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Theory of non-Markovian exciton transport in a one dimensional lattice

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We consider non-Markovian exciton transport in a one dimensional system with nearest neighbor interactions. Kubo's stochastic Liouville equation (SLE) is used to derive a set of coupled equations of motion which are *exact* for a Poisson bath and which also should give a fairly accurate long time description for a Gaussian bath. The SLE is especially suitable for this problem since both cumulunt expansion and projection operator techniques encounter difficulties when the system is quantum mechanical, the stochastic off-diagonal coupling is strong, and the relaxation is non-Markovian. To elucidate the role of correlations in space and time, we consider two different models: (a) Both diagonal and off-diagonal fluctuations arise from the same bath. (b) All the fluctuations arise from uncorrelated baths. We find that model (a) always gives coherent exciton transport even at long times if the mean off-diagonal coupling J is nonzero. Model (b) gives diffusive behavior at long times, but the diffusion constant is very different in the non-Markovian limit from the prediction of Markovian or weak-coupling theories. In the Markovian limit, the expressions for the mean square displacement agree exactly with those of Haken and co-workers and of Grover and Silbey. Some interesting new features of non-Markovian transport are discussed.

I. INTRODUCTION

There has been considerable interest in recent years in the theory of diffusion in one dimensional quantum mechanical systems.[1-14] Much of this interest originates from the fact that a one dimensional model seems capable of explaining some of the essential features of the migration of Frenkel excitons in many molecular crystals.[15-18] At high temperature, the exciton migration is incoherent or diffusive[1-3,15-18] indicating the presence of a random walk type of hopping mechanism for transport. At low temperature, the motion is expected to be coherent[16-18] or wavelike over a distance considerably larger than the lattice spacing before, eventually, becoming incoherent due to scattering by lattice phonons or due to the presence of traps or defects. It has been a major objective of theoretical investigations to explain this transition from incoherence to coherence as the temperature of the system is lowered. In addition to exciton transport, there are other interesting cases where energy transfer in one dimensional quantum mechanical systems plays an important role in explaining experimental results, e.g., long range energy transfer[14] in liquids where the radial distance is randomly modulated by the surrounding liquid. Applications of one dimensional models to chemical rate processes are well known.[12,13]

There exist in the literature three distinct approaches to the problem of exciton migration and the related problem of exciton line shapes. The formalism developed by Haken, Strobl, Reineker and co-workers[2-4] starts with a Hamiltonian of the form

$$H(t)=H_1+H_2(t) \ ,$$

where H_1 includes time-independent off-diagonal coupling and $H_2(t)$ is the fluctuating part of diagonal and off-diagonal couplings of the exciton to the lattice phonons $\langle H_2(t)\rangle=0$. The stochastic forces are assumed to be delta-correlated Gaussian noise so that the exciton motion is Markovian. With the additional assumption of nearest neighbor interaction, these authors[2-4] could solve the problem exactly to obtain an analytic expression for the exciton diffusion constant in an infinite system and also an expression for the width of the line shape of optical absorption in a two molecule system. These expressions have been used to interpret the temperature dependence of diffusion constants and spectral line shapes for triplet excitons in molecular crystals.[1-4,18] One important limitation of this approach is the assumption of white noise. At low temperature, the bath can become correlated over space and time and the assumptions of white noise can break down. An interesting discussion of this approach is presented in Ref. 1.

Perhaps the most extensive study of the dynamics of exciton migration and line shapes has been carried out by Silbey and co-workers.[1,5,7] One important advantage of their formalism is that it treats the phonon bath explicitly and as a result a more consistent and realistic description of exciton dynamics naturally emerges from the theory. This treatment has recently been extended to include memory effects,[5-7] but this extension is not free from objections.[10] The objections mainly concern the truncation of the cumulant expansion[19] at second order. Since the stochastic force becomes a quantum mechanical operator in the interaction representation of the system, proper time ordering[19,20] is required for carrying out the cumulant expansion. If a simple partial ordering prescription is used (as by Silbey and co-workers), then cumulants of *all* orders exist and a truncation at second order can be a serious approximation in the strong coupling limit. In fact, as pointed out by Kenkre[10] and discussed recently by Jackson and Silbey,[7] the occupation probabilities can even become negative. The inadequacy of such a truncation procedure for non-Markovian relaxation was demonstrated quantitatively

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by Abbott and Oxtoby[21] who found that the results of their simulation for vibrational energy relaxation in a two-level system coupled strongly to a Gaussian bath could not be satisfactorily described by a cumulant expansion truncated at second order.

More recently, Kenkre and Knox[8] have initiated a third approach to this problem by using a generalized master equation for the rate of change of occupation probability P_n of the exciton at site n. Kenkre[22] has also pointed out a formal similarity between this theory and that of Silbey and co-workers. However, it has been shown by Silbey[1] that the occupation probability $P_n(t)$ derived by this method can also become negative. Kenkre[10] has discussed in detail the limitations of their approach as well as that of Silbey and co-workers.

It therefore appears that at present there is no formally satisfactory theory for exciton transport in the strong coupling and non-Markovian limit. Another important limitation of all these theories is that they all assume that the stochastic force is Gaussian, which is justified by appealing to the central limit theorem. However, at low temperature, the number of lattice phonons can become small and the central limit theorem may not be applicable.

In this paper we present a theory which is free from some of the limitations of the earlier theories. Our theory is based on the stochastic Liouville equation (SLE) approach developed by Kubo[23] and applied to several interesting problems by Freed and co-workers.[24] The SLE is especially suitable when the system is quantum mechanical but the bath is classical. Moreover, Stillman and Freed[24] have recently shown that one can even include the back reaction from the system onto the bath and the SLE thus modified properly describes the relaxation of the system to thermal equilibrium. Indeed, the SLE seems to be an ideal theory for describing relaxation processes in the non-Markovian limit. Recently, we have shown that the SLE can be used sucessfully to explain results of quantum mechanical simulations of vibrational energy relaxation in liquids.[25] The SLE is especially useful for the Poisson bath because the stochastic diffusion operator has only two bath states, and all calculations can be carried out exactly.[25] For the Gaussian bath, one needs at least six to eight of the infinite number of available bath decay modes in order to obtain good agreement with exact results.[25] However, for long time behavior, a smaller number of these bath modes is sufficient to obtain accurate results, even in the non-Markovian limit.

In this paper, we have applied the SLE to the problem of exciton transport in one dimension. We have derived an exact set of coupled equations to describe the motion of an exciton in the non-Markovian limit. Though this system of equations is exact and closed for a Poisson bath, they can also be considered as limiting equations for a Gaussian bath and should be reasonably accurate for describing the long time behavior. The Poisson bath itself, however, can be a useful model for stochastic forces at low temperatures when the infrequent arrivals of ballistic phonons[26,27] may have a Poisson distribution. At high temperatures, the Poisson bath is of course not realistic. For energy transfer processes in liquids, the Poisson process may model hard core repulsive interactions with neighbors.

In order to investigate the role of diagonal and off-diagonal fluctuations, we have considered two different situations in this paper: (i) Both the diagonal fluctuations on the nearest neighbors and the off-diagonal fluctuations are fully correlated all the time; i.e., they belong to the same bath. This model is expected to mimic the situation at low temperature where the bath degrees of freedom can become correlated over large distances; (ii) the diagonal and off-diagonal fluctuations are completely uncorrelated with each other at all times. In the limit of white noise, this model reduces to that of Haken and co-workers.[2,3]

For both these cases, the SLE gives rise to a set of coupled equations for the occupation probability $P_n(t)$ of the exciton at site n. For case (i), the equations are simple and an explicit expression for the mean squared displacement $\langle x^2(t)\rangle$ is given. In this case, exciton transport is coherent for nonzero values of the time-independent off-diagonal coupling J, diffusive behavior being obtained only for $J=0$. For case (ii), the equations are very complicated and $\langle x^2(t)\rangle$ is evaluated numerically for the general case. Analytic expressions can, however, be obtained in some special limits. In the limit of white noise, $\langle x^2(t)\rangle$ is identical to that of Haken and co-workers. In the non-Markovian limit, the motion is coherent for short times, but becomes diffusive at long times with a diffusion constant which is very different from that predicted by Markovian or weak coupling theories.

