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The microscopic mechanism of electron diffusion in a one-dimensional chain with static and dynamic disorder

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Abstract. We study the mechanism of electron diffusion between localized states for the example of a 1D Anderson chain with static and dynamic disorder. The dynamic disorder is assumed to be periodic in time. The Schrödinger equation is integrated numerically for different frequencies ω , to cover the range from adiabatic to anti-adiabatic coupling between the quasi-stationary states. Our numerical results are analysed in terms of the adiabatic theory and the sudden approximation. We find that—similar to the hopping theory—the elementary diffusion processes depend strongly on the spatial overlap between the quasi-stationary states.

1. Introduction

Since the early days of the theory of disordered systems it has been recognized that the localization of the electron states implies the absence of electron diffusion at zero temperature (Anderson 1958). At finite temperatures the electrons are coupled to the thermal phonons, and diffusion sets in. This problem has been treated in the hopping theory (an early review is given by Mott and Davis (1971)) where the electron diffusion is described in terms of effective transition rates between the unperturbed localized eigenstates at $T = 0$. The transition rates depend on the phonon spectrum, the temperature, as well as the energetic distance and the spatial overlap between the stationary unperturbed electron states. This description of the elementary diffusion processes becomes inadequate in the limit of high temperatures. In particular, it relies on a sufficiently weak electron–phonon coupling that can be treated in low-order perturbation theory. Moreover, only the dynamic coupling between the localized functions is treated, whereas the influence of the phonons on the electron energies is neglected. These approximations break down for high temperatures, where kT is large with respect to typical phonon frequencies, and where the presence of phonons can be described in terms of classical temporal potential fluctuations. In this case a more consistent way would be to describe the electron transition rates with respect to the quasi-stationary states of the system. This approach is attempted in the present paper for the case of a one-dimension (1D) Anderson chain with static and dynamic disorder. In such a 1D system the electronic eigenstates are known to be localized in the presence of static disorder.

The influence of the temporal potential fluctuations on the electron states is treated in the framework of the time-dependent Schrödinger equation. This implies that our system is not coupled to an external heat bath, and that the time evolution of the electron states remains completely reversible. With this in mind it is obvious that our approach does not cover the problem of dissipation but is limited to the description of the elementary processes of diffusion, i.e. the dynamic coupling or 'hopping' between quasi-stationary eigenstates.

Our procedure is straightforward: we place an electron initially in one of the eigenstates of our model Hamiltonian $H(t)$. Two possible kinds of limiting behaviour can then be distinguished: (i) the adiabatic case, in which the electron remains within a quasi-stationary eigenstate of the Hamiltonian $H(t)$; (ii) the anti-adiabatic case, where the electron hops from one quasi-stationary eigenstate to a neighbouring one.

Our results show that—in agreement with intuitive arguments—the adiabatic time evolution becomes important for slowly varying Hamiltonians, whereas anti-adiabatic behaviour is approached for rapid variations. We will discuss the conditions for the occurrence of adiabatic or anti-adiabatic coupling, as well as the respective contributions to electron diffusion.

2. Numerical approach

Our calculations are based on the time-dependent one-band Anderson Hamiltonian, which is given in terms of the Wannier functions $|i\rangle$

$$H(t) = \sum_i \varepsilon_i(t) |i\rangle\langle i| + V \sum_i (|i\rangle\langle i+1| + |i-1\rangle\langle i|). \quad (1)$$

The off-diagonal matrix elements V describe the coupling between nearest neighbours. The disorder—static and dynamic—is introduced through the diagonal elements $\varepsilon_i(t)$ with

$$\varepsilon_i(t) = \varepsilon_i^0 + A \sin(\omega t + \delta_i) \quad (2)$$

where the static disorder is defined through the parameters ε_i^0 , which are statistically equally distributed over the interval $(-W/2, W/2)$. The dynamic part of the disorder is described by the second term in equation (2). For simplicity it is supposed to be periodic in time with a single frequency ω . The phases δ_i are random within the interval $(0, 2\pi)$.

Our numerical calculations have been performed for periodic boundary conditions. The results presented, however, do not depend on the latter, since the periodicity volume is chosen much larger than the extension of the localized states.

The evolution of the electron states with time will be described in terms of the quasi-stationary solutions of the Hamiltonian $H(t)$, which satisfy the Schrödinger equation

$$H(t)|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle. \quad (3)$$

The eigenvectors $|\psi_n(t)\rangle$ can be expressed in terms of the Wannier functions

$$|\psi_n(t)\rangle = \sum_i c_{ni}(t) |i\rangle. \quad (4)$$

For the purposes of our later analysis we define the spatial overlap between two quasi-stationary functions ψ_n and ψ_m by

$$O_{nm}(t) = \sum_i |c_{ni}(t)| |c_{mi}(t)|. \tag{5}$$

The average density of states is given by

$$g(E) = \left\langle \sum_n \delta^\Delta [E_n(t) - E] \right\rangle. \tag{6}$$

The brackets $\langle \dots \rangle$ indicate time averaging, which becomes unimportant for sufficiently large systems, however, where the inter-level spacing is small with respect to the amplitude A of the time-dependent perturbation. The Hamiltonian (1), taken at different times, can then be considered to correspond to different realizations of a disordered chain of the same type. The amplitude of the remaining noise in the energies of the quasi-stationary states is limited by the order of magnitude of boundary effects, which decrease exponentially with the sample size, since the electron states are exponentially localized (Thouless 1977). The participation number

$$p(E) = \frac{1}{g(E)} \left\langle \sum_{ni} \frac{1}{|c_{ni}|^4} \delta^\Delta [E_n(t) - E] \right\rangle \tag{7}$$

measures the average number of sites that are covered by a localized state within the energy interval Δ centred at E .

