Dissipative dynamics of four-site tunneling of H

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(Received 7 December 1999)

We investigate the dissipative properties of a quantum particle which can tunnel among four equivalent sites on a plane. Our four-state system model is of experimental relevance to probe the quantum properties of H or D being trapped by substitutional Zr in Nb. Upon performing a unitary transformation, the problem is reduced to that of effective spin-boson systems. Numerical and analytical results for the population dynamics of the four localized states are obtained. Intriguing *dissipation-assisted* quantum coherent oscillations are predicted to occur even for strong damping.

Low-mass interstitials in solids, such as H or D, may exhibit pronounced quantum effects. These appear as a coherent delocalization of the wave function over *two or more* interstitial sites.[1] Tunneling of H (D) trapped by an interstitial impurity (O, N, and C) in Nb and Ta has been the object of extensive investigations by specific heat, acoustic, and inelastic neutron scattering experiments.[2] Most of the experiments could be quantitatively interpreted by supposing that H tunnels between two equivalent tethraedral sites close to the impurity, thus forming a two-state system (TSS).[3] By taking into account the nonadiabatic interaction with conduction electrons, NbO_xH_y became an ideal test system to verify the predicitions of the thoroughly investigated spin-boson model with Ohmic dissipation.[4,5]

In contrast, very little is known about the dynamics of substitutional-H (-D) pairs in Nb or in semiconductor structures. In these systems H can form a four-state system (FSS) within the four tetrahedral sites of one face of the bcc cubic cell containing the substitutional impurity; cf. Figs. 1. This model has been proposed and found to be consistent with specific heat and anelastic relaxation measurements with substitutional Ti or Zn in Nb,[6] as well as with substitutional

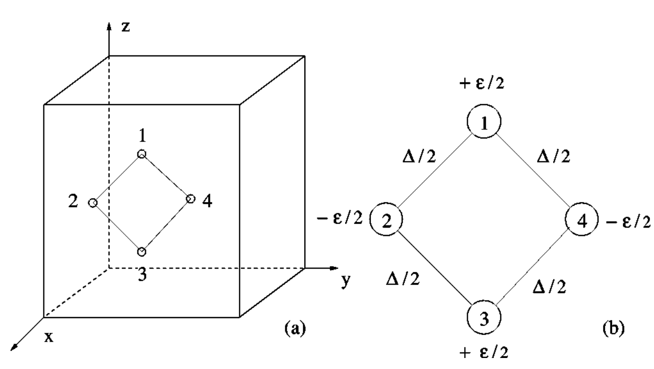

FIG. 1. In a bcc cell containing, e.g., Nb atoms at the vertices, and a substitutional atom in the center, the H atom is supposed to tunnel among the four tetrahedral sites of the same face. In (a) these four sites are shown. In (b) the parameters characterizing the resulting four-state system are depicted.

Zn in GaAs.[7] In this work we systematically investigate the dissipative dynamics of a FSS described by the total Hamiltonian $H = H_{\rm FSS} + H_{\rm int} + H_B$. We shall consider the case, proposed in Ref. 6, that the unperturbed (by the externally applied stress and by the environment) FSS is *centrosymmetric*, since its asymmetry is caused by the long-range strain interactions with the other FSS's present in the sample, and strain is a centrosymmetric tensor. To investigate tunneling properties, in analogy to what is generally done for the TSS, we express the FSS Hamiltonian in the *localized* representation, i.e., in terms of four H wave functions each localized in one of the four sites. This yields the FSS Hamiltonian

$$H_{\rm FSS} = \frac{1}{2}\begin{pmatrix} \varepsilon & \Delta & 0 & \Delta \\ \Delta & -\varepsilon & \Delta & 0 \\ 0 & \Delta & \varepsilon & \Delta \\ \Delta & 0 & \Delta & -\varepsilon \end{pmatrix}, \qquad (1)$$

where the basis vectors read $|1\rangle = [1000]^T$, $|2\rangle = [0100]^T$, $|3\rangle = [0010]^T$, and $|4\rangle = [0001]^T$. Hence Δ represents the tunneling element between adjacent sites, while $\varepsilon_i/2(i = 1,2,3,4)$ is the asymmetry energy of the i site. The case of a perfectly symmetric multisite tunneling system corresponds to $\varepsilon_i = 0$. As mentioned before, this assumption is not suitable to describe the substitutional-H pair.