The coherent propagation of excitons for case (i) is interesting. While it is obvious that this case is not fully realistic because baths must become uncorrelated after some distance, this result does suggest that coherent transport at low temperatures may partly arise from the presence of baths correlated over large distances in space. We discuss the significance of this result in light of the existing explanations in Secs. IV and V.

The organization of the paper is as follows: In Sec. II we introduce the Hamiltonian and in Sec. III we discuss the SLE. In Sec. IV we present the coupled equations for the two cases along with expressions for $\langle x^2(t)\rangle$. Section V concludes with a brief discussion.

II. THE HAMILTONIAN

The Hamiltonian for a coupled exciton–phonon system may be written as[1,2,28–30]

$$H = H_{ex} + H_{ph} + H_{int} \ . \tag{2.1}$$

H_{ex} is defined as

$$H_{ex} = \sum_k E_0 |k\rangle\langle k| + {\sum_{k,l}}' J_{kl} |k\rangle\langle l| \ . \tag{2.2}$$

E_0 is the energy of an electronic exciton localized at site k and J_{kl} is the time independent resonance interaction between excitations at sites k and l. As already noted by Grover and Silbey[28,1] and also by Haken and

Strobl,[2] J_{kl} is responsible for coherent motion of excitons. H_{ph} is the free phonon Hamiltonian and H_{int} is the interaction Hamiltonian between excitons and phonons In describing exciton–phonon interaction, we have two options: (a) We can adopt a harmonic oscillator phonon bath and write down a Taylor series of the exact exciton–phonon interaction in powers of phonon coordinates, as was done by Grover and Silbey[28] and others[29]; or (b) we can consider the total Hamiltonian in the interaction representation of the phonon bath so that H_{int} becomes time dependent and may then be modeled by stochastic functions with known statistical properties. The parameters of the stochastic functions are to be derived from the properties of the phonon bath. This second approach was adopted by Haken and co-workers.[2–4] Under the assumptions of strong exciton–phonon coupling relative to intermolecular coupling and quickly decaying phonon correlation functions, these two approaches lead to identical results.

In this paper, we follow the second approach. The time dependent Hamiltonian $H(t)$ is now given by

$$H(t) = H_{ex} + H_{int}(t) \ , \tag{2.3}$$

where

$$H_{int}(t) = H_d(t) + H_o(t) = \sum_k (|k\rangle\langle k|)\, V_d(t) + \sum_{k,l}{}' (|k\rangle\langle l|)\, V_o(t) \ , \tag{2.4}$$

where $V_d(t)$ and $V_o(t)$ denote diagonal (local) and off-diagonal (nonlocal) parts of the fluctuating Hamiltonian $H_{int}(t)$. Haken and Strobl[2] assumed that $V_d(t)$ and $V_o(t)$ are delta-correlated Gaussian noise and that they are independent of each other at all times. As discussed in the Introduction, these assumptions may not hold in certain realistic situations. Silbey and co-workers[1,5,7] have included memory effects in a Gaussian bath, but as we have discussed earlier, their formalistm is not free from objections.[10]

In this work we have assumed that both $H_o(t)$ and $H_d(t)$ are Poisson stochastic processes, though it is formally straightforward to generalize our method to Gaussian stochastic processes. We have considered two limiting situations. For case (i) (same bath), the Poisson bath jumps at regular intervals between the two states (which we call + and −) at an average rate of $b/2$ and the probability that a jump will occur in a given interval Δt is given by $b/2\exp(-b/2\,\Delta t)$. All the matrix elements $(V_d)_{kk}$ and $(V_o)_{kl}$ also jump together between two values $\pm V$ such that the average values $\langle H_d(t)\rangle = \langle H_o(t)\rangle = 0$. The Gaussian bath is characterized by the exponential correlation function $\langle V^2\rangle e^{-bt}$ and the time dependent fluctuation $V(t)$ obeys an ordinary Langevin equation where the random force is Gaussian white noise. The details of the characteristics of these baths are discussed elsewhere.[21,25]

For case (ii) (independent baths) the nearest neighbor diagonal elements $[V_{k-1,k-1}(t),\ V_{k,k}(t),\ \text{and}\ V_{k+1,k+1}(t)]$ and off-diagonal elements $[V_{k-1,k}(t)\ \text{and}\ V_{k,k+1}(t)]$ are all independent of each other. By symmetry, the nearest neighbor diagonal fluctuations must have the same strength V_d and the same correlation time b_d, although they are independent. Similarly, for off-diagonal fluctuations, $V_{k-1,k}$ and $V_{k,k+1}$ have fluctuations of the same strength V_o and the same correlation time b_o.

The Markovian limit of the exciton motion can be obtained by letting $V\to\infty$, $b\to\infty$ with V^2/b fixed. We define

$$\lim_{V_d,\, b_d\to\infty} \frac{V_d^2}{b_d} = \gamma_0 \ , \tag{2.5}$$

$$\lim_{V_o,\, b_o\to\infty} \frac{V_o^2}{b_o} = \gamma_1 \ . \tag{2.6}$$

γ_0 and γ_1 are the same quantities that appear in the work of Grover and Silbey[28] and of Haken and Strobl[2] to characterize diagonal and off-diagonal fluctuations, respectively. As we shall show later, our expression for the mean squared displacement $\langle x^2(t)\rangle$ of exciton migration reduces in this limit, for the independent bath case [case (ii)], to the well-known expression derived earlier by the above authors.

III. THE STOCHASTIC LIOUVILLE EQUATION

When diagonal and off-diagonal fluctuations arise from coupling of the exciton to the same bath [case (i)], then the time dependent Hamiltonian $H(t)$ depends on only one random variable [say $\lambda(t)$]. In this case, Kubo's stochastic Liouville equation (SLE)[23] is the following equation of motion for the reduced density matrix:

$$\frac{d\sigma}{dt} = -i/h[H(t),\sigma] + \Gamma_\lambda\,\sigma \ , \tag{3.1}$$

where Γ_λ is the stochastic diffusion operator; $\sigma(t)$ and Γ_λ are defined by the following equations:

$$\sigma(t) = \langle\rho(\lambda,t)\rangle = \int d\rho\,\rho P(\lambda,\rho,t) \ , \tag{3.2}$$

$$\frac{dW(\lambda,t)}{dt} = \Gamma_\lambda\, W(\lambda,t) \ , \tag{3.3}$$

where ρ, $P(\lambda,\rho,t)$, and $W(\lambda,t)$ are the total density matrix, the joint probability density of λ and ρ, and the probability density for the random variable $\lambda(t)$, respectively. In deriving Eq. (3.1), the assumption is made that Γ_λ is independent of the motion of the exciton; i.e., the back reaction from the molecular system onto the bath is neglected. Recently, Stillman and Freed[24] have removed this limitation of SLE for classical rotational motion for the special case of a Gaussian stochastic operator. These authors obtained an augmented Fokker–Planck description by following Haken's prescription for incorporating detailed balance into the Fokker–Planck description. This augmented Fokker–Planck equation properly describes relaxation to thermal equilibrium. However, in the present case, the system is quantum mechanical and the stochastic force is Poisson. It is not clear at present how to impose the conditions of detailed balance in this problem. Moreover, this back reaction may not be as important in the motion of the exciton as it can be in vibrational or rotational relaxation since the energy changes involved here are quite small. Therefore, we have used Eq. (3.1) in this paper and have neglected any effect of back reaction.

