Influence of dimensionality on deep tunneling rates: 
a study based on the hydrogen-nickel system

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(Received 26 April 1996)

The tunneling of subsurface hydrogen into a surface site of a nickel crystal is used to investigate deep tunneling phenomena. A method to calculate tunneling lifetimes based on an energy and time filter is developed, enabling converged lifetimes differing by 14 orders of magnitude. It is found that the reduced dimensional approximation always overestimates the tunneling rate. The vibrational adiabatic correction improves dramatically the one-dimensional calculation but nevertheless overestimates the cases of deep tunneling. The isotope effect is studied, pointing to experimental implications. [S0163-1829(96)51332-9]

I. INTRODUCTION

The tunneling motion of hydrogen atoms in metals is an important process with a range of practical applications, such as hydrogen embrittlement, catalysis, and fuel storage. Moreover, tunneling draws fundamental interest since it exhibits dominant quantum effects at low temperatures. Experimentally, for tunneling processes the Arrhenius rate law breaks down, exhibiting a sharp crossover to a temperature-independent rate, as predicted by Wigner in the 1930's.

In molecular dynamics, tunneling phenomena are extreme examples where classical treatments fail. Since quantum calculations scale exponentially with dimension, approximations for the tunneling motion based on a reduced dimensionality description have been developed. It has been established that defining a ‘‘tunneling coordinate’’ and then freezing the perpendicular degrees of freedom causes severe errors in the estimates of tunneling rates. Instead, various studies have employed a reaction path approach, which is essentially an adiabatic approximation suitable when the perpendicular degrees of freedom can be treated as ‘‘fast’’ and the reaction, tunneling coordinate as ‘‘slow.’’ The approximation amounts to adding the ground-state energy of the perpendicular oscillators to the reaction path potential, and will be denoted as the vibrationally adiabatic approximation (VAA).

Schatz et al. have published a comparison of full quantum three-dimensional (3D) calculations of proton transfer reactions vs VAA-type transition-state theory with tunneling treated semiclassically (VAA/ST). They find large departures of the calculated reaction rates, up to a factor of 2.5 at room temperature. Garrett et al. claim that this discrepancy is not necessarily indicative of the quality of the approximation and can also be attributed to differences in potential-energy surfaces or to errors resulting from the numerical implementation of the quantum method. For more conclusive results a simpler solution is necessary.

Motivated by new experiments on the chemistry of bulk hydrogen, the dynamics of a hydrogen atom in a nickel fcc crystal is studied. The atom is located in a subsurface intersitial site from which it tunnels, through a 0.65-eV barrier, to a threefold hollow site on the 111 metal surface.

In this system, degrees of freedom can be divided into two types: those directly belonging to the tunneling atom, and those of the heavy metal atoms — which comprise the crystal vibrational heat bath. The masses associated with each class of degrees of freedom (DOF) are very different, and it is therefore assumed that the hydrogen atom is only weakly coupled to the motion of the crystal. The full 3D hydrogen quantum results are compared with reduced dimensional 2D and 1D calculations, as well as with the 1D vibrational adiabatic approximation (1D-VAA). The treatment of the crystal DOF’s as well as the possibility of exciting the metal electrons will be addressed in a future publication.

II. METHOD OF CALCULATION

The tunneling rate is related to the imaginary component of the complex eigenvalue of the Hamiltonian belonging to an asymptotically outgoing-only eigenstate.

The tunneling eigenvalue spectrum is discrete and complex: $\Lambda_n = E_n - i\Gamma_n/2$, $n = 0, 1, 2, \ldots$, where $E_n$ is the energy of the state and $\Gamma_n$ the tunneling rate. The tunneling states are improper eigenstates of the Hamiltonian, since the negative imaginary part of the eigenvalue imposes a corresponding imaginary value of the outgoing momentum in the asymptotic channel, leading to the divergence of the eigenstate at infinitely large distances. In order to regularize these states, several methods have been developed, such as the complex scaling method and others.

