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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have developed a fairly complete picture of the behavior of a variety of linear excitations nonlinearly coupled to a bath of phonons. The role of solitons and of polarons in the parameter phase space and the nature of the transport of excitation energy in molecular aggregates has been considerably clarified through our work. We now understand a great deal about the effects of quantum and thermal fluctuations on the transport of energy in such systems.

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PUBLICATIONS AND REPORTS

The following publications and reports have been produced as a consequence of the work carried out under this contract:

1. K. Lindenberg and B. J. West, "The First, The Biggest, and Other Such Considerations," *J. Stat. Phys.* **42**, 201 (1986).

We investigate the relation between the underlying dynamics of randomly evolving systems and the extrema statistics for such systems. Independent processes, Fokker-Planck processes and Lévy processes are considered. Our results can be summarized as follows:

a. For statistically independent processes, extrema can be categorized by three types of distributions. Each of these extrema distributions is characterized by parameters determined from phenomenological probability distribution deduced from the data. For many purposes this formulation of extremal statistics is adequate.

b. One may wish to understand the relation of the phenomenological probability distribution to the underlying dynamical process. For diffusive processes this relation is well established and provides analytic asymptotic expressions for the survival probability. These expressions rely entirely on knowledge of the steady-state properties of the system.

c. For nondiffusive processes the relation between the underlying dynamics and the extrema distribution is less well known. We provide approximate results that appear to be satisfactory in those cases where a basis for comparison is available. For nondiffusive processes one needs to know the dynamical behavior (and not just the steady state properties) of the system in order to arrive at these results.

d. One must distinguish between survival probabilities when failure occurs at a preset level from those that involve a probability of failure at each level. In the former case the survival probability depends on the level, whereas in the latter an average over levels is performed. This averaging procedure can profoundly influence the time dependence of the survival probability.

2. D. W. Brown, K. Lindenberg and B. J. West, "On the Dynamics of Polaron Formation in a Deformable Medium," *J. Chem. Phys.* **84**, 1574 (1986).

We consider the standard model for exciton transport in which the energy of interaction between the exciton and the lattice is linear in the lattice coordinates and local in the exciton coordinates. We focus on the dynamics of polaron formation by restricting our analysis to the immobile exciton limit in which the model is exactly solvable. We study the evolution of the many-body system from initial states representing a bare exciton in a quiescent bare lattice and a polaron in a quiescent dressed lattice. The total energy, the dynamical energy content of the bare lattice, the deformation of the bare lattice, and the many-body Green functions are calculated exactly. The reduced density matrix appropriate to each initial contition is obtained exactly for any temperature.

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The picture of the dressing process which emerges from this analysis involves two energy transfer processes which may occur on different time scales. Neither process is that usually connoted by the term "energy transfer", since this term is commonly applied to transport of energy through the resonant processes we have neglected in assigning the resonant transfer matrix element the value zero. The first energy transfer process is the transfer of energy from the bare exciton space into the bare lattice space. We have referred to this process as intersystem energy transfer, since in the present context there can be no confusion with singlet-triplet conversion. The second energy transfer process is the dispersal of the energy transferred into the bare lattice space. We have referred to this process as sound propagation, since we have been able to identify the sound speed as the parameter controlling the dispersal.

We have been able to conclude that while intersystem energy transfer occurs on a time scale which may be arbitrarily short, the dressing process by which a bare immobile exciton evolves toward a polaron-like state proceed on the time scale of sound propagation. this conclusion is reached on the basis of the appearance of similar time dependences in the approaches of the bare lattice deformation, many-body Green functions, and the reduced density matrix to their asymptotic forms, while a distinct time dependence is found for the intersystem energy transfer.

The bare lattice in its asymptotic state is seen to contain a stationary distortion, identical to that found for the polaron, together with paired distortions propagating at the sound velocity away from the excitation region. the difference in the asymptotic condition of the lattice in the two cases is responsible for an important contrast between our Green function and density matrix results: Green functions show that although the asymptotic many-body state is more similar to a polaron state than a bare exciton state, the polaron "component" of the wave function maintains a constant magnitude throughout the dressing process. On the other hand, the reduced density matrix representing an ensemble of initially bare excitons is found at long times to approach the density matrix representing an ensemble of similarly prepared polarons. Thus, while the asymptotic state of an initially bare exciton is only polaron-*like*, the qualifier is needed only to specify a condition of the lattice which is irrelevant to the reduced description of the asymptotic state.