A systematic method of solving Eq. (3.1) is to expand σ in the eigenstates $|b_n\rangle$ of the diffusion operator Γ[25,31]

$$\sigma = \sum_n \sigma_n |b_n\rangle , \tag{3.4}$$

where $|b_n\rangle$ can be obtained by solving the eigenvalue problem

$$\Gamma |b_n\rangle = E_n |b_n\rangle . \tag{3.5}$$

The stochastic operator Γ has a unique equilibrium state $|b_0\rangle$ defined by the equation

$$\Gamma |b_0\rangle = E_0 |b_0\rangle = 0 . \tag{3.6}$$

Equations (3.1) and (3.4) are combined to obtain

$$\frac{d\sigma_m}{dt} = -iH_0^x \sigma_m - iH_1^x \sigma_m - i\sum_{m'} \langle b_m | H_d^x(t) | b_{m'}\rangle - i\sum_{m'} \langle b_m | H_0^x(t) | b_{m'}\rangle - mb\sigma_m . \tag{3.7}$$

For the Poisson bath, Γ is a 2×2 matrix with eigenvalues 0 and $-b$.[25] The stochastic variables $V_d(t)$ and $V_o(t)$ have the following matrix elements in the eigenfunctions of Γ:

$$\langle b_i | V_a(t) | b_j\rangle = V_a , \quad i \neq j ,$$
$$\langle b_i | V_a(t) | b_i\rangle = 0 . \tag{3.8}$$

a in V_a stands for either diagonal or off-diagonal coupling. For the Poisson bath, the stochastic operator depends only on b, so diagonal and off-diagonal fluctuations can have different magnitudes, even though they have the same Γ. This implies that although the fluctuations occur at the same time, they can be of different strength. Equations (3.7) and (3.8) are combined to obtain

$$\frac{d\sigma_m}{dt} = iH_0^x \sigma_m - iH_1^x \sigma_m - iV_d \sum_{m'=0}^{1} (\delta_{m+1,m'} + \delta_{m-1,m'}) \times \Big(\sum_k |k\rangle\langle k|\Big)^x \sigma_{m'} - iV_o \sum_{m'=0}^{1} (\delta_{m+1,m'} + \delta_{m-1,m'}) \times \Big(\sum_{k,l}{}' |k\rangle\langle l|\Big)^x \sigma_{m'} - mb\sigma_m . \tag{3.9}$$

For the Gaussian bath, the diffusion operator is a Fokker–Planck operator; its eigenvalues and eigenfunctions are given in Ref. 25. We here merely quote the expression analogous to Eq. (3.9):

$$\frac{d\sigma_m}{dt} = -iH_0^x\sigma_m - iH_1^x\sigma_m - iV_d \sum_{m'=0}^{\infty} 2^{m'-m-1/2}(\delta_{m',m-1} + 2m\delta_{m',m-1}) \Big(\sum_k |k\rangle\langle k|\Big)^x \sigma_{m'} - iV_o \sum_{m'=0}^{\infty} 2^{m'-m-1/2}(\delta_{m',m+1} + 2m\delta_{m',m-1}) \Big(\sum_{k,l}{}' |k\rangle\langle l|\Big)^x \sigma_{m'} - mb\sigma_m . \tag{3.10}$$

For a Gaussian bath, Γ depends both on V and on b, but the form of Γ (which is a Fokker–Planck operator) is such that the magnitudes V_d and V_o can be different in Eq. (3.10), but b_d and b_o must be the same.

Equations (3.9) and (3.10) can now be used to study the dynamics of exciton transport. In order to find the occupation probability of the exciton at site n at time t, we have to compute $\langle n|\sigma_0(t)|n\rangle$. Due to interactions of this site with its neighbors, the equation of motion of $\langle n|\sigma_0|n\rangle$ is coupled to other matrix elements. The coupled equations will be given in the next section.

The situation is a bit more complicated when the random forces are independent of each other. For case (ii), we have five independent stochastic forces. In this case, the SLE is of the following form[32]:

$$\frac{d\sigma}{dt} = -i[H(t),\sigma] + \sum_{j=1}^{5} \Gamma_j \sigma ,$$

where Γ_j is the stochastic diffusion operator for jth random force. The next step is to expand σ in eigenfunctions of these operators[32]

$$\sigma = \sum_{jklmn} \sigma_{jklmn} |b_j^1\rangle |b_k^2\rangle |b_l^3\rangle |b_m^4\rangle |b_n^5\rangle ,$$

where $|b_i^h\rangle$ denotes the ith bath state of the operator Γ_h. The derivation of the equation of motion for σ_{jklmn} is similar to the one described previously for the same bath case. The occupation probability of the exciton at site n is now given by $\langle n|\sigma_{00000}(t)|n\rangle$ which is coupled to a large number of matrix elements. For some special cases, one can still extract analytic expression for the diffusion constant from the long time behavior, but the general solution must be obtained numerically.

IV. EQUATIONS OF MOTION AND THE MEAN SQUARE DISPLACEMENT

In this section we present the coupled equations of motion for cases (i) and (ii) and give expressions for the mean square displacement for each case.

We are interested in essentially infinite lattice chains and in long time behavior, so we work in the continuum limit where the discrete lattice structure (labeled by n) is replaced by a dependence on a continuous variable x. The results obtained in this way should describe real lattices correctly except at very short times.

A. Same bath for diagonal and off-diagonal fluctuations

The coupled equations for this case are given by

$$\frac{1}{b_o}\ddot{P}_0 + \dot{P}_1 = \frac{2a^2}{b_o}(J^2 + V_o^2) P_0'' + \frac{4JV_o a^2}{b_o} P_1'' - iJZ_0 , \tag{4.1}$$

$$\frac{1}{b_o}\ddot{P}_1+\dot{P}_1=\frac{2a^2}{b_o}(J^2+V_o^2)P_1''+\frac{4JV_oa^2}{b_o}P_0''-iJZ_1\ , \tag{4.2}$$

$$\dot{Z}_0=2iJa^2P_0''+2iV_oa^2P_1''\ , \tag{4.3}$$

$$\dot{Z}_1=2iJa^2P_1''+2iV_oa^2P_0''-b_oZ_1\ , \tag{4.4}$$

where "a" is the lattice spacing and V_o is the strength of fluctuation of off-diagonal matrix elements; the diagonal terms do not contribute for the same bath case. The other quantities are defined in the continuum limit by the following expressions:

$$P_0(x,t)=\langle x|\sigma_0(t)|x\rangle\ ,\quad P_1(x,t)=\langle x|\sigma_1(t)|x\rangle\ ,$$

$$Z_0(x,t)=\langle x+a|\sigma_0(t)|x\rangle+\langle x-a|\sigma_0(t)|x\rangle - \langle x|\sigma_0(t)|x+a\rangle-\langle x|\sigma_0(t)|x-a\rangle\ ,$$

$$Z_1(x,t)=\langle x+a|\sigma_1(t)|x\rangle+\langle x-a|\sigma_1(t)|x\rangle - \langle x|\sigma_1(t)|x+a\rangle-\langle x|\sigma_1(t)|x-a\rangle\ .$$

The dots in Eqs. (4.1)–(4.4) refer to time derivatives and the primes to spatial coordinate derivatives. As we have already mentioned, the *same* set of equations is obtained for the Gaussian bath if only σ_0 and σ_1 are retained and all higher excited bath modes are neglected. Since the higher bath modes have larger eigenvalues, they will decay more rapidly and the long time behavior should be dominated by σ_0 and σ_1. Thus, Eqs. (4.1)–(4.4) should provide a reasonable first order correction to the white noise description of exciton transport with a Gaussian bath.

The coupled equations (4.1)–(4.4) are new. They are interesting in that they have the appearance of diffusion equations and yet are exact for a Poisson bath with full non-Markovian effects. The Markovian limit can be obtained by letting $V\to\infty$, $b\to\infty$ with V^2/b fixed.