An alternative regularization method is achieved by a localized negative imaginary potential (NIP) in the asymptotes. The NIP’s are used to impose an outgoing boundary condition on the eigenstate calculations. By aug-
menting the system Hamiltonian $\hat{H}$ to $\hat{H}' = \hat{H} - i\hat{V}_\text{NIP}$, a nonhermitian Hamiltonian is obtained, and the tunneling states become the right eigenstates. Once a functional form for the imaginary $\hat{V}_\text{NIP}$ is chosen with parameters $\Lambda_k$, $k = 0, 1, \ldots$; the actual parameter values should be optimized for each tunneling eigenvalue separately. The parameter values are selected according to an insensitivity criterion: $(dE_n/d\Lambda_k) = 0$, as has been used in the complex scaling methods. In practice, the spectrum is found to be weakly dependent on the potential parameters.

**A. Algorithm**

The algorithm for calculating tunneling states follows two basic steps. The first step consists of locating the approximate real part $\epsilon_n$ of the energy of the tunneling. The second step consists of repeatedly applying a filter $g_\epsilon(\epsilon_n)$ to a seed state, until convergence to tunneling states is achieved. In both steps the potential and wave function are represented on an equally spaced grid. The calculation is set on a grid employing the Fourier method.

**STEP 1.** The first step consists of calculating the bound states of the well. Bound states are obtained by adding an artificial binding potential in the asymptotic region. Then, the low-lying bound eigenstates $\Phi_n$ are searched for, using a filter-diagonalization scheme. These states constitute an approximation to the tunneling states in the well with a real eigenvalue of $\epsilon_n$, approximately equal to $E_n$, the energies of the tunneling states.

**STEP 2.** Next, the vibrational eigenstates $\Phi_n$ are used as a seed from which the tunneling state $\Psi_n$ is filtered out. When the filter $g_\epsilon(\epsilon_n)$ (see next subsection for details), operates on $\Phi_n$, it enhances the components that have long lifetimes and are close in energy to $\epsilon_n$. Repeated application of the filter results in the purified discrete tunneling state $\Psi_n$, since both the continuum states of the Hamiltonian (short lifetimes) and other tunneling states (different energies) are filtered out.

**B. Energy-lifetime filter**

The energy-lifetime filter used has the following form:

$$g_\epsilon(E) = e^{i(E-H')}\sin\left(\frac{(E-H')\tau}{E-H'}\right),$$

(2.1)

Where, $\tau$ is a real positive parameter. Note that if $\tau$ is large enough, the operator $g_\epsilon(E)$ becomes identical to the Green’s operator $G(E)$: $\lim_{\tau\to\infty} g_\epsilon(E) = (E-H')^{-1} = G(E)$. The limit exists since all the eigenvalues of $H'$ have negative imaginary parts. In practice, $\tau$ is much smaller than $\Gamma^{-1}$ so that the limit is not achieved for low-lying tunneling states. The effect of the filter on a seed state $\Phi_n$ can be seen by expanding it in terms of the eigenstates of $H'$: $\Phi_n = \sum_{k=1}^{N} a_k \Psi_k + \int d\alpha a(\alpha) \Psi(\alpha)$, where $\Psi_n$ are the tunneling eigenstates of $H'$ and $\Psi(\alpha)$ are the continuum eigenstates. Upon application of $g_\epsilon(\epsilon_n)$,

$$g_\epsilon(\epsilon_n)\Psi_n = \sum_{k=1}^{N} a_k e^{i(\epsilon_n-\Lambda_k)\tau} \frac{\sin[(\epsilon_n-\Lambda_k)\tau]}{\epsilon_n-\Lambda_k} \Psi_k + \int d\alpha a(\alpha) e^{i(\epsilon_n-\Lambda(\alpha)\tau)} \frac{\sin[(\epsilon_n-\Lambda(\alpha))\tau]}{\epsilon_n-\Lambda(\alpha)} \Psi(\alpha),$$

(2.2)

the dual operation of the filter is observed: the integral over the continuum vanishes, if $\tau$ is chosen such that $\tau \Gamma(\alpha) \gg 1$ for all $\alpha$; and the discrete sum over the tunneling eigenstates, enhances the component of energy closest to $\epsilon_n$.

