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# Multiquanta states derived from Davydov's $|D_1\rangle$ *ansatz*: I. Equations of motion for the Su–Schrieffer–Heeger Hamiltonian

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**Abstract.** We present equations of motion for the Su–Schrieffer–Heeger (SSH) Hamiltonian derived with the help of *ansatz* states similar to Davydov's so-called  $|D_1\rangle$  state for soliton dynamics in proteins. Such an *ansatz* state allows for quantum effects in the lattice and goes beyond previous calculations which mostly apply adiabatic models. In the most general case, called  $|\Phi_0\rangle$ , which is treated here in detail, we assume that the coherent-state amplitudes for the lattice depend on the site and the molecular orbital of the electrons. The equations of motion are derived from the Lagrangian of the system, a method which is equivalent to the time-dependent variational principle. In the resulting equations we find that, although the SSH Hamiltonian is a one-particle operator, indirect electron–electron interactions are present in the system which originate from the electron–phonon interactions. Inclusion of direct electron–electron interactions, as described in section 8, will give insight into the interplay between electron–electron and electron–phonon interactions which can lead effectively to an attractive force between the electrons in systems other than polyacetylene, where bipolarons are known to be unstable. Further with our time-dependent wavefunction also vibrational details of absorption spectra can be computed. From the equations of motion several approximations can be derived. In a further approximation,  $|\Phi_2\rangle$ , the dependence of the coherent-state amplitudes on the lattice site is neglected. This  $|\Phi_2\rangle$  *ansatz* state consists of a simple product of the electronic and the lattice wavefunctions; however, the electrons are not constrained to follow the lattice dynamics instantaneously as in the adiabatic case. Finally the classical adiabatic case is discussed on which soliton-dynamics simulations are usually based. Further we discuss how to include temperature effects in our model. Applications to soliton dynamics are discussed for the example of the  $|\Phi_2\rangle$  model with emphasis on the dependence of the results on soliton width and temperature. We found that in contrast to results reported in the literature, where a similar *ansatz* is used, but only one electron is treated explicitly, the solitons remain stable also for small soliton widths. This indicates that the interactions of the electrons not occupying the soliton level with the lattice have a stabilizing effect on the soliton. Further our results indicate that the temperature model using random forces and dissipation terms to introduce temperature effects has to be applied with extreme care in this case due to the strong electron–lattice interactions.

## 1. Introduction

Since the introduction of the soliton model and the Su–Schrieffer–Heeger (SSH) Hamiltonian [1] (for a recent comprehensive review see the article of Heeger, Kivelson, Schrieffer, and Su [1]) for the explanation of various properties of *trans*-polyacetylene (*t*-PA), it has been shown that it is necessary to go beyond the simple Hückel-type SSH model. A Hückel-type model e.g. cannot explain the spin densities in *t*-PA measured with the electron-nuclear double-resonance (ENDOR) method [2]. Also for the explanation of  $^{13}\text{C}$ -NMR line shapes the

inclusion of explicit electron–electron interactions in the model turned out to be essential [3]. The observed photoinduced low-energy absorption was assigned to excitations from photogenerated charged soliton pairs which would absorb mid-gap in the SSH model [4]. The origin of the photoinduced high-energy absorption, however, was a matter of considerable debate. Bishop *et al* [5] assign it to a breather excitation left between a separating pair of charged solitons. Wang and Martino [6] found an oscillating charged soliton–antisoliton pair with a breather vibration of the chain between them to be responsible for this absorption, while Su [7] and Kivelson and Wu [8] suggest a neutral (triplet) soliton pair as its origin. Therefore it seems to be established that the inclusion of electron–electron interactions at least on the Pariser–Parr–Pople (PPP) level in mean-field form is necessary to obtain a reasonable model of the dynamics of *t*-PA chains. Nowadays (see discussion and references in [20]) it is established that neutral solitons are indeed responsible for the high-energy absorption.

The computation of the gradient of the electronic energy with respect to the geometrical degrees of freedom can be done in a time-consuming way by a small shift of the coordinate of each CH unit [9–12]; however, the use of exact analytical gradients is more efficient [13]. In *t*-PA the soliton movement is restricted to roughly 50 CH units [2] probably due to impurities, crosslinks, and *cis*-PA segments [14] or interchain interactions. Thus an open chain seems to be a more realistic model than a cyclic one. Wang and Martino [6] used an extended Hubbard model with first-neighbour electron–electron interactions. This seems to be consistent with the first-neighbour truncation of the resonance integrals. However, the resonance integrals decay very rapidly after the first-neighbour term, while the two-electron integrals do not [15]. In our simulations using the full PPP Hamiltonian and the unrestricted Hartree–Fock (UHF) method we found that electron–electron interactions have a considerable influence on soliton properties [15]. Its kinetic mass e.g. is roughly doubled compared to the SSH model [1] and its half width reduced in agreement with MNDO (modified-neglect-of-differential-overlap) calculations [16]. The MNDO method treats all valence electrons explicitly and not only the  $\pi$  electrons as PPP does. However, in [16] restricted-open-shell HF (ROHF) was applied instead of a different-orbitals-for-different-spins (DODS) method like UHF or annihilated UHF (AUHF), which are more appropriate for open-shell systems like neutral solitons in  $(\text{CH})_{2n+1}$  (polymethine) chains.

In a previous work we have studied the influence of isoelectronic substitutions of CH by N,  $\text{NH}^+$ , and  $\text{O}^+$  within the SSH framework [10]. We found that a soliton is able to pass a nitrogen atom but not the oxygen. In another recent paper [17] site and bond impurities have been studied applying also the SSH theory. It was found by Phillpot *et al* [17] that the soliton moves unperturbed in a rather broad range of the impurity strength. Since the soliton properties change considerably upon inclusion of electron–electron interactions [15] it is important to study the effects of site and bond impurities also within the PPP model. This was done in our previous work [18] and we found that in the PPP model free soliton movement is possible within a much smaller range around the parameter values appropriate for carbon than in SSH models [10, 17]. Similar conclusions were obtained from a model where the spin contaminations inherent in the UHF *ansatz* are avoided [19]. In a more recent work we attempted to reparametrize the PPP Hamiltonian for polyenes and found that the electron–phonon interaction parameter has to be much smaller than in the SSH Hamiltonian [20]. The results found from this study confirmed the assignment of the photoinduced low-energy absorption to charged solitons and of the high-energy absorption to neutral solitons.

Since in all our studies using the PPP Hamiltonian we found a rather small soliton half width of about two to three lattice sites the question of the influence of quantum effects on soliton dynamics in the lattice arises (see also the review by Heeger *et al* [1]). In early

work Nakahara and Maki [21] discussed quantum effects on the solitons on the basis of the continuum version of the SSH Hamiltonian. The discrete SSH Hamiltonian was applied by Rukh *et al* [22] who used an *ansatz* which is a product of one-electron states and displaced oscillator states for the lattice. Thus their *ansatz* is similar to the semiclassical  $|D_2\rangle$  *ansatz* state introduced by Davydov [23] for the treatment of protein solitons, where coupled high-frequency oscillators interact with acoustical phonons in the lattice. Rukh *et al* [22] found that quantum effects destroy the solitons when their size is small. Since in the PPP case the soliton size is rather small, one has to investigate quantum effects further. Going beyond the *ansatz* of Rukh *et al* we use an *ansatz* derived from Davydov's more sophisticated  $|D_1\rangle$  state [24] which is a better approximation to the true quantum states of the Davydov Hamiltonian. We call this general *ansatz*  $|\Phi_0\rangle$ . However, in our case the state contains more than one quantum (electron) in contrast to Davydov's considerations. In this paper we concentrate on the derivation of the equations of motion from this *ansatz* for the SSH Hamiltonian [25], as well as on some approximations to it, together with possibilities for the consideration of temperature effects. These approximations include an intermediate one where the coherent-state amplitudes for the lattice phonons depend only on the lattice site and the wavenumber of the phonons and a most simple one where electronic and lattice wavefunctions are separated,  $|\Phi_2\rangle$ , corresponding to Davydov's  $|D_2\rangle$  *ansatz* in proteins. In the second paper (II) of this series we derive the same hierarchy of approximate equations for multiquanta states in the Davydov model.

On the numerical side we restrict ourselves to applications of the equations of motion for the  $|\Phi_2\rangle$ -*ansatz* state, where the product of one-electron states is simply multiplied by a coherent-state for the lattice phonons. However, the electrons are not constrained to follow the lattice dynamics instantaneously, as is the case in the completely adiabatic model. This *ansatz* state is of interest, because Rukh *et al* [22] use a similar model containing a product of electronic states with coherent phonon states, but treat only the electron occupying the soliton level explicitly. They found that in this case the soliton is unstable if its width is as small as approximately one lattice site, as mentioned above. Since small soliton sizes can be easily obtained in the SSH Hamiltonian by using a larger dimerization than the experimental one we restrict ourselves to the SSH model in this work and discuss soliton dynamics within our *ansatz* state as function of soliton width and temperature. In these calculations temperature is included via random-forces and dissipation terms. The results are compared to those obtained from the completely adiabatic model.

Applications of the equations of motion following from the  $|\Phi_0\rangle$ -state *ansatz* which allows for quantum effects in the lattice will be the subject of a forthcoming paper. Also temperature effects will be studied in detail numerically there. After computation of a reliable wavefunction, we can also calculate details of the absorption spectrum of the system, if we deal with an excited state. With the ground-state wavefunction,  $\Phi(t = 0)$ , and the excited state wavefunction  $\Phi(t)$  obtained by our method, one can easily compute numerically the autocorrelation function

$$S(t) \equiv \langle \Phi(t = 0) | \Phi(t) \rangle \quad (1)$$

which contains non-trivial overlap factors between coherent-states belonging to the ground state and to the excited state where the latter coherent-states are time dependent. From this by Fourier transformation the spectrum

$$\sigma(E) \sim \int_{-\infty}^{+\infty} e^{iEt} S(t) dt \quad (2)$$



as

$$\{\hat{A}, \hat{B}\} \equiv \hat{A}\hat{B} + \hat{B}\hat{A} \quad \{\hat{c}_{n\sigma}, \hat{c}_{n'\sigma'}^+\} = \delta_{nn'}\delta_{\sigma\sigma'} \quad \{\hat{c}_{n\sigma}, \hat{c}_{n'\sigma'}\} = \{\hat{c}_{n\sigma}^+, \hat{c}_{n'\sigma'}^+\} = 0. \quad (5)$$

In *t*-PA as can be seen from figure 1 two energetically degenerate bond alternation phases exist. In chains with an odd number of carbons we have an unpaired electron, which occupies a non-bonding level at mid-gap, the soliton level. The soliton is a domain wall where the system switches from one bond alternation phase to the other. Usually the system is treated adiabatically [1], i.e. the units are considered as classical particles moving in the potential created by the  $\pi$  electrons and in the harmonic potential due to the  $\sigma$  electrons. In this case, using the SSH Hamiltonian, one observes a stable and mobile soliton. However, recent calculations have shown that for a small soliton width quantum effects in the lattice might destroy the solitons [22]. In the SSH case the soliton width is quite large (14 lattice units); however, if electron–electron interactions are included the soliton width is drastically reduced [15, 18–20], thus also invalidating considerations based on continuum approximations [21]. Since in the SSH case the soliton width can be chosen freely by the value of the equilibrium dimerization  $u_0$ , this model seems to be a good starting point to study quantum effects in the lattice in more detail. It seems to be reasonable to start with an *ansatz* state similar to Davydov's  $|D_1\rangle$  state for this purpose. The basic differences to the Davydov model are that the electron–phonon coupling appears in the site-off-diagonal terms in contrast to the Davydov model where the exciton–phonon coupling appears in the site-diagonal terms, and further, that instead of bosons (C=O oscillators) we have to deal with fermions (electrons).

The SSH Hamiltonian can be rewritten into a more familiar form by introduction of the usual creation and annihilation operators for the lattice phonons which are of the same form as in the case of the Davydov Hamiltonian and obey Bose commutation relations:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \quad [\hat{b}_k, \hat{b}_{k'}^+] = \delta_{kk'} \quad [\hat{b}_k^+, \hat{b}_{k'}^+] = [\hat{b}_k, \hat{b}_{k'}] = 0. \quad (6)$$

For this purpose we rewrite first the Hamiltonian to get rid of the linear terms which leads to

$$\hat{H}' = \sum_n \left\{ [\beta - (\hat{q}_n - \hat{q}_{n+1})\alpha](\hat{c}_{n\sigma}^+ \hat{c}_{n+1,\sigma} + \hat{c}_{n+1,\sigma}^+ \hat{c}_{n\sigma}) + \frac{\hat{p}_n^2}{2M} + \frac{1}{2}K(\hat{q}_n - \hat{q}_{n+1})^2 \right\} + C. \quad (7)$$

The  $\hat{q}_n$  are displacement operators relative to the minimum geometry of the lattice potential in (3) and are defined in appendix A. The constant  $C$  and the renormalized hopping integral are also given in appendix A. The one-electron SSH Hamiltonian is then given as

$$\hat{H}' = \sum_{n\sigma} \left[ \beta + \sum_k \hbar\omega_k B_{nk}(\hat{b}_k + \hat{b}_k^+) \right] (\hat{c}_{n\sigma}^+ \hat{c}_{n+1,\sigma} + \hat{c}_{n+1,\sigma}^+ \hat{c}_{n\sigma}) + \sum_k \hbar\omega_k (\hat{b}_k^+ \hat{b}_k + \frac{1}{2}) + C. \quad (8)$$

Separation of the constant term leads to

$$\hat{H}' = \hat{H} + D \quad D = \frac{1}{2} \sum_k \hbar\omega_k + C \quad (9a)$$

and the gauge transformation

$$|\psi\rangle = e^{-i/\hbar\{(1/2)\sum_k \hbar\omega_k + Ct\}}|\Phi\rangle = e^{-i/\hbar Dt}|\Phi\rangle. \quad (9b)$$

Therefore

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = (\hat{H} + D)|\psi\rangle \quad (9c)$$

and with the transformed wavefunction we obtain finally

$$D|\Phi\rangle e^{-i/\hbar Dt} + i\hbar e^{-i/\hbar Dt} \frac{\partial}{\partial t}|\Phi\rangle = (\hat{H} + D)|\Phi\rangle e^{-i/\hbar Dt} \Rightarrow i\hbar \frac{\partial}{\partial t}|\Phi\rangle = \hat{H}|\Phi\rangle \quad (9d)$$

with

$$\hat{H} = \sum_{n\sigma} \left[ \beta + \sum_k \hbar\omega_k B_{nk} (\hat{b}_k + \hat{b}_k^+) \right] (\hat{c}_{n\sigma}^+ \hat{c}_{n+1,\sigma} + \hat{c}_{n+1,\sigma}^+ \hat{c}_{n\sigma}) + \sum_k \hbar\omega_k \hat{b}_k^+ \hat{b}_k \quad (9e)$$

where  $\mathbf{B}$  is given by

$$B_{nk} = \frac{\alpha}{\omega_k} \sqrt{\frac{1}{2\hbar\omega_k M}} (V_{n+1,k} - V_{nk}) \quad (10)$$

$\omega_k$  being the eigenfrequencies and  $\mathbf{V}_k$  the coefficient vector of the normal mode  $k$  of the decoupled ( $\alpha_n = 0$ ) lattice, i.e. they are the solutions of the eigenvalue problem

$$\frac{1}{M} \mathbf{K} \mathbf{V}_k = \omega_k^2 \mathbf{V}_k \quad (11a)$$

following from

$$m\ddot{\mathbf{u}} = -\frac{\partial V}{\partial \mathbf{u}} = -\mathbf{K}\mathbf{u} \quad V = \frac{K}{2} \sum_{n=1}^{N-1} (q_n - q_{n+1})^2 \quad (11b)$$

and thus

$$K_{nm} = K \left[ 2(1 - \frac{1}{2}\delta_{n1} - \frac{1}{2}\delta_{nN})\delta_{nm} - \delta_{m,n-1}(1 - \delta_{n1}) - \delta_{m,n+1}(1 - \delta_{nN}) \right]. \quad (11c)$$

The translational mode ( $\omega = 0$ ) has to be excluded from the summations.

## 2.2. The ansatz state

As *ansatz* state one could think of using a Slater determinant (in the Hückel-type SSH case a simple product of one-electron states would be also sufficient) built from the (orthonormal) molecular orbitals

$$|\varphi_i\rangle = \sum_n D_{ni}(c_{ni}, |\beta_{ni}\rangle) \hat{c}_n^+ |0\rangle_e = \sum_n c_{ni}(t) \hat{c}_n^+ |0\rangle_e |\beta_{ni}\rangle \quad (12)$$

where  $|0\rangle_e$  is the electron vacuum and the coherent-states would be given by

$$|\beta_{ni}\rangle = \prod_k |\beta_{nki}\rangle \quad |\beta_{nki}\rangle = e^{-(1/2)|b_{nki}|^2} e^{b_{nki} \hat{b}_k^+} |0\rangle_p = e^{b_{nki} \hat{b}_k^+ - b_{nki}^* \hat{b}_k} |0\rangle_p \quad (13)$$

where  $|0\rangle_p$  denotes the phonon vacuum [27]. However, when forming the Slater determinant or a product state from these MOS, we would obtain products of coherent-states from different sites which do not form a pure coherent-state again. Therefore we have to introduce another form of the *ansatz*.

To this end we first of all introduce creation (annihilation) operators  $\hat{c}_{nj}^+$  ( $\hat{c}_{nj}$ ) which create (annihilate) an electron at site  $n$  in the spin orbital  $j$ . Our full Hamiltonian for  $\nu$  electrons reads then as

$$\hat{H} = \sum_n \left[ \beta + \sum_k \hbar\omega_k B_{nk} (\hat{b}_k + \hat{b}_k^\dagger) \right] \sum_{j=1}^{\nu} (\hat{c}_{nj}^+ \hat{c}_{n+1,j} + \hat{c}_{n+1,j}^+ \hat{c}_{nj}) + \sum_k \hbar\omega_k \hat{b}_k^\dagger \hat{b}_k. \quad (14)$$

Now each of our  $\nu$  electrons ( $j$ ) occupies an atomic orbital at site  $n_j$ . To denote this situation we introduce a row vector  $\mathbf{n} = (n_1, n_2, \dots, n_j, \dots, n_\nu)$ . Thus we can write the electronic part of the wavefunction of this state as a Slater determinant

$$|f_e(\mathbf{n})\rangle = \hat{A} \left[ \prod_{j=1}^{\nu} \hat{c}_{n_j,j}^+ \right] |0\rangle_e \quad \hat{A} = \frac{1}{\sqrt{\nu!}} \sum_P (-1)^P \hat{P} \quad (15)$$

where in the antisymmetrizer  $P$  runs through all possible permutations of the electrons. Here we have to note that in our case of a one-particle Hamiltonian the construction of a Slater determinant is not necessary, because a simple product of the one-electron states leads to the same results.

The electron distribution given in equation (15) causes a polarization of the lattice due to the electron-phonon interaction in the Hamiltonian, leading to a state

$$|f(\mathbf{n})\rangle = |f_e(\mathbf{n})\rangle \hat{U}_{\mathbf{n}} |0\rangle_p. \quad (16)$$

If we assume that the lattice polarizations due to the individual electrons can be superimposed to give the total state of the lattice, we can write the lattice operator in equation (16) as a coherent-state:

$$\hat{U}_{\mathbf{n}} = e^{-(1/2) \sum_k |\sum_{j=1}^{\nu} b_{nj,kj}(t)|^2} e^{\sum_k (\sum_{j=1}^{\nu} b_{nj,kj}(t)) \hat{b}_k^\dagger} \quad (17)$$

where the coherent-state amplitudes  $b_{nkj}$  are functions of time and have to be determined. Then the total wavefunction can be written as a superposition of all states  $|f(\mathbf{n})\rangle$ :

$$|\Phi\rangle = \sum_{\mathbf{n}} C_{\mathbf{n}} |f(\mathbf{n})\rangle. \quad (18)$$

Since we have a one-particle Hamiltonian, the  $N^\nu$  coefficients, where  $\nu$  denotes the number of electrons, decouple to products of the expansion coefficients of one-particle states, the spin orbitals. Introduction of this decoupling leads to our final *ansatz* state

$$|\Phi\rangle = \sum_{n_1, \dots, n_\nu} \left[ \prod_{j=1}^{\nu} c_{n_j,j}(t) \hat{c}_{n_j,j}^+ \right] |0\rangle_e e^{-(1/2) \sum_k |\sum_{j=1}^{\nu} b_{n_j,kj}(t)|^2} e^{\sum_k (\sum_{j=1}^{\nu} b_{n_j,kj}(t)) \hat{b}_k^\dagger} |0\rangle_p \quad (19)$$

where we have already left out the antisymmetrizer, since it is not necessary in a one-particle case. In paper II of this series we will deal with bosons and we can use also a simple product for distinguishable particles and a permanent for indistinguishable ones. A permanent is constructed in the same way as a Slater determinant, except that each term has a positive sign, i.e. instead of the antisymmetrizer one has to use the same sum of permutation operators but without the factor  $(-1)^P$ . However, also for bosons both cases give the same results in a one-particle model. In the next sections we will derive the equations of motion for the parameter sets  $\{c_{nj}(t)\}$  and  $\{b_{nkj}(t)\}$  from this *ansatz* state which will be denoted by  $|\Phi_0\rangle$  in what follows.



