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Quantum Diffusion of H/Ni(111) through a Monte Carlo Wave Function Formalism

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We consider a quantum system coupled to a dissipative background with many degrees of freedom using the Monte Carlo wave function method. Instead of dealing with a density matrix which can be very highly dimensional, the method consists of integrating a stochastic Schrödinger equation with a non-Hermitian damping term in the evolution operator, and with random quantum jumps. The method is applied to the diffusion of hydrogen on the Ni(111) surface below 100 K. We show that the recent experimental diffusion data for this system can be understood through an interband activation process, followed by quantum tunneling.

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The stochastic nature of quantum evolution is described by a sharp crossover from classical diffusion to very weak quantum tunneling regime. In the field emission microscopy study [7] for Ni and W substrates and in the latest scanning tunneling microscopy study for H/Cu(001) [8], a sharp crossover from classical diffusion to very weak quantum tunneling regime is observed. The MCWF method can be used to tackle important transport problems in condensed matter physics in cases where the number of degrees of freedom is large enough (N ≳ 10⁴) to make the density matrix approach unfeasible. We consider here the case of a light adatom moving on a metal surface under conditions where the classical activated hopping rate between potential wells is negligible compared with the corresponding tunneling rate. At present, there does not exist a clear consensus on the details of the crossover from the classical activated behavior to the quantum tunneling regime. In the field emission microscopy (FEM) study [7] for Ni and W substrates and in the latest scanning tunneling microscopy study for H/Cu(001) [8], a sharp crossover from classical diffusion to very weak quantum tunneling regime is observed.
temperature dependence of diffusion was observed at a
temperature in the range of 60–100 K. However, the
quasieelastic helium atom scattering study for H/\text{Pt}(111)
[9] yields no crossover down to \( T = 100 \text{ K} \). For the
H/\text{Ni}(111) system, recent optical studies [10] showed a
crossover behavior from the classical regime to a second activated regime with a lower activation energy below \( T = 100 \text{ K} \). This is in contradiction with the FEM
data on the same system, which showed a crossover to a
temperature independent diffusion at low temperatures
[7]. Thus, while there is strong evidence that diffusion proceeds through quantum tunneling at low temperatures,
the detailed mechanisms for hydrogen diffusion on differ-
ent substrates are not yet understood. Previous theoretical
works do suggest that the details of the crossover are sen-
sitive to the shape of the adsorption potential and not just
determined by the barrier alone [3–5].

We will apply here the MCWF method to study the dy-
namics of H/\text{Ni}(111). The low temperature activated be-
behavior with a barrier of about 90 meV has been attributed
to small polaron type activated tunneling [10]. In our view,
this is a highly implausible explanation. First, the polaron
activation energy for H/\text{Cu}(001) [8] was determined to be
\(~3\text{ meV} \), then the relaxation energy due to the adatom
for H/\text{Ni}(001) was calculated to be 2.72 meV [4], and in
our recent calculations for H/\text{Pt}(111) [11] we also found
a relaxation energy of just a few meV; the polaron activa-
tion energy is a fraction of the relaxation energy [12]. We
will show instead that the data can be explained in terms of
tunneling from the first excited vibrational states of the
H adatom.

We construct a semi-empirical potential \( U(\mathbf{r}) \) based on
available data as follows. The lowest energy adsorption
sites are assumed to be the fcc sites forming a 2D trian-
gular lattice \([1] \) [13] with a lattice constant \( a = 2.581 \text{ Å} \)
(see Fig. 1). Also, the neighboring hcp sites at a distance of
\( s = 1.49 \text{ Å} \) [10] are taken to be equal in energy [10]
(this is also supported by a recent \( \text{ab initio} \) calculation
[14]). Second, we fix the barrier between the fcc and hcp
sites close to the value of 196 meV found in experiments
[10]. We use the vibrational excitation energy of 94 meV
known from [15,16]. \( U(\mathbf{r}) \) is constructed from localized
Gaussians at both the fcc and hcp sites and adjusts the
Gaussian parameters, obtaining a fitting with a band gap
between the centers of the \( A_0 \oplus A_1 \) and the \( E_0 \oplus E_1 \) bands
of \( \Delta = 96 \text{ meV} \) and a separation between the lowest band
and the top of the barrier between fcc and hcp sites of
207 meV.