We have solved these equations with the following initial and boundary values:

$$P_0(x=\pm\infty,t)=0=P_1(x=\pm\infty,t)\ , \tag{4.5}$$

$$P_0(x,t=0)=\delta(x)\ , \tag{4.6}$$

$$P_1(x,t=0)=0=Z_0(x,t=0)\ , \tag{4.7}$$

where we have assumed that the exciton is initially located at $x=0$ in equilibrium with the bath degrees of freedom. The initial conditions (4.6) and (4.7) give $Z_1(x,t=0)=0$.

Equations (4.1)–(4.4) can be solved to obtain the following expression for the mean squared displacement:

$$\langle x^2(t)\rangle=2a^2J^2t^2+\frac{4a^2V_o^2}{b_o}t+\frac{4a^2V_o^2}{b_o^2}e^{-b_ot}-\frac{4a^2V_o^2}{b_o^2}\ . \tag{4.8}$$

Equation (4.8) predicts that exciton transport will remain coherent (mean squared displacement proportional to t^2) whenever the time independent off-diagonal coupling J is nonzero. At short times, the transport is coherent and $\langle x^2(t)\rangle\sim 2a^2(J^2+V_o^2)t^2$, as expected.

Equation (4.8) may appear surprising at first glance, but it obviously arises from the fact that all the fluctuations are correlated at all times. As we shall show later, if either diagonal or off-diagonal fluctuations become uncorrelated (or independent), then we get diffusive behavior at long times. In realistic situations, baths must become uncorrelated after a certain distance due to the presence of traps and impurities or from scattering by short wavelength optical phonons. While we have explicitly considered only a two-state bath, these long time coherent results for case (i) remain if a larger number of bath states is considered, provided that the same bath assumption is retained.

Equation (4.8) can have some interesting consequences. Recent experiments[16–18] have demonstrated that exciton transport becomes coherent at low temperature, at least over intermediate distance scales before impurity scattering becomes important. The transition from incoherent motion at high temperature to coherent motion at low temperatures was explained by Grover and Silbey[28] and also by Haken and Reineker[3] by noting that while J is weakly temperature dependent, V_o increases rapidly with temperature. So, at low temperature J/V_o is large and the motion is coherent while at high temperature J/V_o goes to zero and we recover incoherent motion. Here we find that there can be an alternative explanation: coherent propagation can arise by the bath becoming correlated in space and time. There is now some experimental evidence[26,27] that at very low temperature the scattering process may be dominated by acoustic phonons which have long wavelengths, so that the fluctuations can become correlated over a larger region and thus give rise to coherent migration of excitons. Baths must become uncorrelated eventually and give diffusive behavior at very long times. Over a short distance, however, excitons can propagate coherently for the above mentioned reason.

B. Independent bath fluctuations

In this case, we have five independent bath fluctuations (in the limit of delta time correlation of these fluctuations, this model reduces to that of Haken and Strobl[2]). $\langle n|\dot{\sigma}_{00000}|n\rangle$ in this case is coupled to a large number of other matrix elements; the complete set of coupled equations is collected in the Appendix. Due to the large number of equations, it has not been possible to obtain an analytic expression for $\langle x^2(t)\rangle$, so we have evaluated $\langle x^2(t)\rangle$ numerically in the general case. However, if either diagonal or off-diagonal fluctuations are neglected (which is equivalent to setting either V_d or V_o equal to zero in the system of equations given in the Appendix), then it is possible to obtain an analytic expression for $\langle x^2(t)\rangle$ in the limit of long times. For the former case ($V_d=0$), $\langle x^2(t)\rangle$ is given by

$$\langle x^2(t)\rangle_{t\to\infty}\sim\left[4a^2(V_o^2/b_o)+\frac{2a^2J^2}{(V_o^2/b_o)}\times\left(\frac{12J^4-18J^2V_o^2+8J^2b_o-12V_o^4-6V_o^2b_o^2+b_o^4}{2b_o^4+bJ^2b_o^2+3V_o^2b_o^2}\right)\right]t\ . \tag{4.9}$$

If we take the Markov limit $V\to\infty$, $b\to\infty$ with (V^2/b) fixed, we find

$$\langle x^2(t)\rangle\sim\left[4a^2(V_o^2/b_o)+\frac{J^2a^2}{(V_o^2/b_o)}\right]t \tag{4.10}$$

which gives the following expression for the diffusion constant:

$$D=a^2\left[2\gamma_1+\frac{J^2}{2\gamma_1}\right] \tag{4.11}$$

which agrees exactly with that given by Haken and Reineker for this special case. We would, however, like to point out that Haken and Reineker[3] derived their expression for the diffusion constant by assuming delta correlated *Gaussian* noise. Here we have shown that the same expression [Eq. (4.11)] is also applicable for a *Poisson* stochastic force in the limit of white noise. This is an expected result because in the limit $b\to\infty$, only the first excited bath mode remains important in the dynamics of exciton transport.

Equation (4.9) gives an expression for $\langle x^2(t)\rangle$ for large t. It shows that the motion is diffusive in the non-Markovian limit, but the diffusion constant can be very different from that given by Markovian theory, i.e., Eq. (4.11). Equation (4.9) also demonstrates the fact that the mere proportionality between $\langle x^2(t)\rangle$ and t does not necessarily imply a hopping type random walk mechanism for exciton transport.

As regards the relevance of Eq. (4.9) for a Gaussian bath, we feel that this should give a reasonable first order correction to equation (4.11) in the non-Markovian limit. One expects that this equation will become less accurate as we let $b\to 0$ since then all the excited bath states of the Fokker–Planck operator will become important. Our earlier work on vibrational energy relaxation[21,25] has shown, however, that even in the non-Markovian limit, the long time behavior of Poisson and Gaussian baths are surprisingly similar. Equation (4.9) may therefore have wider validity than expected from purely theoretical arguments. This point deserves further study.

We have also obtained an expression for $\langle x^2(t)\rangle$ at long times when off-diagonal fluctuations are absent ($V_o=0$). In this case $\langle x^2(t)\rangle$ is given by

$$\langle x^2(t)\rangle_{t\to\infty}\sim\left[\frac{2J^2a^2}{(V_d^2/b)}+2J^2a^2\,\frac{6b_d^3+8V_d^2b_d+3J^2b_d+2V_d^2J^2/b_d}{6b_d^4+8V_d^2b_d^2+9b_d^2J^2+10J^2V_d^2}\right]t. \tag{4.12}$$

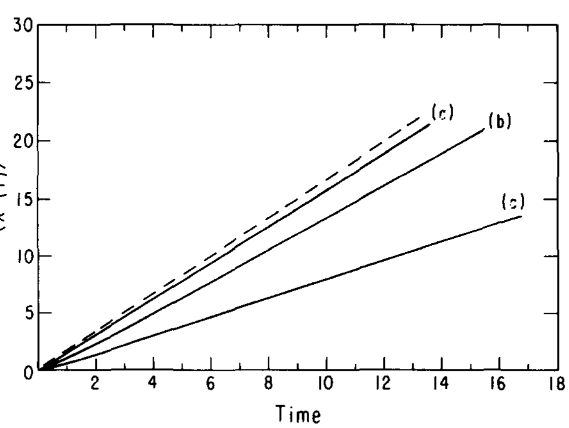

FIG. 1. Convergence of $\langle x^2(t)\rangle$ calculated from this non-Markovian theory, toward the Markovain theory result (dashed line) as V and b are increased keeping V^2/b and J fixed. (a) $V_o=V_d=0.5$, $b_o=b_d=0.625$, $J=0.2$, (b) $V_o=V_d=1.0$, $b_o=b_D=2.5$ (c) $V_o=V_d=2.0$, $b_o=b_d=10.0$.