The relevance of the immobile exciton dynamics to exciton transport is established through the identification of the dissipative kernel in our exciton transport theory with the time-dependent profile of the bare lattice energy in the immobile exciton model.

3.   J. Masoliver, K. Lindenberg and B. J. West, "First-passage Times for Non-Markovian Processes," *Phys. Rev. A* 33, 2177 (1986).

First-passage time statistics for non-Markovian processes have heretofore only been developed for processes driven by dichotomous fluctuations that are themselves Markov. Herein we develop a new method applicable to Markov and non-Markovian dichotomous fluctuation and calculate analytic mean first-passage times for particular examples.

We find that in general for a given value of the mean time between switches of the value of the noise, the mean first-passage time for the process to reach a boundary is longer (shorter) for a process driven by the non-Markovian fluctuations is the initial state is very near to the lower (upper) boundary and the process begins with a positive slope. The differences in the mean first-passage times of the processes driven by Markov and non-Markovian dichotomous fluctuations are most pronounces when the mean distance covered in one interval is comparable to the distance between the boundaries. When the mean distance covered in one interval is very small, the process becomes diffusive, while a larger value of this distance leads in either case to a mean first-passage time representing a direct arrival at the boundary during the first interval.

4.   D. W. Brown, K. Lindenberg and B. J. West, "Applicability of Hamilton's Equations in the Quantum Soliton Problem," *Phys. Rev. A* 33, 4104 (1986).

We test the validity of Hamilton-equation methods for determining the time evolution of trial state vectors in quantum mechanics. Given a trial state vector, we are able to construct a differential operator under which a scalar Hamilton function must be invariant. state vectors composed of single-particle states, coherent-state products, and mixed single-particle states and coherent-state products are considered explicitly. In the latter category, we consider state vectors of the form proposed by Davydov in his treatment of the quantum soliton problem. We find that Davydov's wave vector, as determined by the Hamilton-equation method, is not a solution of the Schrödinger

equation for the Fröhlich Hamiltonian except under very restrictive circumstances. The theoretical justification for a number of conclusions about soliton transport in Fröhlich-type systems is thus called into question.

Unfortunately, the differential invariance condition we have derived does not provide a measure of the deviation of Hamilton-equation solutions having the same initial form. An extensive examination of this difficulty is presented in some of our subsequent papers.

5.   D. W. Brown, B. J. West and K. Lindenberg, "Davydov Solitons: New Results at Variance with Standard Derivations," *Phys. Rev. A* 33, 4110 (1986).

We consider two applications of a method introduced by Davydov for the purpose of modeling energy transport in deformable molecular chains. By specializing to the immobile-exciton limit in which the quantum-mechanical problem is exactly solvable, each application of the method is shown to suffer disagreement with the exact dynamics. Expectation values providing measures of the chain deformation and of the energy content of the chain vibrations are calculated explicitly, as are inner products of model state vectors with corresponding exact state vectors. We show that predictions based on Davydov's methods may differ substantially from the corresponding exact results under experimentally relevant conditions.

6.   J. Masoliver, K. Lindenberg and B. J. West, "First-passage Times for Non-Markovian Processes: Correlated Impacts on a Free Process," *Phys. Rev.* 34, 1481 (1986).

We develop a method to obtain first-passage-time statistics for non-Markovian processes driven by dichotomous fluctuations. The fluctuations themselves need not be Markovian. We calculate analytic first-passage-time distributions and mean first-passage times for exponential, rectangular, and long-tail temporal distributions of the fluctuations.

We conclude that the mean first-passage time is a sensitive function not only of the correlation time of the fluctuations that drive a process but also of the detailed form of the temporal distribution of these fluctuations. It is worth emphasizing that this is the first method capable of dealing analytically with non-Markovian fluctuations. We have also been able to generalize the formalism to dynamical systems subject to a potential.