It is well known that at low temperatures the quantum dynamics of light interstitials in metals is strongly influenced by *nonadiabatic* interaction with conduction electrons. When a charged particle moves in a metal, it drags behind a screening cloud of electron-hole pairs which have bosonic character. At low temperatures the bosonic spectral density $J(\omega)$ has an Ohmic form due to the constant electronic density of states around the Fermi surface. The Ohmic spin-boson model has been successfully used to describe H tunneling in NbO_xH_y.[3,5] We extend the Ohmic spin-boson model to our FSS situation. We consider the case in which the environment effect is to modify the site energies centrosymmetrically,[8] yielding

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$$H=\begin{pmatrix} H_{\rm SB}(\Delta) & \frac{1}{2}\Delta\sigma_x \\ \frac{1}{2}\Delta\sigma_x & H_{\rm SB}(\Delta)\end{pmatrix}, \qquad (2)$$

with the σ_i being the 2×2 Pauli matrices, and (we set $\hbar=k_{\rm B}=1$) where

$$H_{\rm SB}(\Delta)=-\frac{1}{2}[\varepsilon\sigma_z+\Delta\sigma_x]-\frac{1}{2}\sigma_z X+H_{\rm B} \qquad (3)$$

is the well-known spin-boson Hamiltonian.[4,5] Here $H_{\rm B}=\Sigma_i[p_i^2/2m_i+m_i\omega_i^2x_i^2/2]$ represents the bath of bosons, and the collective variable $X=\Sigma_i c_i x_i$ describes the bath polarization as a result of the interaction Hamiltonian $H_{\rm int}$. All effects of the boson bath on the FSS are captured by the spectral density

$$J(\omega)=\frac{\pi}{2}\sum_i \frac{c_i^2}{m_i\omega_i}\delta(\omega-\omega_i).$$

We assume the Ohmic form $J(\omega)=2\pi\alpha\omega e^{-\omega/\omega_c}$, with ω_c being a high-frequency cutoff and α the dimensionless coupling to the conduction electrons. We observe that Eq. (2) captures also the effects of an *externally applied* odd extensional mode[6] upon substituing $\varepsilon\rightarrow\varepsilon+\varepsilon_1$, with $|\varepsilon_1|$ being the external field amplitude. Hence, in the following, ε in Eq. (3) will be interpreted as the total asymmetry energy resulting from internal stresses as well as from external *odd* extensional modes.

Suppose that the FSS has been prepared at time zero in the state $|1\rangle$ with the bath in thermal equilibrium. The dynamical quantities of interest are then the diagonal elements $\rho_{ii}(t)$ of the reduced density matrix (RDM) describing the population of the site *i* at time *t*.

The symmetry of the system is better visualized upon unitary transformation of the Hamiltonian *H*, yielding

$$\tilde{H}=SHS=\begin{pmatrix} H_{\rm SB}(2\Delta) & 0 \\ 0 & H_{\rm SB}(\Delta=0)\end{pmatrix}, \qquad (4)$$

where

$$S=S^\dagger=\frac{1}{\sqrt{2}}\begin{pmatrix} I_2 & I_2 \\ I_2 & -I_2\end{pmatrix} \qquad (5)$$

and I_2 the 2×2 unit matrix. The effect of this rotation is to *decouple* the total Hamiltonian into two unconnected blocks. The new basis reads

$$S|1\rangle\equiv|\alpha\rangle=(|1\rangle+|3\rangle)/\sqrt{2}, \quad S|2\rangle\equiv|\beta\rangle=(|2\rangle+|4\rangle)/\sqrt{2},$$

$$S|3\rangle\equiv|\gamma\rangle=(|1\rangle-|3\rangle)/\sqrt{2}, \quad S|4\rangle\equiv|\delta\rangle=(|2\rangle-|4\rangle)/\sqrt{2}.$$

