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Davydov Soliton Dynamics in Proteins: II. The General Case

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)

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Abstract

We performed long time simulations using the $|D_1>$ approximation for the solution of the Davydov Hamiltonian. In addition we computed expectation values of the relevant operators with the state $\left(\hat{H}_D/J\right)\left|D_1\right\rangle$ and the deviation $|\delta>$ from the exact solution over long times, namely 10 ns. We found that in the very long time scale the $|D_1>$ ansatz is very close to an exact solution, showing expectation values of the relevant physical observables in the state $\left(\hat{H}_D/J\right)\left|D_1\right\rangle$ being about 5-6 orders of magnitudes larger than in the deviation state $|\delta>$. In the intermediate time scale of the ps range such errors, as known from our previous work, are somewhat larger, but still more or less negligibly. Thus we also report results from an investigation of the very short time (in the range 0-0.4 ps) behaviour of the $|D_1>$ state compared with that of an expansion of the exact solution in powers of time t. This expansion is reliable for about 0.12 ps for special cases as shown in the previous paper. However, the accuracy of the exactly known value of the norm and the expectation value of the Hamiltonian finally indicates up to what time a given expansion is valid, as also shown in the preceding paper. The comparison of the expectation values of the operators representing the relevant physical observables, formed with the third order wave function and with the corresponding results of $|D_1>$ simulations has shown, that our expansion is valid up to a time of roughly 0.10-0.15 ps. Within this time the second and third order corrections turned out to be not very important. This is due to the fact that our first order state contains already some terms of the expansion, summed up to inifinite order. Further we found good agreement of the results obtained with our expansion and those from the corresponding $|D_1>$ simulations within the time of about 0.10 ps. At later times, the factors with explicit powers of t in second and third order become dominant, making the expansion meaningless. Possibilities for the use of such expansions for larger times are described. Alltogether we have shown (together with previous work on medium times), that the $|D_1>$ state, although of approximative nature, is very close to an exact solution of the Davydov model on time scales from some femtoseconds up to nanoseconds. Especially the very small time region is of importance, because in this time a possible soliton formation from the initial excitation would start.

Keywords: Proteins, Davydov Model, Nonlinear Dynamics, Expansion of Exact Solutions, Ansätze

Introduction

In the Introduction to the preceding paper [1], we discussed already the basic concepts of the Davydov soliton mechanism for energy transport in proteins [2-5]. Therefeore we refer the reader to that paper and references therein, and especially to the most recent and best review of the state of art in Davydov soliton theory given by Scott [6]. In our preceding paper [1] we studied special cases of the Davydov Hamiltonian. In these cases it turned out that the $|D_1>$ ansatz state of Davydov [3] represents the exact solution, if the initial state is restricted to $|D_2>$ [2] like states with site independent coherent states amplitudes. Further we found that expansions of the exact wave functions in polynomial serieses in time and truncation of these polynomials after the third order yield reliable results for times up to 0.10-0.12 ps for the lattice in the small polaron limit, and 0.6-0.8 ps for the amide-I oscillators in the decoupled case. More important, we found that the accuracy of the norm and of the expectation value of the Hamiltonian (total energy) corresponds exactly to that of the expectation values of the exciton number operators in the decoupled case and that of the displacement and momentum operators in the small polaron limit. Thus norm and total energy are a measure of the time scale within which a given expansion yields reliable results. In the present work which is based on [1] and makes use also of the explicit forms of the wave functions discussed there we determine similar expansions of the exact solution of the full Davydov Hamiltonian up to the third order and compare them on the very short time scale with the results of $|D_1>$ simulations in order to get quantitative informations on the reliability of that ansatz which is not an exact solution of the time dependent Schrödinger equation. Further, using concepts developed in [7] and applied to a medium time scale in the range of a few picoseconds in [8], we study the behaviour of the errors introduced by the use of the $|D_1>$ ansatz on large time scales of the order of nanoseconds.

This study completes our previous one [8], where we concluded that in the subspace of basis functions spanned by the $|D_1>$ ansatz, the errors are negligible within times of a few picoseconds. From this result we concluded, that on this time scale the $|D_1>$ ansatz should be rather close to an exact solution, because we expect that if the exact solution would contain important contributions from basis states not included in $|D_1>$, this should cause large errors also in the space spanned by $|D_1>$. However, the very small time scale is an important one, because in that time a possible soliton formation from a localized initial state starts, especially since the lattice is initially in equilibrium and only driven by the interaction with the localized initial excitation in the chain of amide-I oscillators. In case of a possible soliton formation exactly these initial displacements of the lattice formed in the first few hundredths of a picosecond stabilizes the amide-I excitation against dispersion. To investigate this range of time we expand the exact solution $\left|\Phi\right\rangle = \exp\left[-i\hat{H}_D t/\hbar\right]\Phi_0\rangle$ for the Davydov Hamiltonian ($\hat{H}_D$), where $|\Phi_o>$ is the initial state, in a Taylor series in time and compare the results with those from a $|D_1>$ simulation. Attempts into this direction have been reported previously by Cruzeiro-Hansson, Christiansen and Scott [9]. 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 draw no numerical conclusions from it.

Davydov's Hamiltonian and the $|D_1>$ Approximation

The Hamiltonian, as well as the form of the $|D_1>$ approximation have been discussed extensively in the literature and in the preceding paper [1]. However, for the purpose of clearcut definitions in the following, we repeat here the form of the Hamiltonian as it is used extensively in this work. The full Hamiltonian can be written as

$$\hat{H}_D = \hat{H} + \hat{D} \quad ; \quad \hat{D} \equiv E_0 \sum_{n=1}^{N} \hat{a}_n^+ \hat{a}_n + \tfrac{1}{2} \sum_{k=1}^{N-1} \hbar\omega_k \tag{1}$$

where E_0 is the amide-I excitation energy, $\hat{a}_n$ ($\hat{a}_n^+$) are annihilation (creation) operators of amide-I vibrational quanta at site n in the chain and ω_k are the eigenfrequencies of the decoupled lattice. All definitions and details can be found in [1]. As also shown in [1] the exact state vecor is then

$$\left|\Phi\right\rangle = e^{-\frac{it}{\hbar}\left(E_0 + \frac{1}{2}\sum_{k=1}^{N-1}\hbar\omega_k\right)} \left|\psi\right\rangle \tag{2}$$

where $|\psi>$ obeys the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\left|\psi\right\rangle = \hat{H}\left|\psi\right\rangle \tag{3}$$

with the simplified Hamiltonian

$$\hat{H} = \hat{J} + \hat{\omega} \tag{4}$$

where

$$\hat{J} = -J \sum_{n=1}^{N} \left(\hat{a}_{n+1}^+ \hat{a}_n + \hat{a}_n^+ \hat{a}_{n+1} \right) \tag{5}$$

Here J is the coupling constant between two neighboring amide-I oscillators. Further

$$\hat{\omega} = \sum_{k=1}^{N-1} \hbar\omega_k \left[\hat{b}_k^+ \hat{b}_k + \sum_{n=1}^{N} B_{nk} \left(\hat{b}_k + \hat{b}_k^+ \right) \hat{a}_n^+ \hat{a}_n \right] \tag{6}$$

$$B_{nk} \equiv \frac{\chi}{\omega_k} \frac{1}{\sqrt{2M\hbar\omega_k}} \left[U_{n+1,k} - U_{nk} \right] \quad ; \quad k \neq N$$

where $\hat{b}_k$ ($\hat{b}_k^+$) is the annihilation (creation) operator for an acoustical lattice phonon k, M is the mass of a site and χ the coupling constant between the amide-I oscillators (excitons) and the lattice. The matrix $\underline{\underline{U}}$ contains the normal mode coefficients in the real representation for the decoupled lattice. Again the details are derived in paper [1]. We use for the present study cyclic boundary conditions and chains with an odd number of sites (N), thus n=N+1 equals n=1 and n=0 equals n=N. The $|D_1>$ ansatz for $|\psi>$ has the form (the restriction at the sums over k just excludes the translational mode)

$$\left| D_1 \right\rangle = \sum_{n=1}^{N} a_n(t) \hat{U}_n \hat{a}_n^+ \left| 0 \right\rangle \tag{7}$$

$$\begin{aligned} \hat{U}_n \left| 0 \right\rangle_p &= \exp\left[-\tfrac{1}{2} \sum_{k=1}^{N-1} \left| b_{nk}(t) \right|^2 \right] \cdot \exp\left[\sum_{k=1}^{N-1} b_{nk}(t) \hat{b}_k^+ \right] \left| 0 \right\rangle_p \\ &= \exp\left\{ \sum_{k=1}^{N-1} \left[b_{nk}(t) \hat{b}_k^+ - b_{nk}^*(t) \hat{b}_k \right] \right\} \left| 0 \right\rangle_p \end{aligned}$$

Note, that the last equality holds only if the operator acts on the phonon vacuum $|0>_p$, and that in our notation $|0>=|0>_e|0>_p$, where $|0>_e$ is the vacuum state for the amide-I oscillators (exciton vacuum). The $b_{nk}(t)$ are the coherent state amplitudes and $|a_n(t)|^2$ is the probability to find an amide-I quantum at site n. The equations of motion for these quantities can be obtained with the Euler-Lagrange equations of the second kind (see again [1] and references therein for all details):

$$\begin{aligned} i\hbar\dot{a}_n = &-\frac{i\hbar}{2} \sum_{k=1}^{N-1} \left(\dot{b}_{nk} b_{nk}^* - \dot{b}_{nk}^* b_{nk} \right) a_n + \\ &+ \sum_{k=1}^{N-1} \hbar\omega_k \left[B_{nk} \left(b_{nk} + b_{nk}^* \right) + \left| b_{nk} \right|^2 \right] a_n - \\ &- J \left(D_{n,n+1} a_{n+1} + D_{n,n-1} a_{n-1} \right) \end{aligned} \tag{8}$$

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

where the coherent state overlaps are given by

$$D_{nm} = \exp\left[-\tfrac{1}{2} \sum_{k=1}^{N-1} \left(\left| b_{nk} - b_{mk} \right|^2 + b_{nk} b_{mk}^* - b_{nk}^* b_{mk} \right) \right] \tag{9}$$

Long Time Simulations

In this sub-chapter we want to study the important question of the long-time behaviour of the errors introduced by the $|D_1>$ ansatz. One cannot exclude that these errors, which are very small for intermediate times of some ps (see [1] and references therein for details), might increase with time. In our case, the basis space of $|D_1>$ is incomplete, since it is not an exact solution. However, from the magnitude of the errors introduced within the basis space of $|D_1>$, we can estimate the importance of the basis states missing in the ansatz. If these missing states would be important in the exact solution, one would expect, that the errors made by the ansatz should be rather large already within the subset of the basis space spanned by $|D_1>$. For the numerical investigation of these errors we can use the fact that [7]

$$\left(i\hbar \frac{\partial}{\partial t} - \hat{H}_D \right) \left| D_1 \right\rangle = J \left| \delta \right\rangle \tag{10}$$

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 [7]. In our previous work [8] we have derived expressions for the expectation values of different operators for the two states $\left(\hat{H}_D / J \right) \left| D_1 \right\rangle$ and $|\delta>$ and compared them in numerical calculations. Such a procedure can serve as the appropriate tool to answer our above mentioned question.

As initial state state we use the same one as described in detail in paper [1], section III.3. It consists of a sech-function for the coefficients in the oscillator part and a lattice, populated with phonons according to a temperature of 300K. We performed calculations for different exciton-phonon coupling constants, namely χ = 60 pN, 120 pN, 180 pN, and 240 pN, and chains of length N=21 units. For the fourth order Runge-Kutta simulations we used in case of χ = 60 pN a time step of 0.1 fs and a total simulation time of 10 ns, corresponding to 10^8 time steps. In this period the error in total energy (0.796 eV) was typically between 0 and -7 peV (the exciton-phonon interaction energy was between 0.5 and -4.5 meV) and the error in norm between 0 and -0.006 ppb (parts per billion). The computation time was 2.48 minutes of CPU (Central Processing Unit) time for the simulation of 1 ps and thus 413 hours of CPU time for the complete simulation on an IBM RISC/6000-320H workstation. In the other three calculations we used a time step of 1 fs for the same total simulation time and in these cases the absolute values of the errors in total energy were less than 3 μeV (χ=120 pN, exciton-phonon interaction energy E_{ep} between 0.5 and -12 meV), less than 44 μeV (χ=180 pN, exciton-phonon interaction energy E_{ep} between -5 and -25 meV) and less than 400 μeV (χ=240 pN, exciton-phonon interaction energy E_{ep} between -2 and -45 meV), respectively. The absolute values of the errors in the norms were less than 4 ppm (parts per million, χ=120 pN), 80 ppm (χ=180 pN) and 750 ppm (χ=240 pN). From this it is obvious that a time step of 1 fs is sufficient to obtain correct results for simulation times of 10 ns. Also for the case of χ=60 ps the larger time step caused no significant changes in the results.

Figure1 shows the time evolution of the probability to find an amide-I quantum at a site n for the three different cases. While we observe a complete dispersion of the initial sech-distribution in case of the two smaller couplings, the initial excitation remains localized in the range of the initial distribution up to 10 ns in case of the larger couplings. For χ=60 pN a considerable fraction of the excitation localizes itself at more or less a single site close to the center of the initial excitation after 2-3 ns and remains there until the end of the simulation. Such spontaneous localizations cannot occur for the larger coupling, because in these cases the thermal disorder in the lattice is more strongly coupled to the oscillator system. In Figure 2 we show the norms $S_H(t)=\left\langle (\hat{H}/J)D_1 \middle| (\hat{H}/J)D_1 \right\rangle$ for the four values of the coupling constant. Obviously the norms show a decreasing tendency for increasing coupling, namely from maximum values of roughly 7000 (χ=60 pN) to 1200 (χ=240 pN). For the smallest coupling the function shows a fast oscillation around 5000 when time increases, while for the largest coupling a

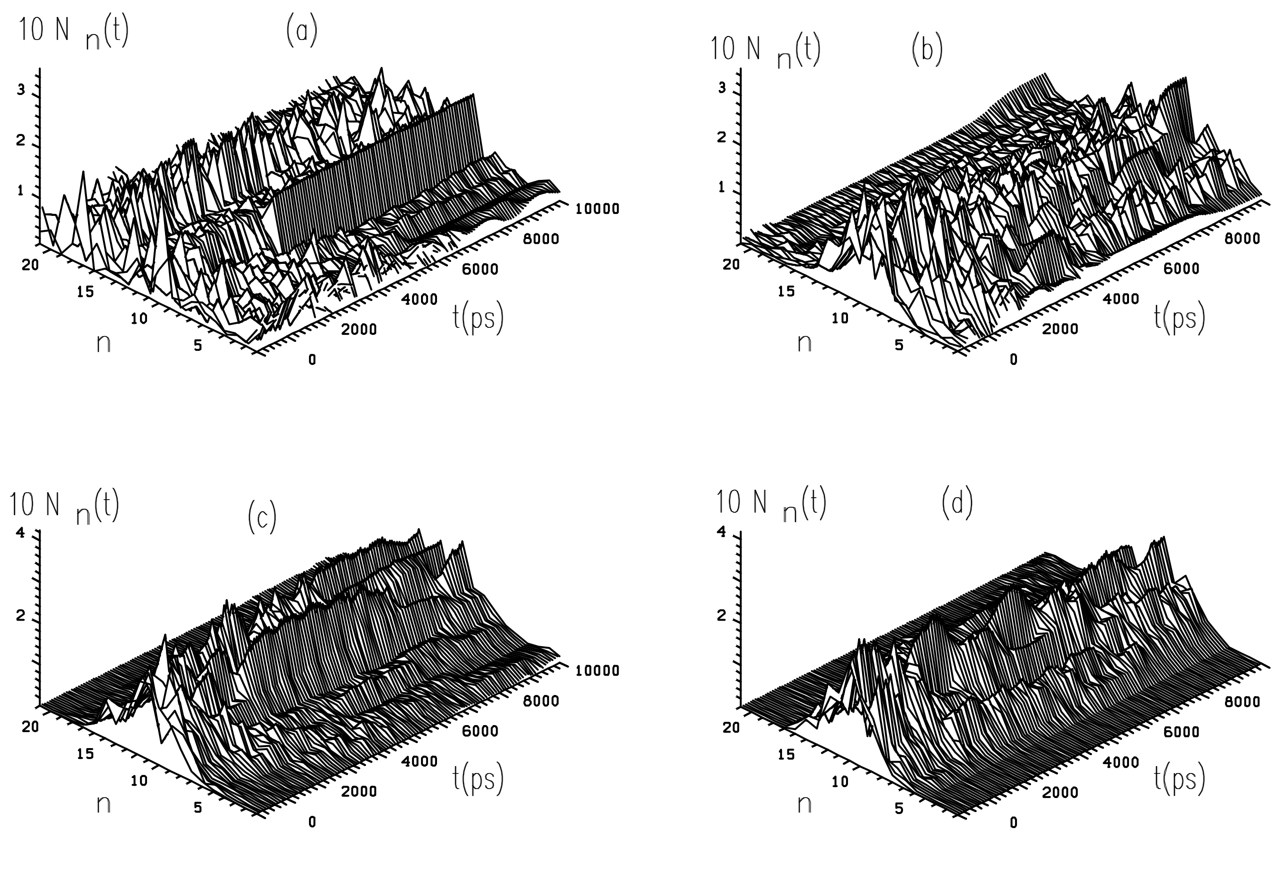


Figure 1: *Long-time evolution of $N_n(t)=\langle D_1|\hat{a}_n^+\hat{a}_n|D_1\rangle$ for four values of the exciton-lattice coupling constant.*
(a) χ=60 pN *(b) χ=120 pN*
(c) χ=180 pN *(d) χ=240 pN*

