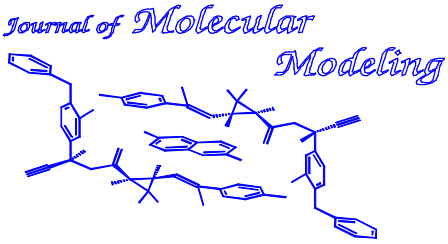
J. Mol. Model. **1996**, *2*, 70 - 102



Davydov Soliton Dynamics in Proteins: I. Initial States and Exactly Solvable Special Cases

Wolfgang Förner

Chair for Theoretical Chemistry and Laboratory of the National Foundation of Cancer Research at the Friedrich-Alexander University Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, FRG. (foerner@pctc.chemie.uni-erlangen.de)

Received: 10 October 1995 / Accepted: 25 March 1996 / Published: 10 May 1996

Abstract

For the Davydov Hamiltonian several special cases are known which can be solved analytically. Starting from these cases we show that the initial state for a simulation using Davydov's $|D_1>$ approximation has to be constructed from a given set of initial lattice displacements and momenta in form of a coherent state with its amplitudes independent of the lattices site, corresponding to Davydov's $|D_2>$ approximation. In the $|D_1>$ ansatz the coherent state amplitudes are site dependent. The site dependences evolve from this initial state exclusively via the equations of motion. Starting the $|D_1>$ simulation from an ansatz with site dependent coherent state amplitudes leads to an evolution which is different from the analytical solutions for the special cases. Further we show that simple construction of such initial states from the expressions for displacements and momenta as functions of the amplitudes leads to results which are inconsistent with the expressions for the lattice energy. The site-dependence of coherent state amplitudes can only evolve through the exciton-phonon interactions and cannot be introduced already in the initial state. Thus also in applications of the $|D_1>$ ansatz to polyacetylene always $|D_2>$ type initial states have to be used in contrast to our previous suggestion [W. Förner, *J. Phys.: Condens. Matter* **1994**, *6*, 9089-9151, on p. 9105]. Further we expand the known exact solutions in Taylor serieses in time and compare expectation values in different orders with the exact results. We find that for an approximation up to third order in time (for the wave function) norm and total energy, as well as displacements and momenta are reasonably correct for a time up to 0.12-0.14 ps, depending somewhat on the coupling strengh for the transportless case. For the oscillator system in the decoupled case the norm is correct up to 0.6-0.8 ps, while the expectation values of the number operators for different sites are reasonably correct up to roughly 0.6 ps, when calculated from the third order wave function. The most important result for the purpose to use such expansions for controlling the validity of ansatz states is, however, that the accuracy of S(t) and H(t) (constant in time, exact values known in all cases) is obviously a general indicator for the time region in which a given expansion yields reliable values also for the other, physically more interesting expectation values.

Keywords: Proteins, Davydov Model, Special Cases, Expansion of Exact Solutions

Introduction

The most recent and best review of the state of art in Davydov soliton theory was given by Scott [1], the leading expert in the field. The problem which Davydov [2-5] attempted to solve with his mechanism was the storage and transport of energy through protein chains. The energy which is to be transported or stored in biological systems is released by the hydrolysis of adenosinetriphosphate (ATP) molecules which amounts to about 0.4 eV (see [2-5] and [1] for further details and references). In Davydov's opinion the best candidate for storing this energy in proteins is the amide-I vibration, which is essentially of C=O stretch type, because one quantum of this vibration has an energy of 0.205 eV, roughly half of the energy released by ATP hydrolysis. From this starting point Davydov developed his physical model for the energy transport. In α–helical proteins the C=O groups of a turn in the helix form hydrogen bonds to the N-H groups in the following turn. As indicated in the following sketch (see section II) these hydrogen bonds form chains parallel to the helix axis and perpendicular to the covalent backbone. There are always three parallel chains of this kind in an α–helix. Within such a chain the C=O oscillators are coupled via their transition dipole moment with each other, where next neighbor coupling is by far the most important term. This type of coupling is a linear one and makes the system dispersive, i.e. an amide-I vibrational quantum at a site would not remain localized, but would be distributed over the complete chain within a few picoseconds (ps).

As next step Davydov considered the fact that the chain of coupled hydrogen bonds forms a phonon system with the peptide units vibrating against each other in the potential due to the hydrogen bonds. These hydrogen bonds are approximated by a harmonic potential. Since the excitation energy of the amide-I oscillators is naturally dependent on the length of the hydrogen bond in which the C=O group takes part, the system of amide-I oscillators is coupled to the acoustic phonon system of the hydrogen bonded chain (the so-called lattice). Considering a linear dependence of the amide-I excitation energy on the length of the hydrogen bond, the coupling constant can be estimated experimentally. Attempts for the theoretical determination of this constant failed (leading mostly even to values with the wrong sign) due to the use of too small atomic basis sets and the lack of electronic correlation in the ab inito Hartree-Fock calculations performed so far (see [1] for a discussion and references). However, the experimental estimates place its value between 35 and 62 pN.

From these considerations Davydov constructed his model Hamiltonian which contains just that details of the protein α–helix which are the most important ones (constructive and destructive) involved in the transport and storage of energy via amide-I vibrations. The Hamiltonian is given in more details in section II. Due to the coupling of the dispersive amide-I system to the lattice, the nonlinear forces occurring can prevent the distribution of an initially localized amide-I excitation over the chain. If the dispersive and the nonlinear forces are balancing each other, the excitation will remain localized on a small number of sites at each time due to the nonlinearity, and the whole system of amide-I excitation together with its stabilizing lattice distortion can move through the system due to dispersion. In other words a solitary wave or a soliton could be formed. However, up to now such solitons have not been observed directly in proteins. Only in acetanilide (ACN) which forms single crystals and contains hydrogen bonded chains of C=O groups as in proteins, pinned solitons (which do not move) of the Davydov-type could be observed spectroscopically by Careri's group (see again Scott's review [1] for a detailed discussion). Since proteins are aperiodic and do not form single crystals an observation of Davydov solitons, if present there, is more or less impossible up to now. Even accurate measurements of the constants appearing in the model is not possible. Therefore it is very important to study the dynamics in the Davydov model theoretically as a function of the parameter values, the degree of disorder and temperature to be able to obtain information whether the formation of solitons is possible at all for reasonable windows in the parameter space or not. Especially it is of utmost importance to obtain approximate solutions of the Schrödinger equation for the Davydov Hamiltonian as close as possible to the unknown exact solutions. This work deals with the latter problem and especially the ansatz states proposed by Davydov for this purpose are investigated. Further we propose a propagation scheme in the conlusion, because in that way the inclusion of temperature effects into the theory is more straightforward than in the case of an ansatz treatment.

These basic concepts of the Davydov soliton mechanism for energy transport in proteins [2-5], as well as the different attempts to include the effects of finite temperature into the model [4-13] and the controversy about thermal stability of protein solitons is discussed in the introduction of Ref. [6]. Therefore we do not want to elaborate on these points here. The extensive discussion on the validity of the different ansatz states used in the literature [14-23] is also reviewed there [6]. The ideas on which the Davydov mechanism is based are nowadays extended also to other systems in more or less similar ways. Davydov himself e.g. used a bisoliton concept to explain high-T_c superconductivity in materials containing copperoxide, and a Hamiltonian similar to that for the description of energy transport in proteins for the explanation of electron transport (electrosoliton) which is important in biological redox processes where proteins serve as catalysators. A wide variety of applications of these ideas is collected and dicussed again by Scott in his review [1].

In a series of papers we dealt mainly with ansatz states which include quantum effects in the lattice into the description and with the inclusion of effects of finite temperature into these theories [6,20, 24-27]. Since already at 0K the $|D_1>$ ansatz is still an approximation, one would like to have a numerical estimate of the errors introduced by this approximate ansatz. Therefore, we presented in Ref. [27] expecta-

tion values of several operators in the state |δ> which represents the error of the $|D_1\rangle$ state if it is substituted into the time dependent Schrödinger equation:

$$\left[i\hbar\left(\partial/\partial t - \hat{H}_D\right)\right] D_1\rangle = J|\delta\rangle \quad .$$

J is one of the parameters in the Hamiltonian (see below). For an exact solution J|δ>=0 would be required. We compared these expectation values with the corresponding ones in the state $\left(\hat{H}_D/J\right)|D_1\rangle$ to get a numerical estimate of the errors occurring. For the sake of comparison the same was done also for the semiclassical so-called $|D_2\rangle$ ansatz [2]. In this study we found that the errors introduced in these expectation values compared to those in the corresponding $\left(\hat{H}_D/J\right)|D_1\rangle$ state are negligible. Since the set of basis states is incomplete when using the $|D_1\rangle$ ansatz, this does not ensure a good quality of the $|D_1\rangle$ approximation, however, it could be expected, that the lack of basis states, if important, should lead to larger errors also within the basis space actually employed, than those we found numerically.

Since we are extending at present the application of $|D_1\rangle$ type ansatz states also to the polyacetylene case [28] it seems to be desirable to obtain some more detailed informations on the limitations of this ansatz. For this purpose we want to expand the exact solution $|\Phi\rangle = \exp\left[-i\hat{H}_D t/\hbar\right]\Phi_0\rangle$ for the Davydov Hamiltonian $\left(\hat{H}_D\right)$, where $|\Phi_o\rangle$ is the initial state, in a Taylor series in time and compare the results with those from a $|D_1\rangle$ simulation. Attempts into this direction have been reported previously by Cruzeiro-Hansson, Christiansen and Scott [29]. However, they restricted their considerations to a dimer and found that second order terms can be neglected only for times much smaller than 0.1 ps. Further they give no comparisons to approximate simulations and for the case of N sites they give a system of equations, but they draw no numerical conclusions from it.

In order to be able to work numerically with such an expansion, we need informations on the time scales in which the different orders are correct. For this purpose we study in the present paper the performance of such expansions for analytically known solutions for some special cases of the Davydov Hamiltonian. We give the analytical solutions and their expansions in Taylor serieses in time. Then we compare norms, total energies, displacements, momenta and expectation values of the number operators for the wave functions in different orders with those obtained from the exact solutions. Further we draw some conclusions on the form of initial states, necessary for reliable $|D_1\rangle$ simulations for these special cases. In the following paper (*J. Mol. Model.*, accepted) we will discuss the results for the complete Davydov Hamiltonian, based on the results of this work.

Finally in the third paper of this series we will present applications of dynamics, obtained with the methods discussed. Specifically we will present vibrational spectra which can be computed directly from simulations obtained with states of $|D_1\rangle$ type. Since the Davydov mechanism was introduced to explain energy storage and transport in proteins, first of all the question of the existence of such solitons in proteins is of utmost important. Our third paper will also deal with this problem. We want to present simulations including temperature effects, and a detailed study on the initial states, from which solitons are formed. Then we need to explain, why in infrared and Raman spectra of polypeptides no signs of solitons in the amide-I region are found, although theoretically they exist. Further, our model after some extensions can be used to study also coupling of the amide-II vibration (where the N-H bonds are stretched) to optical and acoustical lattice phonons. The reason, why such features should be included also is, that experimentally unusual features in the spectra of polypeptides in the amide-II region were found, and still lack an explanation (see [34] for a short review and further references). It is also of importance to apply the model to acetanilide (in modified form, since there the C=O stretching vibration is coupled to optical phonons), because in this case at low temperature the normal amide-I band vanishes and a new solitonic band appears in the Raman spectra (see [1] for discussion and references). Thus the acetanilide case could give additional insight, up to what extent the Davydov model is able to explain measured spectra, especially as function of temperature.

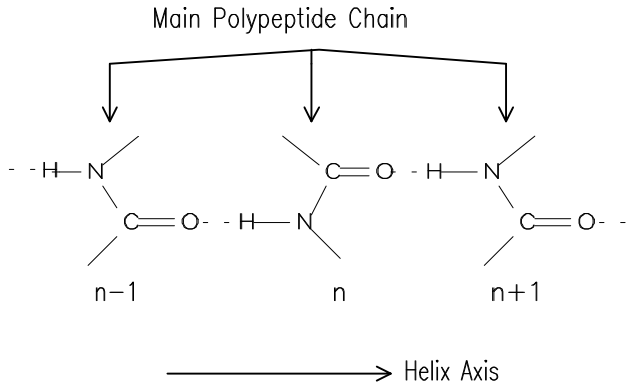
Davydov's Hamiltonian and the $|D_1\rangle$ Approximation

The Hamiltonian, as well as the form of the $|D_1\rangle$ approximation have been discussed extensively in the literature. However, for the purpose of clearcut definitions in the following, we repeat the basic formulas here. The Davydov Hamiltonian for our problem [2] reads as

$$\hat{H}_D = \sum_n \Big[E_0 \hat{a}_n^+ \hat{a}_n - J\left(\hat{a}_n^+ \hat{a}_{n+1} + \hat{a}_{n+1}^+ \hat{a}_n\right) + \frac{\hat{p}_n^2}{2M} + \frac{W}{2}\left(\hat{q}_{n+1} - \hat{q}_n\right)^2 + \chi \hat{a}_n^+ \hat{a}_n \left(\hat{q}_{n+1} - \hat{q}_n\right) \Big] \qquad (1)$$

In equ. (1) $\hat{a}_n^+$ ($\hat{a}_n$) are the usual boson creation (annihilation) operators [4] for the amide-I oscillators at sites n (see sketch at the top of the following page).

From infrared spectra the ground state energy of an isolated amide-I oscillator can be deduced (E_0=0.205 eV). Usually for all parameters in equ. (1) site-independent mean values are used. The average value for the coupling of the transition dipole moments of neighboring amide-I oscillators is J=0.967 meV. The average spring constant of the hydrogen bonds is taken usually to be W=13 N/m, as measured in crystalline formamide. $\hat{p}_n$ is the momentum and $\hat{q}_n$ the position operator of unit n. The mass M of a peptide unit is taken as the mean value of the masses of the units in myosine



(M=114m_p; m_p is the proton mass). The energy of the CO stretching vibration in hydrogen bonds is a function of the length r of the hydrogen bond ($E=E_0+\chi r$). For χ the experimental estimates are between 35 pN and 62 pN. Ab initio calculations on formamide dimers usually lead to χ=30-50 pN, however, with small basis set ab initio calculations even negative values for χ were obtained (see e.g. [1] for a review and references).

The one-particle Hamiltonian [2,3], where one-particle refers to the quanta of the amide-I vibration, in second quantized form is given by

$$\hat{H}_D = \sum_n \left[E_0 \hat{a}_n^+ \hat{a}_n - J\left(\hat{a}_{n+1}^+ \hat{a}_n + \hat{a}_n^+ \hat{a}_{n+1}\right)\right] + \sum_k \hbar\omega_k \left[\hat{b}_k^+ \hat{b}_k + \tfrac{1}{2} + \sum_n B_{nk}\left(\hat{b}_k + \hat{b}_k^+\right)\hat{a}_n^+ \hat{a}_n \right]$$
$$B_{nk} = \frac{\chi}{\omega_k}\frac{1}{\sqrt{2M\hbar\omega_k}}\left[U_{n+1,k} - U_{nk}\right] \qquad (2)$$

$b^\wedge_k{}^+$ ($b^\wedge_k$) are creation (annihilation) operators for acoustic phonons of wave number k. The translational mode has to be excluded from all summations. Note that in the simulations presented we use again the asymmetric interaction model where only the coupling of the oscillator n to the hydrogen bond between n and n+1 in which the oscillator takes part is considered. ω_k denotes the eigenfrequency of the normal mode k and $\underline{\underline{U}}$ contains the normal mode coefficients. $\underline{\omega}$ and $\underline{\underline{U}}$ are obtained by diagonalization of the matrix $\underline{\underline{V}}$ with elements

$$V_{nm} = \frac{W}{M}\left\{2\delta_{nm} - (1-\delta_{nN})\delta_{m,n+1} - (1-\delta_{n1})\delta_{m,n-1} - \delta_{n1}\delta_{mN} - \delta_{nN}\delta_{m1}\right\} \qquad (3)$$

$$\left(\underline{\underline{U}}^+ \underline{\underline{V}}\,\underline{\underline{U}}\right)_{kk'} = \omega_k^2 \delta_{kk'} \quad ; \quad \underline{\underline{U}}^+ \underline{\underline{U}} = \underline{\underline{U}}\,\underline{\underline{U}}^+ = \underline{\underline{1}}$$

The form of $\underline{\underline{V}}$ implies that we use cyclic boundary conditions and N units.

First of all we rewrite our Hamiltonian into the form

$$\hat{H}_D = \hat{H} + E_0 \sum_n \hat{a}_n^+ \hat{a}_n + \tfrac{1}{2}\sum_k \hbar\omega_k \equiv \hat{H} + \hat{D} \quad ;$$
$$\left[\hat{H}, \hat{D}\right] = 0 \qquad (4)$$

For the exact solution the time dependent Schrödinger equation holds:

$$i\hbar \frac{\partial}{\partial t}\left|\Phi\right> = \hat{H}_D \left|\Phi\right> \qquad (5)$$

Now we factorize our exact wave function as

$$\left|\Phi\right> = \exp\left[-\tfrac{it}{\hbar} D\right] \left|\psi\right> \; ; \; D \equiv E_0 + \tfrac{1}{2}\sum_k \hbar\omega_k \qquad (6)$$

Then we obtain (D is a time independent real scalar)

$$\hat{H}_D \left|\Phi\right> = \exp\left[-\tfrac{it}{\hbar} D\right]\cdot\left(\hat{D}\left|\psi\right> + \hat{H}\left|\psi\right>\right)$$
$$i\hbar\tfrac{\partial}{\partial t}\left|\Phi\right> = D\cdot\exp\left[-\tfrac{it}{\hbar} D\right]\left|\psi\right> + \exp\left[-\tfrac{it}{\hbar} D\right]\cdot i\hbar\tfrac{\partial}{\partial t}\left|\psi\right> \qquad (7)$$

We know that the exact wave function can be written in the form

$$\left|\psi\right\rangle = \sum_n \exp\left[\hat{S}_n(t)\right] a_n(t)\hat{a}_n^+ \left|0\right\rangle \qquad (8)$$

where $a_n(t)$ is a complex scalar and |0> the vacuum state. It is known that the generator $\hat{S}_n(t)$ contains only phonon operators and complex scalars (see [16] for details). Therefore we can write

$$\hat{D}\left|\Phi\right\rangle = \exp\left[-\tfrac{it}{\hbar} D\right]\cdot\left(E_0 \sum_{nm} exp\left[\hat{S}_n(t)\right] a_n(t)\hat{a}_m^+ \hat{a}_m \hat{a}_n^+ \left|0\right\rangle + \tfrac{1}{2}\sum_k \hbar\omega_k \left|\psi\right\rangle\right) \qquad (9)$$

$$\hat{a}_m^+ \hat{a}_m \hat{a}_n^+ \left|0\right\rangle = \hat{a}_m^+\left(\delta_{nm} + \hat{a}_n^+ \hat{a}_m\right)\left|0\right\rangle$$
$$\Rightarrow \hat{D}\left|\Phi\right\rangle = D\cdot\exp\left[-\tfrac{it}{\hbar} D\right]\left|\psi\right\rangle$$

