Quantum Simulation of Hydrogen in Metals

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The path-integral method of quantum simulation is applied to an empirical model for hydrogen in niobium. Results for the density distribution of D, H, and the positive muon over the unit cell show the dramatic increase of quantum effects along this series. Calculations on the activation energy for diffusion confirm the importance of excited states at high temperature pointed out by Emin, Baskes, and Wilson and suggest that hydrogen diffusion is approximately classical in this regime.

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Although the study of hydrogen in metals dates back over a century,[1] our understanding of these systems is not fully satisfactory. One reason for this is the difficulty of making realistic model calculations. The purpose of this Letter is to show how the recently developed path-integral technique of quantum simulation[2] can give new insights in this field. I will present illustrative simulation results relevant to (i) the distribution of hydrogen and deuterium and the closely related positive muon[3] in the unit cell and (ii) the temperature dependence of the hydrogen diffusion coefficient in the typical bcc metal niobium.

In the bcc metals, hydrogen and its isotopes reside on the tetrahedral sites.[1] There are two local-mode frequencies ω, which for Nb:H are[4] 26.5 and 43.4 THz ($\hbar\omega/k_{\mathrm{B}}=1270$ and 2070 K). On expects quantum effects to be dominant when the temperature T is low compared with these values. For small enough T, vibrational excitations of the hydrogen will be frozen out, and its diffusion will be dominated by tunneling between vibrational ground states on neighboring sites. The well-known theory of Flynn and Stoneham[5] assumes this ground-state dominance and stresses the crucial role played by lattice distortion in the diffusion process. The theory predicts that, except at very low temperature, diffusion will be thermally activated, the activation energy being the distortion energy needed to bring the ground states on neighboring sites into coincidence. Emin, Baskes, and Wilson[6] (EBW) pointed out that excited vibrational states will become important (and Flynn-Stoneham theory will break down) for T well below $\hbar\omega/k_{\mathrm{B}}$, because of the much greater transition amplitudes for these higher states, and because the frequencies ω are changed by the relevant lattice distortions. Experimentally, one finds two regimes of thermal activation in the bcc metals, with activation energies differing typically by a factor of 2; the break between the regimes is at about 250 K for Nb:H.[1] Very recent calculations of Klamt and Teichler[7] confirm the ideas of EBW and show that diffusion of hydrogen in Nb is ground-state dominated below 250 K, the break in activation energy being due to the increasing importance of excited states above this temperature.

Quantum simulation can be potentially very helpful for this kind of system, because it allows one to make model calculations without analytic approximation. This is particularly relevant in the present context, where more and more excited states come in with increasing T. The path-integral technique I use implicitly performs the thermal averaging over states, without treating all the states individually. A direct calculation of the diffusion coefficient, even with this technique, would be exceedingly difficult,[8] but I will suggest how the activation energy can be studied. The results fully support the ideas of EBW,[6] but imply in addition that the break at 250 K is closely related to the transition from quantum to nearly classical behavior. The density distribution of hydrogen and its isotopes, for which I also report results, is of interest because a comparison with diffraction measurements could give a direct test of the assumed model.

The path-integral (PI) technique of quantum simulation[2] has become increasingly popular in the last five years, and has been used to study several important problems, e.g., liquid helium[9] and the solvated electron.[10] The method is based on Feynman's PI formulation of quantum mechanics,[2] which establishes an isomorphism between the original quantum-statistical system of particles and a purely classical system consisting of cyclic chains of beads (P beads on each chain) coupled by harmonic springs. The isomorphism becomes exact only in the limit $P\rightarrow\infty$, but in practice almost exact results can be obtained with a finite P, which depends on the situation of interest. The spring constant of the chains is equal to $mP/\hbar^2\beta^2$ [m the mass of the quantum particles, β the inverse temperature $(k_{\mathrm{B}}T)^{-1}$]. This implies that for small T, where quantum effects are large (and ground-state dominated for small *enough* T in the present context), the chains become relatively extended, as would be suggested by the uncertainty principle; at high T, the chains shrink to a small size and behave almost like point particles, and one approaches the classical (excited-state dominated) limit. For hydrogen in metals, the metal atoms can be treated classically from the outset, except at temperatures below about $\frac{1}{3}$ of the Debye temperature[6] (i.e., $T \lesssim 80$ K), which will not be of interest here. The classical isomorph then consists of a set of point particles representing the metal atoms and a cyclic chain representing each of the hydrogens.[10] The simulation of the classical isomorph can be done either by Monte Carlo or by molecular dynamics,[10] though the latter gives no dynamical information; either way, one is merely sampling configurations of the system with the correct statistical weight. The results to be described were obtained with the molecular-dynamics sampling procedure. The PI technique is best suited to the calculation of static averages, such as spatial distributions; the *direct* calculation of a diffusion coefficient seems to be impossible at present.