The diagonal elements $\rho_{ii}(t)$ of the RDM in the localized basis $\{|i\rangle\}$ can now be expressed in terms of the matrix elements of the RDM in the transformed basis $\{|\mu\rangle\}$ ($\mu=\alpha,\beta,\gamma,\delta$), yielding for the populations $P_i:=\rho_{ii}$ of the localized states

$$P_1(t)=[\rho_{\alpha\alpha}(t)+2{\rm Re}\rho_{\alpha\gamma}(t)+1/2]/2,$$

$$P_3(t)=[\rho_{\alpha\alpha}(t)-2{\rm Re}\rho_{\alpha\gamma}(t)+1/2]/2,$$

$$P_2(t)=P_4(t)=\rho_{\beta\beta}(t)/2. \qquad (6)$$

Asymptotically ($t\rightarrow\infty$) (cf. below), the coherence $2{\rm Re}\rho_{\alpha\gamma}(t)$ vanishes. This yields, as expected from symmetry arguments, the relation $P_1^\infty=P_3^\infty$, with $P_i^\infty:=P_i(t=\infty)$. Upon observing that

$$\rho_{\alpha\alpha}(t)+\rho_{\beta\beta}(t)=1/2, \qquad (7)$$

the problem is reduced to the evaluation of the RDM elments $\rho_{\alpha\alpha}(t)$ and $\rho_{\alpha\gamma}(t)$. Because of the block-diagonal form of the transformed Hamiltonian $\tilde{H}$, a solution for $\rho_{\alpha\alpha}(t)$ is readily found upon solving the spin-boson problem described by the Hamiltonian $H_{\rm SB}(2\Delta)$ for a particle tunneling between the states $|\alpha\rangle$ and $|\beta\rangle$ and with the constraint (7). In other words, the relation

$$\rho_{\alpha\alpha}(t)=(1+\langle\sigma_z\rangle_t)/4 \qquad (8)$$

holds, where the operator σ_z evolves with respect to $H_{\rm SB}(2\Delta)$ and with the initial condition $\langle\sigma_z\rangle_{t=0}=1$. Note that the resulting TSS has a *doubled* tunneling matrix element 2Δ as compared to the original FSS Hamiltonian. For zero dissipation one finds

$$\rho_{\alpha\alpha}(t)=[1+(\varepsilon/E)^2+(2\Delta/E)^2\cos(Et)]/4,$$

with the energy splitting $E=\sqrt{\varepsilon^2+4\Delta^2}$. For finite dissipation, $\rho_{\alpha\alpha}$ decays towards an asymptotic equilibrium value. Upon observing that $\langle\sigma_z\rangle_{t=\infty}\rightarrow 0$ when $\varepsilon\rightarrow 0$ and $\langle\sigma_z\rangle_{t=\infty}\rightarrow 1$ in the opposite limit $\varepsilon\rightarrow\infty$, we find

$$P_1^\infty\rightarrow 3/8, \quad P_2^\infty\rightarrow 1/8, \quad \varepsilon\ll\Delta,$$

$$P_1^\infty\rightarrow 1/2, \quad P_2^\infty\rightarrow 0, \quad \varepsilon\gg\Delta, \quad T\ll E. \qquad (9)$$

Note that these results are independent of the details of the dissipative mechanism. This tendency is confirmed in Figs. 2, 3, and 4 where the population behavior is shown for two different bias strengths $\varepsilon=1.5\Delta$ and $\varepsilon=0.5\Delta$. To make predictions at intermediate times, the full dynamics must be solved. For finite dissipation, results for $\langle\sigma_z\rangle_t$ covering the whole regimes of temperature and dissipation strength have been reported in the literature.[5] Quite generally,[9] $\langle\sigma_z\rangle_t$ obeys the exact generalized master equation

$$\langle\dot{\sigma}_z\rangle_t=\int_0^t dt'[K_a(t-t')-K_s(t-t')\langle\sigma_z\rangle_{t'}], \qquad (10)$$

where the kernels $K^{s/a}$ are expressed in power series of Δ^2. In the following, we focus on the regime of high temperatures T and/or strong damping, where the so-termed noninteracting-blip approximation (NIBA) correctly describes the dynamics.[4,5] The kernels assume the form

$$K_s(t)=(2\Delta)^2e^{-Q'(t)}\cos[Q''(t)]\cos(\varepsilon t),$$

$$K_a(t)=(2\Delta)^2e^{-Q'(t)}\sin[Q''(t)]\sin(\varepsilon t). \qquad (11)$$

The dissipative effects are encapsulated in the functions Q' and Q'', being the real and imaginary parts, respectively, of the bath correlation function