In the above equations (6) and (7) we have used the filter function

$$\delta^\Delta(E) = \begin{cases} 1 & \text{for } |E| < \Delta/2 \\ 0 & \text{otherwise.} \end{cases} \tag{8}$$

The time evolution of the wavefunctions is calculated by solving the time-dependent Schrödinger equation

$$i\hbar \partial|\varphi(t)\rangle/\partial t = H(t) |\varphi(t)\rangle. \tag{9}$$

In the following we use Rydberg atomic units, i.e. $\hbar = 1$. The corresponding time unit is equal to 5×10^{-17} s.

Different numerical methods can be used for the solution of equation (9). We have used the symmetrized finite-difference scheme

$$\varphi(t + \Delta t) = -2iH(t)\varphi(t) \Delta t + \varphi(t - \Delta t) \tag{10}$$

which is very convenient and rapid. The evaluation of the right-hand side is straightforward in the Wannier basis. The accuracy of the results over the considered time period can easily be controlled by changing the time step Δt .

The above symmetrized version of the finite-difference scheme requires the knowledge of the wavefunction at two previous time steps. To initialize the procedure we choose a quasi-stationary solution of the Hamiltonian $H(t)$ as the initial state and calculate the function after the first time step with the split-operator technique (Fleck *et al* 1976, Feit *et al* 1982)). Its formulation for the case of the Anderson Hamiltonian is straightforward, if one remembers that in the absence of disorder the eigenfunctions of equation (1) are plane waves.

3. Numerical results

3.1. Quasi-stationary case

In our numerical calculations we have used the following parameters

$$N = 100 \quad W = 3 \quad V = 1 \quad A = 0.4.$$

As we will see later, the disorder is sufficiently large to guarantee that the results

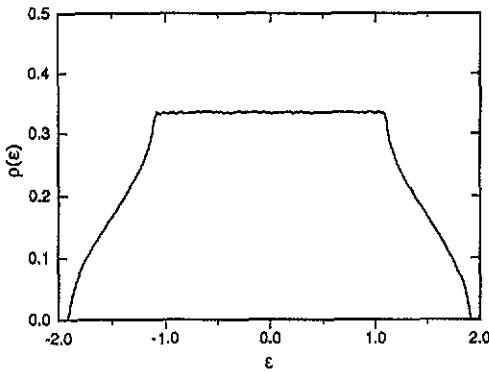


Figure 1. Distribution function for the diagonal elements in the Anderson Hamiltonian with static and dynamic disorder.

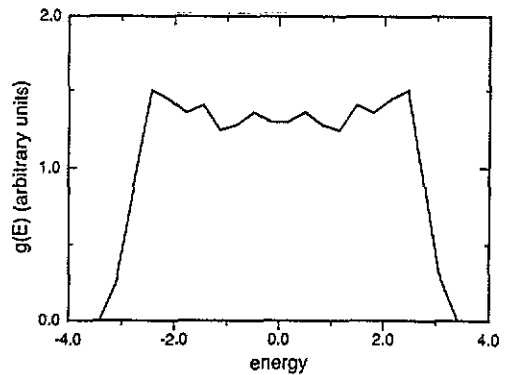


Figure 2. Quasi-stationary case: density of states.

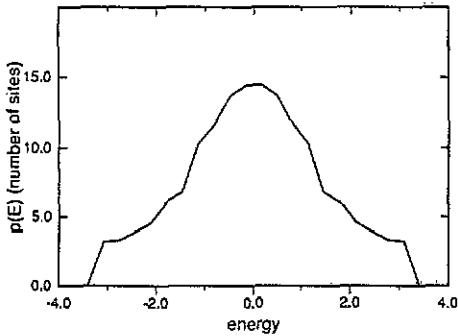


Figure 3. Quasi-stationary case: participation number.

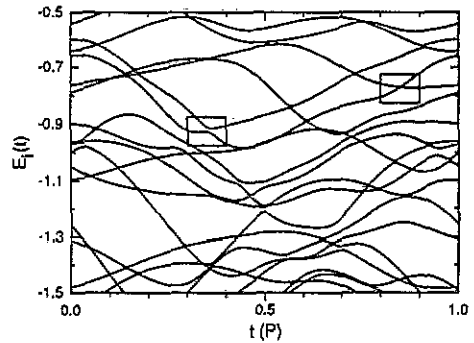


Figure 4. Evolution of the quasi-stationary eigenvalues over the time period P . Chain length $N = 100$.

presented are independent of the boundary conditions. The resulting effective distribution function $\rho(\epsilon)$ for the diagonal elements in the Hamiltonian (1) is given in figure 1. It should be noted that the dynamic disorder is much weaker than the static disorder. The influence of the disorder on the quasi-stationary eigenstates is shown in figures 2 and 3. The Van Hove singularities in the density of states (figure 2) near the band edges have nearly disappeared, and the wavefunctions are localized over only a few sites, as is seen from the participation numbers $p(E)$ in figure 3. As expected, the eigenfunctions are less localized near the band centre where they extend over about 15 sites.

Figure 4 shows the temporal evolution of the eigenvalues of equation (3) within a finite energy window. The results are given for a full time period P . We see that the quasi-stationary eigenvalues change in a rather complicated and uncorrelated manner. Close inspection shows that the lines never cross, but that they always remain separated by a small gap. This behaviour is a consequence of the fact that our Hamiltonian does not possess any symmetries that would give rise to non-accidental level crossings. In future we will therefore use the term 'pseudo-crossing' rather than 'crossing'. The same

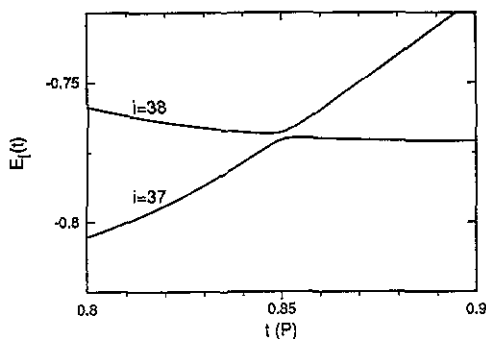


Figure 5. Upper pseudo-crossing of figure 4 in higher resolution.

