Coherent and incoherent motion in a one-dimensional lattice

M. A. Palenberg and R. J. Silbey

*Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

W. Pfluegl

Institut für Theoretische Physik, Johannes-Kepler Universität Linz, A-4040 Linz, Austria
(Received 9 March 2000)

We discuss a generalization of the Haken-Strobl-Reineker model for the diffusion coefficient of a particle (or an excitation) in a one-dimensional lattice. In the original treatment, the characteristic correlation time of the lattice vibrations is assumed to be the smallest time scale in the physical problem. We weaken this requirement and allow for longer correlation times. We discuss previous results in the context of our theory and present numerical examples.

I. INTRODUCTION

The charge transport and energy transfer in organic crystals can be described either as a coherent or an incoherent process, depending on the strength of the interaction of the migrating particle (or excitation) with lattice vibrations. If the interaction is weak, the phases of the wave function of the particle are conserved and the motion is coherent for some time, eventually damping due to interaction with lattice vibrations, finally leading to bandlike motion. In the case of strong interaction, the wave function dephases quickly, leading to an incoherent, hoppinglike motion.

Starting in 1967, Haken and Strobl and later Reineker suggested and worked out a unified theory[1–3] that contains both the coherent and the incoherent limits. In the last 30 years, this concept has been successfully applied to the description of experimentally observed electronic and excitonic properties.[4–12]

A key assumption in the treatment by Haken, Strobl, and Reineker is the fast decay of the correlation of the lattice vibrations. In this paper, we treat and discuss the weakening of this assumption by omitting one of the two constraints on the time scales of the problem.

The paper is organized as follows. In Sec. II we discuss our assumptions, derive the equation of motion for the density matrix of the particle (or the excitation), and discuss its range of validity. In the next section, an expression for the diffusion coefficient is derived. In Sec. IV we compare our result to the result of Haken, Strobl, and Reineker[1–3,12] and to the correlation time expansion of Kitahara and Haus.[13] The next section is devoted to explicit numerical results and we conclude the paper with a summary.

II. EQUATION OF MOTION

We consider a particle moving along a chain of identical molecules with equal equilibrium distances. The thermal motion of the molecules in the chain is taken into account by allowing the site energies $\varepsilon_n(t)$ and and the hopping matrix elements $J_n(t)$ to fluctuate in time. Assuming next neighbor interaction, this leads to the Hamiltonian

$$H(t) = \sum_n \varepsilon_n(t) c_n^\dagger c_n + \sum_n J_n(t)(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n). \quad (1)$$

We decompose the site energy and the hopping matrix element into a constant part that describes the coherent particle motion in a completely rigid chain and into a fluctuating part with zero mean:

$$\varepsilon_n(t) = \varepsilon + \delta\varepsilon_n(t), \quad (2)$$

$$J_n(t) = J + \delta J_n(t) \quad (3)$$

with $\varepsilon = \langle \varepsilon_n(t) \rangle$ and $J = \langle J_n(t) \rangle$. The brackets $\langle \rangle$ represent the thermal average over all molecular vibrations.

Following the approach by Haken, Strobl, and Reineker,[1–3,12] we describe the diagonal fluctuations $[\delta\varepsilon_n(t)]$ and the nondiagonal fluctuations $[\delta J_n(t)]$ as stochastic processes. For the second moments we assume the form suggested by Kitahara and Haus:[13]

$$\langle \delta\varepsilon_n(t) \delta\varepsilon_{n'}(t+\tau) \rangle = \gamma_0 \frac{1}{\tau_c} e^{-|\tau|/\tau_c} \delta_{n,n'}, \quad (4)$$

$$\langle \delta J_n(t) \delta J_{n'}(t+\tau) \rangle = \gamma_1 \frac{1}{\tau_c} e^{-|\tau|/\tau_c} \delta_{n,n'}. \quad (5)$$

This means that energy fluctuations on different sites and fluctuations of the hopping matrix element between different pairs of molecules are not correlated. We have made the additional assumption that $J_n(t)$ is real.

The Hamiltonian (1) leads to a stochastic density-matrix equation. Using the statistical properties of $\delta\varepsilon_n(t)$ and $\delta J_n(t)$, a statistically reduced equation for the migrating particle can be obtained either by a projection operator formalism[14] or by generalized cumulant methods.[14,15] Going to second order in the totally time ordered generalized cumulant expansion,[14] the resulting equation of motion in the interaction picture reads

$$\check{\rho}(t) = -\int_0^t d\tau \langle \delta\tilde{L}(t) \delta\tilde{L}(t-\tau) \rangle \tilde{\rho}(t-\tau), \quad (6)$$

where $\tilde{\rho}(t)$ is the density matrix of the migrating particle in the interaction picture. The Liouville operator $\delta L(t)$ is defined in Appendix A. If we assume that the Liouville operator $\delta L(t)$ is proportional to some quantity α, then Eq. (6) is a second-order equation in the sense that it has the structure

$$\dot{\tilde{\rho}} = \mathcal{A}\tilde{\rho}, \tag{7}$$

where $\mathcal{A}$ is an operator that is known up to order α^2. Some contributions to $\mathcal{A}$ of higher order in α have been neglected.