The Green’s operator in this calculation is expanded by a Chebychev polynomial series, which, when truncated to a finite number of terms $N$ yields $g_\epsilon(E)$, where $N$ determines $\tau$ in a simple linear relation.

**C. Checking the convergence of the tunneling state**

A necessary condition for a state $\Psi$ to be an eigenstate of $\hat{H}$ is that the dispersion is zero: $\sigma^2(\Psi) = \langle \Psi | \hat{H}^2 | \Psi \rangle - \langle \Psi | \hat{H} | \Psi \rangle^2 = 0$. This criterion is used to check the convergence. The filter is applied to a given trial state as many times as needed to obtain $\sigma^2$ smaller than a predefined value. Specifically, with double precision of 16 digits accuracy, $\sigma^2 < 10^{-17}$ was chosen.

Once this criterion is met, convergence is further checked by comparing two different methods of calculating the tunneling rate. First, the rate is calculated from $\Gamma$, which is half the imaginary part of the eigenvalue. Second, the rate is calculated from $J$, the integral of the flux flowing through the surfaces encircling the localized negative imaginary potentials (NIP’s). Since the NIP’s are the only amplitude sinks, the two rates should be equal. The difference $J - \Gamma$ was found to be very sensitive to the quality of the calculation.

The method was first tested by comparing to analytical results. The calculations have also been tested against the sensitivity to the NIP parameters. Very small sensitivity has been found. The accumulation of round-off errors was also checked by comparing the double precision calculations to quadruple precision ones. It was found that round-off errors are small even for the very low tunneling rates (even lower than $10^{-3}$ sec$^{-1}$). It was also found that for all but the lowest tunneling rates, the grid spacing can be determined by the criterion $\Delta x \approx 2P_{\text{max}} < \hbar$, where $P_{\text{max}}^2 = 2m(V_{\text{max}} - V_{\text{min}})$. In the case of very low tunneling states a denser grid was required for convergence.

**III. HYDROGEN IN Ni(111): SUBSURFACE-SURFACE TUNNELING RATES**

The adiabatic potential surface, describing the hydrogen flow to the surface threefold-hollow site was calculated using the embedded-diatomic-in-molecules method of Truong et al. For a single hydrogen atom this approach is similar to the embedded-atom method of Daw and Baskes.

The full three-dimensional calculation was used as a benchmark for the other, reduced dimensional calculations. One- and two-dimensional calculations were performed on the minimum energy path cuts of the 3D potential. Finally,
1D calculations corrected for the zero-point energy of modes perpendicular to the tunneling direction were also performed (VAA). The perpendicular zero-point energy for each point in the reaction coordinate was calculated numerically. The reaction coordinate in this model has no curvature.

The tunneling spectrum, is shown in Fig. 1. The first point to be noted is that the lifetimes span about 14 orders of magnitude. The 2D and more so the 3D spectrum show a complicated nonmonotonic pattern. In general, tunneling rates of similar energies can differ by orders of magnitude. In contrast, the 1D results show a monotonic increasing pattern of tunneling rates vs energy, typically two orders of magnitude higher than the maximum 3D results of similar energy. The adiabatic zero-point correction (VAA) dramatically improves the "naive" 1D calculation. Nevertheless for the low-lying states, rates of similar energies differ by a factor of 7.

The thermal rate of the depletion of the subsurface hydrogen can be calculated from the tunneling spectrum by Boltzmann averaging over the rate constants. Figure 2 shows the thermally averaged tunneling rates calculated using the results shown in Fig. 1.