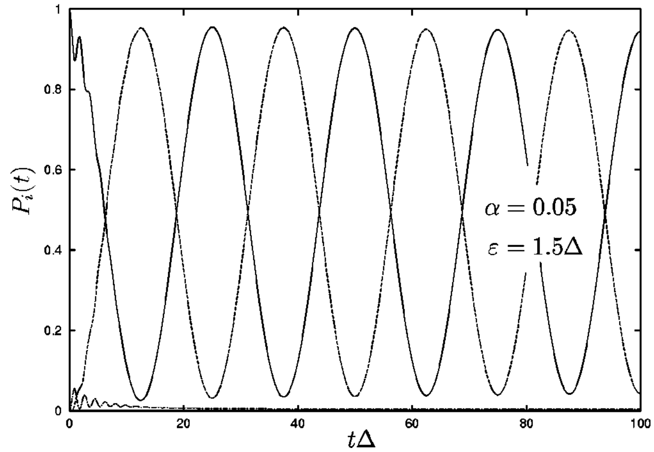

FIG. 2. Dynamics of the populations P_i of a FSS in the presence of weak Ohmic dissipation $\alpha=0.05$ and asymmetry $\varepsilon=1.5\Delta$. Here and in the following figures we choose a temperature $T=\Delta$, a cutoff frequency $\omega_c=50\Delta$, and we depict P_1 with a solid curve, $P_2=P_4$ with a dash-dotted line, and P_3 with a dashed curve. The two populations P_2 and P_4 exhibit a much faster (oscillatory) decay towards equilibrium than P_1 and P_3. Large amplitude oscillations of P_1 and P_3 which decay on quite a long time scale are observed.

$$Q(t)=\int_0^\infty d\omega \frac{J(\omega)}{\omega^2}\left[(1-\cos\omega t)\coth\left(\frac{\omega}{2T}\right)+i\sin\omega t\right]. \tag{12}$$

The Markovian limit of Eq. (10) yields the decaying behavior

$$\langle\sigma_z\rangle_t=e^{-\gamma_s t}[1-P_\infty]+P_\infty, \tag{13}$$

towards the asymptotic equlibrium value $P_\infty=\gamma_a/\gamma_s=\tanh(\varepsilon/2T)$ and where $\gamma_{s/a}:=\int_0^\infty d\tau K_{s/a}(\tau)$.

The evaluation of the coherence $\rho_{\alpha\gamma}(t)$ is not standard. The initial condition $\rho(t=0)=|1\rangle\langle 1|$ implies $\rho_{\alpha\gamma}(t=0)=1/2$, yielding, in the absence of the bath, the result

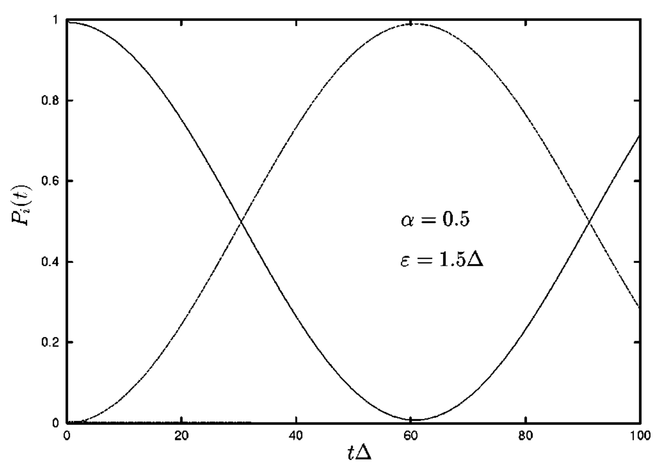

FIG. 3. Population decay for strong Ohmic coupling $\alpha=0.5$ at bias $\varepsilon=1.5\Delta$. The large amplitude oscillations of the occupation probabilities P_1 and P_3 exist also at such strong damping. The oscillation frequency is smaller than in the weak coupling case shown in Fig. 2.

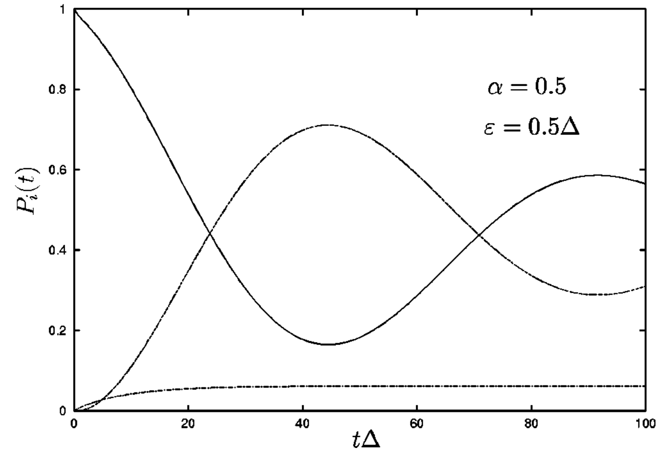

FIG. 4. Population dynamics at strong coupling $\alpha=0.5$ and weak asymmetry $\varepsilon=0.5\Delta$. The decay rate of the populations P_1 and P_3 is strongly enhanced with decreasing asymmetry, as seen by comparison with Fig. 3. Note also the increase in the asymptotic population of states 2 and 4.