### 3. The Lagrangian for the $|\Phi_0\rangle$ ansatz

For a general Hermitian Hamiltonian  $\hat{H} = \hat{H}^\dagger$  with solution  $|\varphi\rangle$  the Lagrangian has to be constructed such that the Euler–Lagrange equations give the time-dependent Schrödinger equation and its Hermitian conjugate:

$$\frac{d}{dt} \frac{\partial L}{\partial \langle \dot{\varphi} |} - \frac{\partial L}{\partial \langle \varphi |} = 0 \Rightarrow i\hbar \frac{\partial}{\partial t} |\varphi\rangle = \hat{H} |\varphi\rangle \quad (20a)$$

$$\frac{d}{dt} \frac{\partial L}{\partial |\dot{\varphi}\rangle} - \frac{\partial L}{\partial |\varphi\rangle} = 0 \Rightarrow -i\hbar \frac{\partial}{\partial t} \langle \varphi | = \langle \varphi | \hat{H}. \quad (20b)$$

The two conditions together are only fulfilled if the Lagrangian is written as

$$L = \frac{i\hbar}{2} \left( \left\langle \varphi \left| \frac{\partial \varphi}{\partial t} \right. \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \varphi \right. \right\rangle \right) - \langle \varphi | \hat{H} | \varphi \rangle. \quad (21)$$

Thus we have to form the corresponding expectation values with our *ansatz* state and Hamiltonian (see e.g. [28]). The form of the different terms occurring in  $L$  can be most easily seen when they are explicitly constructed for a simple three-particle, three-site system. This is done in appendix B. The final form of the Lagrangian for spin orbitals and a chain of  $N$  sites and  $\nu$  electrons (which occupy  $\mu$  spatial orbitals) is then in orbital form

$$\begin{aligned} L = & \frac{i\hbar}{2} \sum_{nj} o_j (\dot{c}_{nj} c_{nj}^* - \dot{c}_{nj}^* c_{nj}) X_j \\ & + \frac{i\hbar}{2} \sum_k \left\{ \sum_{nj} o_j |c_{nj}|^2 \dot{b}_{nkj} \left[ b_{nkj}^* X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'}^* X_{jj'} \right] \right. \\ & \left. - \sum_{nj} o_j |c_{nj}|^2 \dot{b}_{nkj}^* \left[ b_{nkj} X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} X_{jj'} \right] \right\} - H. \quad (22) \end{aligned}$$

$\mu$  is the number of occupied (singly or doubly) spatial orbitals and the  $o_j$  are the occupation numbers. The  $X_j$  and  $X_{jj'}$  are products of molecular-orbital norms and are defined in appendix B. The Hamiltonian function  $H$  is (see appendix B)

$$\begin{aligned} H \equiv \langle \Phi | \hat{H} | \Phi \rangle = & \sum_k \hbar \omega_k \left\{ \sum_{nj} o_j |c_{nj}|^2 b_{nkj}^* \left[ b_{nkj} X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'}^* X_{jj'} \right] \right\} \\ & + \sum_{nj} o_j c_{nj}^* c_{n+1,j} D_{n,n+1,j} \left\{ \left[ \beta + \sum_k \hbar \omega_k B_{nk} (b_{n+1,kj} + b_{nkj}^*) \right] P_{nj} \right. \\ & \left. + \sum_k \hbar \omega_k B_{nk} \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 D_{n,n+1,j}^{mj'} (b_{mkj'} + b_{mkj'}^*) P_{njj'} \right\} \\ & + \sum_{nj} o_j c_{nj} c_{n+1,j}^* D_{n+1,n,j} \left\{ \left[ \beta + \sum_k \hbar \omega_k B_{nk} (b_{n+1,kj}^* + b_{nkj}) \right] P_{nj}^* \right. \\ & \left. + \sum_k \hbar \omega_k B_{nk} \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 D_{n+1,n,j}^{mj'} (b_{mkj'} + b_{mkj'}^*) P_{njj'}^* \right\}. \quad (23) \end{aligned}$$

The derivation of  $H$  is again given in appendix B. The  $D$  and  $P$  values derive from factorized overlap integrals between coherent phonon states (see also appendix B). The  $D$  values are given in (B25)–(B29) and the  $P$  values are

$$P_{nj} \equiv \prod_{j'=1}^{\mu} \left[ \sum_m |c_{mj'}|^2 D_{n,n+1,j}^{mj'} \right]^{o_{j'} - \delta_{jj'}} \quad (24)$$

$$P_{njj'} \equiv \prod_{j''=1}^{\mu} \left[ \sum_m |c_{mj''}|^2 D_{n,n+1,j}^{mj''} \right]^{o_{j''} - \delta_{jj''} - \delta_{j'j''}}$$

To rewrite the Hamiltonian function from the spin-orbital basis ( $\nu$  singly occupied spin orbitals) to the orbital basis ( $\mu$  singly or doubly occupied spatial orbitals) the following replacements

$$\sum_{j=1}^{\nu} Y_j \rightarrow \sum_{j=1}^{\mu} o_j Y_j \quad \sum_{\substack{j'=1 \\ j' \neq j}} Y_{j'} \rightarrow \sum_{j'=1}^{\mu} (o_{j'} - \delta_{jj'}) Y_{j'} \quad (25)$$

$$\prod_{\substack{j'=1 \\ j' \neq j}}^{\nu} Y_{j'} \rightarrow \prod_{j'=1}^{\mu} (Y_{j'})^{o_{j'} - \delta_{jj'}}$$

$$\prod_{\substack{j''=1 \\ j'' \neq jj'}} Y_{j''} \rightarrow \prod_{j''=1}^{\mu} (Y_{j''})^{o_{j''} - \delta_{jj''} - \delta_{j'j''}}$$

had to be performed, where the  $Y$  values stand for any occurring arguments in the sums and products. With these equations the Lagrangian for our  $|\Phi_0\rangle$  ansatz state is completely defined and we can go forward to the derivation of the equations of motion of our time-dependent parameters.

#### 4. Equations of motion for the $|\Phi_0\rangle$ ansatz

From the above-derived Lagrangian in orbital form

$$L = L(\{c_{nj}(t)\}, \{b_{nkj}(t)\}) \quad (26)$$

the equations of motion can be obtained with the Euler–Lagrange equations of the second kind:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{c}_{nj}^*} - \frac{\partial L}{\partial c_{nj}^*} = 0 \quad \frac{d}{dt} \frac{\partial L}{\partial \dot{b}_{nkj}^*} - \frac{\partial L}{\partial b_{nkj}^*} = 0 \quad (27)$$

where  $n$  runs over the  $N$  sites of the chain,  $j$  over the  $\mu$  (doubly or singly) occupied spatial orbitals and  $k$  over the  $(N - 1)$  (non-translational) normal modes of the phonon system. This procedure is equivalent to the time-dependent variational principle (see appendix E) or Heisenberg's operator method, after averaging the equations of motion for the operators with  $|\Phi_0\rangle$ . The derivation of the equations is given in detail in appendix C. As shown there, we have to add Lagrange multipliers to the above Lagrangian in order to conserve the overlap of the orbitals, leading to the equations

$$L' = L + i\hbar \sum_{jj'} \varepsilon_{jj'} (S_{jj'} - \delta_{jj'}) \Rightarrow \frac{d}{dt} \frac{\partial L}{\partial \dot{c}_{nj}^*} - \frac{\partial L}{\partial c_{nj}^*} = i\hbar \sum_{j'} \varepsilon_{jj'} c_{nj'} \quad \frac{d}{dt} \frac{\partial L}{\partial \dot{b}_{nkj}^*} - \frac{\partial L}{\partial b_{nkj}^*} = 0. \quad (28)$$

As shown in detail in appendix D, the equations of motion can be cast into the simple form

$$i\hbar \sum_{mj'} \left\{ P_{nj,mj'} \dot{c}_{mj'} + Q_{mj,mj'} \dot{c}_{mj'}^* + \sum_k [U_{nj,mj'}(k) \dot{b}_{mkj'} + V_{nj,mj'}(k) \dot{b}_{mkj'}^*] \right\} = \sum_{mj'} W_{nj,mj'} c_{mj'} \quad (29)$$

$$i\hbar \sum_{mj'} [\Delta_{nj,mj'}(k) \dot{c}_{mj'} + \Lambda_{nj,mj'}(k) \dot{c}_{mj'}^* + \Theta_{nj,mj'}(k) \dot{b}_{mkj'}] = \sum_{mj'} \Omega_{nj,mj'}(k) b_{mkj'} + J_{nj}(k). \quad (30)$$

Considering  $\{nj\}$  as one combined index we obtain the following system of equations for the determination of the time derivatives of  $c$  and the  $b_k$  from their actual values at a given time:

$$i\hbar \left[ \mathbf{P} \dot{c} + \mathbf{Q} \dot{c}^* + \sum_k \mathbf{U}(k) \dot{b}_k + \sum_k \mathbf{V}(k) \dot{b}_k^* \right] = \mathbf{W} c \quad (31a)$$

$$i\hbar [\Delta(k) \dot{c} + \Lambda(k) \dot{c}^* + \Theta(k) \dot{b}_k] = \Omega(k) b_k + J(k). \quad (31b)$$

The matrices occurring in (29)–(31) depend only on the vectors  $c(t)$  and  $b_k(t)$  and on constants. They are defined in detail in appendix D. From equation (31b) we obtain

$$\dot{b}_k = L(k) + \mathbf{M}(k) \dot{c} + \mathbf{N}(k) \dot{c}^* \quad \dot{b}_k^* = L^*(k) + \mathbf{M}^*(k) \dot{c} + \mathbf{N}^*(k) \dot{c} \quad (32)$$

with

$$L(k) = -\frac{i}{\hbar} \Theta^{-1}(k) [\Omega(k) b_k + J(k)] \quad (33)$$

$$\mathbf{M}(k) = -\Theta^{-1}(k) \Delta(k) \quad \mathbf{N}(k) = -\Theta^{-1}(k) \Lambda(k).$$

Thus each of the  $(N-1)$   $k$  values (translation excluded) requires inversion of an  $(N\mu \times N\mu)$  matrix  $\Theta(k)$ , where again  $N$  is the number of sites and  $\mu$  the number of occupied orbitals. From unpublished, preliminary numerical experience with an approximation to these equations, where the  $D_{nj}^{mj'}$ ,  $P_{nj}$ , and  $P_{njj}$ , are assumed to be constant in time and equal to unity, we conclude that these inversions should not cause any numerical problems. The same holds for the further inversion required later on. Substitution of equation (32) into equation (31a) yields

$$\begin{aligned} \zeta \dot{c} + \kappa \dot{c}^* &= \eta \\ \zeta &\equiv \mathbf{P} + \sum_k [\mathbf{U}(k) \mathbf{M}(k) + \mathbf{V}(k) \mathbf{N}^*(k)] \\ \kappa &= \mathbf{Q} + \sum_k [\mathbf{U}(k) \mathbf{N}(k) + \mathbf{V}(k) \mathbf{M}^*(k)] \\ \eta &= -\frac{i}{\hbar} \mathbf{W} c - \sum_k [\mathbf{U}(k) L(k) + \mathbf{V}(k) L^*(k)]. \end{aligned} \quad (34)$$

From this we obtain

$$\dot{a} = \mu^{-1} \nu \quad (35)$$

where

$$\mu = \begin{pmatrix} [\operatorname{Re}(\zeta) + \operatorname{Re}(\kappa)] & [\operatorname{Im}(\kappa) - \operatorname{Im}(\zeta)] \\ [\operatorname{Im}(\zeta) + \operatorname{Im}(\kappa)] & [\operatorname{Re}(\zeta) - \operatorname{Re}(\kappa)] \end{pmatrix} \quad (36)$$

$$\dot{\alpha} = \begin{pmatrix} \operatorname{Re}(\dot{c}) \\ \operatorname{Im}(\dot{c}) \end{pmatrix} \quad \nu = \begin{pmatrix} \operatorname{Re}(\eta) \\ \operatorname{Im}(\eta) \end{pmatrix}.$$

This step requires inversion of the matrix  $\mu$ , which is of dimension  $(2N\mu \times 2N\mu)$ . Here we have an important point where correctness of programs can be checked. After computation of the time derivatives of the  $c$  values in a time step, one can calculate the time derivative of the overlap matrix from them, which has to be identically equal to zero by construction at any time step.

For the numerical solution of our system of equations we have several options. One would be application of a simple one-step procedure. A way to improve this simple method is the use of a standard Runge–Kutta method, correct up to the fourth order in the time-step  $\tau$ , or for further improvement, Milne's predictor–corrector scheme, which is correct up to  $O(\tau^7)$  [36].

Finally, we want to point out that inspection of the equations of motion in appendix C shows that, in most of the terms occurring, we find products of the coefficients for different molecular orbitals, i.e. for different electrons. This implies that we have an effective electron–electron interaction present in the system, although the SSH Hamiltonian is a one-particle one for the electrons. This effective electron–electron interaction is not a ‘true’ direct interaction, such as the Coulomb interaction, but one which shows up because of the electron–phonon interactions. It might occur that in a Pariser–Parr–Pople model with the  $|\Phi_0\rangle$  ansatz state this can lead naturally to effective attractions between electrons and thus to a counterpart of the ‘negative- $U$ ’ Hubbard Hamiltonians discussed in connection with high- $T_c$  superconductors. However, such a phenomenon cannot occur in  $t$ -PA because it would lead to the formation of bipolarons in doubly charged chains, and it is known that in  $t$ -PA bipolarons are unstable with respect to pairs of free, singly charged solitons and anti-solitons. However, when applied to semi-empirical models of copper oxide planes there might well occur an effective attraction between electrons or holes and thus pairing would show up. Likewise it is known that in many conducting polymers with non-degenerate ground states bipolarons function as spinless charge carriers in the conduction mechanism. Finally, not to forget the phase factors, note that our total wavefunction is given by

$$|\psi\rangle = e^{-i/\hbar((1/2)\sum_k \hbar\omega_k + C)t} \sum_{n_1, \dots, n_\nu} \left[ \prod_{j=1}^{\nu} c_{n_j j}(t) \hat{c}_{n_j j}^+ \right] |0\rangle_e$$

$$\times e^{-(1/2)\sum_k | \sum_{j=1}^{\nu} b_{n_j k j}(t) |^2} e^{\sum_k | \sum_{j=1}^{\nu} b_{n_j k j}(t) | \hat{b}_k^+} |0\rangle_p. \quad (37)$$

These phase factors are important for the computation of autocorrelation functions.

Due to the high degree of non-linearity in our equations it might be difficult to find numerical solutions of them. Thus it would be interesting to examine which approximations to the full  $|\Phi_0\rangle$  theory can be derived. This is the topic of the next section.

## 5. Approximations derived from $|\Phi_0\rangle$

As already mentioned above, due to the complexity and the large degree of non-linearity in the equations of motion for the  $|\Phi_0\rangle$  ansatz state, which make numerical simulations very

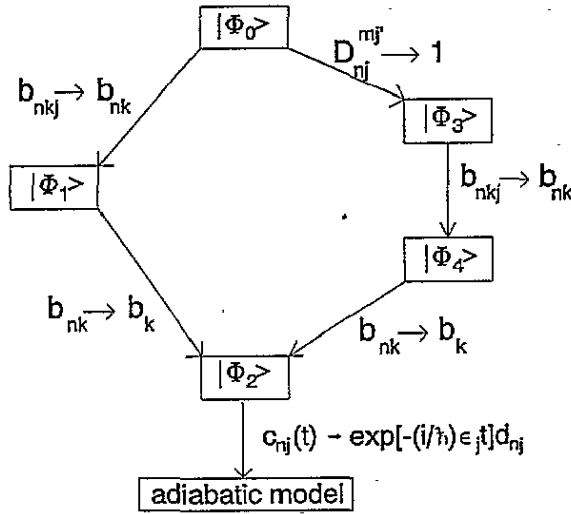


Figure 2.

complicated and time consuming, one has to think about reasonable approximations to this *ansatz* state. There is a natural sequence of possible simplifications which is sketched in figure 2. The definitions of the quantities occurring are given below. In this section we want to discuss briefly these approximate equations of motion.

5.1. The  $|\Phi_1\rangle$  approximation

In this approximation we start from the  $|\Phi_0\rangle$  *ansatz* and neglect as a first step the orbital dependence of the coherent-state amplitudes, i.e. we set  $b_{nkj}(t) = b_{nk}(t)$ , leading to

$$\begin{aligned}
 |\Phi_1\rangle = & e^{-i/\hbar(1/2) \sum_k \hbar \omega_k + C} t \sum_{n_1, \dots, n_\nu} \left[ \prod_{j=1}^{\nu} c_{n_j, j}(t) \hat{c}_{n_j, j}^+ \right] |0\rangle_e \\
 & \times e^{-(1/2) \sum_k | \sum_{j=1}^{\nu} b_{n_j, k}(t) |^2} e^{\sum_k ( \sum_{j=1}^{\nu} b_{n_j, k}(t) ) \hat{b}_k^+} |0\rangle_p.
 \end{aligned}
 \tag{38}$$

Here the  $\omega_k$  are the frequencies of the normal modes of the lattice (phonons),  $C$  is a constant energy (see above), the  $c_{nj}(t)$  are molecular-orbital coefficients, where  $n$  denotes the site and  $j$  the (occupied) spin orbital,  $\hat{c}_{n_j, j}^+$  creates an electron at site  $n$  in spin orbital  $j$ ,  $\nu$  is the number of electrons in the system,  $|0\rangle_e$  is the electron vacuum,  $b_{nk}(t)$  is a coherent-state amplitude for site  $n$  in the normal mode  $k$ ,  $\hat{b}_k^+$  creates a vibrational quantum (phonon) in the  $k$ th normal mode of the lattice, and  $|0\rangle_p$  is the phonon vacuum. Physically, in this approximation we assume that the lattice polarization caused by the population of a given lattice site with electrons does not depend on the individual electron, but only on their total population at the site. This assumption seems to be quite reasonable and leads to a couple of significant simplifications. The Lagrangian and equations of motion for this *ansatz* state can be obtained from those discussed above just by neglecting the orbital index  $j$  at the coherent-state amplitudes. With this approximation the computational work is reduced roughly by a factor of  $\mu$ , because we have to determine only  $N(N - 1)$   $b$  parameters compared to  $\mu N(N - 1)$  before. In addition, the matrices  $\Theta(k)$  which have to be inverted are now of size  $(N \times N)$  compared to  $(\mu N \times \mu N)$  before. However, the

high degree of non-linearity is still present in the  $|\Phi_1\rangle$  equations. The physically interesting indirect electron-electron interactions are also preserved in this approximation. Since the high degree of non-linearity is still there, we switch now to the next level of approximation, where also the site dependence of the  $b$  parameter is neglected.

### 5.2. The $|\Phi_2\rangle$ and the classical approximation

In this approximation the orbital and site dependences of the  $b$  parameters are neglected. Thus we set  $b_{nkj}(t) = b_k(t)$ . From this assumption follows immediately that  $D_{nmj} = 1$ ,  $D_{nj}^{mj} = 1$ ,  $P_{nj} = X_j$ , and  $P_{njj'} = X_{jj'}$ . Physically in this approximation it is assumed that the total distribution of the electrons gives rise to the lattice distortion, no matter what orbital the individual electron occupies or what is the individual electron population at a site. This is a rather crude approximation and it is known from Davydov soliton theory as the  $|D_2\rangle$  approximation. As we will see, in this approximation the lattice is described semiclassically with one coherent state for each normal mode of the decoupled lattice. However, we discuss this approximation in more detail, because it is applied numerically later on.

The *ansatz* state in the  $|\Phi_2\rangle$  case reduces to a simple product of the electronic wavefunction with the lattice coherent states. Thus phase mixing between the electronic and the lattice wavefunctions and therefore quantum effects in the lattice are neglected. With the above simplifications, the *ansatz* can be written as

$$\begin{aligned}
 |\Phi_2\rangle &= \prod_{j=1}^{\nu} |\varphi_j\rangle |\beta\rangle & |\varphi_j\rangle &= \sum_n c_{nj}(t) \hat{c}_{nj}^{\dagger} |0\rangle_e \\
 |\beta\rangle &= \exp\left[-\frac{1}{2} \sum_k |\nu b_k(t)|^2\right] \exp\left[\sum_k \nu b_k(t) \hat{b}_k^{\dagger}\right] |0\rangle_p.
 \end{aligned} \tag{39}$$

This implies that summations over orbitals as occurring in the Lagrangian can be reduced, e.g.

$$\begin{aligned}
 \sum_{nj} o_j |c_{nj}|^2 f(b_{nkj}) X_j &= f(b_k) \sum_{nj} o_j |c_{nj}|^2 X_j = f(b_k) \sum_j o_j X = \nu f(b_k) X \\
 \sum_{nj} o_j |c_{nj}|^2 \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 g(b_{nkj}, b_{mkj'}) X_{jj'} \\
 &= g(b_k) \sum_{nj} o_j |c_{nj}|^2 \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 X_{jj'} \\
 &= g(b_k) \sum_j o_j \sum_{j'} (o_{j'} - \delta_{jj'}) \sum_n |c_{nj}|^2 \sum_m |c_{mj'}|^2 X_{jj'} \\
 &= g(b_k) \sum_j o_j \sum_{j'} (o_{j'} - \delta_{jj'}) X = \nu(\nu - 1) g(b_k) X.
 \end{aligned} \tag{40}$$

Use of these results yields the Lagrangian

$$L = \frac{i\hbar}{2} \sum_{nj} o_j (\dot{c}_{nj} c_{nj}^* - \dot{c}_{nj}^* c_{nj}) X_j + \frac{i\hbar}{2} \nu^2 \sum_k (\dot{b}_k b_k^* - \dot{b}_k^* b_k) X - H \tag{41}$$

with the Hamiltonian

$$H = \sum_{nj} \left[ \beta + \nu \sum_k \hbar \omega_k B_{nk} (b_k + b_k^*) \right] o_j (c_{nj}^* c_{n+1,j} + c_{nj} c_{n+1,j}^*) X_j + \nu^2 \sum_k \hbar \omega_k |b_k|^2 X. \tag{42}$$

Finally we obtain for the lattice displacements and momenta

$$\begin{aligned} q_n(t) &= \nu \sum_k \sqrt{\frac{2\hbar}{M\omega_k}} U_{nk} \operatorname{Re}[b_k(t)] \\ p_n(t) &= \nu \sum_k \sqrt{2\hbar M\omega_k} U_{nk} \operatorname{Im}[b_k(t)]. \end{aligned} \quad (43)$$

Substitution of  $b'_k(t) = \nu b_k(t)$  and renaming  $b'_k(t)$  as  $b_k(t)$  again yields the final Lagrangian and *ansatz* state.

The Euler–Lagrange equations for the  $b_k^*$  together with ( $\nu$  is again the number of electrons in the system, which is constant in time, see below)

$$P_{nn} = \sum_j o_j |c_{nj}|^2 \quad \sum_n P_{nn} = \nu \quad (44)$$

yield the equations of motion

$$i\hbar \dot{b}_k = \hbar\omega_k \left[ b_k + \sum_n (B_{nk} P_{n+1,n} + B_{n-1,k} P_{n-1,n}) \right] \quad (45)$$

which can be shown to be equivalent to

$$\dot{p}_n = K(q_{n+1} - 2q_n + q_{n-1}) + 2\alpha \operatorname{Re}[P_{n,n+1} - P_{n,n-1}]. \quad (46)$$

From this we see that the dynamics of the lattice (without electron–phonon coupling) follow from the classical equations of motion; however, in contrast to the adiabatic model the dynamics of the electrons are taken explicitly into account. Further the  $p_n$  and  $q_n$  here have to be viewed as the expectation values of the operators. Note that equation (46) is identical to the lattice equations in the adiabatic case, since

$$2\alpha \operatorname{Re}[P_{n,n+1} - P_{n,n-1}] = -\frac{\partial E_\pi}{\partial q_n} \quad (47)$$

if  $E_\pi$  and  $\mathbf{P}$  are determined by diagonalization of the Hückel matrix for geometry  $\{q_n\}$ . However, in the  $|\Phi_2\rangle$  case the MO coefficients are determined in a different way. Temperature effects can be included by introduction of random-forces and friction in the above equations in the same way as in the classical case (see appendix F):

$$\dot{p}_n = K(q_{n+1} - 2q_n + q_{n-1}) + 2\alpha \operatorname{Re}[P_{n,n+1} - P_{n,n-1}] + R_n(t) - \Gamma p_n \quad (48)$$

where the random-forces  $R_n(t)$  are created in the same way as described in appendix F. For the orbitals we get from the Euler–Lagrange equations

$$i\hbar \dot{c}_{nj} = (\beta + E_n)c_{n+1,j} + (\beta + E_{n-1})c_{n-1,j} + c_{nj} \sum_k \left[ -\frac{i\hbar}{2} (\dot{b}_k b_k^* - \dot{b}_k^* b_k) + \hbar\omega_k |b_k|^2 \right]. \quad (49)$$

Now we perform a phase transformation

$$a_{nj} = c_{nj} \exp \left\{ -i \sum_k \int_0^t [\operatorname{Im}(\dot{b}_k(t') b_k^*(t')) + \omega_k |b_k(t')|^2] dt' \right\} \quad (50)$$

and arrive after renaming  $a_{nj}$  as  $c_{nj}$  again at the final equations of motion:

$$\begin{aligned} i\hbar\dot{c}_{nj} &= (\beta + E_n)c_{n+1,j} + (\beta + E_{n-1})c_{n-1,j} \\ E_n &= \sum_k \hbar\omega_k B_{nk}(b_k + b_k^*) = -\alpha(q_n - q_{n+1}) \\ \Rightarrow i\hbar\dot{c}_{nj} &= [\beta - \alpha(q_n - q_{n+1})]c_{n+1,j} + [\beta - \alpha(q_{n-1} - q_n)]c_{n-1,j}. \end{aligned} \tag{51}$$

A discussion of numerical results from this *ansatz* are given in section 7. The explicit indirect electron–electron interaction terms are neglected in this approximation.