It is apparent from the figure that the 3D calculation exhibits the lowest thermal rate. For low temperatures the tunneling rate is dominated by the vibrational ground state and is therefore nearly temperature independent. The crossover to temperature-dependent tunneling is at \( \approx 190 \text{ K} \) for the 3D calculations, while it is at approximately 210 K for the 1D/VAA calculations. Below this temperature the rates of the full 3D and 1D/VAA differ by a factor of 7, while for higher temperature, the rates seem to settle to a factor of 1.7. The low-temperature 2D calculation has similar tunneling rates to the 3D one, probably due to the high cylindrical symmetry at the bottom of the potential well. At higher temperature the two rates diverge, reaching factors of 5–6. The 1D calculation exhibits tunneling rates almost two orders of magnitudes too high.

To check the strong isotope effect expected in tunneling, similar calculations were performed for deuterium. For the lowest-energy states, the deuterium tunneling rates calculated by the 1D/VAA approximation are higher by a factor of 80 compared to the full 3D calculations. At higher vibrational states the ratio becomes smaller — down to a factor of 1.7. The deuterium calculations also predict a crossover temperature of 190 K (3D calculations) and 210 K (1D/VAA).

For deep tunneling the isotope effect is enhanced dramatically, as shown in Fig. 3. The figure compares the "thermal programmed depletion" of subsurface hydrogen and deuterium. Here the surface temperature is increased at a constant rate of 2 K/sec, and the rate of the depletion of subsurface sites is simulated.

It is clear that hydrogen leaks out at a significant rate even at low temperatures, peaking at 210 K, while deuterium has negligible leakage at low temperatures with a maximum depletion rate at 250 K. In hydrogen, the 1D/VAA vibrational ground-state tunneling rate is too high, resulting in a fast depletion even at low temperature, with no high-temperature peak, while for deuterium, this approximation
does much better — peaking only 5 K lower than the full 3D calculation. The shape of the depletion curves depend critically on the rate of heating. At 90 K, where subsurface hydrogen experiments were performed, the present calculations predict that subsurface hydrogen will emerge to produce a monolayer within approximately 1 min while the same process for deuterium will take 4 h. The large isotope effect may be the reason that deuterium is easier to stabilize in the subsurface state and thus easier to treat in experiments.

IV. CONCLUSIONS

The dynamics of hydrogen on metal surfaces has been a subject of intensive study. In this context the issue of tunneling is of fundamental importance for all activated processes. Since multidimensional quantum calculations are extremely expensive, reduced dimensional approximations are of the utmost importance. In this study three-dimensional tunneling dynamics have served as a benchmark in understanding the influence of reduced dimensionality. The main conclusions are the following: (i) The tunneling rates are dramatically sensitive to naive reduction of dimensionality and this leads to overestimation of the tunneling rates by orders of magnitude. (ii) The tunneling rates vary monotonically with energy for 1D calculations, while the 3D tunneling rates exhibit a complicated irregular dependence. (iii) The adiabatic VAA approximation dramatically improves the 1D calculations but still overestimates the rate for deep tunneling states. For higher energy the accuracy of the VAA approximation improves. (iv) The tunneling rates of hydrogen are quite distinct from the rates of deuterium, typically three orders of magnitude higher. This fact predicts that subsurface deuterium will be easier to stabilize.

The reduced dimensional approximations fail for two reasons. The first is the variation of the perpendicular zero-point motion along the reaction path, which is corrected by the VAA. The second is the overestimation of the coherence between the two sides of the barrier in all the reduced dimensional calculations. This leads to the final conclusion that even the 3D calculations performed overestimate the tunneling rate.

ACKNOWLEDGMENTS

This research was partially supported by the German Israel Foundation. It was also partially supported by the Israel Atomic Agency commission and the Israel Council for Higher Education. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, GmbH München, FRG.

10 W. H. Miller, in Tunneling (Ref. 3), p. 91.