

Quantum diffusion of hydrogen on metal surfaces

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A quantum mechanical theory is presented for the low temperature diffusion of atomic hydrogen on metal surfaces, based on a band model for the hydrogen motion. The theory is applicable to the diffusion of many interacting particles obeying quantum statistics. At low coverage the hydrogen band motion is limited by collisions between adsorbates, giving rise to a decrease of the diffusion constant with concentration. Other aspects of the hydrogen-hydrogen interaction are introduced to explain the coverage dependence at higher adsorbate concentrations. Comparison with recent low temperature diffusion measurements for H, D, and T on W(110) show that the above model reproduces satisfactorily the main features of the experimental coverage dependence of diffusion. The usefulness and limitations of band treatment for heavy particle diffusion are discussed in the light of these results.

I. INTRODUCTION

Diffusion of atoms and molecules on solid surfaces is of fundamental importance in the study of heterogeneous catalysis and other chemical and physical phenomena.¹ Despite the ubiquity of diffusion at surfaces, very few direct probes of this process exist. Direct imaging is possible with field ion microscopy (FIM) (for metal atoms on metals)² and more recently, with scanning tunneling electron microscopy (also for atoms on nonmetal surfaces).³ Most dynamical studies of adsorbate mobility have been limited so far to species which can be observed either in the FIM, or in the field emission microscope (FEM) in which diffusion is measured by shadowing techniques or from density fluctuations.⁴ Alternative methods based on laser induced desorption are now being developed.⁵ Hydrogen adsorbed on metal surfaces represents an important prototype for study of the mobility of chemisorbed atoms. Hydrogen has a high mobility relative to other adsorbates, just as it also does when dissolved interstitially in the bulk. The binding sites of hydrogen on several metal surfaces are well characterized by electron energy loss spectroscopy (EELS)⁶ and the electronic structure of the hydrogen-metal system has been widely studied by *ab initio* and approximate calculations.^{7,8} The small mass of hydrogen makes it most likely to show quantum effects and the large mass ratio of the three isotopes renders mass effects in both quantum behavior and in coupling to lattice motions clearly visible.

The mobility of hydrogen, and more recently that of the lighter positive muon species, as interstitials in bulk metals has been studied extensively.^{9,10} Based on these studies a qualitative division into nonactivated, activated, and fluid-like behavior in successively higher temperature ranges has

been made.¹¹ However, experimental evidence has only been found for Arrhenius-type activated behavior, and the contribution of tunneling processes, whether direct or phonon-activated, is not clear. The recent observations by Difoggio and Gomer¹² and Wang and Gomer¹³ of temperature independent diffusion for all three isotopes over the range 27–120 K on the W(110) surface thus raise important questions about the quantum mechanical nature of the mobility in this regime. Using the field emission microscope (FEM) fluctuation method¹⁴ they measured the surface diffusion of atomic hydrogen and its isotopes, as a function of both temperature and coverage. These experiments invite a theoretical interpretation and quantitative description because of the following features: (i) The experiments imply that tunneling is the dominant mechanism for diffusion in the range $T < 120$ K, and relatively little is known about tunneling diffusion. (ii) The diffusion coefficient D depends on coverage in an interesting way, suggesting nontrivial interactions between the diffusing species. Tunneling of mutually interacting particles has also not been extensively investigated except for electron motion in metals, where the interaction is strongly shielded. (iii) There may be quantum symmetry effects at high coverages. (iv) A variety of experimental data, including isotopic studies, temperature, and coverage variations, have all been obtained on the same system and this makes it a very good testing ground for theory.

One of the aims of the present study is to investigate the possibility and consequences of band motion for heavy (i.e., atomic) particles. We shall take the hydrogen W(110) surface system at low temperatures as an example. The large mass compared with electrons means that bandwidths will be very much smaller than the \sim eV widths seen for electronic bands in metals and semiconductors. Nevertheless, the possibility of tunneling in the periodic surface potential allows for the formation of energy bands, to an extent deter-

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mined by the other interactions present. In this paper we shall discuss the dynamics of motion in energy bands for atomic hydrogen, and investigate the effects of finite temperature and concentration, as well as the factors inhibiting band type behavior.

Theoretical treatment of the diffusion of hydrogen on metal surfaces is complicated by the strong interactions between many degrees of freedom, none of which are well known in detail. Hydrogen is strongly chemisorbed and the nature of the adsorbed species may be at least partially ionic.¹⁵ Very little is known about the interaction with lattice vibrations. In bulk it is often assumed that the hydrogen is strongly coupled to the local lattice environment, but only a few systems show the predicted temperature dependence.¹¹ In addition, at finite concentrations, interactions between diffusing hydrogen atoms may strongly influence the mobility. As a first step in understanding the mobility of hydrogen on a metal, we shall describe here a quantum mechanical model for surface diffusion of chemisorbed hydrogen atoms at low temperatures and investigate the coverage dependence of diffusion on W(110).

Section II contains a summary of the problem and experimental findings relating to H/W(110). The detailed theory of surface mobility of species with quantum statistics is given in Sec. III. Application to the H/W(110) system is made in Sec. IV, followed by a discussion of the implications and limitations of the comparison. The emphasis throughout will be on identifying the relevant physical features by a simple physical model and numerical calculations will be made to illustrate feasibility.

Section V contains a discussion of the findings relating to band structure and mobility therein, and Sec. VI presents conclusions.

II. LOW TEMPERATURE MOBILITY OF H, D, AND T ON W(110)

When the chemical diffusion coefficient, D , of atomic hydrogen isotopes chemisorbed on W(110) is measured from decay of density fluctuations in the FEM as a function of temperature, there is for all coverages a region from 100–150 K (depending on coverage and isotope) down to 27 K (the lowest temperature measured) over which the diffusion coefficient is independent of temperature.^{12,13} This strongly suggests a tunneling process. The diffusion coefficient D in this regime shows a marked coverage dependence: this is shown in Fig. 1, which is reproduced from Ref. 13. All three isotopes show a nonmonotonic variation but deuterium is unique in showing a sharp increase for $\theta > 0.7$ (θ refers to the coverage, where $\theta = 1$ is experimentally defined as the coverage at saturation of the work function change with dosage).¹² This feature has been attributed to the influence of nuclear symmetry on an elementary jump process.^{12,13} The absolute magnitudes of D for the three isotopes are very close, and although they vary in the direction expected for tunneling processes, the ratio for any pair is much less than would be expected from a simple one-dimensional tunneling picture using the bare masses of the particles.¹²

There are thus three questions to be addressed: (i) the temperature independence of D over a relatively large range of temperature well above 0 K (and approaching $1/2 T_D$,

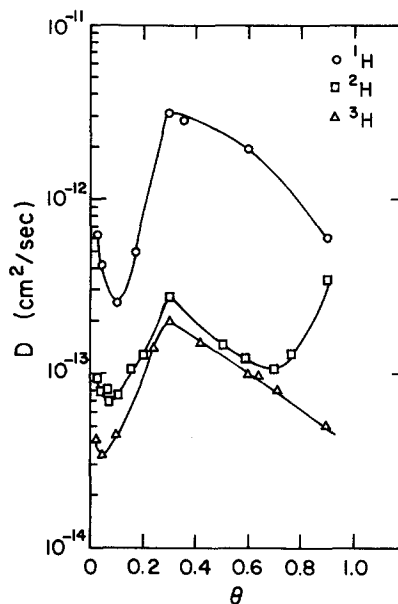


FIG. 1. Log D vs relative coverage θ for ^1H , ^2H , and ^3H as measured by the field emission microscope fluctuation method (Ref. 13) at 27 K. Reproduced with permission from Ref. 13.

where $T_D \sim 200$ K is the surface Debye temperature of W¹⁶), (ii) the coverage dependence, $D(\theta)$, and marked difference in behavior of ^2H and the odd isotopes for $\theta > 0.7$, (iii) the absolute magnitude of D as a function of isotopic mass. Our main focus here will be on the second aspect, but we shall also discuss the other features.

Before attempting a theoretical analysis several important points relating to the coverage dependence seen in the experiment should be noted. First, it is very difficult to measure the absolute number of atoms adsorbed on a surface.¹⁵ Figure 1 actually shows D as a function of relative coverage, θ . The relative coverage θ , for $\theta < 1$, is then extracted from work function measurements assuming a linear dependence of the latter on θ . It is usually further assumed that maximum coverage corresponds to a monolayer in which the ratio H:W is 1:1.¹² However an estimate based on comparison with hydrogen adsorption on W(100) for which absolute flux measurements have been made¹⁷ implies that H:W = 1.28 at saturation of the work function ($\theta = 1$).¹⁸ This fact, together with the known nonlinear dependence of work function on coverage,¹⁵ imply some uncertainty in the θ scale of Fig. 1. Absolute coverage with H:W > 1 is compatible with several possibilities: (i) hydrogen has several binding sites per tungsten atom, (ii) some hydrogen could be adsorbed in subsurface positions, a situation which can be induced by surface reconstruction at higher coverages, (iii) the extra hydrogen could be associated with surface imperfections or boundary structures. Although there is experimental information on the binding sites from several sources,^{15,19,20} no definitive picture of the location of these as a function of coverage has yet emerged. EELS measurements give two vibrational loss peaks at 95 and 160 meV and a possible third at 80 meV.^{19,20} The 160 meV peak is usually assumed to be a normal stretch mode and the other ones vibrations parallel to the surface.^{12,19,20} However the alter-

native, that two of these frequencies are normal stretching frequencies of hydrogen in two different binding sites on the surface, is not ruled out. The evidence from work function changes with coverage,¹⁵ photoemission,²⁰ and electron stimulated desorption measurements²¹ is compatible with either two states or one state whose properties vary with coverage. Surface reconstruction may in addition affect the relative stabilities of different binding sites.²² Since neither exact binding sites nor absolute coverage is known, we shall take the simplest model with H:W = 1:1 at $\theta = 1$ and assume the binding is at the symmetric bridge position¹² at all coverages. The θ scale of Fig. 1 may be changed somewhat if absolute coverage were to be measured. Nevertheless, this will not significantly change our conclusions as to the mechanism causing the variation of D with θ .

