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Quantum Mechanical Theory of Hydrogen Diffusion*

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A quantum mechanical description of low-concentration hydrogen diffusion is presented. Using the Kubo formula for the diffusion coefficent, harmonic wave functions for the hydrogen atoms, and polaronic wave functions for the lattice, an exact expression for the diffusion coefficent can be found. Two interesting predictions of the theory are (i) a decrease in the activation energy with mass for fcc metals, in agreement with experiment, and (ii) an activated form for diffusion between localized states even in the purely tunneling regime.

The diffusion of hydrogen in metals at room temperatures and above has been observed to display features which are not well described by simple classical diffusion theories.[1,2] In particular, the mass dependence of the diffusion constant is strongly dependent on lattice structure and is often found to be highly nonclassical both in the prefactor and in the activation energy.

There have been many attempts to improve the simple classical theory by including a variety of effects[3-5] (e.g., anharmonicity, zero-point motion, and a realistic description of the saddle-point dynamics). However, the applicability of these theories to hydrogen diffusion has not been established.[1,3] Indeed, in a system in which the energy between vibrational eigenstates of the hydrogen atom corresponds to 1370 K,[6] as for niobium, a basically quantum mechanical model is more appropriate. Until now all quantum mechanical treatments of the diffusion process have been restricted to simpler models than presented here: either neglecting the polaron effects[7,8] that

I will show strongly influence the diffusive behavior of hydrogen in metals; or including polaron effects, but treating the higher energy states of the carrier in a qualitative manner[9] or not at all.[10] The present calculation is based on a model which explicitly includes all of these effects, and furthermore, neglect of any of these effects can be shown to alter substantially the predictions of the theory. The model is applicable to hydrogen diffusing in both bcc and fcc metals and is successful in accounting for the observed mass dependences of the activation energies for both cases.

The calculation is based on the Kubo formula for the diffusion constant, employing harmonic-oscillator wave functions for the (tightly bound) hydrogen atoms and conventional polaron-theory wave functions[11] for the lattice. In contrast to polaron theories for electronic or ionic transport,[9,10] all sums over carrier states are explicitly performed.

It will be shown that the decrease of the activation energy with mass evidenced in fcc metals[1] (which leads to heavier isotopes diffusing faster than light isotopes below certain temperatures) can be explained as a result of the importance of transfer processes in which the hydrogen atom absorbs enough energy from the lattice to be excited to a higher energy state before transferring to a neighboring site. Thus at a temperature in which the motion of the lattice distortion about the hydrogen atom behaves classically, contributing a classically activated factor to the diffusion coefficient, the actual activation energy (which, classically, represents the height of the potential barrier between sites) is found to depend on the vibrational energy between the quantum-mechanical hydrogen states. The energy between hydrogen states is smaller for heavier isotopes, resulting in a decrease in the activation energy and hence the observed increase in diffusion rate with mass. Other unusual mass dependences can be found for bcc metals above room temperature and in regions in which the lattice does not behave classically and the diffusion process is a tunneling process for both the lattice deformation and the diffusing atom.

In conventional electron-transport theory an adiabatic approximation, based on the smallness of the carrier (electron) mass compared to the lattice (ion) mass, is usually employed. For hydrogen diffusion the ratio of the carrier mass to the ion mass is of course larger but in some cases still small enough to justify the same adiabatic approximation. I will confine my considerations to low concentrations of hydrogen, to avoid the complications of correlation effects. Assume that the hydrogen atom (for simplicity, neutral) is localized on a single site (as evidenced by neutron-diffraction experiments)[1] and tunnels to a neighboring site only occasionally. In addition, assume an interaction between the hydrogen atom on a given site and the vibrations of the surrounding lattice ions that is linear in the lattice displacements. In contrast to the analogous problem of electronic hopping, the hydrogen atom must reside interstitially rather than on a single ion. This is also in contrast to conventional theories of defect formation and transport.

The Hamiltonian of the system is given by

$$H=\sum_{\vec{q},s}\hbar\omega_{\vec{q},s}(\hat{c}_{\vec{q},s}c_{\vec{q},s}+\tfrac{1}{2})+\sum_{\vec{g}=0,\vec{b}}\sum_{\vec{q},s}(V_{\vec{q},s}{}^{\vec{g}}c_{\vec{q},s}+V_{\vec{q},s}{}^{*\vec{g}}\hat{c}_{\vec{q},s})\sum_{n<b^2/4}\hat{a}_n{}^{\vec{g}}a_n{}^{\vec{g}}$$
$$+\frac{p^2}{2m}+\frac{1}{2}\frac{m\omega^2\vec{x}^2}{1+B'\vec{x}^2}+\frac{1}{2}\frac{m\omega^2(\vec{x}-\vec{b})^2}{1+B'(\vec{x}-\vec{b})^2}, \tag{1}$$