7.   D. W. Brown, K. Lindenberg and B. J. West, "Nonlinear Density-Matrix Approach for the Finite-Temperature Soliton Problem," *Phys. Rev. Letters* 57, 2341 (1986).

The essential ideas of Davydov's theory of molecular solitons are used to develop a variation of the Zwanzig-Nakajima projection technique. The projections operator is time dependent and contains the feedback characteristic of the soliton dynamic. The result is a nonlinear equation of motion for a reduced density matrix. A Markovian approximation is considered which contributes corrections to the Davydov-type evolution. The approximate equation of motion embodies the correct fluctuation-dissipation relation for this system and recovers the known exact results in the transportless limit.

8.   J. Masoliver, B. J. West and K. Lindenberg, "Non-Markovian Dynamics of One-dimensional Trapping Problems," in *Transport and Relaxation in Random Materials*, eds. J. Klafter, R. Rubin and M. F. Shlesinger (World Scientific, Singapore, 1986).

We calculate the trapping times and survival probabilities for an excitation in a one-dimensional system with a random trap distribution. The excitation dynamics are generated by fluctuations that may have a finite correlation time, leading to non-Markovian dynamics of the excitation.

When the survival probabilities are considered as a function of a suitably scaled time, one observes a general scaling phenomenon that would indicate a common stretched exponential behavior with different numerical coefficients and prefactors for all the processes considered in this work. We stress that these results are contingent on the particular choice made here for the distribution of traps. Whether in fact these are general effects which persist independently of the choice of distribution remains an open question.

9.   D. W. Brown, K. Lindenberg and B. J. West, "Nonlinear Density-Matrix Equation for the Study of Finite-Temperature Soliton Dynamics," *Phys. Rev. B* **35**, 6169 (1987).

The essential ideas of Davydov's theory of molecular solitons are used to develop a variation of the Zwanzig-Nakajima projection technique. The new projection operator is time dependent and contains the feedback characteristics of the soliton dynamic. The result is a nonlinear equation of motion for the reduced density matrix of an exciton interacting cooperatively with its thermal environment. As the simplest approximation to the exact projected equation, we consider briefly a factored density operator which corresponds closely to the ansatz state vector used in wave-function treatments. This simplest approximation may be considered to be a statistical generalization of the Davydov system of evolution equations. A Markovian approximation is then considered which goes beyond the simplest approximation and contributes corrections to the Davydov-type evolution. The terms of the Markovian equation are then examined in the light of known exact results. Arguments for specific modifications of the equation are given. The resulting equation of motion embodies the correct fluctuation-dissipation relation for this sytem and recovers the known exact results in the transportless limit. Though the concluding equation is semiphenomenological, the equation contains no phenomenological parameters. All parameters appearing in the final equation are present in the Hamiltonian itself, so that given a well-defines Hamiltonian the final theory contains no adjustable parameters.

10.   D. W. Brown, K. Lindenberg and B. J. West, "Quantum Coherence and the Nonlinear Schrödinger Equation," in *Nonlinearity in Condensed Matter*, eds. A. R. Bishop, D. K. Campbell, P. Kumar and S. E. Trullinger (Springer-Verlag, Berlin, 1987).

We show how the validity of Hamilton equation methods for determining the time evolution of trial state vectors in quantum mechanics may be tested. We show how an ansatz state vector consisting of a product of coherent states allows a differential operator to be constructed under which a scalar Hamilton function must be invariant. Since the Hamilton equations for the coherent state amplitudes are derived without approximation from the exact Heisenberg equations of motion for creation and annihilation operators, the differential invariance condition provides information about the admissibility of coherent state products as state vectors and the validity of the equations of motion subsequently derived. We conclude that the nonlinear Schrödinger equations obtained from the coherent state ansatz do not describe the evolution of a state vector in *any* quantum system.

11.   D. W. Brown, K. Lindenberg and B. J. West, "Towards a Unified Description of Polaron and Soliton Transport," *J. Lumin.* **38**, 116 (1987).

