

Quantum and isotope effects on hydrogen diffusion, trapping and escape in iron



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ABSTRACT

We calculate the rate coefficient as a function of temperature for lattice diffusion of hydrogen and its isotopes in α -iron; and also for trapping and escape from a vacancy. We employ Monte-Carlo and molecular dynamics methods based around the Feynman path integral formulation of the quantum partition function. We find large quantum effects including tunnelling at low temperature and recrossing at high temperature due to the finite extent of the particle probability density. In particular these serve to *increase* the rate of trapping and to *decrease* the rate of escape at low temperature. Our results also show very clear non classical isotope effects.

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1. Introduction

One of the largest known diffusivities in the solid state is that of hydrogen in α -iron [1,2]. There are two reasons for this. One lies in the geometry of the body centered cubic lattice and its tetrahedral interstices; the other arises from the small mass of the proton leading to strong quantum effects, including large zero point energies and tunnelling [3]. It is typical that a rate coefficient may show Arrhenius behaviour at high temperature, T , and be essentially independent or weakly dependent on T otherwise [4] (see Fig. 4). A further complication arises in α -iron in that the transport of H is much attenuated by trapping of protons by crystal defects: dislocations, grain boundaries and vacancies, among others [5]. Hence the measurement of the lattice diffusivity presents many technical challenges [1] so that one would like to be able to separate out the effects of lattice diffusion and trapping by suitable theoretical calculations. We are concerned with the traps' capture probabilities [6]. In addition we are keenly interested in the mean residence time, τ , of a proton trapped at a defect [6]; this is the inverse of the associated rate coefficient for jumping out of the trap. In addressing these matters we arrive at some rather startling conclusions concerning the roles of tunnelling through the barrier and recrossing at the saddle point in the potential energy surface.

We find that an interesting qualitative interpretation can be made from the behaviour of the “beads” in the path integral “necklace” in Feynman's picture.

The most severe approximation that we make is to assume that the hydrogen atom moves in a static lattice of iron atoms. This means that we cannot admit phonon assisted tunnelling [7]. However it allows us to work with a potential energy surface which provides a single degree of freedom in the classical transition state theory [4,8]. We do allow relaxation of the iron atoms, albeit in a rather stilted form: when the proton is in a reactant or product state (before or after a hop) it sees a lattice of iron atoms relaxed about the proton in its metastable position. We also hold the proton in a saddle point position and relax the iron atoms to provide an “activated complex” state. To locate saddle points we use a “nudged elastic band” (NEB) energy minimisation [9]. Interatomic forces that are required for these procedures are obtained from a magnetic tight binding (TB) model of H in iron [10]. This is not a severe approximation, since comparison with density functional theory (DFT) calculations shows good agreement in both concentrated and dilute limits [10]. In Fig. 1 we show a contour plot of the two potential energy surfaces.

Having established potential energy surfaces we calculate position probability densities (PPD) and quantum partition functions employing the Feynman path integral method [11] in a manner described earlier [12] using Wang–Landau Monte Carlo [13]. To address trapping we consider the singly occupied vacancy as an archetypal trap for hydrogen. This is a much studied defect and

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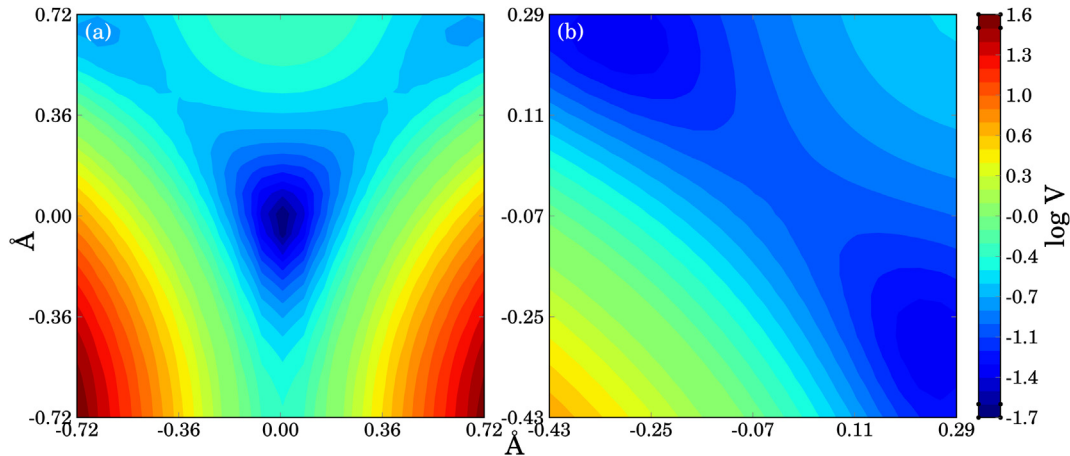


Fig. 1. Calculated potential energy surfaces for a proton in fixed Fe lattices. In (a) the Fe atoms are relaxed about the proton when it is fixed at the bulk tetrahedral site. In (b) the Fe atoms are at the relaxed saddle point configuration. The potential energy, V , is in electron volts. In each case the equilibrium proton position is at the origin of the coordinates.

regarded to have particular significance for the behaviour of H in α -iron [2,14]. The TB model has been shown to give a good account of the atomic structure and energetics of H binding to a vacancy compared to DFT calculations [10,15,16]. Fig. 2 shows a cartoon of the six possible hydrogen absorption sites.