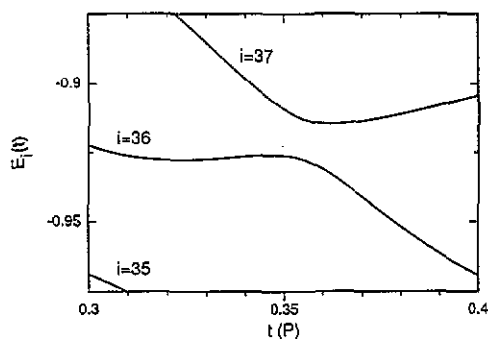


Figure 6. Lower pseudo-crossing of figure 4 in higher resolution.

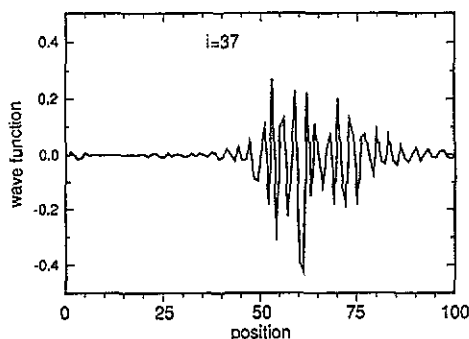


Figure 7. Quasi-stationary eigenfunction of state $i = 37$ before crossing ($t = 0.8P$).

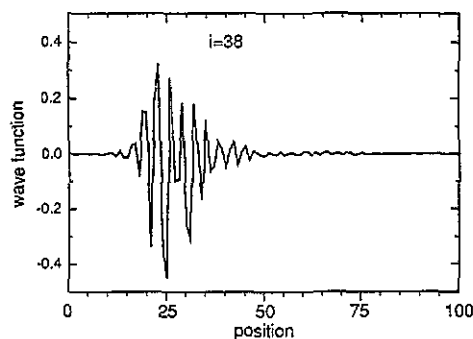


Figure 8. Quasi-stationary eigenfunction of state $i = 38$ before crossing ($t = 0.8P$).

general behaviour of the quasi-stationary eigenstates is found for different realizations ε_i^0 , δ_i of the disorder. In the following we analyse the specific sample corresponding to figure 3. Our results are, however, representative for the whole ensemble of different realizations. This holds equally well for the later discussion of the dynamic evolution of the electron states in section 3.2.

As representative examples of the behaviour of the quasi-stationary states as well as of the dynamic behaviour, we will examine the situation near the indicated pseudo-crossings in figure 4 in detail. These pseudo-crossings are shown with higher resolution in figures 5 and 6. The labels give the ordering of the N states with increasing energy. The behaviour of the two quasi-stationary eigenfunctions near the pseudo-crossing of figure 5 is analysed in figures 7 to 10. Figures 7 and 8 show the quasi-stationary eigenfunctions of the Hamiltonian (1) before the crossing, where the interaction can still be neglected. The situation at the pseudo-crossing, i.e. at the moment where the gap between both states has its minimum, is given in figures 9 and 10. Comparison between both situations shows that at the pseudo-crossing the two states that are formed in the basis of the two uncoupled functions of figures 7 and 8 have bonding and antibonding character. This is confirmed in figure 11, where we present the locally evaluated ratio between the functions of figures 9 and 10. We emphasize that the spatial separation of

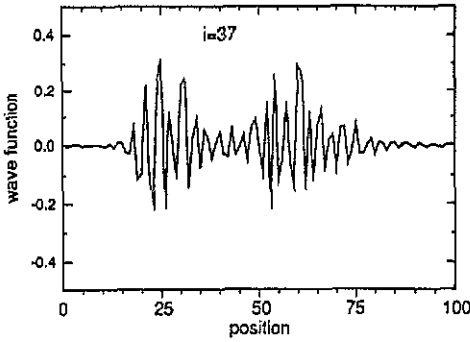


Figure 9. Quasi-stationary eigenfunction of state $i = 37$ at crossing ($t = 0.85P$).

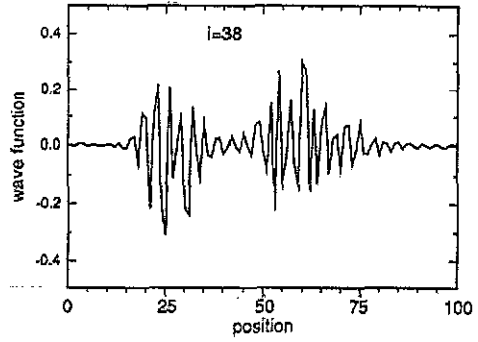


Figure 10. Quasi-stationary eigenfunction of state $i = 38$ at crossing ($t = 0.85P$).

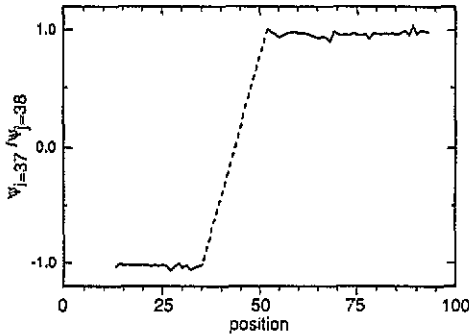


Figure 11. Ratio between the quasi-stationary eigenfunctions of figures 9 and 10.