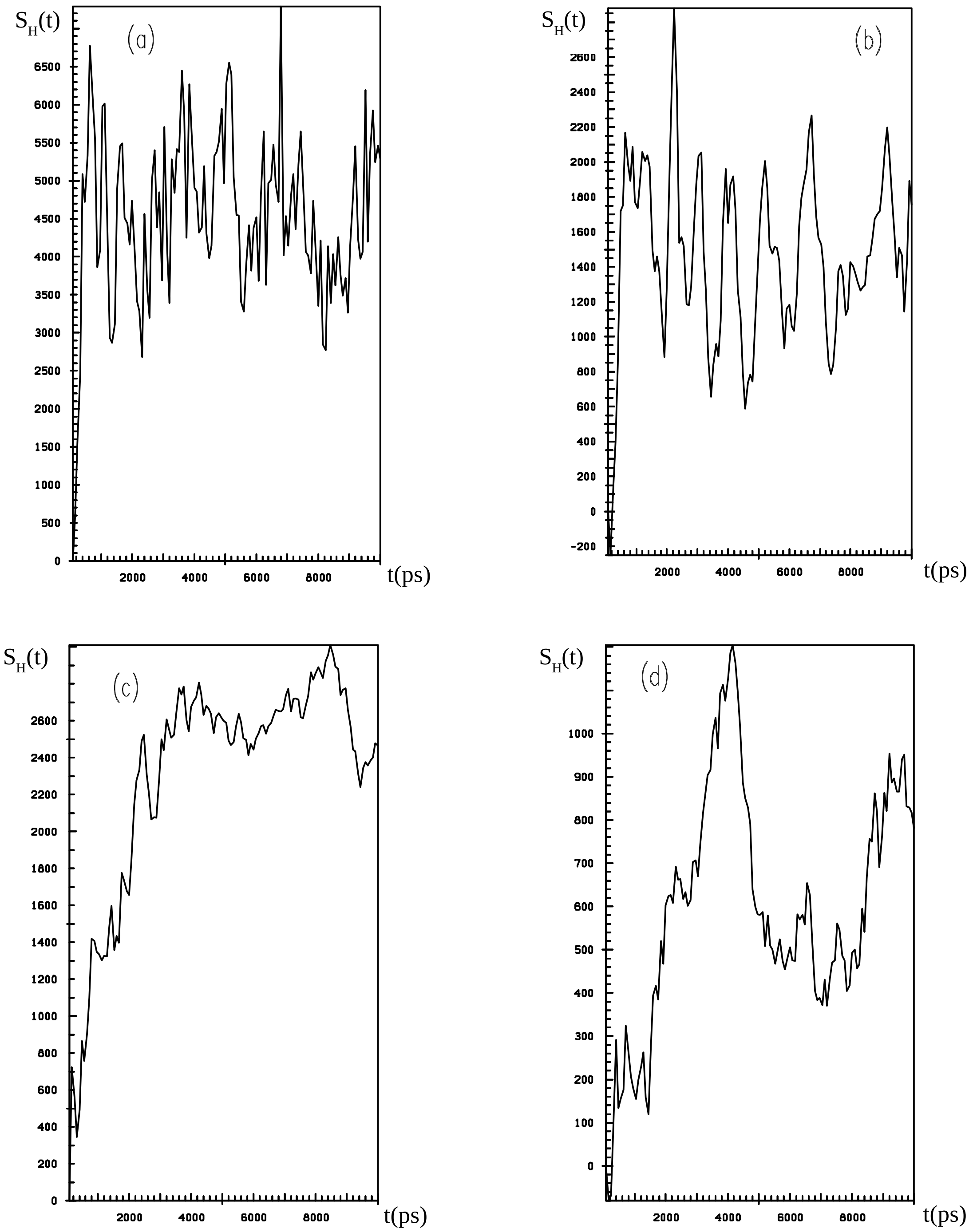


Figure 2: *The norm* $S_H(t)=\left\langle \left(\hat{H}/J\right)D_1 \middle| \left(\hat{H}/J\right)D_1 \right\rangle$ *as function of time for four values of the coupling constant (note that t=80 ps is the first time in the simulation where our program prints out intermediate results, however, in the plots for our long time simulations t=0 and t=80 ps are indistinguishable):*

(a) χ*= 60 pN (*S_H *relative to* S_H*(t=80 ps)=684,827.548170)*
(b) χ*=120 pN (*S_H *relative to* S_H*(t=80 ps)=688,883.505744)*
(c) χ*=180 pN (*S_H *relative to* S_H*(t=80 ps)=694,750.770186)*
(d) χ*=240 pN (*S_H *relative to* S_H*(t=80 ps)=710,240.923822)*

very slow oscillation around 800 starts after roughly 3 ns. Fig. 3 shows S_E(t)=<δ|δ> for the different couplings. In all cases the error remains about 8 orders of magnitude smaller than S_H(t), indicating that within the $|D_1$> basis space no significant errors of the norm of the state occur. Note, that the S_H(t)-plots are drawn relative to S_H(t=80 ps). Moreover, in all cases S_E(t) increases within the first 500 to 1000 ps to values around 2.3 and afterwards decreases to a small amplitude oscillation around 2.03 and 2.00, independent of the value of the coupling constant. Even after 10 ns the mean value of S_E(t) still seems to decrease further very slowly. Therefore

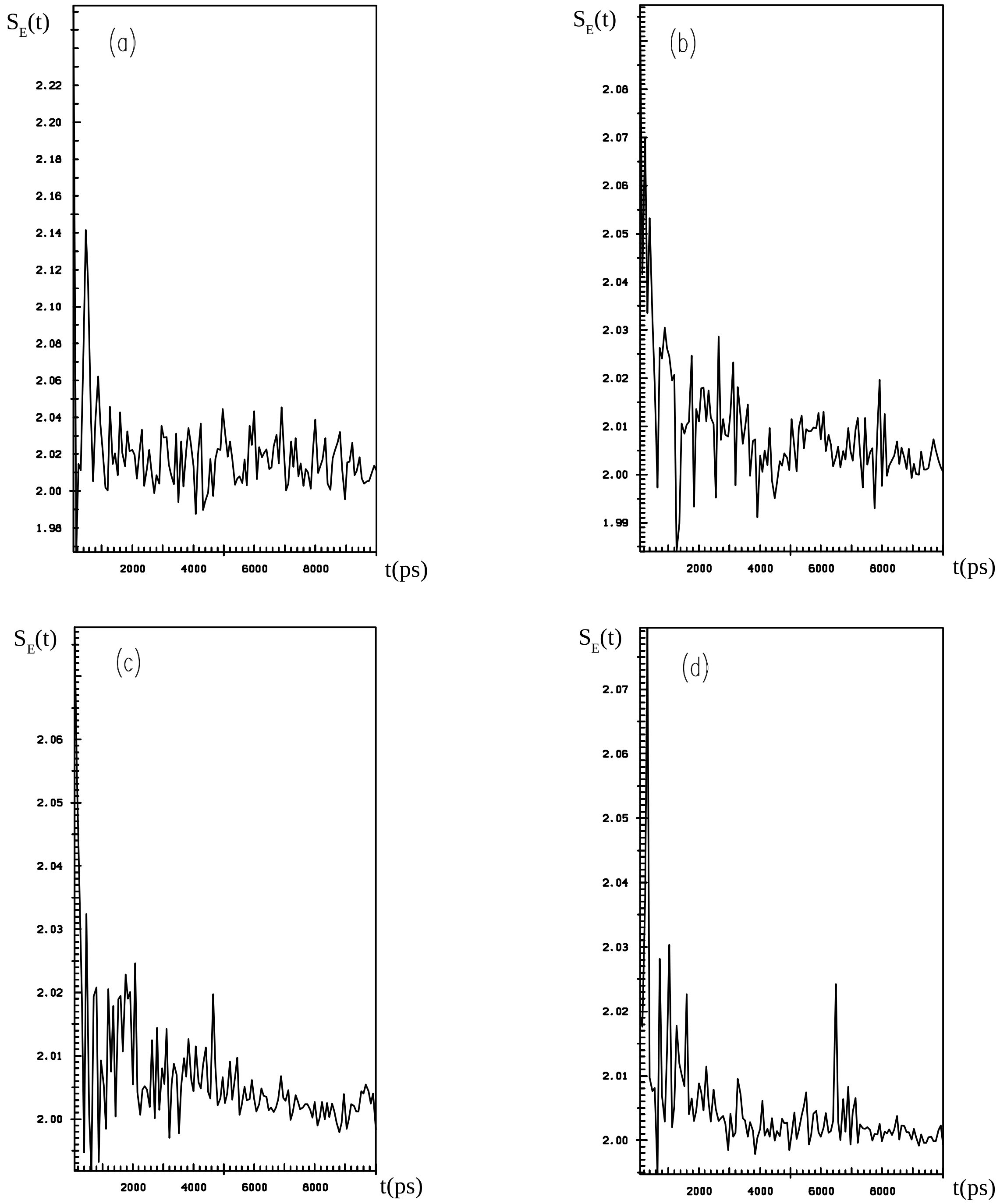


Figure 3: *The norm $S_E(t)=<\delta|\delta>$ as function of time for four values of the coupling constant:*

(a) χ= 60 pN *(b) χ=120 pN*
(c) χ=180 pN *(d) χ=240 pN*

we can conclude, at least on the basis of the norms, that the error introduced by the incomplete basis space of the ansatz decreases in time, and that the $|D_1>$ state becomes more accurate in the long time limit.

Figure 4 shows the time evolution of the number operators for the oscillators, $N_n^H(t)=\left\langle\left(\hat{H}/J\right)D_1\middle|\hat{a}_n^+\hat{a}_n\middle|\left(\hat{H}/J\right)D_1\right\rangle$ and Figure 5 those for the error state $N_n^E(t)=<\delta|\hat{a}_n^+\hat{a}_n|\delta>$. Also here the errors show no tendency to increase with increasing time, in contrast, they have a constant order of magnitude through all 10 ns. They follow closely the time evolution of $N_n^H(t)$, however, being 6 to 7 orders of magnitude smaller, thus as in case of the norms, the deviations are completely negligibly, also over times as large as 10 ns. The same holds

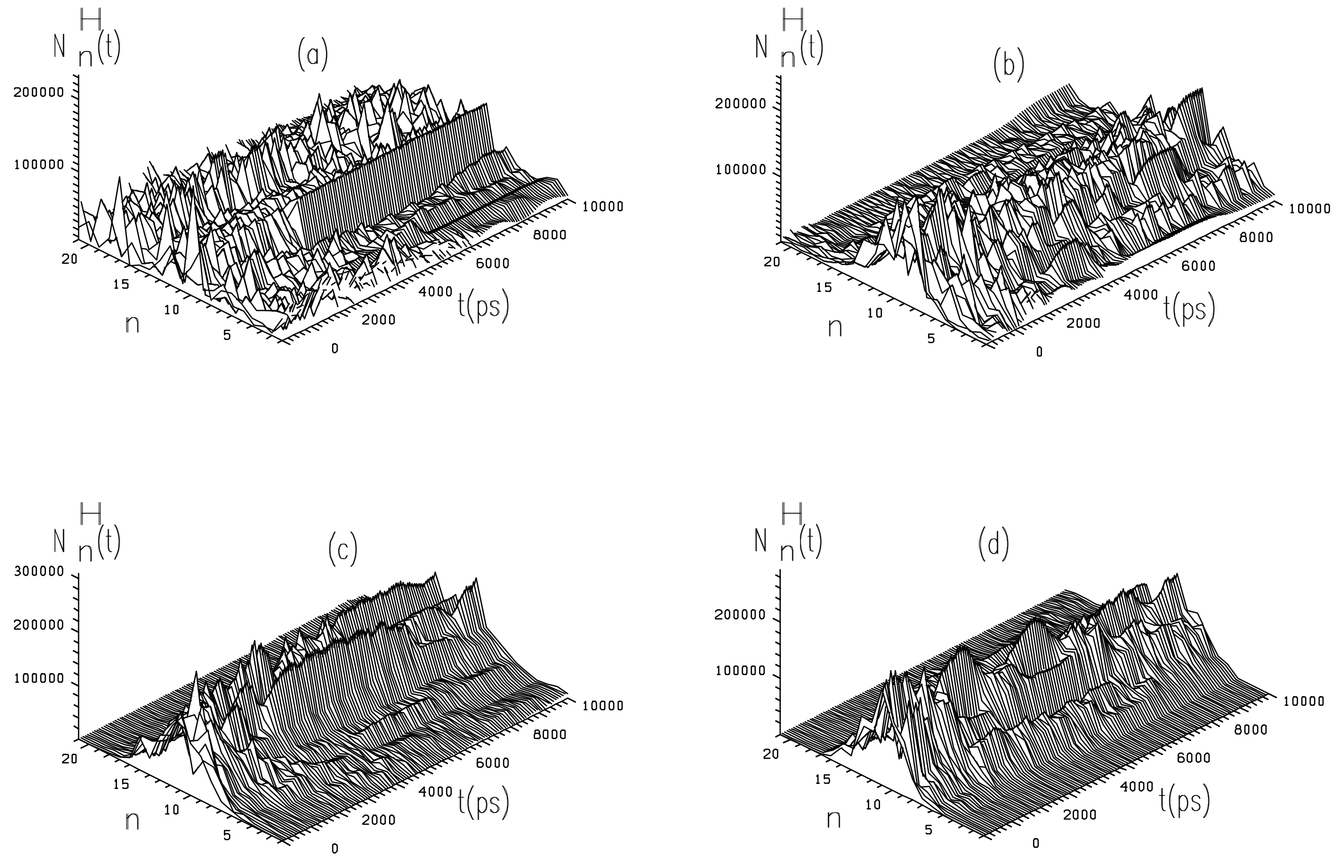


Figure 4:

The expectation values $N_n^H(t) = \left\langle \left(\hat{H}/J\right) D_1 \middle| \hat{a}_n^+ \hat{a}_n \middle| \left(\hat{H}/J\right) D_1 \right\rangle$ *as functions of site and time for the different values of the coupling constant (also here and in Fig. 5-9 the first line drawn in the plot is that at t=80 ps, also the time distance between two lines is 80 ps):*

(a) χ*=60 pN* *(b)* χ*=120 pN*
(c) χ*=180 pN* *(d)* χ*=240 pN*

for the expectation values of the displacement and momentum operators. $q_n^H(t) = \left\langle \left(\hat{H}/J\right) D_1 \middle| \hat{q}_n \middle| \left(\hat{H}/J\right) D_1 \right\rangle$ and $q_n^E(t) = \langle \delta | \hat{q}_n | \delta \rangle$, respectively, as well as $p_n^H(t) = \left\langle \left(\hat{H}/J\right) D_1 \middle| \hat{p}_n \middle| \left(\hat{H}/J\right) D_1 \right\rangle$ and $p_n^E(t) = \langle \delta | \hat{p}_n | \delta \rangle$, respectively, not shown here, exhibit a quasi-random behaviour as it is to be expected because of the „thermal“ excitation in the initial state. However, also here the errors closely follow the corresponding pictures computed from the state $\left(\hat{H}_D/J\right) \left| D_1 \right\rangle$, and are about 5 to 6 orders of magnitude smaller, which does not change in the large time scales of our simulations.

Therefore we can conclude from our results, that for large times $|D_1>$ is close to the exact solution, with nearly negligible deviations. Further we know from our previous simulations on intermediate time scales in the range of ps, that in this region the errors are somewhat larger, although still more or less negligible [8]. In the next section we study the time around 0.1 ps, where a possible soliton formation would start from localized initial states.

Expansion of the Exact Wavefunction

We start, as in our preceding paper [1], from the well-known ansatz for the exact solution of the Schrödinger equation

$$\left| \psi \right\rangle = e^{-\frac{it}{\hbar}\left(\hat{J} + \hat{\omega}\right)} \left| \psi_0 \right\rangle \qquad (11)$$

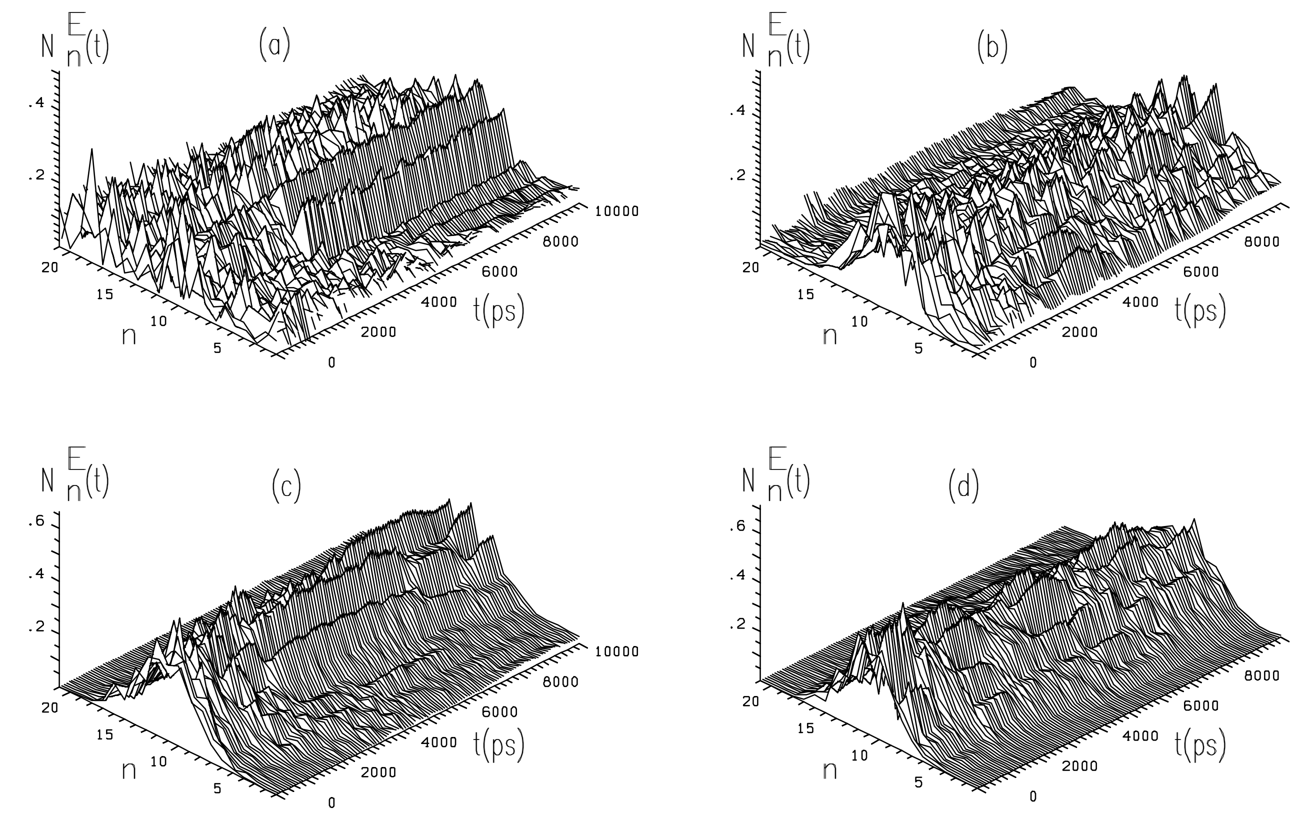


Figure 5: *The expectation values $N^E_n(t)=\langle\delta|\hat{a}_n^+\hat{a}_n|\delta\rangle$ as functions of site and time for the different values of the coupling constant:*

(a) χ=60 pN *(b) χ=120 pN*
(c) χ=180 pN *(d) χ=240 pN*

Note here that the two parts of the Hamiltonian do not commute

$$\left[\hat{\omega},\hat{J}\right]\equiv\hat{\omega}\hat{J}-\hat{J}\hat{\omega}\equiv\hat{C}=\sum_{n=1}^{N}\sum_{k=1}^{N-1}\hbar\omega_k B_{nk}\left(\hat{b}_k^+ +\hat{b}_k\right)\hat{\alpha}_n \tag{12}$$

$$\hat{\alpha}_n\equiv J\left[\left(\hat{a}_{n+1}^+ +\hat{a}_{n-1}^+\right)\hat{a}_n-\hat{a}_n^+\left(\hat{a}_{n+1}+\hat{a}_{n-1}\right)\right]$$

As model system we use a cyclic chain of N (N odd) units and an initial excitation of an amide-I oscillator at site o. The lattice is initially in its groundstate. Thus we have

$$\left|\psi_0\right\rangle=\hat{a}_o^+\left|0\right\rangle \tag{13}$$

Then the exponential in the exact wave function is expanded in a Taylor series yielding

$$\left|\psi(t)\right\rangle=\sum_{\nu=0}^{\infty}\frac{T^\nu}{\nu!}\left(\hat{\omega}+\hat{J}\right)^\nu\left|\psi_0\right\rangle \quad ; \quad T\equiv\left(-\frac{it}{\hbar}\right)$$

$$\begin{aligned}\left|\psi(t)\right\rangle=\Big[&1+T\left(\hat{J}+\hat{\omega}\right)+\frac{T^2}{2}\left(\hat{J}^2+\hat{J}\hat{\omega}+\hat{\omega}\hat{J}+\hat{\omega}^2\right)+\\&+\frac{T^3}{6}\Big(\hat{J}^3+\hat{J}^2\hat{\omega}+\hat{\omega}\hat{J}^2+\hat{\omega}^2\hat{J}+\\&+\hat{J}\hat{\omega}^2+\hat{\omega}\hat{J}\hat{\omega}+\hat{J}\hat{\omega}\hat{J}+\hat{\omega}^3\Big)+\ldots\Big]\left|\psi_0\right\rangle\end{aligned} \tag{14}$$