However, in the above-derived approximation, the dynamics of the electrons are still considered explicitly, while in the usual SSH theory the electrons are assumed to follow the motion of the classically described lattice instantaneously. To arrive at this approximation, we have to assume that the electrons are in a stationary state for each lattice geometry (at every instant of time), i.e.

$$|\varphi_j(t)\rangle = \sum_n c_{nj}(t)\hat{c}_{nj}^+|0\rangle_e = e^{-(i/\hbar)\varepsilon_j t} \sum_n d_{nj}\hat{c}_{nj}^+|0\rangle_e. \tag{52}$$

We obtain by substitution of  $c_{nj}(t) = \exp[-(i/\hbar)\varepsilon_j t]d_{nj}$  into equation (51) an eigenvalue problem

$$\begin{aligned} \varepsilon_j d_{nj} &= [\beta - \alpha(q_n - q_{n+1})]d_{n+1,j} + [\beta - \alpha(q_{n-1} - q_n)]d_{n-1,j} \Rightarrow \mathbf{H}d_j = \varepsilon_j d_j \\ \text{with } H_{nm} &= [\beta - \alpha(q_n - q_{n+1})]\delta_{m,n+1} + [\beta - \alpha(q_{n-1} - q_n)]\delta_{m,n-1} \\ \Rightarrow E_\pi &= \sum_j o_j \varepsilon_j \Rightarrow -\frac{\partial E_\pi}{\partial q_n} = 2\alpha \sum_j o_j \text{Re}[c_{nj}(c_{n+1,j}^* - c_{n-1,j}^*)]. \end{aligned} \tag{53}$$

Substitution of this result into equation (46) yields finally

$$\dot{p}_n = K(q_{n+1} - 2q_n + q_{n-1}) - \frac{\partial E_\pi}{\partial q_n} \tag{54}$$

which is identical to the equations derived in appendix F for the adiabatic approximation which is usually used in simulations of the dynamics of *t*-PA. Therefore, through our series of approximations  $|\Phi_0\rangle \rightarrow |\Phi_1\rangle \rightarrow |\Phi_2\rangle \rightarrow$  adiabatic model we could show up the links between our quantum-mechanical *ansatz* state and the usually used SSH theory.

### 5.3. The $|\Phi_3\rangle$ and $|\Phi_4\rangle$ approximation

As we can see from figure 2, there is another series of approximations which finally also leads to the  $|\Phi_2\rangle$  state. However, from this series it can be expected that it would lead to equations which are numerically more tractable, by conserving the quantum nature of the lattice. In order to arrive at the first one of these approximations,  $|\Phi_3\rangle$ , we do not make assumptions on the  $b$  parameters directly, but on a quantity derived from them, namely their overlap, which contains a series of factors which are simple phase factors. These are factors of the type  $D_{nj}^{m_{j'}}$ . What is the essence of this approximation is to assume the phases in these factors to vanish, i.e. we assume  $D_{nj}^{m_{j'}} = 1$ . This is an approximation not on the level of the *ansatz* state, but on the level of the Lagrangian derived from this state. It has the further consequence that  $P_{nj} = X_j$  and  $P_{njj'} = X_{jj'}$ . Thus first of all, the



most complicated terms in the equations of motion which originate from derivatives of the  $P$  value with respect to the  $b$  parameters vanish and a further simplification stems from the fact that we have shown already that  $X = X_j = X_{jj'} = 1$ . Due to the last fact, the high degree of non-linearity becomes reduced and it is quite probable that neglect of some phases should not be too crude an approximation. The  $|\Phi_3\rangle$  approximation changes the Lagrangian only in the electron-phonon part of the Hamiltonian function. This implies that in the derivation of equations of motion for the  $c$  values (see appendix C), all terms remain, but the  $D$  values have to be set equal to unity, as well as the  $P$  values remaining after differentiation. We note here that the high degree of non-linearity in the former equations is reduced considerably in this approximation, while the indirect electron-electron interactions and the quantum description of the lattice is still preserved.

In the  $|\Phi_4\rangle$  approximation we proceed in the same way as before in going from  $|\Phi_0\rangle$  to  $|\Phi_1\rangle$ , i.e. we neglect the orbital dependence of the  $b$  parameters and set  $b_{nkj}(t) = b_{nk}(t)$ . Finally if we neglect here also the site dependence of the  $b$  parameters we arrive again at the semiclassical  $|\Phi_2\rangle$  equations.

## 6. Initial state and inclusion of temperature effects

For numerical applications of the equations of motion for the  $|\Phi_0\rangle$  model the initial state can be obtained by computing from the usually used end-kink geometry ( $u_n = (-1)^{n+1}u_0$ ,  $p_n = 0$ ) the corresponding  $b_{nki}(t = 0)$ . These quantities can be computed by forming the expectation values of the displacement and momentum operators with our state ( $\mathbf{V}$  contains the normal-mode coefficients of the decoupled lattice)

$$\begin{aligned}
 p_n(t) &= \sum_{kmj} \sqrt{2M\hbar\omega_k V_{nk} o_j} |c_{mj}(t)|^2 \text{Im}[b_{mkj}(t)] \\
 u_n(t) &= \sum_{kmj} \sqrt{\frac{2\hbar}{M\omega_k}} V_{nk} o_j |c_{mj}(t)|^2 \text{Re}[b_{mkj}(t)] + d_n \\
 d_n &= -[n - \frac{1}{2}(N+1)] \frac{A}{K} + \frac{1}{N} \sum_m u_m^{(0)}.
 \end{aligned} \tag{55}$$

The  $c_{nj}(t = 0)$  can be obtained from a static SSH calculation with this geometry. To avoid numerical difficulties due to the matrix inversions in the equations of motion we can use the same approximation as in case of the Davydov soliton [29, 30]. Namely, we can assign each  $c_{nj}(t = 0)$  which is smaller than a given threshold value  $x$  with  $x$ , chosen as a small, physically insignificant number (e.g.  $x = 0.005$ ).

However, multiplication of the above equation for  $u_n$  by  $(M/2\hbar)^{1/2} V_{nk'}$  and summation over  $n$ , yields a factor

$$\sum_n V_{nk'} V_{nk} = \delta_{kk'} \tag{56}$$

due to the orthonormality of the normal modes. After performing the summation over  $k$  we arrive at

$$\begin{aligned}
 \sum_{mj} o_j |c_{mj}|^2 \text{Re}(b_{mk'j}) &= \sum_n \sqrt{\frac{M\omega_{k'}}{2\hbar}} V_{nk'q_n} \\
 \Rightarrow \sum_n \left[ \sum_j o_j |c_{nj}|^2 \text{Re}(b_{nkj}) - \sqrt{\frac{M\omega_k}{2\hbar}} V_{nkq_n} \right] &= 0.
 \end{aligned} \tag{57}$$

Thus from the lattice displacements and momenta we cannot determine the coherent-state amplitudes  $b_{nkj}$  uniquely but only a weighted average of them over the orbitals. Thus we can use

$$\operatorname{Re}[b_{nkj}(t=0)] = \frac{1}{\nu|c_{nj}(t=0)|^2} \sqrt{\frac{M\omega_k}{2\hbar}} V_{nk} q_n(t=0) \quad \sum_j o_j = \nu. \quad (58)$$

In a similar way we obtain

$$\operatorname{Im}[b_{nkj}(t=0)] = \frac{1}{\nu|c_{nj}(t=0)|^2} \sqrt{\frac{1}{2\hbar M\omega_k}} V_{nk} p_n(t=0). \quad (59)$$

For the determination of the  $\{b_{nk}\}$  in the  $|\Phi_1\rangle$  approximation for the simulation start we have again a weighted average:

$$\begin{aligned} \sum_m P_{mm} \operatorname{Re}(b_{mk}) &= \sum_n \sqrt{\frac{M\omega_k}{2\hbar}} V_{nk} q_n \\ \sum_m P_{mm} \operatorname{Im}(b_{mk}) &= \sum_n \sqrt{\frac{1}{2\hbar M\omega_k}} V_{nk} p_n \\ \Rightarrow \sum_n \left[ P_{nn} \operatorname{Re}(b_{nk}) - \sqrt{\frac{M\omega_k}{2\hbar}} V_{nk} q_n \right] &= 0 \\ \sum_n \left[ P_{nn} \operatorname{Im}(b_{nk}) - \sqrt{\frac{1}{2M\hbar\omega_k}} V_{nk} p_n \right] &= 0 \end{aligned} \quad (60)$$

with

$$\mathbf{P} \equiv \sum_j o_j c_j c_j^\dagger \Rightarrow P_{nm} \equiv \sum_j o_j c_{nj} c_{mj}^*. \quad (61)$$

Thus from

$$q_n(0) = (-1)^{n+1} u_0 + [n - \frac{1}{2}(N+1)] \frac{A}{K} - \frac{1}{2} (1 + (-1)^{N+1}) \frac{u_0}{N} \quad p_n(0) = 0 \quad (62)$$

we calculate the initial values of the  $b_{nk}$

$$\operatorname{Re}[b_{nk}(0)] = \frac{1}{P_{nn}} \sqrt{\frac{M\omega_k}{2\hbar}} V_{nk} q_n(0) \quad \operatorname{Im}[b_{nk}(0)] = \frac{1}{P_{nn}} \sqrt{\frac{1}{2\hbar M\omega_k}} V_{nk} p_n(0). \quad (63)$$

The simulation start in the  $|\Phi_2\rangle$  approximation is trivial, since there occur no weighted averages in the transformation to normal modes.

To include temperature in the theory we have several options. One of them is Davydov's method which uses a thermally averaged Lagrangian for the derivation of equations of motion. However, this method has been frequently criticized as being inconsistent with density-matrix theory for mixed states. Further one could use a product of coherent-states at each site where one factor resembles a thermally averaged phonon population [31]. The

Langevin-equation method (see appendix F) should be used only in the classical case. However, because it is frequently applied to model temperature we decided to use it in our numerical simulation to study its behaviour. For later applications we want to use the method of thermal population of the lattice phonons prior to the soliton start which we applied successfully in the case of Davydov solitons [32, 33]. This method has the advantage that the calculated initial displacements of the units can be incorporated in the classical SSH theory (see appendix F), Davydov's semiclassical  $|\Phi_2\rangle$  method, and the quantum-mechanical cases which are discussed here. With the help of the eigenvectors  $\mathbf{V}$  and the eigenfrequencies  $\omega_k$  we can populate each normal mode  $k$  with an energy  $E_k$  according to the Bose-Einstein distribution. Then  $E_k$  is given by [33]

$$E_k = Nk_B T \frac{\hbar\omega_k v_k}{R} \quad v_k = [e^{\hbar\omega_k/k_B T} - 1]^{-1} \quad R = \sum_k \hbar\omega_k v_k. \quad (64)$$

One half of this energy yields the displacements and the other half the momenta of the units due to a given normal mode  $k$  ( $k_B$  is Boltzmann's constant). Superposition of all modes (excluding the translational one) leads to that part of the initial displacements and momenta which are due to temperature effects only:

$$y_n(0) = \sum_k V_{nk} \sqrt{\frac{E_k}{K \sum_m (V_{m+1,k} - V_{mk})^2}} \quad \dot{y}_n(0) = \sum_k V_{nk} \sqrt{\frac{E_k}{M \sum_m V_{mk}^2}}. \quad (65)$$

From these displacements and momenta we can compute the quantities

$$\vartheta_k = \sin^{-1} \left[ \frac{\omega_k}{\zeta_k} \sum_n V_{nk} y_n(0) \right] \quad (66)$$

$$\zeta_k = \sqrt{\omega_k^2 \left[ \sum_n V_{nk} y_n(0) \right]^2 - \left[ \sum_n V_{nk} \dot{y}_n(0) \right]^2}$$

which appear in the final equations for the initial displacements and momenta due to temperature effects. These are obtained by substitution of (66) into the analytical solutions for the decoupled lattice. Superimposed with equation (62) we obtain finally

$$q_n(0, T) = q_n(0) + \sum_k V_{nk} \frac{\zeta_k}{\omega_k} \sin[\omega_k t_0 + \vartheta_k] \quad (67)$$

$$p_n(0, T) = M \dot{q}_n(0, T) = M \sum_k V_{nk} \zeta_k \cos[\omega_k t_0 + \vartheta_k]$$

where  $t_0$  is a lattice equilibration time which can be chosen arbitrarily without effect on the soliton dynamics obtained as was shown numerically for Davydov's soliton in [32]. We chose typically  $t_0 = 100$  ps. The quantities from equation (67) can now be used directly as initial conditions in the classical theory (appendix F), in the semiclassical  $|\Phi_2\rangle$  theory or, transformed according to (58, 59, 63), as initial data for the more sophisticated approximations. However, one has to consider whether due to the strong electron-phonon interactions it would not be more realistic to fit a parabolic potential to the total (electronic-plus-lattice) energy in the potential minimum realized at the start of the simulation and compute the eigenvectors and eigenfrequencies necessary from this potential instead of the

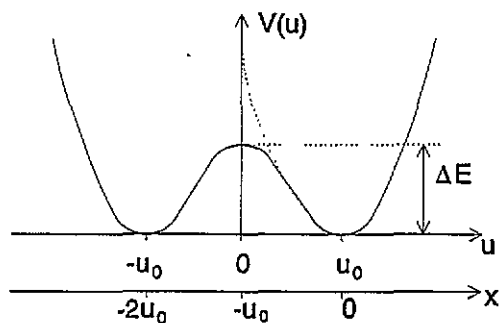


Figure 3.

pure lattice potential. Thus it might be necessary to determine the initial lattice coordinates due to thermal fluctuation not from the decoupled lattice potential  $V_\sigma$  alone but from the total potential energy  $V = E_\pi + V_\sigma$ . Let us consider a geometry  $u_n = (-1)^{n+1}u$  which leads with  $u = \pm u_0$  to the two equilibria of an odd-numbered chain, then we have as potential  $V(u)$  the usual double-well potential as sketched in figure 3.

Note that in the case of an even-numbered finite open chain, we have only one minimum at  $u = u_0$ . Let us define now coordinates  $x_n$  relative to one of the minima. We choose here the minimum  $u = u_0$ , since  $u = -u_0$  is not a minimum of the potential for even-numbered chains. Thus we have

$$x_n = u_n - (-1)^{n+1}u_0 \quad (68)$$

and the above-described geometry is given by

$$x_n = (-1)^{n+1}(u - u_0) \quad (69)$$

and we approximate the right potential well by a parabola centred at the minimum (dashed line in figure 3)

$$\begin{aligned} V(x) = V(u) - V(u_0) &= \frac{W}{2} \sum_n (x_{n+1} - x_n)^2 = \frac{W}{2} \sum_n (-1)^{2n+2} [-(u - u_0) - (u - u_0)]^2 \\ &= \frac{W}{2} \sum_n (-2u + 2u_0)^2 = 2(N - 1)W(u - u_0)^2 \Rightarrow W = \frac{V(u) - V(u_0)}{2(N - 1)(u - u_0)^2} \end{aligned} \quad (70)$$

i.e. we need to compute the total potential of a given chain, via diagonalization of the Hückel matrix and addition of the lattice energy, only at two points, namely at some arbitrary value  $u$  and at  $u_0$  to compute the potential constant  $W$ . However, it might be better to calculate  $W$  for several  $u$  values and take the mean value of them. Then in the usual way we can determine the normal modes of the potential  $V(x)$ , populate them according to the given temperature  $T$  by means of Bose-Einstein statistics, and finally calculate the lattice displacements from equilibrium and the momenta due to thermal excitation as described above for the lattice potential  $V_\sigma$  alone.

At this point a word of caution is appropriate: the above-sketched approach is only applicable if the thermal excitation energy  $Nk_B T$  is less than the barrier height  $\Delta E$ .

Otherwise the harmonic approximation for the potential well breaks down, if states in the energy region around or above  $\Delta E$  are significantly populated. In such cases one needs to use coupled anharmonic oscillators with cubic and quartic anharmonicity for the potential function.

Finally, during a  $|\Phi_0\rangle$  simulation the actual displacements and momenta can be calculated by (note that  $\mathbf{V}$  is real)

$$\begin{aligned}
 p_n &= \sum_{km} \sqrt{2\hbar M \omega_k} V_{nk} \sum_j o_j |c_{mj}|^2 \text{Im}[b_{mkj}] \\
 q_n &= \sum_{km} \sqrt{\frac{2\hbar}{M \omega_k}} V_{nk} \sum_j o_j |c_{mj}|^2 \text{Re}[b_{mkj}] \\
 u_n &= q_n - [n - \frac{1}{2}(N + 1)] \frac{A}{K} + \frac{1}{N} \sum_m u_m^{(0)}.
 \end{aligned} \tag{71}$$

In the following we present for comparison dynamics calculated with the classical SSH model (appendix F), and the semiclassical  $|\Phi_2\rangle$  *ansatz* using Langevin equations for the inclusion of temperature effects.

## 7. Results and discussion

We have computed the dynamics of a chain of 11 units within the fully adiabatic model (as described in appendix F) and the  $|\Phi_2\rangle$  *ansatz* (as described above; for details of the numerical procedure, see appendix G) for different values of the bond-alternation parameter  $u_0$ , since in the SSH model this parameter controls the soliton width. For  $u_0 = 0.03 \text{ \AA}$  the soliton half width is about seven lattice sites and decreases with increasing  $u_0$ , e.g. for  $u_0 = 0.1 \text{ \AA}$  it is about three lattice sites [1]. The case of small soliton widths is interesting for two reasons. First of all our calculations including electron–electron interactions indicated that these interactions mainly reduce the soliton half width to roughly two to three sites [15, 20, 25, 34]. Further the results of Rukh *et al* [22] show that the stability of solitons decreases for decreasing width due to quantum effects. However, in [22], as in the  $|\Phi_2\rangle$  case, a product of an electronic state and coherent phonon states was applied, but treating only the electron in the soliton state explicitly, while in the  $|\Phi_2\rangle$  approach the influence of all electrons on the lattice is considered. As already mentioned, in the  $|\Phi_2\rangle$  *ansatz* the dynamics of the electrons are taken into account explicitly, while in the classical adiabatic case the electrons are assumed to follow the lattice dynamics instantaneously.

As parameters we used the usually quoted SSH values [1] of  $\beta^0 = -2.5 \text{ eV}$  and  $\alpha = 4.1 \text{ eV \AA}$ . In a chain of 11 units this leads to  $K = 15.93 \text{ eV \AA}^{-2}$ ,  $A = -5.36 \text{ eV \AA}$  for  $u_0 = 0.03 \text{ \AA}$ ,  $K = 8.83 \text{ eV \AA}^{-2}$ ,  $A = -4.56 \text{ eV \AA}$  for  $u_0 = 0.2 \text{ \AA}$  and  $K = 5.51 \text{ eV \AA}^{-2}$ ,  $A = -3.75 \text{ eV \AA}$  for  $u_0 = 0.4 \text{ \AA}$ . The time-step size was chosen as 0.05 fs. As starting geometry a so-called end-kink state ( $u_i = (-1)^{i+1} u_0$ ) was used. In this case the chain ends with a long bond and the unpaired electron is localized at this chain end. Since the equilibrium position of a soliton is in the centre of a chain, the kink starts to move away from this position. In figure 4 we show the kinetic energy of the lattice together with the total-energy error for the above-mentioned values of  $u_0$  at temperature  $T = 0 \text{ K}$ . It is obvious that the fluctuations of the kinetic energy due to the soliton movement are, though not completely identical, very similar for the two models. Further there is no tendency, as

one would expect from the results in [22], towards an increase of the differences between the two models with increasing bond alternation, i.e. decreasing soliton width. Obviously the error in total energy increases somewhat in the case of the  $|\Phi_2\rangle$  model, indicating that one should use an even smaller time-step size in this case or a better method for the numerical integration of the equations of motion, like a Runge–Kutta or a predictor–corrector method. However, in cases (b) and (c), where the soliton moves more slowly, the error in total energy is small enough.

In figure 5 we show the time evolution of the electronic energy levels for the three cases as computed with the adiabatic model. As can be seen from the figure a comparatively small fluctuation of the fundamental gap is connected with the soliton movement. The soliton level itself remains at midgap (0 eV) as expected from particle–hole symmetry. The lower edge of the valence band and, in the same way due to particle–hole symmetry, the upper edge of the conduction band, show an oscillation with a smaller amplitude and frequency than the upper edge of the valence band and the lower edge of the conduction band. Figure 6 shows the time evolution of the normalized staggered coordinate  $g_n = \psi_n/u_0$ . At least for the larger values of  $u_0$ , corresponding to smaller soliton widths and also smaller velocities, the movement of the soliton can be clearly followed in the time evolution of the staggered coordinates. Any differences in the two models, if present at all, are too small to be observed from the plots. Clearly during the soliton movement, lattice phonons are also excited. Finally in figure 7 the time evolutions of the spin densities at odd-numbered sites are shown.

In these plots the spin densities at even-numbered sites are not shown, because due to the symmetries of the model they vanish exactly. If electron–electron interactions were included into the model, at even-numbered sites negative spin densities would show up. Also here virtually no differences between the two models are visible. The movement of the soliton, having its centre at the site of maximal spin densities, is clearly visible for the two larger  $u_0$  values. In these cases the solitons have a small width and thus their velocities are rather small. For  $u_0 = 0.4 \text{ \AA}$  already tendencies to lattice pinning show up. For  $u_0 = 0.03 \text{ \AA}$  the soliton is rather broad and fast so that its movement is a little bit difficult to identify in the plot.

Thus in contrast to the results reported in [22] there is no increased instability of the solitons with increasing bond-alternation parameter and consequently decreasing width in the case of the  $|\Phi_2\rangle$  model, although in [22] also products of electronic states with coherent phonon states are used. The difference obviously is due to the fact that in [22] only the dynamics of the electron occupying the soliton level is taken explicitly into account. Obviously the influence of the other electrons on the lattice due to electron–phonon coupling helps to stabilize the solitons in our  $|\Phi_2\rangle$  model.

In figures 8–11 we show the same plots resulting from model calculations including temperature, but only for two values of the bond-alternation parameter, namely  $u_0 = 0.03 \text{ \AA}$  and  $0.40 \text{ \AA}$ . For these model calculations we used random forces and a dissipation term to simulate temperature effects. Here we observe differences in the two models which are most pronounced in the smaller- $u_0$  case. In the adiabatic model the soliton remains stable, however, with an increasing tendency to lattice pinning in the centre of the chain with increasing time. In the  $|\Phi_2\rangle$  model this pinning occurs at smaller times and then the soliton width increases, i.e. the soliton is unstable. In case of the larger bond alternation the soliton remains stable but pinned close to the chain end in both models. However, the plots of the energies show that these findings have to be viewed with some care. The rather large changes in the total energy suggest that the systems are still not in thermal equilibrium after the 0.5 ps total simulation time. This is indicated by the time constants  $\Gamma$  of the heat baths

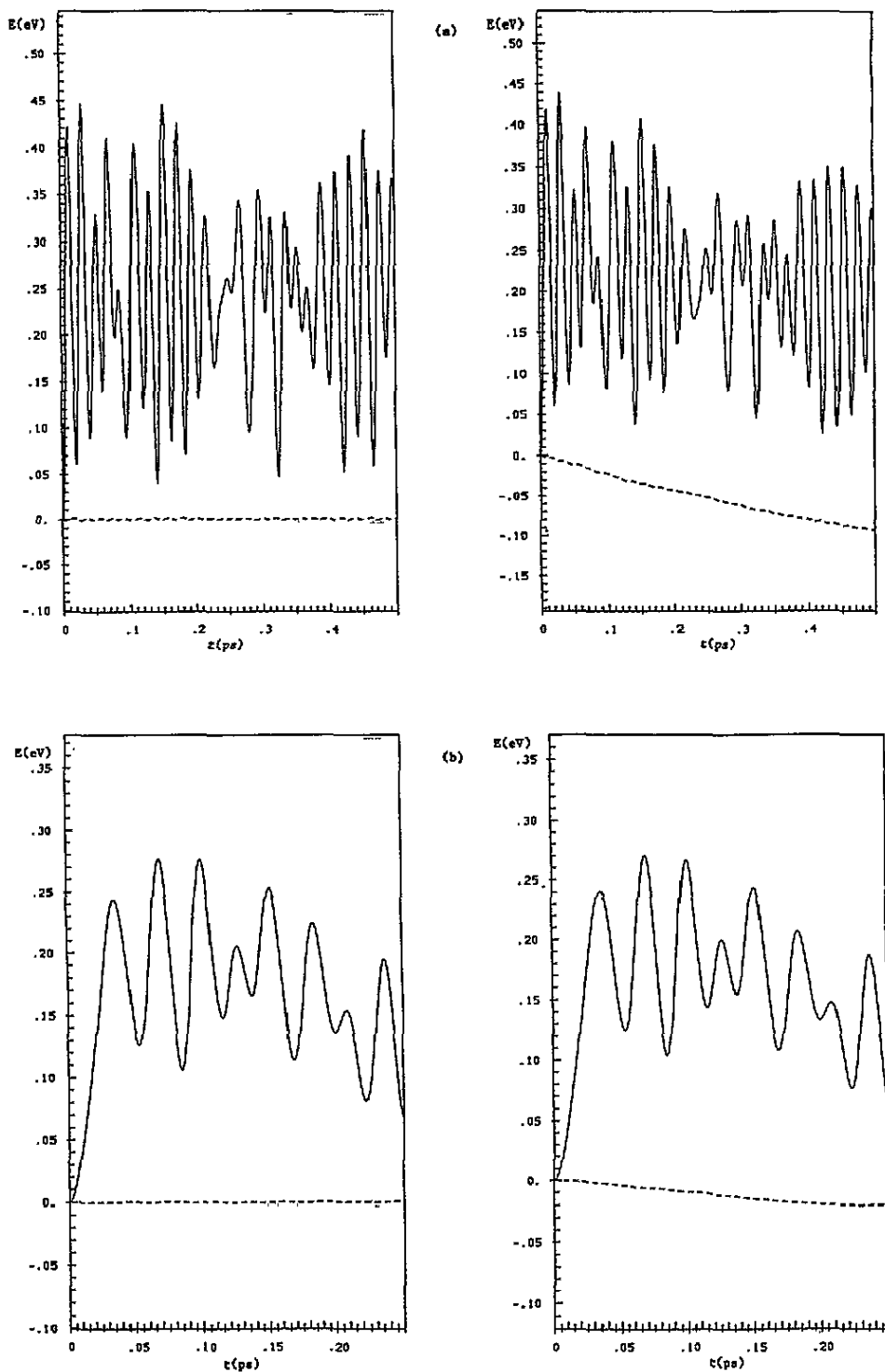


Figure 4. Time evolution of the total kinetic energy (solid line) and the error in total energy (dashed line) for simulations in a chain with 11 units, computed with the adiabatic (left) and the  $|\Phi_2\rangle$  model (right) at  $T = 0 \text{ K}$  for (a)  $u_0 = 0.03 \text{ \AA}$ , (b)  $u_0 = 0.2 \text{ \AA}$ , (c)  $u_0 = 0.4 \text{ \AA}$ .