The adiabatic Hamiltonian \( H_S \) for our model is charac-
terized by Bloch states \( \{|\mathbf{k},m\rangle\} \) with corresponding energy
\( \{\varepsilon_{\mathbf{k},m}\} \). Here \( m \) is the band index and \( \mathbf{k} \)
is the 2D wave vector. The center positions and the bandwidths for the first
few bands are listed in Table 1. The first two branches form
1D representations \( (A_0 \oplus A_1) \) of the symmetry group of
the 2D triangular lattice, while the next four form 2D rep-
resentations \( (E_0 \oplus E_1) \).

We describe the H adatom as a linear superposition of
energy eigenstates:

\[
|\Psi(t)\rangle = \sum_{m,k} b_{\mathbf{k},m}(t) |\mathbf{k},m\rangle,
\]

with \( \sum_{m,k} |b_{\mathbf{k},m}|^2 = 1 \). The frictional coupling to the sub-
strate through electronic and phononic excitations is mod-
eled by a general collision operator \( C_\mu \), (1), through which

\begin{table}[h]
\centering
\caption{Bandwidths \( \Delta\varepsilon_m \) and band centers \( \varepsilon_m \) for branches 1–6. Groups 1–2 and 3–6 form the composite bands \( A_0 \oplus A_1 \) and \( E_0 \oplus E_1 \).}
\begin{tabular}{ccc}
\hline
\( m \) & \( \Delta\varepsilon_m \) (meV) & \( \varepsilon_m \) (meV) \\
\hline
1 (\( A_0 \)) & 0.008 & 104.487 \\
2 (\( A_1 \)) & 0.008 & 104.497 \\
3 (\( E_0 \)) & 0.017 & 200.346 \\
6 & 0.017 & 200.721 \\
4 (\( E_1 \)) & 0.146 & 200.446 \\
5 & 0.146 & 200.621 \\
\hline
\end{tabular}
\end{table}

FIG. 1. (a) Trajectories at \( T = 70 \text{ K} \) (smaller set) and 110 K
(larger set). \( \gamma = 1 \) and the observation time was \( 3.1 \times 10^{-2} \text{ s} \).
(b) Details of the path at \( T = 70 \text{ K} \). The black circles are ex-
citations or deexcitations. Between two such consecutive points
there are usually several random changes of the momentum.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig1}
\caption{FIG. 1. (a) Trajectories at \( T = 70 \text{ K} \) (smaller set) and 110 K
(larger set). \( \gamma = 1 \) and the observation time was \( 3.1 \times 10^{-2} \text{ s} \).
(b) Details of the path at \( T = 70 \text{ K} \). The black circles are ex-
citations or deexcitations. Between two such consecutive points
there are usually several random changes of the momentum.}
\end{figure}
we model both intraband and interband transitions. It is represented as

\[ C_{m_1,m_2,q} = \Gamma_{m_1,m_2,q}^{1/2} \sum_{\mathbf{k}} |\mathbf{k} + \mathbf{q}, m_1\rangle \langle \mathbf{k}, m_2|, \]

where \( \Gamma \) is a (yet unspecified) transition rate, and \( \mu \) in Eq. (1) now becomes a multiple index with two band indices, \( \mu = (m_1,m_2,q) \). Thus the probabilities for scattering \( \delta p_{\mu} \) are given by

\[ \delta p_{\mu} = \langle \Psi(t)|C^+_\mu C_\mu|\Psi(t)\rangle \delta t = \sum_{\mathbf{k}} |b_{\mathbf{k},m}|^2 \Gamma_{\mu,\delta t}. \]

An important feature of the model is that for the low energy bands of interest, \( A_0 \oplus A_1 \) and \( E_0 \oplus E_1 \), the composite bandwidths are much smaller than the energy gap \( \Delta \) separating them (see Table I). This means that we need to consider only two types of transitions: interband transitions between the bands in the two groups and intraband transitions within each group. Since we do not have a microscopic expression for the scattering rates \( \Gamma_{\text{intra}} \) and \( \Gamma_{\text{inter}} \) we make one further simplification that is \( \Gamma_{\text{intra}} = \Gamma_{\text{inter}} = \Gamma \). Below, we will show that the magnitude of \( D \) is controlled by the parameter \( \gamma = \hbar \Gamma/\Delta_E \), where \( \Delta_E \) is the width of the upper composite band defined above.