where $\hbar\omega_{\vec{q},s}$ and $\hat{c}_{\vec{q},s}$ are the energy and creation operator, respectively, for a phonon of wave vector $\vec{q}$ and mode s, $V_{\vec{q},s}{}^{\vec{g}}$ represents the strength of the interaction of the hydrogen atom on site $\vec{g}$ with a phonon of wave vector $\vec{q}$ and mode s, $\hat{a}_n{}^{\vec{g}}$ is the creation operator for a hydrogen atom localized at site $\vec{g}$ with energy E_n, and p, x, ω, and m represent the momentum operator, position operator, frequency of oscillation, and mass of a tightly bound hydrogen atom. It is assumed that b^2 and B' are such that the lowest energy eigenstates of the hydrogen atom are well approximated by harmonic-oscillator wave functions centered at $\vec{x}=0$ and $\vec{x}=\vec{b}$ (i.e., $b^2\gg 1/B'\gg\hbar/m\omega$).

The wave functions of the Hamiltonian H are taken to have the following form:

$$\chi^{\vec{g},n}\{n_{\vec{k}}\}=\chi_{\mathrm{latt}}{}^{\vec{g},n}\{n_{\vec{k}}\}\chi_{\mathrm{H}}{}^{\vec{g},n},$$

where $\chi_{\mathrm{H}}{}^{\vec{g},n}$ is the wave function of the hydrogen atom of energy E_n on site $\vec{g}$, and $\chi_{\mathrm{latt}}{}^{\vec{g},n}\{n_{\vec{k}}\}$ is the wave function of the lattice of $\{n_{\vec{k}}\}$ phonons of wave vector $\{\vec{k}\}$ when the hydrogen atom is on site $\vec{g}$, with energy n. $\chi_{\mathrm{latt}}{}^{\vec{g},n}\{n_{\vec{k}}\}$ has been investigated extensively[11] for the case in which the lattice-carrier interaction is that between a single electron and a single ion. These results can be carried over quite generally to the case of the carrier being an interstitial hydrogen atom, interacting with nearest-neighbor ions, by appropriate changes to the electron-lattice interaction constants.[12] For the purposes of this Letter I will assume $\chi_{1\mathrm{att}}{}^{\vec{g},n}\{n_{\vec{k}}\}$ to be independent of n and use analogs of previously derived expressions[11] for $\chi_{1\mathrm{att}}{}^{\vec{g}}\{n_{\vec{k}}\}$ for the treatment of the lattice wave functions. It can be shown,[14,15] in fact, that the diffusion coefficient can be written in terms of these results:

$$D=\sum_{n,n'}\frac{2}{Z_{\mathrm{H}}}e^{-\beta E_n}e^{-2S}\int_0^{\infty}\cos[F_2(t)-(E_n-E_{n'})t/\hbar]e^{F_1(t)}|\langle\chi_{\mathrm{H}}{}^{g,n}|v_{\mathrm{H}}|\chi^{g'\neq g,n'}\rangle|^2\,dt, \tag{2}$$

where v_{H}, E_n, and Z_{H} are the velocity operator, energy, and partition function, respectively, for the hydrogen atom. If one assumes $kT>\hbar\omega_{\mathrm{D}}$, the Debye energy of the lattice, then it is found that for electrons interacting only with acoustical phonons[15]

$$2S\approx 12E_b kT/(\hbar\omega_{\mathrm{D}})^2,$$

$$F_1(t)\approx[12E_b kT/(\hbar\omega_{\mathrm{D}})^2][\sin(\omega_{\mathrm{D}}t)/\omega_{\mathrm{D}}t],$$

and

$$F_2(t)\approx\frac{6E_b}{(\hbar\omega_{\mathrm{D}})}\frac{[\sin\omega_{\mathrm{D}}t-\omega_{\mathrm{D}}t\cos(\omega_{\mathrm{D}}t)]}{(\omega_{\mathrm{D}}t)^2},$$

where E_b is the binding energy of the lattice deformation. For the present I assume this form for $F_1(t)$ and $F_2(t)$, although the following results will hold in general for any $F_1(t)$ which is a decreasing function of t and which has the same temperature dependence.

For the system of interest, the potential which the hydrogen atom sees can be considered to be harmonic near the site centers. If attention is restricted to low-energy (spatially confined) states, and thus to temperatures low compared with the height of the potential barrier between the two sites, the eigenstates of the true potential of the hydrogen atom may be approximated by three-dimensional harmonic-oscillator wave functions. This does not, however, require that kT be small with respect to the observed activation energy for diffusion.