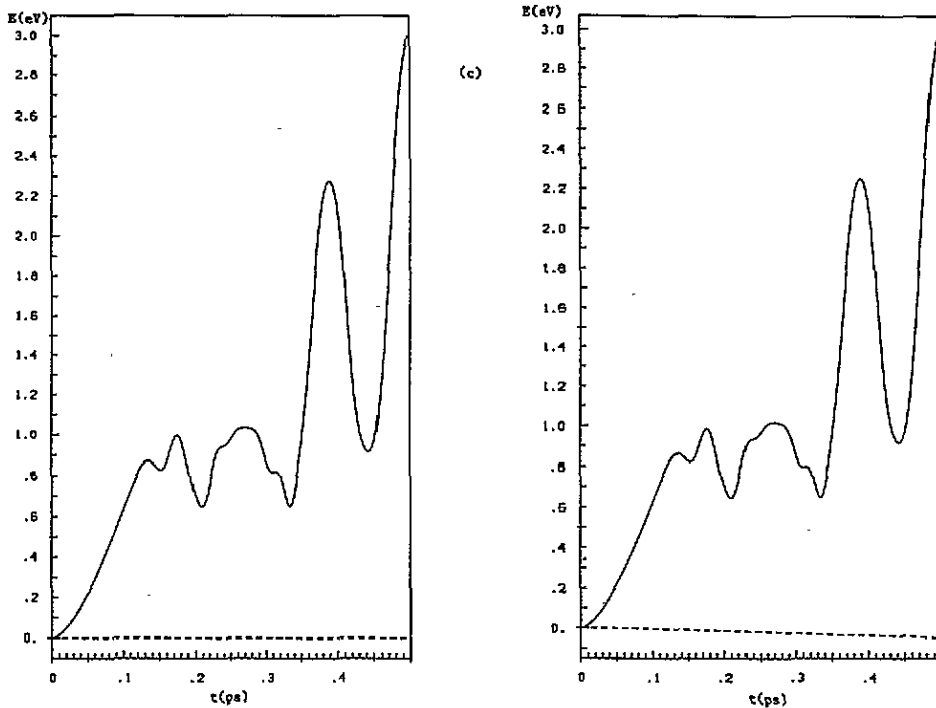


Figure 4. (Continued)

in both cases, whose inverse is 2.04 ps ( $u_0 = 0.03 \text{ \AA}$ ) and 0.4 ps ( $u_0 = 0.4 \text{ \AA}$ ). In figure 12 we show the time average, given for a time-step  $t_l$  by

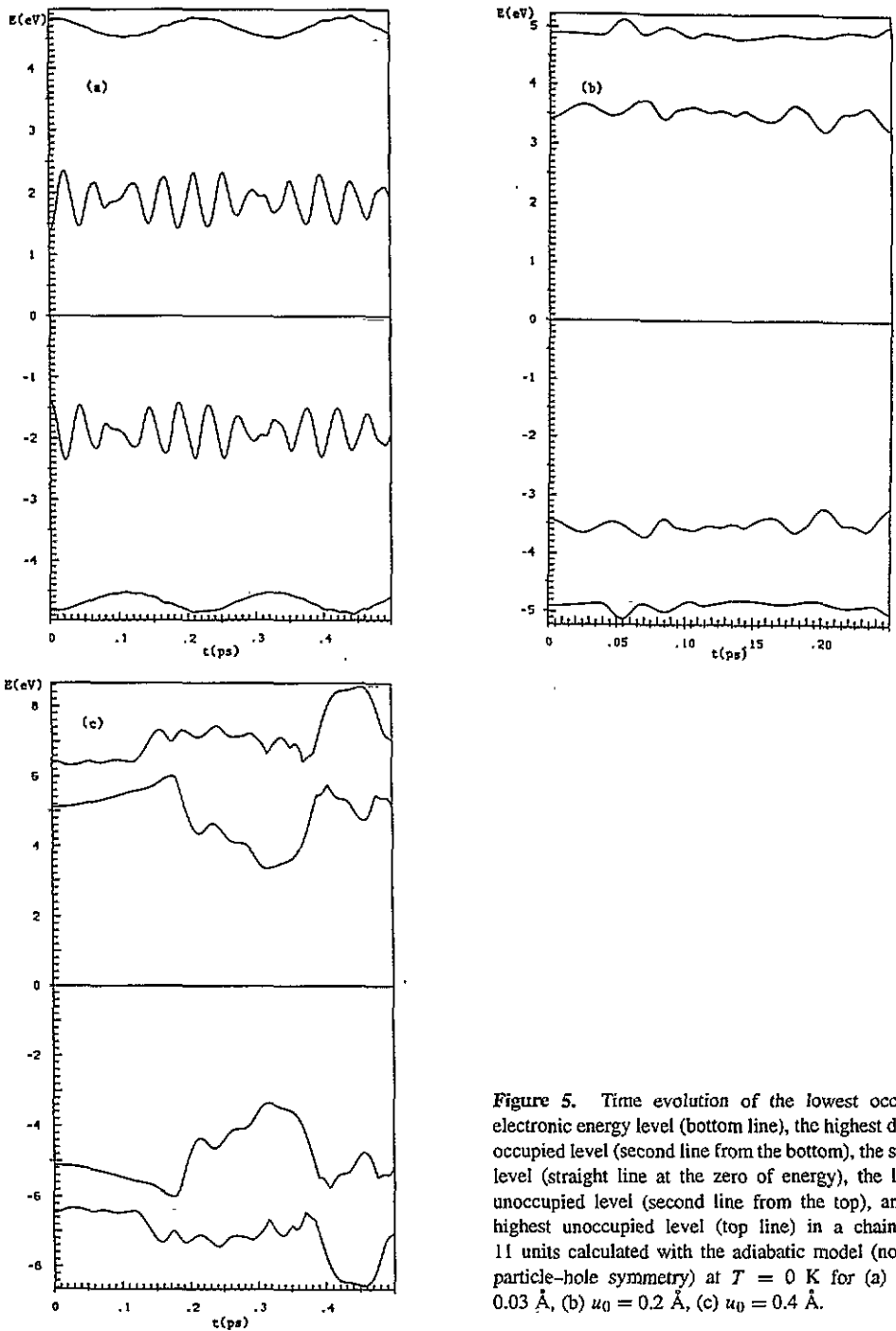
$$A(t_l) = \left\langle \frac{1}{2M} \sum_n p_n^2 \right\rangle / \frac{1}{2} N k_B T = \frac{1}{l} \sum_{k=1}^l \frac{1}{2M} \sum_n p_n^2(t_k) / \frac{1}{2} N k_B T \quad (72)$$

where  $l$  and  $k$  count the time-steps calculated explicitly. As is well known, this has to approach unity in thermal equilibrium for a decoupled lattice. Since the kinetic energy due to soliton movement remains approximately constant,  $A(t)$  has to approach a constant which is equal to  $1 + E_s / (0.5 N k_B T)$ , where  $E_s$  is the time average of the kinetic energy of the soliton, if it is stable. As we see from the plots such a constant value is reached approximately only for the  $|\Phi_2\rangle$  model in case of the smaller bond-alternation parameter. In contrast to the numerical results one would expect that for the larger bond-alternation parameter the thermal equilibrium should be reached faster. However, here we have a small, compact soliton which is quite resistant against thermal fluctuations and one would expect that the presence of this soliton slows down the thermal equilibration of the system. Thus it seems that our model for thermal effects, which is based on a thermal equilibration of the decoupled lattice prior to the soliton start, should overcome this problem of large equilibration times. Further it seems to be more realistic to have the system in thermal equilibrium already prior to the start of the soliton movement.

### 8. Conclusion

We have for the first time derived equations of motion for the SSH Hamiltonian of *trans-*





**Figure 5.** Time evolution of the lowest occupied electronic energy level (bottom line), the highest doubly occupied level (second line from the bottom), the soliton level (straight line at the zero of energy), the lowest unoccupied level (second line from the top), and the highest unoccupied level (top line) in a chain with 11 units calculated with the adiabatic model (note the particle-hole symmetry) at  $T = 0$  K for (a)  $u_0 = 0.03$  Å, (b)  $u_0 = 0.2$  Å, (c)  $u_0 = 0.4$  Å.

polyacetylene, i.e. for electrons coupled to lattice phonons, using *ansatz* states similar to those introduced by Davydov for the case of high-energy vibrations coupled to lattice phonons. We used a  $|\Phi_0\rangle$  *ansatz* in the spirit of Davydov's  $|D_1\rangle$  state, where the quantum nature of the lattice is accounted for. The application of the quantum-mechanical  $|\Phi_0\rangle$

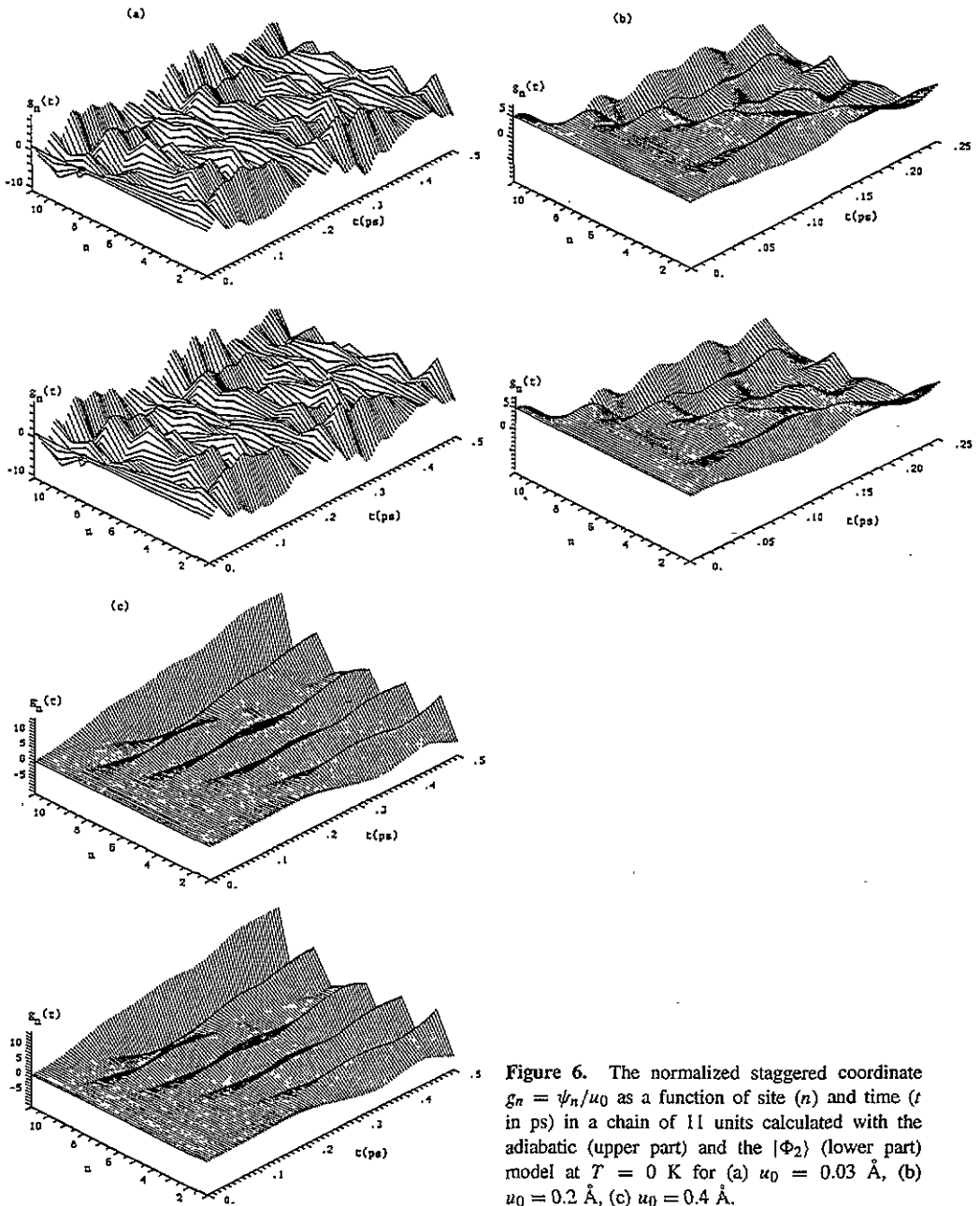


Figure 6. The normalized staggered coordinate  $g_n = \psi_n/u_0$  as a function of site ( $n$ ) and time ( $t$  in ps) in a chain of 11 units calculated with the adiabatic (upper part) and the  $|\Phi_2\rangle$  (lower part) model at  $T = 0$  K for (a)  $u_0 = 0.03 \text{ \AA}$ , (b)  $u_0 = 0.2 \text{ \AA}$ , (c)  $u_0 = 0.4 \text{ \AA}$ .

ansatz state which takes into account quantum fluctuations in the lattice is in progress, and the results of these calculations will be the subject of a forthcoming paper.

Our calculations using the  $|\Phi_2\rangle$  model show that the dynamics are essentially the same in this model and in the classical one, no matter how small the soliton is. Note that the larger the lattice dimerization parameter chosen, the smaller the soliton. Thus treating all electrons on equal footing leads to results different from those of Rukh *et al* [22] who treated only one electron explicitly and found that the soliton becomes unstable, when its width is

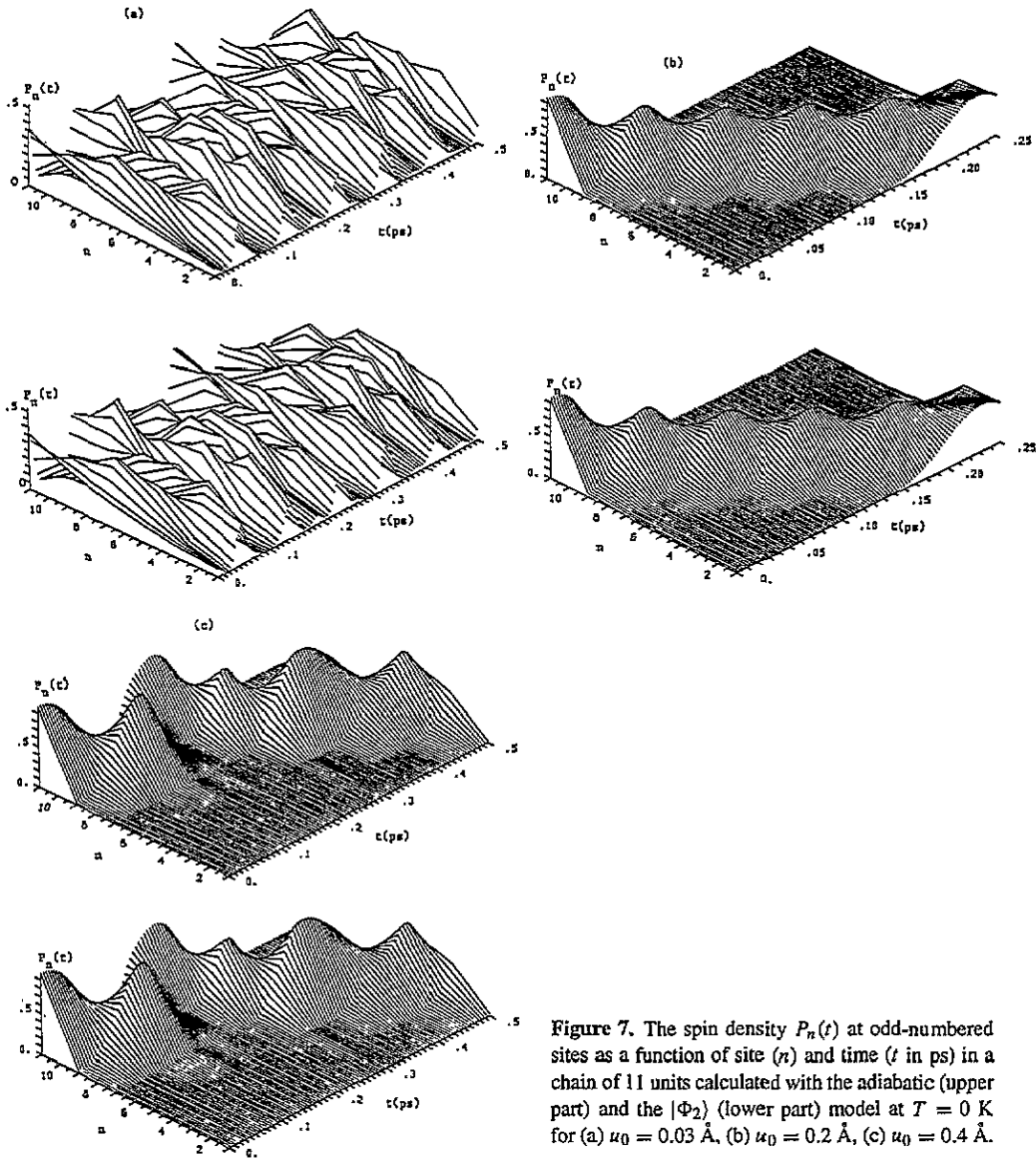
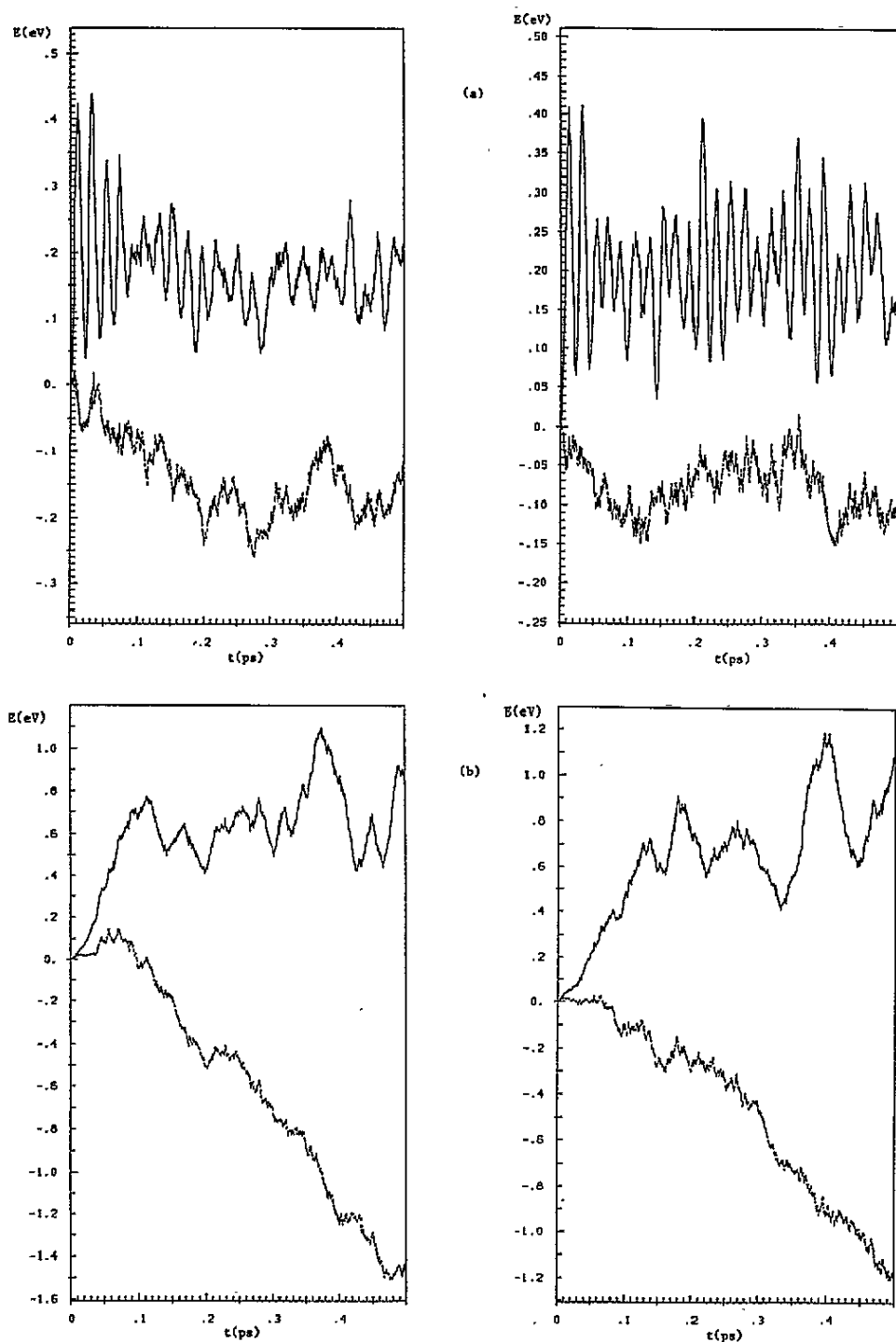


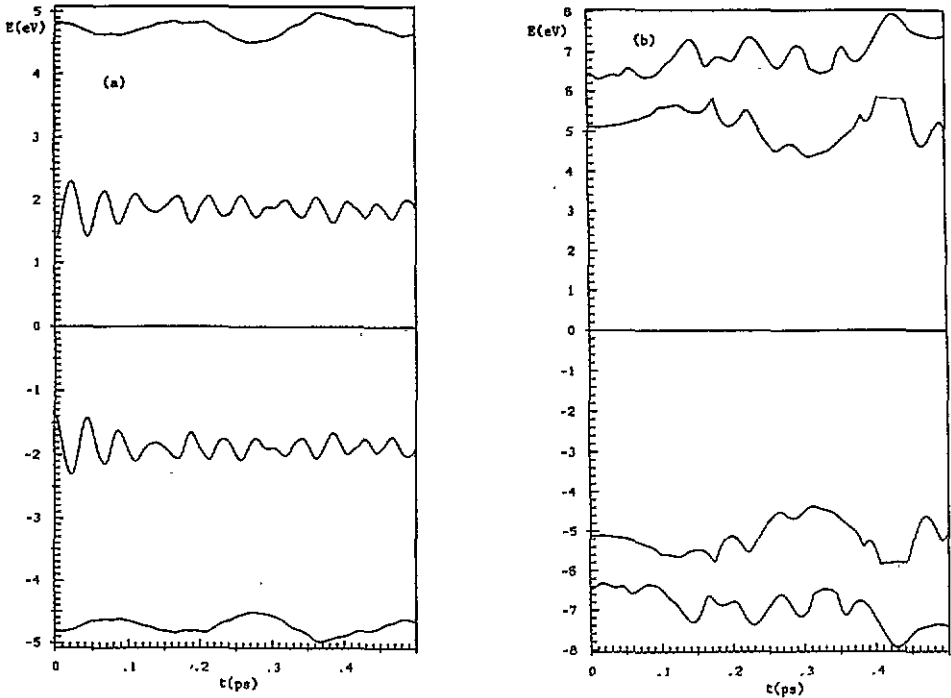
Figure 7. The spin density  $P_n(t)$  at odd-numbered sites as a function of site ( $n$ ) and time ( $t$  in ps) in a chain of 11 units calculated with the adiabatic (upper part) and the  $|\Phi_2\rangle$  (lower part) model at  $T = 0$  K for (a)  $u_0 = 0.03 \text{ \AA}$ , (b)  $u_0 = 0.2 \text{ \AA}$ , (c)  $u_0 = 0.4 \text{ \AA}$ .

smaller or equal to roughly one lattice site. Thus the effective electron–electron interactions are still implicitly present in this approximation via the lattice equations, since the lattice interacts with all electrons simultaneously. The results obtained with the Langevin model for temperature effects suggest that this model is not appropriate for PA in the SSH model, most probably due to the large electron–lattice interactions.