Equation (6) can be written more explicitly as

$$\dot{\tilde{\rho}}(t) = -\frac{1}{\tau_c} \sum_{k_1,k_2,k_3,k_4} \Delta_{k_1,k_2,k_3,k_4} \tilde{d}_{k_1,k_2}(t) \tilde{d}_{k_3,k_4}(t)$$
$$\times \int_0^\infty d\tau\, e^{-\tau/\tau_c} e^{-i(H_{k_3}-H_{k_4})\tau} \tilde{\rho}(t-\tau). \tag{8}$$

The detailed derivation of this equation and the definition of the quantities therein is made in Appendix A. For the present discussion it is sufficient to mention that Δ_{k_1,k_2,k_3,k_4} is proportional to γ_0 and/or γ_1 or is zero.

Equation (8) is the starting point for our further considerations. Since Eq. (8) is a convolution-type equation, a general solution is difficult. Kitahara and Haus[13] have calculated the first orders in τ_c of the diffusion coefficient that results from Eq. (8) by means of a Laplace transform. We will compare their results to the findings of this paper at the end of the next section.

Other approximative solutions depend on the relative magnitude of three different time scales. The kernel of Eq. (8) decays as a function of τ during the time τ_c while oscillating as a function of τ on a time scale $\tau_{coh}=1/J$. The latter time scale is due to the oscillatory exponential in Eq. (8) and can be understood using Eq. (A4) in Appendix A. The third time scale, τ_ρ, defines the time on which the value of the density matrix changes appreciably and will be derived later.

Haken, Strobl, and Reineker[1–3,12] have considered the case that τ_c is the smallest of the three time scales, i.e., $\tau_c \ll \tau_{coh}$ and $\tau_c \ll \tau_\rho$. In this case, the exponential $\exp[-i(H_{k_3}-H_{k_4})\tau]$ as well as the density matrix $\tilde{\rho}(t-\tau)$ in the integral in Eq. (8) can be replaced by their value at $\tau=0$, since they do not change appreciably during the integration over the time interval $t=0\cdots\tau_c$. Later times do not contribute to the integral, since by then the kernel has decayed. The same result is obtained by the original approach by Haken, Strobl, and Reineker that consists in replacing the exponential decay in Eqs. (4) and (5) by a δ function.

In this paper, we will generalize this approach. We will allow the correlation time τ_c to have any value relative to τ_{coh} as long as the change of the density matrix is slow with respect to the correlation time, i.e., $\tau_c \ll \tau_\rho$. To clarify this further, we perform a Taylor expansion of $\tilde{\rho}(t-\tau)$ in Eq. (8) about $\tau=0$ and keep only the first term. This leads to the considerably simplified equation of motion:

$$\dot{\tilde{\rho}}(t) = -\sum_{k_1,k_2,k_3,k_4} \frac{\Delta_{k_1,k_2,k_3,k_4}}{1+i(H_{k_3}-H_{k_4})\tau_c}$$
$$\times \tilde{d}_{k_1,k_2}(t) \tilde{d}_{k_3,k_4}(t)\tilde{\rho}(t). \tag{9}$$

This approximation is good if the first term in the Taylor expansion of $\tilde{\rho}(t-\tau)$ is dominant. This condition can be expressed as $\tau_c \ll \tau_\rho$, with the definition

$$\tau_\rho = \frac{1+\left(\dfrac{2\tau_c}{\tau_{coh}}\right)^2}{\max(\gamma_0,\gamma_1)}. \tag{10}$$

We refer to Appendix B for the derivation.

The time-local equation of motion [Eq. (9)] can also be derived by directly starting from the time-local second-order equation of motion that results from a truncated generalized cumulant expansion with a partial chronological time ordering.[15] However, using this approach the range of applicability explained above is inherent in the construction of the equation and has to be considered carefully.[16,17]

Equation (9) contains, in fact, all the relevant information of a second-order equation because of the following reason. All contributions that have been neglected in the derivation of Eq. (9) represent fourth and higher-order terms in α, using the terminology introduced after Eq. (7). It is not clear whether the partial inclusion of higher-order terms as in Eq. (8) is better or worse than their rigorous omission as in Eq. (9). We will return to this point in Sec. IV B of this paper.