From this expansion we can immediately extract two series

$$\begin{aligned}\left|T_1\right\rangle&=\sum_{\nu=0}^{\infty}\frac{T^\nu}{\nu!}\hat{J}^\nu\left|\psi_0\right\rangle=e^{T\hat{J}}\left|\psi_0\right\rangle=\left|J\right\rangle\\\left|T_2\right\rangle&=\sum_{\nu=0}^{\infty}\frac{T^\nu}{\nu!}\hat{\omega}^\nu\left|\psi_0\right\rangle=e^{T\hat{\omega}}\left|\psi_0\right\rangle=\left|\omega\right\rangle\end{aligned} \tag{15}$$

which are the exact solutions of the separate Schrödinger equations for the two operators. They are derived in detail in paper [1] and can be cast into the form

$$\left|J\right\rangle = \sum_{n=1}^{N} a_n^J(t)\hat{a}_n^+\left|0\right\rangle \quad ; \quad \left|\omega\right\rangle = \hat{U}_o a_o^\omega(t)\hat{a}_o^+\left|0\right\rangle$$
$$\hat{U}_o = U_o(t) e^{\sum_{k=1}^{N-1} b_{ok}(t)\hat{b}_k^+} \quad ; \quad U_o(t) = e^{-\frac{1}{2}\sum_{k=1}^{N-1}\left|b_{ok}(t)\right|^2} \tag{16}$$

where the translational mode of the lattice (ω_N=0) has to be excluded. Note here that

$$\hat{U}_o\left|0\right\rangle \equiv \left|\beta_o\right\rangle \quad ; \quad \hat{b}_k\left|\beta_o\right\rangle = b_{ok}(t)\left|\beta_o\right\rangle$$
$$\left\langle\beta_o\right|\hat{b}_k^+ = \left\langle\beta_o\right| b_{ok}^*(t) \tag{17}$$
$$\left\langle\beta_o|0\right\rangle = \left\langle 0|\beta_o\right\rangle = U_o(t) \quad ; \quad \left\langle\beta_o|\beta_o\right\rangle = 1$$

holds and the time dependent coefficients are given by [1]

$$a_n^J(t) = \frac{1}{N}\sum_{k=1}^{N} e^{\frac{2\pi i}{N}k(n-o)} \cdot e^{2i\frac{Jt}{\hbar}\cos\left(\frac{2\pi}{N}k\right)}$$

$$\sum_{n=1}^{N}\left|a_n^J(t)\right|^2 = 1 \tag{18}$$

$$a_o^\omega(t) = e^{-i\sum_{k=1}^{N-1} B_{ok}^2\left[\sin(\omega_k t)-\omega_k t\right]} \quad ; \quad \left|a_o^\omega(t)\right|^2 = 1$$

$$b_{ok}(t) = B_{ok}\left(e^{-i\omega_k t} - 1\right) \quad ; \quad U_o(t) = e^{\sum_{k=1}^{N-1} B_{ok}^2\left[\cos(\omega_k t)-1\right]}$$

Note, that in case of the amide-I oscillators also the mode with k=N has to be included. Then with

$$\left|\psi(0)\right\rangle = \left|\psi(1)\right\rangle \equiv \left|J\right\rangle + \left|\omega\right\rangle - \left|\psi_0\right\rangle \tag{19}$$

our exact wave function can be written as

$$\left|\psi(t)\right\rangle = \left|\psi(0)\right\rangle + \sum_{\nu=2}^{\infty}\frac{T^\nu}{\nu!}\hat{\Omega}_\nu\left|\psi_0\right\rangle$$
$$\hat{\Omega}_\nu \equiv \left(\hat{\omega}+\hat{J}\right)^\nu - \hat{\omega}^\nu - \hat{J}^\nu \tag{20}$$

Further the different orders μ are defined as

$$\left|\psi(\mu)\right\rangle = \left|\psi(0)\right\rangle + \sum_{\nu=2}^{\mu}\frac{T^\nu}{\nu!}\left|\psi_\nu\right\rangle \quad ; \quad \left|\psi_\nu\right\rangle \equiv \hat{\Omega}_\nu\left|\psi_0\right\rangle \tag{21}$$

$$\hat{\Omega}_1 = 0$$
$$\hat{\Omega}_2 = \hat{\omega}\hat{J} + \hat{J}\hat{\omega}$$
$$\hat{\Omega}_3 = \hat{\omega}\hat{J}^2 + \hat{J}^2\hat{\omega} + \hat{J}\hat{\omega}^2 + \hat{\omega}^2\hat{J} + \hat{\omega}\hat{J}\hat{\omega} + \hat{J}\hat{\omega}\hat{J}$$
$$\ldots$$

In this paper we want to restrict the expansion to μ=3, since the calculation of higher order terms becomes too tedious. This is also the reason why such expansions are only useful for the study of the very short time behaviour of exact solutions, but not for general simulations, where a large amount of high order terms would be necessary to obtain reliable results for times say in the ps-scale. In our previous paper [1] we had studied in detail the time scale on which such a third order expansion is valid. For comparisons with the corresponding results of $|D_1\rangle$ simulations we are interested in the norm of the states of different order in time, the expectation values H(μ,t) of the Hamiltonian, $N_n(\mu,t)$ of the exciton number operators and $B_k(\mu,t)$ of the phonon annihilation operators. From the latter ones we can compute easily expectation values $q_n(\mu,t)$ of the displacement and $p_n(\mu,t)$ of the momentum operators:

$$H(\mu,t) = \left\langle\psi(\mu,t)\right|\hat{\omega}+\hat{J}\left|\psi(\mu,t)\right\rangle$$

$$N_n(\mu,t) = \left\langle\psi(\mu,t)\right|\hat{a}_n^+\hat{a}_n\left|\psi(\mu,t)\right\rangle$$

$$B_k(\mu,t) = \left\langle\psi(\mu,t)\right|\hat{b}_k\left|\psi(\mu,t)\right\rangle$$

$$B_k^*(\mu,t) = \left\langle\psi(\mu,t)\right|\hat{b}_k^+\left|\psi(\mu,t)\right\rangle \tag{22}$$

$$S(\mu,t) = \left\langle\psi(\mu,t)|\psi(\mu,t)\right\rangle = \sum_{n=1}^{N} N_n(\mu,t)$$

$$q_n(\mu,t) = \sum_{k=1}^{N-1}\sqrt{\frac{2\hbar}{M\omega_k}}U_{nk}\ \mathrm{Re}\left[B_k(\mu,t)\right]$$

$$p_n(\mu,t) = \sum_{k=1}^{N-1}\sqrt{2M\hbar\omega_k}U_{nk}\ \mathrm{Im}\left[B_k(\mu,t)\right]$$

where $\underline{\underline{U}}$ is the eigenvector matrix of the decoupled lattice in real representation and is discussed in detail in Appendix B of the preceding paper [1]. The explicit expressions for these expectation values are given in the Appendices, since they are rather massy.

The first order wave function vanishes with our choice of |ψ(0)>, and thus we proceed directly to the second order correction which is given by

$$\left|\psi_2\right\rangle = \hat{\Omega}_2\left|\psi_0\right\rangle = \left(\hat{J}\hat{\omega} + \hat{\omega}\hat{J}\right)\left|\psi_0\right\rangle$$

$$\hat{\omega}\hat{J}\left|\psi_0\right\rangle = -J\sum_{k=1}^{N-1}\hbar\omega_k \hat{b}_k^+\left(B_{o-1,k}\hat{a}_{o-1}^+ + B_{o+1,k}\hat{a}_{o+1}^+\right)\left|0\right\rangle$$

$$\hat{J}\hat{\omega}\left|\psi_0\right\rangle = -J\sum_{k=1}^{N-1}\hbar\omega_k B_{ok}\hat{b}_k^+\left(\hat{a}_{o-1}^+ + \hat{a}_{o+1}^+\right)\left|0\right\rangle \tag{23}$$

$$\left(\sum_{k=1}^{N-1}\hbar\omega_k \hat{b}_k^+\hat{b}_k\left|\psi_0\right\rangle = \sum_{k=1}^{N-1}\hbar\omega_k \hat{b}_k^+\hat{b}_k\hat{J}\left|\psi_0\right\rangle = 0\right)$$

Leading finally to

$$\left|\psi_2\right\rangle = -J\sum_{k=1}^{N-1}\hbar\omega_k \hat{b}_k^+\left(A_{o-1,k}\hat{a}_{o-1}^+ + A_{o+1,k}\hat{a}_{o+1}^+\right)\left|0\right\rangle = \\ = \left(\hat{\Theta}_{-1}\hat{a}_{o-1}^+ + \hat{\Theta}_{+1}\hat{a}_{o+1}^+\right)\left|0\right\rangle \tag{24}$$

$$\hat{\Theta}_{\pm 1} \equiv -J\sum_{k=1}^{N-1}\hbar\omega_k A_{o\pm 1,k}\hat{b}_k^+ \quad ; \quad A_{o\pm 1,k} \equiv B_{ok} + B_{o\pm 1,k}$$

The full second order wave function is then

$$\left|\psi(2)\right\rangle = \left|\psi(0)\right\rangle - \frac{t^2}{2\hbar^2}\left|\psi_2\right\rangle \tag{25}$$

The third order correction is given by

$$\left|\psi_3\right\rangle = \hat{\Omega}_3\left|\psi_0\right\rangle = \\ = \left(\hat{\omega} + \hat{J}\right)\left(\hat{\omega}\hat{J} + \hat{J}\hat{\omega}\right)\left|\psi_0\right\rangle + \hat{\omega}\hat{J}^2\left|\psi_0\right\rangle + \hat{J}\hat{\omega}^2\left|\psi_0\right\rangle = \\ = \left(\hat{\omega} + \hat{J}\right)\left|\psi_2\right\rangle + \hat{\omega}\hat{J}^2\left|\psi_0\right\rangle + \hat{J}\hat{\omega}^2\left|\psi_0\right\rangle \tag{26}$$

With the definition

$$\hat{y}_n = \sum_{k=1}^{N-1}\hbar\omega_k B_{nk}\hat{b}_k \tag{27}$$

we obtain for the different terms, where partially results of the preceding paper are used:

$$\hat{\omega}\hat{J}^2\left|\psi_0\right\rangle = \\ = J^2\sum_{k=1}^{N-1}\hbar\omega_k \hat{b}_k^+\left(B_{o-2,k}\hat{a}_{o-2}^+ + 2B_{ok}\hat{a}_o^+ + B_{o+2,k}\hat{a}_{o+2}^+\right)\left|0\right\rangle \tag{28}$$

$$\hat{J}\hat{\omega}^2\left|\psi_0\right\rangle = \\ = -J\left[\left(\hat{y}_o^+\right)^2 + \sum_{k=1}^{N-1}\left(\hbar\omega_k\right)^2 B_{ok}\left(B_{ok} + \hat{b}_k^+\right)\right]\left(\hat{a}_{o-1}^+ + \hat{a}_{o+1}^+\right)\left|0\right\rangle$$

Further the action of our operators on $|\psi_2>$ yields

$$\hat{J}\left|\psi_2\right\rangle = J^2\sum_{k=1}^{N-1}\hbar\omega_k \hat{b}_k^+\Big[A_{o-1,k}\hat{a}_{o-2}^+ + \\ + \left(A_{o-1,k} + A_{o+1,k}\right)\hat{a}_o^+ + A_{o+1,k}\hat{a}_{o+2}^+\Big]\left|0\right\rangle \tag{29}$$

and

$$\hat{\omega}\left|\psi_2\right\rangle = -J\Bigg\{\sum_{k,k'=1}^{N-1}\hbar\omega_k\hbar\omega_{k'}\hat{b}_k^+\hat{b}_{k'}^+ \cdot \\ \cdot\left[B_{o-1,k}A_{o-1,k'}\hat{a}_{o-1}^+ + B_{o+1,k}A_{o+1,k'}\hat{a}_{o+1}^+\right]\left|0\right\rangle + \\ + \sum_{k=1}^{N-1}\left(\hbar\omega_k\right)^2\Big[\left(B_{o-1,k} + \hat{b}_k^+\right)A_{o-1,k}\hat{a}_{o-1}^+ + \\ + \left(B_{o+1,k} + \hat{b}_k^+\right)A_{o+1,k}\hat{a}_{o+1}^+\Big]\left|0\right\rangle\Bigg\} \tag{30}$$

Collecting all the terms, we can write $|\psi_3>$ in the form

$$\left|\psi_3\right\rangle = \sum_{\nu=-2}^{2}(-1)^\nu\,\hat{\Gamma}_\nu\hat{a}_{o+\nu}^+\left|0\right\rangle \tag{31}$$

where the operators $\hat{\Gamma}_\nu$ contain only phonon creation operators:

$$\hat{\Gamma}_0 \equiv J^2\sum_{k=1}^{N-1}\hbar\omega_k D_k\hat{b}_k^+ \quad ; \quad \hat{\Gamma}_{\pm 2} \equiv J^2\sum_{k=1}^{N-1}\hbar\omega_k D_k^{(\pm)}\hat{b}_k^+$$

$$\hat{\Gamma}_{\pm 1} \equiv J\sum_{k=1}^{N-1}\hbar\omega_k\Bigg[\hbar\omega_k\left(E_k^{(\pm)} + F_k^{(\pm)}\hat{b}_k^+\right) + \\ + \sum_{k'=1}^{N-1}\hbar\omega_{k'}G_{kk'}^{(\pm)}\hat{b}_k^+\hat{b}_{k'}^+\Bigg] \tag{32}$$

and the real scalar quantities:

$$
\begin{aligned}
D_k &\equiv B_{o-1,k} + 4B_{ok} + B_{o+1,k} \\
D_k^{(\pm)} &\equiv B_{ok} + B_{o\pm1,k} + B_{o\pm2,k} \\
E_k^{(\pm)} &\equiv B_{ok}^2 + \left(B_{ok} + B_{o\pm1,k}\right)B_{o\pm1,k} \\
F_k^{(\pm)} &\equiv 2B_{ok} + B_{o\pm1,k} \\
G_{kk'}^{(\pm)} &\equiv B_{ok}B_{ok'} + B_{o\pm1,k}\left(B_{ok'} + B_{o\pm1,k'}\right)
\end{aligned} \tag{33}
$$

With the help of these abbreviations the calculation of expectation values, as given in the Appendices, as well as their programming can be considerably simplified. The total third order wave function is then given by

$$
\begin{aligned}
&\left|\psi(3)\right\rangle = \left|\psi(2)\right\rangle + i\frac{t^3}{6\hbar^3}\left|\psi_3\right\rangle = \\
&= \left|\omega\right\rangle + \left|J\right\rangle - \left|\psi_0\right\rangle - \frac{t^2}{2\hbar^2}\left|\psi_2\right\rangle + i\frac{t^3}{6\hbar^3}\left|\psi_3\right\rangle
\end{aligned} \tag{34}
$$

where the sum of the first three terms is also denoted as $|\psi(0)>$.

With the help of the expectation values as given in the Appendices we performed calculations using cyclic chains of N=21 units for the so-called standard parameters (W=13 N/m, M=114 m_p, J=0.967 meV) and two values of the exciton-phonon coupling constant χ=35 pN and 62 pN as in the preceding paper. In the initial state the lattice is in its equilibrium, i.e. $b_{nk}(0)=0$, and the amide-I excitation is localized at site o=11, i.e. $a_n(0)=\delta_{no}$. As mentioned above, the accuracies of S(t) and H(t) are direct measures of the maximal time a given order of the expansion of the wave function is valid for, we concentrate first on these two functions. The expectation value of the Hamiltonian H(t) (Figure 6 a,c) remains very close to its exact value up to roughly 0.10-0.15 ps in case of the third order expansion. After that the terms which include explicitely powers of t obviously dominate and lead to a fast, unphysical increase. In case of the second order this increase starts somewhat later in time and is less steep. The deviations from the exact value in the first order are rather small and increase very slowly, due to the fact that in first order no explicit powers of t occur. The overall picture for the norm S(t) is qualitatively the same. Also in this case the deviations are tolerable up to a time of about 0.10-0.15 ps. From this, as we have seen in the first paper, we can conlude that also the other expectation values should be reliable at least up to roughly 0.1 ps.

In Figure 7 we show the physically more interesting expectation values of the number operators, displacement and momentum operators for the units o (o=11), where in the initial state the excitation is localized and o+1 for a time of 0.4 ps and the two coupling constants under consideration.

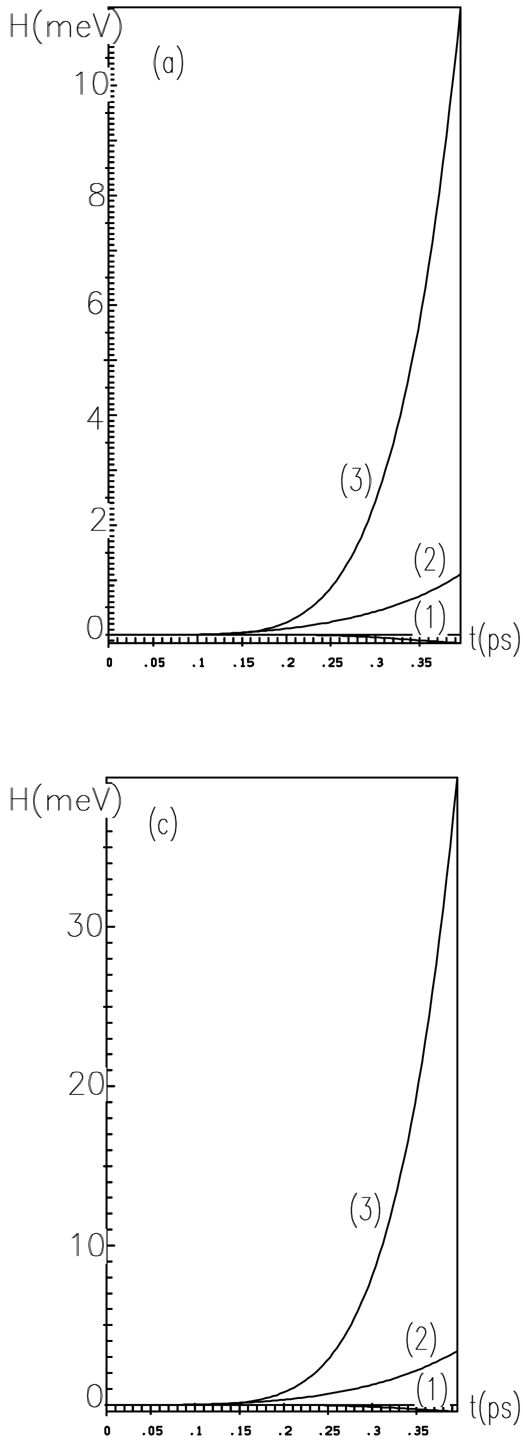
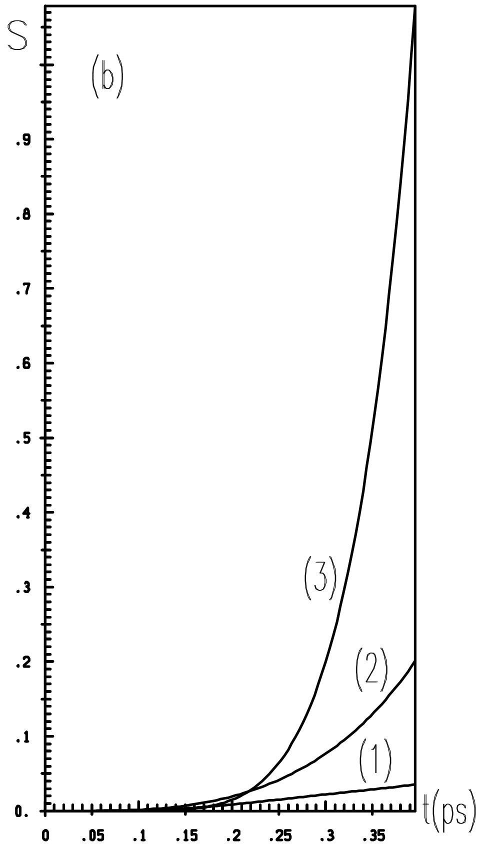
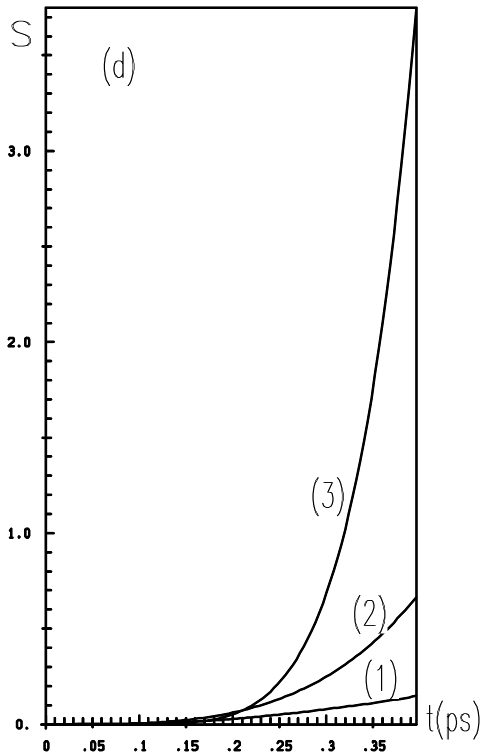