The simulations of Nb:H are based on an empirical model.[11] The metal-metal interactions are described by the recent model of Finnis and Sinclair[12] (FS). The energy U_M of the metal subsystem as a function of the positions $\mathbf{r}_{Mi}$ $(i=1,\ldots,N_M)$ of the N_M metal atoms is

$$U_M = -A\sum_i f(\rho_i) + \frac{1}{2}\sum_{i\neq j} V(|\mathbf{r}_{Mi}-\mathbf{r}_{Mj}|),$$

the "densities" ρ_i being of the pair form

$$\rho_i = \sum_{j(\neq i)} \phi(|\mathbf{r}_{Mi}-\mathbf{r}_{Mj}|).$$

The form $f(\rho)=\rho^{1/2}$ of the "embedding function" and the parametrizations of V and ϕ are those given by FS, except for two modifications. Since vibrations of the metal atoms will play an important role, it is important that the phonon spectrum be roughly correct. With the parameters of FS, the zone-boundary frequencies are too low for Nb by 25%–30%. I correct this by multiplying the energy parameters of FS by the factor 1.9. The FS model also suffers from an instability in $V(r)$ for small r, which I cure by replacing $V(r)$ by $B_0+B_1\exp(-r/d)$ inside the nearest-neighbor distance, with B_0, B_1, and d chosen to ensure continuity of the potential and its first two derivatives. For the metal-hydrogen interaction, I assume an exponential pair potential $C\exp(-r/\sigma)$. The parameters C and σ are fixed uniquely by the requirement that the two local hydrogen frequencies be reproduced; this gives $C=4.12\times10^{-15}$ J, $\sigma=1.62\times10^{-11}$ m. The calculations are all done with a lattice parameter $a_0=3.3008$ Å.

It is useful to know the fully relaxed (classical) energy of the system with a single hydrogen at various positions. Call the tetrahedral and octahedral sites T and O, and the midpoint between neighboring T sites S (Fig. 1). Relaxation calculations with the model show that T is energetically lowest, the S and O sites being higher by 0.127 and 0.156 eV, respectively. The saddle point is not exactly at S, but lies about $\frac{1}{4}$ of the way from S to O, with an energy of 0.104 eV.

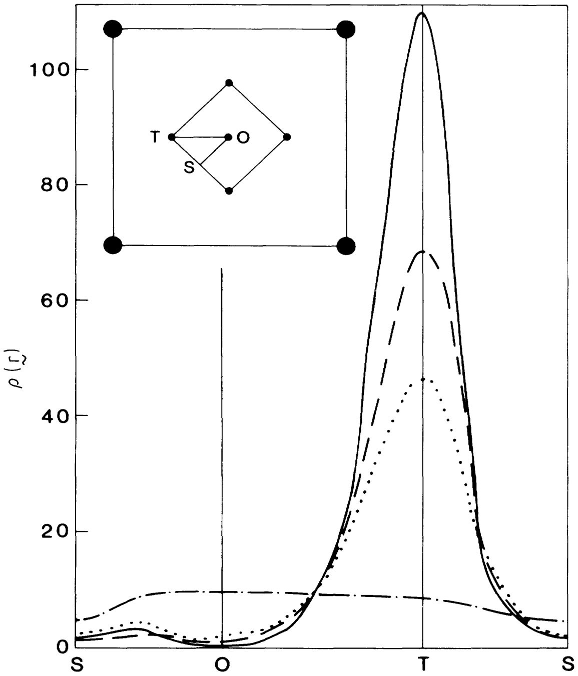

FIG. 1. The simulated density distribution $\rho(\mathbf{r})$ (normalized to the bulk density) for D (dashed line), H (dotted line), and μ^+ (dot-dashed line) in Nb at 300 K; solid line shows the classical prediction. Inset: Points T, O, and S on a face of the bcc cube.