Together with equ. (7) this leads to

$$i\hbar\tfrac{\partial}{\partial t}\left|\Phi\right\rangle = \exp\left[-\tfrac{it}{\hbar} D\right]\cdot\left(D + i\hbar\tfrac{\partial}{\partial t}\right)\cdot\left|\psi\right\rangle$$
$$\hat{H}_D\left|\Phi\right\rangle = \exp\left[-\tfrac{it}{\hbar} D\right]\cdot\left(D + \hat{H}\right)\cdot\left|\psi\right\rangle \qquad (10)$$

and therefore from

$$i\hbar\frac{\partial}{\partial t}|\Phi\rangle = \hat{H}_D|\Phi\rangle = \left(E_0\sum_n \hat{a}_n^+\hat{a}_n + \tfrac{1}{2}\sum_k \hbar\omega_k + \hat{H}\right)|\Phi\rangle \tag{11a}$$

follows

$$|\Phi\rangle = \exp\left[-\frac{it}{\hbar}\left(E_0 + \tfrac{1}{2}\sum_k \hbar\omega_k\right)\right]\cdot|\psi\rangle \tag{11b}$$

where $|\psi\rangle$ has to obey the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{12}$$

with the simplified Hamiltonian

$$\hat{H} = -J\sum_n\left(\hat{a}_{n+1}^+\hat{a}_n + \hat{a}_n^+\hat{a}_{n+1}\right) + \\ + \sum_k \hbar\omega_k\left[\hat{b}_k^+\hat{b}_k + \sum_n B_{nk}\left(\hat{b}_k + \hat{b}_k^+\right)\hat{a}_n^+\hat{a}_n\right] \tag{13}$$

A more simple form of this proof is given in Appendix E. Note, that the zero-point energies in the exponential prefactors are present, whether the coupling between amide-I oscillators and the phonons exists or not, since also if χ=0 holds, the lattice is still present in the Hamiltonian. Thus a remark of Kapor [30] on this topic does not apply. The $|D_1\rangle$ ansatz for $|\psi\rangle$ has the form

$$|D_1\rangle = \sum_n a_n(t)\hat{U}_n\hat{a}_n^+|0\rangle \tag{14}$$

where the coherent state operators are given by

$$\hat{U}_n|0\rangle_p = exp\left[-\tfrac{1}{2}\sum_k|b_{nk}(t)|^2\right]\cdot exp\left[\sum_k b_{nk}(t)\hat{b}_k^+\right]|0\rangle_p \\ = exp\left\{\sum_k\left[b_{nk}(t)\hat{b}_k^+ - b_{nk}^*(t)\hat{b}_k\right]\right\}|0\rangle_p \tag{15}$$

Note, that the second equality holds only if the operator acts on the phonon vacuum $|0\rangle_p$, and that in our notation $|0\rangle=|0\rangle_e|0\rangle_p$, where $|0\rangle_e$ is the vacuum state for the amide-I oscillators (exciton vacuum). A simpler form of this ansatz is the $|D_2\rangle$ state which is a product state:

$$|D_2\rangle = \sum_n a_n(t)\hat{a}_n^+|0\rangle_e\hat{U}|0\rangle_p$$

$$\hat{U}|0\rangle_p = \exp\left[-\tfrac{1}{2}\left|\sum_k b_k(t)\right|^2\right]\cdot exp\left[\sum_k b_k(t)b_k^+\right]|0\rangle_p \\ = \exp\left\{\sum_k b_k(t)\hat{b}_k^+ - b_k^*(t)\hat{b}_k\right\}|0\rangle_p \tag{16}$$

The $b_{nk}(t)$ and the $b_k(t)$, respectively, are the coherent state amplitudes and $|a_n(t)|^2$ is the probability to find an amide-I quantum at site n. These are the quantities which have to be determined.

The equations of motion for these quantities can be obtained with the Euler-Lagrange equations of the second kind (see [6,17,20,24-27]). Note, that with the Hamiltonian method as used previously by Davydov and others incorrect equations are obtained in case of the $|D_1\rangle$ state [17]. The final equations of motion for the $|D_1\rangle$ ansatz are

$$i\hbar\dot{a}_n = -\tfrac{i\hbar}{2}\sum_k\left(\dot{b}_{nk}b_{nk}^* - \dot{b}_{nk}^*b_{nk}\right)a_n + \\ + \sum_k\hbar\omega_k\left[B_{nk}\left(b_{nk} + b_{nk}^*\right) + |b_{nk}|^2\right]a_n + \\ - J\left(D_{n,n+1}a_{n+1} + D_{n,n-1}a_{n-1}\right) \tag{17a}$$

$$i\hbar\dot{b}_{nk} = \hbar\omega_k\left(b_{nk} + B_{nk}\right) - J\left[D_{n,n+1}\left(b_{n+1,k} - b_{nk}\right)\frac{a_{n+1}}{a_n} + \right. \\ \left. + D_{n,n-1}\left(b_{n-1,k} - b_{nk}\right)\frac{a_{n-1}}{a_n}\right]$$

where the coherent state overlaps are given by

$$D_{nm} = \exp\left[-\tfrac{1}{2}\sum_k\left(|b_{nk} - b_{mk}|^2 + b_{nk}b_{mk}^* - b_{nk}^*b_{mk}\right)\right] \tag{17b}$$

Mechtly and Shaw [16] have shown, that for initial conditions $a_n(0)=\delta_{n1}$ and $b_{nk}(0)=0$ the small time behaviour of the system is given by

$$a_n(t) \to \left(2i\frac{J^2M}{\hbar^2W}\right)^{n-1}\frac{t^{n-1}}{(n-1)\,!}$$

$$b_{nk}(t) \to -i\left[\sum_{m=1}^n W_{mk}Q_k\right]\frac{t}{n} \tag{18a}$$

$$W_{mk} = \sqrt{2}\cdot cos\left[k\left(m+\tfrac{1}{2}\right)a\right]\ ;\ Q_k = \sqrt{\frac{4\pi\alpha\omega_k}{(N+1)a}}$$

$$4\pi\alpha \equiv \frac{\chi^2}{2\hbar W}\sqrt{\frac{M}{W}}\ ;\ a \equiv \frac{\hbar}{2J}\sqrt{\frac{W}{M}}$$

where in their case the eigenfrequencies are

$$\omega_k = \tfrac{2}{a}sin\left[\tfrac{ka}{2}\right]\ ;\ k = \tfrac{\pi j}{(N+1)a}\ ;\ j = 1,2,\ldots,N \qquad (18b)$$

Thus two factors in one of the terms in equ. (17a) where $a_n(t)$ occurs in the denominator have for small t the behaviour

$$\lim_{t\to 0}\frac{a_{n-1}(t)}{a_n(t)} \sim \frac{t^{n-2}}{t^{n-1}} = \frac{1}{t}$$

$$\lim_{t\to 0}\left[b_{n-1,k}(t) - b_{nk}(t)\right] \sim t \qquad (18c)$$

and therefore the product of both approaches a constant as t approaches zero. The other term has the behaviour

$$\lim_{t\to 0}\frac{a_{n+1}(t)}{a_n(t)} \sim \frac{t^n}{t^{n-1}} = t \qquad (18d)$$

and vanishes when t approaches zero. Thus in principle the denominators $a_n(t)$ in equ. (17a) pose no difficulties, although if they vanish for t approaching zero. However, in [16] it is reported that instabilities are encountered when the short time solutions are incorporated into a program. To avoid such problems we follow the suggestion given in [16] and all a_n which vanish in the initial state are put to $a_n(0)=x$, where x is a small, physically insignificant number, e.g. x=0.005 [16].

The equations for the $|D_2>$ state, transformed from the normal mode to the coordinate representation, are

$$\begin{aligned} i\hbar\dot{a}_n &= -J\left(a_{n+1}+a_{n-1}\right)+\chi\left(q_{n+1}-q_n\right)a_n \\ \dot{p}_n &= W\left(q_{n+1}-2q_n+q_{n-1}\right)+\chi\left(\left|a_n\right|^2-\left|a_{n-1}\right|^2\right) \\ \dot{q}_n &= \frac{p_n}{M} \end{aligned} \qquad (19)$$

The numerical solution of all these equations can be accomplished with the help of a fourth order Runge-Kutta method. Note, that the lattice parts of equ. (19) are not entirely classical as their form might suggest, but the q_n's and p_n's have to be viewed as expectation values of the corresponding quantum mechanical operators rather than as classical variables. However, the $|D_2>$ state is the exact solution for $\hat{H}_p$ if the operators of the displacements and momenta are replaced by real numbers $q_n(t)$ and $p_n(t)$, respectively [31,32].

Initial States

In this subchapter we want to discuss the question of the correctness of the $|D_1>$ state in the decoupled (χ=0) and in the transportless (or small polaron) case (J=0). Especially it is interesting to investigate whether or not this poses restrictions on the form of the initial state. This is an important problem, since for the initial state (time t=0) we have the physical situation that a set of coefficients for the amide-I oscillators in the wave function, $\{a_n(0)\}$, and a set of displacements and momenta $\{q_n(0),p_n(0)\}$ is given. The question is now, how to compute coherent state amplitudes from these sets of initial values.

The Small Polaron Limit

First we want to discuss the transportless case, also called the small polaron limit (J=0). Since here we have an excitation which is not transported along the chain, but deforms the lattice, it can be called a polaron and further if the initial excitation is localized, it is called a small polaron. Brown et al. stated in 1986 (Ref. [14], second paper) that with $|D_1>$ dynamics incorrect values for the displacements and consequently also for the phonon energy are obtained. This result is due to the use of the Hamiltonian method introduced by Davydov [2,3] which yields incorrect equations of motion in the $|D_1>$ case [17]. In his paper from 1988 (Ref. [14], last paper), Brown concluded that $|D_1>$ satisfies the Schrödinger equation in the small polaron limit, but derives no equations of motion. Again in 1988 (Ref. [14], third paper) Brown et al. stated that an ansatz treatment yields correct displacements but incorrect phonon energies. This statement was based on the $|D_2>$ ansatz, where it is certainly correct, however, since no direct reference to $|D_2>$ was made there, it could lead to the impression, that any ansatz treatment would be plagued by the same problem, what is not the case. To avoid any misunderstandings, we give in Appendix A a complete derivation of the exact solution for the small polaron limit which is a $|D_1>$ state, together with the expressions for the relevant expectation values.

Assuming now a set of initial conditions for the lattice $\{q_n(0),p_n(0)\}$, then the lattice energy is clearly given by

$$E_{lat}(0) = \sum_n\left\{\frac{W}{2}\left[q_{n+1}(0)-q_n(0)\right]^2 + \frac{p_n^2(0)}{2M}\right\} \qquad (20)$$

Let us construct now from these initial conditions a set $\{b_{nk}(0)\}$ of coherent state amplitudes following the suggestion given by us in [28]:

$$P_{nn} = \left|a_n(0)\right|^2 \qquad (21)$$

$$b_{nk}(0) = \frac{1}{P_{nn}}\sqrt{\frac{M\omega_k}{2\hbar}}U_{nk}q_n(0) + \frac{i}{P_{nn}}\sqrt{\frac{1}{2\hbar M\omega_k}}U_{nk}p_n(0)$$

which clearly gives the correct displacements and momenta back, and thus leads also to a correct exciton-lattice interaction term, which is linear in the phonon operators. However, substitution into that part of equ. (A23) which represents the energy of the decoupled lattice as derived in Appendix A leads to

$$E_{lat} = \sum_n \frac{1}{P_{nn}} \left[\frac{M}{2} \sum_k U_{nk} \omega_k^2 U_{nk} q_n^2(0) + \frac{p_n^2(0)}{2M} \sum_k U_{nk}^2 \right]$$
$$= \sum_n \frac{1}{P_{nn}} \left[W q_n^2(0) + \frac{p_n^2(0)}{2M} \right] \tag{22}$$

which obviously differs from equ. (20) and is therefore incorrect. Analytical expressions for $\underline{\omega}$ and $\underline{\underline{U}}$ (in real representation) are given in Appendix B. From that we conclude that the choice for $b_{nk}(0)$ is consistent with the exciton-lattice interaction but not with the lattice energy. The reason is, that the averaged equations which the $b_{nk}(0)$ have to obey

$$\sum_n \left\{ P_{nn}\, Re\left[b_{nk}(0)\right] - \sqrt{\frac{M\omega_k}{2\hbar}} U_{nk} q_n(0) \right\} = 0$$

$$\sum_n \left\{ P_{nn}\, Im\left[b_{nk}(0)\right] - \sqrt{\frac{1}{2M\hbar\omega_k}} U_{nk} p_n(0) \right\} = 0 \tag{23}$$

$$\sum_n \left\{ \hbar\omega_k \left|b_{nk}(0)\right|^2 P_{nn} - \tfrac{W}{2}\left[q_{n+1}(0) - q_n(0)\right]^2 - \frac{p_n(0)^2}{2M} \right\} = 0$$

simply do not contain enough information to determine the $b_{nk}(0)$ uniquely. Further the most obvious choice for a solution, namely to set each term in the first two sums individually to zero (from this equ. (21) follows) does not yield a solution which could fulfill all three equations.

However, we can derive a consistent choice for the initial conditions, if we assume the $b_{nk}(0)$ as site independent ($b_{nk}(0)=b_k(0)$), i.e. if we choose the initial state to be of $|D_2\rangle$ form. From this initial state the site dependence of the b's present in the evolution governed by the complete Hamiltonian evolves naturally from the $|D_1\rangle$ equations of motion. If we set $b_{nk}(0)=b_k(0)$ in the above equations, we get instead of a weighted average simply factors $\Sigma_n P_{nn}=1$, and thus the initial values

$$\mathrm{Re}\left[b_{nk}(0)\right] = \sum_{n'} \sqrt{\frac{M\omega_k}{2\hbar}} U_{n'k} q_{n'}(0) \tag{24}$$

$$\mathrm{Im}\left[b_{nk}(0)\right] = \sum_{n'} \sqrt{\frac{1}{2M\hbar\omega_k}} U_{n'k} p_{n'}(0)$$

With this choice we obtain again the correct values for $q_n(0)$ and $p_n(0)$ back and thus also the correct exciton lattice interaction. Further, this ansatz yields also the correct lattice energy:

$$E_{lat} = \sum_{nk} \hbar\omega_k \left|b_{nk}(0)\right|^2 P_{nn} =$$
$$= \frac{M}{2} \sum_{nn'} \sum_k U_{n'k} \omega_k^2 U_{nk} q_{n'}(0) q_n(0) +$$
$$+ \frac{1}{2M} \sum_{nn'} \sum_k U_{n'k} U_{nk} p_{n'}(0) p_n(0) = \tag{25}$$
$$= \frac{W}{2} \sum_{nn'} V_{n'n} q_{n'}(0) q_n(0) + \sum_n \frac{p_n^2(0)}{2M}$$

where $\underline{\underline{V}}$ is defined in Appendix B.

In the case of ν bosons occupying the same state the initial variables are given by

$$Re\left[b_{nk}(0)\right] = \frac{1}{\nu} \sum_{n'} \sqrt{\frac{M\omega_k}{2\hbar}} U_{n'k} q_{n'}(0)$$
$$Im\left[b_{nk}(0)\right] = \frac{1}{\nu} \sum_{n'} \sqrt{\frac{1}{2M\hbar\omega_k}} U_{n'k} p_{n'}(0) \tag{26}$$

However, here we have [28] alternatively

$$q_n = \nu \sum_{n'k} \sqrt{\frac{2\hbar}{M\omega_k}} U_{nk} \left|a_{n'}\right|^2 \mathrm{Re}\left[b_{n'k}\right]$$
$$p_n = \nu \sum_{n'k} \sqrt{2M\hbar\omega_k}\, U_{nk} \left|a_{n'}\right|^2 \mathrm{Im}\left[b_{n'k}\right] \tag{27}$$
$$E_{lat} = \nu^2 \sum_{nk} \hbar\omega_k \left|b_{nk}\right|^2 \left|a_n\right|^2 ; \quad \sum_n \left|a_n\right|^2 = 1$$

Therefore it is obvious, that in order to obtain a correct initial state we have to start from a $|D_2\rangle$ like ansatz at t=0, calculated from the initial set of displacements and momenta. Otherwise we would obtain an incorrect lattice energy and consequently an incorrect time evolution.

The Decoupled Case

In the decoupled case (χ=0) we have the Hamiltonian

$$\begin{aligned}\hat{H}_{DC} &= \hat{J} + \hat{H}_{lat} \\ \hat{J} &\equiv -J\sum_n \left(\hat{a}_n^+ \hat{a}_{n+1} + \hat{a}_{n+1}^+ \hat{a}_n\right) \\ \hat{H}_{lat} &\equiv \sum_k \hbar\omega_k \hat{b}_k^+ \hat{b}_k\end{aligned} \tag{28a}$$

Since the two parts of the Hamiltonian are independent, the exact solution is a product of a state for the excitons with a state for the phonons. The separation ansatz leads to

$$\begin{aligned}&|\psi_l\rangle\left[i\hbar\tfrac{\partial}{\partial t}|\psi_e\rangle - \hat{J}|\psi_e\rangle\right] = \\ &-|\psi_e\rangle\left[i\hbar\tfrac{\partial}{\partial t}|\psi_l\rangle - \hat{H}_{lat}|\psi_l\rangle\right]\end{aligned} \tag{28b}$$

which can only be fulfilled if both sides of the equation vanish independently. Here $|\psi_e\rangle$ is the exciton and $|\psi_l\rangle$ the lattice (phonon) state. The phonon operator is a sum of operators for each normal mode and its solution is a product of coherent states for each mode:

$$\begin{aligned}|\psi_l\rangle &= \prod_k |\beta_k\rangle = e^{\sum_k \left[b_k(t)\hat{b}_k^+ - b_k^*(t)\hat{b}_k\right]}|0\rangle = \\ &= e^{-\frac{1}{2}\sum_k |b_k(t)|^2} e^{\sum_k b_k(t)\hat{b}_k^+}|0\rangle\end{aligned} \tag{29}$$

Thus the exact solution of

$$i\hbar\tfrac{\partial}{\partial t}|\psi_l\rangle = \hat{H}_{lat}|\psi_l\rangle \tag{30}$$

is given by our ansatz if

$$b_k(t) = b_k(0)e^{-i\omega_k t} \tag{31}$$

where $b_k(0)$ has to be constructed from the initial displacements and momenta as described in the previous chapter. The exact solution of the Schrödinger equation for the oscillator system is given in Appendix C. It is obvious that the exact solution is a $|D_2\rangle$ state which is identical to a $|D_1\rangle$ state with site independent $b_{nk}(t)$.

Thus we have to show, that from the equations of motion for the $|D_1\rangle$ ansatz the $b_{nk}(t)$ remain site independent if we start from a site independent initial state in the case χ=0:

$$\begin{aligned}i\hbar\dot{b}_{nk} = \hbar\omega_k b_{nk} - J\Big[&\left(b_{n-1,k} - b_{nk}\right)D_{n,n-1}\frac{a_{n-1}}{a_n} + \\ &+\left(b_{n+1,k} - b_{nk}\right)D_{n,n+1}\frac{a_{n+1}}{a_n}\Big]\end{aligned} \tag{32}$$

Thus we obtain

$$\begin{aligned}-\frac{i\hbar}{2}\sum_k\left(\dot{b}_{nk}b_{nk}^* - \dot{b}_{nk}^* b_{nk}\right)a_n = &-\sum_k \hbar\omega_k |b_{nk}|^2 a_n + \\ &+\frac{J}{2}\sum_k\Big[\left(b_{n-1,k}b_{nk}^* - |b_{nk}|^2\right)D_{n,n-1}\frac{a_{n-1}}{a_n} + \\ &+\left(b_{n+1,k}b_{nk}^* - |b_{nk}|^2\right)D_{n,n+1}\frac{a_{n+1}}{a_n} + \\ &+\left(b_{n-1,k}^* b_{nk} - |b_{nk}|^2\right)D_{n,n-1}^*\frac{a_{n-1}^*}{a_n^*} + \\ &+\left(b_{n+1,k}^* b_{nk} - |b_{nk}|^2\right)D_{n,n+1}^*\frac{a_{n+1}^*}{a_n^*}\Big]a_n\end{aligned} \tag{33}$$

and together with equ. (17) we have

$$\begin{aligned}i\hbar\dot{a}_n = &-J\left(D_{n,n-1}a_{n-1} + D_{n,n+1}a_{n+1}\right) + \\ &+\frac{J}{2}\sum_k\Big[\left(b_{n-1,k}b_{nk}^* - |b_{nk}|^2\right)D_{n,n-1}\frac{a_{n-1}}{a_n} + \\ &+\left(b_{n+1,k}b_{nk}^* - |b_{nk}|^2\right)D_{n,n+1}\frac{a_{n+1}}{a_n} + \\ &+\left(b_{n-1,k}^* b_{nk} - |b_{nk}|^2\right)D_{n,n-1}^*\frac{a_{n-1}^*}{a_n^*} + \\ &+\left(b_{n+1,k}^* b_{nk} - |b_{nk}|^2\right)D_{n,n+1}^*\frac{a_{n+1}^*}{a_n^*}\Big]a_n\end{aligned} \tag{34}$$

At the beginning of the first time step, i.e. at t=0 we can replace $b_{nk}(0)$ by $b_k(0)$ from our initial state and the equations of motion yield

$$\begin{aligned}&D_{nm}(0) = 1 \quad ; \quad i\hbar\dot{a}_n(0) = -J\left[a_{n+1}(0) + a_{n-1}(0)\right] \\ &i\hbar\dot{b}_{nk}(0) = \hbar\omega_k b_k(0)\end{aligned} \tag{35}$$

Thus after the first time step (t=τ) we obtain

$$D_{nm}(\tau)=1 \quad ; \quad a_n(\tau)=a_n(0)+\frac{iJ}{\hbar}\left[a_{n-1}(0)+a_{n+1}(0)\right]\tau$$
$$b_{nk}(\tau)=b_k(0)(1-i\omega_k\tau) \tag{36}$$

Obviously the b's remain site independent after the first time step, thus consequently for all times, and therefore the time simulation with the equations of motion for the $|D_1>$ state yields the correct solution of $|D_2>$ form, provided the initial state is of this form. Note, that for site-independent b's also the, for the decoupled case artificial coupling terms in equ.'s (32) and (34) vanish and that further we have $D_{nm}(t)=1$.