The second point to be borne in mind when analyzing $D(\theta)$ is the occurrence of phase transitions. The experimental diffusion coefficients of all isotopes show pronounced dips at temperatures of 80–90 K, depending on coverage, which were shown by Difoggio and Gomer¹² to be related to order–disorder transitions of the adsorbed layer. When translated into a phase diagram,¹² this information suggests that the disordered phase existing at low coverage is replaced by a mixture of ordered and disordered phases. Since the observed diffusion coefficient for given θ is the same above and below this transition (i.e., for both the two phase and the one phase regions; perhaps because the ordered component exists in small islands) it appears that the contribution of ordering to coverage variations may be neglected.

Phase transitions in adsorbed atomic hydrogen on W(110) have also been observed by low energy electron diffraction (LEED) by Gonchar *et al.*²³ They see disordered and ordered phases. From measurements of transition temperatures above 100 K they propose a phase diagram yielding a sequence of four phases as θ varies from zero to one at temperatures below 100 K [$0 < \theta < 0.3$, disordered; $0.3 < \theta < 0.6$, $p(2 \times 1)$; $0.6 < \theta < 0.9$, $p(2 \times 2)$; $0.9 < \theta$, $p(1 \times 1)$]. However no direct measurement of transition temperature was made below 100 K. Relating the phase transitions observed by LEED even at higher temperatures to the evidence of transitions in the FEM fluctuation method is complicated by differences in surface size probed and possible dependence on surface reconstruction.¹² Thus while the evidence clearly indicates that a disordered atomic hydrogen phase at low coverage is replaced by one or more ordered phases at larger θ , it does not appear that the presence of order has any significant effect on the chemical diffusion coefficient as measured from density fluctuations.

Finally, we comment on the absolute magnitude of the diffusion coefficient obtained from FEM measurements, relative to estimates obtained for the surface and bulk by other methods. The presence of order as detected by LEED measurements of H and D on W(110) has been taken to imply some mobility at 5 K, but there is no reformation of the ordered phase within a few hours after electron stimulated disordering.²³ This would suggest diffusion is much slower than is seen in the FEM results, if diffusion over the coherence length of LEED ($\sim 100 \text{ \AA}$) is the controlling factor in reformation of a LEED pattern. However the rate of change

of LEED superstructure reflection intensity does not necessarily reflect the time scale of adsorbate diffusion: it is possible that once destroyed it is hard to nucleate again the ordered phase because of instability of small ordered islands, and not because of absence of diffusive motion. Measurements of diffusion in bulk tungsten are also relevant. The only measurements of diffusion of hydrogen isotopes in bulk tungsten at low temperatures of which we are currently aware are a lower bound estimate of $(1-10) \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ at 29 K by Macrander and Seidman²⁴ and the observation by Panitz²⁵ that deuterium is immobile at 80 K. These findings were interpreted as suggesting nonclassical behavior for ^1H and a very large isotope effect.²⁴

III. THEORY

We propose here a collision limited band propagation model for the diffusion of hydrogen on surfaces at low temperatures. The basis for this model is that at low coverage θ , the hydrogen atoms move independently in the periodic surface potential. This can give rise to energy bands in which we suggest diffusive motion comes about as a result of collisions between hydrogen atoms. The duration of these collisions is short relative to the natural lifetime of the band states.

There is obviously a question concerning the validity of a band picture for atomic motion in bulk solids and on solid surfaces, even though such bands exist for static perfect lattices and have been calculated for, e.g., H on Ni surfaces^{7,26} and H in bcc metals.²⁷ As we show later, the experimental results for the diffusion of the three hydrogen isotopes on W(110) can be described within a band picture only if we postulate renormalized masses which lead to bandwidths of $\sim 10^{-9} \text{ meV}$. A strong objection to the band picture may be raised on the ground that the coherent nature of the motion in such narrow bands may be destroyed by the thermal motion of the lattice. Even at 0 K the zero point motion of the lattice should affect to some extent the narrow band hydrogen motion.

On the other side of this picture there is some evidence (discussed below) for extremely narrow bands in other systems.^{28–30} The insensitivity of the observed diffusion to temperature for $T \lesssim 120 \text{ K}$ ^{12,13} suggests that most of the effect of phonons in this temperature range is taken by the mass renormalization [note that the bandwidth for the bare H mass is $\sim 10^{-3} \text{ meV}$ (Sec. IV)]. It thus appears that band motion is possible at low hydrogen coverage even though its detailed quantitative nature may be substantially more complicated than the simple model used in this work. It is also possible that coherent band motion exists only within the finite distance range ($\gtrsim 100 \text{ \AA}$) probed by the FEM method.

In Sec. III A, we describe the band structure and review other situations where energy bands are formed by atomic particles. Section III B presents the collisional picture of the adsorbate dynamics. We develop a semiclassical theory of hydrogen mobility in narrow bands which is analogous to that of electron mobility in metals, using the relaxation time concept to deal with scattering events. The relative contributions of impurity, phonon, and interparticle scattering to the H/W(110) system are discussed. Quantum statistics of the

diffusing particles are naturally included in this formalism, which is not the case in theories of hopping mobility. The band picture is valid up to a certain maximum coverage which is determined by the interactions. At higher coverages we retain an effective independent particle picture and use more qualitative reasoning to analyze the effects of interactions on $D(\theta)$. Section III C gives a discussion of the sources of interactions between hydrogen atoms chemisorbed on metal surfaces and evaluates the relaxation time. Section III D presents the extension of the band model to higher coverages, together with a brief discussion of its limits.

A. Energy bands for hydrogen on metal surfaces

We shall neglect any lattice imperfections and assume, for simplicity, a square lattice. Complete decoupling between parallel and perpendicular vibrations of the hydrogen is also assumed, the latter giving rise to discrete energy levels. At low temperatures it is only the band structure of the ground state energy levels for parallel motion in the two dimensional periodic potential which is of relevance. Since this implies motion at energies well below the barrier for lateral propagation, the tight binding description applies. Then the two dimensional energy band is given by³¹

$$\epsilon(\mathbf{k}) = \epsilon^0 - 2\beta \cos(k_x l) - 2\beta \cos(k_y l). \quad (3.1)$$

Here ϵ^0 is the zeroth order, ground state, local site energy (plus a small shift independent of \mathbf{k} which we neglect), β the resonance integral³¹ and l the lattice parameter.

Energy bands are in principle a suitable framework for describing mass transport and migration whenever a particle is situated in a periodic potential, but because of their narrow width for high mass particles, are rarely seen for systems other than electrons. This is particularly true in the tight binding regime, where the bandwidth falls off exponentially with the mass. However the possibility of band states has been suggested before for hydrogen adsorbed on metal surfaces^{26,32} and also when dissolved interstitially in bulk metals (excited states only).²⁷ Other nonelectronic species likely to form delocalized states are the positive muon^{10,30} and helium isotopes. The helium isotopes are believed to form two-dimensional bands of width $\lesssim 1$ meV when physisorbed on certain surfaces.²⁷ Evidence for such bands is seen in selective adsorption³³ and in the thermodynamic properties of physisorbed monolayers.³⁴ Low concentrations of defects in quantum crystals of He are also proposed to form energy bands, of width $\sim 10^{-8}$ meV.²⁹ In the latter case the dynamics have been studied extensively for spin diffusion of ^3He in solid ^4He at temperatures below 1 K.²⁹ However there is as yet no evidence for bands of such narrow widths at higher temperatures. If narrow bands are predicted to occur for atomic particles such as H or μ^+ , then the width of the bands at finite temperatures and effects on them of both interadsorbate and particle-lattice interactions will be of prime importance. At temperatures above, e.g., 30 K, thermal lattice motion is not negligible and whether band type motion is possible in the presence of thermal fluctuations will depend specially on the exact details of coupling to the lattice vibrations. In Sec. IV we show that application of our band model to the H/W(110) system implies diffusive mo-

tion in bands much narrower than kT after a mass renormalization due to hydrogen-lattice interactions is taken into account.

B. Collision limited dynamics of band propagation

In the equilibrium state, at each coverage θ the chemisorbed hydrogen atoms will be distributed over the band states (3.1) according to the quantum distribution function

$$f^0(\epsilon(\mathbf{k})) = \frac{1}{e^{[\epsilon(\mathbf{k}) - \mu]/kT} \pm 1}, \quad (3.2)$$

where $+1$ refers to fermions and -1 to bosons. The chemical potential μ is obtained by solving numerically the expression for the density

$$n = n_0\theta = g_s \int \frac{d\mathbf{k}}{(2\pi)^2} f^0(\epsilon(\mathbf{k})), \quad (3.3)$$

where n_0 is the absolute density in atoms cm^{-2} at maximum coverage and g_s the spin degeneracy. We shall now consider how the mobility and hence diffusion coefficient may be derived from the semiclassical treatment of transport in bands. In the semiclassical theory the rate of change of the nonequilibrium distribution function $f(\mathbf{k}, \mathbf{r}, t)$ in the presence of a time independent external force \mathbf{F} is given in the steady state by the Boltzmann equation

$$\mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}}(\mathbf{k}, \mathbf{r}, t) + \mathbf{F} \cdot \frac{1}{\hbar} \frac{\partial f}{\partial \mathbf{k}}(\mathbf{k}, \mathbf{r}, t) = \left[\frac{\partial f}{\partial t}(\mathbf{k}, \mathbf{r}, t) \right]_c, \quad (3.4)$$

where $(\partial f / \partial t)_c$ is the rate of change of $f(\mathbf{k}, \mathbf{r}, t)$ due to scattering mechanisms unrelated to the applied field. The semiclassical assumption is implicit here in the substitution of \mathbf{v} for $\dot{\mathbf{r}}$ and \mathbf{F} for $\hbar \dot{\mathbf{k}}$. In linear response, when only terms first order in the applied field are retained, Eq. (3.4) becomes

$$\mathbf{v} \cdot \left\{ - \frac{\partial f^0}{\partial \epsilon}(\epsilon(\mathbf{k})) \right\} \left[\nabla \mu + \frac{(\epsilon - \mu)}{T} \nabla T - \mathbf{F} \right] = \left(\frac{\partial f}{\partial t}(\mathbf{k}, \mathbf{r}, t) \right)_c, \quad (3.5)$$

where ∇ is the spatial gradient. In the most usual form of the relaxation time approximation (RTA) the collision term is replaced by

$$\left(\frac{\partial f}{\partial t}(\mathbf{k}, \mathbf{r}, t) \right)_c = - \frac{[f(\mathbf{k}, \mathbf{r}, t) - f^0(\epsilon(\mathbf{k}))]}{\tau(\epsilon(\mathbf{k}))}, \quad (3.6)$$

whereupon Eq. (3.5) yields

$$f(\mathbf{k}, \mathbf{r}, t) = f^0(\epsilon(\mathbf{k})) - \tau(\epsilon(\mathbf{k})) \left(- \frac{\partial f^0}{\partial \epsilon}(\epsilon(\mathbf{k})) \right) \mathbf{v} \cdot \left[\nabla \mu - \frac{(\epsilon - \mu)}{T} \nabla T - \mathbf{F} \right]. \quad (3.7)$$