$$2\,\mathrm{Re}\rho_{\alpha\gamma}(t)=\cos\left(\frac{Et}{2}\right)\cos\left(\frac{\varepsilon t}{2}\right)+\left(\frac{\varepsilon}{E}\right)\sin\left(\frac{Et}{2}\right)\sin\left(\frac{\varepsilon t}{2}\right).$$

It describes the quantum coherent motion of the FSS between the states (α,γ) and (β,γ) of the RDM in the transformed basis $\{|\mu\rangle\}$. The dissipative effects of the bath result in a damping of the quantum coherent motion. To evaluate the latter we employ a real time path integral approach (cf., e.g., Ref. 5) which allows an exact evaluation of the trace over the bath degrees of freedom. Then, $\rho_{\alpha\gamma}(t)$ is expressed as a double path integral over forward and backward spin paths $\sigma(\tau)$ and $\sigma'(\tau)$, respectively. The piecewise constant forward path $\sigma(\tau)$ describes a sequence of transitions between the states $|\alpha\rangle(\sigma=1)$ and $|\beta\rangle(\sigma=-1)$. On the contrary, the backward path is constant, $\sigma'(\tau)=1$, as it corresponds to a permanence of the system in the state $|\gamma\rangle$. It is convenient to switch to the path combinations $\eta(\tau)=[\sigma(\tau)+\sigma'(\tau)]/2$ and $\xi(\tau)=[\sigma(\tau)-\sigma'(\tau)]/2$. Then, $\rho_{\alpha\gamma}(t)$ is expressed in terms of a double path sum

$$\rho_{\alpha\gamma}(t)=\int \mathcal{D}\xi\mathcal{D}\eta\mathcal{A}[\xi,\eta]\exp\{\Phi'_{FV}[\xi]+i\Phi''_{FV}[\xi,\eta]\},$$

where $\mathcal{A}$ is the path weight in the absence of the bath coupling and the influence function is

$$\Phi_{FV}[\xi,\eta]=\int_0^t dt_2\int_0^{t_2}dt_1\dot{\xi}(t_2)\times[Q'(t_2-t_1)\dot{\xi}(t_1)+iQ''(t_2-t_1)\dot{\eta}(t_1)]. \tag{14}$$

In this way the expression (14) formally resembles the solution for a TSS, with the ''sojourn'' path $\eta(t)=0$ if in the RDM state (β,γ), and $\eta(t)=1$ if in (α,γ). Likeways, the ''blip'' path is $\xi(t)=0$ if in (α,γ), and $\xi(t)=-1$ if in (β,γ). Upon generalizing[9] to our case, we obtain an exact master equation for the vector $X:=(\mathrm{Re}\rho_{\alpha,\gamma},\mathrm{Im}\rho_{\alpha\gamma})^T$, i.e.,

$$\dot{X}(t) = -\int_0^t dt' Y(t-t') X(t'), \tag{15}$$

where the matrix elements of the rate matrix Y are expressed in power series of Δ^2. Quite generally, this implies that $\mathrm{Re}\rho_{\alpha\gamma}^{\infty} = 0$. Within the NIBA, the kernel matrix reads $Y(t) = \Sigma_R(t) I_2 - i\Sigma_I(t)\sigma_y$, where $\Sigma_R(t)$ and $\Sigma_I(t)$ are the real and imaginary parts, respectively, of the bath correlation function

$$\Sigma(t) = \Delta^2 e^{-Q(t) - i\varepsilon t}. \tag{16}$$

In the Markovian limit Eq. (15) with Eq. (16) yields the solution

$$\mathrm{Re}\rho_{\alpha\gamma}(t) = \Delta^2 e^{-\gamma t}\cos(\Omega t), \tag{17}$$