III. DIFFUSION COEFFICIENT

In this section we calculate the diffusion coefficient from the equation of motion derived previously. Transforming Eq. (9) to the Schrödinger picture we obtain for the density matrix in the wave-vector basis

$$\dot{\rho}_{k+q,k} = -i(H_{k+q}-H_k)\rho_{k+q,k} - \sum_K W^o_{k+q,k\to K+q,K}\rho_{k+q,k}$$
$$+ \sum_K W^i_{K+q,K\to k+q,k}\rho_{K+q,K} \tag{11}$$

with the generalized rates

$$W^i_{k+q,k\to K+q,K} = \frac{\gamma_{k=0}+\gamma_{k+K+q}-\dfrac{\gamma_0}{N}}{1+i\tau_c(H_K-H_{k+q})} + \frac{\gamma_{k=0}+\gamma_{k+K}-\dfrac{\gamma_0}{N}}{1+i\tau_c(H_k-H_K)},$$

$$W^o_{K+q,K\to k+q,k} = \frac{\gamma_q+\gamma_{k+K+q}-\dfrac{\gamma_0}{N}}{1+i\tau_c(H_K-H_k)}$$
$$+ \frac{\gamma_q+\gamma_{k+K+q}-\dfrac{\gamma_0}{N}}{1+i\tau_c(H_{k+q}-H_{K+q})}. \tag{12}$$

The diffusion coefficient is given by

$$D = -\frac{1}{2}\lim_{t\to\infty}\lim_{q\to 0}\partial_q^2 \sum_k \dot{\rho}_{k+q,k}, \tag{13}$$

which follows directly from the definition of the diffusion coefficient in the site representation $2D = \lim_{t\to\infty}(1/t)\sum_n n^2\rho_{n,n}$. Inserting Eq. (11) into definition (13), we obtain

$$D = 2\gamma_1 F + \frac{4J^2}{\gamma_1} \frac{1}{N} \sum_k \sin^2 k (1 - G_1) u_k. \quad (14)$$

The function u_k is determined by the equation

$$u_k \Gamma_{kk} = 1 + G_2 - \frac{4}{N} \sum_K \frac{\sin^2 K}{1 + \epsilon^2 (\cos K - \cos k)^2} u_K, \quad (15)$$

with $\epsilon = 2J\tau_c$. The quantities F, G_1, and G_2 are functions of $J\tau_c$, $\gamma_0 \tau_c$, and $\gamma_1 \tau_c$ and are given in Appendix C. Γ_{kk} is given by

$$\Gamma_{kk} = \frac{2}{N} \sum_K \frac{\gamma_0/\gamma_1 + 2 + 2\cos k \cos K}{1 + \epsilon^2 (\cos K - \cos k)^2} \quad (16)$$

$$= \frac{2\,\mathrm{Re}\sqrt{z}}{|z|} \{\gamma_0/\gamma_1 + 2 + 2\cos^2 k\} - \frac{4\,\mathrm{Im}\sqrt{z}}{\epsilon|z|} \cos k \quad (17)$$

with

$$z = \epsilon^2 + (1 + i\epsilon \cos k)^2, \quad \epsilon = 2J\tau_c. \quad (18)$$

Expression (14) for the diffusion coefficient is the central result of this paper. It represents the generalization of the result of Haken, Strobl, and Reineker to larger correlation times τ_c, provided that the density matrix is slowly varying. As in the original Haken-Strobl-Reineker model, the diffusion coefficient (14) is the sum of an incoherent and a coherent part, where the names are chosen according to the fact that the first (incoherent) part does not vanish when the hopping matrix element J goes to zero while the second (coherent) part does. The incoherent part increases with γ_1 and reflects the motion of a particle that is generated by the nondiagonal dynamical fluctuations. The coherent part represents the band motion of a particle that is hindered by diagonal as well as nondiagonal fluctuations. Here the fluctuating site energies and hopping matrix elements act as disorder that tends to stop the free band motion.

In Appendix C we show that in the present approximation of a slowly varying density matrix, the functions G_1 and G_2 are both small compared to unity and can therefore be neglected, simplifying the expression (14) for D further.

In the special case of diagonal fluctuations ($\gamma_1 \to 0$), Eq. (15) is analytically solvable and, neglecting the small contributions of G_1 and G_2, we obtain for the diffusion coefficient of a system with only diagonal fluctuations

$$D_{(\gamma_1 = 0)} = \frac{2J^2}{\gamma_0} \sum_k \frac{\sin^2 k}{\displaystyle\sum_K \frac{1}{1 + \epsilon^2 (\cos K - \cos k)^2}} \quad (19)$$

$$= \frac{2J^2}{\gamma_0} \frac{1}{\pi} \int_0^\pi dk \frac{|z| \sin^2 k}{\mathrm{Re}\sqrt{z}}, \quad (20)$$

with z defined in Eq. (18).

If both γ_0 and γ_1 differ from zero, Eq. (15) can be approximated by iteration as long as the local fluctuations are dominant ($\gamma_1 \ll \gamma_0$). If γ_1 is of the same order of magnitude as γ_0, the iterative method does not converge. Fortunately,

in the general case of diagonal and nondiagonal fluctuations, a Fourier analysis of u_k in Eq. (15) leads to good results. We therefore write

$$u_k = \sum_n C_n \cos(kn) \quad (21)$$

and upon insertion into Eq. (14) for the diffusion coefficient, we remark that only the coefficients C_0 and C_2 contribute to D, since

$$\frac{1}{N} \sum_k \sin^2 k\, u_k = \frac{1}{N} \sum_k \sin^2 k \sum_n C_n \cos(kn) = \frac{C_0}{2} - \frac{C_2}{4}. \quad (22)$$