If only the transitions from a single site $\vec{g}$ to a single site $\vec{g}'$ (keeping lowest-order terms in the transfer integrals and lowest-order terms in B') are considered, the sum over carrier states of

$$2\sum_{n,n'}e^{-\beta E_n}|\langle\chi_{\mathrm{H}}{}^{\vec{g},n}|v_{\mathrm{H}}|\chi^{\vec{g}'n'}\rangle|^2\cos[(E_n-E_{n'})t/\hbar-F_2(t)] \tag{3}$$

can be performed exactly.

The sum in (3) can be evaluated by means of a number of straightforward algebraic manipulations, which will only be outlined briefly here. The eigenfunction of a harmonic oscillator of frequency ω, energy E_n, and mass m centered at site $\vec{g}'$, expressed in terms of the eigenfunctions of an oscillator centered at $\vec{g}$, $|\vec{g}-\vec{g}'|=b$, can be used to calculate the relevant matrix element which appears in the Kubo relation for the diffusion constant:

$$2|\langle\chi_{\mathrm{H}}{}^{\vec{g},n}|v_{\mathrm{H}}|\chi_{\mathrm{H}}{}^{\vec{g},n'}\rangle|^2=\frac{\hbar\omega}{m}e^{-\bar{b}^2}\frac{n'!}{n!}(\bar{b}^2)^{n-n'-1}\{n\mathcal{L}_{n'}{}^{n-n'-1}(\bar{b}^2)-\bar{b}^2\mathcal{L}_{n'}{}^{n-n'+1}(\bar{b}^2)\}^2, \tag{4}$$

where $\bar{b}^2=b^2(m\omega/2\hbar)$ and the $\mathcal{L}_n{}^{\alpha}$ are Laguerre polynomials.[16] Inserting expression (4) into the sum (3) and writing out the explicit forms for the $\mathcal{L}_n{}^{\alpha}$, one can recognize the expression to contain a sum over Kummer's functions.[16] Thus the sum over n' can be accomplished with the use of published formulas, yielding

$$\mathrm{Re}\frac{\hbar\omega}{m}\sum_n\frac{e^{-\beta\hbar\omega_n}}{Z_H}e^{-Z'}[e^{i\omega t}n\,{}_1F_1(n,1,X)-n(n+1)X\,{}_1F_1(n+2,3,X)+e^{-i\omega t}(n+1)\,{}_1F_1(n+2,1,X), \tag{5}$$

where $X=2\bar{b}^2(\cos\omega t-1)$, $Z'=\bar{b}^2(e^{i\omega t}-1)$, and the ${}_1F_1(x,y,z)$ are Kummer's functions. The sum in Eq. (5) can also be accomplished using published formulas,[16] yielding for the diffusion coefficient (2)

$$D=\frac{\hbar\omega}{m}\frac{e^{-2S}}{(1-e^{-\beta\hbar\omega})}\mathrm{Re}\int_0^{+\infty}dt\{\exp[F_1(t)-iF_2(t)]\}\left[\exp\left(\bar{b}^2\frac{(1+e^{-\beta\hbar\omega})}{(1-e^{-\beta\hbar\omega})}(\cos\omega t-1)-i\bar{b}^2\sin\omega t\right)G(\omega t)\right], \tag{6}$$

where

$$G(\omega t) = e^{-i\omega t} + e^{i\omega t - \beta\hbar\omega} + \bar{b}^2(1 - e^{-\beta\hbar\omega})\left[\frac{(1+e^{-\beta\hbar\omega})}{(1-e^{-\beta\hbar\omega})}(\cos\omega t - 1) - i\sin\omega t\right]^2 .$$

Some of the properties of this expression in the temperature regime characteristic of most hydrogen-diffusion experiments will now be considered. In this regime the lattice distortion behaves classically. Consistent with the earlier requirement that the height of the potential barrier between (low-lying) hydrogen bound states be large compared to kT, it is required that $\frac{1}{4}\bar{b}^2\hbar\omega \gg \frac{1}{2}m\omega^2(1/B') \gg kT$. In addition, assume that the lattice-hydrogen interaction is strong enough that the principal contribution to the time integral occurs at short times compared with $1/\omega_D$. In this case

$$F_1(t) - 2S = \frac{-2E_b kT}{\hbar^2}t^2, \quad F_2(t) = \frac{2E_b}{\hbar}t .$$

In the evaluation of Eq. (6) two limits can be immediately distinguished: (i) $\omega^2 \gg 2E_b kT/\hbar^2$ and (ii) $\omega^2 \ll 2E_b kT/\hbar^2$. In case (i) the lattice transfers energy to the hydrogen atom typically over time scales long compared to the vibrational period of the hydrogen atom. This is the case that may apply to niobium and other bcc metals near and below room temperature. Although this case will not be discussed in detail here, an approximate evaluation of Eq. (6) in this limit results in a mass-dependent term in the activation energy that agrees to within 30% with the corresponding term observed for niobium. However, such agreement with experiment must necessarily be considered qualitative since the condition (i) is only approximate for niobium.