The Complete Hamiltonian

After we have shown, that in both special cases, the initial state has to be of $|D_2>$ form, i.e. with site independent coherent state amplitudes $b_{nk}(0)$, if a simulation using a $|D_1>$ ansatz should lead to the correct analytical solution, we have to ask how such an initial state evolves in time when we apply the complete Hamiltonian. Since in this case, the basis space of $|D_1>$ is incomplete we have to study the errors developing through the use of this ansatz. For this purpose we can use the fact that [17]

$$\left(i\hbar\frac{\partial}{\partial t}-\hat{H}_D\right)|D_1\rangle = J|\delta\rangle \tag{37}$$

where the form of the error state $|\delta>$ as function of $\{a_n(t),b_{nk}(t)\}$ as computed in a $|D_1>$ simulation is known [17]. In our previous work [26] we have derived expressions for the expectation values of different operators for the two states $\left(\hat{H}/J\right)|D_1\rangle$ and $|\delta>$ and compared them in numerical calculations. Such a procedure can serve as the appropriate tool to answer our above mentioned question. Therefore we introduced cyclic boundary conditions into our program [26] and performed simulations for χ=0,10,20,30,40 pN. For χ=0 we found that all the expectation values computed for the state $|\delta>$ from a numerical $|D_1>$ simulation vanish, as it is to be expected because in this case $|D_1>$ yields the exact solution for site independent amplitudes $b_{nk}(0)$.

To be more precise we applied as initial conditions for the oscillator system

$$a_n(0)=R\cdot sech\left[\frac{(n-o)X^2}{4WJ}\right] \tag{38}$$

where R is a normalization constant, J=0.967 meV, W=13 N/m, X=62 pN (note, that X is used only in the initial state for all cases, in contrast to χ), and the maximum of the function was put at site o=11 in a chain of N=21 units. The displacements and momenta of the lattice were chosen such that kinetic and potential energy each equal $0.5(N-1)k_BT$ for T=300K. This energy was distributed according to Bose-Einstein statistics on the normal modes, excluding the translation:

$$q_n(0)=\sum_k U_{nk}\sqrt{\frac{e_k}{W\sum_{n'}\left(U_{n'k}-U_{n'+1,k}\right)^2}}$$

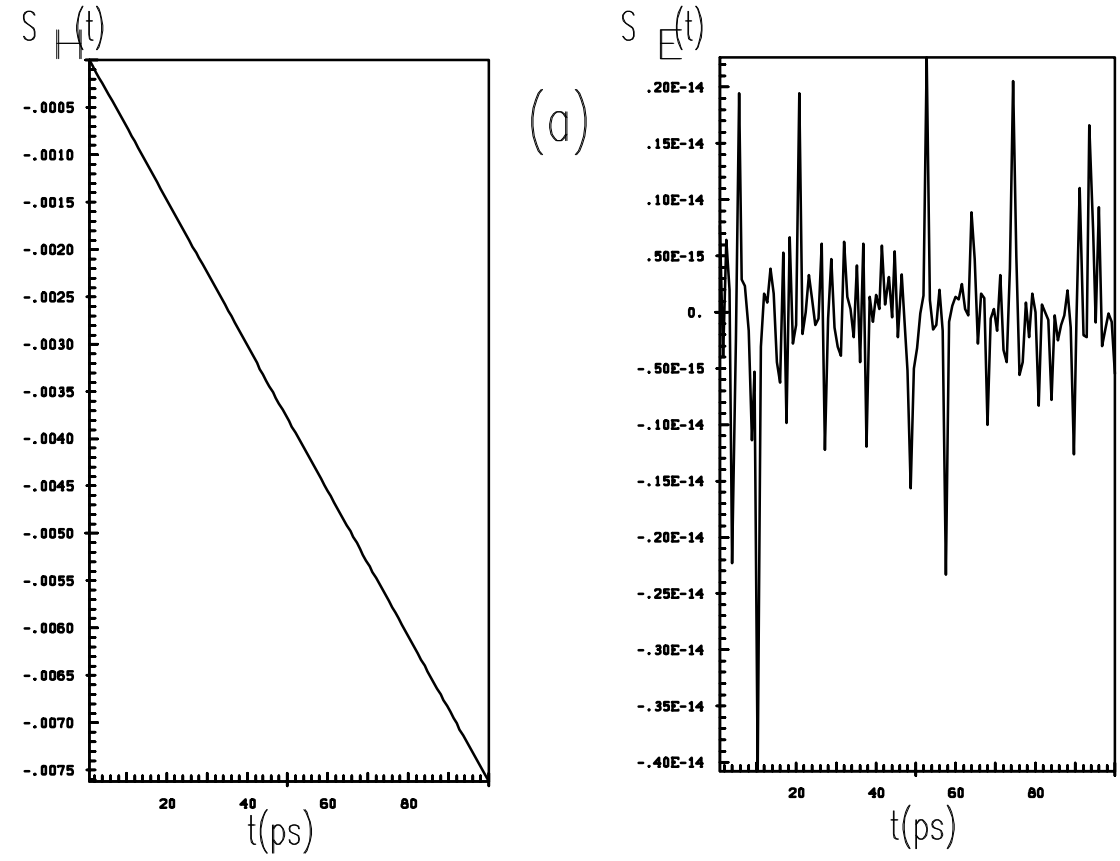
$$p_n(0)=\sum_k U_{nk}\sqrt{\frac{e_k}{M\sum_{n'}U_{n'k}^2}} \tag{39}$$

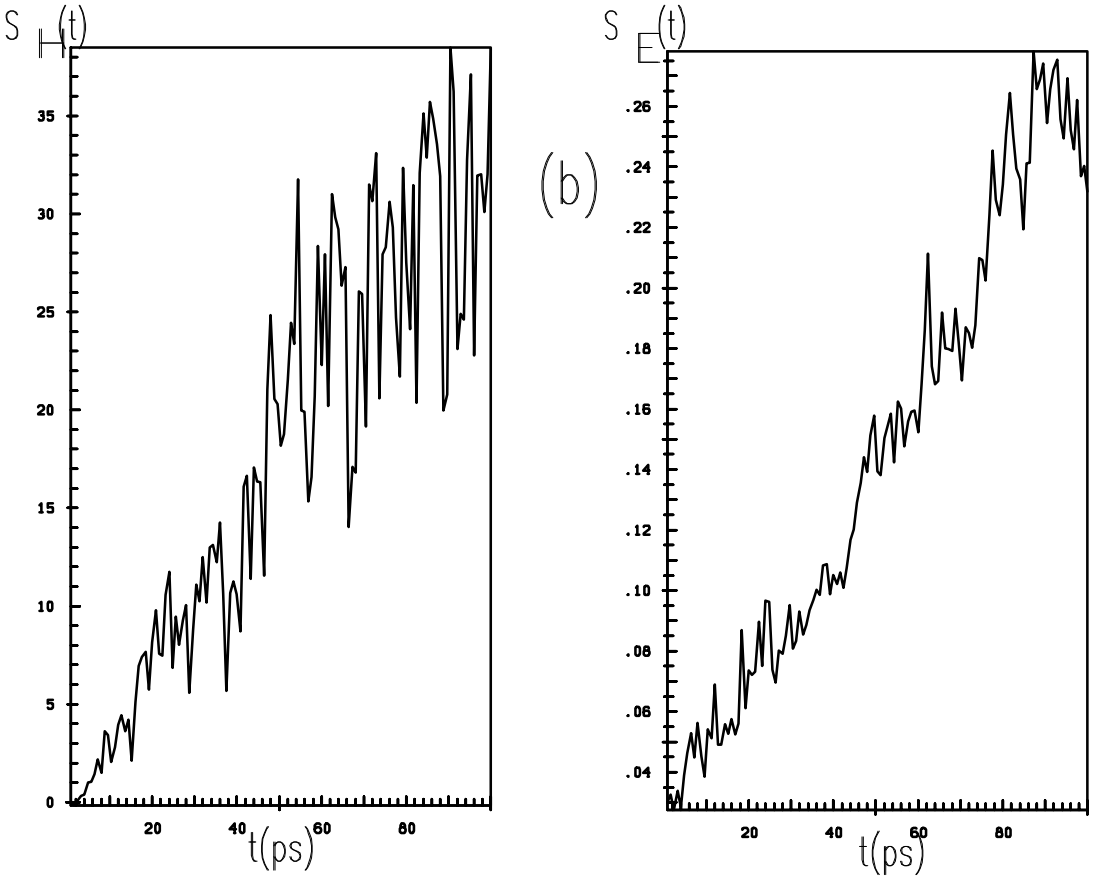
$$e_k=(N-1)k_BT\hbar\omega_k f_k/S$$

$$f_k=\left[e^{\frac{\hbar\omega_k}{k_BT}}-1\right]^{-1} \quad ; \quad S=\sum_k \hbar\omega_k f_k$$

where M=114 m_p, and k_B is Boltzmann's constant. For the fourth order Runge-Kutta simulations we used a time step of 1 fs and a total simulation time of 100 ps, corresponding to 100,000 time steps. In this period the error in total energy was typically less than 5-10 peV (much less than 0.1 % of the exciton phonon interaction energies) and the error in norm around 1 ppb (parts per billion).

In Fig. 1 we show the norms $S_H(t)=\left\langle\left(\hat{H}/J\right)D_1\middle|\left(\hat{H}/J\right)D_1\right\rangle$ and $S_E(t)=<\delta|\delta>$ for three values of χ, namely 0, 10, and 20 pN. Note, that for these coupling strengths no solitons are present in the system. Here we see, that for the decoupled case (Fig.1a) the norm of the error state is below machine accuracy, since here we obtain the analytical solution from our simulations. The norm of $\left(\hat{H}/J\right)|D_1\rangle$ decreases slightly in the course of the simulation. When we switch on the coupling to a small value of χ=10 pN (Fig.1b), the increase of $S_H(t)$ with time becomes rather large, up to more than 35. However, the increase of the error $S_E(t)$ is much smaller, between 0 and 0.27, indicating the accuracy of the $|D_1>$ simulation. For the larger coupling χ=20 pN (Fig. 1c) $S_H(t)$ increases by a factor of 10 up to values around 350. The increase of the error is much smaller, namely up to a value of 1.5. If we increase χ further up to 30 and 40 pN (not shown here), the increase of $S_H(t)$ per 10 pN increase in coupling remains the same, while the maximum values of $S_E(t)$ start to converge to maximum values around 2.2-2.3. When increasing the coupling further we reach the values already discussed in [26]. Thus it is obvious, that the error in the norm starts to increase smoothly with χ increasing from its value of 0 where $|D_1>$ is the exact


S H(t)
-.0005
-.0010
-.0015
-.0020
-.0025
-.0030
-.0035
-.0040
-.0045
-.0050
-.0055
-.0060
-.0065
-.0070
-.0075
20
40
60
80
t(ps)
(a)
S E(t)
.20E-14
.15E-14
.10E-14
.50E-15
0.
-.50E-15
-.10E-14
-.15E-14
-.20E-14
-.25E-14
-.30E-14
-.35E-14
-.40E-14
20
40
60
80
t(ps)


S H(t)
35
30
25
20
15
10
5
0
20
40
60
80
t(ps)
(b)
S E(t)
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
20
40
60
80
t(ps)

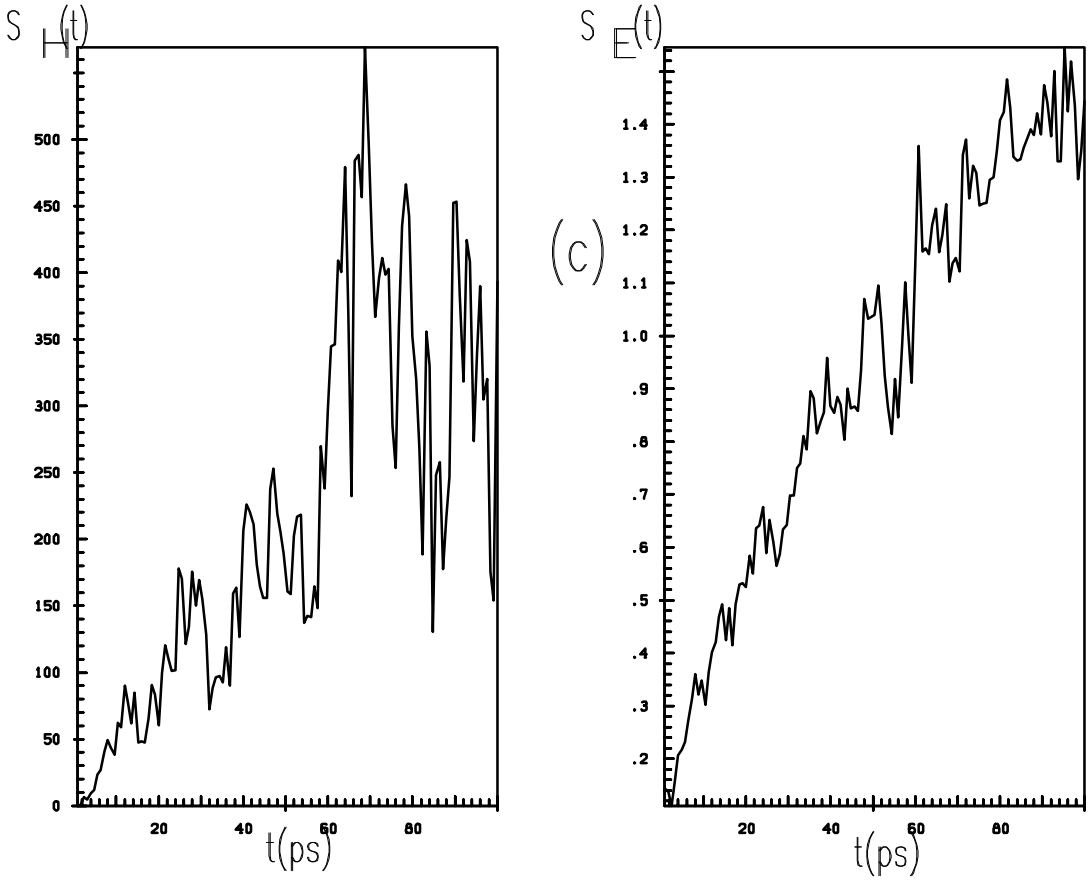


Figure 1: *The norms* $S_H(t) = \left\langle \left(\hat{H}/J\right) D_1 \middle| \left(\hat{H}/J\right) D_1 \right\rangle$ *and* $S_E(t) = \langle \delta | \delta \rangle$ *for the two states under consideration as function of time for three values of the coupling constant:*

(a) $\chi = 0$ *pN (*S_H *relative to* $S_H(0) = 675{,}827.93106$*)*
(b) $\chi = 10$ *pN (*S_H *relative to* $S_H(0) = 676{,}851.60694$*)*
(c) $\chi = 20$ *pN (*S_H *relative to* $S_H(0) = 677{,}877.52615$*)*

solution, when the simulation is started from an initial $|D_2\rangle$ like state. Fig. 2 shows the probabilities $N_n(t) = \langle D_1 | \hat{a}_n^+ \hat{a}_n | D_1 \rangle$ to find an amide-I quantum at site n as function of time for the three values of the coupling constant.The results show that in all three cases no soliton is formed from the initial sech-distribution. The dispersion of this distribution becomes less regular with increasing coupling strength, because the phonons, coupled with increasing strength to the oscillators, are initially excited with an energy corresponding to a temperature of 300K, which leads to a large aperiodicity in the lattice coordinates.

In Fig. 3 finally we show the expectation values $N_n^H = \left\langle \left(\hat{H}/J\right) D_1 \middle| \hat{a}_n^+ \hat{a}_n \middle| \left(\hat{H}/J\right) D_1 \right\rangle$ and $N^E{}_n(t) = \langle \delta | \hat{a}_n{}^+ \hat{a}_n | \delta \rangle$ of the number operators again for the three values of the coupling constant.

Naturally, for the decoupled case the error is less than machine accuracy, because in this case our evolution is exact. With increasing coupling strength, we find a slight increase of the errors, however, about six orders of magnitude smaller than the corresponding values of $N^H{}_n(t)$. Thus also here the deviation of our results from the exact solution of the Schrödinger equation is very small, even more or less negligible, when using the $|D_1\rangle$ ansatz starting from an initial $|D_2\rangle$ like state. We do not discuss the expectation values of displacement and momentum operators here, because they behave rather similar as those of the number operators we have just studied. Thus our conclusion drawn from the analytically solvable special cases as discussed in the previous subchapters remain valid also when we apply the complete Hamilton operator in numerical simulations.

Therefore, we can savely draw as final conclusion, that indeed the initial state has to have the form of a $|D_2\rangle$ state, i.e. site independent coherent state amplitudes $b_{nk}(0)$, in order to be able to obtain reliable results from $|D_1\rangle$ simulations.