The obvious next step after completion of these calculations is the explicit inclusion of electron–electron interactions in the model. For this purpose we need a representation of the two electron integrals in terms of phonon creation and annihilation operators. These are given by (SI units)



**Figure 8.** Time evolution of the total kinetic energy (solid line) and the error in total energy (dashed line) for simulations in a chain with 11 units, computed with the adiabatic (left) and the  $|\Phi_2\rangle$  model (right) at  $T = 300 \text{ K}$  (random-forces-dissipation model) for (a)  $u_0 = 0.03 \text{ \AA}$  ( $Nk_B T = 0.1293 \text{ eV}$ ,  $\Gamma = \nu_{\min} = 0.4909 \text{ ps}^{-1}$ ,  $\sigma = 0.6888 \text{ (eV \AA)}^2$ ), (b)  $u_0 = 0.40 \text{ \AA}$  ( $Nk_B T = 0.1293 \text{ eV}$ ,  $\Gamma = \nu_{\min} = 2.8873 \text{ ps}^{-1}$ ,  $\sigma = 4.0514 \text{ (eV \AA)}^2$ ).



**Figure 9.** Time evolution of the lowest occupied electronic energy level (bottom line), the highest doubly occupied level (second line from the bottom), the soliton level (straight line at the zero of energy), the lowest unoccupied level (second line from the top), and the highest unoccupied level (top line) in a chain with 11 units calculated with the adiabatic model (note the particle-hole symmetry) at  $T = 300$  K (random-forces-dissipation model) for (a)  $u_0 = 0.03 \text{ \AA}$  ( $Nk_B T = 0.1293 \text{ eV}$ ,  $\Gamma = \nu_{\min} = 0.4909 \text{ ps}^{-1}$ ,  $\sigma = 0.6888 \text{ (eV \AA)}^2$ ), (b)  $u_0 = 0.40 \text{ \AA}$  ( $Nk_B T = 0.1293 \text{ eV}$ ,  $\Gamma = \nu_{\min} = 2.8873 \text{ ps}^{-1}$ ,  $\sigma = 4.0514 \text{ (eV \AA)}^2$ ).

$$\gamma_{nm} = b \left[ \left( \frac{2b}{\gamma_n + \gamma_m} \right)^2 + R_{nm}^2 \right]^{-1/2} \quad b = \frac{e^2}{4\pi\epsilon_0} \tag{73}$$

where  $e$  is the elementary charge,  $\epsilon_0$  the dielectric constant of the vacuum, sometimes also called the electric field constant ( $\epsilon_0 = 8.854 \text{ II} \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1}$ ), and the  $\gamma_n$  are the so-called on-site Coulomb repulsion parameters of the atom at site  $n$ , usually calculated as the difference between the ionization potential and the electron affinity of that atom.  $R_{nm}$  is the distance between sites  $n$  and  $m$  and is given by

$$R_{nm} = \sqrt{[(n - m)a_0 + u_n - u_m]^2 + [(-1)^n - (-1)^m]^2 y_0^2} \tag{74}$$

where  $a_0$  is the lattice constant of the equidistant chain and  $y_0$  the distance of the sites from the chain axis which is defined by the centre points of the CC bonds.

Since the displacements are very small compared to the distance between the atoms in the equidistant chain, we can expand the integrals in a Taylor series in the displacements and truncate the series after the linear term to be consistent with the truncation of the similar expansion for the resonance integrals. Thus we obtain

$$\gamma_{nm} = \gamma_{nm}^{(0)} + \frac{\partial \gamma_{nm}}{\partial u_n} \Big|_{u_n=u_m=0} u_n + \frac{\partial \gamma_{nm}}{\partial u_m} \Big|_{u_n=u_m=0} u_m \quad \gamma_{nm}^{(0)} = \gamma_{nm}(u_n = u_m = 0). \tag{75}$$

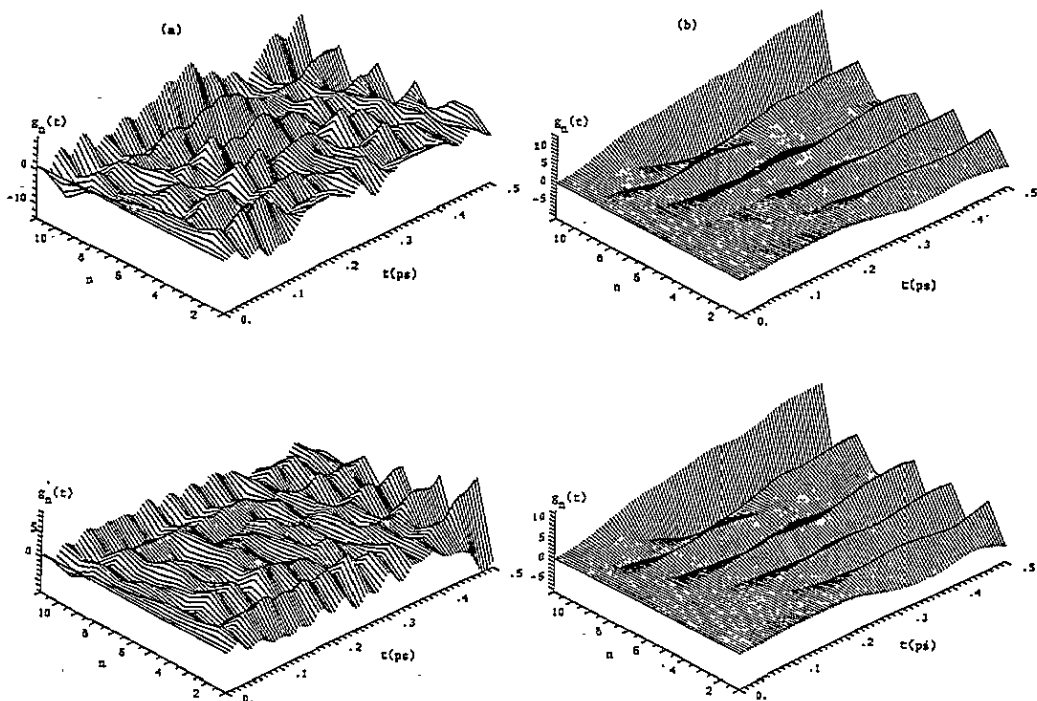


Figure 10. The normalized staggered coordinate  $g_n = \psi_n/u_0$  as a function of site ( $n$ ) and time ( $t$  in ps) in a chain of 11 units calculated with the adiabatic (upper part) and the  $|\Phi_2\rangle$  (lower part) model at  $T = 300$  K (random forces-dissipation model) for (a)  $u_0 = 0.03$  Å ( $Nk_B T = 0.1293$  eV,  $\Gamma = \nu_{\text{min}} = 0.4909$  ps $^{-1}$ ,  $\sigma = 0.6888$  (eV Å) $^2$ ), (b)  $u_0 = 0.40$  Å ( $Nk_B T = 0.1293$  eV,  $\Gamma = \nu_{\text{min}} = 2.8873$  ps $^{-1}$ ,  $\sigma = 4.0514$  (eV Å) $^2$ ).

The derivatives are

$$a \equiv \left. \frac{\partial \gamma_{nm}}{\partial u_n} \right|_{u_n=u_m=0} = -\frac{(\gamma_{nm}^{(0)})^3}{b^2} (n-m) a_0 = -\left. \frac{\partial \gamma_{nm}}{\partial u_m} \right|_{u_n=u_m=0} \quad (76)$$

and thus

$$\gamma_{nm} = \gamma_{nm}^{(0)} + a(u_n - u_m). \quad (77)$$

In table 1 we compare this linear approximation for a next-neighbour integral with the exact values computed from the Ohno formula for different displacements. It is obvious from the table that in the region of displacements which usually occur in simulations the linear approximation agrees satisfactorily with the exact Ohno formula.

The two-electron operator which has to be added to the Hamiltonian is

$$\hat{H}_2 = \frac{1}{2} \sum_{\sigma_1, \sigma_2} \sum_{nm} \gamma_{nm} \hat{c}_{n\sigma_1}^+ \hat{c}_{m\sigma_2}^+ \hat{c}_{m\sigma_2} \hat{c}_{n\sigma_1}. \quad (78)$$

Substitution of the expansion of the  $\gamma$  values leads then to

$$\hat{H}_2 = \frac{1}{2} \sum_{\sigma_1, \sigma_2} \sum_{nm} [\gamma_{nm}^{(0)} + a(\hat{u}_n - \hat{u}_m)] \hat{c}_{n\sigma_1}^+ \hat{c}_{m\sigma_2}^+ \hat{c}_{m\sigma_2} \hat{c}_{n\sigma_1}. \quad (79)$$

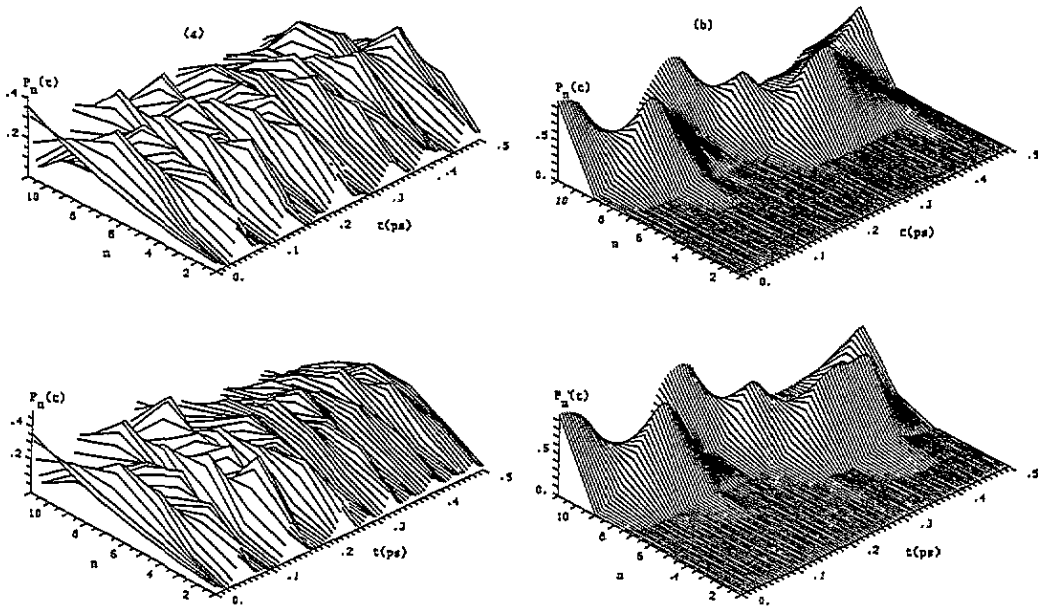


Figure 11. The spin density  $P_n(t)$  at odd-numbered sites as a function of site ( $n$ ) and time ( $t$  in ps) in a chain of 11 units calculated with the adiabatic (upper part) and the  $|\Phi_2\rangle$  (lower part) model at  $T = 300$  K (random forces-dissipation model) for (a)  $u_D = 0.03$  Å ( $Nk_B T = 0.1293$  eV,  $\Gamma = \nu_{\min} = 0.4909$  ps $^{-1}$ ,  $\sigma = 0.6388$  (eV Å) $^2$ ), (b)  $u_D = 0.40$  Å ( $Nk_B T = 0.1293$  eV,  $\Gamma = \nu_{\min} = 2.8873$  ps $^{-1}$ ,  $\sigma = 4.0514$  (eV Å) $^2$ ).

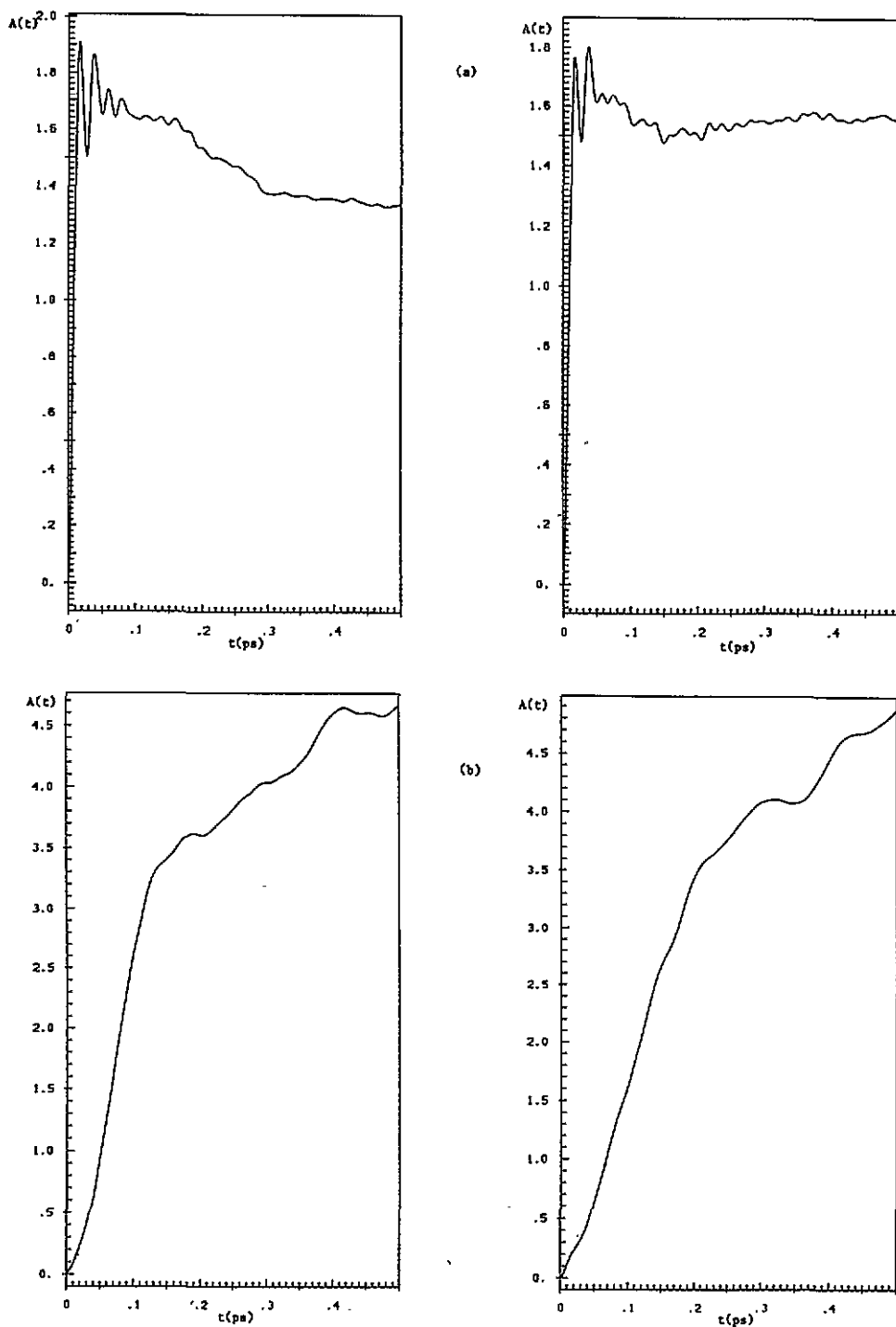
The equations of motion, derived from an SSH Hamiltonian including in addition this term together with the  $|\Phi_0\rangle$  ansatz could be used to define effective electron-electron interaction parameters which incorporate indirect interactions between the electrons. These effective parameters, depending on the interplay between electron-electron and electron-phonon interactions, could give rise to an effective attraction between the electrons. This would be an analogue to the 'negative- $U$ ' models, discussed in connection with high- $T_c$  superconductors; however, the effective parameters would be well defined and the role the phonons play would be more obvious. However, it is clear that in  $t$ -PA the direct Coulomb interactions would play the major role, because it is known that in  $t$ -PA bipolarons are unstable against charged solitons which interact repulsively. But in other conducting polymers, bipolarons are well known as charge carriers. Thus in such systems the effective attraction between electrons due to electron-phonon interaction is stronger than the bare Coulomb repulsion.

The displacement operators can be transformed to

$$\hat{u}_n - \hat{u}_m = \hat{q}_n - \hat{q}_m - (n - m) \frac{A}{K} \Rightarrow \gamma_{nm}^{(0)} + a(\hat{u}_n - \hat{u}_m) = \bar{\gamma}_{nm}^{(0)} + a(\hat{q}_n - \hat{q}_m) \quad (80)$$

$$\bar{\gamma}_{nm}^{(0)} \equiv \gamma_{nm}^{(0)} - (n - m) \frac{A}{K} a$$

as discussed in appendix A. Transformation to phonon operators gives then finally



**Figure 12.** Time average of the total kinetic energy of the lattice divided by  $0.5Nk_B T(A(t))$  as a function of time at  $T = 300$  K (random-forces-dissipation model) calculated with the adiabatic (left) and the  $|\Phi_2\rangle$  model (right) for (a)  $u_0 = 0.03 \text{ \AA}$  ( $Nk_B T = 0.1293 \text{ eV}$ ,  $\Gamma = \nu_{\min} = 0.4909 \text{ ps}^{-1}$ ,  $\sigma = 0.6888 \text{ (eV \AA)}^2$ ), (b)  $u_0 = 0.40 \text{ \AA}$  ( $Nk_B T = 0.1293 \text{ eV}$ ,  $\Gamma = \nu_{\min} = 2.8873 \text{ ps}^{-1}$ ,  $\sigma = 4.0514 \text{ (eV \AA)}^2$ ).



**Table 1.** Exact ( $\gamma_{12}$ ) and linearly approximated ( $\gamma_{12}^a$ ) values of the two-electron integral (Ohno approximation) between two neighbouring sites ( $\gamma_0 = 11.25$  eV,  $b = 14.39$  eV Å,  $a_0 = 1.2$  Å,  $\gamma_0 = 0.35$  Å,  $u_0 = 0.03$  Å) as a function of  $u$  for the cases (A)  $u_1 = u$ ,  $u_2 = -u_0$  and (B)  $u_1 = -u_2 = u$  ( $u$  is given in Å and the  $\gamma$  values are in eV).

$u$	$\gamma_{12}$ (A)	$\gamma_{12}^a$ (A)	$\gamma_{12}$ (B)	$\gamma_{12}^a$ (B)
-0.06	10.04	10.03	9.52	9.48
-0.05	10.10	10.10	9.63	9.60
-0.04	10.16	10.16	9.75	9.72
-0.03	10.22	10.22	9.86	9.85
-0.02	10.28	10.28	9.98	9.97
-0.01	10.35	10.34	10.10	10.10
0.00	10.41	10.41	10.22	10.22
0.01	10.47	10.47	10.35	10.34
0.02	10.54	10.53	10.47	10.47
0.03	10.60	10.59	10.60	10.59
0.04	10.67	10.65	10.74	10.72
0.05	10.74	10.72	10.87	10.84
0.06	10.80	10.78	11.01	10.96

$$\begin{aligned} \hat{H}_2 &= \frac{1}{2} \sum_{\sigma_1, \sigma_2} \sum_{nm} [\bar{\gamma}_{nm}^{(0)} + a(\hat{q}_n - \hat{q}_m)] \hat{c}_{n\sigma_1}^{\dagger-} \hat{c}_{m\sigma_2}^{\dagger+} \hat{c}_{m\sigma_2} \hat{c}_{n\sigma_1} \\ &= \frac{1}{2} \sum_{\sigma_1, \sigma_2} \sum_{nm} \left[ \bar{\gamma}_{nm}^{(0)} + \sum_k \hbar\omega_k A_{nmk} (\hat{b}_k^{\dagger+} + \hat{b}_k) \right] \hat{c}_{n\sigma_1}^{\dagger+} \hat{c}_{m\sigma_2}^{\dagger+} \hat{c}_{m\sigma_2} \hat{c}_{n\sigma_1} \end{aligned} \quad (81)$$

$$A_{nmk} \equiv \frac{a}{\omega_k} \sqrt{\frac{1}{2M\hbar\omega_k}} (V_{nk} - V_{mk}).$$

The expectation value of the two-electron operator calculated with the  $|\Phi_0\rangle$  *ansatz* state has to be added to that of the one-particle operator. Note that in this case we have to build a Slater determinant from the one-particle states and we have to introduce different orbitals for different spins for states which are not singlets. Further, in PPP theory the Coulomb repulsion between the ionic cores appears explicitly in the total energy in the form

$$H_I = \frac{1}{2} \sum_{nm} z_n z_m \gamma_{nm} (1 - \delta_{nm}) \quad (82)$$

where  $z_n$  is the charge of the ionic core  $n$ , i.e. in the  $t$ -PA case we have  $\text{CH}^+$  ions and consequently  $z_n = 1$ . This term could be absorbed into  $V_\sigma$ , leading to another minimum geometry on which then the phonon operators would have to be based. Alternatively one can expand the integrals in equation (82) and add the new operator to the Hamiltonian:

$$\hat{H}_I = \frac{1}{2} \sum_{nm} z_n z_m \left[ \bar{\gamma}_{nm}^{(0)} + \sum_k \hbar\omega_k A_{nmk} (\hat{b}_k^{\dagger+} + \hat{b}_k) \right] (1 - \delta_{nm}). \quad (83)$$

In this way electron–electron interactions can be included in the model. In this term already the modification of the electron–electron interactions due to phonons is obvious. The electrons do not interact as bare particles any more, but the interaction parameters are modified by phonon terms. The actual strength of this modification, however, can be only calculated after introduction of the *ansatz* state. Note, that according to the previous discussions already from the one-electron terms effective electron–electron interactions of an indirect nature show up due to the coupling to the lattice phonons.

Finally we want to point out the differences of our model from the electrosoliton concept of Davydov [35], introduced for the electron transport in proteins, and later extended to a bisoliton concept in the high- $T_c$  materials. The SSH Hamiltonian for *t*-PA contains the electron-phonon interaction in the terms off-diagonal in the electron creation and annihilation operators, while in Davydov's theory for proteins it appears in terms diagonal in these operators, which is an *ansatz* which cannot be used for *t*-PA, since here the resonance integrals depend strongly on geometry, while the dependence of the diagonal Hückel parameters on it is, if present at all, very weak. Further in Davydov's model only one electron is treated explicitly and the *ansatz* is a  $|D_2\rangle$  state only. However, the case of the Davydov Hamiltonian and the electrosoliton concept is dealt with in paper II of this series.