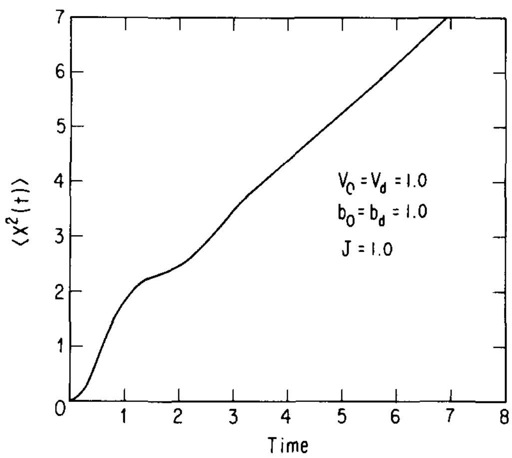

FIG. 2. Root mean square displacement in the intermediate strength and intermediate memory regime.

If we take the limit $V\to\infty$, $b\to\infty$, V^2/b fixed, then Eq. (4.12) reduces exactly to the analogous expression of Haken and Reineker.[3] Equations (4.9) and (4.12) show the dependence of the diffusion constant on both the strength V and the rate of change b of the fluctuations, whereas the only parameter that enters in a Markovian theory is the combination V^2/b. Thus, the expressions (4.9) and (4.12) are more general than those previously obtained by Haken and Reineker.[3]

From Eqs. (4.9) and (4.12), we can also study the behavior of $\langle x^2(t)\rangle$ in other limiting cases. For example, if we keep both J and V fixed, but let $b\to\infty$, then both Eqs. (4.9) and (4.12) give diffusion constants proportional to b (i.e., the diffusion constant becomes very large). On the other hand, if we keep J and b fixed but let $V\to\infty$, then Eq. (4.9) predicts that the diffusion constant would become large, while Eq. (4.12) gives a diffusion constant independent of V.

Due to the complicated structure of the coupled equations for the case when both diagonal and off-diagonal fluctuations are nonzero (see the Appendix for the complete set of equations), we have solved them numerically by using the fourth order Runge–Kutta–Gills method.[33] Figure 1 shows the convergence of the numerical results from our exact calculation toward the Markovian theory result of Haken and Reineker[3] as the strengths of fluctuations (V_d and V_o) and the rates of change of the fluctuations (b_d and b_o) are increased, keeping the ratios V^2/b constant. This figure also demonstrates the fact that at long times $\langle x^2(t)\rangle$ is proportional to the time even in the limit where the Markovian theory does not hold.

Figure 2 shows the behavior of $\langle x^2(t)\rangle$ in the intermediate coupling ($V_d=V_o=J$) and intermediate memory regime. It clearly shows coherent or wavelike propagation at short times and diffusive propagation at long times. There is an interesting oscillatory behavior in the intermediate or crossover region. It is not clear whether this oscillatory behavior is a general feature of the crossover from coherent to diffusive motion or is just an artifact of the Poisson bath. Further investigation of this behavior is needed for complete understanding.

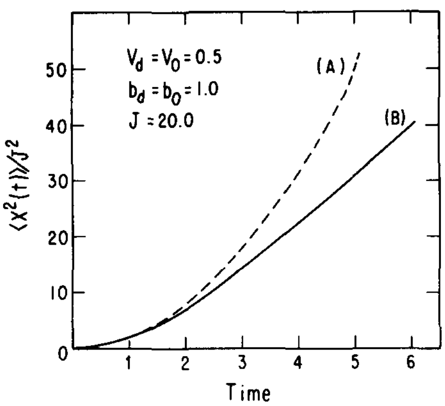

FIG. 3. Comparison between cases (A) and (B) for a large value of the mean off-diagonal coupling J.

When the temperature of the system is lowered, the strengths of the time-dependent couplings become small and the time-independent off-diagonal coupling J begins to play an important role in the exciton migration. In this limit, model (B) should show coherent propagation over a distance considerably larger than the lattice spacing, and should be similar to the prediction of model (A) (same bath). Figure 3 compares the prediction for $\langle x^2(t)\rangle$ from these two models. As expected, values of $\langle x^2(t)\rangle$ lie close to each other over a considerable distance. Model (A) stays coherent even at long times, whereas model (B) becomes diffusive.

Haken and Strobl[2] have put forward the following criteria to determine whether exciton motion is coherent or incoherent. If $\gamma_0 > 2J$, then the motion is incoherent; otherwise it is coherent. Figure 3 clearly shows that the motion can very easily be diffusive even if $V_d^2/b_d > 2J$. Hence, special care must be taken in order to arrive at a physical criterion for diffusive motion. Diffusive behavior in exciton motion does not necessarily mean that the Haken–Strobl limit is valid and a white noise theory is applicable.

V. DISCUSSION

Let us first summarize the basic features of this paper. We have used Kubo's stochastic Liouville equation to investigate the dynamics of exciton migration in the non-Markovian limit. We have considered two different cases of bath fluctuations (i) and (ii) and derived a set of coupled equations for each case which are then solved exactly to obtain the mean squared displacement. These equations are exact when the stochastic baths are Poisson, but, as we have already discussed, they should also have some validity in the long time limit for a Gaussian bath. It is rather pleasing to note that in the framework of the SLE, the Poisson bath naturally arises as a limiting case of the Gaussian bath. Since all the previous calculations on this problem were done for Gaussian baths, the present calculation with a Poisson bath should be regarded as complementary to the earlier theories.

One main result of this work is that exciton migration is coherent at all times for the same bath case [case (i)]. This suggests that at low temperature coherent propagation of excitons can arise from baths becoming correlated over large distances. This interpretation is conceptually somewhat different from the existing explanation[1-3] that the coherent motion at low temperature arises because the ratio J/V becomes very large at low temperature. It is likely that both these mechanisms are responsible for giving rise to coherent motion at low temperature.

For the case of independent bath fluctuations, the exciton migration becomes diffusive at long times in both the Markovian and the non-Markovian limit. If a "van Hove" limit is taken, then we recover the expression of Haken and co-workers for the diffusion constant, but in the non-Markovian limit, the value of the diffusion constant is very different from that predicted by Markovian or weak coupling theories. Since a simple hopping type mechanism of exciton transport is not possible in the non-Markovian limit (where memory effects are important), the long time diffusive behavior ($\langle x^2(t)\rangle \propto t$) is rather interesting. This is similar physically to our earlier work on vibrational energy relaxation[25,32] where we also obtained an exponential decay of population even in the non-Markovian limit with a rate which is very different from the prediction of the weak coupling theories.

There are several questions that can be raised regarding the relevance of the above results to realistic systems. First, at low temperatures, where a Poisson stochastic process may be a reasonable model for the bath, the quantum nature of the bath may become important as well. This will certainly change the quantitative details of our predictions, but we believe that the qualitative features predicted in this paper will remain relevant over a wide range of temperature. Second, the two-level Poisson bath is no doubt an idealization of a more complicated process occurring in real systems and may never be strictly realized in nature. However, we would like to refer to our earlier work[25,32] where we showed that the long time behavior for the two-level Poisson bath and the Gaussian bath (which has an *infinite* number of bath states) is remarkably similar. This indicates that the long-time behavior predicted in this paper, especially the expressions for the diffusion constant, should be semiquantitatively reliable for more general baths. We do not expect the same to be true for short time behavior which will definitely change if we choose a different stochastic bath. An exact calculation for short time exciton transport for a general bath is, unfortunately, very difficult, since the cumulant expansion is unreliable especially at short time in the non-Markovian limit and our formalism becomes numerically less tractable for a general stochastic bath. Third, we have presented expressions for the mean square displacement $\langle x^2(t)\rangle$, but this quantity is generally not directly measured in experiments (although one can conceive of experiments where one region of a crystal is excited and another, a given distance away, is probed). Instead, most experiments involve detection of emission from traps formed by impurities, either isotopic or chemical. Fayer and co-workers[15,26] have discussed extensively the relationship between trapping experiments and exciton motion. We plan to extend our approach to include trap effects in the future, as well as to see the effect on exciton line shapes.