For the coefficients C_n, we obtain a system of coupled equations

$$C_n = A_n + \sum_m B_{nm} C_m \quad (23)$$

with

$$A_0 = \frac{1}{\pi} \int_0^\pi dk \frac{1}{\Gamma_{kk}}, \quad (24)$$

$$A_{n>0} = \frac{2}{\pi} \int_0^\pi dk \frac{\cos(kn)}{\Gamma_{kk}} \quad (25)$$

and

$$B_{0,m} = -\frac{4}{\pi} \int_0^\pi dk \frac{I_m(k)}{\Gamma_{kk}}, \quad (26)$$

$$B_{n>0,m} = -\frac{8}{\pi} \int_0^\pi dk \frac{I_m(k)\cos(kn)}{\Gamma_{kk}} \quad (27)$$

with Γ_{kk} as given in Eq. (17). The integrals $I_m(k)$ are given by

$$I_m(k) = \frac{1}{\pi} \int_0^\pi dK \frac{\sin^2 K \cos(Km)}{1 + \epsilon^2 (\cos K - \cos k)^2} \quad (28)$$

and can easily be solved to give

$$I_0(k) = \frac{\mathrm{Re}\sqrt{z} - 1}{\epsilon^2}, \quad (29)$$

$$I_1(k) = \frac{\mathrm{Re}\sqrt{z} - 2}{\epsilon^2} \cos k + \frac{\mathrm{Im}\sqrt{z}}{\epsilon^3}, \quad (30)$$

$$I_2(k) = \frac{\mathrm{Re}\sqrt{z}(2\cos^2 k - 1) - 6\cos^2 k + 2}{\epsilon^2} + 4\frac{\mathrm{Im}\sqrt{z}}{\epsilon^3}$$

$$- 2\frac{\mathrm{Re}\sqrt{z} - 1}{\epsilon^4} \quad (31)$$

$$\vdots$$

with z as defined in Eq. (18). The system of Eq. (23) is simplified by the fact that $B_{n,m} = 0$ for all odd sums $n + m$. This leads to decoupling for even and odd indices and since

we are only interested in the coefficients C_0 and C_2 the coefficients with odd indices do not need to be considered further.

In this formalism, the diffusion coefficient can be written as

$$D = 2\gamma_1 F + \frac{J^2}{\gamma_1}(2C_0 - C_2), \tag{32}$$

where the coefficients C_0 and C_2 are determined by the system of equations in Eq. (23). The coefficient C_2 is generally much smaller than C_0 and can sometimes be neglected. For a practical calculation, the system of equations is solved for a finite cutoff $n_{max} \geq n, m$. For a qualitative estimate, it suffices to take into account the trivial solution for $n_{max} = 0$, while the cutoff $n_{max} = 2$ approximates the exact result very well. For example, taking $\epsilon = 1$, the relative error made by the cutoff $n_{max} = 0$ is smaller than 6% for all values of γ_0 and γ_1, while the cutoff $n_{max} = 2$ yields results with relative errors smaller than 0.05%. The relative errors made with either cutoff are roughly linear in ϵ.

IV. COMPARISON TO PREVIOUS RESULTS

A. Haken, Strobl, and Reineker model

In the original treatment of the problem of mixed coherent and incoherent particle motion, Haken, Strobl, and Reineker assumed the correlation time τ_c to be smaller than all other time scales in the problem. We retrieve their result by setting $\tau_c = 0$ in Eqs. (14) and (15). In this limit, the equation for u_k reads

$$u_k 2(\gamma_0/\gamma_1 + 2) = 1 - \frac{4}{N}\sum_K \sin^2 K u_K \tag{33}$$

which can readily be solved for the quantity $1/N\sum_k \sin^2 k u_k$ needed in Eq. (14) for the diffusion coefficient. With $1/N\sum_k \sin^2 k u_k = \gamma_1/(4\gamma_0 + 12\gamma_1)$ we obtain the result of Haken, Strobl, and Reineker,

$$D = 2\gamma_1 + \frac{J^2}{\gamma_0 + 3\gamma_1}. \tag{34}$$

B. Kitahara's and Haus' result

Starting from the second-order Eq. (8), Kitahara and Haus have calculated the first terms in an expansion of the diffusion coefficient in powers of the correlation time τ_c.[13] The zeroth-order term in this expansion is given by the result of Haken, Strobl, and Reineker [Eq. (34)].

We will show how their result for a correction linear in the correlation τ_c can be reproduced within the present formalism and then make some general remarks about the expansion in powers of τ_c.