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**Appendix A. Lattice phonons**

To define the lattice phonons we have to start from the potential of the decoupled lattice as a function of the displacement coordinates  $u_n$ , which are measured relative to an equidistant chain of length  $(N - 1)a_0$  with  $a_0 = 1.212 \text{ \AA}$ , leading with a dimerization parameter  $u_0 = 0.03 \text{ \AA}$  to the geometry of undoped polyacetylene:

$$V = \frac{K}{2} \sum_{n=1}^{N-1} (u_n - u_{n+1})^2 - A \sum_{n=1}^{N-1} (u_n - u_{n+1}) = \frac{K}{2} \sum_{n=1}^{N-1} (u_n - u_{n+1})^2 - A(u_1 - u_N). \quad (A1)$$

For definition of the phonons we have to find the minimum geometry  $u_n^e$  of this potential. Thus we have to differentiate the potential with respect to  $u_n$ :

$$\begin{aligned} \frac{\partial V}{\partial u_1} &= K(u_1 - u_2) - A & \frac{\partial V}{\partial u_n} &= K(-u_{n-1} + 2u_n - u_{n+1}) \\ \frac{\partial V}{\partial u_N} &= -K(u_{N-1} - u_N) + A. \end{aligned} \quad (A2)$$

Now we have to solve the system of equations

$$\left. \frac{\partial V}{\partial u_n} \right|_{u_n=u_n^e} = 0. \quad (A3)$$

From these equations we obtain

$$u_n^e = u_1^e - (n - 1) \frac{A}{K} \quad (A4)$$

corresponding to the equidistant chain of length  $(N - 1)(a_0 - A/K)$ . The parameter  $u_1^e$  can be chosen arbitrarily and just corresponds to a translation of the whole chain which does not change its potential energy. Now we define new displacements relative to the equilibrium geometry  $q_n = u_n - u_n^e$  given by

$$q_n = u_n + (n - 1)\frac{A}{K} - u_1^e \quad u_n = q_n - (n - 1)\frac{A}{K} + u_1^e. \tag{A5}$$

Thus we have  $u_n - u_{n+1} = q_n - q_{n+1} + (A/K)$  and we can define a renormalized hopping integral  $\beta$  via

$$t_{n,n+1} = \beta^0 - (u_n - u_{n+1})\alpha = \beta^0 - \frac{A}{K}\alpha - (q_n - q_{n+1})\alpha \equiv \beta - (q_n - q_{n+1})\alpha \tag{A6}$$

with  $\beta = \beta^0 - (A/K)\alpha$ . Substitution of  $u_n - u_{n+1}$  into the potential yields

$$V = \frac{K}{2} \sum_{n=1}^{N-1} \left( q_n - q_{n+1} + \frac{A}{K} \right)^2 - A \sum_{n=1}^{N-1} \left( q_n - q_{n+1} + \frac{A}{K} \right) = \frac{K}{2} \sum_{n=1}^{N-1} (q_n - q_{n+1})^2 + C \tag{A7}$$

with  $C = -(N - 1)A^2/(2K)$ . The phonon operators are now defined in the usual way with respect to the displacements  $q_n = 0$ . Since for the momenta  $p_n = M(du_n/dt) = M(dq_n/dt)$  holds, we obtain

$$\hat{q}_n = \sum_k \sqrt{\hbar/(2M\omega_k)} V_{nk} (\hat{b}_k^+ + \hat{b}_k) \quad \hat{p}_n = i \sum_k \sqrt{M\hbar\omega_k/2} V_{nk} (\hat{b}_k^+ - \hat{b}_k). \tag{A8}$$

The translation  $u_1^e$  can be determined such that the starting geometry  $\{q_n^{(0)}\}$  has its centre of mass at zero. From the starting geometry  $\{u_n^{(0)}\}$  we obtain finally our transformation

$$q_n = u_n + [n - \frac{1}{2}(N + 1)]\frac{A}{K} - \frac{1}{N} \sum_m u_m^{(0)}. \tag{A9}$$

**Appendix B. Derivation of the Lagrangian for a three-site system**

The general structure of the different terms in the Lagrangian can be most easily visualized by deriving them for a simple three-site, three-electron system. In this case our *ansatz* state, formulated for spin orbitals, i.e. each orbital is occupied by one electron and contains a spin function, which we do not write out explicitly, is given by

$$|\Phi\rangle = \sum_{nml} c_{n1} c_{n2} c_{l3} \hat{c}_{n1}^+ \hat{c}_{m2}^+ \hat{c}_{l3}^+ |0\rangle_e |\beta_{nml}\rangle \tag{B1}$$

$$|\beta_{nml}\rangle = \exp \left[ -\frac{1}{2} \sum_k |b_{nk1} + b_{mk2} + b_{lk3}|^2 \right] \exp \left[ \sum_k (b_{nk1} + b_{mk2} + b_{lk3}) \hat{b}_k^+ \right] |0\rangle_p$$

where  $\hat{c}_{nj}^+$  creates an electron at site  $n$  in spin orbital  $j$ . The Lagrangian is given by

$$L = \frac{i\hbar}{2} \left( \left\langle \Phi \left| \frac{\partial}{\partial t} \Phi \right. \right\rangle - \left\langle \frac{\partial}{\partial t} \Phi \left| \Phi \right. \right\rangle \right) - \langle \Phi | \hat{H} | \Phi \rangle. \tag{B2}$$

The time derivative of  $|\Phi\rangle$  can be straightforwardly computed to

$$\begin{aligned} \left| \frac{\partial}{\partial t} \Phi \right\rangle = & \sum_{nml} \sum_k \{ \dot{c}_{n1} c_{m2} c_{l3} + c_{n1} \dot{c}_{m2} c_{l3} + c_{n1} c_{m2} \dot{c}_{l3} \\ & - \frac{1}{2} c_{n1} c_{m2} c_{l3} [(\dot{b}_{nk1} + \dot{b}_{mk2} + \dot{b}_{lk3})(b_{nk1}^* + b_{mk2}^* + b_{lk3}^*) \\ & + (b_{nk1} + b_{mk2} + b_{lk3})(\dot{b}_{nk1}^* + \dot{b}_{mk2}^* + \dot{b}_{lk3}^*)] \\ & + c_{n1} c_{m2} c_{l3} (\dot{b}_{nk1} + \dot{b}_{mk2} + \dot{b}_{lk3}) \hat{b}_k^+ \} \hat{c}_{n1}^+ \hat{c}_{m2}^+ \hat{c}_{l3}^+ |0\rangle_e |\beta_{nml}\rangle. \end{aligned} \tag{B3}$$

The expectation value formed with  $\langle \Phi |$  and using

$$\langle \beta_{nml} | \hat{b}_k^+ | \beta_{nml} \rangle = b_{nk1}^* + b_{mk2}^* + b_{lk3}^* \tag{B4}$$

is given then by

$$\begin{aligned} \left\langle \Phi \left| \frac{\partial}{\partial t} \Phi \right. \right\rangle = & \sum_{nml} [\dot{c}_{n1} c_{n1}^* |c_{m2}|^2 |c_{l3}|^2 + |c_{n1}|^2 \dot{c}_{m2} c_{m2}^* |c_{l3}|^2 + |c_{n1}|^2 |c_{m2}|^2 \dot{c}_{l3} c_{l3}^*] \\ & + \frac{1}{2} \sum_{nml} |c_{n1}|^2 |c_{m2}|^2 |c_{l3}|^2 \sum_k [(\dot{b}_{nk1} + \dot{b}_{mk2} + \dot{b}_{lk3})(b_{nk1}^* + b_{mk2}^* + b_{lk3}^*) \\ & - (\dot{b}_{nk1}^* + \dot{b}_{mk2}^* + \dot{b}_{lk3}^*)(b_{nk1} + b_{mk2} + b_{lk3})]. \end{aligned} \tag{B5}$$

Now we can write the first term as a single summation over spin orbitals  $j$  and the second term can be split into six summations according to the time derivatives occurring. Further in these terms we interchange summation indices, and finally, with the definition

$$X_j \equiv \prod_{j' \neq j} \left( \sum_n |c_{nj'}|^2 \right) \tag{B6}$$

we obtain

$$\begin{aligned} \left\langle \Phi \left| \frac{\partial}{\partial t} \Phi \right. \right\rangle = & \sum_{nj} \dot{c}_{nj} c_{nj}^* X_j + \frac{1}{2} \sum_k \left\{ \sum_{nml} |c_{n1}|^2 \dot{b}_{nk1} |c_{m2}|^2 |c_{l3}|^2 (b_{nk1}^* + b_{mk2}^* + b_{lk3}^*) \right. \\ & + \sum_{nml} |c_{n2}|^2 \dot{b}_{nk2} |c_{m1}|^2 |c_{l3}|^2 (b_{mk1}^* + b_{nk2}^* + b_{lk3}^*) \\ & \left. + \sum_{nml} |c_{n3}|^2 \dot{b}_{nk3} |c_{l1}|^2 |c_{m2}|^2 (b_{lk1}^* + b_{mk2}^* + b_{nk3}^*) - (cc) \right\}. \end{aligned} \tag{B7}$$

Here the symbol CC in the curly brackets denotes the complex conjugate of the other terms in the curly brackets. Now we look at the first term in curly brackets and split into three summations (T1):

$$\begin{aligned} T1 = & \sum_n |c_{n1}|^2 \dot{b}_{nk1} b_{nk1}^* \sum_m |c_{m2}|^2 \sum_l |c_{l3}|^2 \\ & + \sum_n |c_{n1}|^2 \dot{b}_{nk1} \left[ \sum_m |c_{m2}|^2 b_{mk2} \sum_l |c_{l3}|^2 + \sum_m |c_{m3}|^2 b_{mk3} \sum_l |c_{l2}|^2 \right] \\ = & \sum_n |c_{n1}|^2 \dot{b}_{nk1} b_{nk1}^* \left[ X_1^* + \sum_m \sum_{j' \neq 1} |c_{mj'}|^2 b_{mkj'} X_{1j'} \right]. \end{aligned} \tag{B8}$$

We obtain such a term from each spin orbital and thus we have

$$\begin{aligned} \left\langle \Phi \left| \frac{\partial}{\partial t} \Phi \right. \right\rangle &= \sum_{nj} \dot{c}_{nj} c_{nj}^* X_j + \frac{1}{2} \sum_k \left\{ \sum_{nj} |c_{nj}|^2 \dot{b}_{nkj} b_{nkj}^* X_j \right. \\ &\quad \left. + \sum_{nj} |c_{nj}|^2 \dot{b}_{nkj} \sum_m \sum_{j' \neq j} |c_{mj'}|^2 b_{mkj'}^* X_{jj'} - (\text{CC}) \right\} \end{aligned} \quad (\text{B9})$$

with

$$X_{jj'} \equiv \prod_{j'' \neq j, j'} \left( \sum_n |c_{nj''}|^2 \right). \quad (\text{B10})$$

Therefore with

$$\left\langle \frac{\partial}{\partial t} \Phi \middle| \Phi \right\rangle = \left( \left\langle \Phi \middle| \frac{\partial}{\partial t} \Phi \right\rangle \right)^* \quad (\text{B11})$$

we obtain

$$\begin{aligned} \frac{i\hbar}{2} \left( \left\langle \Phi \middle| \frac{\partial}{\partial t} \Phi \right\rangle - \left\langle \frac{\partial}{\partial t} \Phi \middle| \Phi \right\rangle \right) &= \frac{i\hbar}{2} \sum_{nj} (\dot{c}_{nj} c_{nj}^* - c_{nj}^* \dot{c}_{nj}) X_j \\ &\quad + \frac{i\hbar}{2} \sum_k \left\{ \sum_{nj} |c_{nj}|^2 \dot{b}_{nkj} \left[ b_{nkj}^* X_j + \sum_m \sum_{j' \neq j} |c_{mj'}|^2 b_{mkj'}^* X_{jj'} \right] \right. \\ &\quad \left. - \sum_{nj} |c_{nj}|^2 \dot{b}_{nkj}^* \left[ b_{nkj} X_j + \sum_m \sum_{j' \neq j} |c_{mj'}|^2 b_{mkj'} X_{jj'} \right] \right\}. \end{aligned} \quad (\text{B12})$$

Finally we perform the spin summations and obtain

$$\begin{aligned} \frac{i\hbar}{2} \left( \left\langle \Phi \middle| \frac{\partial}{\partial t} \Phi \right\rangle - \left\langle \frac{\partial}{\partial t} \Phi \middle| \Phi \right\rangle \right) &= \frac{i\hbar}{2} \sum_{nj} o_j (\dot{c}_{nj} c_{nj}^* - c_{nj}^* \dot{c}_{nj}) X_j \\ &\quad + \frac{i\hbar}{2} \sum_k \left\{ \sum_{nj} o_j |c_{nj}|^2 \dot{b}_{nkj} \left[ b_{nkj}^* X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'}^* X_{jj'} \right] \right. \\ &\quad \left. - \sum_{nj} o_j |c_{nj}|^2 \dot{b}_{nkj}^* \left[ b_{nkj} X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} X_{jj'} \right] \right\} \end{aligned} \quad (\text{B13})$$

where  $j, j'$  run now over the spatial orbitals only and the  $o_j$  are their occupation numbers.  $\mathbf{X}$  and  $\mathbf{X}$  read now as

$$X_j = \prod_{j'} \left( \sum_n |c_{nj'}|^2 \right)^{o_j - \delta_{jj'}} \quad X_{jj'} = \prod_{j''} \left( \sum_n |c_{nj''}|^2 \right)^{o_{j''} - \delta_{j''j} - \delta_{j''j'}}. \quad (\text{B14})$$

Note that  $X_{jj}$  is not equal to  $X_j$  in the case of spatial orbitals which might be doubly occupied. Note further that terms  $X_{jj}$  and later on their derivatives cancel out by the factors  $(o_{j'} - \delta_{jj'})$  in the summations.

Now we have to evaluate the expectation value of the Hamiltonian with  $|\Phi\rangle$ . For this purpose we start with the phonon part:

$$\hat{H}_p = \sum_k \hbar\omega_k \hat{b}_k^+ \hat{b}_k.$$

We use the fact that a coherent state  $|\beta_{nk}\rangle$  is an eigenstate of the annihilation operator with the coherent state amplitude as eigenvalue

$$|\beta_n\rangle = \prod_{k'} |\beta_{nk'}\rangle \Rightarrow \hat{b}_k |\beta_n\rangle = \left( \sum_j b_{nj,kj} \right) |\beta_n\rangle \quad \langle \beta_n | \hat{b}_k^+ = \langle \beta_n | \left( \sum_j b_{nj,kj}^* \right). \quad (\text{B15})$$

Thus we obtain

$$\begin{aligned} \langle \Phi | \hat{H}_p | \Phi \rangle &= \sum_k \hbar\omega_k \sum_{nml} |c_{n1}|^2 |c_{m2}|^2 |c_{l3}|^2 \langle \beta_n | \hat{b}_k^+ \hat{b}_k | \beta_n \rangle \\ &= \sum_k \hbar\omega_k \sum_{nml} |c_{n1}|^2 |c_{m2}|^2 |c_{l3}|^2 (b_{nk1}^* + b_{mk2}^* + b_{lk3}^*) (b_{nk1} + b_{mk2} + b_{lk3}). \end{aligned} \quad (\text{B16})$$

The first term in the first bracket ( $T_1$ ) gives

$$T_1 = \sum_k \hbar\omega_k \sum_n |c_{n1}|^2 b_{nk1}^* \left[ b_{nk1} X_1 + \sum_m \sum_{j' \neq 1} |c_{mj'}|^2 b_{mkj'} X_{1j'} \right]. \quad (\text{B17})$$

From the remaining two terms in the first bracket in (B16) we obtain similar contributions where e.g.  $T_2$  reads after exchange of summation indices

$$T_2 = \sum_k \hbar\omega_k \sum_n |c_{n2}|^2 b_{nk2}^* \left[ b_{nk2} X_2 + \sum_m \sum_{j' \neq 2} |c_{mj'}|^2 b_{mkj'} X_{2j'} \right]. \quad (\text{B18})$$

Thus altogether we have

$$\langle \Phi | \hat{H}_p | \Phi \rangle = \sum_k \hbar\omega_k \sum_{nj} |c_{nj}|^2 b_{nkj}^* \left[ b_{nkj} X_j + \sum_m \sum_{j' \neq j} |c_{mj'}|^2 b_{mkj'} X_{jj'} \right]. \quad (\text{B19})$$

Performing the spin summations leads finally to

$$\langle \Phi | \hat{H}_p | \Phi \rangle = \sum_k \hbar\omega_k \sum_{nj} o_j |c_{nj}|^2 b_{nkj}^* \left[ b_{nkj} X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} X_{jj'} \right]. \quad (\text{B20})$$

For the next terms we need the expectation value

$$\langle \Phi | \hat{b}_k | \Phi \rangle = \sum_{nml} |c_{n1}|^2 |c_{m2}|^2 |c_{l3}|^2 (b_{nk1} + b_{mk2} + b_{lk3}) = \sum_{nj} |c_{nj}|^2 b_{nkj} X_j \quad (\text{B21})$$

or in orbital form

$$\langle \Phi | \hat{b}_k | \Phi \rangle = \sum_{nj} o_j |c_{nj}|^2 b_{nkj} X_j \quad \langle \Phi | \hat{b}_k^+ | \Phi \rangle = \sum_{nj} o_j |c_{nj}|^2 b_{nkj}^* X_j. \quad (\text{B22})$$

Further we have to compute overlap integrals  $D(\mathbf{b}_1, \mathbf{b}_2) = \langle \beta(\mathbf{b}_1) | \beta(\mathbf{b}_2) \rangle$ , where  $\mathbf{b}_1 = (b_{nk1} + b_{mk2} + b_{lk3})$  and, e.g.,  $\mathbf{b}_2 = (b_{n+1,k1} + b_{mk2} + b_{lk3})$ , or

$$D(\mathbf{b}_1, \mathbf{b}_2) = {}_p \langle 0 | e^{-(1/2) \sum_k |\sum_j b_{nj,kj}|^2} e^{\sum_k b_{nkj}^* \hat{b}_k} e^{-(1/2) \sum_k |\sum_j b_{nj+\delta_{j1},kj}|^2} e^{\sum_k b_{nj+\delta_{j1},kj} \hat{b}_k^*} | 0 \rangle_p. \quad (\text{B23})$$

In general such an overlap between coherent states is given by

$$D(\mathbf{b}_1, \mathbf{b}_2) = \exp \left[ -\frac{1}{2} \sum_k (|\mathbf{b}_1 - \mathbf{b}_2|^2 + \mathbf{b}_1^* \mathbf{b}_2 - \mathbf{b}_2^* \mathbf{b}_1) \right]. \quad (\text{B24})$$

For our example we obtain from that

$$D(\mathbf{b}_1, \mathbf{b}_2) = \exp \left\{ -\frac{1}{2} \sum_k [ |b_{nk1} - b_{n+1,k1}|^2 + (b_{nk1}^* + b_{mk2}^* + b_{lk3}^*) (b_{n+1,k1} + b_{mk2} + b_{lk3}) - (b_{nk1} + b_{mk2} + b_{lk3}) (b_{n+1,k1}^* + b_{mk2}^* + b_{lk3}^*) ] \right\}. \quad (\text{B25})$$

Now we can factor out a term

$$D_{n,n+1,j} = \exp \left[ -\frac{1}{2} \sum_k (|b_{nkj} - b_{n+1,kj}|^2 + b_{nkj}^* b_{n+1,kj} - b_{nkj} b_{n+1,kj}^*) \right] \quad (\text{B26})$$

leading to

$$\begin{aligned} D(\mathbf{b}_1, \mathbf{b}_2) &= D_{n,n+1,1} \exp \left\{ -\frac{1}{2} \sum_k [ b_{nk1}^* (b_{mk2} + b_{lk3}) + (b_{mk2}^* + b_{lk3}^*) (b_{n+1,k1} + b_{mk2} + b_{lk3}) - b_{nk1} (b_{mk2}^* + b_{lk3}^*) - (b_{mk2} + b_{lk3}) (b_{n+1,k1}^* + b_{mk2}^* + b_{lk3}^*) ] \right\} \\ &= D_{n,n+1,1} \exp \left\{ -\frac{1}{2} \sum_k [ (b_{nk1}^* b_{mk2} + b_{mk2}^* b_{n+1,k1}) - (b_{nk1} b_{mk2}^* + b_{mk2} b_{n+1,k1}^*) ] \right\} \\ &\quad \times \exp \left\{ -\frac{1}{2} \sum_k [ (b_{nk1}^* b_{lk3} + b_{lk3}^* b_{n+1,k1}) - (b_{nk1} b_{lk3}^* + b_{lk3} b_{n+1,k1}^*) ] \right\} \quad (\text{B27a}) \end{aligned}$$

and finally

$$D(\mathbf{b}_1, \mathbf{b}_2) = D_{n,n+1,1} D_{n,n+1,1}^{m2} D_{n,n+1,1}^{l3} \quad (\text{B27b})$$

or in general

$$D(\mathbf{b}_1, \mathbf{b}_2) = D_{n,n+1,j} \prod_{j' \neq j} D_{n,n+1,j'}^{m_j j'} \quad (\text{B28})$$

where

$$\begin{aligned}
 D_{n,n+1,j} &= \exp \left\{ -\frac{1}{2} \sum_k [|b_{nkj} - b_{n+1,k,j}|^2 + b_{nkj}^* b_{n+1,kj} - b_{nkj} b_{n+1,kj}^*] \right\} \\
 D_{nj}^{mj'} &= \exp \left\{ -\frac{1}{2} \sum_k [b_{nkj}^* b_{mkj'} - b_{nkj} b_{mkj'}^*] \right\} \\
 D_{n,n+1,j}^{mj'} &= D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* \\
 |\beta(b_1)\rangle &= \exp \left\{ -\frac{1}{2} \sum_k \left| \sum_{j'} b_{n_j k j'} \right|^2 \right\} \exp \left\{ \sum_k \left( \sum_{j'} b_{n_j k j'} \right) \hat{\delta}_k^+ \right\} |0\rangle_p \\
 |\beta(b_2)\rangle &= \exp \left\{ -\frac{1}{2} \sum_k \left| \sum_{j' \neq j} b_{n_j k j'} + b_{n_{j+1}, k j} \right|^2 \right\} \exp \left\{ \sum_k \left( \sum_{j' \neq j} b_{n_j k j'} + b_{n_{j+1}, k j} \right) \hat{\delta}_k^+ \right\} |0\rangle_p \\
 D(b_1, b_2) &= \langle \beta(b_1) | \beta(b_2) \rangle.
 \end{aligned} \tag{B29}$$

With this we can compute the expectation value of the inter-site interaction part of our Hamiltonian e.g. for electron 1:

$$\begin{aligned}
 \langle \Phi | \sum_{n''} (\hat{c}_{n''1}^+ \hat{c}_{n''+1,1} + \hat{c}_{n''+1,1}^+ \hat{c}_{n''1}) | \Phi \rangle &= \sum_{nml} \sum_{n'm'l'} c_{l3}^* c_{m2}^* c_{n1}^* c_{n'1} c_{m'2} c_{l'3} \langle \beta(nml) | \hat{c}_{l3} \hat{c}_{m2} \hat{c}_{n1} \\
 &\quad \times \sum_{n''} (\hat{c}_{n''1}^+ \hat{c}_{n''+1,1} + \hat{c}_{n''+1,1}^+ \hat{c}_{n''1}) \hat{c}_{n'1}^+ \hat{c}_{m'2}^+ \hat{c}_{l'3}^+ | \beta(n'm'l') \rangle \\
 &= \sum_{ml} \sum_{n'm'} |c_{m2}|^2 |c_{l3}|^2 c_{n1}^* c_{n'1} \langle \beta(nml) | \hat{c}_{n1} \\
 &\quad \times \sum_{n''} (\hat{c}_{n''1}^+ c_{n''+1,1} + \hat{c}_{n''+1,1}^+ \hat{c}_{n''1}) \hat{c}_{n'1}^+ | \beta(n'ml) \rangle \\
 &= \sum_{ml} |c_{m2}|^2 |c_{l3}|^2 \sum_n [c_{n1}^* c_{n+1,1} \langle \beta(nml) | \beta(n+1, ml) \rangle \\
 &\quad + c_{n+1,1}^* c_{n1} \langle \beta(n+1, ml) | \beta(nml) \rangle].
 \end{aligned} \tag{B30}$$