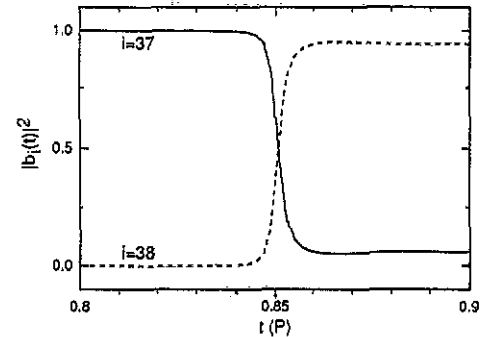


Figure 12. Dynamic behaviour of the functions $i = 37$ and $i = 38$ for $\omega = 0.001$ at the crossing of figure 5. The coupling is completely anti-adiabatic.

the uncoupled crossing states before the crossing—as found in figures 7 and 8—is not fortuitous. It can be seen from first-order perturbation theory that pseudo-crossings will predominantly involve states that are localized at distant centres, since they are exposed to different temporal potential fluctuations. After the crossing the eigenfunctions again become essentially the same as before the crossing, and we regain the situation shown in figures 7 and 8. If we order the eigenstates according to their energies, the corresponding eigenfunctions are simply interchanged after the crossing. This behaviour is due to the fact that the time interval during which the crossing states interact is very small with respect to the period P . This means that the changes in the Hamiltonian (1) are sufficiently small to be described within first-order perturbation theory.

3.2. Dynamic case

The dynamic behaviour of the solutions of the time-dependent Schrödinger equation (9) near the level crossings of figures 5 and 6 was calculated for different frequencies ω . For the following discussion we express the resulting wavefunctions in terms of the initial

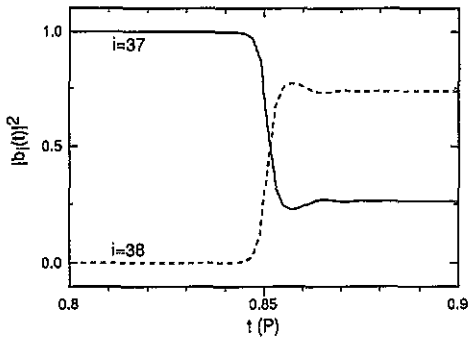


Figure 13. Same as figure 12, but for $\omega = 0.0002$. The coupling is predominantly adiabatic.

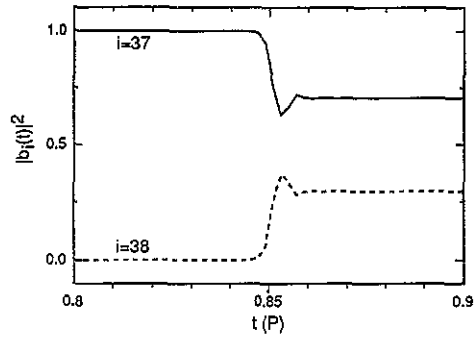


Figure 14. Same as figures 12 and 13, but for $\omega = 0.00005$. The coupling is predominantly anti-adiabatic.

quasi-stationary functions at time $t = t_0$ before the crossing, where the levels do not yet interact, i.e.

$$|\varphi(t)\rangle = \sum_i b_i(t) |\psi_i(t_0)\rangle. \tag{11}$$

The results for the pseudo-crossing of figure 5 are shown in figures 12 to 14, where we present the evolution of the expansion coefficients $a_i(t)$ in equation (11) with time. The initial conditions are

$$b_{i=37}(t = 0.8P) = 1 \quad b_{i=38}(t = 0.8P) = 0$$

i.e. the considered electron is supposed to be initially in the quasi-stationary state with label 37. We see that near the pseudo-crossing and for sufficiently large ω ($\omega \geq 0.001$, figure 12) the behaviour is fully anti-adiabatic, i.e. the electron transits from one quasi-stationary state to the other. The adiabatic contributions increase with decreasing ω , as can be seen from figures 13 and 14. Complete adiabatic behaviour will be approached in the limit $\omega \rightarrow 0$. The dynamic behaviour for ω values smaller than $\omega = 0.00005$ was not calculated, since the numerical calculations become rather time-consuming.

The dynamical behaviour near the pseudo-crossing in figure 6 is shown in figures 15 and 16, where it is assumed that the electron is initially in state 36. In this case the gap is much larger (see figure 6) than in the previous case and we find already a large adiabatic contribution at $\omega = 0.001$. Complete adiabatic behaviour is obtained at $\omega = 0.00005$. It is seen that in the limit of large ω -values the dynamic evolution will become completely anti-adiabatic.

Our results suggest that the electron dynamics depends strongly on the gap at the pseudo-crossing: for a given ω the electron dynamics is anti-adiabatic for sufficiently small gaps and adiabatic for sufficiently large gaps. The independence of the above results with respect to the chain length N is tested in figures 17 and 18, where the calculations corresponding to figures 5 and 15 are repeated for the doubled chain length $N = 200$. The dynamic coupling with the new states, which are represented by the broken curves in figure 17, is completely anti-adiabatic. Thus the dynamics of figure 15 is not affected by the presence of the additional states. This is in agreement with our above findings: the gaps at the pseudo-crossings between the old and the new states are

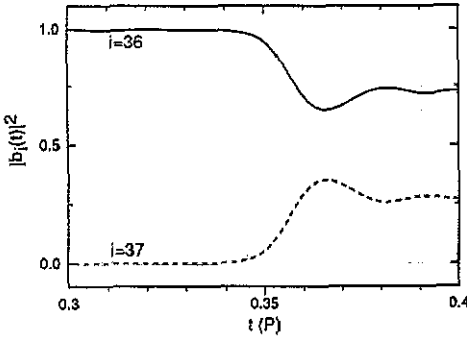


Figure 15. Dynamic behaviour of the functions $i = 36$ and $i = 37$ for $\omega = 0.001$ at the crossing of figure 6. The coupling is partly anti-adiabatic.