From Eqs. (14) and (15), the first order of D in a correlation time expansion can easily be calculated and yields

$$D^{[1]} = \epsilon J \frac{\gamma_0 + \gamma_1}{\gamma_0 + 3\gamma_1}. \tag{35}$$

This result differs from Kitahara's and Haus' result, which in our notation is

$$D_{KH}^{[1]} = -\epsilon J \frac{2\gamma_1}{\gamma_0 + 3\gamma_1}. \tag{36}$$

The discrepancy can be explained by the fact that Kitahara and Haus include a fourth-order contribution in the equation of motion that is neglected in our treatment. To understand this better, we explicitly write down the corresponding density-matrix equations. Expanding the density matrix in powers of the correlation time τ_c,

$$\tilde{\rho}(t) = \tilde{\rho}^{[0]}(t) + \tilde{\rho}^{[1]}(t) + \tilde{\rho}^{[2]}(t) + \cdots \tag{37}$$

with $\tilde{\rho}(t)^{[n]} \sim \tau_c^n$, the second-order Eq. (8) for the contribution linear in τ_c reads

$$
\begin{aligned}
\dot{\tilde{\rho}}^{[1]}(t) = &-\sum_{k_1,k_2,k_3,k_4} \Delta_{k_1,k_2,k_3,k_4} \tilde{d}_{k_1,k_2}(t)\tilde{d}_{k_3,k_4}(t)\tilde{\rho}^{[1]}(t) \\
&+ i\tau_c \sum_{k_1,k_2,k_3,k_4} \Delta_{k_1,k_2,k_3,k_4}(H_{k_3} - H_{k_4}) \\
&\times \tilde{d}_{k_1,k_2}(t)\tilde{d}_{k_3,k_4}(t)\tilde{\rho}^{[0]}(t) \\
&- \tau_c \sum_{k_1,k_2,k_4} \Delta_{k_1,k_2,k_4}\tilde{d}_{k_1,k_2}(t)\tilde{d}_{k_3,k_4}(t) \\
&\times \sum_{k_1',k_2',k_3'k_4'} \Delta_{k_1',k_2',k_3',k_4'}\tilde{d}_{k_1',k_2'}(t)\tilde{d}_{k_3',k_4'}(t)\tilde{\rho}^{[0]}(t).
\end{aligned}
\tag{38}
$$

If this equation is used for the calculation of $D^{[1]}$, Kitahara's and Haus' result [Eq. (36)] is found. On the other hand, our simplified Eq. (9) leads to an equation for $\tilde{\rho}^{[1]}$ that is given by Eq. (38) without the last term of the right side. This term generates a contribution to the diffusion coefficient equal to $-\epsilon J$ and is responsible for the difference between ours and Kitahara's and Haus' results.

At this point, a clarification is necessary. Both the convolution-type Eq. (8) and the time-local Eq. (9) are equivalent second-order equations in the sense that the operator $\mathcal{A}$ connecting $\dot{\rho}$ with $\tilde{\rho}$ [Eq. (7)] is identical in both equations up to second order in a small parameter α which here is essentially given by $\alpha = \sqrt{\Delta}$ where Δ is the magnitude of Δ_{k_1,k_2,k_3,k_4} and proportional to either γ_0 or γ_1. The third term of the right side in Eq. (38) that is responsible for the difference of Kitahara's and Haus' and our result is clearly a fourth-order term, since it carries the factors $\Delta_{k_1,k_2,k_3,k_4}\Delta_{k_1',k_2',k_3',k_4'} \sim \Delta^2 \sim \alpha^4$. This term, although being of fourth order, nevertheless contributes to $D_{KH}^{[1]}$ [Eq. (36)] with similar magnitude as the part in Eq. (35) that does not include the additional term. This might seem surprising at first sight, but can be explained by the fact that the long time limit of the density matrix, and hence also the diffusion coefficient, cannot be expanded in a power series in powers of α (or Δ), since such an expansion would diverge for large times.[18] Therefore nonanalytic contributions (e.g., of order $1/\Delta$) may occur in the course of solving the equation of motion and lower the order of the final result. This is exactly what happens in the calculation of $D^{[1]}$.
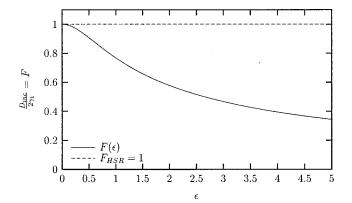
FIG. 1. The incoherent part of the diffusion coefficient divided by $2\gamma_1$.

The expansion of the diffusion coefficient in powers of the correlation time should therefore be considered with care, since the result depends on higher-order terms in the equation of motion. Comparing the second-order Eqs. (8) and (9) it is hard to tell which expression for $D^{[1]}$ is physically more reasonable. While the time-local Eq. (9) takes no higher-order contributions into account, the convolution-type Eq. (8) does take them into account partly, which can be better or worse.

A rigorous calculation of the contribution $D^{[1]}$ to the diffusion coefficient should have a fourth-order equation as a starting point, that will lead to the same result for $D^{[1]}$, no matter what kind of fourth-order equation is chosen as a starting point. In this case, the problem discussed above is encountered on the next higher level: the quadratic contribution $D^{[2]} \sim \tau_c^2$ again depends on the higher-order contributions (α^6 and higher) in the equation of motion.