In field emission microscopy the adsorbate is at constant temperature and, on a macroscopic scale, also at constant chemical potential. (Measurement of diffusion by FEM is based on the diffusion equation for gradients of concentration fluctuations rather than macroscopic concentration gradients,¹⁴ which is valid for long wavelength fluctuations.³⁵) The particle flux \mathbf{J} in the presence of the force \mathbf{F} is given by

$$\mathbf{J} = n\gamma\mathbf{F} = g_s \int \frac{d\mathbf{k}}{(2\pi)^2} \mathbf{v}(\mathbf{k}) f(\mathbf{k}) \quad (3.8)$$

which defines the mobility tensor γ as the ratio of velocity \mathbf{v} to force \mathbf{F} . Inserting Eq. (3.7) into Eq. (3.8) we obtain

$$\gamma = \frac{g_s}{n} \int \frac{d\mathbf{k}}{(2\pi)^2} \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k}) \tau(\epsilon(\mathbf{k})) \left(- \frac{\partial f^0}{\partial \epsilon}(\epsilon(\mathbf{k})) \right). \quad (3.9)$$

The mobility is related to the chemical diffusion coefficient D by the Stokes–Einstein relation which we generalize from classical Boltzmann to the quantum distributions (3.2) by

$$D = \gamma \left(\frac{1}{n} \frac{\partial n}{\partial \mu} \right)^{-1}. \quad (3.10)$$

Both Eqs. (3.9) and (3.10) remain valid in the limit as the external field goes to zero and thus yield the diffusion tensor corresponding to collision limited band propagation, where the effects of collisions are entirely described by the single parameter τ , the relaxation time.

The semiclassical approximation is naturally appropriate for atomic particles in bands since their wavelength is short compared with the length scale of the interactions involved and of variations in the external field. Introduction of a single relaxation time τ precludes interband transitions, which is easily valid for hydrogen adsorbed on W(110) where the bandwidth is orders of magnitude narrower than the separation between ground and first excited band (Sec. IV). More importantly, the RTA assumes that collisions, whatever their origin, are random, uncorrelated events, which are short relative to the natural lifetime of the band states. This means that the approximation is valid as long as

$$\Delta \tau \gg \hbar, \quad (3.11)$$

where $\Delta = 8\beta$ is the bandwidth, β being the resonance integral (3.1).

There are several mechanisms which can in principle be responsible for the relaxation time τ . Anything which causes deviations, temporal or static, from perfect periodicity of the surface causes scattering of the independent particle states. The relevant mechanisms for hydrogen are: (i) impurity or defect scattering, (ii) hydrogen–phonon scattering, and (iii) hydrogen–hydrogen scattering. These are directly analogous to the mechanisms responsible for electrical resistance of metals but the relative importance of these is very different for hydrogen and for electrons. In particular, the electron–electron interaction is generally unimportant in metals except at very low temperatures and resistance is primarily due to electron–phonon scattering at most temperatures. The unimportance of electron–electron interactions is of course due to the efficient screening of the Coulomb potential.³¹ For chemisorbed hydrogen however, it appears (because of the strong coverage dependence and lack of temperature dependence) that the hydrogen–hydrogen interaction is not so effectively shielded and is more important than any dynamic hydrogen–phonon interaction in determining the relaxation time.

If all three mechanisms are present, acting independently, the resulting relaxation time is given by

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_p} + \frac{1}{\tau_H} \quad (3.12)$$

with τ_i the relaxation time from impurity scattering, τ_p that from hydrogen–phonon scattering, and τ_H that from hydrogen–hydrogen scattering. Impurity scattering will not cause any concentration dependence of D (unless significant sur-

face reconstruction occurs). It will only cause some change in the absolute magnitude of $D(\theta)$ so although it must be relevant if $H:W \neq 1$ at maximum coverage,¹⁸ we shall neglect this in our analysis of $D(\theta)$.

The question of the extent and effect of hydrogen interactions with lattice vibrations is more important, both in determining the absolute magnitude of $D(\theta)$ and its variation with θ . Muttalib and Sethna³⁶ have suggested that a phonon mechanism may account for the coverage dependence of diffusion at low temperatures. Unfortunately details of these interactions depend crucially on both the hydrogen–lattice coupling and the surface phonon spectrum, neither of which is known. Furthermore, the surface phonon spectrum may be altered by adsorbate–surface interactions. Coupling to lattice nuclear motions can in general have two kinds of effects: (i) introduction of a mass renormalization or Franck–Condon factors, according to the relative time scales of hydrogen and lattice motions,³⁷ (ii) dephasing arising from energy level fluctuations. The latter act as a source of scattering for motion in the average periodic potential and if sufficiently strong, can destroy the coherence necessary for band motion. They also lead to phonon assisted tunneling, which is an activated process.^{38,39} However theoretical treatments of the mobility of hydrogen interstitials in bulk metals find strong temperature dependence in the case when dephasing is important (small polaron limit).^{38,39} For example, a 3D Debye model predicts T^{-9} dependence of band type propagation and T^{+7} dependence of hopping motion for $T < T_{D/2}$ ($T_D =$ Debye temperature): for H on W(110) with $T_D = 226$ K¹⁶ this means a 10^5 -fold decrease in band mobility from 27 to 100 K and a 10^{+4} -fold increase in hopping mobility over the same range. Although the exponents will differ for 2D phonon spectra, the fact that no inverse temperature dependence and no minimum in D is seen below the Arrhenius regime suggest that this is therefore not the appropriate situation for the H/W(110) system. For this reason we assume that the nuclear lattice distortions effect only a mass renormalization of the adsorbed atoms which otherwise continue to move in the average periodic potential, and disregard the possibility of additional scattering resulting from lattice motion. Then the delocalized or localized nature of the adsorbate states will be determined by the hydrogen–hydrogen interactions.

In using a mass renormalization we follow Muttalib and Sethna³⁶ who used the additive mass renormalization at 0 K to account for the small isotopic differences in D in the tunneling regime. Within a band picture it gives rise to an effective narrowing of the band (3.1). We do not analyze the temperature dependence of the additive renormalization factor here, assuming it to be constant over the range 27–120 K.

The relaxation time derived from hydrogen–hydrogen scattering may be derived at two levels. Firstly, if the relative motion of the hydrogen atoms is neglected, i.e., each hydrogen is considered to scatter from a static array of randomly distributed hydrogens, the collision term is given by

$$\left(\frac{\partial f}{\partial t}(\epsilon(\mathbf{k})) \right)_c = - \int \frac{d\mathbf{k}'}{(2\pi)^2/A} W_{\mathbf{k}\mathbf{k}'} [f(\mathbf{k}) - f(\mathbf{k}')] \quad (3.13)$$

with $W_{\mathbf{k}\mathbf{k}'}$ the transition rate for scattering from \mathbf{k} to \mathbf{k}' and A the surface area. When the energy levels are taken as approximately isotropic in \mathbf{k} , Eqs. (3.6) and (3.13) yield the following relaxation time for elastic scattering³¹:

$$\frac{1}{\tau(\epsilon(\mathbf{k}))} = \int \frac{d\mathbf{k}'}{(2\pi)^2/A} W_{\mathbf{k}\mathbf{k}'} (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'). \quad (3.14)$$

When $W_{\mathbf{k}\mathbf{k}'}$ is given by the Golden rule

$$W_{\mathbf{k}\mathbf{k}'} = \frac{2\pi}{\hbar} |V_{\mathbf{k}\mathbf{k}'}|^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'}) \quad (3.15)$$

with the potential matrix element $V_{\mathbf{k}\mathbf{k}'}$ related to the scattering amplitude $F(k, \Theta)$ in the two dimensional Born approximation

$$|F(k, \Theta)|^2 = \frac{m^2}{2\pi\hbar^4 k} |V_{\mathbf{k}\mathbf{k}'}|^2 A^2, \quad (3.16)$$

$$|V_{\mathbf{k}\mathbf{k}'}| = \left| \int \frac{d\mathbf{r}}{A} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} V_{\text{H}}(\mathbf{r}) \right|, \quad (3.17)$$

$$\cos \Theta = \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}' \quad (3.18)$$

(m being the mass of the scattered H atom and Θ the lab. frame scattering angle) we find that

$$\frac{1}{\tau_{\text{H}}(\epsilon(k))} = n v(\epsilon) \int d\Theta (1 - \cos \Theta) |F(k, \Theta)|^2. \quad (3.19)$$

Because of the implicit assumption of isotropic energy surfaces, $v(\epsilon) = \hbar k / m$ and $k = |\mathbf{k}|$ are average quantities at energy ϵ and $\tau_{\text{H}}(\epsilon(k))$ is now independent of the orientation of k . We shall define $v(\epsilon)$ and k more precisely in Sec. III C. $V_{\text{H}}(r)$ is the hydrogen-hydrogen interaction. The Born approximation is used here merely on a semiquantitative footing and in view of the fact that the collisions involved are governed by relatively weak long range interparticle interactions. An exact numerical evaluation of the scattering amplitude is possible but does not seem justified at the present relatively crude level of our present treatment.