In order to make the theory presented here realistic, so that experimental verification of the predictions is possible, we must have some knowledge of the parameters V_o, V_d, b_o, b_d, and J which must be estimated in a separate microscopic calculation. For a harmonic exciton–bath interaction, it should be possible to carry out such a calculation. For experimental investigation, it is especially important to know the temperature dependences of these quantities. Qualitatively, as temperature is increased, b_o and b_d should increase rapidly, while V_o, V_d, and J, being static properties, should show weaker temperature dependence. Since the temperature dependences of V_o^2/b_o and V_d^2/b_d are known in the Markovian limit (from results of Grover and Silbey[28] and of Haken and Reineker[3]), a reasonable estimate of the temperature dependences of b_o and b_d can easily be obtained.

An important limitation of our approach is that initial conditions appropriate for certain experimental situations may not be easy to incorporate. This is due to the fact that when the molecules are identical, electromagnetic radiation will excite a large number of lattice sites; i.e., the initial exciton will be delocalized. If we are interested only in the long time behavior of exciton migration, then this limitation should not pose a serious problem but the short time behavior may be significantly dependent on the nature of the excitation used to prepare the initial state.

We are now carrying out calculations on the effects of non-Markovian relaxation on the optical line shapes of excitonic states. The effects of correlations in stochastic forces can be more pronounced in this case and the SLE should be a powerful technique for this problem.

ACKNOWLEDGMENTS

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APPENDIX: EQUATIONS OF MOTION FOR THE GENERAL INDEPENDENT BATH CASE

Here we give the complete set of equations for the general independent bath case which involve five independent baths. The first three indices i, j, k in σ_{ijklm} denote the three diagonal fluctuations $V_{k-1,k-1}$, $V_{k,k}$, and $V_{k+1,k+1}$, respectively. The last two indices l and m correspond to $V_{k-1,k}(=V_{k,k-1})$ and $V_{k,k+1}(=V_{k+1,k})$, respectively. In all, there are 44 coupled equations. First we introduce the notation of different terms involved:

$$P_0=\langle x|\sigma_{00000}|x\rangle\ , \tag{A1}$$

$$Z_0=\langle x-a|\sigma_{00000}|x\rangle-\langle x|\sigma_{00000}|x-a\rangle+\langle x+a|\sigma_{00000}|x\rangle-\langle x|\sigma_{00000}|x+a\rangle\ , \tag{A2}$$

$$Z_1=\langle x-a|\sigma_{00010}|x\rangle-\langle x|\sigma_{00010}|x-a\rangle+\langle x+a|\sigma_{00001}|x\rangle-\langle x|\sigma_{00001}|x+a\rangle\ , \tag{A3}$$

$$\begin{aligned}\tilde{Z}_1=&\langle x-a|\sigma_{10000}|x\rangle+\langle x|\sigma_{10000}|x-a\rangle-\langle x-a|\sigma_{01000}|x\rangle\\&-\langle x|\sigma_{01000}|x-a\rangle-\langle x|\sigma_{01000}|x+a\rangle-\langle x+a|\sigma_{01000}|x\rangle+\langle x|\sigma_{00100}|x+a\rangle+\langle x+a|\sigma_{00100}|x\rangle\ ,\end{aligned} \tag{A4}$$

$$Z_2=\langle x|\sigma_{00010}|x\rangle-\langle x-a|\sigma_{00010}|x-a\rangle+\langle x|\sigma_{00001}|x\rangle-\langle x+a|\sigma_{00001}|x+a\rangle\ , \tag{A5}$$

$$Z_3=\langle x|\sigma_{11000}|x-a\rangle-\langle x-a|\sigma_{11000}|x\rangle+\langle x|\sigma_{01100}|x+a\rangle-\langle x+a|\sigma_{01100}|x\rangle\ , \tag{A6}$$

$$Z_4=\langle x-a|\sigma_{11000}|x-a\rangle-\langle x|\sigma_{11000}|x\rangle+\langle x+a|\sigma_{01100}|x+a\rangle-\langle x|\sigma_{01100}|x\rangle\ , \tag{A7}$$

$$Z_5=\langle x-a|\sigma_{11010}|x-a\rangle-\langle x|\sigma_{11010}|x\rangle+\langle x+a|\sigma_{01101}|x+a\rangle-\langle x|\sigma_{01101}|x\rangle\ , \tag{A8}$$

$$Z_6=\langle x+a|\sigma_{00010}|x\rangle-\langle x|\sigma_{00010}|x+a\rangle+\langle x-a|\sigma_{00001}|x\rangle-\langle x|\sigma_{00001}|x-a\rangle\ , \tag{A9}$$

$$Z_7=\langle x+a|\sigma_{00011}|x\rangle-\langle x|\sigma_{00011}|x+a\rangle+\langle x-a|\sigma_{00011}|x\rangle-\langle x|\sigma_{00011}|x-a\rangle\ , \tag{A10}$$

$$\begin{aligned}Z_8=&\langle x-a|\sigma_{10010}|x\rangle-\langle x-a|\sigma_{01010}|x\rangle-\langle x|\sigma_{01010}|x-a\rangle+\langle x|\sigma_{10010}|x-a\rangle\\&+\langle x+a|\sigma_{00101}|x\rangle-\langle x+a|\sigma_{01001}|x\rangle-\langle x|\sigma_{01001}|x+a\rangle+\langle x|\sigma_{00101}|x+a\rangle\ ,\end{aligned} \tag{A11}$$

$$Z_9=\langle x|\sigma_{11000}|x+a\rangle-\langle x+a|\sigma_{11000}|x\rangle+\langle x|\sigma_{01100}|x-a\rangle-\langle x-a|\sigma_{01100}|x\rangle\ , \tag{A12}$$

$$Z_{10}=\langle x|\sigma_{11010}|x-a\rangle-\langle x-a|\sigma_{11010}|x\rangle+\langle x|\sigma_{01101}|x+a\rangle-\langle x+a|\sigma_{01101}|x\rangle\ , \tag{A13}$$

$$Z_{11}=\langle x|\sigma_{11001}|x+a\rangle-\langle x+a|\sigma_{11001}|x\rangle+\langle x|\sigma_{01110}|x-a\rangle-\langle x-a|\sigma_{01110}|x\rangle\ , \tag{A14}$$

$$Z_{12}=\langle x|\sigma_{11010}|x+a\rangle-\langle x+a|\sigma_{11010}|x\rangle+\langle x|\sigma_{01101}|x-a\rangle-\langle x-a|\sigma_{01101}|x\rangle\ , \tag{A15}$$

$$Z_{13}=\langle x|\sigma_{11011}|x+a\rangle-\langle x+a|\sigma_{11011}|x\rangle+\langle x|\sigma_{01111}|x-a\rangle-\langle x-a|\sigma_{01111}|x\rangle\ , \tag{A16}$$

$$Z_{14}=\langle x|\sigma_{00010}|x\rangle-\langle x+a|\sigma_{00010}|x+a\rangle+\langle x|\sigma_{00001}|x\rangle-\langle x-a|\sigma_{00001}|x-a\rangle\ , \tag{A17}$$

$$\begin{aligned}Z_{15}=&\langle x+a|\sigma_{00110}|x\rangle-\langle x+a|\sigma_{01010}|x\rangle-\langle x|\sigma_{01010}|x+a\rangle+\langle x|\sigma_{00110}|x+a\rangle\\&+\langle x-a|\sigma_{10001}|x\rangle-\langle x-a|\sigma_{01001}|x\rangle-\langle x|\sigma_{01001}|x-a\rangle+\langle x|\sigma_{10001}|x-a\rangle\ ,\end{aligned} \tag{A18}$$

$$Z_{16}=2\langle x|\sigma_{00011}|x\rangle-\langle x+a|\sigma_{00011}|x+a\rangle-\langle x-a|\sigma_{00011}|x-a\rangle\ , \tag{A19}$$