From this, together with the overlaps between coherent states, we can write this part of the Hamiltonian function for an arbitrary number of electrons as

$$\begin{aligned}
 \sum_{nj} c_{nj}^* c_{n+1,j} D_{n,n+1,j} \prod_{j' \neq j} \left( \sum_m |c_{mj'}|^2 D_{n,n+1,j}^{mj'} \right) \\
 + \sum_{nj} c_{n+1,j}^* c_{nj} D_{n+1,n,j} \prod_{j' \neq j} \left( \sum_m |c_{mj'}|^2 D_{n+1,n,j}^{mj'} \right).
 \end{aligned} \tag{B31}$$

For the products we introduce the abbreviations

$$\begin{aligned}
 P_{nj} &= \prod_{j' \neq j} \left( \sum_m |c_{mj'}|^2 D_{n,n+1,j}^{mj'} \right) = \prod_{j' \neq j} \left[ \sum_m |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* \right] \\
 P_{nj}^* &= \prod_{j' \neq j} \left( \sum_m |c_{mj'}|^2 D_{n+1,n,j}^{mj'} \right) = \prod_{j' \neq j} \left[ \sum_m |c_{mj'}|^2 (D_{nj}^{mj'})^* D_{n+1,j}^{mj'} \right].
 \end{aligned} \tag{B32}$$



Now we want to discuss one of the electron-phonon interaction terms:

$$\begin{aligned}
 \langle \Phi | \sum_n (\hat{c}_{n1}^+ \hat{c}_{n+1,1} + \hat{c}_{n+1,1}^+ \hat{c}_{n1}) \hat{b}_k | \Phi \rangle &= \sum_n c_{n1}^* c_{n+1,1} D_{n,n+1,1} \\
 &\times \sum_m |c_{m2}|^2 D_{n,n+1,1}^{m2} \sum_l |c_{l3}|^2 D_{n,n+1,1}^{l3} (b_{n+1,k1} + b_{mk2} + b_{lk3}) \\
 &= \sum_n c_{n1}^* c_{n+1,1} D_{n,n+1,1} b_{n+1,k1} \sum_m |c_{m2}|^2 D_{n,n+1,1}^{m2} \sum_l |c_{l3}|^2 D_{n,n+1,1}^{l3} \\
 &+ \sum_n c_{n1}^* c_{n+1,1} D_{n,n+1,1} \sum_m |c_{m2}|^2 D_{n,n+1,1}^{m2} b_{mk2} \sum_l |c_{l3}|^2 D_{n,n+1,1}^{l3} \\
 &+ \sum_n c_{n1}^* c_{n+1,1} D_{n,n+1,1} \sum_m |c_{m2}|^2 D_{n,n+1,1}^{m2} \sum_l |c_{l3}|^2 D_{n,n+1,1}^{l3} b_{lk3}. \quad (B33)
 \end{aligned}$$

From this the general form of this kind of term can be deduced:

$$\begin{aligned}
 \langle \Phi | \sum_{nj} (\hat{c}_{nj}^+ \hat{c}_{n+1,j} + \hat{c}_{n+1,j}^+ \hat{c}_{nj}) \hat{b}_k | \Phi \rangle &= \sum_{nj} c_{nj}^* c_{n+1,j} D_{n,n+1,j} \\
 &\times \left[ b_{n+1,kj} P_{nj} + \sum_m \sum_{j' \neq j} |c_{mj'}|^2 D_{n,n+1,j}^{mj'} b_{mkj'} P_{njj'} \right] \quad (B34)
 \end{aligned}$$

$$P_{njj'} = \prod_{j'' \neq j, j'} \left[ \sum_m |c_{mj''}|^2 D_{nj}^{mj''} (D_{n+1,j}^{mj''})^* \right].$$

Finally we obtain for these parts ( $H_e$ ) of the Hamiltonian function in spin-orbital form

$$\begin{aligned}
 H_e &= \beta \sum_{nj} [c_{nj}^* c_{n+1,j} D_{n,n+1,j} P_{nj} + c_{nj} c_{n+1,j}^* D_{n+1,n,j} P_{nj}^*] \\
 &+ \sum_{nj} \sum_k \hbar \omega_k B_{nk} \left\{ c_{nj}^* c_{n+1,j} D_{n,n+1,j} \left[ (b_{n+1,kj} + b_{nkj}^*) P_{nj} \right. \right. \\
 &+ \left. \sum_m \sum_{j' \neq j} |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* (b_{mkj'} + b_{mkj}^*) P_{njj'} \right] \\
 &+ c_{nj} c_{n+1,j}^* D_{n+1,n,j} \left[ (b_{n+1,kj}^* + b_{nkj}) P_{nj}^* \right. \\
 &+ \left. \left. \sum_m \sum_{j' \neq j} |c_{mj'}|^2 (D_{nj}^{mj'})^* D_{n+1,j}^{mj'} (b_{mkj'}^* + b_{mkj'}) P_{njj'}^* \right] \right\}. \quad (B35)
 \end{aligned}$$

Note that here the orbital indices run from one to  $\nu$ , the number of singly occupied spin orbitals. Further

$$H_e = \langle \Phi | \hat{H}_e | \Phi \rangle = \langle \Phi | \sum_{nj} \left[ \beta + \sum_k \hbar \omega_k B_{nk} (\hat{b}_k + \hat{b}_k^+) \right] (\hat{c}_{nj}^+ \hat{c}_{n+1,j} + \hat{c}_{n+1,j}^+ \hat{c}_{nj}) | \Phi \rangle. \quad (B36)$$

In orbital form  $H_e$  is given by

$$\begin{aligned}
 H_e = & \beta \sum_{nj} o_j [c_{nj}^* c_{n+1,j} D_{n,n+1,j} P_{nj} + c_{nj} c_{n+1,j}^* D_{n+1,n,j} P_{nj}^*] \\
 & + \sum_{nj} o_j \sum_k \hbar \omega_k B_{nk} \left\{ c_{nj}^* c_{n+1,j} D_{n,n+1,j} \left[ (b_{n+1,kj} + b_{nkj}^*) P_{nj} \right. \right. \\
 & + \left. \left. \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* (b_{mkj'} + b_{mkj'}^*) P_{njj'} \right] \right. \\
 & + c_{nj} c_{n+1,j}^* D_{n+1,n,j} \left[ (b_{n+1,kj}^* + b_{nkj}) P_{nj}^* \right. \\
 & \left. \left. + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 (D_{nj}^{mj'})^* D_{n+1,j}^{mj'} (b_{mkj'}^* + b_{mkj'}) P_{njj'}^* \right] \right\} \quad (B37)
 \end{aligned}$$

where now the orbital indices run from one to  $\mu$ , the number of (singly and doubly occupied) spatial orbitals. Further the products  $P$  are given now by

$$\begin{aligned}
 Q_{njj'} & \equiv \sum_m |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* & P_{nj} & = \prod_{j'=1}^{\mu} Q_{njj'}^{o_{j'} - \delta_{jj'}} \\
 P_{njj'} & = \prod_{j''=1}^{\mu} Q_{njj''}^{o_{j''} - \delta_{jj''} - \delta_{j'j''}} = P_{nj} / Q_{njj'} & P_{jj'j''} & = P_{nj} / (Q_{njj'} Q_{njj''})
 \end{aligned} \quad (B38)$$

Terms with possibly occurring negative exponents in the products  $P$  and their derivatives cancel out via factors  $(o_{j'} - \delta_{jj'})$  in the summations. With this all terms in the Lagrangian are calculated, and we can proceed with the derivation of the equations of motion for the  $c$  and the  $b$  values.

### Appendix C. Equations of motion, conservation of overlap and Lagrange multipliers

Here we have to show first of all that our Lagrangian conserves the norm of the orbitals. This must necessarily hold, because the Hamiltonian conserves the number of particles. Conservation of the norm implies that we have to show that  $X(t) = N_j(t) = X_j(t) = X_{jj'}(t) = 1$  independent of time, provided that the orbitals are normalized in the initial state, i.e.  $N_j(t=0) = 1$ . This is equivalent to showing that  $(dN_j/dt) = 0$ . For this purpose we start with the Lagrangian in orbital form. The Lagrangian is divided into several terms which then can be differentiated step by step:

$$L = \sum_{\eta=1}^6 T_{\eta} \quad (C1)$$

with

$$\begin{aligned}
 T_1 & = \frac{i\hbar}{2} \sum_{nj} o_j (\dot{c}_{nj} c_{nj}^* - \dot{c}_{nj}^* c_{nj}) X_j \\
 T_2 & = \frac{i\hbar}{2} \sum_k \left\{ \sum_{nj} o_j |c_{nj}|^2 \dot{b}_{nkj} \left[ b_{nkj}^* X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'}^* X_{jj'} \right] \right. \\
 & \quad \left. - \sum_{nj} o_j |c_{nj}|^2 \dot{b}_{nkj}^* \left[ b_{nkj} X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} X_{jj'} \right] \right\}. \quad (C2)
 \end{aligned}$$

Further we have the terms arising from the Hamiltonian:

$$T_3 = - \sum_k \hbar \omega_k \left\{ \sum_{nj} o_j |c_{nj}|^2 b_{nkj}^* \left[ b_{nkj} X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} X_{jj'} \right] \right\} \tag{C3a}$$

$$T_4 = - \sum_{nj} o_j \{ \gamma_{nj} c_{nj}^* c_{n+1,j} D_{n,n+1,j} P_{nj} + \gamma_{nj}^* c_{nj} c_{n+1,j}^* D_{n+1,n,j} P_{nj}^* \}$$

$$\gamma_{nj} \equiv \beta + \sum_k \hbar \omega_k B_{nk} (b_{n+1,kj} + b_{nkj}^*) \tag{C3b}$$

$$P_{nj} = \prod_{j'} \left[ \sum_m |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* \right]^{o_{j'} - \delta_{jj'}}$$

and

$$T_5 = - \sum_k \hbar \omega_k \sum_{nj} B_{nk} o_j c_{nj}^* c_{n+1,j} D_{n,n+1,j} \times \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* (b_{mkj'}^* + b_{mkj'}) P_{njj'}. \tag{C3c}$$

Finally we have the term  $T_6 = T_5^*$ . Now we have to build the equations of motion for the  $c$  values from the Euler–Lagrange equations of the second kind:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{c}_{nj}^*} - \frac{\partial L}{\partial c_{nj}^*} = 0. \tag{C4}$$

This leads to

$$\begin{aligned} \frac{\partial L}{\partial \dot{c}_{nj}^*} &= \frac{\partial T_1}{\partial \dot{c}_{nj}^*} = -\frac{i\hbar}{2} o_j c_{nj} X_j = -\frac{i\hbar}{2} o_j c_{nj} \prod_{j'} \left( \sum_m |c_{mj'}|^2 \right)^{o_{j'} - \delta_{jj'}} \\ \frac{d}{dt} \frac{\partial L}{\partial \dot{c}_{nj}^*} &= -\frac{i\hbar}{2} o_j (\dot{c}_{nj} X_j + c_{nj} \dot{X}_j) \end{aligned} \tag{C5a}$$

where

$$\begin{aligned} \dot{X}_j &= \frac{d}{dt} \prod_{j'} \left( \sum_m |c_{mj'}|^2 \right)^{o_{j'} - \delta_{jj'}} \\ &= \sum_{mj'} (o_{j'} - \delta_{jj'}) (\dot{c}_{mj'} c_{mj'}^* + \dot{c}_{mj'}^* c_{mj'}) \prod_{j''} \left( \sum_{m'} |c_{m'j''}|^2 \right)^{o_{j''} - \delta_{j''j} - \delta_{j''j'}} \\ &= \sum_{mj'} (o_{j'} - \delta_{jj'}) (\dot{c}_{mj'} c_{mj'}^* + \dot{c}_{mj'}^* c_{mj'}) X_{jj'}. \end{aligned} \tag{C5b}$$

As the next step we have to differentiate the individual terms in  $L$  with respect to  $c_{nj}^*$ . For  $T_1$  this yields

$$\frac{\partial T_1}{\partial c_{nj}^*} = \frac{i\hbar}{2} o_j \dot{c}_{nj} X_j + \frac{i\hbar}{2} \sum_{mj'} o_{j'} (\dot{c}_{mj'} c_{mj'}^* - \dot{c}_{mj'}^* c_{mj'}) \frac{\partial X_{j'}}{\partial c_{nj}^*} = \frac{i\hbar}{2} o_j \dot{c}_{nj} X_j + \frac{i\hbar}{2} A_j o_j c_{nj}. \tag{C6}$$

Together with

$$\begin{aligned} \frac{\partial X_{j'}}{\partial c_{nj}^*} &= \sum_{j''} (o_{j''} - \delta_{j'j''}) \left[ \frac{\partial}{\partial c_{nj}^*} \sum_m |c_{mj''}|^2 \right] \prod_{j'''} \left( \sum_{m'} |c_{m'j'''}|^2 \right)^{o_{j'''} - \delta_{j''j'''} - \delta_{j''j'''}} \\ &= \sum_{j''} (o_{j''} - \delta_{j'j''}) \delta_{j''j} c_{nj} X_{j'j''} = (o_j - \delta_{jj'}) c_{nj} X_{jj'} \end{aligned} \tag{C7}$$

we can define  $A_j$ :

$$\begin{aligned} \frac{o_{j'}}{o_j} (o_j - \delta_{jj'}) &= \left\{ \begin{array}{ll} o_{j'} & j \neq j' \\ o_j - 1 = o_{j'} - 1 & j = j' \end{array} \right\} = (o_{j'} - \delta_{jj'}) \\ \Rightarrow A_j &\equiv \sum_{mj'} (o_{j'} - \delta_{jj'}) (\dot{c}_{mj'} c_{mj'}^* - \dot{c}_{mj'}^* c_{mj'}) X_{jj'} = 2i \operatorname{Im} \left[ \sum_{mj'} (o_{j'} - \delta_{jj'}) \dot{c}_{mj'} c_{mj'}^* X_{jj'} \right]. \end{aligned} \tag{C8}$$

Thus vector  $\mathbf{A}$  is imaginary ( $A_j^* = -A_j$ ). The derivative of  $T_2$  we split into two terms, the first one arising from differentiation of the factors at the  $X_j$  and  $X_{jj'}$ , the second one from differentiation of the  $X$  values, leading to

$$\frac{\partial T_2}{\partial c_{nj}^*} = \frac{i\hbar}{2} (B_{nj} + C_j) o_j c_{nj} \tag{C9}$$

with

$$\begin{aligned} \frac{\partial T_2}{\partial c_{nj}^*} &= \frac{i\hbar}{2} C_j o_j c_{nj} + \frac{i\hbar}{2} o_j c_{nj} \sum_k \left\{ (\dot{b}_{nkj} b_{nkj}^* - \dot{b}_{nkj}^* b_{nkj}) X_j \right. \\ &\quad \left. + \sum_{mj'} (o_{j'} - \delta_{jj'}) (\dot{b}_{nkj} b_{mkj'}^* - \dot{b}_{nkj}^* b_{mkj'} + \dot{b}_{nkj}^* b_{mkj'} - b_{nkj} \dot{b}_{mkj'}^*) X_{jj'} \right\} \end{aligned} \tag{C10}$$

and thus

$$\begin{aligned} B_{nj} &= \sum_k \left\{ (\dot{b}_{nkj} b_{nkj}^* - \dot{b}_{nkj}^* b_{nkj}) X_j \right. \\ &\quad \left. + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 (\dot{b}_{nkj} b_{mkj'}^* - \dot{b}_{nkj}^* b_{mkj'} + \dot{b}_{nkj}^* b_{mkj'} - b_{nkj} \dot{b}_{mkj'}^*) X_{jj'} \right\} = -B_{nj}^* \end{aligned} \tag{C11}$$

and therefore matrix  $\mathbf{B}$  is purely imaginary. By differentiation of the factors  $X_j$  and  $X_{jj'}$  which yields

$$\begin{aligned} \frac{\partial X_{j'}}{\partial c_{nj}^*} &= (o_j - \delta_{jj'}) c_{nj} X_{jj'} & \frac{\partial X_{j'j''}}{\partial c_{nj}^*} &= (o_j - \delta_{jj'} - \delta_{j'j''}) c_{nj} X_{j'j''} \\ X_{j'j''} &= \prod_{j'''} \left( \sum_m |c_{mj'''}|^2 \right)^{o_{j'''} - \delta_{j''j'''} - \delta_{j'j''} - \delta_{j''j'''}} \end{aligned} \tag{C12a}$$

and

$$\frac{\partial T_2}{\partial c_{nj}^*} = \frac{i\hbar}{2} B_{nj} o_j c_{nj} + \frac{i\hbar}{2} \sum_k \sum_{mj'} o_{j'} |c_{mj'}|^2 \left\{ (\dot{b}_{mkj'} b_{mkj'}^* - \dot{b}_{mkj'}^* b_{mkj'}) \frac{\partial X_{j'}}{\partial c_{nj}^*} \right. \\ \left. + \sum_{m'j''} (o_{j''} - \delta_{j'j''}) |c_{m'j''}|^2 (\dot{b}_{mkj'} b_{m'kj''}^* - \dot{b}_{mkj'}^* b_{m'kj''}) \frac{\partial X_{j'j''}}{\partial c_{nj}^*} \right\} \quad (C12b)$$

and since one can easily show that

$$\sum_{j'j''} \frac{o_{j'}}{o_j} (o_{j''} - \delta_{j'j''}) (o_j - \delta_{jj'} - \delta_{jj''}) A_{jj'j''} = \sum_{j'j''} (o_{j''} - \delta_{jj''}) (o_{j'} - \delta_{jj'} - \delta_{j'j''}) A_{jj'j''} \quad (C12c)$$

holds, where  $A_{jj'j''}$  is any arbitrary argument of such a summation, we obtain

$$C_j = \sum_k \sum_{mj'} |c_{mj'}|^2 \left\{ (o_{j'} - \delta_{jj'}) (\dot{b}_{mkj'} b_{mkj'}^* - \dot{b}_{mkj'}^* b_{mkj'}) X_{jj'} \right. \\ \left. + \sum_{m'j''} (o_{j''} - \delta_{jj''}) (o_{j'} - \delta_{jj'} - \delta_{j'j''}) |c_{m'j''}|^2 (\dot{b}_{mkj'} b_{m'kj''}^* - \dot{b}_{mkj'}^* b_{m'kj''}) X_{jj'j''} \right\} \\ = -C_j^* \quad (C13)$$

and thus vector  $C$  is also imaginary. The term  $T_3$  leads again to two terms  $D_{nj}$ , resulting from differentiation of the factors at  $X_j$  and  $X_{jj'}$ , and  $E_j$  from differentiation of the  $X$  values themselves, where

$$D_{nj} = - \sum_k \hbar \omega_k \left[ |b_{nkj}|^2 X_j + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 (b_{nkj} b_{mkj'}^* + b_{nkj}^* b_{mkj'}) X_{jj'} \right] = D_{nj}^* \\ E_j = - \sum_k \hbar \omega_k \sum_{mj'} |c_{mj'}|^2 b_{mkj'}^* \left[ b_{mkj'} (o_{j'} - \delta_{jj'}) X_{jj'} \right. \\ \left. + \sum_{m'j''} (o_{j''} - \delta_{jj''}) (o_{j'} - \delta_{jj'} - \delta_{j'j''}) |c_{m'j''}|^2 b_{m'kj''} X_{jj'j''} \right] = E_j^* \quad (C14)$$

$$\frac{\partial T_3}{\partial c_{nj}^*} = (D_{nj} + E_j) o_j c_{nj}$$

Again, both terms are real. The differentiation of  $T_4$  can again be split into two different terms, one resulting from the factors at the products  $P$ , the other one,  $F'_{nj'}$  from differentiation of the products  $P$ . From

$$\frac{\partial T_4}{\partial c_{nj}^*} = -o_j \{ \gamma_{nj} c_{n+1,j} D_{n,n+1,j} P_{nj} + \gamma_{n-1,j}^* c_{n-1,j} D_{n,n-1,j} P_{n-1,j}^* \} \\ - \sum_{mj'} o_{j'} \left\{ \gamma_{mj'} c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} \frac{\partial P_{mj'}}{\partial c_{nj}^*} + \gamma_{mj'}^* c_{mj'} c_{m+1,j'}^* D_{m+1,m,j'} \frac{\partial P_{mj'}^*}{\partial c_{nj}^*} \right\} \quad (C15)$$

with

$$\begin{aligned}
 P_{mj'} &= \prod_{j''} [\mathcal{Q}_{mj'j''}]^{o_{j''} - \delta_{j'j''}} \equiv \prod_{j''} \left[ \sum_{m'} |c_{m'j''}|^2 D_{mj''}^{m'j''} (D_{m+1,j'}^{m'j''})^* \right]^{o_{j''} - \delta_{j'j''}} \\
 \frac{\partial \mathcal{Q}_{mj'j''}}{\partial c_{nj}^*} &= \delta_{jj''} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* c_{nj} \\
 \Rightarrow \frac{\partial P_{mj'}}{\partial c_{nj}^*} &= \sum_{j''} (o_{j''} - \delta_{j'j''}) \left[ \frac{\partial \mathcal{Q}_{mj'j''}}{\partial c_{nj}^*} \right] \prod_{j''} [\mathcal{Q}_{mj'j''}]^{o_{j''} - \delta_{j'j''} - \delta_{j''j''}} c_{nj} \\
 &= (o_j - \delta_{jj'}) D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} c_{nj} \quad P_{mj'j} \equiv \prod_{j''} [\mathcal{Q}_{mj'j''}]^{o_{j''} - \delta_{j''} - \delta_{j'j''}}
 \end{aligned} \tag{C16}$$

we can write these terms as

$$\begin{aligned}
 \frac{\partial T_4}{\partial c_{nj}^*} &= -o_j [\gamma_{nj} c_{n+1,j} D_{n,n+1,j} P_{.j} + \gamma_{n-1,j}^* c_{n-1,j} D_{n,n-1,j} P_{n-1,j}^*] + F'_{nj} o_j c_{nj} \\
 F'_{nj} &= - \sum_{mj'} (o_{j'} - \delta_{jj'}) [\gamma_{mj'} c_{m+1,j'}^* D_{m,m+1,j'} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} \\
 &\quad + \gamma_{mj'}^* c_{m+1,j'} c_{m+1,j'}^* D_{m+1,mj'} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j}^*] = F'_{nj}^*
 \end{aligned} \tag{C17}$$