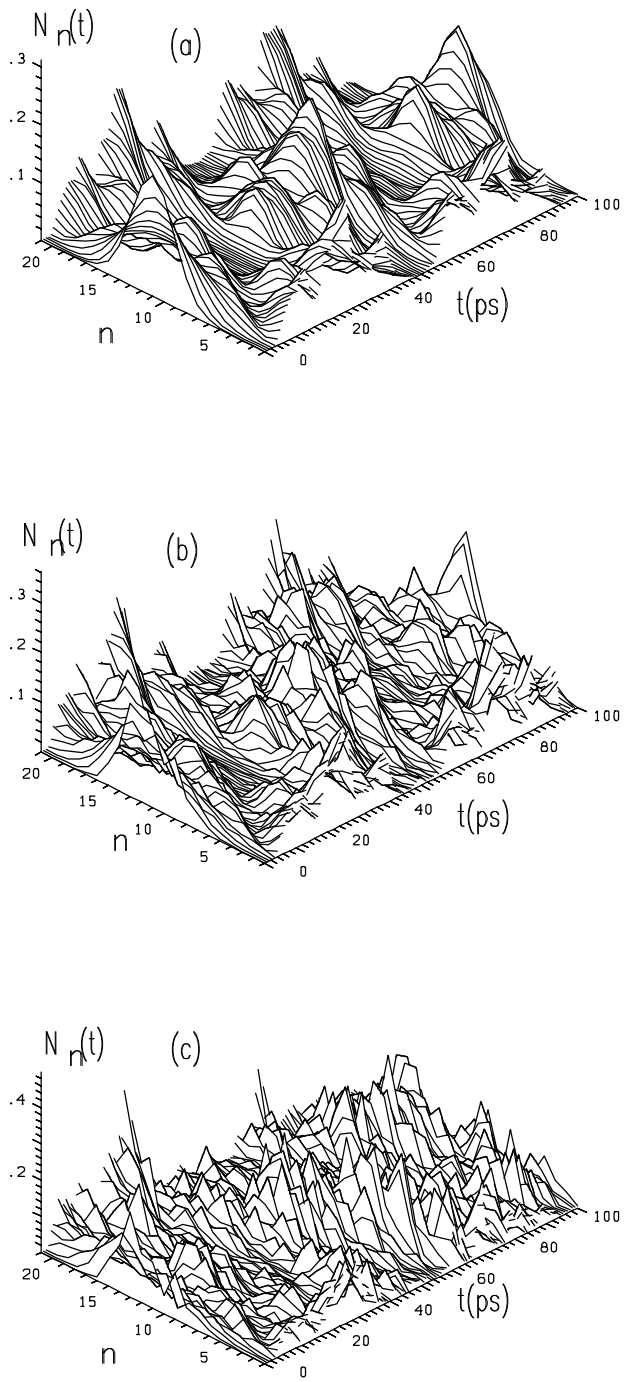


Figure 2: *The probability $N_n(t)=\langle D_1|\hat{a}_n^{+}\hat{a}_n|D_1\rangle$ to find an amide-I vibrational quantum at site n as function of time for three values of the coupling constant:*
(a) χ=0 pN (b) χ=10 pN (c) χ=20 pN

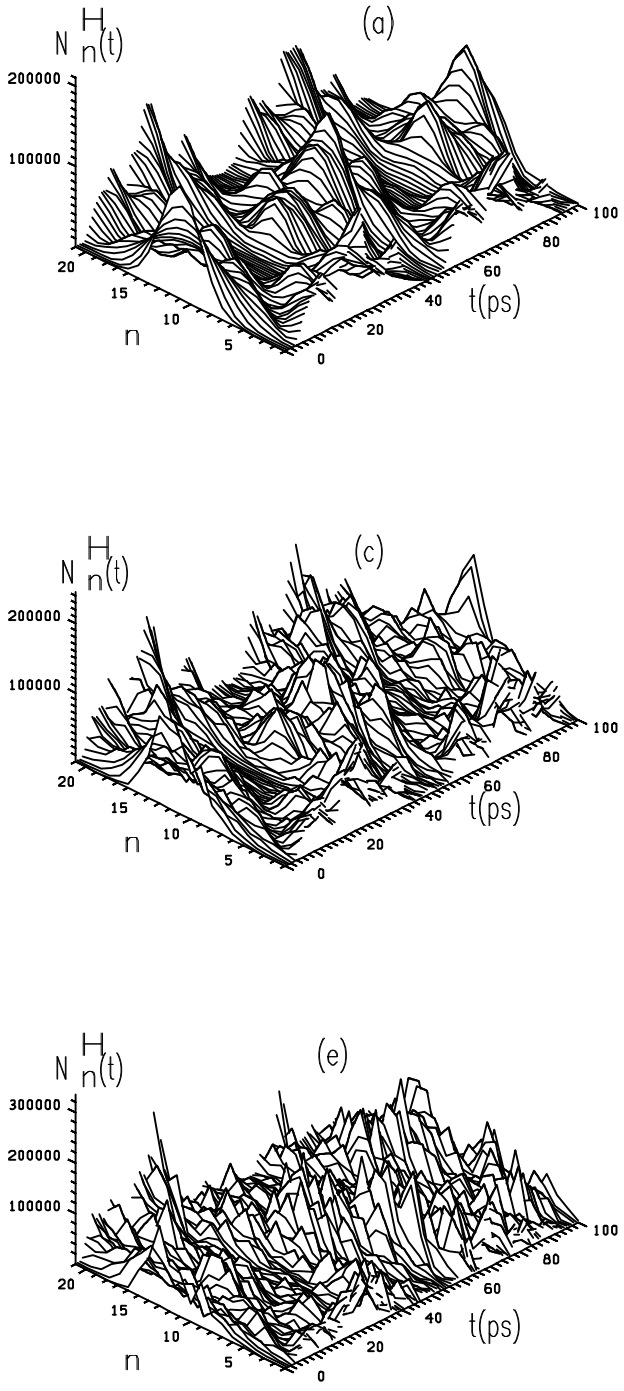


Figure 3: *The expectation values*
$N_n^H = \left\langle \left(\hat{H}/J\right)D_1 \middle| \hat{a}_n^{+}\hat{a}_n \middle| \left(\hat{H}/J\right)D_1 \right\rangle$ (a,c,e) as functions of site and time for three values of the coupling constant:

(a,b) χ=0 pN (c,d) χ=10 pN (e,f) χ=20 pN

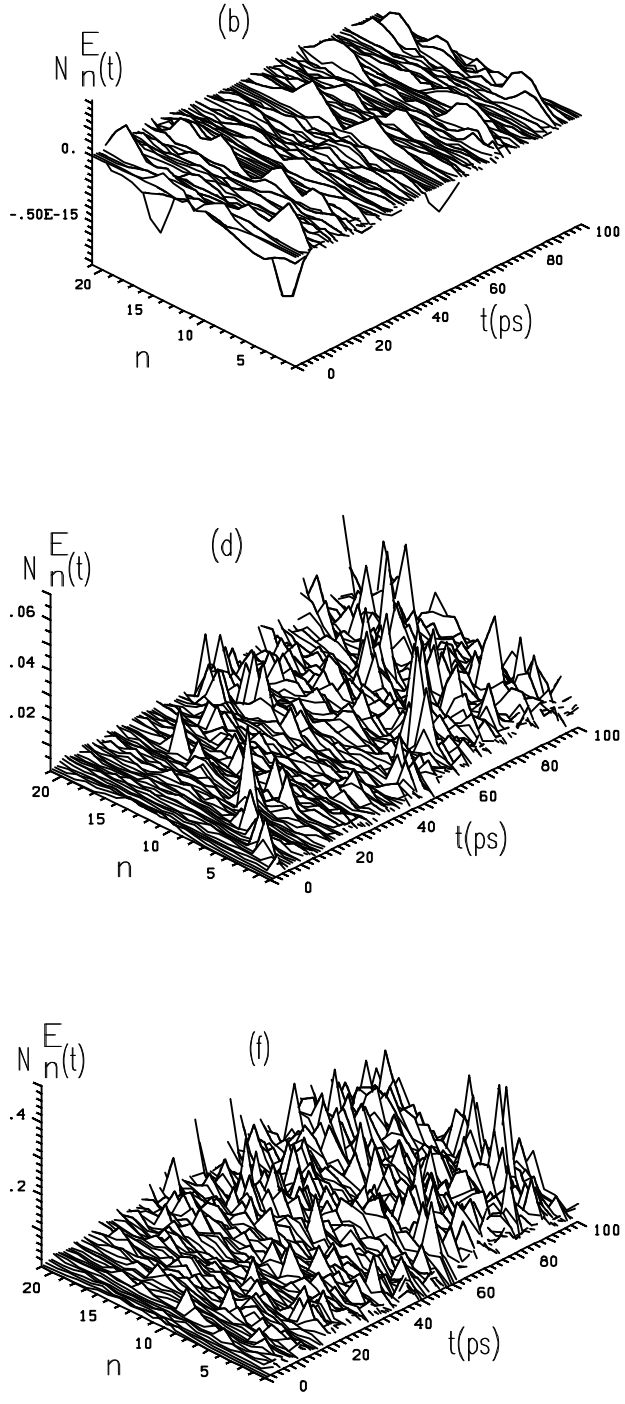


Figure 3 (continued): *The expectation values* $N^E_n(t)=<\delta|\hat{a}_n^+\hat{a}_n|\delta>$ *(b,d,f) as functions of site and time for three values of the coupling constant:*

(a,b) χ*=0 pN (c,d)* χ*=10 pN (e,f)* χ*=20 pN*

Expansions of Exact Solutions

Since in the following paper we want to use for the general case expansions of the exact wave functions in polynomials in time, it is very important to get a reliable tool to judge up to which time a given order of the expansion can be considered as reliable. The best way to do so is the expansion of exactly known solutions in such polynomials and to compare the results of different orders with the exact states. There are in principle two ways to compute such expansions. The simplest one is to expand directly the exact solution. The other one, which has to be used in cases where the exact solution is not known, is to expand the formally exact wave function

$$\left|\psi(t)\right\rangle = e^{T\hat{H}}\left|\psi(0)\right\rangle \quad ; \quad T \equiv -\frac{it}{\hbar}$$
$$\Rightarrow \left|\psi(t)\right\rangle = \sum_{\nu=0}^{\infty}\frac{T^\nu}{\nu!}\hat{H}^\nu\left|\psi(0)\right\rangle \tag{40}$$

Thus a given order μ can be written as

$$\left|\psi(\mu)\right\rangle \equiv \sum_{\nu=0}^{\mu}\frac{T^\nu}{\nu!}\hat{H}^\nu\left|\psi(0)\right\rangle = \sum_{\nu=0}^{\mu}\frac{T^\nu}{\nu!}\left|\psi_\nu\right\rangle$$
$$\left|\psi_\nu\right\rangle = \hat{H}\left|\psi_{\nu-1}\right\rangle = \hat{H}^\nu\left|\psi_0\right\rangle \quad ; \quad \left|\psi_0\right\rangle = \left|\psi(0)\right\rangle \tag{41}$$

In the present work we used both methods, just to avoid errors in the calculation. Then expectation values for any operator $\hat{O}$ can be computed from expectation values in lower order by

$$\left|\psi(\mu)\right\rangle = \left|\psi(\mu-1)\right\rangle + \frac{T^\mu}{\mu!}\left|\psi_\mu\right\rangle \tag{42}$$

$$O(\mu) \equiv \left\langle\psi(\mu)\middle|\hat{O}\middle|\psi(\mu)\right\rangle = O(\mu-1) +$$
$$+\frac{1}{\mu!}\left[\left(T^*\right)^\mu\left\langle\psi_\mu\middle|\hat{O}\middle|\psi(\mu-1)\right\rangle + T^\mu\left\langle\psi(\mu-1)\middle|\hat{O}\middle|\psi_\mu\right\rangle\right] +$$
$$+\frac{|T|^{2\mu}}{(\mu!)^2}\left\langle\psi_\mu\middle|\hat{O}\middle|\psi_\mu\right\rangle$$

In case of $\hat{O}$ being hermitian, the second term reduces to

$$\frac{2}{\mu!}Re\left[T^\mu\left\langle\psi(\mu-1)\middle|\hat{O}\middle|\psi_\mu\right\rangle\right] \tag{43}$$

Further the expectation value can be expanded in any case to yield

$$\left\langle \psi_\mu \middle| \hat{O} \middle| \psi(\mu-1) \right\rangle = \sum_{\nu=0}^{\mu-1} \frac{T^\nu}{\nu!} \left\langle \psi_\mu \middle| \hat{O} \middle| \psi_\nu \right\rangle \tag{44}$$

The properties of the different orders can further be used to transform expectations values of the Hamiltonian to overlap integrals:

$$\left\langle \psi_\mu \middle| \hat{H} \middle| \psi_\nu \right\rangle = \left\langle \psi_{\mu+1} \middle| \psi_\nu \right\rangle = \left\langle \psi_\mu \middle| \psi_{\nu+1} \right\rangle \tag{45}$$

We do not want to elaborate here on more details of the sometimes tedious calculations and proceed to the two cases under consideration.

The Oscillator System in the Decoupled Case

Here the relevant expectation values to be computed are $S(\mu,t) = \left\langle \psi(\mu) \middle| \psi(\mu) \right\rangle$, $H(\mu,t) = \left\langle \psi(\mu) \middle| \hat{H} \middle| \psi(\mu) \right\rangle$ and $N_n(\mu,t) = \left\langle \psi(\mu) \middle| \hat{a}_n^+ \hat{a}_n \middle| \psi(\mu) \right\rangle$. These functions have to be compared with the corresponding results obtained from the exact solution, namely S(t)=1, H(t)=0 and $N_n(t)$ as given in Appendix C for an initial state, where the excitation is localized at one site o, i.e. $\left| \psi(0) \right\rangle = \left| \psi_0 \right\rangle = \hat{a}_o^+ \left| 0 \right\rangle$. The Hamiltonian in spatial representation is given by

$$\begin{aligned} \hat{J} &= -J \sum_n \left(\hat{a}_n^+ \hat{a}_{n+1} + \hat{a}_{n+1}^+ \hat{a}_n \right) \\ \hat{J} \hat{a}_n^+ \left| 0 \right\rangle &= -J \left(\hat{a}_{n-1}^+ + \hat{a}_{n+1}^+ \right) \left| 0 \right\rangle \end{aligned} \tag{46}$$

Thus we can directly write down the first three orders of the exact solution

$$\begin{aligned} \left| \psi_0 \right\rangle &= \hat{a}_o^+ \left| 0 \right\rangle \\ \left| \psi_1 \right\rangle &= -J \left(\hat{a}_{o-1}^+ + \hat{a}_{o+1}^+ \right) \left| 0 \right\rangle \\ \left| \psi_2 \right\rangle &= J^2 \left(\hat{a}_{o-2}^+ + 2\hat{a}_o^+ + \hat{a}_{o+2}^+ \right) \left| 0 \right\rangle \\ \left| \psi_3 \right\rangle &= -J^3 \left(\hat{a}_{o-3}^+ + 3\hat{a}_{o-1}^+ + 3\hat{a}_{o+1}^+ + \hat{a}_{o+3}^+ \right) \left| 0 \right\rangle \end{aligned} \tag{47}$$

Obviously in any order μ the excitation is at maximum transported only μ sites away from the initial excitation. Since we can also perform a direct expansion of the state to any arbitrary order, it seems to be more advantegeous to use for this purpose the normal mode representation (Appendix C)

$$\hat{J} = -J \underline{\hat{a}}^+ \underline{\underline{X}} \underline{\hat{a}} = -J \underline{\hat{c}}^+ \underline{\underline{\lambda}} \underline{\hat{c}} = -J \sum_k \lambda_k \hat{c}_k^+ \hat{c}_k \quad ; \quad \underline{\hat{a}} = \underline{\underline{R}} \underline{\hat{c}} \tag{48}$$

$$R_{nk} = \frac{1}{\sqrt{N}} e^{\frac{2\pi i}{N} nk} \quad ; \quad \lambda_k = 2 \cdot \cos\left(\frac{2\pi}{N} k \right)$$

$$\left| \psi_0 \right\rangle = \sum_k c_k(0) c_k^+ \left| 0 \right\rangle$$

With the transformations (here $a_n(0)=\delta_{no}$)

$$c_k(0) = \sum_n R_{nk}^* a_n(0) \quad ; \quad a_n(t) = \sum_k R_{nk} c_k(t) \tag{49}$$

we can write down the solution in any order in time by expansion of the exact wave function as

$$\begin{aligned} \left| \psi(\mu) \right\rangle &= \sum_n a_n(\mu,t) \hat{a}_n^+ \left| 0 \right\rangle = \\ &= \frac{1}{N} \sum_{nk} e^{\frac{2\pi i}{N} k(n-o)} \sum_{\nu=0}^{\mu} \frac{1}{\nu!} \left(i \frac{J\lambda_k}{\hbar} t \right)^\nu \hat{a}_n^+ \left| 0 \right\rangle \end{aligned} \tag{50}$$

The expectation values of the number operators are consequently

$$\begin{aligned} N_n(\mu,t) &= \left| a_n(\mu,t) \right|^2 = \\ &= \frac{1}{N^2} \sum_{kk'} e^{\frac{2\pi i}{N}(k-k')(n-o)} \sum_{\nu,\nu'=0}^{\mu} \frac{\lambda_k^\nu (-\lambda_{k'})^{\nu'}}{\nu!\nu'!} \left(i \frac{J}{\hbar} t \right)^{\nu+\nu'} \end{aligned} \tag{51}$$

However, in the form $N_n(\mu,t)=|a_n(\mu,t)|^2$, where $a_n(\mu,t)$ is actually calculated from equ. (50), the expectation values are most easily programmed for arbitrary order. From (51) we obtain

$$S(\mu,t) = \sum_n N_n(\mu,t) = \frac{1}{N} \sum_k \sum_{\nu,\nu'=0}^{\mu} \frac{(-1)^{\nu'}}{\nu!\nu'!} \left(i \frac{J\lambda_k}{\hbar} t \right)^{\nu+\nu'} \tag{52}$$

The expectation value of the Hamiltonian is obtained as

$$\begin{aligned} H(\mu,t) &= \sum_{nn'} a_n(\mu,t) a_{n'}^*(\mu,t) \left\langle 0 \middle| \hat{a}_{n'} \hat{J} \hat{a}_n^+ \middle| 0 \right\rangle = \\ &= -\frac{J}{N} \sum_{nn'} a_n(\mu,t) a_{n'}^*(\mu,t) \sum_k \lambda_k e^{\frac{2\pi i}{N} k(n-n')} \end{aligned} \tag{53}$$

Substitution of the explicit values for the coefficients yields the final expression

$$H(\mu,t) = -\frac{J}{N}\sum_k \lambda_k \sum_{\nu,\nu'=0}^{\mu} \frac{(-1)^{\nu'}}{\nu!\nu'!}\left(i\frac{J\lambda_k}{\hbar}t\right)^{\nu+\nu'} \qquad (54)$$

Note that all the double sums over the different orders in (52) and (54) are real, because each term $T_{\nu\nu'}$ occurs twice. The $T_{\nu\nu}$ are anyway real. Therefore we always obtain combinations ($T_{\nu\nu'}+T_{\nu'\nu}$) which can only be imaginary, if one of the indices is odd and the other one even. However, just in this case due to the minus signs we have $T_{\nu\nu'}=-T_{\nu'\nu}$, and thus all imaginary contributions vanish, and the sum can be restricted to terms where (ν+ν') is even. Therefore we can write after some reordering

$$H(\mu,t) = -\frac{J}{N}\sum_{\substack{\nu,\nu'=0 \\ (\nu+\nu')even}}^{\mu} \frac{(-1)^{\nu'}}{\nu!\nu'!}\left(i\frac{Jt}{\hbar}\right)^{\nu+\nu'} \sum_k \lambda_k^{\nu+\nu'+1} \qquad (55)$$

Since we have

$$\sum_{k=1}^{N}\lambda_k^n = \sum_k\left(e^{\frac{2\pi i}{N}k}+e^{-\frac{2\pi i}{N}k}\right)^n = \sum_{m=0}^{n}\binom{n}{m}\sum_{k=1}^{N}e^{\frac{2\pi i}{N}k(n-2m)} =$$

$$= N\sum_{m=0}^{n}\binom{n}{m}\delta_{n,2m} = \begin{cases} 0 \quad ; \quad \text{if n is odd} \\ \dfrac{N\cdot n!}{\left[(n/2)!\right]^2} \quad ; \quad \text{if n is even or 0} \end{cases} \qquad (56)$$

and our summation is restricted to even values of (ν+ν'), we have in the k-summation only odd exponents (ν+ν'+1) at λ_k, and thus H(ν,t)=0. This result can be used to check together with equation (53) the correctness of the program. Since in S(μ,t) we have in the k-summations only even exponents (ν+ν') at the λ_k, this quantitity does not vanish:

$$S(\mu,t) = \sum_{\substack{\nu,\nu'=0 \\ (\nu+\nu')even}}^{\mu} \frac{(-1)^{(3\nu'+\nu)/2}(\nu+\nu')!}{(\nu!)+(\nu'!)\left\{\left[(\nu+\nu')/2\right]!\right\}^2}\left(\frac{Jt}{\hbar}\right)^{\nu+\nu'} \qquad (57)$$