A second, more accurate description takes the relative motion of the hydrogen atoms into account. This is obtained using the general collision term in the Boltzmann equation

$$\begin{aligned} \left(\frac{\partial f(\epsilon(\mathbf{k}))}{\partial t} \right)_c = & \iint \frac{d\mathbf{k}_1}{(2\pi)^2/A} d\Theta W_{\mathbf{k}\mathbf{k}_1, \mathbf{k}'\mathbf{k}'_1} \\ & \times [f(\mathbf{k}') f(\mathbf{k}'_1) (1 \mp f(\mathbf{k})) (1 \mp f(\mathbf{k}_1)) \\ & - f(\mathbf{k}) f(\mathbf{k}_1) (1 \mp f(\mathbf{k}')) (1 \mp f(\mathbf{k}'_1))] \end{aligned} \quad (3.20)$$

with Θ the scattering angle in the c.m. frame and $W_{\mathbf{k}\mathbf{k}_1, \mathbf{k}'\mathbf{k}'_1}$ the transition rate for scattering from \mathbf{k}, \mathbf{k}_1 to $\mathbf{k}, \mathbf{k}'_1$, where \mathbf{k} and \mathbf{k}_1 correspond to the two atoms involved in the collision. With the previous form of $W_{\mathbf{k}\mathbf{k}_1, \mathbf{k}'\mathbf{k}'_1}$, and approximation of isotropic energy surfaces we obtain

$$\begin{aligned} \frac{1}{\tau_{\text{H}}(\epsilon)} = & g_s \int d\epsilon_1 d\phi_1 \left(\frac{m}{m_r} \right) \delta(E_{\mathbf{k}_r} - E_{\mathbf{k}'_r}) \int d\Theta V_r |F(k_r, \Theta)|^2 \\ & \times \frac{f^0(\epsilon_1) (1 \mp f^0(\epsilon')) (1 \mp f^0(\epsilon'_1))}{(1 \mp f^0(\epsilon))} [1 + \eta - \eta' - \eta'_1], \end{aligned} \quad (3.21)$$

where m_r is the reduced mass of the colliding atoms, v_r and k_r are the velocity and wave vector of relative motion between \mathbf{k} and \mathbf{k}_1 , ϵ' and ϵ'_1 the final particle energies after scattering, and $E_{\mathbf{k}_r}$, $E_{\mathbf{k}'_r}$ the total energy before and after collision. The quantities η, η', η'_1 are scalars defined in terms of the angles between unit vectors $\hat{\mathbf{k}}, \hat{\mathbf{k}}_1, \hat{\mathbf{k}}'$, and $\hat{\mathbf{k}}'_1$,

$$\eta = \hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}, \quad \eta' = \hat{\mathbf{k}}_1 \cdot \hat{\mathbf{k}}'_1, \quad \eta'_1 = \hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}'_1. \quad (3.22)$$

For scattering of identical particles with spins the two dimensional scattering amplitude $F(k, \Theta)$ is given by the symmetrized expression⁴⁰

$$F_F(k, \Theta) = \frac{s+1}{2s+1} F_a(k, \Theta) + \frac{s}{2s+1} F_s(k, \Theta) \quad (3.23)$$

for fermions and

$$F_B(k, \Theta) = \frac{s+1}{2s+1} F_s(k, \Theta) + \frac{s}{2s+1} F_a(k, \Theta) \quad (3.24)$$

for bosons, where F_s and F_a are the symmetric and antisymmetric amplitudes respectively:

$$F_s(k, \Theta) = F(k, \Theta) + F(k, \Pi + \Theta), \quad (3.25)$$

$$F_a(k, \Theta) = F(k, \Theta) - F(k, \Pi + \Theta). \quad (3.26)$$

The mobility γ [Eq. (3.8)] is then evaluated with the isotropic relaxation time $\tau(\epsilon)$ as

$$\gamma = \frac{g_s}{n} \int_0^{8\pi} d\epsilon \left(\frac{-\partial f^0(\epsilon)}{\partial \epsilon} \right) \tau(\epsilon) \int_{S(\epsilon)} \frac{dk_s}{(2\pi)^2} \frac{\mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\nabla_{\mathbf{k}} \epsilon(\mathbf{k})|}, \quad (3.27)$$

where $S(\epsilon)$ is the contour in \mathbf{k} space at constant energy ϵ and dk_s the differential length element on $S(\epsilon)$. Integration over $S(\epsilon)$ is done exactly and does not assume an isotropic energy surface. From now on the band energy is defined with respect to zero at the bottom of the band.

We now discuss the hydrogen interaction and evaluate the scattering amplitudes (3.23)–(3.26).

C. Hydrogen-hydrogen interactions on metal surfaces

There are several possible contributions to interactions between chemisorbed hydrogen atoms. The repulsive part of the direct interaction gives us an approximate hard core interaction radius while the long range direct component can be assumed to have a negligible effect at low concentrations. Indirect interaction mediated by the surface may be: (i) between surface induced dipoles, (ii) elastic interaction transmitted by lattice displacements, or (iii) electronic interactions mediated by conduction electrons. Induced surface dipoles for hydrogen are negligible, and the lack of temperature dependence in the low temperature regime leads us to regard (ii) as unimportant, as was discussed above. The third interaction arises essentially from the superposition of the potential between two protons and that between one proton and the image charge of the other.^{41,42} Calculations based on jellium models yield a screened oscillatory long range interaction when the hydrogen atoms are effectively ionized and within the surface electron density (the situation relevant to strong chemisorption), and a slowly decaying repulsive interaction when the atoms are located outside the surface electron density.^{41,42} For our purposes it is suffi-

cient to take the longer range repulsive component into account in τ_H by calculating $F(k, \Theta)$ by scattering from a hard core with radius a larger than the atomic radius, a was adjusted to yield reasonable relaxation times, a value of 1.5 Å having been found suitable.

Our relaxation time τ_H in Eq. (3.19) is derived from collisions between free particles with wave vector k determined by the energy ϵ . At the lower band edge k is related to ϵ by the effective mass m^* :

$$\epsilon = \frac{\hbar^2 k^2}{2m^*}, \quad (3.28)$$

where

$$m^* = \frac{\hbar^2}{2\beta l^2} \quad (3.29)$$

[l = lattice spacing Eq. (3.1)]. We use this expression to evaluate an effective wave vector k_{eff} at all energies ϵ within the band. This semiclassical approximation is strictly valid at the band edges and slightly overestimates the scattering amplitude at the center of the band. (Here the true effective mass is infinite, hence k_{eff} also and the scattering cross section approaches its classical value.) The scattering amplitude $F(k_{\text{eff}}, \Theta)$ for hard core scattering in two dimensions may be solved for analytically⁴³ to yield

$$F(k_{\text{eff}}, \Theta) = \sqrt{\frac{2i}{\pi k_{\text{eff}}}} \sum_{m=0}^{\infty} \rho_m e^{2i\delta_m(k_{\text{eff}} a)} \times \sin[\delta_m(k_{\text{eff}} a)] \cos m\theta, \quad (3.30)$$

where $\rho_1 = 1$, $\rho_m = 2$ for $m > 0$ and $\delta_m(k_{\text{eff}} a)$ is defined by

$$\tan \delta_m(k_{\text{eff}} a) = \frac{-J_m(k_{\text{eff}} a)}{N_m(k_{\text{eff}} a)}, \quad (3.31)$$

where J_m , N_m the regular and irregular Bessel functions of order m , and a the hard core radius. In the generalized expression for τ_H , Eq. (3.21), effective k vectors are defined in a similar way from ϵ and ϵ_1 , which are then combined to give the relative k vector k_r . The masses m and m_r are also defined in terms of the effective mass m^* , i.e., $m = m^*$, $m_r = m^*/2$.

D. Effect of hydrogen-hydrogen interactions on energy level structure

In our model so far hydrogen-hydrogen interactions have been assumed to affect only the dynamics of the adsorbed hydrogens by the short lived two body collisions represented in τ_H . This is valid at low coverage θ , but at higher coverage the effect of these interactions on the energy levels of the adsorbed hydrogens cannot be neglected. At finite concentrations each hydrogen moves in a potential which is a sum of the underlying periodic potential and its interactions with other hydrogen atoms. If the latter is of the range of a lattice spacing and is of the same order of magnitude as the periodic potential, then it cannot be ignored at higher coverages.

A full description would require solution of the energy level structure for interacting particles which tunnel in an external periodic potential. In order to analyze the localized or delocalized nature of the resulting adsorbate states, addi-

tional wave function information would be necessary. Such analysis goes beyond the aims and scope of the present study. Instead we treat the interactions approximately by replacing the periodic potential $V(r)$ by an effective potential $\bar{V}(r)$ which contains a static average of the hydrogen-hydrogen interactions in addition to the underlying periodic term. This is illustrated in Fig. 2 for coverage $\theta = 0.4$ which corresponds to an average of two nearest neighbors for each hydrogen. As a hydrogen atom tunnels from site A to site B it interacts with its two nearest neighbors at C_1 and at C_2 which are assumed to be stationary. Interactions with these stationary neighbors of the initial site A are included in the effective potential $\bar{V}(r)$. At any point P on the tunneling path

$$\bar{V}(x) = V(x) + V_H(r_1) + V_H(r_2), \quad (3.32)$$

where x is the tunneling coordinate ($0 < x < l$), r_1 and r_2 are the distances PC_1 and PC_2 , respectively (Fig. 2), $V(x)$ the periodic potential, and $V_H(r)$ the hydrogen-hydrogen interaction.