$$\begin{aligned}Z_{17}=&\langle x+a|\sigma_{00111}|x\rangle-\langle x+a|\sigma_{01011}|x\rangle-\langle x|\sigma_{01011}|x+a\rangle+\langle x|\sigma_{00111}|x+a\rangle\\&+\langle x-a|\sigma_{10011}|x\rangle-\langle x-a|\sigma_{01011}|x\rangle-\langle x|\sigma_{01011}|x-a\rangle+\langle x|\sigma_{10011}|x-a\rangle\ ,\end{aligned} \tag{A20}$$

$$Z_{18}=\langle x+a|\sigma_{11000}|x+a\rangle-\langle x|\sigma_{11000}|x\rangle+\langle x-a|\sigma_{01100}|x-a\rangle-\langle x|\sigma_{01100}|x\rangle\ , \tag{A21}$$

$$Z_{19}=\langle x+a|\sigma_{11001}|x+a\rangle-\langle x|\sigma_{11001}|x\rangle+\langle x-a|\sigma_{01110}|x-a\rangle-\langle x|\sigma_{01110}|x\rangle\ , \tag{A22}$$

$$Z_{20}=\langle x|\sigma_{10000}|x+a\rangle+\langle x+a|\sigma_{10000}|x\rangle+\langle x|\sigma_{00100}|x-a\rangle+\langle x-a|\sigma_{00100}|x\rangle\ , \tag{A23}$$

$$Z_{21}=\langle x|\sigma_{11100}|x+a\rangle+\langle x+a|\sigma_{11100}|x\rangle+\langle x|\sigma_{11100}|x-a\rangle+\langle x-a|\sigma_{11100}|x\rangle\ , \tag{A24}$$

$$Z_{22}=\langle x|\sigma_{10001}|x+a\rangle+\langle x+a|\sigma_{10001}|x\rangle+\langle x|\sigma_{00110}|x-a\rangle+\langle x-a|\sigma_{00110}|x\rangle\ , \tag{A25}$$

$$Z_{23}=\langle x|\sigma_{11101}|x+a\rangle+\langle x+a|\sigma_{11101}|x\rangle+\langle x|\sigma_{11110}|x-a\rangle+\langle x-a|\sigma_{11110}|x\rangle\ , \tag{A26}$$

$$Z_{24}=\langle x+a|\sigma_{11010}|x+a\rangle-\langle x|\sigma_{11010}|x\rangle+\langle x-a|\sigma_{01101}|x-a\rangle-\langle x|\sigma_{01101}|x\rangle\ , \tag{A27}$$

$$Z_{25}=\langle x+a|\sigma_{11011}|x+a\rangle-\langle x|\sigma_{11011}|x\rangle-\langle x-a|\sigma_{01111}|x-a\rangle-\langle x|\sigma_{01111}|x\rangle\ , \tag{A28}$$

$$Z_{26}=\langle x|\sigma_{10010}|x+a\rangle+\langle x+a|\sigma_{10010}|x\rangle+\langle x|\sigma_{00101}|x-a\rangle+\langle x-a|\sigma_{00101}|x\rangle\ , \tag{A29}$$

$$Z_{27}=\langle x|\sigma_{11110}|x+a\rangle+\langle x+a|\sigma_{11110}|x\rangle+\langle x|\sigma_{11101}|x-a\rangle+\langle x-a|\sigma_{11101}|x\rangle\ , \tag{A30}$$

$$Z_{28}=\langle x|\sigma_{10011}|x+a\rangle+\langle x+a|\sigma_{10011}|x\rangle+\langle x|\sigma_{00111}|x-a\rangle+\langle x-a|\sigma_{00111}|x\rangle\ , \tag{A31}$$

$$Z_{29}=\langle x|\sigma_{11111}|x+a\rangle+\langle x+a|\sigma_{11111}|x\rangle+\langle x|\sigma_{11111}|x-a\rangle+\langle x-a|\sigma_{11111}|x\rangle\ , \tag{A32}$$

$$Z_{30}=\langle x|\sigma_{01110}|x+a\rangle-\langle x+a|\sigma_{01110}|x\rangle+\langle x|\sigma_{11001}|x-a\rangle-\langle x-a|\sigma_{11001}|x\rangle\ , \tag{A33}$$

$$Z_{31}=\langle x|\sigma_{01111}|x+a\rangle-\langle x+a|\sigma_{01111}|x\rangle+\langle x|\sigma_{11011}|x-a\rangle-\langle x-a|\sigma_{11011}|x\rangle\ , \tag{A34}$$

$$Z_{32}=\langle x|\sigma_{10100}|x+a\rangle-\langle x+a|\sigma_{10100}|x\rangle+\langle x|\sigma_{10100}|x-1\rangle-\langle x-1|\sigma_{10100}|x\rangle\ , \tag{A35}$$

$$Z_{33}=\langle x|\sigma_{10101}|x+a\rangle-\langle x+a|\sigma_{10101}|x\rangle+\langle x|\sigma_{10110}|x-a\rangle-\langle x-a|\sigma_{10110}|x\rangle\ , \tag{A36}$$

$$Z_{34}=\langle x+a|\sigma_{10110}|x\rangle-\langle x|\sigma_{10110}|x+a\rangle+\langle x-a|\sigma_{10101}|x\rangle-\langle x|\sigma_{10101}|x-a\rangle\ , \tag{A37}$$

$$Z_{35}=\langle x+a|\sigma_{10111}|x\rangle-\langle x|\sigma_{10111}|x+a\rangle+\langle x-a|\sigma_{10111}|x\rangle-\langle x|\sigma_{10111}|x-a\rangle\ , \tag{A38}$$

$$Z_{36}=\langle x+a|\sigma_{01110}|x+a\rangle-\langle x|\sigma_{01110}|x\rangle+\langle x-a|\sigma_{11001}|x-a\rangle-\langle x|\sigma_{11001}|x\rangle\ , \tag{A39}$$

$$Z_{37}=\langle x+a|\sigma_{01111}|x+a\rangle-\langle x|\sigma_{01111}|x\rangle+\langle x-a|\sigma_{11011}|x-a\rangle-\langle x|\sigma_{11011}|x\rangle\ , \tag{A40}$$

$$Z_{38}=\langle x+a|\sigma_{10100}|x+a\rangle+\langle x-a|\sigma_{10100}|x-a\rangle-2\langle x|\sigma_{10100}|x\rangle\ , \tag{A41}$$

$$Z_{39}=\langle x+a|\sigma_{10101}|x+a\rangle-\langle x|\sigma_{10101}|x\rangle+\langle x-a|\sigma_{10110}|x-a\rangle-\langle x|\sigma_{10110}|x\rangle\ , \tag{A42}$$

$$Z_{40}=\langle x|\sigma_{10110}|x\rangle+\langle x|\sigma_{10101}|x\rangle-\langle x+a|\sigma_{10110}|x+a\rangle-\langle x-a|\sigma_{10101}|x-a\rangle\ , \tag{A43}$$

$$Z_{41}=\langle x+a|\sigma_{10111}|x+a\rangle+\langle x-a|\sigma_{10111}|x-a\rangle-2\langle x|\sigma_{10111}|x\rangle\ . \tag{A44}$$