In our numerical calculations, the substrate is represented by a 2D hexagonal box consisting of \( 180 \times 180 \) unit cells, with fully periodic boundary conditions. The size of the system is chosen such that the H adatom does not spread outside the boundary during the observation time \( t \). To calculate the spatial \( \alpha \beta \) elements of the tracer diffusion coefficient of H, we used the expression

\[ D_{\alpha\beta}(t) = \lim_{t \to \infty} \frac{1}{2t} \langle \hat{x}_\alpha - \langle \hat{x}_\alpha \rangle_0 \rangle \langle \hat{x}_\beta - \langle \hat{x}_\beta \rangle_0 \rangle, \]

where \( \hat{x} \) is the position operator. The average \( \langle \cdots \rangle \) in Eq. (8) represents both the quantum mechanical average in a given state as well as the ensemble average over different initial states. Statistical averages to compute \( D \) were performed with \( 1500-6000 \) initial states, for time intervals containing up to \( 10^5 \) collisions. With a code parallelized on four processors, one point on the Arrhenius plot takes 2–4 h, depending on the collision rates.

The symmetry of the lattice implies that the diffusion tensor \( D_{\alpha\beta} \) is diagonal. Figure 2 shows the temperature dependence of \( D \) for \( \gamma = 1, 5, 10 \) on an Arrhenius plot. There is clear activated behavior \( D \propto e^{-E_a/\hbar \omega} \), with an activation energy \( E_a = 98.1 \pm 0.5 \) meV. This is in excellent agreement with the experimental data of Cao et al. [10], shown in Fig. 2 as well, in the temperature regime below 100 K, where \( E_a = 105 \) meV. Obviously, with the inclusion of only the lowest bands in the present calculation, we cannot account for the classical high temperature region above 100 K, where \( E_a = 196 \) meV [10]. We can give a good qualitative description of the quantum regime, though, where the numerical results above indicate that the observed Arrhenius behavior for \( D \) corresponds to activated quantum tunneling.
it suffers a collision. It is found that asymptotically $P_\ell$ decreases exponentially with $\ell$, while it obeys a Poisson-like distribution at small values of $\ell$ ($\ell \approx s$). This is similar to the jump distribution in the classical regime [20]. Regarding the dependence of $D$ on $\gamma$, we have done simulations at $T = 70$ K and $T = 110$ K in the range $0.1 \leq \gamma \leq 10$ and found that $D \propto \gamma^{-1}$ in this range. This inverse power law dependence on $\gamma$ is similar to the dependence of $D$ on the microscopic friction $\eta$ in the classical regime [21,22]. However, the influence of the geometrical factor on the dependence of the jump distribution on $\gamma$ seems rather different from the classical case. The crossover of the dependence on $\gamma$ or $\eta$ from quantum to classical behavior is a subject worthy of further investigations.

To summarize, we have demonstrated through a model study of H diffusion on Ni(111) that the MCWF method is a powerful tool in the study of quantum transport problems with many degrees of freedom. In addition, the real space nature of the method allows one to extract interesting information about the dynamics of wave functions, not easily available with other means. As opposed to the small polaron mechanism suggested earlier [10], our results suggest that the low temperature diffusion behavior observed in the work of Cao et al. for H/Ni(111) [10] has its origin in the tunneling of the hydrogen adatom from the first vibrational excited state. We plan to apply the same MCWF formalism to investigate other quantum diffusion systems, such as H/Pt(111) [9] and H/Cu(001) [8], which show qualitatively different behaviors from H/Ni(111) [10]. The key is to start with a reliable adsorption potential through a combination of first-principles calculation and empirical inputs.

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[13] The present assumption of a 2D model should be well justified based on recent evidence that there is no significant mixing between the vertical and horizontal modes, due to the very different characteristic frequencies [15].