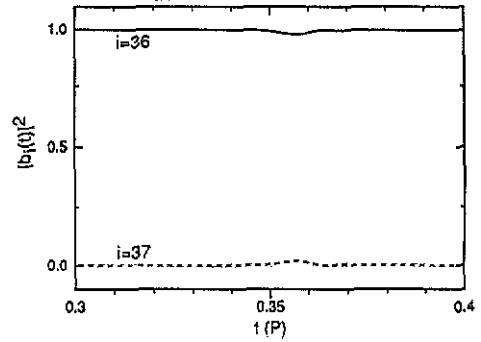


Figure 16. Same as figure 15, but for $\omega = 0.00005$. The coupling is completely adiabatic.

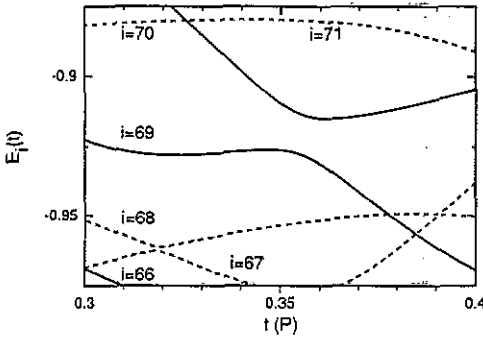


Figure 17. Evolution of the quasi-stationary eigenvalues near the pseudo-crossing of figure 6 for an increased chain length $N = 200$. The broken curves correspond to the additional states with respect to figure 6.

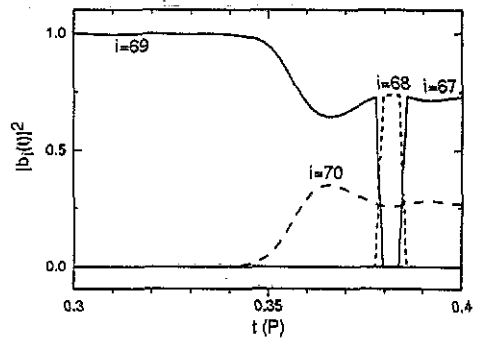


Figure 18. Dynamic coupling of the states of figure 17 for $\omega = 0.001$. The effective diffusion is the same as in figure 15. The broken curves represent the additional states.

negligibly small, which is a consequence of their large spatial separation and the corresponding small spatial overlap of the corresponding quasi-stationary eigenfunctions, and thus the dynamic behaviour at $\omega = 0.001$ is already fully anti-adiabatic. The reasons for this behaviour will be analysed in more detail in the following.

4. Theoretical description

4.1. Quasi-stationary case

Near a pseudo-crossing the quasi-stationary problem is essentially determined by the interaction between the two crossing levels i and k . In the following we will therefore neglect any interaction with other states. We define the crossing time t_1 by the condition that the gap $|E_k(t) - E_i(t)|$ assumes its minimum at $t = t_1$. Because of their time-dependent separation in energy the levels interact only during a finite time interval (t_0, t_2) ,

where $t_0 < t_1$ is the time closest to t_1 where the interaction can still be neglected, and $t_2 > t_1$ is the time where the interaction has again become negligibly small. The times t_0 , t_1 and t_2 may be chosen in a symmetric way, such that

$$t_1 - t_0 = t_2 - t_1 = \frac{1}{2}\delta t \quad \delta t = t_2 - t_0. \tag{12}$$

Starting from the solutions at $t = t_1$ we obtain for the corresponding quasi-stationary solutions in the time interval (t_0, t_2)

$$\begin{pmatrix} E_i(t_1) + S_i(t, t_1) - E & \Delta(t, t_1) \\ \Delta^*(t, t_1) & E_k(t_1) + S_k(t, t_1) - E \end{pmatrix} \begin{pmatrix} c_i(t) \\ c_k(t) \end{pmatrix} = 0 \tag{13}$$

with the matrix elements

$$\begin{aligned} \Delta(t, t_1) &= \langle \psi_i(t_1) | H(t) - H(t_1) | \psi_k(t_1) \rangle \\ S_i(t, t_1) &= \langle \psi_i(t_1) | H(t) - H(t_1) | \psi_i(t_1) \rangle \\ S_k(t, t_1) &= \langle \psi_k(t_1) | H(t) - H(t_1) | \psi_k(t_1) \rangle. \end{aligned} \tag{14}$$

We further assume that

$$\frac{\Delta(t_0, t_1)}{|E_k(t_1) - E_i(t_1)|} \gg 1 \quad \frac{\Delta(t_2, t_1)}{|E_k(t_1) - E_i(t_1)|} \ll -1. \tag{15}$$

An eventual simultaneous change of the signs in the above two expressions does not influence the results of the following discussion.