Figure 6 (continues next page): *The functions H(μ,t) (in meV, relative to H(t)=H(0)=0) and S(μ,t) (relative to S(t)=S(0)=1; the graphs corresponding to the different orders are marked by μ):*

(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*





In the rather short simulation time at sites n<o-1 or n>o+2 no important dynamics evolve. In all the figures the results of the corresponding $|D_1>$ simulations are plotted as dashed lines and those of the expansion as solid lines with the order indicated at them. The time step in the simulations was 4 fs. Thus we have 100 time steps exactly at the times where we computed the expectation values for the expansion. In these simulations the absolute value of the errors in total energy were less than 6 peV (exciton-phonon interaction energy between 0 and -2.4 meV) and the absolute values of the errors in the norm less than 1 ppb (parts per billion). As mentioned previously in paper I, we need as initial state for $|D_1>$ simulations the form

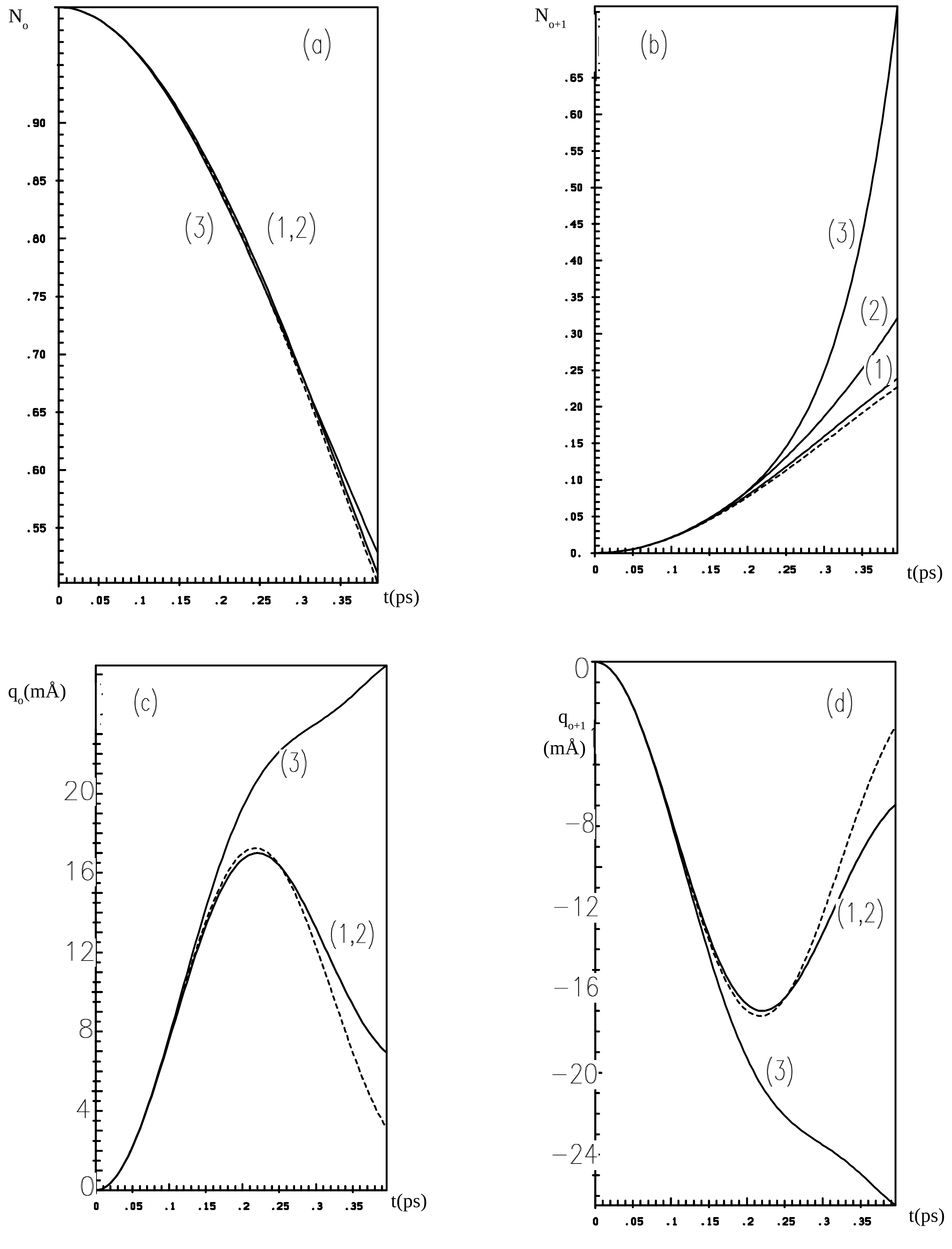
$$a_n(0)=\frac{\delta_{no}+x(1-\delta_{no})}{\sqrt{1+(N-1)|x|^2}} \tag{35}$$

where N is the number of sites in the chain, o the initial excitation site and x a small, real scalar. This is necessary to avoid numerical problems due to a_n occuring in the denominators in the equations of motion. However, if we use $x=5\cdot10^{-3}$, which is physically irrelevant in long time simulations, we obtain for very short times between 0 and 0.1 ps spurious minima e.g. in the expectation values of the number operators $N_n(t)$ for n<o-1 and n>o+1 of a depth of about 5 ppm. These spurious minima, not found in the expansions, can be avoided if x is reduced to $x=5\cdot10^{-5}$.

The first six parts of Figure 7 show the relevant expectation values for the smaller coupling constants. It is obvious, that up to a time of roughly 0.15 ps the $|D_1>$ results agree perfectly well with those from the three orders of the expansion, which in this region of time do not differ very much from each other. In most cases of differences (Fig. 7e,f) obviously the second order starts to deviate from the first one and then the third order correction brings the curve again closer to the first order. After about 0.2 ps the explicit factors

Figure 7 (following pages): *The expectation values of the number operators $N_o(\mu,t)$ and $N_{o+1}(\mu,t)$ together with the corresponding $|D_1>$ results, the displacements $q_o(\mu,t)$ and $q_{o+1}(\mu,t)$ together with the corresponding $|D_1>$ results (in mÅ) and the momenta $p_o(\mu,t)$ and $p_{o+1}(\mu,t)$ together with the corresponding $|D_1>$ results (in meVps/Å; o=11, N=21). The $|D_1>$ curves are given as dashed lines, the solid lines are marked with numbers to indicate the different orders μ.*

(a) $N_o(\mu,t)$; χ=35 pN *(b) $N_{o+1}(\mu,t)$; χ=35 pN*
(c) $q_o(\mu,t)$; χ=35 pN *(d) $q_{o+1}(\mu,t)$; χ=35 pN*
(e) $p_o(\mu,t)$; χ=35 pN *(f) $p_{o+1}(\mu,t)$; χ=35 pN*
(g) $N_o(\mu,t)$; χ=62 pN *(h) $N_{o+1}(\mu,t)$; χ=62 pN*
(i) $q_o(\mu,t)$; χ=62 pN *(j) $q_{o+1}(\mu,t)$; χ=62 pN*
(k) $p_o(\mu,t)$; χ=62 pN *(l) $p_{o+1}(\mu,t)$; χ=62 pN*
(m) $q_{o+2}(\mu,t)$; χ=35 pN *(n) $p_{o+2}(\mu,t)$; χ=35 pN*



N_o
(a)
(3)
(1,2)
.90
.85
.80
.75
.70
.65
.60
.55
0
.05
.1
.15
.2
.25
.3
.35
t(ps)
N_o+1
(b)
(3)
(2)
(1)
.65
.60
.55
.50
.45
.40
.35
.30
.25
.20
.15
.10
.05
0.
t(ps)
q_o(mÅ)
(c)
(3)
(1,2)
20
16
12
8
4
0
t(ps)
q_o+1 (mÅ)
(d)
(1,2)
(3)
0
−8
−12
−16
−20
−24
t(ps)

Figure 7a-d

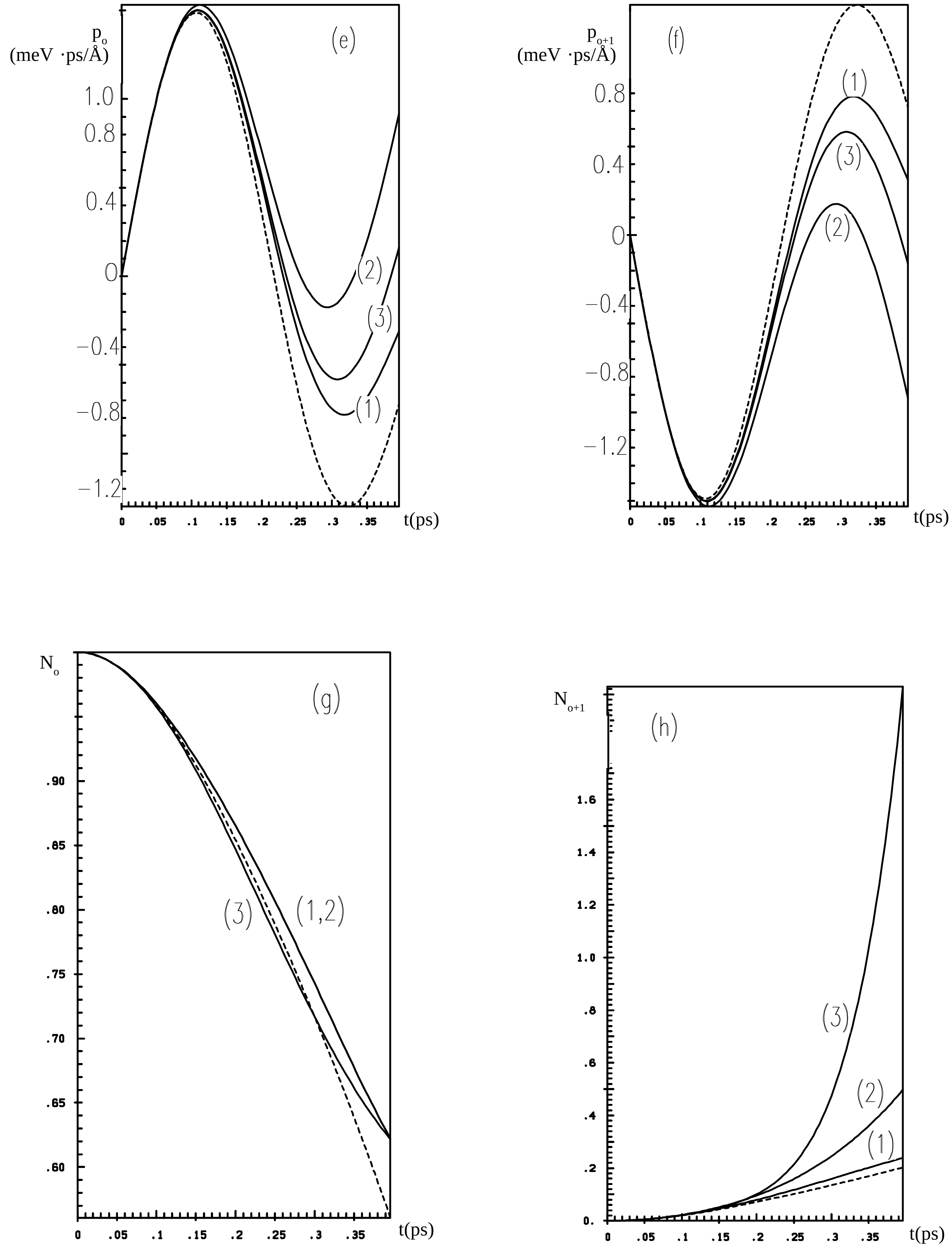
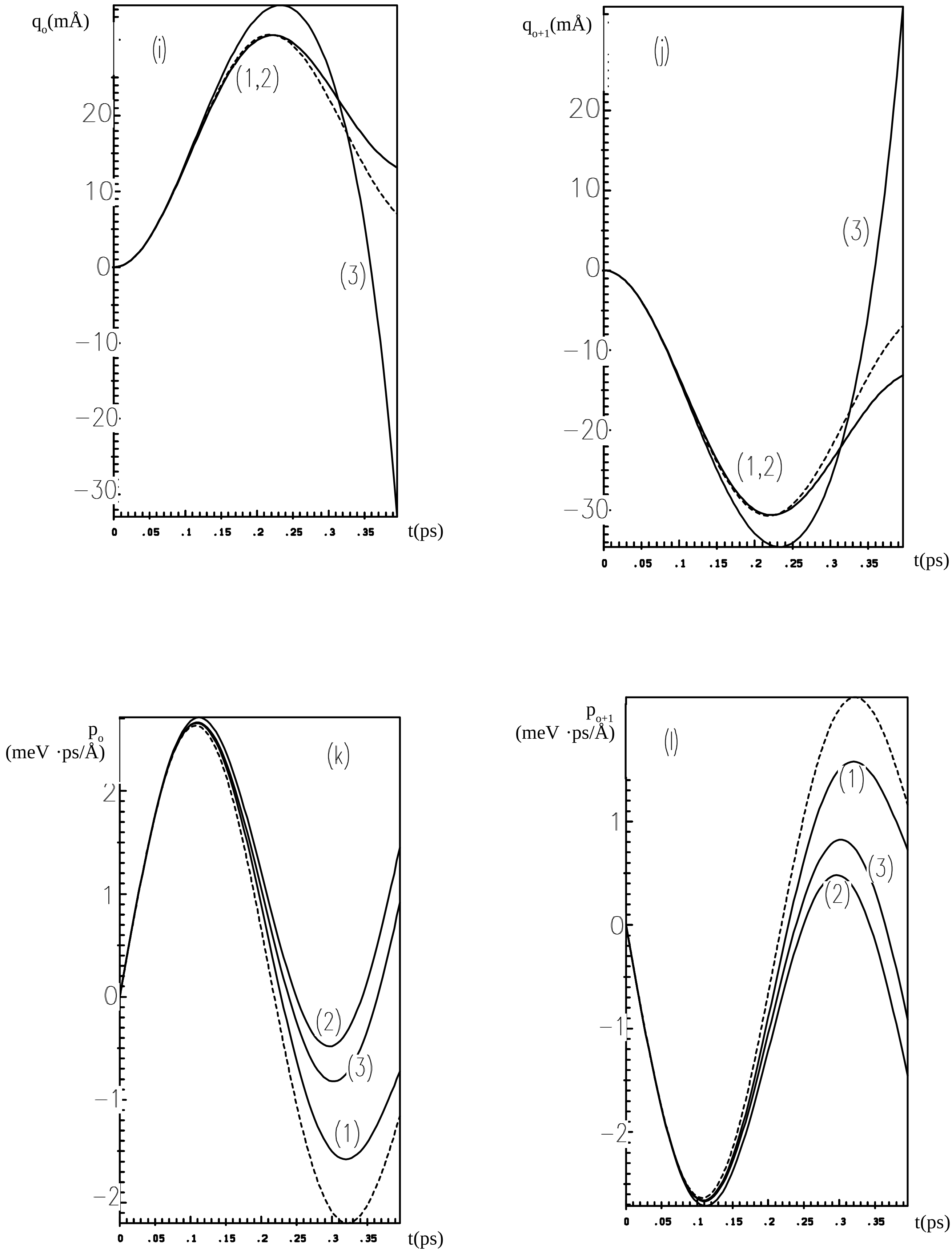

p_o
(meV ·ps/Å)
(e)
1.0
0.8
0.4
0
−0.4
−0.8
−1.2
(2)
(3)
(1)
0 .05 .1 .15 .2 .25 .3 .35
t(ps)
p_o+1
(meV ·ps/Å)
(f)
0.8
0.4
0
−0.4
−0.8
−1.2
(1)
(3)
(2)
t(ps)
N_o
(g)
.90
.85
.80
.75
.70
.65
.60
(3)
(1,2)
t(ps)
N_o+1
(h)
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0.
(3)
(2)
(1)
t(ps)

Figure 7e-h



q_o(mÅ)
(i)
(1,2)
(3)
20
10
0
−10
−20
−30
0 .05 .1 .15 .2 .25 .3 .35
t(ps)
q_{o+1}(mÅ)
(j)
(3)
(1,2)
20
10
0
−10
−20
−30
0 .05 .1 .15 .2 .25 .3 .35
t(ps)
p_o
(meV ·ps/Å)
(k)
(2)
(3)
(1)
2
1
0
−1
−2
0 .05 .1 .15 .2 .25 .3 .35
t(ps)
p_{o+1}
(meV ·ps/Å)
(l)
(1)
(3)
(2)
1
0
−1
−2
0 .05 .1 .15 .2 .25 .3 .35
t(ps)