with γ and Ω being the real and imaginary parts, respectively, of $\int_0^\infty d\tau \Sigma(\tau)$. Equation (17) is quite intriguing, and shows that the coherence $\rho_{\alpha\gamma}(t)$ exhibits damped coherent oscillations, whose amplitude and frequency are determined by the details of the bath. Upon comparison of Eq. (17) with Eq. (13), and with the use of the relation $\gamma_a/\gamma_s = \tanh(\varepsilon/2T)$, we find

$$\gamma_s = 2\gamma[1 + \exp(-\varepsilon/T)] \geqslant 2\gamma, \tag{18}$$

implying that the coherence $\rho_{\alpha\gamma}$ decays with a *smaller* rate than the diagonal element $\rho_{\alpha\alpha}$. Up to here we did not need to specify the dissipative mechanism. In the case of Ohmic dissipation and in the scaling limit $\omega_c \gg T$, Δ, the function $Q(t)$ in Eq. (12) takes the form[5]

$$Q'(t) = 2\alpha \ln[(\omega_c/\pi T)\sinh(\pi T t)],$$

$$Q''(t) = \pi\alpha\,\mathrm{sgn}(t) \quad \text{with} \quad Q''(0) = 0. \tag{19}$$

This yields for the decay rate γ_s of $\rho_{\alpha\alpha}$ the result[5]

$$\gamma_s = \frac{\Delta^2}{\omega_c}\left(\frac{\beta\omega_c}{2\pi}\right)^{1-2\alpha} \frac{|\Gamma(\alpha + i\beta\varepsilon/2\pi)|^2}{\Gamma(2\alpha)} \cosh(\beta\epsilon/2), \tag{20}$$

with $\Gamma(z)$ being the gamma function. The decay rate γ of the coherence $\rho_{\alpha\gamma}$ immediately follows from Eq. (20) together with Eq. (18). Numerical results, obtained upon solving the dissipative dynamics described by the FSS Hamiltonian (2) within the noninteracting-blip approximation, are shown in Figs. 2, 3, and 4. In Figs. 2 and 3 the time evolution of the populations is investigated for two different values $\alpha = 0.05$ and $\alpha = 0.5$, respectively, of the Ohmic coupling strength. As expected, the two populations $P_2 = P_4$ decay towards equilibrium with a much faster decay rate than the two other populations P_1 and P_3. In fact, in virtue of Eq. (6), these two latter probabilities turn out to be characterized by *two* different decay times. The faster one γ_s, being the same as that of the P_2 and P_4 populations, determines the transient dynamics at short times. The smaller one γ dominates the transient dynamics at longer times. In Fig. 2, where a small value of the coupling constant is chosen, the decay towards equilibrium determined by γ is very slow. In this regime the two occupation probabilities P_1 and P_3 exhibit characteristic underdamped quantum coherent oscillations, with frequency $\Omega(\alpha, T)$; cf. Eq. (17). Upon increasing the damping strength (cf. Fig. 3), the oscillations persist. Interestingly enough, the amplitude and period $2\pi/\Omega$ of the oscillation *increases* with α. In Fig. 4 the effects of the asymmetry variation are investigated. We observe that a *weaker* asymmetry strongly enhances the decay rate γ. As expected from Eq. (9), the asymptotic occupation of states 2 and 4 increases in the more symmetric situation corresponding to smaller ε.

In conclusion, we solved the dissipative dynamics of a dissipative centrosymmetric four-state system (FSS) with periodic boundary conditions upon mapping the problem to that of two effective spin-boson systems. Analytical and numerical results were presented. The peculiar symmetries of a centrosymmetric FSS (cf. Fig. 1) are reflected nicely in the properties of the populations of the four localized states. In particular, for a FSS initially localized at the site 1 (cf. Fig. 1, the relation $P_2(t) = P_4(t)$ holds at any time. These two populations are characterized by a much faster decay towards equilibrium than the two occupation probabilities $P_1(t)$ and $P_3(t)$. In particular, P_1 and P_3 undergo damped coherent oscillations even at relatively strong damping strengths. In a two-state system characterized by the same asymmetry energy and tunneling matrix element, quantum coherent oscillations are damped away by the environment at much lower temperatures and/or smaller damping strengths.[5]

We hope that our results will contribute to a better understanding of the tunneling dynamics of H in Nb or in semiconductor structures.

We acknowledge support by the European Community Project No. FMRX-CT97-0143 (M.G.) and Grant No. SFB-382 (M.W.) of the Deutsche Forschungsgemeinschaft.

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