The excited states of a regular molecular aggregate differ from the corresponding excited states of a single molecule in two ways: The intermolecular excited state interactions lead to the formation of extended states that form a band, and the interactions of the excited states with the mechanical motions of the medium lead to lattice distortions that accompany the electronic (or vibronic) excitations. A ubiquitous problem in these systems is the treatment of this patter interaction, which is typically strong and cannot be dealt with perturbatively. It is universally agreed that the cooperative interaction of an excited state with the deformation or polarization modes of the medium results in dynamics profoundly different from those of the uncoupled entities, but the nature of the resulting dynamics is still a matter of much controversy.

Much of the literature on the problem makes use of "dressing" transformations to find a set of "polaron" states that are "almost" eigenstates of the Hamiltonian. A growing body of work approaches the problem in a completely different way, making use of variational principles that lead to the identification of the quasiparticle as a "soliton". The connection between these two approaches has remained obscure.

We have developed a new description of the dynamics of an excitation interacting cooperatively with a fluctuating medium. All exact and many approximate known results can be recovered from this equation in appropriate limits. Guided by this development we have begun a detailed "parameter space" characterization of the known features of energy transport and mapped out the known behavior as a function of the four important energy parameters of the system: the exciton bandwidth, the phonon bandwidth, the exciton-photon interaction and the temperature. We find that soliton theory is applicable only in a small region of parameter space, and that the nature of the energy transport process is unknown for most parameter values.

12.   D. W. Brown, K. Lindenberg and B. J. West, "Polaron Band Theory as Linearized Soliton Theory," *Phys. Rev B* **37**, 2946 (1988).

A nonlinear equation of motion developed by us for the study of finite-temperature soliton dynamics is linearized and compared with corresponding results from traditional polaron theory. Numerous points of agreement are found, and points of disagreement are interpreted in the context of the full nonlinear theory. New interpretations of well-known features of traditional polaron theory are made possible through this approach. We have found significant points of agreement in our comparison of the memory functions of the linearized dynamics with the memory functions which characterize polaron band theory. On the other hand, significant differences suggest alternatives to the common interpretations of memory function structure.

13.   K. Lindenberg, D. W. Brown and X. Wang, "A Review of Current Issues in the Quantum Theory of Envelope Solitons," in *Far From Equilibrium Phase Transitions*, ed. L. Garrido (Springer-Verlag, Berlin, 1988).

This chapter presents a review of the theory of envelope solitons based on the original model of Davydov as understood at the time that this review was written. The principal points have been made in the papers preceding this one in this report, and there is therefore no useful purpose gained by repeating them.

At the end of this review we make some comments about the experimental situation surrounding these issues that are still relevant today. It is difficult to design an experiment that will unequivocally distinguish the precise nature of an excitation from among various possibilities. spectral measurements may identify red-shifts (i.e. energy lowering mechanisms), but it is difficult to say whether the collective excitation being observed is a polaron or soliton or yet another structure. such red-shifts have been observed, for instance, in ACN crystals, and have been used to infer the presence of a soliton. Subsequently the observations have been re-interpreted as arising from a polaron. Less equivocal information can be obtained from transport measurements of mobile excitations, a goal that has proven elusive.

14.   D. W. Brown, K. Lindenberg X. Wang, "A Brief Survey of Analytical and Numerical Results from the Theory of Davydov Solitons," in *Singular Behavior and Nonlinear Dynamics*, ed. S. Pnevmatikos, T. Bountis and S. Pnevmatikos (World Scientific, Singapore, 1988).

In this review we focus on two issues. One is the quantum character of the so-called Davydov soliton, and the other is the question of its thermal stability. We briefly preview some of the Monte Carlo results described in more detail in a subsequent paper.

15.   D. W. Brown, B. J. West and K. Lindenberg, "Response of an Insulating Material to Photoexcitation,"in *Unconventional Photoactive solids*, ed. H. Sher (Plenum, New York, 1988).

We focus on the dynamics of polaron formation following photoexcitation of a deformable insulator. A bare exciton is seen to evolve toward a polaron-like state by shedding energy into the vibrations of the medium. The radiated energy propagates away from the excitation region in the form of sound waves, resulting in the emergence of a persistent deformation of the medium about the excitation region.

