes on the Cu(001)-surface by Lauhon and Ho [21]. In this work, the authors reported the first direct observations of quantum tunneling of individual atoms. Using a combination of repeated-imaging and single-atom tracking techniques, the hop rate for hydrogen (H) and deuterium (D) as function of temperature $T$ was determined quantitatively. The main experimental findings are the following: For H the hop rate first decreases with decreasing temperature according to an Arrhenius law. However, around $T = 60$ K the temperature dependence changes abruptly and levels off at a nearly constant value. In contrast, for D the hop rate follows an Arrhenius law over the entire investigated temperature range until at $T = 50$ K the rate drops below the experimentally accessible value. At this temperature, the measured rates for H and D differ by three orders of magnitude, while for $T > 60$ K they are nearly identical. This is a clear manifestation of H diffusion by quantum tunneling. A closer inspection of the H behavior in the low-temperature regime even shows a small decrease of the hop rate between 60 and 25 K (consistent with phonon-assisted tunneling [22]) followed by an increase of the hop rate below 25 K (consistent with tunneling limited by a non-adiabatic response of excited electron–hole pairs [23]). These observations strongly suggest that H diffusion in the low-temperature regime can only be described by including a coupling to the lattice and electronic degrees of freedom of the substrate.

Several theoretical works on the quantum motion of hydrogen on metal surfaces have demonstrated the accuracy and versatility of calculations based on the density-functional theory (DFT) [24–27]. The diffusion of H and D on a rigid Cu(001) surface has previously been studied by Kua et al. [28]. However, calculating accurate tunneling rates is an intrinsically difficult problem due to the exponential dependence of tunneling matrix elements on the shape of the potential energy barrier separating adjacent sites. Therefore, it is well motivated to investigate further the relative importance of including a renormalization of the hop rate due to the adsorbate-induced lattice distortion and excitation of electron–hole pairs in the substrate [29].

## 2. Methods

The theory of migration of light interstitials in solids is a well-established subject [30,31]. It is most readily formulated in terms of diffusive jumps between so-called self-trapped states: A hydrogen adsorbed at a stable site on a perfect crystal will distort the positions of surrounding metal atoms in the substrate. This lowers the total energy of the system further by an amount known as the self-trapping energy. As a consequence, the translational symmetry is broken so that if hydrogen is moved from its initial site $i$ to another site $f$, without allowing the substrate to readjust, the potential energy will be higher. The minimum energy required to establish a configuration where hydrogen levels on two neighboring sites become equivalent is known as the coincidence energy. It is related to the activation energy for phonon-assisted