V. NUMERICAL RESULTS

A. Incoherent part of the diffusion coefficient

The incoherent part of the diffusion coefficient (32) is proportional to the magnitude γ_1 of the nondiagonal fluctuations and to the function F defined in Eq. (C7),

$$D_{\text{inc}} = 2\gamma_1 F. \tag{39}$$

In Fig. 1 we plot $F = D_{\text{inc}}/(2\gamma_1)$ as a function of $\epsilon = 2J\tau_c$. The line $F = 1$ represents the results obtained with the Haken-Strobl-Reineker model. As expected, the deviations from the Haken-Strobl-Reineker model become quite dramatic for large values of ϵ, indicating the violation of the assumption $\tau_c \ll \tau_{\text{coh}}$ (or $J\tau_c \ll 1$) made by Haken, Strobl, and Reineker. With increasing ϵ, the function F decreases monotonically. However, this does not imply that the incoherent part of the diffusion coefficient decreases as well, since in general γ_1 depends on J and τ_c. This dependence has to be calculated separately. In a concrete example,[19] some of us have obtained dependencies of the form $\gamma_1 \sim J^2$ and $\gamma_1 \sim \tau_c$, leading to an incoherent part of the diffusion coefficient that increases with J and τ_c.

B. Coherent part of the diffusion coefficient

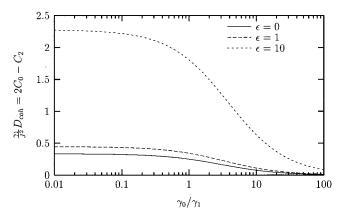Neglecting the small contributions G_1 and G_2, the coherent part of the diffusion coefficient is given by

FIG. 2. The coherent part of the diffusion coefficient multiplied by γ_1/J^2.

$$D_{\text{coh}} = \frac{J^2}{\gamma_1}(2C_0 - C_2). \tag{40}$$

The coefficients C_0 and C_2 have to be determined numerically by the method described in Sec. III. They depend on $\epsilon = 2J\tau_c$ and the ratio γ_0/γ_1.

In Fig. 2 we show the quantity $2C_0 - C_2 = (\gamma_1/J^2)D_{\text{coh}}$ as a function of the ratio γ_0/γ_1 for different values of ϵ. We have used the truncation $n_{\text{max}} = 2$ for this calculation which approximates the exact result with an error of less than 0.5%.

For a ratio $\gamma_0/\gamma_1 \ll 1$, the quantity $(\gamma_1/J^2)D_{\text{coh}}$ approaches a constant value. This means that in this limit the coherent part of the diffusion coefficient is proportional to J^2/γ_1 which is the same behavior observed in the original Haken-Strobl-Reineker model. However, its overall magnitude is larger than in the original model.

The opposite limit ($\gamma_0/\gamma_1 \gg 1$) can be understood best in Fig. 3 where we plot the quantity $(\gamma_0/J^2)D_{\text{coh}}$ as a function of the ratio γ_0/γ_1. In this case the curves approach constant values for large ratios $\gamma_0/\gamma_1 \gg 1$, indicating that the coherent part of the diffusion coefficient is proportional to J^2/γ_0, again in agreement with the original Haken-Strobl-Reineker model.

Independent of the ratio γ_0/γ_1, the diffusion coefficient D_{coh} is linear in ϵ for large epsilon ($\epsilon \gg 1$) and approaches asymptotically the Haken-Strobl-Reineker value for $\epsilon \to 0$.
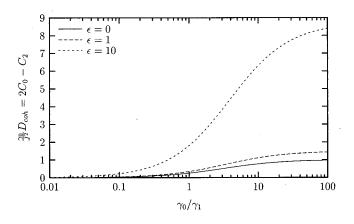

FIG. 3. The coherent part of the diffusion coefficient multiplied by γ_0/J^2.

VI. SUMMARY

In this paper we have calculated the diffusion coefficient for a migrating particle on a one-dimensional chain of molecules with dynamical disorder described as diagonal and nondiagonal fluctuations. We have generalized the result previously obtained by Haken, Strobl, and Reineker to larger correlation times, provided that the density matrix is slowly varying.

We have shown that the calculation of an expansion of the diffusion constant in powers of the correlation time is problematic, since the result depends on what type of second-order equation is chosen as a starting point. The different results can be explained by inclusion of higher-order contributions.