The energy band structure (3.1) is determined by the ground state resonance integral β which we evaluate by relating it to the one dimensional tunneling integral⁴⁴

$$\beta = 4 \left(\frac{\hbar\omega}{2\pi} \right) \exp \left[-\frac{\sqrt{2m}}{\hbar} \int_{x_1}^{x_2} \sqrt{\bar{V}(x) - \hbar\omega/2} dx \right], \quad (3.33)$$

where $\bar{V}(x)$ is the one dimensional barrier between binding sites (3.32), ω is the parallel vibration frequency of H in a local site, and x_1 , x_2 the turning points on either side of the barrier. Regarding $V(x)$, little is known about the barrier shape or size apart from an activation energy of ~ 200 meV derived from high temperature diffusion measurements^{12,13} which gives an estimate of the barrier height. In the diffusion calculations presented in Sec. IV we shall therefore use the simplest model, of a rectangular barrier. To show the effect of $V_H(r)$ however, we shall first consider a more realistic barrier shape. Figure 3 shows a one dimensional barrier potential $V(x)$ which was constructed by taking a one dimensional path between sites on the H/W(110) surface calculat-

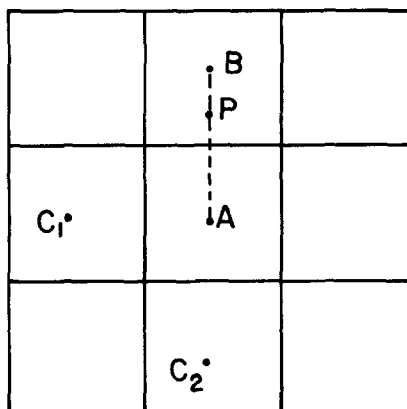


FIG. 2. Diagram showing the tunneling path (---) of a chemisorbed hydrogen atom between nearest neighbor sites A and B in the presence of two nearest neighbors C_1 , C_2 of the initial site A. The tunneling coordinate x is measured from A to B. r_1 and r_2 are the rectilinear distances C_1P and C_2P at any point P on the tunneling path.

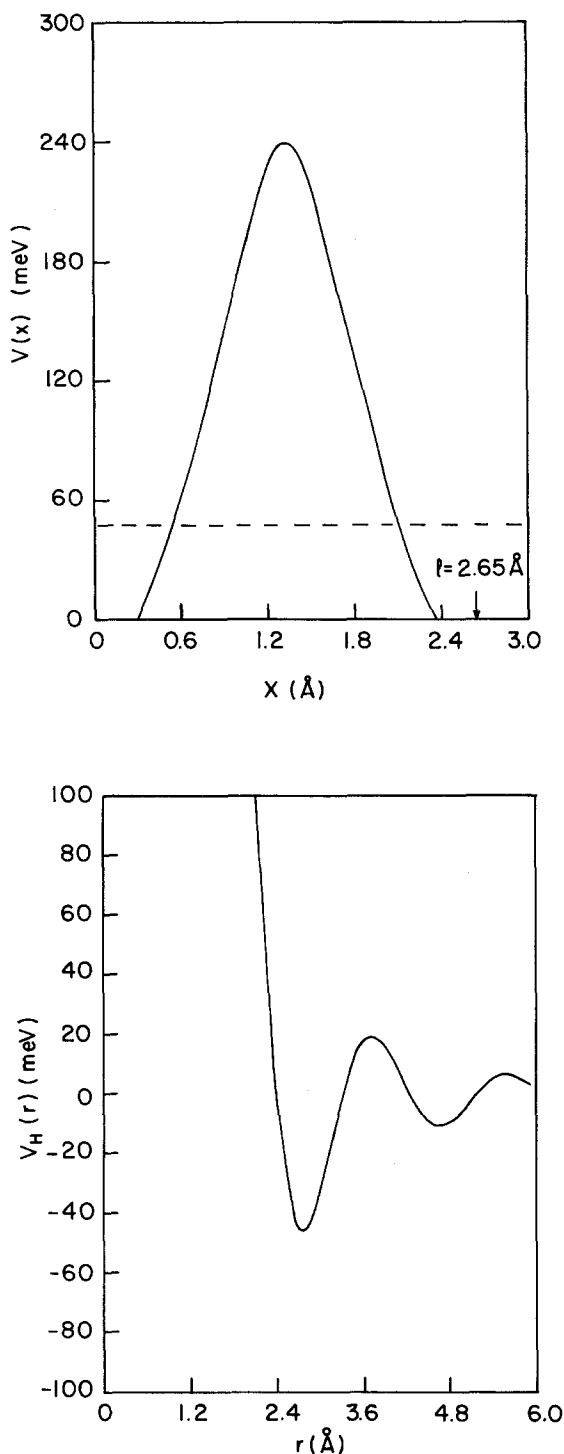


FIG. 3. (a) Quasi-one-dimensional potential barrier between neighboring adsorption sites on the H/W(110) surface. The model was calculated by interpolating between the potential energy surface values of Nordlander *et al.* (Ref. 8) and scaling this potential to give a barrier height of 240 meV. The dashed line (---) indicates the ground state energy of the parallel vibrational motion of adsorbed H, $\hbar\omega/2 = 47.5$ meV. (b) Interaction potential $V_H(r)$ between two adsorbed hydrogen atoms on tungsten. This result was derived as an analytic approximation for a situation intermediate between the results of Ref. 42 for hydrogen adsorbed on sodium and on aluminum, calculated within a jellium model. $V_H(r)$ is given here by $V_H(r) = -V_0\{\cos[2k_0(r-r_0)]/r_0^2\}$, $r > 1.9$ Å with $V_0 = 150$ meV Å², $k_0 = 1.7$ Å⁻¹, and $r_0 = 1.0$ Å. Hydrogen is here assumed to be inside the electron density of the jellium, i.e., strongly chemisorbed.

ed by Nordlander *et al.*⁸ and scaling this to give a barrier of 240 meV. Taking the parallel frequency from EELS measurements as 95 meV for ¹H, gives an estimated activation energy of 193 meV for ¹H which agrees well enough with the experimental value.^{12,13} For $V_H(r)$ we now take the oscillatory electronic surface mediated interaction appropriate to strongly chemisorbed hydrogen,⁴² shown in Fig. 3(b). [The form shown here is intermediate between that estimated in Ref. 42 for Na ($r_s = 3.9$) and Al ($r_s = 2.1$) within the jellium model: it is reasonable to assume that W lies between these two metals.] The tunneling integral (3.33) is now calculated with the potential $\bar{V}(x)$, Eq. (3.32). The bandwidth Δ resulting for ¹H is given as a function of θ and of the average number and type of nearest neighbors in Table I. We see that within this simple additive mean field model there is a two order of magnitude increase in Δ as θ increases, due to an effective decrease in barrier height resulting from the attractive component in $V_H(r)$ at $r < l$.

Equation (3.32) contains additive interactions: however it is expected that the indirect interaction will be nonadditive and saturate at some coverage, since polarization of the metal electron distribution will not be linearly related to addition of successive hydrogens. Since very little is known for interactions between more than two hydrogens, in our simplified model we shall assume the interactions to be additive at low coverage but also introduce a saturation limit at $\theta = 0.3$ (see Sec. IV B) which corresponds to the maximum in the experimental $D(\theta)$ (Fig. 1).

The increased bandwidth in our one particle mean field effective periodic potential is a result of the strong chemical forces between adsorbed hydrogen atoms and the nonmonotonic variation of these with distance. As θ is further increased these interactions affect the density of available states in a more drastic way as the local fluctuations in site energy levels prevent the coherent propagation between sites, i.e., inducing localization. It is not our aim here to attempt a detailed analysis of the extent and dynamical effects of localization, which would be a major undertaking. We can only give a heuristic argument here. At high coverage the repulsions between hydrogen atoms prevent multiple occupation of sites. Then a primitive estimate of the density of delocalized states which can still contribute to tunneling

TABLE I. Bandwidth Δ as a function of number and type nearest neighbors of the initial site A. θ is the coverage ($\theta = 1$ corresponds to H:W = 1) $\Delta = 8\beta$ is calculated from the tunneling integral (3.33) with the potential (3.32) shown in Fig. 3. The lattice renormalized mass of ¹H ($m = 6.5$) is used in this calculation.

θ	No. nearest neighbors	Configuration	Δ (meV)
0	0		1.2(-9)
0.25	1	C_1	1.3(-7)
		C_2	1.3(-9)
0.4	2	C_1C_1	6.7(-6)
		C_1C_2	1.0(-7)

mobility at a given coverage is given by multiplying the density of states from Eq. (3.1) by the mean area not covered by repulsive forces, i.e., the density of delocalized states is given by

$$\rho(\epsilon) = \int_{S(\epsilon)} \frac{dk_s (1 - \theta)}{(2\pi)^2 |\nabla_{\mathbf{k}} \epsilon(\mathbf{k})|}, \quad (3.34)$$

where integration is over an energy contour, $S(\epsilon)$.

Before presenting the results of applying the band model to diffusion of hydrogen isotopes on W(110) we briefly discuss its limitations. We have already noted one restriction on Eq. (3.9), which is necessary if the RTA is to hold Eq. (3.11). Independently of this we expect that band motion will no longer be obeyed above a critical coverage θ_c at which the local fluctuations in localized site energy levels which result from hydrogen interactions prevent coherent propagation from site to site. Klinger⁴⁵ has given a criterion for θ_c for the quantum diffusion of defects in quantum crystals when motion is limited by impurities. This criterion says that band propagation is no longer possible when the difference between energy fluctuations on adjacent sites due to the presence of a defect on some other site become larger than the bandwidth. Defining the length r^* (a property of the impurity potential) by

$$|\delta\epsilon(r^*) - \delta\epsilon(r^* + l)| \simeq l \left| \frac{\partial \delta\epsilon(r)}{\partial r} \right|_{r=r^*} = \Delta, \quad (3.35)$$

where $\delta\epsilon(r)$ is the shift induced in a localized site energy level induced by the presence of other hydrogen atoms at distance r , Δ is the bandwidth, and l is the lattice spacing, then the critical coverage θ_c beyond which band motion is destroyed is given by

$$(r^*)^2 \theta_c = l^2. \quad (3.36)$$

Even when band propagation is not allowed, one can nevertheless have coherent tunneling motion over a finite length which is greater than or equal to the lattice spacing. Such "coherent hopping" is a nonactivated process. In the next section, after analyzing the results for hydrogen on W(110) we show how the results at intermediate and high coverage can also be qualitatively described by such a hopping model.