Next we present the coupled equations of motion. In these equations, dots refer to time derivatives and primes to spatial coordinate derivatives:

$$\dot{P}_0=iJZ_0-iV_0Z_1\ , \tag{A45}$$

$$Z_0=2iJ^2P_0''-iV_d\tilde{Z}_1-2iV_0Z_2\ , \tag{A46}$$

$$\dot{Z}_1=-2iJZ_2-iV_dZ_8+2iV_0a^2P_0''-b_0Z_1\ , \tag{A47}$$

$$\dot{\tilde{Z}}_1=-2iV_dZ_0-2iV_dZ_3-b_d\tilde{Z}_1\ , \tag{A48}$$

$$\dot{Z}_2=-2iJZ_1-iJZ_6-2iV_0Z_0-iV_0Z_7-b_0Z_2\ , \tag{A49}$$

$$\dot{Z}_3=-2iJZ_4-iV_d\tilde{Z}_1-2iV_0Z_5-2b_dZ_3\ , \tag{A50}$$

$$\dot{Z}_4=-2iJZ_3-iJZ_9-2iV_0Z_{10}-iVZ_{11}-2b_dZ_4\ , \tag{A51}$$

$$\dot{Z}_5=-2iJZ_{10}-iJZ_{12}-2iV_0Z_3-iV_0Z_{13}-2b_dZ_5-b_0Z_5\ , \tag{A52}$$

$$\dot{Z}_6=-2iJZ_{14}-iV_dZ_{15}-2iV_0Z_{16}-b_0Z_6\ , \tag{A53}$$

$$\dot{Z}_7=-2iJZ_{16}-2iV_0Z_{14}-iV_dZ_{17}-2b_0Z_7\ , \tag{A54}$$

$$\dot{Z}_8=-2iV_dZ_1-2iV_dZ_{10}-(b_o+b_d)Z_8\ , \tag{A55}$$

$$\dot{Z}_9=-2iJZ_{18}-2iV_0Z_{19}-iV_dZ_{20}+iV_dZ_{21}-2b_dZ_9\ , \tag{A56}$$

$$\dot{Z}_{10}=-2iJZ_5-2iV_0Z_4-iV_dZ_8-(2b_d+b_0)Z_{10}\ , \tag{A57}$$

$$\dot{Z}_{11} = -2iJZ_{19} - 2iV_0 Z_{18} - iV_d Z_{22} + iV_d Z_{23} - (2b_d + b_0) Z_{11} , \tag{A58}$$

$$\dot{Z}_{12} = -2iJZ_{24} - 2iV_0 Z_{25} + iV_d Z_{26} - iV_d Z_{27} - (2b_d + b_0) Z_{12} , \tag{A59}$$

$$\dot{Z}_{13} = -2iJZ_{25} - 2iV_0 Z_{24} - iV_d Z_{28} + iV_d Z_{29} - (2b_d + 2b_0) Z_{13} , \tag{A60}$$

$$\dot{Z}_{14} = -iJZ_1 - 2iJZ_6 - iV_0 Z_0 - 2iV_0 Z_7 - b_0 Z_{14} , \tag{A61}$$

$$\dot{Z}_{15} = -2iV_d Z_6 - 2iV_d Z_{30} - (b_0 + b_d) Z_{15} , \tag{A62}$$

$$\dot{Z}_{16} = -a^2 P''_{00011} ; \quad P_{00011} = \langle x | \sigma_{00011} | x \rangle , \tag{A63}$$

$$\dot{P}_{00011} = -iJZ_7 - iV_0 Z_6 - 2b_0 P_{00011} , \tag{A64}$$

$$\dot{Z}_{17} = -2iV_d Z_7 - 2iV_d Z_{31} - (b_d + 2b_0) Z_{17} , \tag{A65}$$

$$\dot{Z}_{18} = -2iJZ_9 - 2iV_0 Z_{11} - iV_0 Z_{10} - 2b_d Z_{18} , \tag{A66}$$

$$\dot{Z}_{19} = -2iJZ_{11} - iJZ_{30} - 2iV_0 Z_9 - iV_0 Z_{31} - (2b_d + b_0) Z_{19} , \tag{A67}$$

$$\dot{Z}_{20} = -iV_d Z_9 + iV_d Z_{32} - b_d Z_{20} , \tag{A68}$$

$$\dot{Z}_{21} = -iV_d Z_{32} + iV_d Z_9 - 3b_d Z_{21} , \tag{A69}$$

$$\dot{Z}_{22} = -iV_d Z_{11} + iV_d Z_{33} - (b_0 + b_d) Z_{22} , \tag{A70}$$

$$\dot{Z}_{23} = -iV_d Z_{33} + iV_d Z_{11} - (3b_d + b_0) Z_{23} , \tag{A71}$$

$$\dot{Z}_{24} = -2iJZ_{12} - iJZ_{10} - 2iV_0 Z_{13} - iV_0 Z_3 - (2b_d + b_0) Z_{24} , \tag{A72}$$

$$\dot{Z}_{25} = -2iJZ_{13} - iJZ_{31} - 2iV_0 Z_{12} - iV_0 Z_{30} - (2b_d + 2b_0) Z_{25} , \tag{A73}$$

$$\dot{Z}_{26} = -iV_d Z_{12} - iV_d Z_{34} - (b_0 + b_d) Z_{26} , \tag{A74}$$

$$\dot{Z}_{27} = iV_d Z_{12} + iV_d Z_{34} - (3b_d + b_0) Z_{27} , \tag{A75}$$

$$\dot{Z}_{28} = -iV_d Z_{13} - iV_d Z_{35} - (b_d + b_0) Z_{28} , \tag{A76}$$

$$\dot{Z}_{29} = iV_d Z_{13} + iV_d Z_{35} - (3b_d + 2b_0) Z_{29} , \tag{A77}$$

$$\dot{Z}_{30} = -2iJZ_{36} - 2iV_0 Z_{37} - iV_d Z_{15} - (2b_d + b_0) Z_{30} , \tag{A78}$$

$$\dot{Z}_{31} = -2iJZ_{37} - 2iV_0 Z_{36} - iV_d Z_{17} - (2b_d + 2b_0) Z_{31} , \tag{A79}$$

$$\dot{Z}_{32} = -2iJZ_{38} - 2iV_0 Z_{39} + iV_d Z_{20} - iV_d Z_{21} - 2b_d Z_{32} , \tag{A80}$$

$$\dot{Z}_{33} = -2iJZ_{39} - 2iV_0 Z_{38} + iV_d Z_{22} - iV_d Z_{23} - (2b_d + b_0) Z_{33} , \tag{A81}$$

$$\dot{Z}_{34} = -2iJZ_{40} + 2iV_0 Z_{41} - iV_d Z_{26} + iV_d Z_{27} - (2b_d + b_0) Z_{34} , \tag{A82}$$

$$\dot{Z}_{35} = 2iJZ_{41} - 2iV_0 Z_{40} - iV_d Z_{28} + iV_d Z_{29} - (2b_d + 2b_0) Z_{35} \tag{A83}$$

$$\dot{Z}_{36} = -2iJZ_{30} - 2iV_0 Z_{31} - (2b_d + b_0) Z_{36} , \tag{A84}$$

$$\dot{Z}_{37} = -2iJZ_{31} - 2iV_0 Z_{30} - (2b_d + 2b_0) Z_{37} , \tag{A85}$$

$$\dot{Z}_{38} = a^2 P''_{10100} ; \quad P_{10100} = \langle x | \sigma_{10100} | x \rangle , \tag{A86}$$

$$\dot{P}_{10100} = -iJZ_{32} - iV_0 Z_{33} - 2b_d P_{10100} , \tag{A87}$$

$$\dot{Z}_{39} = -2iJZ_{33} - 2iV_0 Z_{32} + iJZ_{34} + iV_0 Z_{35} - (2b_d + b_0) Z_{39} , \tag{A88}$$

$$\dot{Z}_{40} = -2iJZ_{34} + iJZ_{33} - 2iV_0 Z_{35} + iV_0 Z_3 - (2b_d + b_0) Z_{40} , \tag{A89}$$

$$\dot{Z}_{41} = a^2 P''_{10111} ; \quad P_{10111} = \langle x | \sigma_{10111} | x \rangle , \tag{A90}$$

$$\dot{P}_{10111} = -iJZ_{35} - iV_0 Z_{34} - (2b_d + 2b_0) P_{10111} . \tag{A91}$$

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