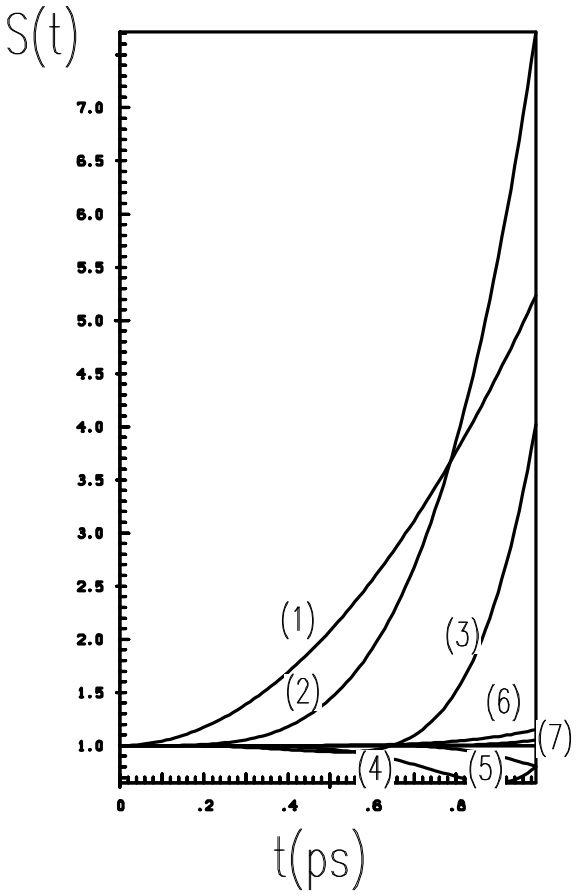


Figure 4: *The norm S(μ,t) of the state vector in the decoupled case for different orders μ (μ=1-7) of the wave function (indicated by numbers at the different curves) as function of time (the exact value is S(t)=1).*

Note, that (3ν'+ν)/2 is integer, because (ν'+ν) is even. Finally, from equ. (52) we obtain

$$S(t) = \lim_{\mu\to\infty} S(\mu,t) = \frac{1}{N}\sum_{k=1}^{N} e^{i\frac{J\lambda_k}{\hbar}t}e^{-i\frac{J\lambda_k}{\hbar}t} = 1 \qquad (58)$$

We have calculated these expectation values for the case J=0.967 meV up to the 7th order of the state vector, as described above. In all these calculations, the total energy was in absolute value smaller than 10^{-17} eV, i.e. it is vanishing within machine accuracy. In Fig. 4 we show the norms S(μ,t). We draw all computed orders in one plot. The time covered was 1 ps. It is obvious, that starting from third order, the norm is reasonably correct up to a time of roughly 0.6-0.8 ps, while in larger orders it is correct in the full interval of 1 ps. In Fig. 5 we show the time evolution of the expectation values of the number operators $N_n(t)$ for the exact state vector (Fig. 5a).

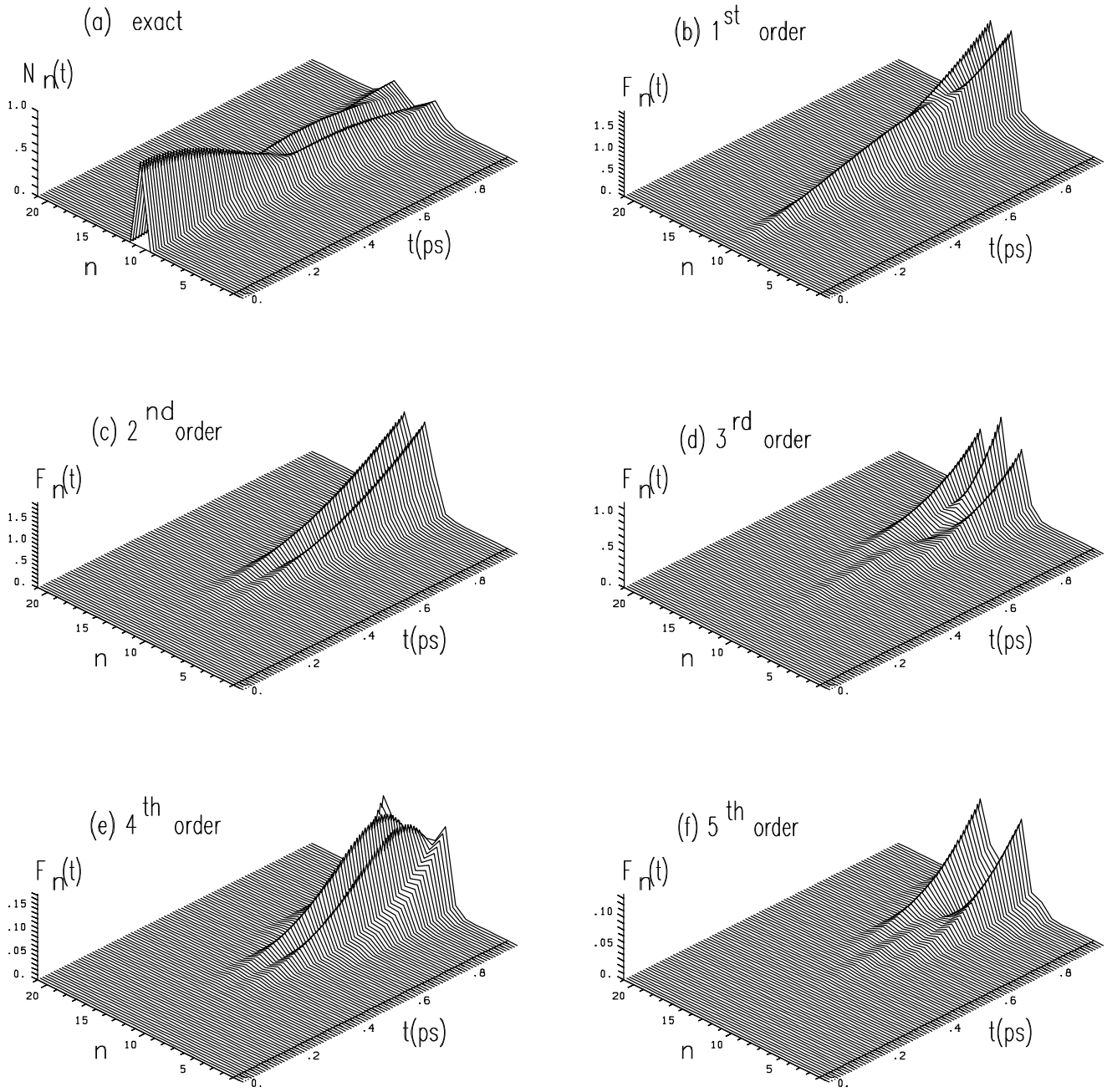


Figure 5. (continued on next page)

Obviously, within 1 ps the initially localized excitation spreads only over a few sites left and right of the initial excitation site. In the further parts of Fig. 5 we plot the errors of the corresponding expectation values $N_n(\mu,t)$, $F_n(\mu,t)=|N_n(t)-N_n(\mu,t)|$, for the state vectors in the different orders μ in time. It is clear that in first or second order, only in a small time interval of 0.1 ps (1st order) or 0.3 ps (2nd order) the errors are reasonably small, while in third order already a time interval of 0.6 ps is covered. In the higher orders, μ=4-7, the fine structure of the transport evolves, and the errors are reasonably small over the whole interval of 1 ps. In the highest (7th) order the maximum error within this time is around 0.02. Therefore, if we want to compare results as obtained from the $|D_1>$ state with those from an expansion as described (see following paper) we are only able to do that up to roughly 0.6 ps time if we want to restrict ourselves to a third order expansion.

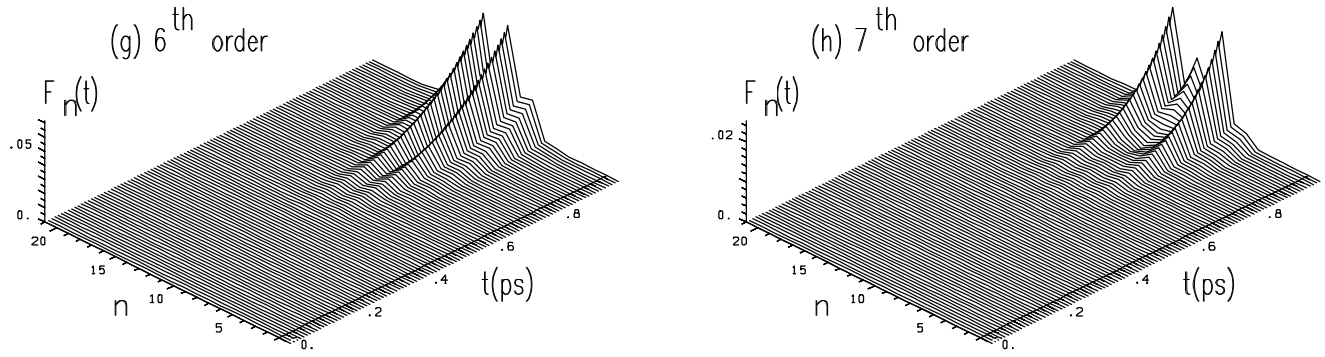


Figure 5: *The expectation values of the number operators $N_n(t)$ calculated from the exact state vector and the errors $F_n(\mu,t)=|N_n(t)-N_n(\mu,t)|$ for different orders μ of the state vector as function of site and time in the decoupled case:*
(a) $N_n(t)$ (b) $\mu=1$ (c) $\mu=2$ (d) $\mu=3$
(e) $\mu=4$ (f) $\mu=5$ (g) $\mu=6$ (h) $\mu=7$

The Phonon System in the Small Polaron Limit

The conclusion drawn in the last subchapter holds only for a freely dispersing excitation in the oscillator subsystem. In the complete system this time evolution is perturbed by the interaction with the phonons. Thus we have to study also, how well the lattice is described by such an expansion. To this end we turn now to the small polaron limit with a localized excitation at a site o (o=11 in our case of a chain with 21 units). Via the interaction of strength χ this localized excitation interacts with the initially unexcited lattice ($b_{nk}(0)=0$). It excites a shock wave in the lattice which travels roughly with the speed of sound through the chain. The excitation itself remains at its initial site, because J=0. The exact solution for this case $|\omega>$ is given in equ. (A14) in Appendix A. The time evolution of the displacements and momenta, as computed from the exact state vector, for our case (W=13 N/m, χ=62 pN and M=114 m_p) is shown in Fig. 6.

Our Hamiltonian in this case is given in equ. (A1) in Appendix A. The expansion of the wave function in a power series in time is obtained both by direct Taylor expansion of all the time dependent terms in the exact solution, equ. (A14), and ordering according to the powers of t, as well as by succesive action of the Hamiltonian on the initial state, where one has to commute the annihilation operators for phonons occurring in the operator through the expression for the preceding order until they act on the vacuum and vanish. This has to be done, until the final form of the state contains only phonon creation operators. The calculation is rather simple, but lengthy.

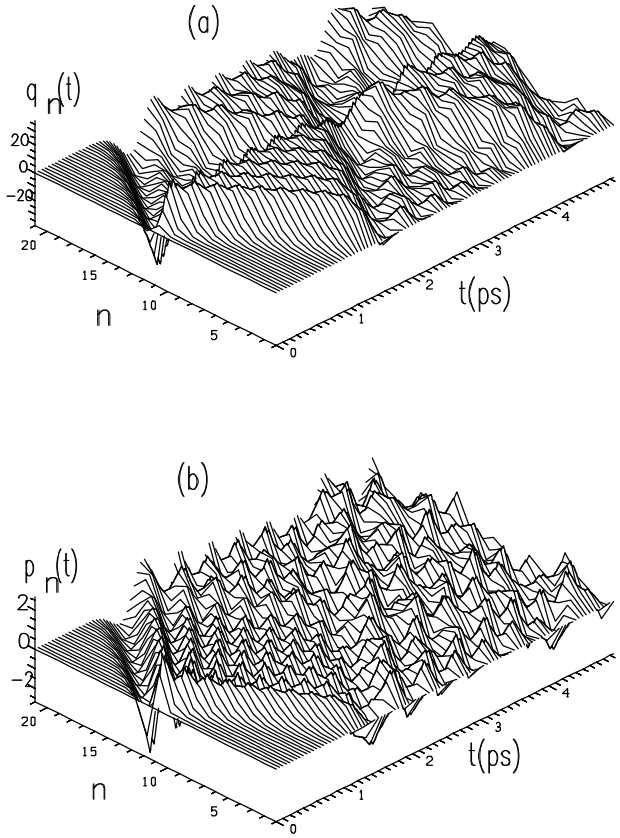


Figure 6: *The time evolution of diplacements $q_n(t)$ (in mÅ, part a) and momenta $p_n(t)$ (in meVps/Å, part b) in the small polaron limit as computed from the exact state vector for χ=62 pN (the plots of the time evolution for χ=35 pN are very similar, only the absolute values of $q_n(t)$ and $p_n(t)$ are of roughly half the magnitude).*

Therefore we show here only the final results, which are identical in both procedures described:

$$\left|\psi(\mu)\right\rangle = \sum_{\nu=1}^{\mu} \frac{T^{\nu}}{\nu!}\left|\psi_{\nu}\right\rangle \quad ; \quad T = -\frac{it}{\hbar}$$
$$\left|\psi_{\nu}\right\rangle = \hat{\omega}\left|\psi_{\nu-1}\right\rangle \quad ; \quad \left|\psi_{0}\right\rangle = \hat{a}_o^{+}\left|0\right\rangle \tag{59}$$

From this the components of the state vector in the first three orders μ are obtained as

$$\left|\psi_0\right\rangle = \hat{a}_o^{+}\left|0\right\rangle$$

$$\left|\psi_1\right\rangle = \hat{\omega}\left|\psi_0\right\rangle = \hat{y}_o^{+}\hat{a}_o^{+}\left|0\right\rangle \quad ; \quad \hat{y}_o^{+} \equiv \sum_k \hbar\omega_k B_{ok}\hat{b}_k^{+}$$

$$\left|\psi_2\right\rangle = \hat{\omega}\left|\psi_1\right\rangle =$$
$$= \left[\left(\hat{y}_o^{+}\right)^2 + \sum_k \left(\hbar\omega_k\right)^2 B_{ok}\left(B_{ok} + \hat{b}_k^{+}\right)\right]\hat{a}_o^{+}\left|0\right\rangle \tag{60}$$

$$\left|\psi_3\right\rangle = \hat{\omega}\left|\psi_2\right\rangle = \left[\left(\hat{y}_o^{+}\right)^3 + \right.$$
$$\left. + \sum_k \left(\hbar\omega_k\right)^2 B_{ok}\left(B_{ok} + \hat{b}_k^{+}\right)\left(3\hat{y}_o^{+} + \hbar\omega_k\right)\right]\hat{a}_o^{+}\left|0\right\rangle$$

The relevant expectation values in this case are the norm of the state S(μ,t)=<ψ(μ,t)|ψ(μ,t)>, the expectation value of the Hamiltonian and those of the phonon operators

$$S(\mu,t) = \left\langle\psi(\mu,t)\middle|\psi(\mu,t)\right\rangle$$
$$H(\mu,t) = \left\langle\psi(\mu,t)\middle|\hat{\omega}\middle|\psi(\mu,t)\right\rangle$$
$$B_k(\mu,t) = \left\langle\psi(\mu,t)\middle|\hat{b}_k\middle|\psi(\mu,t)\right\rangle \tag{61}$$
$$q_n(\mu,t) = \sum_k \sqrt{\frac{2\hbar}{M\omega_k}}U_{nk}\,\mathrm{Re}\left[B_k(\mu,t)\right]$$
$$p_n(\mu,t) = \sum_k \sqrt{2M\hbar\omega_k}U_{nk}\,\mathrm{Im}\left[B_k(\mu,t)\right]$$

The calculation of these expectation values is again rather tedious, so we refer the reader for some details and the explicit expressions to Appendix D and turn now to the numerical results.

As mentioned above we show in Figure 6 displacements and momenta as computed from the exact solution for χ=62 pN. The corresponding plots for χ=35 pN (not shown here), are looking very similar, however, in that case the absolute values are roughly half of that for the larger coupling. The results show the usual shock wave in the lattice, caused by the localized excitation at site o (o=11 in chains of 21 units). The wave clearly disperses and becomes enhanced when its front passes the initial excitation for the second time after roughly 2-3 ps. Figure 7, which shows the time evolution of H(μ,t) and of S(μ,t) indicates clearly, that the third order wave function is reasonably accurate on a time scale which is much smaller than that for the corresponding third order function in the decoupled oscillator system discussed before. The reason for this is that the characteristic times of the oscillations in the lattice are much smaller than the characteristic time of the oscillator system, as can be seen from Table 1.