IV. APPLICATION TO LOW TEMPERATURE DIFFUSION OF HYDROGEN ON W(110)

A. Low coverage $\theta < 0.1$

We first consider the results from the independent particle model in the energy band structure calculated without hydrogen interactions (Secs. III A–III C). The diffusion calculations are carried out with a rectangular barrier of height V_B and width X_B chosen such that the same argument in the exponential of Eq. (3.33) is obtained with both the rectangular barrier and the potential of Fig. 3(a). All parameters for the diffusion calculations are given in Table II, together with the hard core radius a and the lattice parameter l . The latter is chosen to yield an adsorbate density $1.42 \times 10^{15} \text{ cm}^{-2}$ at $\theta = 1.0$ for a square lattice, while the former can vary somewhat when the long range interactions are taken into account. When the diffusion coefficient is calculated at very low coverage with the parameters of Table II,

TABLE II. Parameters for the resonance integral β , Eq. (3.32), which determines the energy band structure (3.1) at zero coverage. The bandwidth is given by $\Delta = 8\beta$.

Frequency (¹ H)	$\omega = 95 \text{ meV}$
Barrier height	$V_B = 300 \text{ meV}$
Barrier width	$X_B = 0.95 \text{ \AA}$
Lattice spacing	$l = 2.65 \text{ \AA}$
Hard core radius	$a = 1.5 \text{ \AA}$

Bandwidth Δ (meV) for the three H isotopes with and without additive mass renormalization Δm (amu).

	$\Delta m = 0$	$\Delta m = 5.5$
Δ (¹ H)	1.35 (−2)	1.19 (−9)
Δ (² H)	8.34 (−4)	5.35 (−11)
Δ (³ H)	1.79 (−6)	4.51 (−12)

we find that simultaneous agreement with the experimental values for all three isotopes is only possible if the mass in Eq. (3.33) is renormalized by an additive amount, $\Delta m = 5.5$ amu. A similar conclusion was reached by Muttalib and Sethna³⁶ and confirms the conclusion of DiFoggio and Gomer on the inadequacy of a tunneling model with no effects of interaction with lattice motion.¹² In principle the renormalized mass may depend on the coverage. The effect of this on the tunneling will then be similar to changing the effective barrier with adsorbate concentration. In order to provide the simplest theory we incorporate coverage effects only on the effective potential (see Sec. III D).

The most striking consequence of the calculation are the very narrow bandwidths Δ (Table II). It can be shown from Eqs. (3.2), (3.9), and (3.10) that when $\Delta \ll kT$ all quantum statistical factors cancel except for the scattering amplitude $F(k, \Theta)$ and we find, e.g.,

$$D_{xx}(\theta) = \beta^2 l^2 \tau_H(\beta) \left(\frac{8g_s}{4\pi^2 \hbar^2} \right) \times \int_0^\pi dx' \sqrt{1 + \left(\frac{dy'}{dx'} \right)^2} \frac{\sin x' \sin x'}{\sqrt{\sin^2 x' + \sin^2 y'}}, \quad (4.1)$$

where

$$x' = \frac{2\pi}{l} k_x, \quad y' = \frac{2\pi}{l} k_y \quad (4.2)$$

are scaled coordinates of the reciprocal lattice. The integral in Eq. (4.1) is taken along the contour defined by the energy ϵ :

$$\frac{\epsilon}{\beta} = -2 \cos x' - 2 \cos y' + 4. \quad (4.3)$$

Equation (4.2) together with Eq. (3.19) imply that $D \sim n^{-1} (D = D_{xx} = D_{yy}$ from now on).

Figure 4 shows the concentration dependence of D for all three isotopes with ²H treated as a boson of spin 1, and ¹H, ³H as fermions of spin 1/2. The inverse concentration dependence at small θ agrees with the experimental findings¹³ but we find no structure at higher coverages and in particular no

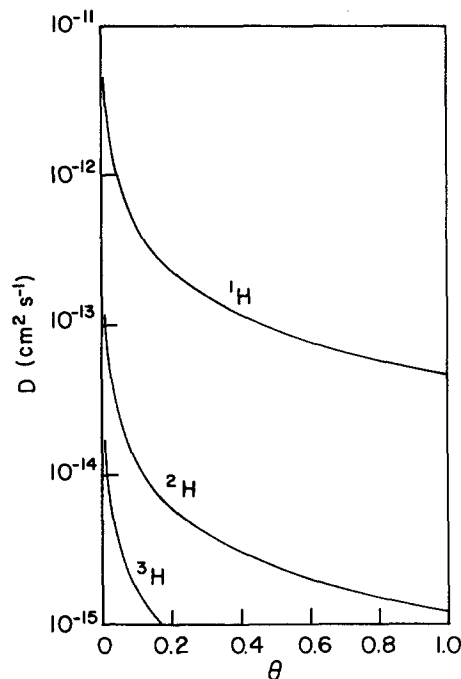


FIG. 4. Log D vs relative coverage θ for ^1H , ^2H , and ^3H at 27 K calculated within the independent particle model of Sec. III C. The band structure is independent of hydrogen interactions here. ($D = D_{xx} = D_{yy}$.)

difference between fermions and bosons at any coverage. The result is similar when τ_{H} is calculated according to Eq. (3.21). Thus we conclude that the initial fall in $D(\theta)$ for $\theta < 0.1$ is consistent with a band model for motion of the hydrogens in very narrow bands with effective hard core collisions between particles. Extrapolation of the experimental results to $\theta = 0$ will thus give τ_i for impurity scattering, which when inserted in Eq. (3.12) will remove the singularity in (4.1). {The origin of this singularity is the inverse concentration dependence of τ_{H} [Eq. (3.19)], which in our treatment is the only explicit component of the relaxation time τ [Eq. (3.12)].} However the rapid decrease in $D(\theta)$ makes extrapolation uncertain and since we are not interested in the constant effect of impurities we shall not include τ_i here.

The fact that D remains finite at $\theta = 1.0$ is a trivial consequence of the model, resulting from taking nonunity spin degeneracy g_s . When $g_s = 1$ however, we find for fermions $D \rightarrow 0$ as it should for filled bands, while for bosons a finite value is obtained. Inspection of Eqs. (3.2) and (3.9) shows that this is necessarily the case for bands narrow relative to kT since $\partial f^0(\epsilon)/\partial \epsilon$ cannot be zero for bosons, which means γ and D remain finite at all θ . This is an interesting observation in view of the experimentally observed rise in $D(\theta)$ for $\theta > 0.7$ (Fig. 1), but is of course a result of the independent particle picture in the band structure at the dilute limit, which is not appropriate at these high coverages.

Quantitatively these results vary slightly with small changes in the parameters and given the various sources of uncertainty, we regard Table II as a representative best fit set. No temperature dependence is seen over the range 30–120 K, as expected since $\Delta \ll kT$.

B. Intermediate and high coverage $\theta > 0.1$

To investigate the diffusion for $\theta > 0.1$ we now include the effects of hydrogen–hydrogen interactions on the energy level structure in the qualitative fashion outlined in Sec. III D. The diffusion coefficient $D(\theta)$ is now calculated with a coverage dependent bandwidth $\Delta(\theta)$ (Table I) and the modified density of states (3.34). The effect of $V_{\text{H}}(r)$ is simplified for the rectangular barrier model by taking V_B to decrease linearly with coverage and saturating at $\theta = 0.3$:

$$V_B(\theta) = \begin{cases} V_B - \lambda\theta, & \theta < 0.3, \\ V_B - 0.3\lambda, & \theta > 0.3. \end{cases} \quad (4.4)$$

with $\lambda = 250$ meV, the bandwidth for ^1H increases from $\Delta = 1.2(-9)$ meV at $\theta = 0$ to $\Delta = 0.9(-7)$ meV at $\theta = 0.3$. The effect of interactions upon the dynamics are still calculated within the relaxation time expression for τ_{H} . The result of this is shown in Fig. 5 in which we now find a minimum in $D(\theta)$ at $\theta \sim 0.1$. The location of the minimum moves to lower coverage as the isotope mass increases from ^1H to ^3H , as seen in the experimental result (Fig. 1). For $\theta > 0.3$ after the mean field potential $\bar{V}(r)$ has saturated, $D(\theta)$ decreases again. This is now faster than n^{-1} due to the reduction in the density of states, Eq. (3.34). This also forces $D(\theta)$ to go to zero at $\theta = 1$, regardless of the spin degeneracy.

In neither situation, with or without the factor of $(1 - \theta)$ in Eq. (3.34), does the diffusion coefficient for ^2H when treated as a boson show any increase for high coverage, i.e., $\theta > 0.6$. This is a consequence of the narrowness of the energy bands, which eliminates all differences between fermions and bosons as mentioned above and which also suppresses all concentration dependence except that from the collision rate (3.19). In order to further investigate whether

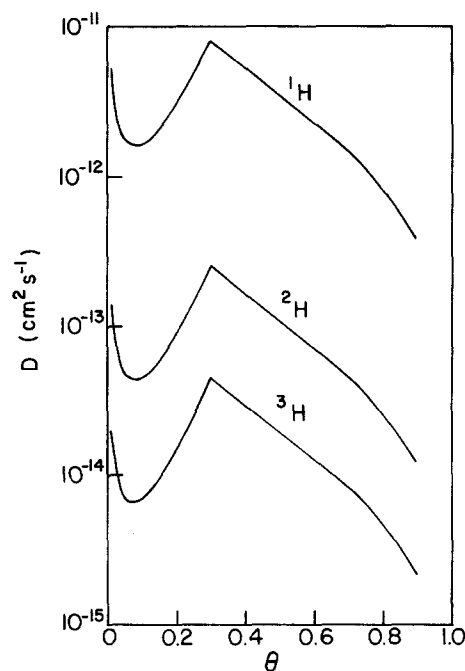


FIG. 5. Log D vs coverage θ for ^1H , ^2H , and ^3H at 27 K calculated taking the effect of hydrogen interactions on the band structure into account, Sec. III D.

this increase is a consequence of the quantum statistics a proper many body treatment of the dynamics at high densities is required. At the current time it is an open question whether this apparent increase for ^2H is really due to quantum statistics or the particular energetics for this isotope. (An explanation based on overlap of spin wave functions within a hopping tunneling model has recently been advanced by Tringides and Gomer.⁴⁶)

C. Tunneling between localized states

The above discussion shows that all the coverage dependence of $D(\theta)$ except the increase for ^2H at $\theta > 0.7$ may be qualitatively understood within a tunneling model based on band type propagation. However we do not expect that the mobility is true collision controlled band motion over the entire range of θ , but that tunneling between localized sites, or over some finite localization length, occurs above a certain coverage. Nevertheless, the behavior of $D(\theta)$ is expected to be qualitatively the same within both a delocalized and a localized model of adsorbate states, being determined essentially by the nature of the hydrogen-hydrogen interactions. To confirm this we now investigate a hopping tunneling model and consider the effects of finite hydrogen concentration on this.