Figure 7i-l

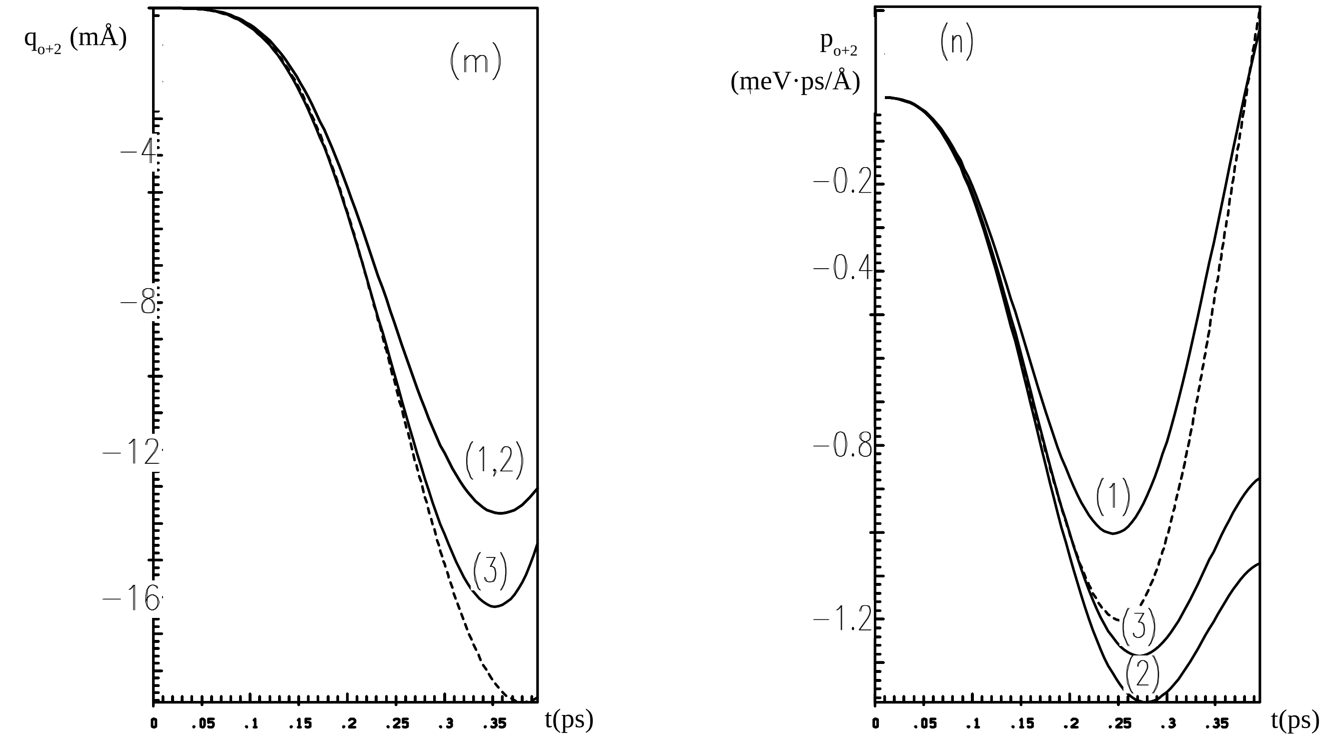


Figure 7m-n

with powers of t especially in the third order curves start to dominate and make the expansion unreliable. To obtain an „exact" wave function for larger times higher orders of the expansion would be necessary. One might wonder, why for N_o, q_o and q_{o+1} the second order curves coincide completely with the first order ones. For N_o the reason is simple, as equation (A9) shows: second order corrections simply show up only for sites o-1 and o+1, but not for site o. The fact that for the q's also the second order corrections vanish, while this is not the case for the p's implies that the second order corrections in the expectation values $B_k(2)$ must be purely imaginary as equation (22) indicates. Equation (B6) shows that the only complex factors in the expression for the corrections are a_{o-1}^{J} and a_{o+1}^{J}. We looked at the numerical values for these coefficients, and indeed, within the first 0.4 ps their real part is less than 10^{-16} and their imaginary part varies between 0 and 0.5. Therefore it is clear that the second order corrections influence only the momenta but not the displacements. The situation for the larger coupling constant (Fig. 7 g-l) is similar to that for the smaller one, therefore we don't want to discuss it in detail. The most important result of both calculations is, that the $|D_1>$ results agree very well with those from the expansion within 0.10-0.15 ps, the time in which the expansion can be considered as „exact" solution. This time is also the most important one for a possible soliton formation, because the lattice is driven only by exciton-phonon coupling in these first 100-150 fs where the excitation starts to move from the initial excitation site to its nearest neighbors. During this process the lattice deforms in a way which stabilizes the excitation to an extent, that a soliton can be formed or not. In Fig. 7g we show for completeness q_{o+2} and p_{o+2}. In the short time intervall their values are smaller than the ones discussed above, however, here the first order becomes worse and the $|D_1>$ curves are nearly identical to the third order results up to roughly 0.25 ps.

Conclusion

In an attempt to study the properties of the $|D_1>$ approximation numerically, we have performed long time simulations over a period of 10 ns and computed the relevant expectation values of the deviation state and compared them to those computed from the state $\left(\hat{H}_D/J\right)\left|D_1\right\rangle$. This study complements our previous investigations of the medium time scale in the order of 100 ps [8]. The expectation values of the deviation state, which were already neglegible in the medium time scale turned out to decrease even in the course of time.

Further we expanded the formally exact solution of the Davydov Hamiltonian in a Taylor series in the time t, to assess the very short time behaviour also. We found that such an expansion around t=0 up to third order is valid within a time of 0.10-0.15 ps. Further the second and third order corrections turned out to be more or less negligible in this range of time. This is probably due to the fact, that as first order we chose already a state in which some of the terms in the expansion are summed to infinite order, resulting in the solutions of the decoupled oscillator system and the small polaron limit, respectively. Therefore we conclude that on this time-scale the two limiting cases govern the dynamics of the system. However, for larger times the first order becomes incorrect, because in the small polaron limit, starting from a localized initial excitation, only the initial excitation site is affected by the exciton-phonon interaction, while due to the dipole interaction the amide-I excitation spreads over the neighboring sites also within the |ψ(1)> state. For the time in which the expansion is valid, however, the results obtained from the $|D_1>$ simulation agree very well with it. Thus, together with the long-time results and our previous work on medium time scales, we conclude that the $|D_1>$ approximation must be very close to the exact solution for times from 0 up to 10 ns.

As it was to be expected from the beginning, an expansion of the exact solution around a single point in time, i.e. t=0, cannot replace methods using ansatz states for simulation on longer time scales. One could think to compute simply higher orders of the expansion. The draw back of this approach is, that for longer time rather high orders would be necessary, leading to prohibitively complicated expressions. Also it is known, that attempts to expand wave functions only around a single point in time usually lead into problems, when they are applied for longer times. However, there is another possibility to use the expansion method also up to larger times, namely to use a given expansion only for a small time interval, say τ, and use the state obtained as initial state for a further expansion around t=τ and so forth. If the time interval is small enough, e.g. τ=0.05-0.10 ps, the expansion could even be restricted to the first order. However, in this case the first order becomes more complicated.

Assume time steps ℓτ with ℓ=0,1,... and 0<t<τ, then for ℓ=0 we have the same expansion as discussed above. However, at t=τ we have the new initial state

$$\left|\psi_0(1,\tau)\right\rangle = \sum_n \left(a_n^J(\tau)-\delta_{no}\right)\hat{a}_n^+\left|0\right\rangle + a_o^\omega(\tau)\hat{U}_o(\tau)\hat{a}_o^+\left|0\right\rangle \tag{36}$$

Then our first order state in the second time interval is

$$\left|\psi(1,\tau+t)\right\rangle = \left(e^{-\frac{it}{\hbar}\hat{\omega}} + e^{-\frac{it}{\hbar}\hat{J}} - 1\right)\left|\psi_0(1,\tau)\right\rangle \tag{37}$$

where the different terms can be derived from the exact special case solutions given in detail in paper I. For the small polaron contribution we obtain

$$\left|\omega(\tau+t)\right\rangle = e^{-\frac{it}{\hbar}\hat{\omega}}\left|\psi_0(1,\tau)\right\rangle = \tag{38}$$

$$= e^{-\frac{it}{\hbar}\hat{\omega}}\sum_n \left(a_n^J(\tau)-\delta_{no}\right)\hat{a}_n^+\left|0\right\rangle + e^{-\frac{it}{\hbar}\hat{\omega}} a_o^\omega(\tau)\hat{U}_o(\tau)\hat{a}_o^+\left|0\right\rangle$$

where the first term can be obtained from equation (A12) of paper I by insertion of the new initial conditions

$$a_n(0) = a_n^J(\tau)-\delta_{no} \quad ; \quad b_{nk}(0)=0 \tag{39}$$

and the second term also from equation (A12) by insertion of

$$a_n(0) = e^{-i\sum_k B_{ok}^2\left[\sin(\omega_k\tau)-\omega_k\tau\right]}\cdot\delta_{no} \tag{40}$$

$$b_{nk}(0) = B_{ok}\left(e^{-i\omega_k\tau}-1\right)\delta_{no}$$

A similar decomposition can be performed for the oscillator part:

$$\left|J(\tau+t)\right\rangle = e^{-\frac{it}{\hbar}\hat{J}}\left|\psi_0(1,\tau)\right\rangle =$$

$$= e^{-\frac{it}{\hbar}\hat{J}}\sum_n \left(a_n^J(\tau)-\delta_{no}\right)\hat{a}_n^+\left|0\right\rangle + a_o^\omega(\tau)\hat{U}_o(\tau)e^{-\frac{it}{\hbar}\hat{J}}\hat{a}_o^+\left|0\right\rangle \tag{41}$$

where both terms can be computed from equation (C9) of paper I. For coherent state operators, as occurring in the second part one only needs to note that the exponential operator for the oscillator system commutes with them. Thus for time steps ℓτ with ℓ>1 with arbitrary coefficients $d_n(\ell\tau)$ one has to treat cases like this as a superposition of exact solutions for the decoupled oscillator system:

$$e^{-\frac{it}{\hbar}\hat{J}}\sum_n d_n(\ell\tau)\hat{U}_n(\ell\tau)\hat{a}_n^+\left|0\right\rangle =$$

$$= \sum_n \hat{U}_n(\ell\tau)d_n(\ell\tau)\left[e^{-\frac{it}{\hbar}\hat{J}}\hat{a}_n^+\left|0\right\rangle\right] \tag{42}$$

where all the terms can be calculated individually for each n as an exact solution of the decoupled oscillator system with an initial excitation localized at site n, leading to

$$e^{-\frac{it}{\hbar}\hat{J}}\sum_n d_n(\ell\tau)\hat{U}_n(\ell\tau)\hat{a}_n^+\left|0\right\rangle =$$

$$= \frac{1}{N}\sum_{nmk}\hat{U}_n(\ell\tau)d_n(\ell\tau)e^{\frac{2\pi i}{N}k(m-n)}e^{2i\frac{Jt}{\hbar}\cos\left(\frac{2\pi}{N}k\right)}\hat{a}_m^+\left|0\right\rangle \tag{43}$$

In this way for any time step the contributions to |ψ(1,ℓτ+t)> can be calculated, using always |ψ(1,ℓτ)> as initial state, and thus the first order approximation can be propagated through larger times. However, the time step τ has to be chosen small enough, that the first order is a reliable representation of the exact solution. According to the present work τ should be around 0.05-0.10 ps. Investigations along this line are in progress, which, as we hope, will lead at least for a few picoseconds to a state which is nearly identical to the exact solution. However, the expressions obtained become more complicated at each time step (see Appendix D), especially for the computation of expectation values. A simpler possibility would be, to calculate at each τ from $|\psi(1,\ell\tau)>$ the set $\{a_n(\ell\tau),q_n(\ell\tau),p_n(\ell\tau)\}$ and to construct a $|D_2>$ like state from them, which in turn could be used as initial state for the next period. However, in this approximation one could miss the quantum mechanical phase mixing between phonons and excitons, which is described by $|D_1>$ like states. This possibility has to be checked by numerical calculations.

The final step of these investigations will be the introduction of temperature into such expansion methods and to compare the results with the usually used methods for the treatment of temperature effects, e.g. Davydov's method, which uses an averaged Hamiltonian or our lattice population ansatz, where the lattice is populated with thermal phonons prior to the start of the simulation. For this purpose we would have to start with an initial state of the form [8]

$$\left|\psi_\nu(0)\right\rangle = \sum_n a_n(0)\hat{a}_n^+\left|0\right\rangle_e\left|\nu\right\rangle$$
$$\left|\nu\right\rangle = \prod_k \frac{\left(\hat{b}_k^+\right)^{\nu_k}}{\sqrt{\nu_k!}}\left|0\right\rangle_p \qquad (44)$$

where ν denotes any one of the possible phonon distributions in the lattice. Then in the usual way we can write down the exact time evolution as

$$\left|\psi_\nu(t)\right\rangle = e^{-\frac{it}{\hbar}\hat{H}}\left|\psi_\nu(0)\right\rangle \qquad (45)$$

with expectation values for an arbitrary operator

$$A_\nu(t) = \left\langle\psi_\nu(t)\right|\hat{A}\left|\psi_\nu(t)\right\rangle = \left\langle\psi_\nu(0)\right|e^{\frac{it}{\hbar}\hat{H}}\hat{A}e^{-\frac{it}{\hbar}\hat{H}}\left|\psi_\nu(0)\right\rangle \qquad (46)$$

Finally a thermal average results in the desired expectation value at a temperature T

$$A(t,T) = \sum_\nu \rho_\nu(T)A_\nu(t)$$
$$\rho_\nu(T) = \frac{\left\langle\nu\right|e^{-\frac{\hat{H}_p}{k_BT}}\left|\nu\right\rangle}{\sum_\mu\left\langle\mu\right|e^{-\frac{\hat{H}_p}{k_BT}}\left|\mu\right\rangle} \qquad (47)$$

where k_B is Boltzmann's constant and $\hat{H}_p$ is the phonon part of the Hamiltonian. Then the final expansion is given by

$$A(t,T) = \sum_\nu \rho_\nu(T)\sum_{k,l=0}^{\infty}\frac{(-1)^l\left(\frac{it}{\hbar}\right)^{k+l}}{k!l!}\cdot \left\langle\psi_\nu(0)\right|\hat{H}^k\hat{A}\hat{H}^l\left|\psi_\nu(0)\right\rangle \qquad (48)$$

We want to use such an expansion again up to the third order in both k and l for the case of the small polaron limit and to compare it then to the results of the different models for inclusion of temperature effects into the theory.

In the third and final paper of this series we will present, on the basis of the discussions in this work and paper I, applications of the $|D_1>$ model to proteins with emphasis on the question, whether or not Davydov solitons are stable in such systems at 0K and at physiological temperatures. Further we will present vibrational spectra of proteins, calculated from the dynamics as obtained with our model.

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Appendix A: Expectation Values of the Exciton Number Operators and the Norm

The expectation values of the number operators for the excitons in the different orders m of the wave function are given by

$$N_n(\mu,t)=\left\langle\psi(\mu,t)\middle|\hat{a}_n^+\hat{a}_n\middle|\psi(\mu,t)\right\rangle \tag{A1}$$

and the norm of the states can be obtained by direct calculation of S(μ,t)=<ψ(μ,t)|ψ(μ,t)> or by summation of the $N_n(\mu,t)$ over all sites n, since the total number of excitons equals 1. The zeroth order results in

$$N_n(0)=\left\langle\psi(0)\middle|\hat{N}_n\middle|\psi(0)\right\rangle=\left\langle\omega+J-\psi_0\middle|\hat{N}_n\middle|\omega+J-\psi_0\right\rangle \tag{A2}$$

which is easily evaluated and yields (since there is no first order correction $N_n(1)=N_n(0)$ and |ψ(0)>=|ψ(1)> holds)

$$\begin{aligned} N_n(1)&=2\left\{1+\mathrm{Re}\left[\left(a_o^{\omega}\right)^*\left(a_o^J-1\right)\right]U_o-\mathrm{Re}\left[a_o^J\right]\right\}\delta_{no}+\left|a_n^J\right|^2 \\ U_o&=e^{-\frac{1}{2}\sum_{k=1}^{N-1}\left|b_{ok}\right|^2}=e^{\sum_{k=1}^{N-1}B_{ok}^2\left[\cos(\omega_k t)-1\right]} \end{aligned} \tag{A3}$$

Summation over n yields the norm:

$$S(1)=\sum_{n=1}^{N}N_n(1)=3-2\,\mathrm{Re}\left[\left(a_o^{\omega}\right)^*\left(1-a_o^J\right)\right]U_o-2\,\mathrm{Re}\left[a_o^J\right] \tag{A4}$$

In second order we have to evaluate

$$N_n(2)=\left\langle\psi(2)\middle|\hat{N}_n\middle|\psi(2)\right\rangle=\left\langle\psi(1)-\frac{t^2}{2\hbar^2}\psi_2\middle|\hat{N}_n\middle|\psi(1)-\frac{t^2}{2\hbar^2}\psi_2\right\rangle=N_n(1)-\frac{t^2}{\hbar^2}\mathrm{Re}\left[\left\langle\psi(1)\middle|\hat{N}_n\middle|\psi_2\right\rangle\right]+\frac{t^4}{4\hbar^4}\left\langle\psi_2\middle|\hat{N}_n\middle|\psi_2\right\rangle \tag{A5}$$

Due to the phonon operators in $|\psi_2>$ we have

$$\left\langle J\middle|\hat{N}_n\middle|\psi_2\right\rangle=\left\langle\psi_0\middle|\hat{N}_n\middle|\psi_2\right\rangle=0 \tag{A6}$$

Further, since in <ω| only the exciton operator for site o occurs, while in $|\psi_2>$ only those for sites o+1 and o-1 are present

$$\left\langle\omega\middle|\hat{N}_n\middle|\psi_2\right\rangle=\left\langle\psi(1)\middle|\hat{N}_n\middle|\psi_2\right\rangle=0 \tag{A7}$$

holds. Together with

$$\left\langle\psi_2\middle|\hat{N}_n\middle|\psi_2\right\rangle=J^2\sum_{k=1}^{N-1}(\hbar\omega_k)^2\left(A_{o-1,k}^2\delta_{n,o-1}+A_{o+1,k}^2\delta_{n,o+1}\right) \tag{A8}$$

we obtain

$$N_n(2) = N_n(1) + \left(\frac{Jt}{2\hbar}\right)^2 \sum_{k=1}^{N-1} (\omega_k t)^2 \left(A_{o-1,k}^2 \delta_{n,o-1} + A_{o+1,k}^2 \delta_{n,o+1}\right) \tag{A9}$$

which summed over n yields the norm

$$S(2) = \sum_{n=1}^{N} N_n(2) = S(1) + \left(\frac{Jt}{2\hbar}\right)^2 \sum_{k=1}^{N-1} (\omega_k t)^2 \left(A_{o-1,k}^2 + A_{o+1,k}^2\right) \tag{A10}$$

The third order is more complicated and needs evaluation of

$$\begin{gathered} N_n(3) = \left\langle \psi(2) + \frac{i}{6}\left(\frac{t}{\hbar}\right)^3 \psi_3 \middle| \hat{N}_n \middle| \psi(2) + \frac{i}{6}\left(\frac{t}{\hbar}\right)^3 \psi_3 \right\rangle = N_n(2) - \frac{t^3}{3\hbar^3} \operatorname{Im}\left[\left\langle \psi(2) \middle| \hat{N}_n \middle| \psi_3 \right\rangle\right] + \frac{t^6}{36\hbar^6} \left\langle \psi_3 \middle| \hat{N}_n \middle| \psi_3 \right\rangle \\ \left\langle \psi(2) \middle| \hat{N}_n \middle| \psi_3 \right\rangle = \left\langle \omega + J - \psi_0 \middle| \hat{N}_n \middle| \psi_3 \right\rangle - \frac{t^2}{2\hbar^2} \left\langle \psi_2 \middle| \hat{N}_n \middle| \psi_3 \right\rangle \end{gathered} \tag{A11}$$

Using the well known commutation relations of our operators we obtain

$$\begin{gathered} \left\langle \omega \middle| \hat{N}_n \middle| \psi_3 \right\rangle = J^2 \left(a_o^\omega\right)^* \sum_{k=1}^{N-1} \hbar\omega_k D_k b_{ok}^* U_o \delta_{no} \quad ; \quad \left\langle \psi_0 \middle| \hat{N}_n \middle| \psi_3 \right\rangle = 0 \\ \left\langle J \middle| \hat{N}_n \middle| \psi_3 \right\rangle = -J \sum_{n=1}^{N-1} (\hbar\omega_k)^2 \left(E_k^{(+)} \left(a_{o+1}^J\right)^* \delta_{n,o+1} + E_k^{(-)} \left(a_{o-1}^J\right)^* \delta_{n,o-1} \right) \end{gathered} \tag{A12}$$