I have used the potential model to make PI simulations for hydrogen $(m=1)$ and deuterium $(m=2)$, and also for the positive muon $(m=0.1126)$. It is interesting to examine the distribution $\rho(\mathbf{r})$ of the quantum particles, i.e., the thermal equilibrium probability density of finding one at position $\mathbf{r}$ in the unit cell. Calculations of $\rho(\mathbf{r})$ were made at a temperature of 300 K with a periodically repeating system of 54 metal atoms and 5 quantum particles in the case of H and D, and a single quantum particle in the case of μ^+. For H and D, a chain number P equal to 20 is sufficient; for μ^+, I have used $P=80$, which is probably overcautious. The results for $\rho(\mathbf{r})$ are shown in Fig. 1, with the classical prediction $P=1$ for comparison. For the hydrogen isotopes, the distribution is strongly concentrated on the T sites, in accord with experiment.[1] The quantum broadening is very marked, however, and the density is quite substantial all along the "corridor" joining T sites. This implies that diffraction experiments, which measure this density, could be used to get information about the metal-hydrogen potential over a range of separations. Available diffraction results[13] for deuterium in Nb show a measurable density between the interstitial sites and could, with improvement, provide the required comparison. For the muon, $\rho(\mathbf{r})$ is spread evenly over the T–O region. The μ^+ will spend most of its time in the region of T, since there are twice as many of these sites. This is consistent with experiment,[3] but the balance may be delicate, since experiment shows that in vanadium the μ^+ resides partly on the O site.[3]

I now want to argue that simulation can be used to help interpret the meaning of the break in the experimental Arrhenius slope. First, let us see what happens if one calculates the diffusion coefficient D by ordinary (classical) molecular dynamics. Results for D obtained in this way from the slope of the time-dependent mean square displacement are compared in Fig. 2 with measured values.[14] The qualitative agreement between the two at temperatures above the experimental change of slope is remarkable. The activation energy from simulation is 0.101 eV (essentially the same as our classical saddle-point energy, as expected), which is in close agreement with the experimental value of 0.106 eV. This suggests that classical mechanics provides at least a rough guide to the diffusion behavior above ~250 K (but see discussion below).

Since path-integral simulation cannot give D directly, the study of the break in Arrhenius slope requires an indirect method. The idea is that the transition rate between sites is governed by the probability of finding the center of mass (c.m.) of the quantum chain at the saddle point separating the sites. If $F(\mathbf{r})$ is the free energy of the system when the c.m. of the chain is fixed at $\mathbf{r}$, the probability distribution of the c.m. is rigorously $\rho_{\text{c.m.}}(\mathbf{r}) = \alpha \exp[-\beta F(\mathbf{r})]$. One expects that F will have its minimum value at the T site and will have a saddle point somewhere near the classical saddle point. Let ΔF be the difference of F between these two positions, and $\Delta E \equiv \partial(\beta \Delta F)\partial\beta$ be the corresponding energy. Now it is clearly correct to identify ΔE with the activation energy for diffusion at high temperature: The quantum chain is then contracted to a small size, ΔF and ΔE go to their classical values, and the identification just corresponds to classical transition-state theory. At low temperatures, the chain becomes extended, but then ΔE becomes equal to the energy difference between the ground states associated with the relaxed saddle-point and T-site configurations. But this is just the activation energy given by the Flynn-Stoneham theory[5] for diffusion in the quantum regime. Since ΔF yields the correct activation energies in both the high-temperature quasiclassical regime and the low-temperature quantum regime, it seems at least plausible that it will exhibit the transition between the two at roughly the correct temperature. The proposed method constitutes the natural generalization of transition-state theory: The transition rate is proportional to the probability of finding the system at the appropriate saddle point, but the saddle point is now in the configuration space extended to include the degrees of freedom of the quantum chain. This idea is not new, and is implicit in recent discussions of the general problem of quantum barrier crossing.[15]

To find the difference of $F(\mathbf{r})$ between any two points $\mathbf{r}$, I use the fact that $F(\mathbf{r})$ is the potential of mean force for the c.m. of the chain: If $\mathbf{f}(\mathbf{r})$ is the mean force acting on the chain when the c.m. is fixed at $\mathbf{r}$, then $\mathbf{f}(\mathbf{r}) = -\nabla F(\mathbf{r})$. Then ΔF can be expressed as $\Delta F = -\int d\mathbf{s}\cdot\mathbf{f}$, along any integration path joining the two points. I use a path going from T to S and then along the lines $S-O$ to the point where $\mathbf{f}$ vanishes. The calculation of $\mathbf{f}$ at seven points along this path allows an accurate numerical integration to obtain ΔF. I have calculated ΔF for hydrogen and deuterium at seven temperatures ranging from 68 to 763 K. The required value of P varies strongly with temperature, going from 50 to 10 over this range. The results are shown in Fig. 3 as a plot of $-\beta\Delta F$ vs β, i.e., as an Arrhenius plot of $\rho_{\text{c.m.}}$ at the saddle point divided by its value at site T. For hydrogen, a marked change of behavior is clear at ~250 K, which is close to the observed transition (cf. Fig. 2). The low-