In Sec. III we mentioned two criteria for validity of the band mobility, Eqs. (3.11) and (3.35). The calculation displayed in Fig. 5 obeys the relaxation time consistency requirement (3.11) for $\theta < 0.2$. Condition (3.35) together with $V_{\text{H}}(r)$ (Fig. 4) yields an estimate of a critical concentration θ_c above which coherent band type propagation between successive sites is not possible. The large uncertainty in estimating $V_{\text{H}}(r)$ from jellium models for the metal⁴² renders a realistic estimate impossible but if we invert Eq. (3.36) we find that if $\theta_c = 0.1$, then $r^* = 8.4 \text{ \AA}$ and if $\theta_c = 0.2$, then $r^* = 5.9 \text{ \AA}$, both of which are reasonable with the model potential of Fig. 4 and condition (3.35).

The nature of the hydrogen mobility above θ_c is an interesting question. It is not pure band motion but nor is it a thermally or phonon activated hopping process since it shows no temperature dependence. The exact nature depends on some coherence length, by which we mean the

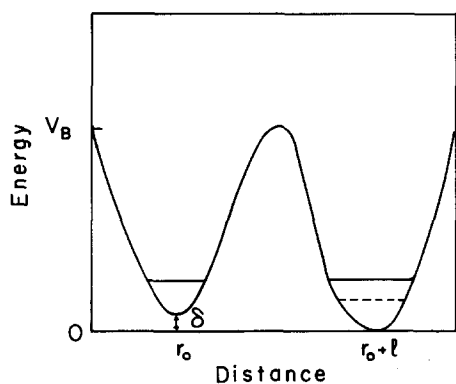


FIG. 6. Energy levels of neighboring adsorption sites in the presence of external interactions with, e.g., other adsorbed hydrogen atoms. The level shift δ in the right well relative to the left well results from these interactions.

range into which the wave function of the particle is effectively confined. If this is equal to the sample length over which diffusion is experimentally measured ($\sim 100 \text{ \AA}$), then motion may indeed appear band-like, but if the localization length is of the order of a lattice spacing, a hopping process must be involved. Since two is a marginal dimension for localization, the length scale of localized states can vary enormously. We shall not go into this aspect here, but will consider only the most extreme case where coherence of the motion is destroyed between consecutive tunneling events.

For a hopping process, the diffusion coefficient in two dimensions is given by

$$D = \frac{1}{4} l^2 W, \quad (4.5)$$

where W is the averaged rate of transition from one site to the next (assuming nearest neighbor hops only). If fluctuations in the energy levels destroy resonance between adjacent sites one can nevertheless still have tunneling between these adjacent sites, which will however occur at a rate very much less than the resonance enhanced process. The assumption of nearest neighbor hops only implies that fluctuations are large enough to entirely eliminate coherent motion over two or more lattice spacings. This results in a model where the particle moves over the surface in a series of disconnected tunneling events to nearest neighbor sites. The events are separated by long residence times at each site. The energies of any two neighboring sites fluctuate due to interactions with the surrounding hydrogen atoms which is expressed by an asymmetry parameter, δ (Fig. 6). One way to construct the averaged transition rate W is to assume the fluctuations result in a distribution of asymmetries δ , and to integrate the tunneling rate for a particle in an asymmetric double minimum over this distribution. Then

$$W = \int P(\delta) W(\delta) d\delta, \quad (4.6)$$

where $P(\delta)$ is the probability of having an asymmetry δ due to the interactions, and $W(\delta)$ is the tunneling rate from left to right in the double minimum potential of Fig. 6. We shall assume the asymmetry, δ , to be Lorentzian distributed with width Γ :

$$P(\delta) = \frac{\Gamma}{\pi(\delta^2 + \Gamma^2)}. \quad (4.7)$$

The model assumes, in effect, that the symmetric (pure resonant) situation is the most probable one. This appears reasonable for low coverages. In general however, δ for which $P(\delta)$ is maximum should depend on concentration. The tunneling rate in the symmetrical potential, $W(0)$, is the resonance enhanced rate given by⁴⁴

$$W(0) = (2\Delta')/h \quad (4.8)$$

with Δ' the symmetrical level splitting. We use the semiclassical expression for Δ' , as in Sec. III C,⁴⁴

$$\Delta' = \frac{\hbar\omega}{\pi} \exp \left[-\frac{\sqrt{2m}}{\hbar} \int_{x_1}^{x_2} \sqrt{V(x) - \hbar\omega/2} dx \right]. \quad (4.9)$$

Here ω is the frequency in one of the equivalent minima and $\hbar\omega/2$ the energy at which tunneling occurs. When an asymmetry δ is introduced, the corresponding tunneling rate from left to right, $W(\delta)$, is given by

$$W(\delta) = W(0) \left[\frac{2(\Delta')^2}{\delta^2 + (\Delta')^2 + \delta\sqrt{\delta^2 + (\Delta')^2}} - \frac{(\Delta')^4}{[\delta^2 + (\Delta')^2 + \delta\sqrt{\delta^2 + (\Delta')^2}]^2} \right]. \quad (4.10)$$

Equation (4.10) is derived in Appendix A. In performing the integral (4.6) we note that for $\Gamma \gg \Delta'$ or $\Gamma \ll \Delta'$ most of the contribution to the integrand comes from regions where the term $\delta\sqrt{\delta^2 + (\Delta')^2}$ may be replaced by δ^2 (if $\Delta' \ll \delta$) or neglected (if $\Delta' \gg \delta$). In this approximation, for $\Gamma \gg \Delta'$ we get

$$W = W(0) \left[\frac{\Delta'(3\sqrt{2}\Gamma/2 - 2\Delta')}{(2\Gamma^2 - (\Delta')^2)} + \frac{(\Delta')^3(\sqrt{2}\Gamma - \Delta')}{((\Delta')^2 - 2\Gamma^2)^2} \right] \quad (4.11)$$

and for $\Gamma \gg \Delta'$ this reduces to

$$W \cong \frac{3\sqrt{2}}{2} \frac{(\Delta')^2}{h\Gamma}, \quad (4.12)$$

where

$$D = l^2 \frac{3\sqrt{2}}{8} \frac{(\Delta')^2}{h\Gamma}. \quad (4.13)$$

These results deserve some comment. Equation (4.10) is a perturbative result insofar that it was assumed $\Delta < \delta$ (Appendix A). However the limit $\Gamma \rightarrow 0$ is well defined in both Eqs. (4.10) and (4.11), and gives $W(0)$. In contrast, Eq. (4.12) is identical except for numerical factors, to the result of a Golden rule perturbative analysis of tunneling from one well defined state to a distribution of states (Appendix A). Here the limit $\Gamma \rightarrow 0$ is not well defined, which causes an apparent discontinuity between the rate of the perturbative process for which $D \propto (\Delta')^2$ and the rate of the resonance enhanced process, for which $D \propto \Delta'$, Eqs. (4.5) and (4.8). [The band diffusion is of the same order of magnitude as the latter since the relaxation time is proportional to β in Eq. (4.1).] If one includes the contribution from off resonant tunneling, as in Eq. (4.10), this discontinuity is properly eliminated. Finally note that if the "dephasing" width Γ arises from phonon interactions the rate W would be temperature dependent ($\Gamma \sim T^9$ at low temperatures³⁹).

We now have an expression for the diffusion coefficient in the presence of fluctuations larger than the bandwidth $\Delta = 16\Delta'$ the width Γ being a measure of the energy range of the fluctuations. [β is related to Δ' in Eq. (3.33) by equating the semiclassical frequency for transition between neighboring wells, $\nu = 2\Delta'/\hbar$, with the average group velocity in one dimension divided by the lattice spacing, i.e., β/\hbar . This gives $\beta = 2\Delta'$, which implies $\Delta = 8\beta = 16\Delta'$.] Although we do not currently have a theory for the dependence of the fluctuations on coverage, we can expect these to increase with concentration. On the basis of our previous discussion of hydrogen-hydrogen interactions, the symmetric tunneling rate (4.8) will also be expected to increase with coverage because of the effective reduction in barrier height at finite coverages (Sec. III C), until some saturation point is reached. A simple calculation based on the parameters of Table II then shows that the coherent hopping diffusion rate (4.13) can show an initial increase to a maximum, which is followed by a monotonic decrease at higher coverages. (The correct order of magnitude diffusion coefficient for ^1H is

obtained with a width $\Gamma \sim \Delta'/10$ if $\Delta m = 5.5$ amu, a larger width being compatible with a smaller mass renormalization Δm .) Thus within this simple model of hopping diffusion based on tunneling between localized sites, we can also account for the coverage dependence at intermediate and high coverages, though not yet for the initial decrease at low coverage.

Although the above estimate is very crude and is based on a static uniform distribution of adsorbed hydrogen atoms, it is consistent within a model of coherent tunneling between localized sites, provided the fluctuations destroying further long range coherence are derived from the electron mediated hydrogen-hydrogen interaction. Work is now in progress on a more realistic treatment, based on a self-consistent field description of the interacting diffusing particles. The distributions of the hydrogen in such a self-consistent field treatment should be quantitative, and quantities such as $P(\Gamma)$ obtainable from first principles.

V. HYDROGEN DIFFUSION AND THE ENERGY BAND MODEL

We have seen that the coverage dependence of the mobility of chemisorbed hydrogen isotopes on tungsten (110) is consistent with a collision limited band propagation at low concentrations. The variations in $D(\theta)$ at coverages greater than 0.1 could be explained in terms of the hydrogen interactions mediated by the metal electron distribution, within either a band or a hopping tunneling model of the atom motion. However the criteria for band propagation were fulfilled only for $\theta < 0.1$, so we rely quantitatively on the picture of band motion only for coverages less than 0.1.