Fig. 3 shows the PPD of H trapped at an α -iron vacancy. It is very significant that at 50 K, although the centroid of the particle (in the language of path integral theory [17]) is constrained to remain at the dividing surface, the PPD clearly indicates that the proton has *tunnelled* through the barrier and largely escaped from the trap (indeed the proton has “split into two”). Note also, that at high T the proton is by no means localised and samples a considerable region of configuration space orthogonal to the reaction path, *ie*, in the region of the “dividing surface” having potential energies greater than at the saddle point. Therefore we would expect quantum effects effectively to *lower* the activation barrier at low T , but to *raise* it at high T .

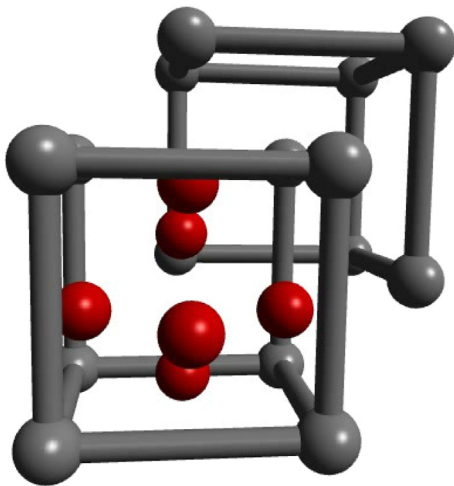


Fig. 2. The six absorption sites of a hydrogen atom bound to a vacancy in bcc Fe. Up to six hydrogen atoms may be absorbed exothermically from bulk tetrahedral sites. The vacant site itself is not a trap site. Roughly, each proton is found near a tetrahedral site on the faces bounding the vacancy; however each is displaced slightly towards the vacancy and in some cases there are small lateral shifts. For precise locations, see Refs. [16,10].

2. Theory and results

The Feynman path integral method is a means to obtain quantum partition functions. We illustrate this for a single particle whose equation of motion is Schrödinger's equation in a potential energy $V(x)$ (which becomes our potential energy surface in the configuration space of all the atoms in our simulations). The partition function of this particle is [11,19].

$$\begin{aligned} Z &= \sum_i e^{-\beta E_i} = \int dx \rho(x, x, T) \\ &= \int \mathcal{D}x(u) e^{-S/\hbar} \end{aligned} \quad (1)$$

Here, E_i are eigenvalues of the Schrödinger equation, ρ is the one particle density matrix, and the particle's probability density (see Fig. 3) is $\rho(x, x, T)/Z$. Equation (1) is an integral of the action in imaginary time

$$S[x(u)] = \int_0^{\beta\hbar} du \left[\frac{1}{2} m \dot{x}^2(u) + V(x(u)) \right]$$

the symbol $\mathcal{D}x(u)$ indicating that the integral in (1) is taken over all paths in configuration space starting at time $u = 0$ and finishing at $u = \beta\hbar$, where $\beta = 1/k_B T$ and k_B is the Boltzmann constant. The paths over which (1) is taken are closed in the sense that the particle starts and finishes at the same point, x , in configuration space. The integral in (1) can be discretised for numerical purposes and this furnishes us with the approximate formula [19].

$$\begin{aligned} Z &\approx \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{\frac{P}{2}} \int dx_1 \dots dx_P \\ &\times \exp \left\{ -\beta \sum_{s=1}^P \left[\frac{1}{2} \frac{mP}{\beta^2 \hbar^2} (x_{s+1} - x_s)^2 + P^{-1} V(x_s) \right] \right\} \end{aligned}$$

again over all *closed* paths having $x_{i+P} = x_i$, $\forall i$ [17]. But this is more than just a numerical convenience. It reveals that the partition function of a quantum particle is identical to that of a necklace of P classical particles, or *beads*, moving in a reduced potential energy $V(x)/P$ and connected by springs of stiffness $mP/\beta^2 \hbar^2$. Note that the stiffness is proportional to T^2 which means that at high T the necklace tightens towards a point particle (the classical limit) while

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