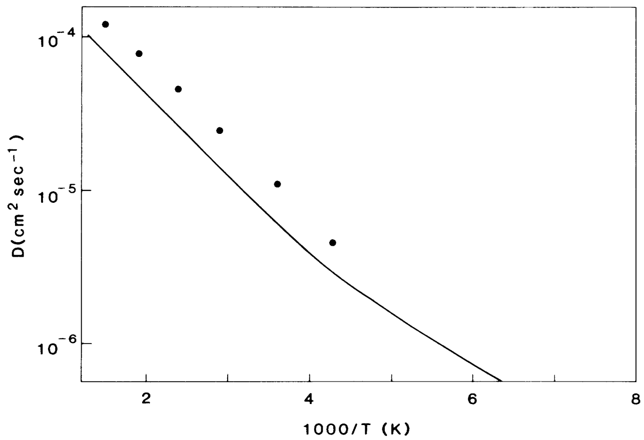

FIG. 2. Results of classical simulation (dots) for the diffusion coefficient of H in Nb compared with experiment (Ref. 11). Note the experimental break in Arrhenius slope at ~250 K.

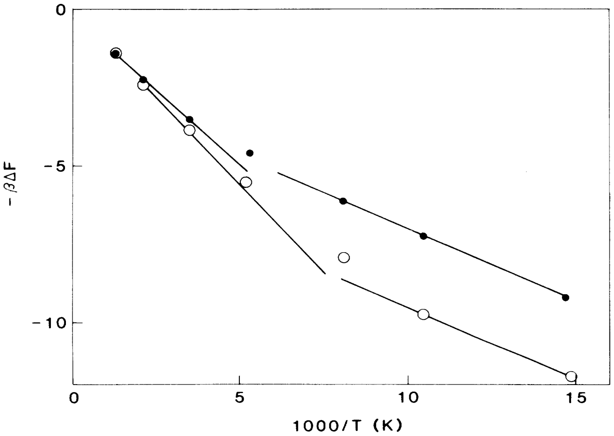

FIG. 3. The simulated free-energy difference ΔF for the center of mass of the quantum chain at the saddle point and at the T site (H: filled circles, D: open circles). Slopes of the straight lines give the activation energies at low and high temperatures.

temperature ΔE is 0.041 eV, which is in qualitative accord with (actually some 40% smaller than) the observed activation energy in this region; the high-temperature ΔE is 0.084 eV ($\sim$20% lower than experiment). As expected, the transition for deuterium is at a lower temperature ($\sim$140 K); the low-temperature ΔE is the same as for hydrogen, while the high-temperature value is 0.094 eV. This is consistent with experiments for deuterium, which so far go down only to $\sim$150 K, and find no break of slope in this range. My results agree with experiment that the high-temperature ΔE for D is greater than for H. Note that our high-temperature ΔE for both H and D lie below our classical saddle-point energy (0.104 eV). Although, as noted above, they must become equal to it for high enough T, we expect some reduction because of tunneling through (spreading of the quantum chain across) the barrier top. The experimental fact[14] that the isotope effect above the transition temperature deviates from the classical prediction shows that diffusion cannot be *fully* classical in this region. Nevertheless, my calculations show that the near equality of the high-temperature ΔE and the classical saddle-point energy is no accident, and suggest that the quantum effects in this region may be regarded as *corrections* to the classical description. I stress that the simulation results are fully consistent with the ideas of EBW[6]: The increasing dominance of excited states which causes the change of Arrhenius slope corresponds to the contraction of the quantum chains in the PI description.

The main point of this Letter is that quantum simulation opens up new ways of studying models for hydrogen in metals. One quantity that can be readily calculated is the density distribution, and the comparison of this with diffraction data could be used to test and improve models. Available data appear not to be adequate for this purpose, and it is to be hoped that new measurements will be made. My results relating to thermally activated diffusion suggest that the observed transition in bcc metals is related to the transition from quantum to nearly classical behavior.

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