Collecting the terms yields

$$\left\langle \psi(1) \middle| \hat{N}_n \middle| \psi_3 \right\rangle = J \sum_{k=1}^{N-1} \hbar\omega_k \left[J \cdot D_k \left(a_o^\omega\right)^* b_{ok}^* U_o \delta_{no} - \hbar\omega_k \left(E_k^{(-)} \left(a_{o-1}^J\right)^* \delta_{n,o-1} + E_k^{(+)} \left(a_{o+1}^J\right)^* \delta_{n,o+1} \right) \right] \tag{A13}$$

Together with the fact that

$$\left\langle \psi_2 \middle| \hat{N}_n \middle| \psi_3 \right\rangle = J^2 \sum_{k=1}^{N-1} (\hbar\omega_k)^3 \left(A_{o-1,k} F_k^{(-)} \delta_{n,o-1} + A_{o+1,k} F_k^{(+)} \delta_{n,o+1} \right) \tag{A14}$$

is real and

$$\left\langle \psi_3 \middle| \hat{N}_n \middle| \psi_3 \right\rangle = \sum_{\nu=-2}^{2} \left\langle 0 \middle| \hat{\Gamma}_\nu^+ \hat{\Gamma}_\nu \middle| 0 \right\rangle \delta_{n,o+\nu} \tag{A15a}$$

$$\left\langle \psi_3 \middle| \hat{N}_{o\pm2} \middle| \psi_3 \right\rangle = J^4 \sum_{k=1}^{N-1} \left(\hbar\omega_k D_k^{(\pm)} \right)^2 \tag{A15b}$$

$$\left\langle\psi_3\left|\hat{N}_{o\pm1}\right|\psi_3\right\rangle = J^2\left\{\left[\sum_{k=1}^{N-1}(\hbar\omega_k)^2 E_k^{(\pm)}\right]^2 + \sum_{k=1}^{N-1}\left[(\hbar\omega_k)^2 F_k^{(\pm)}\right]^2 + \sum_{k,k'=1}^{N-1}(\hbar\omega_k\hbar\omega_{k'})^2\left[\left(G_{kk'}^{(\pm)}\right)^2 + G_{kk'}^{(\pm)}G_{k'k}^{(\pm)}\right]\right\}$$

$$\left\langle\psi_3\left|\hat{N}_o\right|\psi_3\right\rangle = J^4\sum_{k=1}^{N-1}(\hbar\omega_k D_k)^2 \tag{A15c}$$

we finally obtain

$$\begin{aligned}
N_n(3) = {} & N_n(2) + \delta_{n,o-2}\left\{\frac{1}{36}\left(\frac{Jt}{\hbar}\right)^4\sum_{k=1}^{N-1}\left(\omega_k t D_k^{(-)}\right)^2\right\} + \delta_{n,o-1}\left\{\frac{1}{3}\frac{Jt}{\hbar}\sum_{k=1}^{N-1}(\omega_k t)^2 E_k^{(-)}\,\mathrm{Im}\left[\left(a_{o-1}^J\right)^*\right] + \right.\\
& \left. + \frac{1}{36}\left(\frac{Jt}{\hbar}\right)^2\left[\left(\sum_{k=1}^{N-1}(\omega_k t)^2 E_k^{(-)}\right)^2 + \sum_{k=1}^{N-1}\left((\omega_k t)^2 F_k^{(-)}\right)^2 + \sum_{k,k'=1}^{N-1}(\omega_k t\cdot\omega_{k'}t)^2\left(\left(G_{kk'}^{(-)}\right)^2 + G_{kk'}^{(-)}G_{k'k}^{(-)}\right)\right]\right\} + \\
& + \delta_{no}\left(\frac{Jt}{\hbar}\right)^2\sum_{k=1}^{N-1}(\omega_k t)\left\{\frac{1}{36}\left(\frac{Jt}{\hbar}\right)^2\omega_k t D_k^2 + \frac{1}{3}\mathrm{Im}\left[a_o^{\omega} b_{ok}\right]D_k U_o\right\} + \delta_{n,o+1}\left\{\frac{1}{3}\frac{Jt}{\hbar}\sum_{k=1}^{N-1}(\omega_k t)^2 E_k^{(+)}\,\mathrm{Im}\left[\left(a_{o+1}^J\right)^*\right] + \right.\\
& \left. + \frac{1}{36}\left(\frac{Jt}{\hbar}\right)^2\left[\left(\sum_{k=1}^{N-1}(\omega_k t)^2 E_k^{(+)}\right)^2 + \sum_{k=1}^{N-1}\left((\omega_k t)^2 F_k^{(+)}\right)^2 + \sum_{k,k'=1}^{N-1}(\omega_k t\cdot\omega_{k'}t)^2\left(\left(G_{kk'}^{(+)}\right)^2 + G_{kk'}^{(+)}G_{k'k}^{(+)}\right)\right]\right\} + \\
& + \delta_{n,o+2}\left\{\frac{1}{36}\left(\frac{Jt}{\hbar}\right)^4\sum_{k=1}^{N-1}\left(\omega_k t D_k^{(+)}\right)^2\right\}
\end{aligned} \tag{A16}$$

The norm S(3) is then simply given by summation of $N_n(3)$ over the sites n:

$$S(3) = \sum_{n=1}^{N} N_n(3) \tag{A17}$$

The explicit expression for S(3) is obtained from (A16) by replacing on the right hand side the term $N_n(2)$ with S(2) and by leaving out the Kronecker δ's.

Appendix B: Expectation Values of the Phonon Operators

In this Appendix we want to calculate the expectation values of the phonon annihilation operators. Note that their complex conjugates are the expectation values of the phonon creation operator. These expectation values are

$$B_k(\mu) = \left\langle\psi(\mu)\left|\hat{b}_k\right|\psi(\mu)\right\rangle \tag{B1}$$

The first expectation value in this series, $B_k(0)=B_k(1)$ is given by

$$B_k(1) = \left\langle \psi(1) \middle| \hat{b}_k \middle| \psi(1) \right\rangle = \left\langle \omega + J - \psi_0 \middle| \hat{b}_k \middle| \omega + J - \psi_0 \right\rangle = \left\langle \omega + J - \psi_0 \middle| \hat{b}_k \middle| \omega \right\rangle$$

$$\left\langle \omega \middle| \hat{b}_k \middle| \omega \right\rangle = \left| a_o^\omega \right|^2 \left\langle \beta_o \middle| \hat{b}_k \middle| \beta_o \right\rangle = b_{ok}$$

$$\left\langle J \middle| \hat{b}_k \middle| \omega \right\rangle = a_o^\omega \left(a_o^J \right)^* \left\langle 0 \middle| \hat{b}_k \middle| \beta_o \right\rangle = a_o^\omega \left(a_o^J \right)^* b_{ok} U_o \tag{B2}$$

$$\left\langle \psi_0 \middle| \hat{b}_k \middle| \omega \right\rangle = a_o^\omega b_{ok} U_o$$

$$B_k(1) = b_{ok} \left\{ 1 + a_o^\omega \left[\left(a_o^J \right)^* - 1 \right] U_o \right\}$$

For $B_k(2)$ we have to evaluate

$$B_k(2) = \left\langle \psi(2) \middle| \hat{b}_k \middle| \psi(2) \right\rangle = \left\langle \psi(1) - \frac{t^2}{2\hbar^2} \psi_2 \middle| \hat{b}_k \middle| \psi(1) - \frac{t^2}{2\hbar^2} \psi_2 \right\rangle$$

$$= B_k(1) - \frac{t^2}{2\hbar^2} \left[\left\langle \psi(1) \middle| \hat{b}_k \middle| \psi_2 \right\rangle + \left\langle \psi_2 \middle| \hat{b}_k \middle| \psi(1) \right\rangle \right] + \frac{t^4}{4\hbar^4} \left\langle \psi_2 \middle| \hat{b}_k \middle| \psi_2 \right\rangle \tag{B3}$$

where the terms are

$$\left\langle \psi(1) \middle| \hat{b}_k \middle| \psi_2 \right\rangle = \left\langle \omega + J - \psi_0 \middle| \hat{b}_k \middle| \psi_2 \right\rangle = \left\langle J \middle| \hat{b}_k \middle| \psi_2 \right\rangle = -J\hbar\omega_k \left[\left(a_{o-1}^J \right)^* A_{o-1,k} + \left(a_{o+1}^J \right)^* A_{o+1,k} \right]$$

$$\left\langle \psi_2 \middle| \hat{b}_k \middle| \psi(1) \right\rangle = \left\langle \psi_2 \middle| \hat{b}_k \middle| \omega + J - \psi_0 \right\rangle = 0 \tag{B4}$$

and

$$\left\langle \psi_2 \middle| \hat{b}_k \middle| \psi_2 \right\rangle = J^2 \sum_{k'k''} \hbar\omega_{k'} \hbar\omega_{k''} \left(A_{o-1,k'} A_{o-1,k''} + A_{o+1,k'} A_{o+1,k''} \right) \cdot \left\langle 0 \middle| \hat{b}_{k'} \hat{b}_k \hat{b}_{k''}^+ \middle| 0 \right\rangle = 0 \tag{B5}$$

and thus the final result reads as

$$B_k(2) = B_k(1) + \frac{1}{2} \frac{Jt}{\hbar} \omega_k t \left[\left(a_{o-1}^J \right)^* A_{o-1,k} + \left(a_{o+1}^J \right)^* A_{o+1,k} \right] \tag{B6}$$

For the third order wave function we have to compute

$$B_k(3) = \left\langle \psi(3) \middle| \hat{b}_k \middle| \psi(3) \right\rangle = \left\langle \psi(2) + \frac{i}{6} \frac{t^3}{\hbar^3} \psi_3 \middle| \hat{b}_k \middle| \psi(2) + \frac{i}{6} \frac{t^3}{\hbar^3} \psi_3 \right\rangle$$

$$= B_k(2) + \frac{i}{6} \frac{t^3}{\hbar^3} \left[\left\langle \psi(2) \middle| \hat{b}_k \middle| \psi_3 \right\rangle - \left\langle \psi_3 \middle| \hat{b}_k \middle| \psi(2) \right\rangle \right] + \frac{1}{36} \frac{t^6}{\hbar^6} \left\langle \psi_3 \middle| \hat{b}_k \middle| \psi_3 \right\rangle \tag{B7}$$

The two mixed terms can be reduced to

$$\hat{b}_k \left| J - \psi_0 \right\rangle = 0 \Rightarrow \left\langle \psi_3 \middle| \hat{b}_k \middle| \psi(2) \right\rangle = \left\langle \psi_3 \middle| \hat{b}_k \middle| \omega \right\rangle - \frac{1}{2}\frac{t^2}{\hbar^2}\left\langle \psi_3 \middle| \hat{b}_k \middle| \psi_2 \right\rangle$$

$$\left\langle \psi(2) \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \left\langle J + \omega - \psi_0 \middle| \hat{b}_k \middle| \psi_3 \right\rangle - \frac{1}{2}\frac{t^2}{\hbar^2}\left\langle \psi_2 \middle| \hat{b}_k \middle| \psi_3 \right\rangle \qquad \text{(B8)}$$

Now we have to evaluate the individual expectation values:

$$\left\langle \psi_3 \middle| \hat{b}_k \middle| \omega \right\rangle = \sum_{\nu=-2}^{2} (-1)^{\nu} a_o^{\omega} \left\langle 0 \middle| \hat{\Gamma}_{\nu}^{+} \hat{a}_{o+\nu} \hat{b}_k \hat{a}_o^{+} \hat{U}_o \middle| 0 \right\rangle = a_o^{\omega} b_{ok} \left\langle 0 \middle| \Gamma_0^{+} \middle| \beta_o \right\rangle = J^2 a_o^{\omega} b_{ok} U_o \sum_{k'=1}^{N-1} \hbar\omega_{k'} D_{k'} b_{ok'}$$

$$\text{(B9)}$$

$$\left\langle \psi_3 \middle| \hat{b}_k \middle| \psi_2 \right\rangle = \sum_{\nu=-2}^{2} (-1)^{\nu} \left\langle 0 \middle| \hat{\Gamma}_{\nu}^{+} \hat{a}_{o+\nu} \hat{b}_k \left(\hat{\Theta}_{-1} \hat{a}_{o-1}^{+} + \hat{\Theta}_{+1} \hat{a}_{o+1}^{+} \right) \middle| 0 \right\rangle = -\left[\left\langle 0 \middle| \hat{\Gamma}_{-1}^{+} \hat{b}_k \hat{\Theta}_{-1} \middle| 0 \right\rangle + \left\langle 0 \middle| \hat{\Gamma}_{+1}^{+} \hat{b}_k \hat{\Theta}_{+1} \middle| 0 \right\rangle \right]$$

$$= J^2 \hbar\omega_k \left[A_{o-1,k} \sum_{k'=1}^{N-1} (\hbar\omega_{k'})^2 E_{k'}^{(-)} + A_{o+1,k} \sum_{k'=1}^{N-1} (\hbar\omega_{k'})^2 E_{k'}^{(+)} \right]$$

Collecting the terms, this yields

$$-\frac{i}{6}\frac{t^3}{\hbar^3}\left\langle \psi_3 \middle| \hat{b}_k \middle| \psi(2) \right\rangle = \frac{i}{6}\left(\frac{Jt}{\hbar}\right)^2 \Bigg\{ -a_o^{\omega} b_{ok} U_o \sum_{k'=1}^{N-1} (\omega_{k'} t) D_{k'} b_{ok'} +$$

$$+ \frac{1}{2}(\omega_k t)\left[A_{o-1,k} \sum_{k'=1}^{N-1} (\omega_{k'} t)^2 E_{k'}^{(-)} + A_{o+1,k} \sum_{k'=1}^{N-1} (\omega_{k'} t)^2 E_{k'}^{(+)} \right] \Bigg\} \qquad \text{(B10)}$$

The contributions to the next term are

$$\left\langle J \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \sum_{\nu=-2}^{2} (-1)^{\nu} \left(a_{o+\nu}^{J} \right)^{*} \left\langle 0 \middle| \hat{b}_k \hat{\Gamma}_{\nu} \middle| 0 \right\rangle$$

$$= J^2 \hbar\omega_k \left[\left(a_{o-2}^{J}\right)^{*} D_k^{(-)} + \left(a_o^{J}\right)^{*} D_k + \left(a_{o+2}^{J}\right)^{*} D_k^{(+)} \right] - J(\hbar\omega_k)^2 \left[\left(a_{o-1}^{J}\right)^{*} F_k^{(-)} + \left(a_{o+1}^{J}\right)^{*} F_k^{(+)} \right]$$

$$\left\langle \psi_0 \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \left\langle 0 \middle| \hat{b}_k \hat{\Gamma}_0 \middle| 0 \right\rangle = J^2 \hbar\omega_k D_k \qquad \text{(B11)}$$

$$\left\langle \omega \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \left(a_o^{\omega}\right)^{*} \left\langle \beta_o \middle| \hat{b}_k \hat{\Gamma}_0 \middle| 0 \right\rangle = J^2 \hbar\omega_k \left(a_o^{\omega}\right)^{*} D_k U_o$$

and therefore

$$\left\langle \omega + J - \psi_0 \middle| \hat{b}_k \middle| \psi_3 \right\rangle = -J(\hbar\omega_k)^2 \left\{ \left(a_{o-1}^{J}\right)^{*} F_k^{(-)} + \left(a_{o+1}^{J}\right)^{*} F_k^{(+)} \right\} +$$

$$+ J^2 \hbar\omega_k \left\{ \left(a_{o-2}^{J}\right)^{*} D_k^{(-)} + \left[\left(a_o^{\omega}\right)^{*} U_o + \left(a_o^{J}\right)^{*} - 1 \right] D_k + \left(a_{o+2}^{J}\right)^{*} D_k^{(+)} \right\} \qquad \text{(B12)}$$

Further

$$\left\langle \psi_2 \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \sum_{\nu=-2}^{2} (-1)^{\nu} \langle 0 \left| \left[\hat{\Theta}^+_{-1} \hat{a}_{o-1} + \hat{\Theta}^+_{+1} \hat{a}_{o+1} \right] \hat{b}_k \hat{a}^+_{o+\nu} \hat{\Gamma}_{\nu} \right| 0 \rangle = -\left[\left\langle 0 \middle| \hat{\Theta}^+_{-1} \hat{b}_k \hat{\Gamma}_{-1} \middle| 0 \right\rangle + \left\langle 0 \middle| \hat{\Theta}^+_{+1} \hat{b}_k \hat{\Gamma}_{+1} \middle| 0 \right\rangle \right]$$
$$= J^2 \hbar\omega_k \sum_{k'=1}^{N-1} (\hbar\omega_{k'})^2 \left[A_{o-1,k'} \left(G^{(-)}_{kk'} + G^{(-)}_{k'k} \right) + A_{o+1,k'} \left(G^{(+)}_{kk'} + G^{(+)}_{k'k} \right) \right] \tag{B13}$$

and thus

$$\frac{i}{6} \frac{t^3}{\hbar^3} \left\langle \psi(2) \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \frac{i}{6} \left\{ -\frac{Jt}{\hbar} (\omega_k t)^2 \left[\left(a^J_{o-1} \right)^* F^{(-)}_k + \left(a^J_{o+1} \right)^* F^{(+)}_k \right] + \right.$$
$$+ \left(\frac{Jt}{\hbar} \right)^2 \omega_k t \left[\left(a^J_{o-2} \right)^* D^{(-)}_k + \left(\left(a^{\omega}_o \right)^* U_o + \left(a^J_o \right)^* - 1 \right) D_k + \left(a^J_{o+2} \right)^* D^{(+)}_k \right] -$$
$$\left. - \frac{1}{2} \left(\frac{Jt}{\hbar} \right)^2 \omega_k t \sum_{k'=1}^{N-1} (\omega_{k'} t)^2 \left[A_{o-1,k'} \left(G^{(-)}_{kk'} + G^{(-)}_{k'k} \right) + A_{o+1,k'} \left(G^{(+)}_{kk'} + G^{(+)}_{k'k} \right) \right] \right\} \tag{B14}$$