Nevertheless, the fact that the bandwidths that we estimate are extremely narrow raises questions as to the consistency of our model with the existing interactions within the system. Should one not be concerned with the fact that inelastic scattering by phonons will effectively destroy the bands? Although it is an extremely hard question to investigate from first principles, the existence of such extremely narrow bands ($\sim 10^{-9}$ meV) at low temperatures seems to us possible on the basis of several experimental and theoretical arguments: Our considerations of accepting that such narrow bands persist despite coupling to phonons are the following.

(i) Evidence for the existence of very narrow bands was found in the somewhat similar case of spin diffusion of ^3He in solid ^4He .²⁹ In that case the theoretical interpretation invoked the existence of bands of width $\sim 10^{-8}$ meV. The temperature of the spin diffusion experiments is however lower (1 K) than the temperature range considered in the present work. Furthermore, diffusion of muons in the bulk of some metals has also been argued to proceed by tunneling at low temperatures, with matrix elements of the order of 10^{-3} meV³⁰ at temperatures up to 20 K, which approaches the range studied here.

(ii) The experiments of Gomer *et al.*^{12,13} which we attempt to interpret here, show no temperature dependence of the tunneling rate. It is highly unphysical that inelastic phonon scattering can play a role in this process without giving rise to significant temperature dependence. It should

be stressed that one major type of phonon effect is included in our treatment, namely mass renormalization. This is, however, a static effect which persists down to zero temperature and which, we assume, does not change significantly within the experimentally relevant temperature range (27–100 K). We thus make here the assumption that dynamical phonon effects (i.e., inelastic scattering) do not play a role, as the simplest framework which is consistent with the experimental evidence of temperature independence.

(iii) Theoretical considerations also suggest that dynamical phonon effects may be weak. For instance, phonon inelastic scattering leading to intraband transitions is unlikely to play any role because the phonon density of states leading to such transitions is extremely low given the narrow bandwidth. On the other hand, interband transitions, which could also destroy the band structure if sufficiently strong, require at least two phonons of high frequencies which are modes not significantly populated in our temperature range. Thus both interband and intraband phonon dynamical coupling effects are likely to be extremely weak. Finally, dephasing effects by low frequency acoustic phonons is limited by the long scale of their wavelength. Acoustic phonons, if populated, can destroy coherent band states which extend over several unit cells. However such coherence domains may be larger than those probed in the H/W(110) experiment ($\sim 100 \text{ \AA}$).

Clearly the above arguments are merely suggestive in nature. It should be stressed that even if our assumptions regarding the coherent motion of the H atoms at low temperature holds, the band treatment as used here is too simplistic. It seems reasonable to expect that this coherent motion should be affected by the zero point motion of the substrate atoms (it is well known however that zero point motion alone cannot destroy the coherence). The hope is that the concepts advanced here will remain largely intact in a more rigorous theory that will probably lead to additional renormalization of some of the parameters (which are anyway used in the present work only to fit the experimental observations). Such more rigorous theory and additional experimental work are clearly needed.

In this context it would be of considerable interest to repeat the diffusion experiments at lower temperatures, e.g., $T \sim 1 \text{ K}$, to ascertain whether $D(T)$ remains constant at its present low temperature value or whether any increase is observed as T is lowered, suggesting a decrease in phonon participation. Spectroscopic measurements can also give more information relating to band motion. In addition to clarifying the binding sites and assigning frequencies, spectroscopic linewidths can be related to widths of the adsorbed states.²⁷ Also it seems very desirable to carry out more quantitative theoretical estimates of phonon inelastic scattering on band states of diffusing atoms in realistic systems in order to obtain an indication if and under what conditions do the bands survive the dynamical coupling to the phonons.

There are other situations where hydrogen may move in energy bands, such as when present as impurities in rare gas crystals,⁴⁵ or the more well known proton in ice.^{44,47} The easy accessibility of surface experiments to controlled concentration variations, however, makes further experiments

with hydrogen on metals and other surfaces and with measurement of the diffusion dynamics by several independent means extremely desirable. The recently developed laser induced desorption techniques show some promise for providing a new method of measuring surface diffusion.⁵ The relation between diffusion and the rate of reformation of ordered structures after induced disordering in LEED²³ deserves further attention, particularly since the role of formation of islands of ordered phases and the effect of size and stability of these on the microscopic dynamics has not been extensively investigated.

V. CONCLUSION

We have developed a model for quantum diffusion of hydrogen metal surfaces and applied it to the H/W(110) system. The model of collision limited band mobility was considered and shown to be feasible for this system, although very narrow bandwidths appear to result from mass renormalization due to lattice vibrations. The band model seems to be applicable at low coverages, $\theta < 0.1$, where it quantitatively explains the coverage dependence of the diffusion in the low temperature regime. The results assert the usefulness of the band model for mass transport of *atomic* particles on periodic surfaces, although in special limiting conditions. The behavior at higher coverages is qualitatively explicable in terms of the indirect hydrogen–hydrogen interactions on the surface, which are mediated by the metal electrons and which reduce the effective barrier for tunneling. Both the band and tunneling hopping models can account for the experimental observation for $\theta > 0.1$ with a reasonable choice of parameters, but the inconsistencies in the width requirements for band motion at these concentrations lead us to prefer the hopping model. In no situation do the quantum statistics of the adsorbed species play any noticeable role. The observed increase in diffusion of ^2H at $\theta > 0.7$ remains unexplained within our model.

This study has illuminated the importance of adsorbate–adsorbate interactions in determining the many particle dynamics of the chemical diffusion coefficient, $D(\theta)$. We have not attempted to provide a rigorous theory of the dynamics of strongly interacting particles in periodic lattices, but clearly this is a fundamental question raised by the present investigation and in particular by the absence of a quantitative theory at high concentrations. Another intriguing question raised by this work is the possibility of using collisional models to analyze diffusion of interacting particles in the classical or thermally activated regime. These questions invite further study.

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APPENDIX

The tunneling rate in a symmetric double well ($\delta = 0$ in Fig. 6) can be defined in terms of the residence time τ^0 in a single minimum

$$\tau^0 = h / (2\Delta'), \quad (\text{A1})$$

where Δ' is the energy splitting.⁴⁴ This concept of residence time was generalized by Brickmann and Zimmerman⁴⁸ to tunneling in asymmetric double minima to yield

$$\tau = h / (8c_1^2 c_2^2 \Delta'), \quad (\text{A2})$$

where c_1, c_2 are coefficients of the eigenfunction expansion

$$\psi_a = c_1 \phi_1 - c_2 \phi_2, \quad (\text{A3})$$

$$\psi_b = c_2 \phi_1 + c_1 \phi_2.$$

ψ_a, ψ_b are eigenfunctions of the isolated minima, ϕ_1, ϕ_2 are the ground and first excited states of the double minimum potential. The rate of tunneling in the asymmetric system, $W(\delta)$ is then given by

$$W(\delta) = 4c_1^2 c_2^2 W(0). \quad (\text{A4})$$

Neglecting the contribution of excited states, the lowest two energy levels in the asymmetric system are given by eigenvalues of the matrix

$$\begin{pmatrix} \epsilon_a & J \\ J & \epsilon_b \end{pmatrix}, \quad (\text{A5})$$

where J is the tunneling matrix element and ϵ_a, ϵ_b the (unequal) ground state eigenvalues of the isolated minima. Defining for this discussion

$$\epsilon_a = 0, \quad \epsilon_b = \delta \quad (\text{A6})$$

we find

$$\epsilon = \delta \pm \sqrt{\delta^2 + (\Delta')^2}, \quad (\text{A7})$$

where

$$\Delta' = 2J \quad (\text{A8})$$

is the symmetric energy level splitting.⁴⁴ The normalized coefficients c_1 and c_2 are then given by

$$c_1 = \frac{\delta + \sqrt{\delta^2 + (\Delta')^2}}{[2\delta^2 + 2(\Delta')^2 + 2\delta\sqrt{\delta^2 + (\Delta')^2}]^{1/2}}, \quad (\text{A9})$$

$$c_2 = \frac{-\Delta'}{[2\delta^2 + 2(\Delta')^2 + 2\delta\sqrt{\delta^2 + (\Delta')^2}]^{1/2}}, \quad (\text{A10})$$

and

$$4c_1^2 c_2^2 = \frac{2(\Delta')^2}{[\delta^2 + (\Delta')^2 + \delta\sqrt{\delta^2 + (\Delta')^2}] - \frac{(\Delta')^4}{[\delta^2 + (\Delta')^2 + \delta\sqrt{\delta^2 + (\Delta')^2}]}}. \quad (\text{A11})$$

Inserting Eq. (A11) into Eq. (A4) we obtain

$$W(\delta) = W(0) \left[\frac{2(\Delta')^2}{[\delta^2 + (\Delta')^2 + \delta\sqrt{\delta^2 + (\Delta')^2}] - \frac{(\Delta')^4}{[\delta^2 + (\Delta')^2 + \delta\sqrt{\delta^2 + (\Delta')^2}]}} \right]. \quad (\text{A12})$$

This gives $W(0)$ as the correct limit of $W(\delta)$ as $\delta \rightarrow 0$.

It is instructive to compare this result with the Golden rule for resonant tunneling from ϵ_a to a distribution of final states ϵ_b defined by some width Γ . The Golden rule rate is

$$W(\Gamma) = \frac{2\pi}{\hbar} J^2 \rho(\epsilon_b) \delta(\epsilon_b - \epsilon_a - \hbar\omega). \quad (\text{A13})$$

If we take the distribution of final states to be Lorentzian with width Γ ,

$$\rho(\epsilon_b) = \frac{\Gamma \Pi^{-1}}{(\epsilon_b - \epsilon_a)^2 + \Gamma^2}, \quad (\text{A14})$$

we obtain

$$W(\Gamma) = \frac{2J^2}{\hbar\Gamma} = W(0) \frac{J}{\Gamma}. \quad (\text{A15})$$

This yields the coefficient of diffusion for a hopping process over jumps of length l as

$$D = \frac{l^2 (\Delta')^2}{2 \hbar\Gamma}. \quad (\text{A16})$$

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