The labels i, k are defined such that $E_i(t) < E_k(t)$ for all times, i.e. $k = i + 1$ in our case. With this convention we obtain for the solutions of equation (13) at the end points of the interaction interval (t_0, t_2)

$$\begin{aligned} E_i(t_0) &= \frac{1}{2}[E_i(t_1) + E_k(t_1) + S_i(t_0, t_1) + S_k(t_0, t_1)] - |\Delta(t_0 - t_1)| \\ E_k(t_0) &= \frac{1}{2}[E_i(t_1) + E_k(t_1) + S_i(t_0, t_1) + S_k(t_0, t_1)] + |\Delta(t_0 - t_1)| \\ E_i(t_2) &= E_i(t_0) + \frac{1}{2}[S_i(t_2, t_1) + S_k(t_2, t_1) - S_i(t_0, t_1) - S_k(t_0, t_1)] \\ E_k(t_2) &= E_k(t_0) + \frac{1}{2}[S_i(t_2, t_1) + S_k(t_2, t_1) - S_i(t_0, t_1) - S_k(t_0, t_1)]. \end{aligned} \tag{16}$$

The respective eigenfunctions are

$$\begin{aligned} |\psi_i(t_0)\rangle &= (1/\sqrt{2})[|\psi_i(t_1)\rangle - |\psi_k(t_1)\rangle] & |\psi_i(t_2)\rangle &= |\psi_k(t_0)\rangle \\ |\psi_k(t_0)\rangle &= (1/\sqrt{2})[|\psi_i(t_1)\rangle + |\psi_k(t_1)\rangle] & |\psi_k(t_2)\rangle &= |\psi_i(t_0)\rangle. \end{aligned} \tag{17}$$

As was already mentioned in section 2.1, the interacting quasi-stationary functions will in general be localized at different centres. It follows from equation (17) that the centre of localization of a quasi-stationary wavefunction with a given label changes during the crossing. This property will be responsible for the diffusion in the adiabatic regime.

If we express the solutions at $t = t_1$ in the basis of the functions $\psi_i(t_0)$ and $\psi_k(t_0)$, we get from equation (17)

$$\begin{aligned} |\psi_i(t_1)\rangle &= (1/\sqrt{2})[|\psi_i(t_0)\rangle + |\psi_k(t_0)\rangle] \\ |\psi_k(t_1)\rangle &= (1/\sqrt{2})[|\psi_i(t_0)\rangle - |\psi_k(t_0)\rangle]. \end{aligned} \quad (18)$$

This confirms our numerical result, that the solutions at $t = t_1$ are the bonding or antibonding combinations of the interaction-free functions at $t = t_0$.

4.2. Adiabatic case

For the discussion of the adiabatic case we start from the quasi-stationary solutions, which were discussed in the previous section. The solutions of the time-dependent Schrödinger equation (9) can then be written (Schiff 1955)

$$|\varphi(t)\rangle = \sum_i a_i(t) |\psi_i(t)\rangle \exp\left(-i \int_0^t E_i(t') dt'\right). \quad (19)$$

Insertion of the above expression in equation (9) yields

$$\frac{\partial a_k(t)}{\partial t} = \sum_{i \neq k} G_{ki}(t) a_i(t). \quad (20)$$

The term $G_{kk}(t)$ vanishes because of the particular choice of the phase factors in equation (19) (Schiff 1955). The coupling coefficients $G_{ki}(t)$ are given by

$$G_{ki}(t) = \frac{1}{E_k(t) - E_i(t)} \left(\frac{\partial H(t)}{\partial t} \right)_{ki} \exp\left(i \int_0^t [E_k(t') - E_i(t')] dt'\right) \quad (21)$$

with

$$\left(\frac{\partial H(t)}{\partial t} \right)_{ki} = \langle \psi_k(t) | \frac{\partial H(t)}{\partial t} | \psi_i(t) \rangle. \quad (22)$$

According to equation (20) the coupling coefficients $G_{ki}(t)$ determine the non-adiabaticity of the evolution of state k with time. In the following we estimate their orders of magnitude. With equations (2) and (4) we obtain

$$\left(\frac{\partial H(t)}{\partial t} \right)_{ki} = A\omega \sum_n c_{kn}^*(t) c_{in}(t) \cos(\omega t + \delta_n) \quad (23)$$

and therefore

$$\left| \left(\frac{\partial H(t)}{\partial t} \right)_{ki} \right| \leq A\omega \sum_n |c_{kn}^*(t)| |c_{in}(t)| = A\omega O_{ki}(t) \quad (24)$$

where we have used the expression (5) for the overlap between the quasi-stationary states. The upper limit for the strengths of the coupling coefficients (equation (21)) becomes

$$|G_{ki}(t)| \leq A\omega O_{ki}(t) / |E_k(t) - E_i(t)|. \quad (25)$$

It follows that the dynamic coupling between the quasi-stationary states decreases with their distance in energy. In the case of large dynamic disorder, where the variations of $E_i(t)$ over a period are important, non-adiabatic behaviour will therefore only occur

near a pseudo-crossing. The coupling parameter G_{ki} reaches its maximum at $t = t_1$, where $O_{ki}(t_1) = 1$. We have

$$|G_{ki}(t_1)| \leq A\omega/|E_k(t_1) - E_i(t_1)|. \tag{26}$$

In agreement with our numerical results we find that the adiabatic behaviour is approached in the limit of small 'adiabatic parameters' $A\omega$ and/or large gaps.