Table 1: *The characteristic times of the different lattice oscillations, $T_k=1/\omega_k$, and for the amide-I oscillator subsystem, $T_0 = \hbar/J$, for the chain discussed in the main text (the different coupling constants do not influence these times).*

k	T_k(ps)	T_o(ps)
1,20	0.406	
2,19	0.205	
3,18	0.139	
4,17	0.107	
5,16	0.089	0.681
6,15	0.077	
7,14	0.070	
8,13	0.065	
9,12	0.062	
10,11	0.061	
21	∞	

For the case of the smaller coupling (χ=35 pN, m=114 m_p) the third order curve is close to the corresponding exact one for a time of roughly 0.12-0.14 ps and up to 0.12 ps for the larger coupling (χ=62 pN). This is due to the fact that for larger interaction the shock wave has a larger amplitude, which is excited on the same time scale. Thus with increasing coupling it becomes more difficult to describe the exact curves with a low order wave function. In Figure 8 we show the evolution of the displacements and momenta for sites o and o+1. In our very small region of time only these two sites are excited to a non-negligible extent. Already at sites

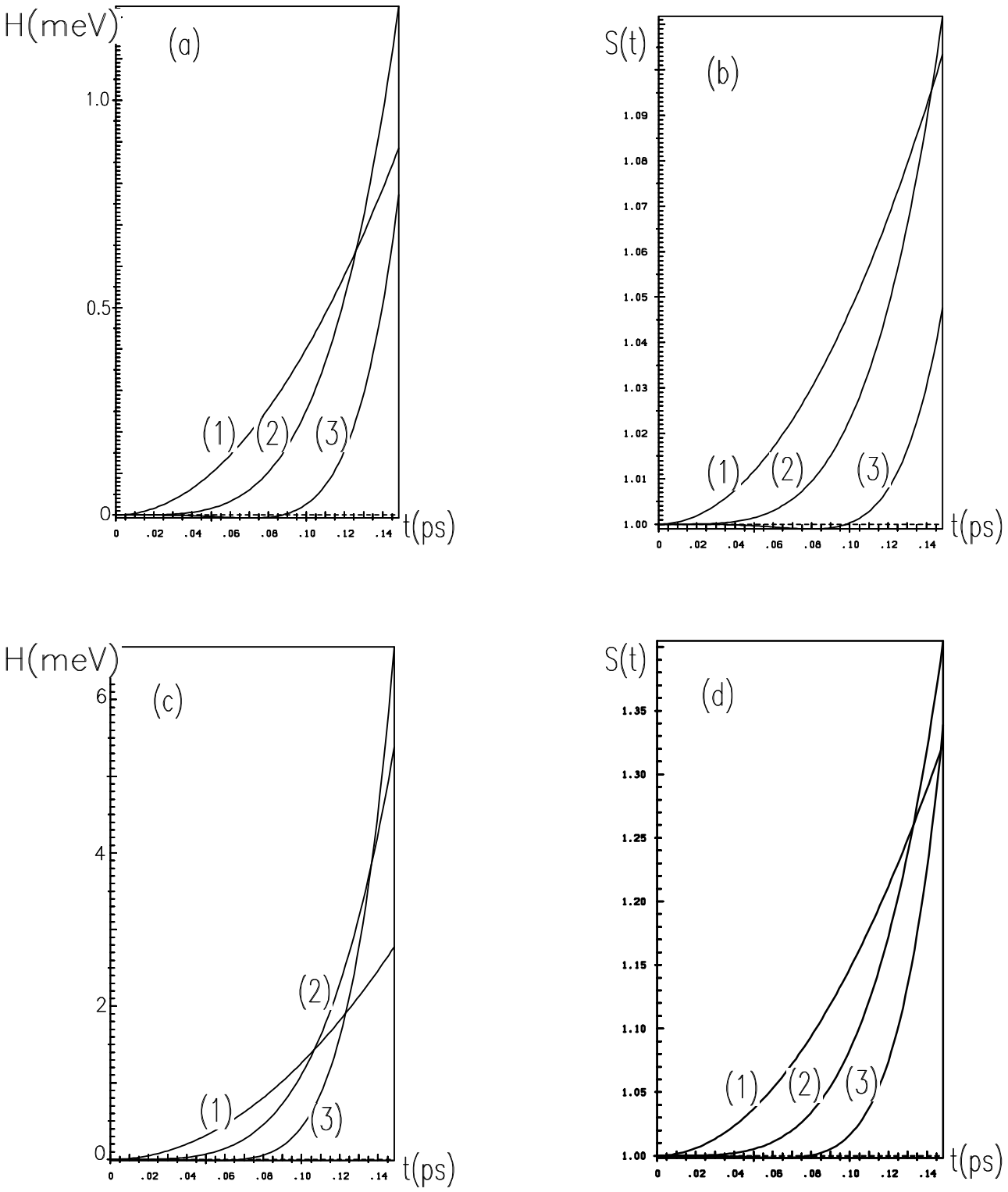


Figure 7: *The functions H(μ,t) (in meV) and S(μ,t) in the small polaron limit (the graphs corresponding to the different orders are marked by μ)*
(a) H(μ,t), χ=35 pN (b) S(μ,t), χ=35 pN
(c) H(μ,t), χ=62 pN (d) S(μ,t), χ=62 pN

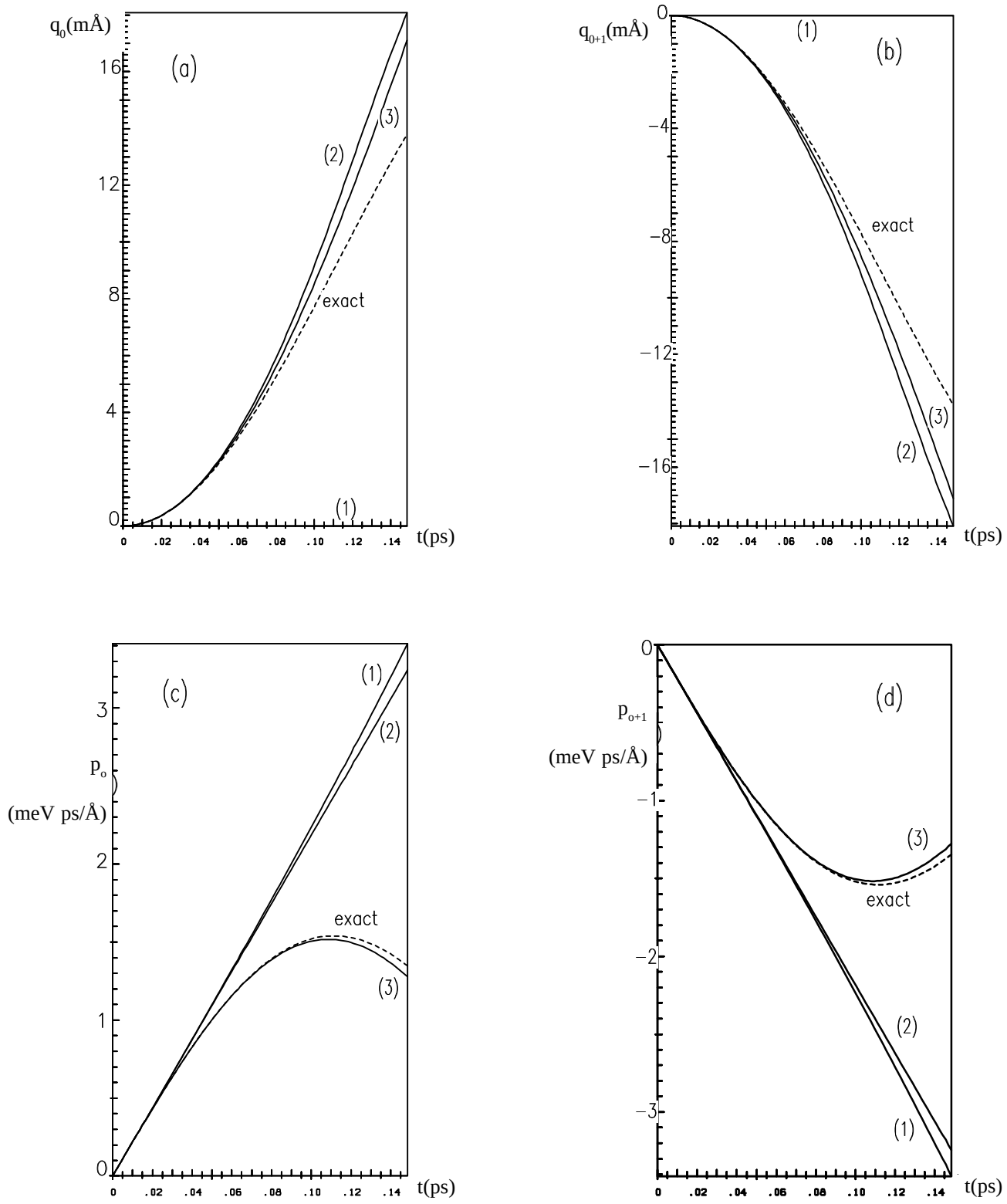
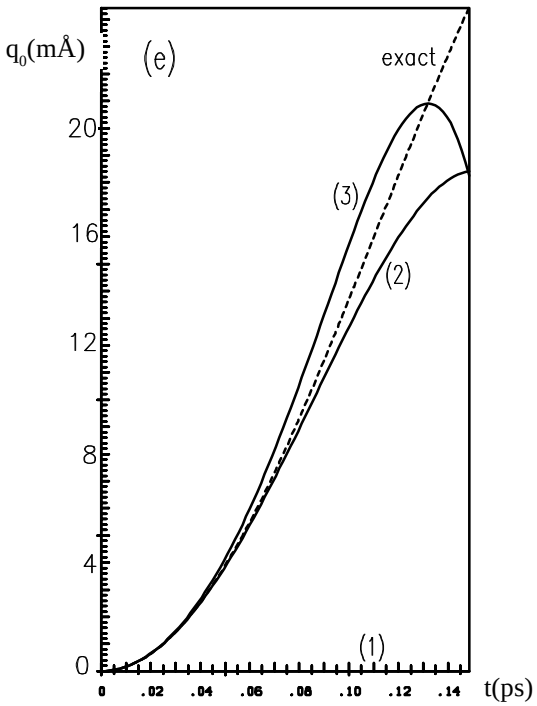
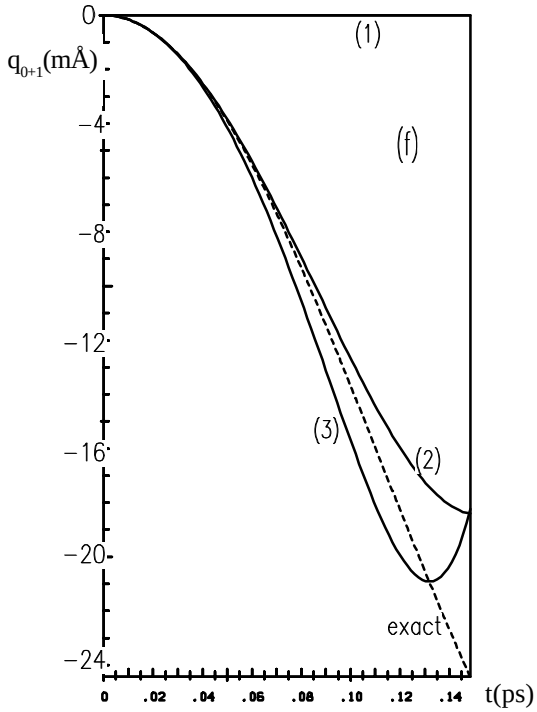
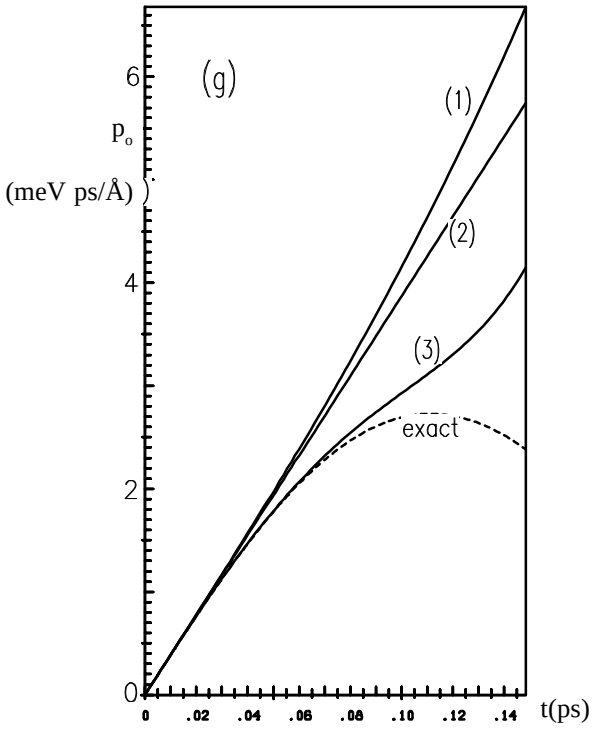


Figure 8 (continued on next page): *The displacements $q_o(\mu,t)$ and $q_{o+1}(\mu,t)$ together with the corresponding exact curves (in mÅ) and the momenta $p_o(\mu,t)$ and $p_{o+1}(\mu,t)$ together with the corresponding exact curves (in meVps/Å) in the small polaron limit (o=11, N=21):*

(a) $q_o(\mu,t)$; χ=35 pN *(b) $q_{o+1}(\mu,t)$; χ=35 pN*
(c) $p_o(\mu,t)$; χ=35 pN *(d) $p_{o+1}(\mu,t)$; χ=35 pN*
(e) $q_o(\mu,t)$; χ=62 pN *(f) $q_{o+1}(\mu,t)$; χ=62 pN*
(g) $p_o(\mu,t)$; χ=62 pN *(h) $p_{o+1}(\mu,t)$; χ=62 pN*







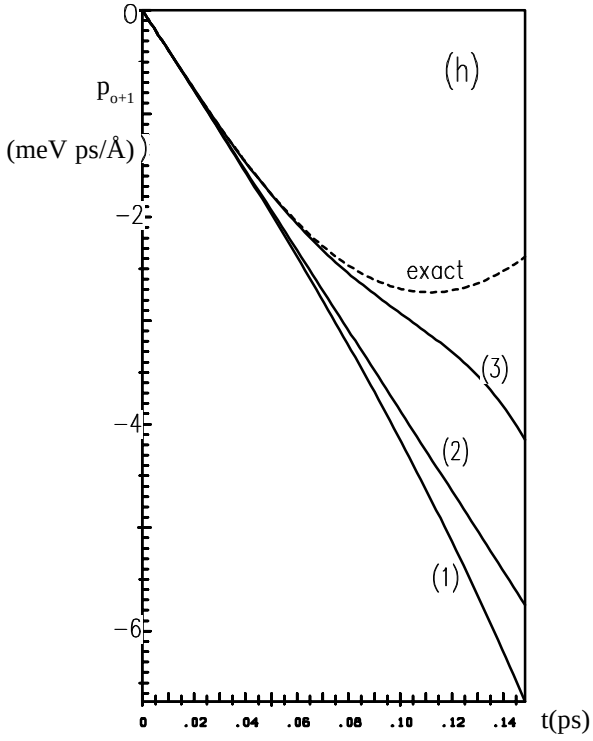


Figure 8 (continued)

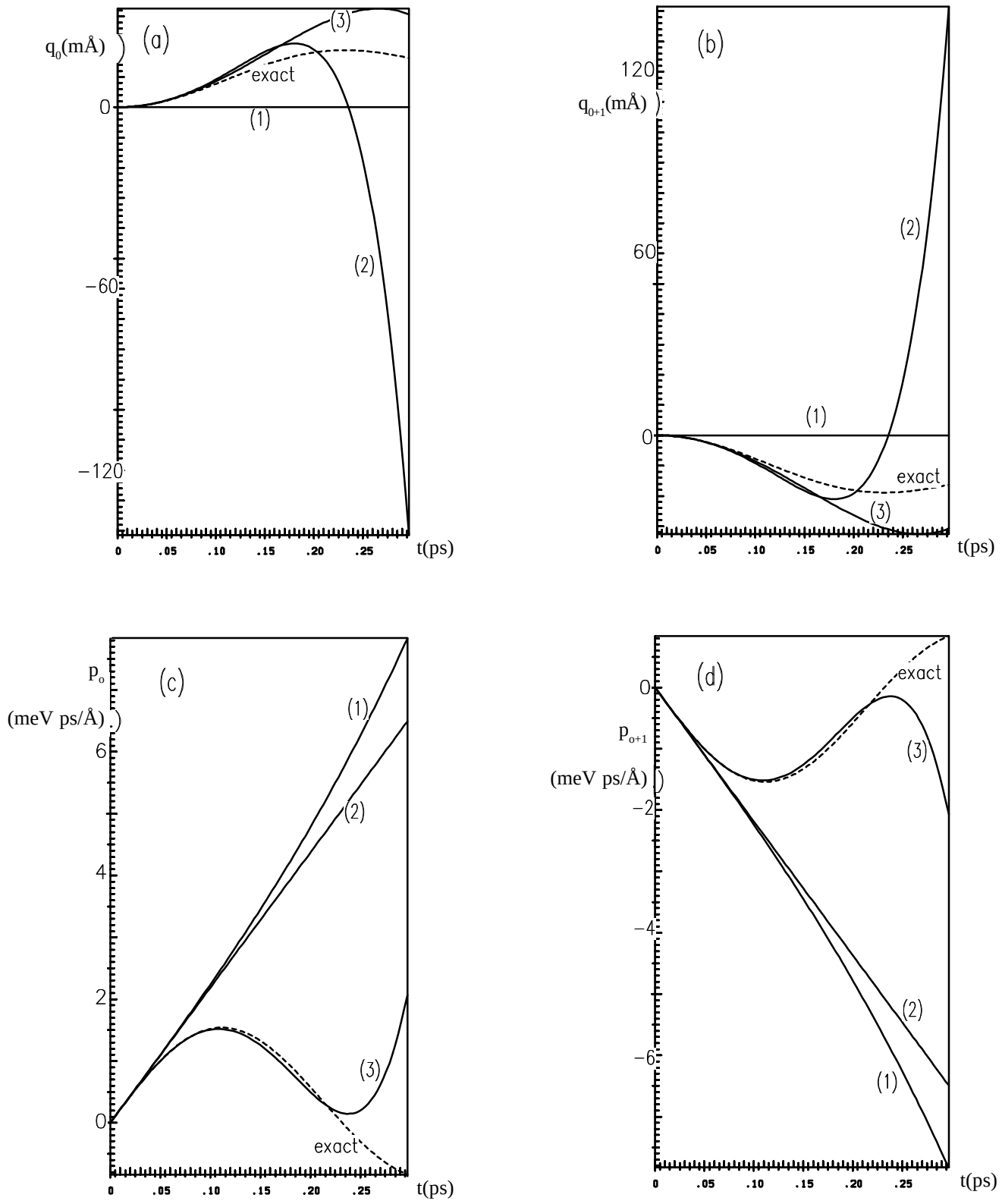


Figure 9: *As Figure 8 but for a longer time (χ=35 pN):*
(a) $q_o(\mu,t)$ (b) $q_{o+1}(\mu,t)$
(c) $p_o(\mu,t)$ (d) $p_{o+1}(\mu,t)$

o-1 and o+2 the excitations within 0.15 ps are negligible (a maximum of 0.1 mÅ for q_{o-2}, of 1.8 mÅ for q_{o-1}, of 0.05 meV ps/Å for p_{o-2}, and of 0.7 meV ps/Å for p_{o-1} in case of the smaller coupling). Thus on our small time scale we deal mainly with a dimer. In Figure 8a to d the displacements and momenta for the small coupling case are shown. The reliability of the third order curves in this case obviously corresponds to that of the total energy and the norm as discussed above. Thus also for displacements and momenta the third order wave function is a reasonable approximation to the exact one up to 0.12-0.14 ps in the small coupling case and up to around 0.12 ps for the larger coupling (Figure 8e to h). The situation for the momenta is somewhat strange, because at least for the small coupling the momenta in third order are reasonably correct on a larger time scale than the displacements, as can be seen in Fig. 9, and even the displacements are qualitatively tolerable up to more than 0.2 ps, although the norm and total energy of the third order state differ to a quite large extent from their correct values. However, this does not hold for larger coupling constants, like χ=62 pN, because in this case the unphysical increase of the factors containing explicit powers of t starts to dominate earlier. This is due to the fact, that for increasing coupling shock waves with increasing amplitudes are excited on the same time scale as for smaller couplings.

Conclusion

We have expanded for the exactly solvable transportless and the decoupled case of the Davydov Hamiltonian the exact wave functions in power serieses in time. From this one can conclude up to what times such expansions of the exact wave functions in the general case are reliable. This information is important for studies of the short time behaviour of the $|D_1>$, or also generally of other ansatz states. We found that in the case of coupling between a localized excitation of an amide-I oscillator in a cyclic chain (small polaron or transportless limit) to the lattice phonons a third order expansion of the exact wave function gives reliable results for the relevant variables of the lattice up to 0.12 ps for the larger coupling of χ=62 pN, and up to about 0.12-0.14 ps for a smaller coupling constant of χ=35 pN. The calculation of higher orders becomes very tedious and is for this reason not feasible. In the case of a decoupled oscillator system a third order wave function yields reasonable expectation values for about 0.6-0.8 ps. However, for our expansion of the exact wave function in the general case, which is the subject of the following paper, we have to restrict the study of its short time behaviour to the smaller one of the two time scales. Only in this case we can be confident that expectation values computed with a third order expansion are reasonable. More important, we have seen that the accuracy of S(t) and H(t) (constant in time for exact solutions and initial values known) parallels completely that of the other, physically more interesting expectation values for a given expansion in both systems studied. Thus S(t) and H(t) are indicators for the time up to which an expansion yields reliable results. In any case, one has to conclude that expansions of the kind used here are not useful for the investigation of long time dynamics, since to this end very large orders would be required, which are prohibitively tedious to compute. Therefore one cannot get rid in this way of the requirement to use ansatz states for such purposes.

Further we found that, although the $|D_1>$ ansatz state contains site dependent coherent state amplitudes, the initial state has to be constructed in form of a $|D_2>$ wave function, i.e. with site independent amplitudes, from the initial set of lattice displacements and momenta. Otherwise in case of the decoupled limit $|D_1>$ dynamics would not lead to the exact solution. Further, the known requirements for computation of correct amplitudes b_{nk} from a given set of displacements and momenta do not lead to a unique set of b_{nk}'s and only the use of site independent b_k's yields consistent values of the lattice energy.