For case (ii) the lattice typically transfers energy to the hydrogen atom on time scales short compared to the vibrational time of the hydrogen atom. This case may be typical of fcc metals at high temperatures. When $kT \gtrsim \hbar\omega$ the diffusion coefficient is given by

$$D = \frac{1}{m}\left(\frac{\pi\hbar^2 kT}{2(E_b + \frac{1}{2}\hbar\omega\bar{b}^2)}\right)^{1/2} \exp\left(\frac{-(E_b + \frac{1}{2}\hbar\omega\bar{b}^2)}{2kT} - \frac{\hbar\omega}{2kT(2\bar{b}^2 + Eb/\hbar\omega)}\right). \tag{7}$$

The quantity $\frac{1}{4}\bar{b}^2\hbar\omega$, which is an upper bound on the size of the potential barrier between the two stationary wells of the hydrogen atom, is independent of mass. Thus the pre-exponential term in expression (7) is proportional to m^{-1}, while the activation energy contains a small term proportional to m^{-1}. This additional term in the activation energy can be directly related to the importance of tunneling processes in which the hydrogen atom transfers to a higher energy state, by absorbing energy from the lattice, before tunneling. It is always small compared to other terms in the activation energy, and is in rough agreement with the observed results in fcc metals.[1] [Note that in the special case when $E_b/2$ is negligible compared to the potential barrier between wells (hence $E_b << \frac{1}{2}\bar{b}^2\hbar\omega$), the lattice serves only as a thermal reservoir in a quantum mechanical description of Brownian motion between two wells.[17] In this case and when $\bar{b}^2 = 1$, Eq. (7) agrees with the high-temperature results of Weiner and Partom.[7]]

It should be noted that the prefactor of the diffusion constant obtained from experiments on fcc metals is often found to have the $m^{-1/2}$ behavior predicted by classical theory, although considerable deviation from this behavior is also seen. The results given here do not reproduce this dependence, so it is clear that this is far from a complete description. Modifications of the approach to include a more satisfactory treatment of over-the-barrier hops and of the hydrogen-phonon interaction are being considered. In addition it should be possible to apply this model to the study of hydrogen-ion diffusion, specifically the case-(ii) results which presume a strong hydrogen-ion–lattice interaction.

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Quasiparticle-Injection-Induced Superconducting Weak Links*

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Superconducting weak links are studied in which the weak region is created by locally driving the superconductor out of equilibrium using an independent source of quasiparticles. The characteristics of these weak links can be varied electrically or optically at any temperature below T_c. A simple model which describes the dependence of weak-link critical current on quasiparticle-injection rate is presented.

A common feature of all superconducting weak links is a localized region of depressed superconducting order parameter separating two superconductors. The size of the localized weak region must be comparable with or smaller than a characteristic length of the superconductor, generally supposed to be the temperature-dependent coherence length $\xi(T)$. This condition imposes rather severe constraints on the fabrication and operation of weak links. The link dimensions must be at the micrometer level and desired operating characteristics can often be achieved only within a rather restricted temperature interval. We report here some initial experimental observations on a new class of weak links in which the weak region is not a result of a fabrication process, but is created by locally driving the superconductor out of equilibrium using a source of quasiparticles which is independent of the primary weak-link circuit.[1] The characteristics of these weak links can be electrically or optically varied at any temperature below T_c. We also present a simple model, based on current understanding of the nonequilibrium superconductor, which accounts for the dependence of the weak-link critical current on quasiparticle-injection rate.

Consider a narrow thin-film strip of superconductor, a microbridge of width W. Suppose it is possible by some means to inject or create excess quasiparticles over a length L of the microbridge. The resulting excess quasiparticle density will be position dependent, varying slowly within L and falling to zero outside L in a distance of the order of the quasiparticle diffusion length $\lambda = (v_{\mathrm{qp}} l \tau_{\mathrm{eff}}/3)^{1/2}$. Here v_{qp} is an average quasiparticle velocity approximately equal to the Fermi velocity, l is the quasiparticle elastic scattering mean free path, and τ_{eff} is a characteristic quasiparticle relaxation time, probably the effective quasiparticle-recombination time. The excess quasiparticles will depress the superconducting order parameter over some distance $\Lambda \sim L + 2\lambda$, creating a weak link if Λ is sufficiently small and the depression sufficiently strong. The characteristics of this weak link, e.g., the critical current, depend basically on Λ and on Δ_{min}, the gap parameter at its minimum within L. These parameters in turn depend in a rather complicated