APPENDIX A: DERIVATION OF THE EQUATION OF MOTION

The equation of motion assumes a particularly simple form in the wave-vector representation. We therefore define

$$\tilde{c}_k^\dagger(t) = \frac{1}{\sqrt{N}} \sum_n e^{-ikn} \tilde{c}_n^\dagger(t), \tag{A1}$$

$$\tilde{c}_k(t) = \frac{1}{\sqrt{N}} \sum_n e^{ikn} \tilde{c}_n(t), \tag{A2}$$

$$\gamma_k = \frac{1}{N}(\gamma_0 + 2\gamma_1 \cos k), \tag{A3}$$

$$H_k = \varepsilon + 2J \cos k \tag{A4}$$

and rewrite the Hamiltonian [Eq. (1)] as

$$H(t) = H_0 + \delta H(t) \tag{A5}$$

$$= \sum_k H_k c_k^\dagger c_k + \sum_{k,k'} (t) c_k^\dagger c_{k'}. \tag{A6}$$

The second moments [Eqs. (4) and (5)] can now be written as

$$\langle \delta H_{k_1,k_2}(t) \delta H_{k_3,k_4}(t-\tau) \rangle = \Delta_{k_1,k_2,k_3,k_4} \frac{1}{\tau_c} e^{-|\tau|/\tau_c} \tag{A7}$$

with

$$\Delta_{k_1,k_2,k_3,k_4} = \delta_{k_1-k_2+k_3-k_4,0} \left(\gamma_{k_2-k_3} + \gamma_{k_2+k_4} - \frac{\gamma_{n=0}}{N} \right). \tag{A8}$$

The interaction picture quantities are related to their counterparts in the Schrödinger picture by

$$\tilde{\rho}(t) = e^{iL_0 t} \rho(t), \tag{A9}$$

$$\delta\tilde{L}(t) = e^{iL_0 t} \delta L(t) e^{-iL_0 t}, \tag{A10}$$

with $L_0 = [H_0, \ldots]$ and $\delta L(t) = [\delta H(t), \ldots]$. Using Eqs. (A5)–(A10), Eq. (6) takes the form

$$\dot{\tilde{\rho}}(t) = -\frac{1}{\tau_c} \sum_{k_1,k_2,k_3,k_4} \Delta_{k_1,k_2,k_3,k_4} \tilde{d}_{k_1,k_2}(t)$$
$$\times \int_0^t d\tau \tilde{d}_{k_3,k_4}(t-\tau) e^{-\tau/\tau_e} \tilde{\rho}(t-\tau) \tag{A11}$$

with $\tilde{d}_{k,k'}(t) = [\tilde{c}_k^\dagger(t)\tilde{c}_{k'}(t), \ldots]$. Since the time dependence of the creation and destruction operators in the interaction picture is known we can express $\tilde{d}_{k_3,k_4}(t-\tau)$ by its value at time t,

$$\tilde{d}_{k_3,k_4}(t-\tau) = e^{-i(H_{k_3}-H_{k_4})\tau} \tilde{d}_{k_3,k_4}(t). \tag{A12}$$

As long as we are not interested in the short-time behavior $(t < \tau_c)$ of the density matrix, we can safely replace the upper integration limit by infinity and using Eq. (A12) we obtain the equation of motion

$$\dot{\tilde{\rho}}(t) = -\frac{1}{\tau_c} \sum_{k_1,k_2,k_3,k_4} \Delta_{k_1,k_2,k_3,k_4} \tilde{d}_{k_1,k_2}(t) \tilde{d}_{k_3,k_4}(t)$$
$$\times \int_0^\infty d\tau\, e^{-\tau/\tau_e} e^{-i(H_{k_3}-H_{k_4})\tau} \tilde{\rho}(t-\tau). \tag{A13}$$

APPENDIX B: DERIVATION OF THE TIME-LOCAL EQUATION OF MOTION

Expanding $\rho(t-\tau)$ into a Taylor series around $\tau = 0$ and performing the integrals, we obtain

$$\dot{\tilde{\rho}}(t) = -\sum_{k_1,k_2,k_3,k_4} \frac{\Delta_{k_1,k_2,k_3,k_4}}{1+i\tau_c(H_{k_3}-H_{k_4})} \tilde{d}_{k_1,k_2}(t) \tilde{d}_{k_3,k_4}(t)$$
$$\times \left\{ \dot{\tilde{\rho}}(t) - \frac{\tau_c}{1+i\tau_c(H_{k_3}-H_{k_4})} \dot{\tilde{\rho}}(t) \right.$$
$$\left. + \frac{\tau_c^2}{[1+i\tau_c(H_{k_3}-H_{k_4})]^2} \ddot{\tilde{\rho}}(t) - \cdots \right\}. \tag{B1}$$

We now assume that the first term in the Taylor expansion is dominant, i.e.,

$$|\tilde{\rho}(t)| \gg \left| \frac{\tau_c}{1+i\tau_c(H_{k_3}-H_{k_4})} \dot{\tilde{\rho}}(t) \right|, \tag{B2}$$

which is equivalent to

$$\left|\tilde{\rho}(t)\right| \gg \left| \frac{\tau_c}{1+i\tau_c(H_{k_3}-H_{k_4})} \right.$$

$$\times \sum_{k_1',k_2',k_3',k_4'} \frac{\Delta_{k_1',k_2',k_3',k_4'}}{1+i\tau_c(H_{k_3'}-H_{k_4'})}$$

$$\times \tilde{d}_{k_1',k_2'}(t)\tilde{d}_{k_3',k_4'}(t)\tilde{\rho}(t) \bigg|. \qquad (B3)$$