In conlusion, the present work lead to the foundations for a thorough investigation of the very small time behaviour of $|D_1>$ dynamics (or generally for all ansatz states) in comparison to the exact wave function, which is the subject of the following paper.

Acknowledgement The financial support of the „Deutsche Forschungsgemeinschaft“ (project no. Fo 175/3-1) and of the „Fond der Chemischen Industrie“ is gratefully acknowledged.

References

1. Scott, A.C. *Phys. Rep.* **1992**, *217*, 1.
2. Davydov, A.S.; Kislukha, N.I. *Phys. Stat. Sol.* **1973**, *B59*, 465; Davydov, A.S. *Phys. Scripta* **1979,** *20*, 387.
3. Davydov, A.S. *Zh. Eksp. Teor. Fiz.* **1980**, *78*, 789; *Sov. Phys. JETP* **1980**, *51*, 397.
4. Scott, A.C. *Phys. Rev.* **1982**, *A26*, 57; *Physica Scripta* **1984**, *29*, 279; Mac Neil, L.; Scott, A.C. *Physica Scripta* **1984**, *29*, 284; *Phil. Trans. Roy Soc. London* **1985**, *A315*, 423.
5. Förner, W.; Ladik, J. In *Davydov's Soliton Revisited*; Christiansen, P.L.; Scott, A.C., Eds.; NATO ASI, Series B -Physics, Vol. 243; Plenum, New York (1991), 267.
6. Förner, W. *J. Phys.: Condensed Matter* **1993**, *5*, 803.
7. Halding, J.; Lomdahl, P.S. *Phys. Lett.* **1984**, *A124*, 37.
8. (a) Lomdahl, P.S.; Kerr, W.C. *Phys. Rev. Lett.* **1985**, *55*, 1235; and in *Davydov's Soliton Revisited*, Christiansen, P.L.; Sott, A.C., Eds. NATO ASI, Series B - Physics, Vol. 243, Plenum, New York (1991), 259.
   (b) Kerr, W.C.; Lomdahl, P.S. *Phys. Rev.* **1987**, *B35*, 3629.
   (c) Kerr, W.C.; Lomdahl, P.S. In *Davydov's Soliton Revisited*, Christiansen, P.L.; Scott, A.C., Eds.; NATO ASI,

Series B - Physics, Vol. 243, Plenum, New York (1991), 23.
9. Lawrence, A.F.; McDaniel, J.C.; Chang, D.B.; Pierce, B.M.; Birge, R.R. *Phys. Rev.* **1986**, *A33*, 1188.
10. Bolterauer, H. In *Structure Coherence and Chaos in Dynamical Systems*, Christiansen, P.L.; Parmentier, R.D., Eds.; Proc. MIDIT 1986 Workshop, Manchester University Press, Englsnd (1986); Bolterauer, H. In *Davydov's Soliton Revisited*, Christiansen, P.L.; Scott, A.C., Eds.; NATO ASI, Series B - Physics, Vol. 243, Plenum, New York (1991), 99, and 309.
11. Cottingham, J.P.; Schweitzer, J.W. *Phys. Rev. Lett.* **1989**, *62*, 1792; Schweitzer, J.W.; Cottingham, J.P. In *Davydov's Soliton Revisited*, Christiansen, P.L.; Scott, A.C., Eds.; NATO ASI, Series B - Physics, Vol. 243, Plenum, New York (1991), 285.
12. Motschmann, H.; Förner, W.; Ladik, J. *J. Phys.: Cond. Matter* **1989**, *1*, 5083.
13. (a) Förner, W. *J. Phys.: Cond. Matter* **1991**, *3*, 4333. (b) Förner, W. *J. Comput. Chem.* **1992**, *13*, 275.
14. Brown, D.W.; Linderberg, K.; West, B.J. *Phys. Rev.* **1986**, *A33*, 4104, 4110; *Phys. Rev.* **1987**, *B35*, 6169; *Phys. Rev.* **1988**, *B37*, 2946; Brown, D.W. *Phys. Rev.* **1988**, *A37*, 5010.
15. Cruzeiro, L.; Halding, J.; Christiansen, P.L.; Skovgaard, O.; Scott, A.C. *Phys. Rev.* **1988**, *A37*, 880.
16. Mechtly, B.; Shaw, P.B. *Phys.Rev.* **1988**, *B38*, 3075.
17. Skrinjar, M.J.; Kapor, D.V; Stojanovic, S.D. *Phys. Rev.* **1988**, *A38*, 6402.
18. Förner, W. *Phys. Rev.* **1991**, *A44*, 2694; *J. Mol. Struct. (Theochem)* **1993**, *282*, 223.
19. Förner, W. *Nanobiology* **1992**, *1*, 413.
20. Förner, W. *J. Phys.: Cond. Matter* **1992**, *4*, 1915.
21. Wang, X.; Brown, D.W.; Linderberg, K. *Phys. Rev. Lett.* **1989**, *62*, 1796.
22. Scott, A.C. Presented at the *Conference on Nonlinear Sciences: The Next Decade*, Los Alamos, National Laboratory, on May 21, 1990.
23. Brown, D.W.; Ivic, Z. *Phys. Rev.* **1989**, *B40*, 9876.
24. Förner, W. *J. Phys.: Cond. Matter* **1993**, *5*, 823.
25. Förner, W. *J. Phys.: Cond. Matter* **1993**, *5*, 3883.
26. Förner, W. *J. Phys.: Cond. Matter* **1993**, *5*, 3897.
27. Förner, W. *Physica* **1993**, *D68*, 68.
28. Förner, W. *J. Phys.: Cond. Matter* **1994**, *6*, 9089.
29. Cruzeiro-Hansson, L.; Christiansen, P.L.; Scott, A.C. In *Davydov's Soliton Revisited*, Christiansen, P.L.; Scott, A.C., Eds.; NATO-ASI Series B - Physics, No. 243; Plenum Press New York (1991), 325.
30. Kapor, D. Remark in *Davydov's Soliton Revisited*, Christiansen, P.L.; Scott, A.C., Eds.; Nato ASI Series No. 243, Plenum Press, New York (1991), 29.
31. Cruzeiro-Hansson, L.; Okhonin, V.A.; Khlebopros, R.G.; Yassievich, I.N. *Nanobiology* **1992**, *1*, 395.
32. Cruzeiro-Hansson, L. *Phys. Rev. Lett.* **1994**, *73*, 2927.
33. Förner, W. *J. Mol. Struct. (Theochem)* **1996**, *362*, 101.
34. Barthes, M. In *Nonlinear Excitations in Biomolecules*, Peyrard, M., Ed.; Springer, Berlin, Heidelberg, New York, (1995), 209.

Appendix A: Treatment of the Small Polaron Limit Using the $|D_1>$ Ansatz

The Hamiltonian $\hat{H}_{sp}$ in this case and the $|D_1>$ ansatz are given by

$$\hat{H}_{SP} \equiv \hat{\omega} = \sum_{nk} \hbar\omega_k B_{nk}\left(\hat{b}_k^+ + \hat{b}_k\right)\hat{a}_n^+\hat{a}_n + \sum_k \hbar\omega_k \hat{b}_k^+\hat{b}_k$$

$$\left|D_1\right\rangle = \sum_n a_n(t)\hat{a}_n^+\left|0\right\rangle_e\left|\beta_n\right\rangle \tag{A1}$$

$$\left|\beta_n\right\rangle = \exp\left[-\tfrac{1}{2}\sum_k \left|b_{nk}(t)\right|^2\right]\cdot\exp\left[\sum_k b_{nk}(t)\hat{b}_k^+\right]\left|0\right\rangle_p$$

First of all we have to show that our ansatz satisfies the Schrödinger equation for the Hamiltonian given in (A1). The left hand side of the equation is readily calculated and yields

$$i\hbar\tfrac{\partial}{\partial t}\left|D_1\right\rangle = i\hbar\sum_n\left\{-\sum_k\left[\dot{b}_{nk}\left(\tfrac{1}{2}b_{nk}^* - \hat{b}_k^+\right) + \tfrac{1}{2}\dot{b}_{nk}^* b_{nk}\right]a_n + \dot{a}_n\right\}\left|\beta_n\right\rangle\hat{a}_n^+\left|0\right\rangle_e \tag{A2}$$

To eliminate the time derivatives in (A2) we need the equations of motion for the $|D_1>$ ansatz under the condition J=0. From equ. (17) in the main text follows

$$i\hbar\dot{a}_n = -\frac{i\hbar}{2}\sum_k\left(\dot{b}_{nk}b_{nk}^* - \dot{b}_{nk}^* b_{nk}\right)a_n + \sum_k \hbar\omega_k\left[B_{nk}\left(b_{nk} + b_{nk}^*\right) + \left|b_{nk}\right|^2\right]a_n \tag{A3}$$

$$i\hbar\dot{b}_{nk} = \hbar\omega_k\left(b_{nk} + B_{nk}\right) \tag{A4}$$

Substitution of (A4) into (A3) yields

$$i\hbar\dot{a}_n = \tfrac{1}{2}\sum_k \hbar\omega_k B_{nk}\left(b_{nk} + b_{nk}^*\right)a_n \tag{A5}$$

The use of (A5) together with (A4) leads to the final form of (A2)

$$i\hbar\tfrac{\partial}{\partial t}\left|D_1\right\rangle = \sum_{nk}\hbar\omega_k\left[B_{nk}b_{nk} + \left(b_{nk} + B_{nk}\right)\hat{b}_k^+\right]\left|\beta_n\right\rangle a_n\hat{a}_n^+\left|0\right\rangle_e \tag{A6}$$

With the help of the eigenvalue equation for coherent states

$$\hat{b}_k\left|\beta_n\right\rangle = b_{nk}\left|\beta_n\right\rangle \tag{A7}$$

we obtain (A8) for the different terms on the right hand side of the Schrödinger equation and comparison with (A6) shows that the equation is fulfilled, and thus $|D_1>$ together with the equations of motion (A4) and (A5) is the exact solution for the small polaron limit:

$$\begin{aligned}\hat{\omega}\left|D_1\right\rangle &= \sum_n\left[\sum_{mk}\hbar\omega_k B_{mk}\left(\hat{b}_k^+ + \hat{b}_k\right)\hat{a}_m^+\hat{a}_m + \sum_k \hbar\omega_k\hat{b}_k^+\hat{b}_k\right]\left|\beta_n\right\rangle a_n\hat{a}_n^+\left|0\right\rangle_e = \\ &= \sum_{nk}\hbar\omega_k\left[B_{nk}\hat{b}_k^+ + B_{nk}b_{nk} + b_{nk}\hat{b}_k^+\right]\left|\beta_n\right\rangle a_n\hat{a}_n^+\left|0\right\rangle_e = i\hbar\tfrac{\partial}{\partial t}\left|D_1\right\rangle\end{aligned} \tag{A8}$$

The explicit form of this solution is obtained by direct integration of (A4):

$$\int_{b_{nk}(0)}^{b_{nk}(t)}\frac{db'_{nk}}{b'_{nk}+B_{nk}} = -i\omega_k\int_0^t dt' \tag{A9}$$

and thus

$$b_{nk}(t) = b_{nk}(0)e^{-i\omega_k t} + B_{nk}\left(e^{-i\omega_k t} - 1\right) \tag{A10}$$

Further, together with (A10), we can integrate (A5)

$$i\hbar \int_{a_n(0)}^{a_n(t)} \frac{da'_n}{a'_n} = \tfrac{1}{2}\sum_k \hbar\omega_k B_{nk} \int_0^t \left[b_{nk}(t') + b^*_{nk}(t')\right]dt' \tag{A11}$$

which yields the general solution for the transportless case

$$|D_1\rangle = \sum_n \exp\left\{\sum_k \left[b_{nk}(t)\hat{b}^+_k - b^*_{nk}(t)\hat{b}_k\right]\right\} a_n(t)\hat{a}^+_n|0\rangle \tag{A12}$$

$$a_n(t) = a_n(0)\cdot \exp\left\{-i\sum_k B^2_{nk}\left[\sin(\omega_k t) - \omega_k t\right]\right\}\cdot \exp\left\{-i\sum_k B_{nk}\left\{\mathrm{Re}\left[b_{nk}(0)\right]\sin(\omega_k t) + \mathrm{Im}\left[b_{nk}(0)\right]\left[1-\cos(\omega_k t)\right]\right\}\right\}$$

$$b_{nk}(t) = b_{nk}(0)e^{-i\omega_k t} + B_{nk}\left(e^{-i\omega_k t} - 1\right)$$

where Re[x] (Im[x]) denotes the real (imaginary) part of a complex number x. For later considerations we need also the special case, that we start from an undistorted lattice and an excitation localized at one site o, i. e. $b_{nk}(0)=0$ and $a_n(0)=\delta_{no}$:

$$a_n(t) = e^{-i\sum_k B^2_{ok}\left[\sin(\omega_k t)-\omega_k t\right]}\delta_{no} \quad ; \quad b_{nk}(t) = B_{nk}\left(e^{-i\omega_k t} - 1\right) \tag{A13}$$

with the total state vector

$$|\omega\rangle = e^{-i\sum_k B^2_{ok}\left[\sin(\omega_k t)-\omega_k t\right]}\cdot e^{\sum_k \left[b_{ok}(t)\hat{b}^+_k - b^*_{ok}(t)\hat{b}_k\right]}\hat{a}^+_o|0\rangle$$
$$b_{ok}(t) = B_{ok}\left(e^{-i\omega_k t} - 1\right) \tag{A14}$$

For the computation of expectation values we concentrate first on the same case as Brown et al. [14], namely an undistorted lattice $b_{nk}(0)=0$, but an arbitrary excitation $a_n(0)$. Then the lattice energy is given by

$$E_{lat} = \sum_k \hbar\omega_k \left\langle D_1\left|\hat{b}^+_k\hat{b}_k\right|D_1\right\rangle = \sum_{nk}\hbar\omega_k |a_n|^2 |b_{nk}|^2 \tag{A15}$$

With the help of

$$|a_n(t)|^2 = |a_n(0)|^2 \equiv P_{nn} \quad ; \quad |b_{nk}(t)|^2 = 2B^2_{nk}\left[1-\cos(\omega_k t)\right] \tag{A16}$$

we obtain

$$E_{lat} = 2\sum_{nk} \hbar\omega_k B^2_{nk} P_{nn}\left[1-\cos(\omega_k t)\right] \tag{A17}$$

which is identical to the exact result given by Brown et al. (Ref. [14], second paper). The exciton-lattice interaction energy is

$$E_{\mathrm{int}} = \sum_{nk}\hbar\omega_k B_{nk}\left\langle D_1\left|\left(\hat{b}^+_k + \hat{b}_k\right)\hat{a}^+_n\hat{a}_n\right|D_1\right\rangle = 2\sum_{nk}\hbar\omega_k B_{nk}\,\mathrm{Re}\left[b_{nk}\right]|a_n|^2 = 2\sum_{nk}\hbar\omega_k B^2_{nk}P_{nn}\left[\cos(\omega_k t) - 1\right] = -E_{lat} \tag{A18}$$

Therefore, as to be expected, the total energy is conserved and vanishes in this case. The expectation values of the phonon operators are

$$B_k \left\langle D_1 \middle| \hat{b}_k \middle| D_1 \right\rangle = \sum_n |a_n|^2 b_{nk} = \sum_n P_{nn} B_{nk} \left(e^{-i\omega_k t} - 1 \right) \quad ; \quad B_k^* = \left\langle D_1 \middle| \hat{b}_k^+ \middle| D_1 \right\rangle \tag{A19}$$

From this we obtain the displacements as

$$q_n(t) = \sum_k \sqrt{\frac{2\hbar}{M\omega_k}} U_{nk} \, \mathrm{Re}[B_k] = \sum_{mk} \sqrt{\frac{2\hbar}{M\omega_k}} P_{mm} U_{nk} B_{mk} \left[\cos(\omega_k t) - 1 \right] \tag{A20}$$

where matrix $\underline{\underline{U}}$ contains the normal mode coefficients (see Appendix B for details). This is again identical to the exact quantity given by Brown et al. Finally the momenta are given by

$$p_n(t) = \sum_k \sqrt{2M\hbar\omega_k} U_{nk} \, \mathrm{Im}[B_k] = -\sum_{mk} \sqrt{2M\hbar\omega_k} P_{mm} U_{nk} B_{mk} \sin(\omega_k t) \tag{A21}$$

For the general case we have

$$\begin{aligned} E_{lat} &= \sum_{nk} \hbar\omega_k \left\{ |b_{nk}(0)|^2 + 2B_{nk}^2 \left[1 - \cos(\omega_k t) \right] + 2B_{nk} \left[x_{nk} \left[1 - \cos(\omega_k t) \right] - y_{nk} \sin(\omega_k t) \right] \right\} \cdot P_{nn} \\ E_{\mathrm{int}} &= \sum_{nk} \hbar\omega_k \left\{ 2B_{nk}^2 \left[\cos(\omega_k t) - 1 \right] + 2B_{nk} \left[x_{nk} \cos(\omega_k t) + y_{nk} \sin(\omega_k t) \right] \right\} \cdot P_{nn} \end{aligned} \tag{A22}$$

where the abbreviations x_{nk}=Re[$b_{nk}(0)$] and y_{nk}=Im[$b_{nk}(0)$] were used. Finally the conserved total energy $E_{tot}=E_{lat}+E_{int}$ is given by

$$E_{tot} = \left\langle D_1 \middle| \hat{\omega} \middle| D_1 \right\rangle = \sum_{nk} \hbar\omega_k \left\{ |b_{nk}(0)|^2 + B_{nk} \left[b_{nk}(0) + b_{nk}^*(0) \right] \right\} \cdot P_{nn} \tag{A23}$$

Appendix B: Normal Mode Coefficients for the Lattice

The solution of the classical normal mode problem for a cyclic chain of oscillators leads to the problem of diagonalization of a matrix $\underline{\underline{V}}$:

$$\begin{aligned} &\underline{\ddot{q}} = -\underline{\underline{V}} \; \underline{q} \Rightarrow \underline{\underline{U}}^+ \underline{\ddot{q}} = -\underline{\underline{U}}^+ \underline{\underline{V}} \; \underline{\underline{U}} \; \underline{\underline{U}}^+ \underline{q} \Rightarrow \underline{\underline{U}}^+ \underline{\ddot{q}} = -\underline{\underline{\omega}}^2 \underline{\underline{U}}^+ \underline{q} \quad ; \quad \omega_{kk'}^2 \equiv \omega_k^2 \delta_{kk'} \\ &V_{nm} = \frac{W}{M} \left\{ 2\delta_{nm} - (1 - \delta_{nN}) \delta_{m,n+1} - (1 - \delta_{n1}) \delta_{m,n-1} - \delta_{n1} \delta_{mN} - \delta_{nN} \delta_{m1} \right\} \end{aligned} \tag{B1}$$

For this purpose we split the matrix in the form

$$\begin{aligned} \underline{\underline{V}} &= \frac{W}{M} \left(2 \cdot \underline{\underline{1}} - \underline{\underline{X}} \right) \\ X_{nm} &= (1 - \delta_{nN}) \delta_{m,n+1} + (1 - \delta_{n1}) \delta_{m,n-1} + \delta_{n1} \delta_{mN} + \delta_{nN} \delta_{m1} \end{aligned} \tag{B2}$$

Instead of the eigenvalue problem $\underline{\underline{V}}\underline{u}_k = \omega_k^2 \underline{u}_k$ we solve the related problem $\underline{\underline{X}}\underline{u}_k = \lambda_k \underline{u}_k$. The relation is, that both matrices have the same eigenvectors and the relation of the eigenvalues is

$$\underline{\underline{V}}\underline{u}_k = \frac{W}{M}\left(2\cdot\underline{\underline{1}} - \underline{\underline{X}}\right)\underline{u}_k = 2\frac{W}{M}\underline{u}_k - \frac{W}{M}\lambda_k\underline{u}_k = \frac{W}{M}\left(2-\lambda_k\right)\underline{u}_k \Rightarrow \omega_k^2 = \frac{W}{M}\left(2-\lambda_k\right) \tag{B3}$$