The final expectation value is

$$\left\langle \psi_3 \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \sum_{\nu,\mu=-2}^{2} (-1)^{\nu+\mu} \left\langle 0 \middle| \hat{a}_{o+\nu} \hat{\Gamma}^+_{\nu} \hat{b}_k \hat{\Gamma}_{\mu} \hat{a}^+_{o+\mu} \middle| 0 \right\rangle = \sum_{\nu=-2}^{2} \left\langle 0 \middle| \hat{\Gamma}^+_{\nu} \hat{b}_k \hat{\Gamma}_{\nu} \middle| 0 \right\rangle \tag{B15}$$

where

$$\left\langle 0 \middle| \hat{\Gamma}^+_{\pm 2} \hat{b}_k \hat{\Gamma}_{\pm 2} \middle| 0 \right\rangle = J^4 \sum_{k'k''} \hbar\omega_{k'} \cdot \hbar\omega_{k''} D^{(\pm)}_{k'} D^{(\pm)}_{k''} \left\langle 0 \middle| \hat{b}_{k'} \hat{b}_k \hat{b}^+_{k''} \middle| 0 \right\rangle = 0$$
$$\left\langle 0 \middle| \hat{\Gamma}^+_{\pm 1} \hat{b}_k \hat{\Gamma}_{\pm 1} \middle| 0 \right\rangle = J^2 (\hbar\omega_k)^2 F^{(\pm)}_k \sum_{k'=1}^{N-1} (\hbar\omega_{k'})^2 E^{(\pm)}_{k'} + J^2 \hbar\omega_k \sum_{k'=1}^{N-1} (\hbar\omega_{k'})^3 F^{(\pm)}_{k'} \left(G^{(\pm)}_{kk'} + G^{(\pm)}_{k'k} \right) \tag{B16}$$
$$\left\langle 0 \middle| \hat{\Gamma}^+_0 \hat{b}_k \hat{\Gamma}_0 \middle| 0 \right\rangle = J^4 \sum_{k'k''} \hbar\omega_{k'} \hbar\omega_{k''} D_{k'} D_{k''} \left\langle 0 \middle| \hat{b}_{k'} \hat{b}_k \hat{b}^+_{k''} \middle| 0 \right\rangle = 0$$

and thus

$$\frac{1}{36} \frac{t^6}{\hbar^6} \left\langle \psi_3 \middle| \hat{b}_k \middle| \psi_3 \right\rangle = \frac{1}{36} \left(\frac{Jt}{\hbar} \right)^2 \omega_k t \sum_{k'=1}^{N-1} (\omega_{k'} t)^2 \left\{ \omega_k t \left[F^{(-)}_k E^{(-)}_{k'} + F^{(+)}_k E^{(+)}_{k'} \right] + \right.$$
$$\left. + \omega_{k'} t \left[F^{(-)}_{k'} \left(G^{(-)}_{kk'} + G^{(-)}_{k'k} \right) + F^{(+)}_{k'} \left(G^{(+)}_{kk'} + G^{(+)}_{k'k} \right) \right] \right\} \tag{B17}$$

Then $B_k(3)$ is given by

$$B_k(3) = B_k(2) + \frac{i}{6}\left\{-\frac{Jt}{\hbar}(\omega_k t)^2\left[\left(a^J_{o-1}\right)^* F_k^{(-)} + \left(a^J_{o+1}\right)^* F_k^{(+)}\right] + \right.$$
$$+\left(\frac{Jt}{\hbar}\right)^2 \omega_k t\left[\left(a^J_{o-2}\right)^* D_k^{(-)} + \left(\left(a^\omega_o\right)^* U_o + \left(a^J_o\right)^* - 1\right)D_k + \left(a^J_{o+2}\right)^* D_k^{(+)}\right] -$$
$$\left. -\frac{1}{2}\left(\frac{Jt}{\hbar}\right)^2 \omega_k t \sum_{k'=1}^{N-1}(\omega_{k'} t)^2\left[A_{o-1,k'}\left(G^{(-)}_{kk'} + G^{(-)}_{k'k}\right) + A_{o+1,k'}\left(G^{(+)}_{kk'} + G^{(+)}_{k'k}\right)\right]\right\} + \tag{B18}$$
$$+\frac{i}{6}\left(\frac{Jt}{\hbar}\right)^2\left\{-a^\omega_o b_{ok} U_o \sum_{k'=1}^{N-1}(\omega_{k'} t) D_{k'} b_{ok'} + \frac{1}{2}(\omega_k t)\left[A_{o-1,k}\sum_{k'=1}^{N-1}(\omega_{k'} t)^2 E^{(-)}_{k'} + A_{o+1,k}\sum_{k'=1}^{N-1}(\omega_{k'} t)^2 E^{(+)}_{k'}\right]\right\} +$$
$$+\frac{1}{36}\left(\frac{Jt}{\hbar}\right)^2 \omega_k t \sum_{k'=1}^{N-1}(\omega_{k'} t)^2\left\{\omega_k t\left[F_k^{(-)}E^{(-)}_{k'} + F_k^{(+)}E^{(+)}_{k'}\right] + \omega_{k'} t\left[F^{(-)}_{k'}\left(G^{(-)}_{kk'} + G^{(-)}_{k'k}\right) + F^{(+)}_{k'}\left(G^{(+)}_{kk'} + G^{(+)}_{k'k}\right)\right]\right\}$$

The expectation values of the displacement and momentum operators can be computed simply from $B_k(\mu)$ and $B_k^*(\mu)$ as decribed in the main text.

Appendix C: Expectation Values of the Hamiltonian

Since the Hamilton operator is hermitian, we can write for the expectation value for the first order wave function, omitting the vanishing contributions of the total of 18:

$$H(0) = H(1) = \left\langle \omega + J - \psi_0 \middle| \hat{\omega} + \hat{J} \middle| \omega + J - \psi_0 \right\rangle = 2\,\mathrm{Re}\left[\left\langle \omega|\hat{\omega}|J\right\rangle - \left\langle \omega|\hat{\omega}|\psi_0\right\rangle + \left\langle \omega|\hat{J}|J\right\rangle - \left\langle J|\hat{J}|\psi_0\right\rangle\right] \tag{C1}$$

where

$$\left\langle J|\hat{J}|\psi_0\right\rangle = -J\left[\left(a^J_{o-1}\right)^* + \left(a^J_{o+1}\right)^*\right]$$
$$\left\langle \omega|\hat{\omega}|J\right\rangle = a^J_o\left(a^\omega_o\right)^* U_o \sum_{k=1}^{N-1}\hbar\omega_k B_{ok} b^*_{ok} \tag{C2}$$

$$\left\langle \omega|\hat{\omega}|\psi_0\right\rangle = \left(a^\omega_o\right)^* U_o \sum_{k=1}^{N-1}\hbar\omega_k B_{ok} b^*_{ok}$$
$$\left\langle \omega|\hat{J}|J\right\rangle = -J\left(a^\omega_o\right)^*\left(a^J_{o-1} + a^J_{o+1}\right)U_o$$

and thus we obtain finally for H(1)

$$H(1) = 2U_o\sum_k \hbar\omega_k B_{ok}\,\mathrm{Re}\left[a^\omega_o b_{ok}\left(\left(a^J_o\right)^* - 1\right)\right] + 2J\left\{\mathrm{Re}\left[a^J_{o-1} + a^J_{o+1}\right] - U_o\,\mathrm{Re}\left[\left(a^\omega_o\right)^*\left(a^J_{o-1} + a^J_{o+1}\right)\right]\right\} \tag{C3}$$

For the second order we need the following expectation values for $|\psi_2>$ [with equation (29)]

$$\left\langle \psi_2|\hat{\omega}|\psi_2\right\rangle = J^2\sum_{k=1}^{N-1}(\hbar\omega_k)^3\left(A^2_{o-1,k} + A^2_{o+1,k}\right) \tag{C4}$$

$$\left\langle \psi_2 \middle| \hat{J} \middle| \psi_2 \right\rangle = 0 \Rightarrow \left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle = \left\langle \psi_2 \middle| \hat{\omega} \middle| \psi_2 \right\rangle$$

and the total function H(2) is given by

$$H(2) = H(1) - \frac{t^2}{\hbar^2} \mathrm{Re}\left[\left\langle \psi(1) \middle| \hat{H} \middle| \psi_2 \right\rangle\right] + \frac{t^4}{4\hbar^4} \left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle \tag{C5}$$

Since of the six individual expectation values contained in $\left\langle \psi(1) \middle| \hat{H} \middle| \psi_2 \right\rangle$ four are vanishing we arrive at

$$\begin{aligned} &\left\langle \psi(1) \middle| \hat{H} \middle| \psi_2 \right\rangle = \left\langle \omega \middle| \hat{J} \middle| \psi_2 \right\rangle + \left\langle J \middle| \hat{\omega} \middle| \psi_2 \right\rangle \\ &\left\langle \omega \middle| \hat{\omega} \middle| \psi_2 \right\rangle = \left\langle J \middle| \hat{J} \middle| \psi_2 \right\rangle = \left\langle \psi_0 \middle| \hat{\omega} \middle| \psi_2 \right\rangle = \left\langle \psi_0 \middle| \hat{J} \middle| \psi_2 \right\rangle = 0 \end{aligned} \tag{C6}$$

where

$$\left\langle \omega \middle| \hat{J} \middle| \psi_2 \right\rangle = J^2 \left(a_o^{\omega}\right)^* U_o \sum_{k=1}^{N-1} \hbar\omega_k b_{ok}^* \left(A_{o-1,k} + A_{o+1,k}\right) \tag{C7}$$

$$\left\langle J \middle| \hat{\omega} \middle| \psi_2 \right\rangle = -J \sum_{k=1}^{N-1} (\hbar\omega_k)^2 \left[A_{o-1,k} B_{o-1,k} \left(a_{o-1}^J\right)^* + A_{o+1,k} B_{o+1,k} \left(a_{o+1}^J\right)^*\right]$$

Thus finally we obtain

$$\begin{aligned} H(2) = H(1) + \frac{1}{4}\left(\frac{Jt}{\hbar}\right)^2 \sum_{k=1}^{N-1} \hbar\omega_k (\omega_k t)^2 \left(A_{o-1,k}^2 + A_{o+1,k}^2\right) - \\ -\left(\frac{Jt}{\hbar}\right)^2 U_o \sum_{k=1}^{N-1} \hbar\omega_k \left(A_{o-1,k} + A_{o+1,k}\right) \mathrm{Re}\left[b_{ok} a_o^{\omega}\right] + J \sum_{k=1}^{N-1} (\omega_k t)^2 \left\{A_{o-1,k} B_{o-1,k} \,\mathrm{Re}\left[a_{o-1}^J\right] + A_{o+1,k} B_{o+1,k} \,\mathrm{Re}\left[a_{o+1}^J\right]\right\} \end{aligned} \tag{C8}$$

For the third order correction we have to evaluate

$$H(3) = \left\langle \psi(2) + \frac{i}{6}\frac{t^3}{\hbar^3}\psi_3 \middle| \hat{H} \middle| \psi(2) + \frac{i}{6}\frac{t^3}{\hbar^3}\psi_3 \right\rangle = H(2) - \frac{1}{3}\frac{t^3}{\hbar^3} \mathrm{Im}\left[\left\langle \psi(2) \middle| \hat{H} \middle| \psi_3 \right\rangle\right] + \frac{1}{36}\frac{t^6}{\hbar^6} \left\langle \psi_3 \middle| \hat{H} \middle| \psi_3 \right\rangle \tag{C9}$$

$$\left\langle \psi(2) \middle| \hat{H} \middle| \psi_3 \right\rangle = \left\langle \psi(1) \middle| \hat{H} \middle| \psi_3 \right\rangle - \frac{1}{2}\frac{t^2}{\hbar^2} \left\langle \psi_2 \middle| \hat{H} \middle| \psi_3 \right\rangle$$

Since

$$\left\langle \psi_2 \middle| \hat{H} \middle| \psi_3 \right\rangle = \langle 0 | \left[\hat{\Theta}_{-1}^{+} \hat{a}_{o-1} + \hat{\Theta}_{+1}^{+} \hat{a}_{o+1}\right] \left(\hat{\omega} + \hat{J}\right) \sum_{\nu=-2}^{2} (-1)^{\nu} \hat{\Gamma}_{\nu} \hat{a}_{o+\nu}^{+} | 0 \rangle \tag{C10}$$

is obviously real, and thus $\mathrm{Im}\left[\left\langle \psi_2 \middle| \hat{H} \middle| \psi_3 \right\rangle\right] = 0$, it remains to calculate

$$H(3) = H(2) - \frac{1}{3}\frac{t^3}{\hbar^3} \mathrm{Im}\left[\left\langle \omega + J - \psi_0 \middle| \hat{H} \middle| \psi_3 \right\rangle\right] + \frac{1}{36}\frac{t^6}{\hbar^6} \left\langle \psi_3 \middle| \hat{H} \middle| \psi_3 \right\rangle \tag{C11}$$

where we obtain for $|\psi_0\rangle$

$$\hat{H}\left|\psi_0\right\rangle = -J\left(\hat{a}^+_{o-1} + \hat{a}^+_{o+1}\right)\left|0\right\rangle + \sum_{k=1}^{N-1} \hbar\omega_k B_{ok} \hat{b}^+_k \hat{a}^+_o \left|0\right\rangle \tag{C12}$$

$$\left\langle\psi_o\middle|\hat{H}\middle|\psi_3\right\rangle = J\left(\left\langle 0\middle|\hat{\Gamma}_{-1}\middle|0\right\rangle + \left\langle 0\middle|\hat{\Gamma}_{+1}\middle|0\right\rangle\right) + \sum_{k=1}^{N-1} \hbar\omega_k B_{ok}\left\langle 0\middle|\hat{b}_k\hat{\Gamma}_o\middle|0\right\rangle = J^2 \sum_{k=1}^{N-1}\left(\hbar\omega_k\right)^2\left(E_k^{(-)} + B_{ok}D_k + E_k^{(+)}\right)$$

Note, that $\left\langle\psi_0\middle|\hat{H}\middle|\psi_3\right\rangle$ is real. The action of the Hamiltonian on $|\omega\rangle$ yields

$$\hat{H}\left|\omega\right\rangle = -Ja_o^\omega\left(\hat{a}^+_{o+1} + \hat{a}^+_{o-1}\right)\left|\beta_o\right\rangle + a_o^\omega \sum_{k=1}^{N-1}\hbar\omega_k\left[B_{ok}b_{ok} + \left(B_{ok} + b_{ok}\right)\hat{b}^+_k\right]\hat{a}^+_o\left|\beta_o\right\rangle \tag{C13}$$

and thus

$$\left\langle\omega\middle|\hat{H}\middle|\psi_3\right\rangle = \left(a_o^\omega\right)^* J\left[\left\langle\beta_o\middle|\hat{\Gamma}_{-1}\middle|0\right\rangle + \left\langle\beta_o\middle|\hat{\Gamma}_{+1}\middle|0\right\rangle\right] + \left(a_o^\omega\right)^* \sum_{k=1}^{N-1}\hbar\omega_k\left[B_{ok}b^*_{ok}\left\langle\beta_o\middle|\hat{\Gamma}_0\middle|0\right\rangle + \left(B_{ok} + b^*_{ok}\right)\left\langle\beta_o\middle|\hat{b}_k\hat{\Gamma}_0\middle|0\right\rangle\right] \tag{C14}$$

The explicit evaluation of the expectation values results in

$$\begin{aligned}\left\langle\omega\middle|\hat{H}\middle|\psi_3\right\rangle = J^2\left(a_o^\omega\right)^* U_o \sum_{k=1}^{N-1}\hbar\omega_k\Bigg\{&\sum_{k'=1}^{N-1}\hbar\omega_{k'}b^*_{ok}b^*_{ok'}\left[G^{(-)}_{kk'} + G^{(+)}_{kk'} + B_{ok}D_{k'}\right] + \\ &+\hbar\omega_k\left[\left(E_k^{(-)} + E_k^{(+)}\right) + b^*_{ok}\left(F_k^{(-)} + F_k^{(+)}\right) + \left(B_{ok} + b^*_{ok}\right)D_k\right]\Bigg\}\end{aligned} \tag{C15}$$

Finally, the action of the Hamiltonian on $|J\rangle$ leads to

$$\hat{H}\left|J\right\rangle = \sum_{n=1}^{N}\left[-J\left(a^J_{n+1} + a^J_{n-1}\right) + a^J_n \sum_{k=1}^{N-1}\hbar\omega_k B_{nk}\hat{b}^+_k\right]\hat{a}^+_n\left|0\right\rangle \tag{C16}$$

and thus the expectation value of the Hamiltonian is given by

$$\left\langle J\middle|\hat{H}\middle|\psi_3\right\rangle = \sum_{\nu=-2}^{2}(-1)^\nu\left\{-J\left[\left(a^J_{o+\nu-1}\right)^* + \left(a^J_{o+\nu+1}\right)^*\right]\left\langle 0\middle|\hat{\Gamma}_\nu\middle|0\right\rangle + \sum_{k=1}^{N-1}\hbar\omega_k B_{o+\nu,k}\left(a^J_{o+\nu}\right)^*\left\langle 0\middle|\hat{b}_k\hat{\Gamma}_\nu\middle|0\right\rangle\right\} \tag{C17}$$

which yields

$$\begin{aligned}\left\langle J\middle|\hat{H}\middle|\psi_3\right\rangle = -J\sum_{k=1}^{N-1}\left(\hbar\omega_k\right)^3\left[\left(a^J_{o-1}\right)^* B_{o-1,k}F_k^{(-)} + \left(a^J_{o+1}\right)^* B_{o+1,k}F_k^{(+)}\right] + \\ +J^2\sum_{k=1}^{N-1}\left(\hbar\omega_k\right)^2\left[\left(a^J_{o-2}\right)^* B_{o-2,k}D_k^{(-)} + \left(a^J_{o-2} + a^J_o\right)^* E_k^{(-)} + \left(a^J_o\right)^* B_{ok}D_k + \left(a^J_o + a^J_{o+2}\right)^* E_k^{(+)} + \left(a^J_{o+2}\right)^* B_{o+2,k}D_k^{(+)}\right]\end{aligned} \tag{C18}$$

and thus

$$
\begin{aligned}
H'(3) = -\frac{1}{3}\frac{t^3}{\hbar^3}\,\mathrm{Im}\Big[\big\langle\psi(1)\big|\hat{H}\big|\psi_3\big\rangle\Big] = \frac{1}{3}\left(\frac{Jt}{\hbar}\right)^2 U_o \sum_{k=1}^{N-1}\omega_k t \Bigg\{ \sum_{k'=1}^{N-1}\hbar\omega_{k'}\,\mathrm{Im}\big[a_o^{\omega} b_{ok} b_{ok'}\big]\Big[G_{kk'}^{(-)} + G_{kk'}^{(+)} + B_{ok}D_{k'}\Big] + \\
+\hbar\omega_k\Big[\mathrm{Im}\big[a_o^{\omega}\big]\Big(E_k^{(-)}+E_k^{(+)}\Big) + \mathrm{Im}\big[a_o^{\omega} b_{ok}\big]\Big(F_k^{(-)}+F_k^{(+)}\Big) + \Big(\mathrm{Im}\big[a_o^{\omega}\big]B_{ok} + \mathrm{Im}\big[a_o^{\omega} b_{ok}\big]\Big)D_k\Big]\Bigg\} - \\
-\frac{J}{3}\sum_{k=1}^{N-1}(\omega_k t)^3\Big[\mathrm{Im}\big[a_{o-1}^J\big]B_{o-1,k}F_k^{(-)} + \mathrm{Im}\big[a_{o+1}^J\big]B_{o+1,k}F_k^{(+)}\Big] + \\
+\frac{J}{3}\frac{Jt}{\hbar}\sum_{k=1}^{N-1}(\omega_k t)^2\Big[\mathrm{Im}\big[a_{o-2}^J\big]B_{o-2,k}D_k^{(-)} + \mathrm{Im}\big[a_{o-2}^J + a_o^J\big]E_k^{(-)} + \\
+\mathrm{Im}\big[a_o^J\big]B_{ok}D_k + \mathrm{Im}\big[a_o^J + a_{o+2}^J\big]E_k^{(+)} + \mathrm{Im}\big[a_{o+2}^J\big]B_{o+2,k}D_k^{(+)}\Big]
\end{aligned}
\tag{C19}
$$