16.   X. Wang, D. W. Brown and K. Lindenberg, "Quantum Monte Carlo Simulation of the Davydov Model," *Phys. Rev Letter* **62**, 1796 (1989).

Through an application of the quantum Monte Carlo technique, we investigate the thermal equilibrium properties of the one-dimensional model proposed by Davydov for the description of energy transport processes in the α-helix. The deformation of the lattice about a single (moving) excitation is computed over a wide range of temperatures. On the basis of the quantum Monte Carlo calculations we arrive at the following conclusions: 1) A coherent structure exists for temperatures below $7K$; 2) The basic unit of this coherent stricture is highly localized and bears a close resemblance to the Davydov soliton; and 3) above $7K$ thermal fluctuations are effective in destroying the

internal coherence of this basic unit, its destruction being essentially complete above $11.2K$. The *equilibrium* quantity we have presented is not seriously affected by quantum fluctuations, but it is likely that *dynamical* properties would be affected by the presence of intrinsic quantum noise.

17.   X. Wang, D. W. Brown and K. Lindenberg, "Vibron Solitons," *Phys. Rev B* 37, 5366 (1989).

Starting from a general Hamiltonian describing the dynamics of vibrons coupled to acoustic phonons, equations of motion for the dynamical variables are obtained by eliminating the phonon degrees of freedom. Specific results are obtained for the form of this Hamiltonian proposed by Takeno. Vibron number is not conserved in general, which distinguishes our study from others based on the Fröhlich Hamiltonian in which the analogous bosons are conserved. Solitary-wave solutions are found for approximate continuum wave equations obtained employing a coherent-state ansatz under a rotating-wave approximation. Regimes of validity are determined, and within these regimes physically meaningful quantities are computed, including energy - wave-vector relations, frequency - wave-vector relations, binding energies, and effective masses. The role of these in spectroscopy is discussed. Several instabilities are encountered and their origins are traced. Certain of these are argued to be generic and intrinsic to the physics of the problem, while others can be shown to be artifacts of the particular model chosen for specific calculations. The modification of our results caused by discreteness corrections is considered, and the role of thermal fluctuations is discussed.

By examining the dependence of the energy on the mean number of vibron quanta and on the wave vector, we have been able to infer certain characteristics of the mechanisms controlling the decay of an excited state toward thermal equilibrium/ First, we have shown that these exists a unique family of solitary waves which should be highly stable and should dominate dynamics. The existence of these states can be inferred from the fact that the solitary-wave energy band possesses a minimum-energy envelope. The existence of the minimum-energy envelope depends only on the qualitative requirement that the effective local potential softens with increasing amplitude. Second, we have shown that the thermal fluctuations in the Takeno model do not conserve vibron number, and hence allow transitions between solitary-wave families of different vibron quanta. This opens up channels for decay which are forbidden to conserved quanta, and which would appear to destabilize solitary wave states. Indeed, it would appear that over most of **k** space the greatest energy gain is to be had by changing vibron number and hence decaying out of a particular solitary-wave family labeled by the number of quanta/ However, all such decays bring the state of the system closer to the unique family of solitary waves which comprise minimum-energy envelopes.

These findings contrast with well-known characteristics of the Davydov model in which thermal fluctuations are number conserving. The principal effect which number-conserving fluctuations have on a state is to decrease energy through phase randomization - damping - one manifestation of which is a decreasing group velocity. In the Davydov model, decreasing group velocity is accompanied by a *broadening* of the solitary-wave state toward the characteristic width of the zero-wave-vector state set by the coupling strength and the (fixed) number of quanta. The number-conserving fluctuations in the Takeno model also cause damping, which would be manifested on the minimum-energy envelope by movement toward $k = 0$. Unlike any fixed quantum number family of solitary waves in either the Takeno or Davydov models, movement toward $k = 0$ along the minimum-energy envelope is accompanied by a *narrowing* of the solitary wave towards its minimum value at $k = 0$. We conclude that global energy minimization favors energy localization.

18.   X. Wang, D. W. Brown and K. Lindenberg, "A Study of Vibron Solitons," *J. Molec. Liquids* 41, 123 (1989).

This paper is a short version of the previous one for a celebratory issue in honor of Professor G. Careri.