This is fulfilled if

$$\frac{\max(\gamma_0,\gamma_1)\tau_c}{1+\epsilon^2} \ll 1, \quad \epsilon = 2J\tau_c. \qquad (B4)$$

APPENDIX C: CALCULATION OF F, G_1, and G_2

The quantities F, G_1, and G_2 are derivatives of the generalized rates [Eq. (12)]:

$$F = \frac{1}{4\gamma_1}\frac{1}{N}\sum_{k,K}\left(\frac{\partial^2 W^o_{k+q,k\to K+q,K}}{\partial q^2}\bigg|_{q=0} \right.$$

$$\left. -\frac{\partial^2 W^i_{k+q,k\to K+q,K}}{\partial q^2}\bigg|_{q=0} \right), \qquad (C1)$$

$$G_1 = \frac{1}{2iJ\sin k}\sum_{K}\left(\frac{\partial W^o_{k+q,k\to K+q,K}}{\partial q}\bigg|_{q=0} \right.$$

$$\left. -\frac{\partial W^i_{k+q,k\to K+q,K}}{\partial q}\bigg|_{q=0} \right), \qquad (C2)$$

$$G_2 = -\frac{1}{2iJ\sin k}\sum_{K}\left(\frac{\partial W^o_{k+q,k\to K+q,K}}{\partial q}\bigg|_{q=0} \right.$$

$$\left. -\frac{\partial W^i_{K+q,K\to k+q,k}}{\partial q}\bigg|_{q=0} \right). \qquad (C3)$$

After some algebra we can rewrite this as

$$F = \frac{1}{N^2}\sum_{k,K}\frac{1+\cos k\cos K}{1+\epsilon^2(\cos K-\cos k)^2}, \qquad (C4)$$

$$G_1 = \frac{4\gamma_1\tau_c}{N}\sum_{K}\cos K\frac{\cos K-\cos k}{1+\epsilon^2(\cos K-\cos k)^2}, \qquad (C5)$$

$$G_2 = \frac{2\tau_c}{N}\sum_{K}(\gamma_0+2\gamma_1+2\gamma_1\cos k\cos K)$$

$$\times\frac{1-\epsilon^2(\cos K-\cos k)^2}{[1+\epsilon^2(\cos K-\cos k)^2]^2} \qquad (C6)$$

with $\epsilon = 2J\tau_c$. Converting the sum (C4) into an integral, we obtain

$$F = \frac{(1+4\epsilon^2)K(2i\epsilon)-E(2i\epsilon)}{\pi\epsilon^2}, \qquad (C7)$$

where $K(x)$ and $E(x)$ are the complete elliptic integrals of the first and second kind, respectively.

The expressions for G_1 and G_2 can easily be integrated as well, but since both quantities are of the order of magnitude of $\max(\gamma_0,\gamma_1)\tau_c/(1+\epsilon^2)$ which is assumed to be much smaller than unity [Eq. (B4)], they can be neglected and will not be given here.

[1] H. Haken and G. Strobl, in *The Triplet State*, edited by A. Zahlan (Cambridge University Press, London, 1967), p. 311.

[2] H. Haken and P. Reineker, Z. Phys. **249**, 253 (1972).

[3] H. Haken and G. Strobl, Z. Phys. **262**, 135 (1973).

[4] E. K. L. Yeow, D. J. Haines, K. P. Ghiggino, and M. N. Paddon-Row, J. Phys. Chem. A **103**, 6517 (1999).

[5] C. Warns, I. Barvik, and P. Reineker, Phys. Rev. E **57**, 3928 (1998).

[6] C. K. Law, R. S. Knox, and J. H. Eberly, Chem. Phys. Lett. **258**, 352 (1996).

[7] G. D. Scholes and K. P. Ghiggino, J. Chem. Phys. **103**, 8873 (1995).

[8] D. G. Evans and R. D. Coalson, J. Chem. Phys. **102**, 5658 (1995).

[9] P. Guyot-Sionnest, P. H. Lin, and E. M. Hiller, J. Chem. Phys. **102**, 4269 (1995).

[10] A. Kruger, C. Kryschi, L. Valkunas, and D. Schmid, Chem. Phys. **157**, 243 (1991).

[11] K. Kassner, Z. Phys. B: Condens. Matter **70**, 229 (1988).

[12] P. Reineker, in *Exciton Dynamics in Molecular Crystals and Aggregates*, edited by G. Höhler (Springer-Verlag, Berlin, 1982).

[13] K. Kitahara and J. W. Haus, Z. Phys. B **32**, 419 (1979).

[14] B. Yoon, J. M. Deutch, and J. H. Freed, J. Chem. Phys. **62**, 4687 (1975).

[15] R. Kubo, J. Math. Phys. **4**, 174 (1963).

[16] N. G. van Kampen, Physica A **74**, 215 (1974).

[17] N. G. van Kampen, Physica A **74**, 239 (1974).

[18] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (Elsevier, Amsterdam, 1997).

[19] M. A. Palenberg, R. J. Silbey, M. Malagoli, and J.-L. Brédas, J. Chem. Phys. **112**, 1541 (2000).