We will now discuss the behaviour of the coupling coefficients in somewhat more detail. Defining the times t_0 , t_1 and t_2 as before and using equation (18), we obtain for the gap at $t = t_1$

$$\begin{aligned} E_i(t_1) - E_k(t_1) &= \langle \psi_i(t_1) | H(t_1) | \psi_i(t_1) \rangle - \langle \psi_k(t_1) | H(t_1) | \psi_k(t_1) \rangle \\ &= \langle \psi_i(t_0) | H(t_1) | \psi_k(t_0) \rangle + \text{cc}. \end{aligned} \tag{27}$$

With equations (1) and (2) we can write

$$H(t_1) = H(t_0) + A \sum_n [\sin(\omega t_1 + \delta_n) - \sin(\omega t_0 + \delta_n)] |n\rangle \langle n| \tag{28}$$

and with equations (5) and (27)

$$\begin{aligned} |E_i(t_1) - E_k(t_1)| &\leq 2A \sum_n |c_{in}^*(t_0)| |c_{kn}(t_0)| |\sin(\omega t_1 + \delta_n) - \sin(\omega t_0 + \delta_n)| \\ &\leq 4A O_{ki}(t_0). \end{aligned} \tag{29}$$

This relates the minimum value of the gap to the overlap between the unperturbed quasi-stationary functions before the pseudo-crossing. The overlap between distant localized states decreases exponentially with their relative distance. Therefore we can conclude from equations (26) and (29) that for given $A\omega$ quasi-stationary states beyond a critical distance may be coupled dynamically, i.e. the time evolution will possibly be non-adiabatic. This behaviour will be confirmed in the following chapter. In order to avoid any confusion, we emphasize that the dynamic coupling is described with respect to the quasi-stationary states. It follows from equation (17) and the discussion in section 4.1 that electron diffusion is correlated with adiabatic behaviour. We will see in the next section that strong dynamic coupling leaves the initial electron state unchanged over the level pseudo-crossing, and thus does not contribute to the diffusion.

4.3. Anti-adiabatic case

As in the previous chapter, we consider again a pair of quasi-stationary eigenstates near a pseudo-crossing. The times t_0 , t_1 and t_2 are defined as before. For the following analysis it is convenient to express the solution of the time-dependent Schrödinger equation in the time interval (t_0, t_2) in terms of the quasi-stationary functions at $t = t_0$

$$\varphi(t) = \sum_{i=i,k} b_i(t) \psi_i(t_0) \tag{30}$$

which has already been used for the discussion of the numerical results. We assume the same initial conditions as before, i.e. $\varphi(t_0) = \psi_k(t_0)$, or

$$b_k(t_0) = 1 \quad b_i(t_0) = 0. \tag{31}$$

For short interaction times $\delta t = t_2 - t_0$ it is convenient to start from the 'sudden approximation' (Messiah 1964), which gives $\varphi(t_2) = \psi_k(t_0)$, or

$$b_k(t_2) = 1 \quad b_i(t_2) = 0 \tag{32}$$

i.e. the initial state remains unchanged and we have no contribution to electron diffusion.

The diffusion is related to the term $b_i(t_2)$, which determines the transition rate between the initial quasi-stationary state $\psi_k(t_0)$ and the crossing state $\psi_i(t_0)$. The first-order correction for $b_i(t_2)$ is

$$b_i(t_2) = -i \int_{t_0}^{t_2} \exp[i\{E_i(t') - E_k(t')\}t'] W_{ik}(t') dt' \quad (33)$$

with

$$\begin{aligned} W_{ik}(t) &= \langle \psi_i(t_0) | H(t) - H(t_0) | \psi_k(t_0) \rangle \\ &= A \sum_n c_{in}^*(t_0) c_{kn}(t_0) [\sin(\omega t + \delta_n) - \sin(\omega t_0 + \delta_n)]. \end{aligned} \quad (34)$$

For the last expression we have made use of equations (4) and (28). Assuming that the interaction interval $\delta t = t_2 - t_0$ is small compared with the period P of the time-dependent perturbation, we obtain after development of $\sin(\omega t + \delta_n)$ at $t = t_0$

$$W_{ik}(t) \approx A\omega(t - t_0) \sum_n c_{in}^*(t_0) c_{kn}(t_0) \cos(\omega t_0 + \delta_n) \quad (35)$$

and with equation (5)

$$|W_{ik}(t)| \leq A\omega(t - t_0) O_{ik}(t_0). \quad (36)$$

Insertion in equation (33) yields

$$|b_i(t_2)| \leq A\omega O_{ik}(t_0) \int_{t_0}^{t_2} (t' - t_0) dt' = \frac{1}{2} A\omega O_{ik}(t_0) \delta t^2. \quad (37)$$

The interaction time δt can be estimated from the quasi-stationary Schrödinger equation (13), which describes the interaction between the levels i and k . Starting from equation (14) we obtain in the same way as for equations (34) to (36)

$$\Delta(t, t_1) = A\omega(t - t_1) \sum_n c_{in}^*(t_1) c_{kn}(t_1) \cos(\omega t_1 + \delta_n). \quad (38)$$

Remembering that $O_{ik}(t_1) = 1$ we get for the upper bound at $t = t_2$

$$|\Delta(t_2, t_1)| \leq \frac{1}{2} A\omega \delta t. \quad (39)$$

It follows from equation (13) that the interaction increases with the ratio between $\Delta(t_2, t_1)$ and the minimum gap at $t = t_1$. We may therefore characterize the interaction strength by

$$K = \Delta(t_2, t_1) / |E_k(t_1) - E_i(t_1)|. \quad (40)$$

From equations (39) and (40) we obtain for the interaction time

$$\delta t = 2K |E_k(t_1) - E_i(t_1)| / A\omega. \quad (41)$$

It is evident that the minimum gap at $t = t_1$ is related to the overlap between the states i and k . According to equation (29) it disappears for vanishing overlap $O_{ik}(t_0)$. It is

therefore reasonable to assume that both are proportional, with a constant of proportionality depending on the disorder. This leads to

$$\delta t = CO_{ik}(t_0)/A\omega. \tag{42}$$

Together with equation (37) we obtain for the first-order correction $b_i(t_2)$

$$|b_i(t_2)| \leq D |O_{ik}(t_0)|^3/A\omega \tag{43}$$

where D is a constant that depends on the strength of the static as well as the dynamic disorder. Equation (43) shows that the adiabatic corrections become rapidly less important for increasing spatial distance between the crossing states—in agreement with the results of the previous section. Thus, for a given adiabatic parameter $A\omega$, states that are separated by more than a critical distance will merely contribute to the diffusion. This point will be discussed in more detail in the following section.