19.   D. W. Brown, "Damping and Undamping in a Simple Model of Quantum Self-Trapping," *Phys. Rev. B* 39, 8122 (1989).

We examine dissipative effects caused by nontrivial lattice memory in a simple model of the self-trapping of a quantum particle in a deformable medium. Dissipation in the transport degrees of freedom can be shown to appear and disappear as a function of time-scale disparity. Evolution in the dissipative regime is strongly influenced by the existence of a favored "reaction path." The properties of this reaction path allow a qualitative characterization of the

equilibrium distribution of a self-trapped quantum particle in a fluctuating environment.

We find that there is a combination of parameters that leads to maximum damping in the regime where lattice and transport time scales are nondisparate. In the nondisparate regime the global structure of the phase flow is determined by a curve of fixed points we have described as a reaction path. Evolutions near the reaction path undergo localization in a two-step process of phase correlation followed by growing asymmetrization of the site occupation probabilities. a knowledge of fixed-point properties allows the thermal equilibrium distribution to be characterized as a quasi-one-dimensional figure sheathing the reaction path.

20. T-M. Wu, D. W. Brown and K. Lindenberg, "A Polaron Mechanism for the Y and E States of Excimer Crystals," *J. Lumin.* **45**, 245 (1990).

We present a model of excimer formation in dimerized materials such as α-perylene. Exact diagonalization of a model Hamiltonian identifies the Y and E states inferred from excimer fluorescence spectra with antisymmetric and symmetric pair states of an exciton confined to a dimer. Our model gives rise to a phonon-assisted transition between the Y and E states which, through an application of the Fermi golden rule, is found to be thermally activated, consistent with experimental findings. Our most significant single result is the conclusion that a satisfactory fit of the α-perylene data requires a large nonlocal exciton-phonon interaction relative to the local one.

21. K. Lindenberg, X. Wang and D. W. Brown, "Vibron Solitons: A Semiclassical Approach," in *Davydov's Solitons Revisited*, eds. P. L. Christiansen and A. C. Scott (Plenum Press, New York, 1990).

The central copy of the conference to which these proceedings are contributed revolved around the soliton mechanism first proposed by Davydov and coworkers as a means of transporting energy in molecular (mainly biological) aggregates. The considerable amount of theoretical advances made in this field have not yet unequivocally answered the question of the possible importance of soliton mechanisms in mechanisms in the transport of biological energy since the starting model in most theories (one-dimensional Fröhlich Hamiltonian) may be well removed from what goes on in real proteins. However, *if* the model is indeed appropriate, then the weight of the evidence suggests that at least in the α-helix soliton transport at room temperature (or even at low temperatures) should not play an important role.

The Fröhlich Hamiltonian describes two linear fields, e.g. an electronic excitation or an intramolecular vibration, and a collection of phonons, interacting nonlinearly with one another. The model contains several features that one may wish to question if one is to relate it to a real physical or biological system. For example, in the Fröhlich interaction one field modulates the local site-energy of the other but not the transfer of excitation from one site to the other. The Fröhlich Hamiltonian conserves the number of excitations in one of the two fields, a restriction which may not be appropriate when the excitation is an intramolecular vibration as in the α-helix. We consider a Hamiltonian first introduced by Takeno that relaxes the second of these restrictions. We find that this opens an avenue for processes that may indeed stabilize the existence of solitons. In particular, we find that in this picture energy relaxation actually *favors* energy localization.

22. T-M. Wu, D. W. Brown and K. Lindenberg, "On the Possible Role of Phonon-Modulated Tunneling in Excimer Formation," in *Davydov's Solitons Revisited*, eds. P. L. Christiansen and A. C. Scott (Plenum Press, New York, 1990).

We present a model of excimer formation based only on the most generic of features of dimerized lattices such as those found in the excimer-forming molecular crystal α-perylene. The modulation of resonance integrals by lattice vibrations is found to cause significant effects consistent with the known characteristics of excimers and the related Y states. A specific calculation of the thermally-activated transition rate from the Y state to the excimer state is in good agreement with experimental observations.

8. **SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:**

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