Since $\underline{\underline{X}}$ is a reducible representation of the rotation group C_N we can write down its eigenvector matrix $\underline{\underline{U}}$ without further calculation:

$$\underline{\underline{U}} \equiv \left(\underline{u}_1 \quad \underline{u}_2 \quad \dots \quad \underline{u}_N\right) \;\; ; \;\; U_{nk} = \frac{1}{\sqrt{N}} e^{\frac{2\pi i}{N}nk} \;\; ; \;\; \Rightarrow U_{nk} = U_{N+1,k} \;\; ; \;\; U_{nk} = U_{n,N+k} \;\; ; \;\; U_{n,N-k} = U_{nk}^*$$
$$\sum_k U_{nk}U_{n'k}^* = \delta_{nn'} \;\; ; \;\; \sum_n U_{nk}^* U_{nk'} = \delta_{kk'} \tag{B4}$$

Since in our cyclic system, the choice of the numbering is arbitrary, we assume n and k to run from 1 to N. The eigenvalues are obtained by explicitely performing the matrix product

$$\left(\underline{\underline{U}}^+ \underline{\underline{X}}\,\underline{\underline{U}}\right)_{kk'} = \lambda_k \delta_{kk'} \tag{B5}$$

using the relation

$$\delta_{kk'} = \frac{1}{N}\sum_{n=1}^{N} e^{\frac{2\pi i}{N}n(k-k')} \tag{B6}$$

From this calculation the eigenvalues of $\underline{\underline{X}}$ and $\underline{\underline{V}}$ are found to be

$$\lambda_k = 2\cdot\cos\left(\frac{2\pi}{N}k\right) \;\; ; \;\; \omega_k^2 = 2\frac{W}{M}\left[1-\cos\left(\frac{2\pi}{N}k\right)\right] \tag{B7}$$

Using $1-\cos(2\alpha)=2\sin^2(\alpha)$ we obtain

$$\omega_k = 2\sqrt{\frac{W}{M}}\cdot\sin\left(\frac{\pi}{N}k\right) \tag{B8}$$

Obviously with exception of k=N each eigenvalue is doubly degenerate (we concentrate here and in the rest of the paper on odd numbers N), namely $\omega_k=\omega_{N-k}$, which is easily shown, using the trigonometric relation $\sin(\alpha-\beta)=\sin(\alpha)\cos(\beta)-\cos(\alpha)\sin(\beta)$. Therefore, any linear combination of the two eigenvectors belonging to the eigenvalues ω_k and ω_{N-k} yields also eigenvectors of $\underline{\underline{V}}$. Thus from the set of degenerate eigenvectors, we can form a new set of real and orthonormal eigenvectors by

$$\varphi_{nk}^{(1)} = \frac{1}{\sqrt{2}}\left(U_{nk} + U_{n,N-k}\right) = \sqrt{\frac{2}{N}}\cdot\cos\left(\frac{2\pi}{N}nk\right)$$
$$\varphi_{nk}^{(2)} = -\frac{i}{\sqrt{2}}\left(U_{nk} - U_{n,N-k}\right) = \sqrt{\frac{2}{N}}\cdot\sin\left(\frac{2\pi}{N}nk\right) \tag{B9}$$
$$k = 1,\dots,\frac{N-1}{2}$$

Since the new eigenvectors belong still to degenerate eigenvalues, we can form again another set of orthonormal eigenvectors by the linear combination:

$$\psi_{nk}^{(1,2)} = \frac{1}{\sqrt{2}}\left(\varphi_{nk}^{(1)} \pm \varphi_{nk}^{(2)}\right) \tag{B10}$$

leading to

$$\cos(\alpha)+\sin(\alpha) = \sqrt{2}\cos\left(\alpha - \frac{\pi}{4}\right) \Rightarrow \psi_{nk}^{(1)} = \sqrt{\frac{2}{N}}\cos\left(\frac{2\pi}{N}nk - \frac{\pi}{4}\right) \tag{B11a}$$

and

$$\cos(\alpha)-\sin(\alpha) = \sqrt{2}\cos\left(\alpha + \frac{\pi}{4}\right) \Rightarrow \psi_{nk}^{(2)} = \sqrt{\frac{2}{N}}\cos\left(\frac{2\pi}{N}nk + \frac{\pi}{4}\right) \tag{B11b}$$

where k runs again from 1 to (N-1)/2. To get rid of the unpleasent fact of having two functions for one k, we use in the second function (B11b) the index k'=N-k instead of k, but with k' running from [(N-1)/2+1] to (N-1). After performing this substitution and using the relation $\cos(\alpha+\beta)=\cos\alpha\cos\beta-\sin\alpha\sin\beta$ with $\alpha=2\pi n$ we arrive at

$$\begin{aligned}
&\psi_{nk}^{(1)} = \sqrt{\frac{2}{N}}\cos\left(\frac{2\pi}{N}nk - \frac{\pi}{4}\right) \quad ; \quad k = 1,\ldots,\frac{N-1}{2} \\
&\psi_{nk'}^{(2)} = \sqrt{\frac{2}{N}}\cos\left(\frac{2\pi}{N}nk' - \frac{\pi}{4}\right) \quad ; \quad k' = \left(\frac{N-1}{2}+1\right),\ldots,(N-1)
\end{aligned} \tag{B12}$$

Since $\cos\left[2\pi n - (\pi/4)\right] = 1/\sqrt{2}$ we have now our final set of real eigenvalues and we substitute it for the eigenvector matrix $\underline{\underline{U}}$:

$$\begin{aligned}
\omega_k &= 2\sqrt{\frac{W}{M}}\cdot\sin\left(\frac{\pi}{N}k\right) \\
U_{nk} &= \sqrt{\frac{2}{N}}\cos\left(\frac{2\pi}{N}nk - \frac{\pi}{4}\right) \quad ; \quad k = 1,\ldots,N \quad ; \quad N \text{ odd} \\
\underline{\underline{U}}^{+}\underline{\underline{U}} &= \underline{\underline{U}}\;\underline{\underline{U}}^{+} = \underline{\underline{1}}
\end{aligned} \tag{B13}$$

This form of the normal mode coefficients can also be used to develop an ab inito Hartree-Fock Crystal Orbital formalism based on real numbers only. However, in this case it does not lead to a complete block-diagonalization, because it leaves the pairwise degenerate sets unresolved [33].

Appendix C: Analytical Solution of the Oscillator System in the Decoupled Case

The Hamiltonian for the oscillator system in the decoupled (χ=0) case reads as

$$\hat{J} = -J\sum_{n}\left(\hat{a}_n^{+}\hat{a}_{n+1} + \hat{a}_{n+1}^{+}\hat{a}_n\right) \tag{C1}$$

With the ansatz

$$\left|\psi_e\right\rangle = \sum_{n} a_n(t)\hat{a}_n^{+}\left|0\right\rangle_e \tag{C2}$$

the Schrödinger equation can be exactly solved and is transformed to

$$-\frac{i\hbar}{J}\dot{\underline{a}} = \underline{\underline{X}}\,\underline{a} \tag{C3}$$

where $\underline{\underline{X}}$ is the same matrix as defined in Appendix B, equ. (B2). Therefore we have again the same eigenvector matrix $\underline{\underline{R}}$ and eigenvalues λ_k:

$$\lambda_k = 2\cos\left(\frac{2\pi}{N}k\right) \quad ; \quad R_{nk} = \frac{1}{\sqrt{N}} e^{\frac{2\pi i}{N}nk} \quad ; \quad k = 1,\ldots,N \tag{C4}$$

However, here we keep its complex form and name it $\underline{\underline{R}}$. Then with the transformation $\underline{\underline{R}}^{+}\,\underline{a} = \underline{c}$ our equation becomes

$$-\frac{i\hbar}{J}\dot{\underline{c}} = \underline{\underline{\lambda}}\,\underline{c} \quad ; \quad \lambda_{kk'} = \lambda_k \delta_{kk'} \tag{C5}$$

which is simple to integrate:

$$\int_{c_k(0)}^{c_k(t)} \frac{dc'_k}{c'_k} = i\frac{J}{\hbar}\lambda_k \int_0^t dt' \Rightarrow c_k(t) = c_k(0) e^{i\frac{J}{\hbar}\lambda_k t} \tag{C6}$$

The backtransformation is simply done by multiplying the result for $\underline{c}$(t) from the left with $\underline{\underline{R}}$ and replacing $\underline{c}$(0) by $\underline{\underline{R}}^{+}\,\underline{a}(0)$:

$$\underline{a}(t) = \underline{\underline{R}}\,\underline{c}(t) = \underline{\underline{R}} \cdot e^{i\frac{J}{\hbar}\underline{\underline{\lambda}}t}\,\underline{\underline{R}}^{+}\,\underline{a}(0) \quad ; \quad \left(e^{i\frac{J}{\hbar}\underline{\underline{\lambda}}t}\right)_{kk'} = e^{i\frac{J}{\hbar}\lambda_k t}\delta_{kk'} \tag{C7}$$

or without matrix notation:

$$a_n(t) = \frac{1}{N}\sum_{n'=1}^{N}\sum_{k=1}^{N} e^{\frac{2\pi i}{N}k(n-n')} \cdot e^{2i\frac{Jt}{\hbar}\cos\left(\frac{2\pi}{N}k\right)} \cdot a_{n'}(0) \tag{C8}$$

Thus the total wave function is given by

$$\left|\psi_e\right\rangle = \frac{1}{N}\sum_{n,n'=1}^{N}\sum_{k=1}^{N} e^{\frac{2\pi i}{N}k(n-n')} \cdot e^{2i\frac{Jt}{\hbar}\cos\left(\frac{2\pi}{N}k\right)} \cdot a_{n'}(0)\hat{a}_n^{+}\left|0\right\rangle_e \tag{C9}$$

The expectation values N_n of the number operators $\hat{a}_n^{+}\hat{a}_n$ are given by

$$N_n(t) = \left|a_n(t)\right|^2 = \frac{1}{N^2}\sum_{kk'}\sum_{n'n''} e^{\frac{2\pi i}{N}n(k-k')} \cdot e^{\frac{2\pi i}{N}(k'n''-kn')} \cdot e^{2i\frac{Jt}{\hbar}\left[\cos\left(\frac{2\pi}{N}k\right)-\cos\left(\frac{2\pi}{N}k'\right)\right]} \cdot a_{n'}(0)a^{*}_{n''}(0) \tag{C10}$$

For calculation of the norm of the state we have to sum N_n over n. Then the first exponential can be summed over n and yields together with the factor 1/N the Kronecker symbol $\delta_{kk'}$. When the sum over k' is performed the time dependent exponent

vanishes. Then the summation over k can be performed, leading together with the second factor 1/N to $\delta_{n'n''}$. Thus the norm is conserved and equals the norm of the initial state.
The total energy is given by

$$E_{tot} = -J\sum_n \left(a_n^*(t)a_{n+1}(t) + a_n(t)a_{n+1}^*(t)\right) = -2J\sum_n \mathrm{Re}\left[a_n^*(t)a_{n+1}(t)\right] = -2J\sum_n \mathrm{Re}\left[a_n^*(0)a_{n+1}(0)\right] \tag{C11}$$

where the last equality is obtained with the help of the same summation procedure as above, with the only difference that instead of $\delta_{n'n''}$ in this case a factor $\delta_{n'',n'+1}$ is obtained.

For later use we want to give finally the wave function coefficients for the special case of an initial excitation localized at just one site o, i.e. $a_n(0)=\delta_{on}$:

$$|J\rangle = \frac{1}{N}\sum_{nk} e^{\frac{2\pi i}{N}k(n-o)} \cdot e^{2i\frac{Jt}{\hbar}\cos\left(\frac{2\pi}{N}k\right)} \cdot \hat{a}_n^+ |0\rangle_e \tag{C12}$$

In this case the total energy vanishes and N_n is given by

$$N_n(t) = \frac{1}{N^2}\sum_{kk'} e^{\frac{2\pi i}{N}(n-o)(k-k')} \cdot e^{2i\frac{Jt}{\hbar}\left[\cos\left(\frac{2\pi}{N}k\right)-\cos\left(\frac{2\pi}{N}k'\right)\right]} \tag{C13}$$

Appendix D: The Relevant Expectation Values for the Phonon System in the Small Polaron Limit

First of all we compute the norm of the states in different order. In 0th order we have simply S(0,t)=1, and in 1st order

$$S(1,t) = 1 + \sum_k \left(B_{ok}\omega_k t\right)^2 \tag{D1}$$

Then in 2nd order we obtain

$$S(2,t) = \left\langle \psi(1,t) + \frac{1}{2}T^2\psi_2 \middle| \psi(1,t) + \frac{1}{2}T^2\psi_2 \right\rangle =$$

$$= S(1,t) - \frac{t^2}{\hbar^2}\mathrm{Re}\left[\langle\psi_0|\psi_2\rangle\right] + \frac{t^3}{\hbar^3}\mathrm{Im}\left[\langle\psi_1|\psi_2\rangle\right] + \frac{1}{4}\frac{t^4}{\hbar^4}\langle\psi_2|\psi_2\rangle = \frac{3}{4}\left[\sum_k \left(B_{ok}\omega_k t\right)^2\right]^2 + \frac{1}{4}\sum_k B_{ok}^2\left(\omega_k t\right)^4 \tag{D2}$$

In this way we simplify all expectation values to the corresponding one of the preceding order and a series of expectation values between the $|\psi_\mu>$. Further we calculate S(3,t) to

$$S(3,t) = -\frac{1}{3}S(2,t) + \frac{5}{12}\left[\sum_k \left(B_{ok}\omega_k t\right)^2\right]^3 + \frac{5}{18}\left[\sum_k B_{ok}^2\left(\omega_k t\right)^3\right]^2 + \frac{5}{12}\sum_k B_{ok}^2\left(\omega_k t\right)^4 \sum_{k'} \left(B_{ok'}\omega_{k'} t\right)^2 + \frac{1}{36}\sum_k B_{ok}^2\left(\omega_k t\right)^6 \tag{D3}$$

For calculation of the expectation values of the Hamiltonian we split the expression into two terms leading to

$$H(\mu,t) = \sum_k \hbar\omega_k \left\langle \psi(\mu,t)\middle|\hat{b}_k^+\hat{b}_k\middle|\psi(\mu,t)\right\rangle + 2\sum_k \hbar\omega_k B_{ok}\ \mathrm{Re}\left[B_k(\mu,t)\right] \tag{D4}$$

This leads to H(0,t)=0 and further to

$$H(1,t)=\sum_k \hbar\omega_k\left(B_{ok}\omega_k t\right)^2$$

$$H(2,t)=\frac{5}{4}\sum_k \hbar\omega_k\left(B_{ok}\omega_k t\right)^2\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2+\frac{1}{4}\sum_k \hbar\omega_k B_{ok}^2\left(\omega_k t\right)^4 \tag{D5}$$

$$H(3,t)=-\frac{1}{3}H(2,t)+\frac{7}{12}\sum_k \hbar\omega_k B_{ok}^2\left(\omega_k t\right)^4\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2+$$
$$+\sum_k \hbar\omega_k\left(B_{ok}\omega_k t\right)^2\left\{\frac{35}{12}\left[\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2\right]^2+\frac{35}{36}\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^4\right\}+\frac{1}{36}\sum_k \hbar\omega_k B_{ok}^2\left(\omega_k t\right)^6$$

Further we give the expectation values of the phonon annihilation operators, where $B_k(0,t)=0$:

$$B_k(1,t)=-iB_{ok}\omega_k t$$

$$B_k(2,t)=-iB_{ok}\omega_k t\left[1+\frac{1}{2}\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2\right]+\frac{1}{2}B_{ok}\omega_k t\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^3-\frac{1}{2}B_{ok}\left(\omega_k t\right)^2\left[1-\frac{1}{2}\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2\right] \tag{D6}$$

$$B_k(3,t)=B_k(2,t)+\frac{i}{2}B_{ok}\omega_k t\left\{\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2-\frac{1}{2}\left[\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2\right]^2-\frac{1}{6}\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^4\right\}-$$
$$-\frac{i}{6}B_{ok}\left(\omega_k t\right)^2\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^3+\frac{i}{6}B_{ok}\left(\omega_k t\right)^3\left[1-\frac{1}{2}\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2\right]+$$
$$+B_{ok}\omega_k t\left\{\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^3\left[-\frac{2}{3}+\frac{5}{6}\sum_{k''}\left(B_{ok''}\omega_{k''}t\right)^2\right]+\frac{1}{12}\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^5\right\}+\frac{1}{36}B_{ok}\left(\omega_k t\right)^3\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^3+$$
$$+\frac{1}{2}B_{ok}\left(\omega_k t\right)^2\left[-\sum_{k'}\left(B_{ok'}\omega_{k'}t\right)^2+\frac{1}{2}\left[\sum_{k'}B_{ok'}\left(\omega_{k'}t\right)^2\right]^2+\frac{1}{6}\sum_{k'}B_{ok'}^2\left(\omega_{k'}t\right)^4\right]$$

Finally note, that

$$B_k^*(\mu,t)=\left\langle\psi(\mu,t)\middle|\hat{b}_k^+\middle|\psi(\mu,t)\right\rangle \tag{D7}$$

holds.

Appendix E: Separation of the Phase Factor of the Exact Solution

We have found that the operators $\hat{D}$ and $\hat{H}$ commute [see equ.(4)]. Further we know that the initial single exciton state must be of the form

$$\left|\Phi(0)\right\rangle = \sum_n \hat{B}_n(0) a_n(0) \hat{a}_n^+ \left|0\right\rangle \tag{E1}$$

where the operator $\hat{B}_n(0)$ creates the initial set of displacements and momenta from the phonon vacuum. Thus $\hat{B}_n(0)$ can contain only complex scalars and phonon operators. Then

$$e^{T\hat{D}}\left|\Phi(0)\right\rangle = \sum_{\nu=0}^{\infty} \frac{T^\nu}{\nu!} \hat{D}^\nu \hat{B}_n(0) a_n(0) \hat{a}_n^+ \left|0\right\rangle \quad ; \quad T \equiv \left(-\frac{it}{\hbar}\right) \tag{E2}$$

holds. Since

$$\hat{D}\hat{a}_n^+\left|0\right\rangle = \left[\sum_m E_0 \hat{a}_m^+ \hat{a}_m + \frac{1}{2}\sum_k \hbar\omega_k\right]\hat{a}_n^+\left|0\right\rangle = \left[E_0 + \frac{1}{2}\sum_k \hbar\omega_k\right]\hat{a}_n^+\left|0\right\rangle \tag{E3}$$

we have

$$\hat{D}^\nu \hat{a}_n^+\left|0\right\rangle = \left[E_0 + \frac{1}{2}\sum_k \hbar\omega_k\right]^\nu \hat{a}_n^+\left|0\right\rangle \tag{E4}$$

and therefore

$$e^{T\hat{D}}\left|\Phi(0)\right\rangle = e^{T\left(E_0+\frac{1}{2}\sum_k \hbar\omega_k\right)}\left|\Phi(0)\right\rangle \tag{E5}$$

Finally we obtain

$$\left|\Phi(t)\right\rangle = e^{T\left(\hat{H}+\hat{D}\right)}\left|\Phi(t)\right\rangle = e^{T\hat{H}} e^{T\hat{D}}\left|\Phi(0)\right\rangle = e^{-\frac{it}{\hbar}\left(E_0+\frac{1}{2}\sum_k \hbar\omega_k\right)} e^{T\hat{H}}\left|\Phi(0)\right\rangle \tag{E6}$$

which is the same separation as discussed in the main text.