For the above discussion we have assumed that the interaction time δt is small with respect to the time period P , i.e. we have excluded the case of quasi-stationary states with a flat crossing behaviour. This assumption will be valid for most crossings, in particular if the considered states are far apart such that their overlap is negligible (see equation (42)). However, the case of flat crossing can also be treated in a quite similar manner. In this case we start again from equation (34), which leads to

$$W_{ik}(t) \leq 2AO_{ik}(t_0). \tag{44}$$

The interaction takes place throughout the full period P . We obtain with equation (33)

$$b_i(P) \leq 2APO_{ik}(t_0) = (4\pi A/\omega)O_{ik}(t_0). \tag{45}$$

Comparison with equation (43) shows that as before the adiabatic correction increases with $1/\omega$ and is limited by the spatial overlap $O_{ik}(t_0)$. The dependence on the overlap is, however, weaker than in equation (43). The inverse dependence on the amplitude in equations (43) and (45) is due to the fact that in the limit of short interaction times δt is proportional to $1/A$ (equation (41)), whereas it becomes independent of A in the case of flat crossings.

The behaviour of the dynamic coupling for $A\omega \rightarrow 0$ cannot be predicted in an unambiguous manner. From the above estimate, equation (43), it cannot be excluded that the coupling remains anti-adiabatic at a given pseudo-crossing, and thus does not contribute to the diffusion. Such a situation is, however, not found in our numerical calculations.

4.4. *Size dependence of the diffusion*

In the preceding section we have found that, for a given adiabatic parameter $A\omega$, spatially distant states will not contribute to the electron diffusion. The argumentation is, however, not completely satisfactory, because up to now we have neglected the fact that the number of pseudo-crossings increases with the sample size. Therefore, we have still to control whether the above estimate remains true in the limit of infinite chains. To this end we consider a chain of length N_0 and an initial state k , which is localized near the centre of the chain. N_0 is supposed to be large compared with the localization lengths of the electron states. We now ask for the change of the dynamic behaviour of the initial quasi-stationary state k , if we add a site at each side of the considered chain. For the following estimation we will assume that the original N_0 states of the unperturbed chain remain practically unchanged. The new chain then contains just two additional states i ,

with $i = N_0 + 1, N_0 + 2$. Their distance with respect to the centre will increase as $N_0/2 + 1$. Under these assumptions we can calculate an upper bound for the first-order correction χ to the anti-adiabatic dynamics ('adiabatic correction'), which results from the presence of the two additional states. Since the overlap between the initial state k and the states i is negligible, it is adequate to start from equation (43), which is valid for steep crossings. We obtain

$$\chi(N_0 + 2) = 2|b_i(t_2)|^2 \leq 2D^2|O_{ik}(t_0)|^6/A^2\omega^2 \quad (46)$$

where the overlap term can be approximated by

$$O_{ik}(t_0)^6 \leq \exp[-\lambda(\frac{1}{2}N_0 + 1)]. \quad (47)$$

Here λ is proportional to the minimum of the reciprocal localization lengths, which describe the exponential decrease of the wavefunctions at large distances. Here we have supposed that the considered quasi-stationary states k and i are sufficiently close in energy to cross under the influence of the time-dependent perturbation, as was required for the derivation of equation (43). However, equation (46) still holds if the energy difference between states i and k remains large for all times. In this case the states remain uncoupled, and $\chi(N_0 + 2) = 0$.

If we add in the same manner more and more sites on both sides of the chain we get finally for an infinite chain

$$\chi_{\text{tot}} = \sum_{n=1}^{\infty} \chi(N_0 + 2n) \leq \frac{2D^2}{A^2\omega^2} \sum_{n=1}^{\infty} \exp[-\lambda(\frac{1}{2}N_0 + n)] = \frac{2D^2}{A^2\omega^2} \exp[-\lambda(\frac{1}{2}N_0)] \frac{e^{-\lambda}}{1 - e^{-\lambda}}. \quad (48)$$

The above expression shows that even in the limit $N \rightarrow \infty$ the contributions of the additional states remain negligible, provided that N_0 is already sufficiently large. Even if flat crossing behaviour is not very likely for far distant states, we note that also in this case a similar result is found starting from equation (45) instead of equation (43).

5. Conclusions

We have investigated the microscopic mechanism of electron diffusion in a 1D chain with static and dynamic disorder. The dynamic behaviour of the electron states has been described in the basis of the quasi-stationary eigenfunctions of the time-dependent model Hamiltonian. We have shown that the elementary electronic diffusion processes correspond to adiabatic coupling of crossing quasi-stationary states. For a given adiabatic parameter $A\omega$, the diffusion processes are limited to a finite range in real space. This range increases with decreasing $A\omega$.

As was mentioned in the introduction, our present study can be understood as a first step of an extension of the hopping theory to high temperatures. In order to obtain the temperature dependence of the high-temperature hopping rates, our transition rates (which correspond to a given amplitude of the potential fluctuations) must still be weighted by a Boltzmann factor, which accounts for the statistical distribution of the amplitudes. We find that, even in our high-temperature model, the electron diffusion is strongly limited by the spatial overlaps between the involved electronic functions—similar to the hopping model for low temperatures. There is, however, an important difference: the hopping theory is expressed in terms of the eigenstates of the stationary

Hamiltonian at $T = 0$; in our high-temperature limit these must be replaced by the quasi-stationary eigenstates of the time-dependent Hamiltonian.

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