Finally we have to calculate the three parts of the expectation value of the Hamiltonian with the state $|\psi_3>$. As first step we evaluate the exciton-phonon interaction part:

$$
\begin{aligned}
&\sum_{n=1}^{N} B_{nk}\hat{a}_n^{+}\hat{a}_n|\,\psi_3\rangle = \sum_{n=1}^{N} B_{nk}\sum_{\nu=-2}^{2}(-1)^{\nu}\,\hat{\Gamma}_{\nu}\hat{a}_n^{+}\hat{a}_n\hat{a}_{o+\nu}^{+}|\,0\rangle = \sum_{\nu=-2}^{2}(-1)^{\nu}B_{o+\nu,k}\hat{\Gamma}_{\nu}\hat{a}_{o+\nu}^{+}|\,0\rangle \\
&\sum_{n=1}^{N} B_{nk}\Big\langle\psi_3\Big|\Big(\hat{b}_k^{+}+\hat{b}_k\Big)\hat{a}_n^{+}\hat{a}_n\Big|\psi_3\Big\rangle = \sum_{\nu=-2}^{2}B_{o+\nu,k}\Big\langle 0\Big|\hat{\Gamma}_{\nu}^{+}\Big(\hat{b}_k^{+}+\hat{b}_k\Big)\hat{\Gamma}_k\Big|0\Big\rangle = 2\sum_{\nu=-2}^{2}B_{o+\nu,k}\,\mathrm{Re}\Big[\Big\langle 0\Big|\hat{\Gamma}_{\nu}^{+}\hat{b}_k\hat{\Gamma}_{\nu}\Big|\Big\rangle\Big]
\end{aligned}
\tag{C20}
$$

The expectation values occurring in (C20) had been calculated already in Appendix B and thus we can write directly

$$
\begin{aligned}
&\Big\langle\psi_3\,\Big|\sum_{n=1}^{N}\sum_{k=1}^{N-1}\hbar\omega_k B_{nk}\Big(\hat{b}_k^{+}+\hat{b}_k\Big)\hat{a}_n^{+}\hat{a}_n\Big|\,\psi_3\Big\rangle = \\
&= 2J^2\sum_{k,k'=1}^{N-1}(\hbar\omega_k)^2(\hbar\omega_{k'})^2\Big\{\hbar\omega_k\Big[B_{o-1,k}F_k^{(-)}E_{k'}^{(-)} + B_{o+1,k}F_k^{(+)}E_{k'}^{(+)}\Big] + \\
&+\hbar\omega_{k'}\Big[B_{o-1,k}F_{k'}^{(-)}\Big(G_{kk'}^{(-)}+G_{k'k}^{(-)}\Big) + B_{o+1,k}F_{k'}^{(+)}\Big(G_{kk'}^{(+)}+G_{k'k}^{(+)}\Big)\Big]\Big\}
\end{aligned}
\tag{C21}
$$

The phonon part yields

$$
\begin{aligned}
&\Big\langle\psi_3\,\Big|\sum_{k=1}^{N-1}\hbar\omega_k\hat{b}_k^{+}\hat{b}_k\Big|\,\psi_3\Big\rangle = \sum_{k=1}^{N-1}\hbar\omega_k\sum_{\nu=-2}^{2}\Big\langle 0\Big|\hat{\Gamma}_{\nu}^{+}\hat{b}_k^{+}\hat{b}_k\hat{\Gamma}_{\nu}\Big|0\Big\rangle \\
&\Big\langle 0\Big|\hat{\Gamma}_{\pm 2}^{+}\hat{b}_k^{+}\hat{b}_k\hat{\Gamma}_{\pm 2}\Big|0\Big\rangle = J^4(\hbar\omega_k)^2\Big(D_k^{(\pm)}\Big)^2 \\
&\Big\langle 0\Big|\hat{\Gamma}_{\pm 1}^{+}\hat{b}_k^{+}\hat{b}_k\hat{\Gamma}_{\pm 1}\Big|0\Big\rangle = J^2(\hbar\omega_k)^2\Big\{(\hbar\omega_k)^2\Big(F_k^{(\pm)}\Big)^2 + \sum_{k'=1}^{N-1}\Big[\hbar\omega_{k'}\Big(G_{kk'}^{(\pm)}+G_{k'k}^{(\pm)}\Big)\Big]^2\Big\}
\end{aligned}
\tag{C22}
$$

$$\left\langle 0\left|\hat{\Gamma}_o^+\hat{b}_k^+\hat{b}_k\hat{\Gamma}_0\right|0\right\rangle = J^4(\hbar\omega_k)^2 D_k^2$$

Finally we have to evaluate the expectation value of the operator $\hat{J}$:

$$\hat{J}\left|\psi_3\right\rangle = -J\sum_{\mu=-2}^{2}(-1)^{\mu}\hat{\Gamma}_{\mu}\left(\hat{a}^+_{o+\mu-1}+\hat{a}^+_{o+\mu+1}\right)\left|0\right\rangle \tag{C23}$$

From this we obtain

$$\begin{aligned}\left\langle\psi_3\left|\hat{J}\right|\psi_3\right\rangle &= -J\sum_{\nu,\mu=-2}^{2}(-1)^{\nu+\mu}\left\langle 0\left|\hat{\Gamma}_\nu^+\hat{\Gamma}_\mu\cdot\left(\hat{a}_{o+\nu}\hat{a}^+_{o+\mu-1}+\hat{a}_{o+\nu}\hat{a}^+_{o+\mu+1}\right)\right|0\right\rangle = \\ &= J\sum_{\nu=-1}^{2}\left[\left\langle 0\left|\hat{\Gamma}^+_{\nu-1}\hat{\Gamma}_\nu\right|0\right\rangle+\left\langle 0\left|\hat{\Gamma}^+_\nu\hat{\Gamma}_{\nu-1}\right|0\right\rangle\right] = 2J\sum_{\nu=-1}^{2}\mathrm{Re}\left[\left\langle 0\left|\hat{\Gamma}^+_{\nu-1}\Gamma_\nu\right|0\right\rangle\right] = \\ &= 2J^4\sum_{k=1}^{N-1}(\hbar\omega_k)^3\left[D_k^{(-)}F_k^{(-)}+D_k\left(F_k^{(-)}+F_k^{(+)}\right)+D_k^{(+)}F_k^{(+)}\right]\end{aligned} \tag{C24}$$

Then the complete expectation value, multiplied with the appropriate factor is given by

$$\begin{aligned} H''(3) &= \frac{1}{36}\frac{t^6}{\hbar^6}\left\langle\psi_3\left|\hat{H}\right|\psi_3\right\rangle = \frac{1}{36}\frac{t^6}{\hbar^6}\left\langle\psi_3\left|\hat{J}+\hat{\omega}\right|\psi_3\right\rangle = \\ &= \frac{J}{18}\left(\frac{Jt}{\hbar}\right)^3\sum_{k=1}^{N-1}(\omega_k t)^3\left[D_k^{(-)}F_k^{(-)}+D_k\left(F_k^{(-)}+F_k^{(+)}\right)+D_k^{(+)}F_k^{(+)}\right]+ \\ &+\frac{1}{36}\left(\frac{Jt}{\hbar}\right)^2\sum_{k=1}^{N-1}\hbar\omega_k(\omega_k t)^2\left\{\left(\frac{Jt}{\hbar}\right)^2\left[\left(D_k^{(-)}\right)^2+D_k^2+\left(D_k^{(+)}\right)^2\right]+\right. \\ &\left.+(\omega_k t)^2\left[\left(F_k^{(-)}\right)^2+\left(F_k^{(+)}\right)^2\right]+\sum_{k'=1}^{N-1}(\omega_{k'}t)^2\left[\left(G_{kk'}^{(-)}+G_{k'k}^{(-)}\right)^2+\left(G_{kk'}^{(+)}+G_{k'k}^{(+)}\right)^2\right]\right\}+ \\ &+\frac{1}{18}\left(\frac{Jt}{\hbar}\right)^2\sum_{k,k'=1}^{N-1}(\omega_k t)^2(\omega_{k'}t)^2\left\{\hbar\omega_k\left[B_{o-1,k}F_k^{(-)}E_{k'}^{(-)}+B_{o+1,k}F_k^{(+)}E_{k'}^{(+)}\right]+\right. \\ &\left.+\hbar\omega_{k'}\left[B_{o-1,k}F_{k'}^{(-)}\left(G_{kk'}^{(-)}+G_{k'k}^{(-)}\right)+B_{o+1,k}F_{k'}^{(+)}\left(G_{kk'}^{(+)}+G_{k'k}^{(+)}\right)\right]\right\}\end{aligned} \tag{C25}$$

Then our final result is given by

$$\begin{aligned} &H(3) = H(2)+H'(3)+H''(3) \\ &H(2) = \left\langle\psi(2)\left|\hat{H}\right|\psi(2)\right\rangle \qquad \text{[equ. (C8)]} \\ &H'(3) = -\frac{1}{3}\frac{t^3}{\hbar^3}\,\mathrm{Im}\left[\left\langle\psi(1)\left|\hat{H}\right|\psi_3\right\rangle\right] \qquad \text{[equ. (C19)]} \\ &H''(3) = \frac{1}{36}\frac{t^6}{\hbar^6}\left\langle\psi_3\left|\hat{H}\right|\psi_3\right\rangle \qquad \text{[equ. (C25)]}\end{aligned} \tag{C26}$$

Appendix D: Propagation of the First Order Wave Function to Larger Times

In this Appendix we want to show for some time steps τ the explicit formulas for the dynamics as they result from the calculation of the individual terms. The index μ=1 we drop from the states in the following. We consider steps $\ell\tau$, ℓ=0,1,... and times t with $0 \le t \le \tau$. As already mentioned in the main text we have for the first period, ℓ=0:

$$\left|\psi(t)\right\rangle = \sum_n \left(a_n^J(t) - \delta_{no}\right)\hat{a}_n^+\left|0\right\rangle + a_o^\omega(t)\hat{U}_o(t)\hat{a}_o^+\left|0\right\rangle \tag{D1}$$

From this we obtain for t=τ:

$$\left|\psi(\tau)\right\rangle = \sum_n \left(a_n^J(\tau) - \delta_{no}\right)\hat{a}_n^+\left|0\right\rangle + a_o^\omega(\tau)\hat{U}_o(\tau)\hat{a}_o^+\left|0\right\rangle \tag{D2}$$

which is the initial state for the first order term in the second period, ℓ=1:

$$\left|\psi(\tau+t)\right\rangle = \left(e^{-\frac{it}{\hbar}\hat{\omega}} + e^{-\frac{it}{\hbar}\hat{J}} - 1\right)\left|\psi(\tau)\right\rangle \tag{D3}$$

Before explicitely writing down the states resulting from equation (D3), we want to define some quantities to keep the final formulas shorter:

$$\varphi_k(t) \equiv e^{2i\frac{Jt}{\hbar}\cos\left(\frac{2\pi}{N}k\right)} \quad ; \quad k = 1,\ldots,N$$

$$\gamma_n(t) \equiv e^{-i\sum_{k=1}^{N-1} B_{nk}^2\left[\sin(\omega_k t) - \omega_k t\right]}$$

$$\zeta_{nk}(t) \equiv B_{nk}\left(e^{-i\omega_k t} - 1\right) \quad ; \quad k = 1,\ldots,N-1 \tag{D4a}$$

$$b_{nk}^{(0)}(t) \equiv b_{nk}(t)$$

$$\hat{U}_n^{(j)}(t) \equiv e^{-\frac{1}{2}\sum_{k=1}^{N-1}\left|b_{nk}^{(j)}(t)\right|^2} e^{\sum_{k=1}^{N-1} b_{nk}^{(j)}(t)\hat{b}_k^+} \quad ; \quad \hat{U}_n^{(0)}(t) \equiv \hat{U}_n(t)$$

$$\vartheta_n^{(j)}(t) \equiv e^{-i\sum_{k=1}^{N-1}\Omega_{nk}^{(j)}(t)} \tag{D4b}$$

$$\Omega_{nk}^{(j)}(t) \equiv \mathrm{Re}\left[b_{nk}^{(j)}(\tau)\right]\sin(\omega_k t) + \mathrm{Im}\left[b_{nk}^{(j)}(\tau)\right]\left[1 - \cos(\omega_k t)\right]$$

This yields for the first term, together with the expressions for the small polaron limit from paper I:

$$e^{-\frac{it}{\hbar}\hat{\omega}}\left|\psi(\tau)\right\rangle = \sum_n a_n^{(1)}(t)\hat{U}_n^{(1)}(t)\hat{a}_n^+\left|0\right\rangle + a_o^{(2)}(t)\hat{U}_o^{(2)}(t)\hat{a}_o^+\left|0\right\rangle$$

$$a_n^{(1)}(t) = \left[a_n^J(\tau) - \delta_{no}\right]\gamma_n(t) \quad ; \quad b_{nk}^{(1)}(t) = \zeta_{nk}(t) \tag{D4c}$$

$$a_o^{(2)}(t) = a_o^\omega(\tau)\gamma_o(t)\vartheta_o^{(0)}(t) \quad ; \quad b_{ok}^{(2)}(t) = b_{ok}(\tau)e^{-i\omega_k t} + \zeta_{nk}(t)$$

Further we act with the second operator on the initial state, observing that the exponential operator and coherent state operators commute with each other. This yields:

$$e^{-\frac{it}{\hbar}\hat{J}}\left|\psi(\tau)\right\rangle = \sum_n \left[a_n^{(3)}(t) + \hat{U}_o(\tau)a_n^{(4)}(t)\right]\hat{a}_n^+|0\rangle$$

$$a_n^{(3)}(t) = \frac{1}{N}\sum_{n'}\sum_{k=1}^{N} e^{\frac{2\pi i}{N}k(n-n')}\varphi_k(t)\left[a_{n'}^J(\tau) - \delta_{n'o}\right] \tag{D5}$$

$$a_n^{(4)}(t) = \frac{a_o^{\omega}(\tau)}{N}\sum_{k=1}^{N} e^{\frac{2\pi i}{N}k(n-o)}\varphi_k(t)$$

Collecting the terms and substracting the initial state leads to

$$\left|\psi(\tau+t)\right\rangle = \sum_n \left[d_n^{(1)}(t) + a_n^{(1)}(t)\hat{U}_n^{(1)}(t) + a_n^{(4)}(t)\hat{U}_o(\tau)\right]\hat{a}_n^+|0\rangle + \left[a_o^{(2)}(t)\hat{U}_o^{(2)}(t) - a_o^{\omega}(\tau)\hat{U}_o(\tau)\right]\hat{a}_o^+|0\rangle$$
$$d_n^{(1)}(t) = a_n^{(3)}(t) - a_n^J(\tau) + \delta_{no} \tag{D6}$$

This yields directly the initial state for the third period:

$$\left|\psi(2\tau)\right\rangle = \sum_n \left[d_n^{(1)}(\tau) + a_n^{(1)}(\tau)\hat{U}_n^{(1)}(\tau) + a_n^{(4)}(\tau)\hat{U}_o(\tau)\right]\hat{a}_n^+|0\rangle + \left[a_o^{(2)}(\tau)\hat{U}_o^{(2)}(\tau) - a_o^{\omega}(\tau)\hat{U}_o(\tau)\right]\hat{a}_o^+|0\rangle \tag{D7}$$

From this state we obtain

$$e^{-\frac{it}{\hbar}\hat{J}}\left|\psi(2\tau)\right\rangle = \sum_n \left[d_n^{(2)}(t) + a_n^{(5)}(t)\hat{U}_o(\tau) + a_n^{(6)}(t)\hat{U}_o^{(2)}(\tau) + \sum_{n'} f_{nn'}^{(1)}(t)\hat{U}_{n'}^{(1)}(\tau)\right]\hat{a}_n^+|0\rangle \tag{D8}$$

where the coefficients are given by

$$d_n^{(2)}(t) = \frac{1}{N}\sum_{n'}\sum_{k=1}^{N} d_{n'}^{(1)}(\tau)e^{\frac{2\pi i}{N}k(n-n')}\varphi_k(t)$$

$$f_{nn'}^{(1)}(t) = \frac{1}{N}\sum_{k=1}^{N} a_{n'}^{(1)}(\tau)e^{\frac{2\pi i}{N}k(n-n')}\varphi_k(t) \tag{D9}$$

$$a_n^{(5)}(t) = \frac{1}{N}\sum_{k=1}^{N}\left[\sum_{n'} a_{n'}^{(4)}(\tau)e^{\frac{2\pi i}{N}k(n-n')} - a_o^{\omega}(\tau)e^{\frac{2\pi i}{N}k(n-o)}\right]\varphi_k(t)$$

$$a_n^{(6)}(t) = \frac{a_o^{\omega}(\tau)}{N}\sum_{k=1}^{N} e^{\frac{2\pi i}{N}k(n-o)}\varphi_k(t)$$

Further we can write

$$e^{-\frac{it}{\hbar}\hat{\omega}}\left|\psi(2\tau)\right\rangle = \sum_{j=3}^{7}\sum_n e_n^{(j)}(t)\hat{U}_n^{(j)}(t)\hat{a}_n^+|0\rangle \tag{D10}$$

with the different coherent state amplitudes

$$b_{nk}^{(3)}(t)=\zeta_{nk}(t) \quad ; \quad b_{nk}^{(4)}(t)=b_{nk}^{(1)}(\tau)e^{-i\omega_k t}+\zeta_{nk}(t) \quad ; \quad b_{nk}^{(5)}(t)=b_{ok}(\tau)e^{-i\omega_k t}\delta_{no}+\zeta_{nk}(t)$$
$$b_{nk}^{(6)}(t)=\left[b_{ok}^{(2)}(\tau)e^{-i\omega_k t}+\zeta_{ok}(t)\right]\delta_{no} \quad ; \quad b_{nk}^{(7)}(t)=\left[b_{ok}(\tau)e^{-i\omega_k t}+\zeta_{ok}(t)\right]\delta_{no} \tag{D11}$$

and coefficients

$$e_n^{(3)}(t)=d_n^{(1)}(\tau)\gamma_n(t) \quad ; \quad e_n^{(4)}(t)=a_n^{(1)}(\tau)\vartheta_n^{(1)}(t)\gamma_n(t) \quad ; \quad e_n^{(5)}(t)=a_n^{(4)}(\tau)\vartheta_o^{(0)}(t)\gamma_o(t)$$
$$e_n^{(6)}(t)=a_o^{(2)}(\tau)\vartheta_o^{(2)}(t)\gamma_o(t)\delta_{no} \quad ; \quad e_n^{(7)}=-a_o^{\omega}(\tau)\vartheta_o^{(0)}(t)\gamma_o(t)\delta_{no} \tag{D12}$$

Now we can write down the state vector for the third interval:

$$\left|\psi(2\tau+t)\right\rangle=\sum_n\left[\sum_{j=3}^{7}e_n^{(j)}(t)\hat{U}_n^{(j)}(t)+d_n^{(2)}(t)+a_n^{(5)}(t)\hat{U}_o(\tau)+a_n^{(6)}(t)\hat{U}_o^{(2)}(\tau)-d_n^{(1)}(\tau)-a_n^{(1)}(\tau)\hat{U}_n^{(1)}(\tau)-\right.$$
$$\left.-a_n^{(4)}(\tau)\hat{U}_o(\tau)+\sum_{n'}f_{nn'}^{(1)}(t)U_{n'}^{(1)}(\tau)\right]\hat{a}_n^{+}\left|0\right\rangle-\left[a_o^{(2)}(\tau)\hat{U}_o^{(2)}(\tau)-a_o^{\omega}(\tau)\hat{U}_o(\tau)\right]\hat{a}_o^{+}\left|0\right\rangle \tag{D13}$$

From this expression we can compute now the initial state for the fourth period and so on. It is obvious that with each period the expressions for the state vectors become more complicated. However, the calculation of expectation values from these states is rather simple, because they are all just superpositions of free exciton, $|D_1>$- and $|D_2>$-type states. The problem is that their derivation becomes lengthy and tedious. Currently we try to find out whether or not it is possible to establish a kind of recursive algorithm for this task.