From the term  $T_5 + T_6$  we obtain in a very similar way the terms

$$\frac{\partial}{\partial c_{nj}^*} (T_5 + T_6) = o_j [G'_{nj} c_{n+1,j} + G_{n-1,j}^* c_{n-1,j} + F''_{nj} c_{nj}] \tag{C18a}$$

where from differentiation of the first sum over  $c$  values in equation (C3) we have

$$G'_{nj} = - \sum_k \hbar \omega_k B_{nk} D_{n,n+1,j} \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* (b_{mkj'}^* + b_{mkj'}) P_{njj'} \tag{C18b}$$

while the second summation and differentiation of the products  $P$  yield with

$$\begin{aligned}
 \frac{\partial P_{mj'j''}}{\partial c_{nj}^*} &= \sum_{j''} (o_{j''} - \delta_{j'j''} - \delta_{j''j''}) \left[ \frac{\partial \mathcal{Q}_{mj'j''}}{\partial c_{nj}^*} \right] P_{mj'j''} \\
 &= (o_j - \delta_{jj'} - \delta_{jj''}) c_{nj} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j''}
 \end{aligned} \tag{C18c}$$

$$P_{mj'j''} \equiv \prod_{j''} [\mathcal{Q}_{mj'j''}]^{o_{j''} - \delta_{j'j''} - \delta_{j''j''} - \delta_{j''j''}} = P_{mj'j} / (\mathcal{Q}_{mj'j} \mathcal{Q}_{mj'j''})$$

the factor

$$\begin{aligned}
 F''_{nj} &= - \sum_k \hbar \omega_k (b_{nkj}^* + b_{nkj}) \sum_{mj'} B_{mk} (o_{j'} - \delta_{jj'}) \{ c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} \\
 &\quad + c_{mj'} c_{m+1,j'}^* D_{m+1,mj'} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j}^* \} \\
 &\quad - \sum_k \hbar \omega_k \sum_{mj'} B_{mk} \sum_{m'j''} (o_{j'} - \delta_{j'j''} - \delta_{j''j''}) (o_{j''} - \delta_{j''j''}) |c_{m'j''}|^2 (b_{m'kj''}^* + b_{m'kj''}) \\
 &\quad \times \{ c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} D_{mj'}^{m'j''} (D_{m+1,j'}^{m'j''})^* D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j''} \\
 &\quad + c_{mj'} c_{m+1,j'}^* D_{m+1,mj'} (D_{mj'}^{m'j''})^* D_{m+1,j'}^{m'j''} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j''}^* \}.
 \end{aligned} \tag{C18d}$$

With  $F_{nj} = F'_{nj} + F''_{nj}$ ,

$$G_{nj} = -\gamma_{nj} D_{n,n+1,j} P_{nj} + G'_{nj} \quad (\text{C19})$$

and

$$\begin{aligned} \frac{\partial L}{\partial c_{nj}^*} &= o_j \left[ \frac{i\hbar}{2} \dot{c}_{nj} X_j + H_{nj} c_{nj} + G_{nj} c_{n+1,j} + G_{n-1,j}^* c_{n-1,j} \right] \\ H_{nj} &\equiv \frac{i\hbar}{2} (A_j + B_{nj} + C_j) + D_{nj} + E_j + F_{nj} = H_{nj}^* \end{aligned} \quad (\text{C20})$$

we can write the equations of motion (divided by  $o_j$ ) in the form

$$\begin{aligned} i\hbar \dot{c}_{nj} X_j &= -\frac{i\hbar}{2} \dot{X}_j c_{nj} + \sum_m K_{nmj} c_{mj} \\ K_{nmj} &= -H_{nj} \delta_{nm} - G_{nj} \delta_{m,n+1} (1 - \delta_{nN}) - G_{n-1,j}^* \delta_{m,n-1} (1 - \delta_{n1}). \end{aligned} \quad (\text{C21})$$

Thus the matrix  $\mathbf{K}_j$  has real diagonal elements, and only the first off-diagonal ones are non-vanishing. For these elements the following holds:

$$\begin{aligned} K_{n,n+1,j} &= -G_{nj} \\ K_{n+1,nj} &= \sum_m \delta_{m,n+1} K_{m,m-1,j} = -\sum_m \delta_{m,n+1} G_{m-1,j}^* = -G_{nj}^* \\ &= K_{n,n+1,j}^* \Rightarrow \mathbf{K}_j = \mathbf{K}_j^+. \end{aligned} \quad (\text{C22})$$

Therefore, since  $H_{nj}$  is real, the matrices  $\mathbf{K}_j$  are Hermitian, i.e.  $K_{nmj} = K_{mnj}^*$  ( $\mathbf{K}_j = \mathbf{K}_j^+$ ). From this we obtain for the norms of the orbitals

$$\begin{aligned} i\hbar \dot{N}_j &= i\hbar \frac{d}{dt} \sum_n c_{nj} c_{nj}^* = \sum_n [(i\hbar \dot{c}_{nj}) c_{nj}^* - (-i\hbar \dot{c}_{nj}^*) c_{nj}] \\ \Rightarrow i\hbar \dot{N}_j &= -i\hbar \frac{\dot{X}_j}{X_j} N_j + \frac{1}{X_j} \sum_{nm} (K_{nmj} c_{mj} c_{nj}^* - K_{nmj}^* c_{mj}^* c_{nj}) \\ \sum_{nm} K_{nmj}^* c_{mj}^* c_{nj} &= \sum_{mn} K_{mnj}^* c_{nj}^* c_{mj} = \sum_{nm} K_{nmj} c_{nj}^* c_{mj} \\ \Rightarrow \dot{N}_j X_j + N_j \dot{X}_j &= 0 \Rightarrow \frac{d}{dt} (N_j X_j) = \dot{X} = \frac{d}{dt} \left( \prod_j N_j \right) = 0. \end{aligned} \quad (\text{C23})$$

Thus the product of the norms of the orbitals is conserved. From this we obtain the equality

$$\begin{aligned} \frac{\dot{X}_j}{X_j} &= -\frac{\dot{N}_j}{N_j} \quad \dot{X} = 0 \Rightarrow X(t) = X(t=0) = 1 \quad X = X_j N_j = 1 \Rightarrow X_j = \frac{1}{N_j} \\ \Rightarrow i\hbar \dot{c}_{nj} &= \frac{i\hbar}{2} \frac{\dot{N}_j}{N_j} c_{nj} + N_j \sum_m K_{nmj} c_{mj}. \end{aligned} \quad (\text{C24})$$

Let us assume that we have found a solution of the equation (which follows also from the substitution  $c_{nj} = (N_j)^{1/2} a_{nj}$ )

$$i\hbar \dot{c}_{nj} = N_j \sum_m K_{nmj} c_{mj}. \tag{C25}$$

From (C25) follows

$$i\hbar \dot{N}_j = N_j \sum_{nm} (K_{nmj} c_{mj} c_{nj}^* - K_{nmj}^* c_{mj}^* c_{nj}) = 0. \tag{C26}$$

Therefore a solution of (C26) is also a solution of (C24), since it conserves the norms of the orbitals and thus  $N_j(t) = N_j(t=0) = 1$  and  $(dN_j/dt) = 0$ .

Thus we are concerned simply with the equation

$$i\hbar \dot{c}_{nj} = \sum_m K_{nmj} c_{mj}. \tag{C27}$$

Now we could partition  $H_{nj}$  into two terms  $H_{nj} = Z_j + Y_{nj}$  with

$$Z_j = \frac{i\hbar}{2} (A_j + C_j) + E_j \quad Y_{nj} = \frac{i\hbar}{2} B_{nj} + D_{nj} + F_{nj}. \tag{C28}$$

Because  $Z_j$  is real and is simply multiplied by  $c_{nj}$  on the right-hand side of the equations of motion, we could remove it from the equations by a phase transformation, i.e. the orbitals resulting from solution of the equations without  $Z_j$  would have to be multiplied by the phase factor  $\exp[i\varphi_j(t)]$  where the phase is given by

$$\varphi_j(t) = \frac{1}{\hbar} \int_0^t Z_j(t') dt' \tag{C29}$$

and could be calculated during the simulation by numerical integration. However, since our equations as they are do not conserve the orbital overlap (see below) and  $Z_j$  contains time derivatives of our unknown functions this transformation is not appropriate at this step.

Now we are in the position to compute the time derivative of the overlap matrix:

$$\begin{aligned} i\hbar \dot{S}_{ij} &= i\hbar \frac{d}{dt} \left( \sum_n c_{ni}^* c_{nj} \right) = \sum_n [(i\hbar \dot{c}_{nj}) c_{ni}^* - (-i\hbar \dot{c}_{ni}^*) c_{nj}] \\ i\hbar \dot{S}_{ij} &= \sum_{nm} (K_{nmj} c_{mj} c_{ni}^* - K_{nmj}^* c_{mj}^* c_{nj}) = \sum_{nm} (K_{nmj} - K_{nmi}) c_{ni}^* c_{mj}. \end{aligned} \tag{C30}$$

Since all terms in  $\mathbf{K}_j$  depend on  $j$ , our equations of motion conserve only the norm of the orbitals, but not their overlap. Therefore, our Lagrangian  $L$  leads to equations of motion for the  $c$  values which conserve the norms of the orbitals, but not their overlap. Since we deal with fermions we must force our system to overlap conservation by introduction of Lagrange multipliers  $\varepsilon_{jl}$ . Let us denote the orbital overlap by  $\mathbf{S}$ . We have to deal with a modified Lagrangian (in orbital form)

$$L' = L + i\hbar \sum_{jl} \varepsilon_{jl} (S_{jl} - \delta_{jl}) \tag{C31}$$



and the equations of motion

$$\frac{d}{dt} \frac{\partial L'}{\partial \dot{c}_{nj}^*} - \frac{\partial L'}{\partial c_{nj}^*} = 0 \Rightarrow \frac{d}{dt} \frac{\partial L}{\partial \dot{c}_{nj}^*} - \frac{\partial L}{\partial c_{nj}^*} - i\hbar \frac{\partial}{\partial c_{nj}^*} \sum_{il} \varepsilon_{il} \left( \sum_m c_{mi}^* c_{ml} - \delta_{il} \right) = 0$$

$$\frac{d}{dt} \frac{\partial L'}{\partial \dot{b}_{nkj}^*} - \frac{\partial L'}{\partial b_{nkj}^*} = 0 \Rightarrow \frac{d}{dt} \frac{\partial L}{\partial \dot{b}_{nkj}^*} - \frac{\partial L}{\partial b_{nkj}^*} = 0.$$
(C32)

Now let us denote all terms on the right-hand side of the equations of motion, resulting from differentiation of  $L$  alone, by  $A_{nj}$ . Then we have

$$i\hbar \dot{c}_{nj} = A_{nj} - \frac{i\hbar}{O_j} \sum_{il} \varepsilon_{il} \left( \sum_m c_{ml} \delta_{mn} \delta_{ij} \right) = A_{nj} - \frac{i\hbar}{O_j} \sum_l \varepsilon_{jl} c_{nl}$$

$$- i\hbar \dot{c}_{nj'}^* = A_{nj'}^* + \frac{i\hbar}{O_{j'}} \sum_l \varepsilon_{j'l}^* c_{nl}^*$$

$$A_{nj} \equiv \sum_m K_{nmj} c_{mj}.$$
(C33)

From this we can compute the time derivative of the orbital overlap  $\mathbf{S}$  as

$$i\hbar \dot{S}_{j'j} = \sum_n [(i\hbar \dot{c}_{nj}) c_{nj'}^* - (-i\hbar \dot{c}_{nj'}^*) c_{nj}]$$

$$= \sum_n (A_{nj} c_{nj'}^* - A_{nj'}^* c_{nj}) - \frac{i\hbar}{O_j} \sum_{nl} \varepsilon_{jl} c_{nl} c_{nj'}^* - \frac{i\hbar}{O_{j'}} \sum_{nl} \varepsilon_{j'l}^* c_{nl}^* c_{nj}$$

$$= i\hbar x_{j'j} - i\hbar \sum_l \left[ \frac{\varepsilon_{jl}}{O_j} \sum_n c_{nl} c_{nj'}^* + \frac{\varepsilon_{j'l}^*}{O_{j'}} \sum_n c_{nl}^* c_{nj} \right]$$
(C34)

where we have defined

$$i\hbar x_{j'j} \equiv \sum_n (A_{nj} c_{nj'}^* - A_{nj'}^* c_{nj}) = \sum_{nm} (K_{nmj} - K_{nmj}') c_{mj} c_{nj'}^*.$$
(C35)

Since we demand that our orbital overlap should not change in time, we have (where 0 denotes  $t = 0$ )

$$\dot{S}_{j'j} = 0 \quad \sum_n \dot{c}_{nl} c_{nj} = S_{lj}(0) \quad \sum_n \dot{c}_{nj'}^* c_{nl} = S_{j'l}(0)$$
(C36)

and thus

$$0 = x_{j'j} - \sum_l \left[ \frac{\varepsilon_{jl}}{O_j} S_{j'l}(0) + \frac{\varepsilon_{j'l}^*}{O_{j'}} S_{lj}(0) \right].$$
(C37)

Since at the beginning of simulation we have orthonormalized orbitals and thus  $S_{ij}(0) = \delta_{ij}$  this leads to

$$\sum_l \left( \varepsilon_{jl} \frac{\delta_{j'l}}{O_j} + \varepsilon_{j'l}^* \frac{\delta_{jl}}{O_{j'}} \right) = x_{j'j} \Rightarrow \frac{\varepsilon_{jj'}}{O_j} + \frac{\varepsilon_{j'j}^*}{O_{j'}} = x_{j'j}.$$
(C38)

Use of the hermiticity of  $\underline{\varepsilon}$ , which results from the hermiticity of  $\mathbf{S}$  and its time derivative, yields

$$\varepsilon_{jj'} \left( \frac{1}{o_j} + \frac{1}{o_{j'}} \right) = x_{jj'} \Rightarrow \varepsilon_{jj'} = \frac{o_j o_{j'}}{o_j + o_{j'}} x_{jj'}. \quad (\text{C39})$$

Since  $\mathbf{x}$  is nothing else than the time derivative of the orbital overlap obtained above from the equations of motion without Lagrange multipliers, we get the final expression

$$\begin{aligned} \varepsilon_{jj'} &= \frac{i}{\hbar} \frac{o_j o_{j'}}{o_j + o_{j'}} \sum_{nm} (K_{nmj'} - K_{nmj}) c_{mj} c_{nj'}^* \\ &= -\frac{i}{\hbar} \frac{o_j o_{j'}}{o_j + o_{j'}} \sum_n [(H_{nj'} - H_{nj}) c_{nj} c_{nj'}^* + (G_{nj'} - G_{nj}) c_{n+1,j} c_{nj'}^* \\ &\quad + (G_{n-1,j'}^* - G_{n-1,j}^*) c_{n-1,j} c_{nj'}^*]. \end{aligned} \quad (\text{C40})$$

Thus our equations of motion are

$$\begin{aligned} i\hbar \dot{c}_{nj} &= \sum_m K_{nmj} c_{mj} + \sum_{j'} R_{jj'} c_{nj'} \\ R_{jj'} &= -\frac{o_{j'}}{o_j + o_{j'}} \left[ \sum_m [(H_{mj'} - H_{mj}) c_{mj} c_{mj'}^* + (G_{mj'} - G_{mj}) c_{m+1,j} c_{mj'}^* \right. \\ &\quad \left. + (G_{m-1,j'}^* - G_{m-1,j}^*) c_{m-1,j} c_{mj'}^* \right]. \end{aligned} \quad (\text{C41})$$

Now we have to derive the equations for the  $b$  values. As first term we obtain in orbital form

$$\frac{\partial L}{\partial \dot{b}_{nkj}^*} = \frac{\partial T_2}{\dot{b}_{nkj}^*} = -\frac{i\hbar}{2} o_j |c_{nj}|^2 \left[ b_{nkj} + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} \right]. \quad (\text{C42})$$

From this we obtain further

$$\begin{aligned} \frac{d}{dt} \frac{\partial L}{\partial \dot{b}_{nkj}^*} &= -\frac{i\hbar}{2} o_j (\dot{c}_{nj} c_{nj}^* + \dot{c}_{nj}^* c_{nj}) \left[ b_{nkj} + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} \right] \\ &\quad - \frac{i\hbar}{2} o_j |c_{nj}|^2 \sum_{mj'} (o_{j'} - \delta_{jj'}) (\dot{c}_{mj'} c_{mj'}^* + \dot{c}_{mj'}^* c_{mj'}) b_{mkj'} \\ &\quad - \frac{i\hbar}{2} o_j |c_{nj}|^2 \left[ \dot{b}_{nkj} + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 \dot{b}_{mkj'} \right]. \end{aligned} \quad (\text{C43})$$

From the derivative of  $L$  with respect to  $b_{nkj}^*$  we obtain the following different terms:

$$\begin{aligned} \frac{\partial T_1}{\partial b_{nkj}^*} &= 0 \\ \frac{\partial T_2}{\partial b_{nkj}^*} &= \frac{i\hbar}{2} o_j |c_{nj}|^2 \left[ \dot{b}_{nkj} + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 \dot{b}_{mkj'} \right] \\ \frac{\partial T_3}{\partial b_{nkj}^*} &= -\hbar \omega_k o_j |c_{nj}|^2 \left[ b_{nkj} + \sum_{mj'} (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 b_{mkj'} \right]. \end{aligned} \quad (\text{C44})$$

The contributions arising from the differentiation of  $(T_4 + T_5 + T_6)$  we partition into four terms. The first one,  $T(1)$ , is derived from differentiation of the directly occurring  $b^*$  factors:

$$\begin{aligned}
 T(1) = & -\tilde{\hbar}\omega_k (B_{nk}c_{n+1,j}D_{n,n+1,j}P_{nj} + B_{n-1,k}c_{n-1,j}D_{n,n-1,j}P_{n-1,j})o_jc_{nj}^* \\
 & - \sum_{mj'} (o_j - \delta_{jj'})o_{j'}|c_{nj}|^2\tilde{\hbar}\omega_k B_{mk}[c_{mj'}^*c_{m+1,j'}D_{m,m+1,j'}D_{mj'}^{nj'}(D_{m+1,j'}^{nj'})^*P_{mj'j} \\
 & + c_{mj'}c_{m+1,j'}^*D_{m+1,m,j'}(D_{mj'}^{nj'})^*D_{m+1,j'}^{nj'}P_{mj'j}^*]. \tag{C45}
 \end{aligned}$$

The term  $T(2)$  arises from differentiation of the  $D_{m,m+1,j}$  factors, i.e. from

$$\begin{aligned}
 \frac{\partial D_{m,m+1,j'}}{\partial b_{nkj}^*} &= [b_{n+1,kj}\delta_{mn} - \frac{1}{2}b_{nkj}(\delta_{mn} - \delta_{m,n-1})]D_{m,m+1,j}\delta_{jj'} \\
 \frac{\partial D_{m+1,m,j'}}{\partial b_{nkj}^*} &= [b_{n-1,kj}\delta_{n,m+1} - \frac{1}{2}b_{nkj}(\delta_{mn} - \delta_{m,n-1})]D_{m+1,m,j}\delta_{jj'}
 \end{aligned} \tag{C46}$$

we obtain

$$\begin{aligned}
 T(2) = & -o_j\{(b_{n+1,kj} - \frac{1}{2}b_{nkj})c_{n+1,j}^*D_{n,n+1,j}\Gamma_{n,n+1,j} - \frac{1}{2}b_{nkj}c_{n-1,j}^*c_{nj}D_{n-1,nj}\Gamma_{n-1,nj} \\
 & + (b_{n-1,kj} - \frac{1}{2}b_{nkj})c_{n-1,j}^*D_{n,n-1,j}\Gamma_{n-1,nj}^* - \frac{1}{2}b_{nkj}c_{n+1,j}^*c_{nj}D_{n+1,nj}\Gamma_{n,n+1,j}^*\}
 \end{aligned} \tag{C47}$$

with

$$\begin{aligned}
 \Gamma_{nn'j} \equiv & \beta P_{nn'j} + \sum_{k'} \tilde{\hbar}\omega_{k'} B_{nk'} \left[ (b_{nk'j}^* + b_{n'k'j})P_{nn'j} \right. \\
 & \left. + \sum_{m'j'} (o_{j'} - \delta_{jj'})|c_{m'j'}|^2 D_{nj}^{m'j'} (D_{n'j}^{m'j'})^* (b_{m'k'j'}^* + b_{m'k'j'})P_{nn'jj'} \right]
 \end{aligned} \tag{C48}$$

$$P_{nn'j} = \prod_{j'} \left[ \sum_{m'} |c_{m'j'}|^2 D_{nj}^{m'j'} (D_{n'j}^{m'j'})^* \right]^{o_{j'} - \delta_{jj'}}.$$

The term  $T(3)$  results from differentiation of factors of the type  $D_{nj}^{mj'}(D_{n+1,j}^{mj'})^*$ . With

$$\begin{aligned}
 \frac{\partial}{\partial b_{nkj}^*} D_{mj'}^{m'j''} &= [-\frac{1}{2}b_{m'kj''}\delta_{nm}\delta_{jj''} + \frac{1}{2}b_{mkj'}\delta_{nm'}\delta_{jj''}]D_{mj'}^{m'j''} \\
 \frac{\partial}{\partial b_{nkj}^*} (D_{m+1,j'}^{m'j''})^* &= [\frac{1}{2}b_{m'kj''}\delta_{n,m+1}\delta_{jj''} - \frac{1}{2}b_{m+1,kj'}\delta_{nm'}\delta_{jj''}](D_{m+1,j'}^{m'j''})^*
 \end{aligned} \tag{C49}$$

we can evaluate

$$\begin{aligned}
 T(3) = & - \sum_{mj'} o_{j'} \sum_{k'} \tilde{\hbar}\omega_{k'} \left\{ B_{mk'}c_{mj'}^*c_{m+1,j'}D_{m,m+1,j'} \sum_{m''j''} (o_{j''} - \delta_{j'j''})|c_{m''j''}|^2 \left[ \left( \frac{\partial}{\partial b_{nkj}^*} D_{mj'}^{m'j''} \right) \right. \right. \\
 & \times (D_{m+1,j'}^{m'j''})^* + D_{mj'}^{m'j''} \frac{\partial}{\partial b_{nkj}^*} (D_{m+1,j'}^{m'j''})^* \left. \right] (b_{m'k'j''}^* + b_{m'k'j''})P_{mj'j''} \\
 & + B_{mk'}c_{mj'}^*c_{m+1,j'}D_{m+1,m,j'} \sum_{m''j''} (o_{j''} - \delta_{j'j''})|c_{m''j''}|^2 \left[ \left( \frac{\partial}{\partial b_{nkj}^*} (D_{mj'}^{m'j''})^* \right) D_{m+1,j'}^{m'j''} \right. \\
 & \left. \left. + (D_{mj'}^{m'j''})^* \frac{\partial}{\partial b_{nkj}^*} D_{m+1,j'}^{m'j''} \right] (b_{m'k'j''}^* + b_{m'k'j''})P_{mj'j''}^* \right\}
 \end{aligned} \tag{C50}$$

as

$$\begin{aligned}
 T(3) = & -\frac{1}{2} \sum_{mj'} o_{j'} (o_j - \delta_{jj'}) |c_{nj}|^2 \sum_{k'} \hbar \omega_{k'} B_{mk'} (b_{mkj'} - b_{m+1,kj'}) \\
 & \times [c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} \\
 & - c_{mj'} c_{m+1,j'}^* D_{m+1,m,j'} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j}^*] (b_{nk'j} + b_{nk'j}^*) \\
 & + \frac{1}{2} \sum_{mj'} o_j (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 \sum_{k'} \hbar \omega_{k'} (b_{mk'j'} + b_{mk'j'}^*) b_{mkj'} \Upsilon_{nm,jj'}^k \quad (C51a)
 \end{aligned}$$

where

$$\begin{aligned}
 \Upsilon_{nm,jj'}^k = & B_{nk'} [c_{nj}^* c_{n+1,j} D_{n,n+1,j} D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* P_{njj'} - c_{nj} c_{n+1,j}^* D_{n+1,nj} (D_{nj}^{mj'})^* D_{n+1,j}^{mj'} P_{njj'}^*] \\
 & - B_{n-1,k'} [c_{n-1,j}^* c_{nj} D_{n-1,nj} D_{n-1,j}^{mj'} (D_{nj}^{mj'})^* P_{n-1,jj'} \\
 & - c_{n-1,j} c_{nj}^* D_{n,n-1,j} (D_{n-1,j}^{mj'})^* D_{n-1,j}^{mj'} P_{n-1,jj'}^*]. \quad (C51b)
 \end{aligned}$$

This can be rewritten as

$$T(3) = -\lambda'_{nj}(k) - \sum_{mj'} \omega'_{nj,mj'}(k) b_{mkj'} \quad (C52)$$

with

$$\begin{aligned}
 \lambda'_{nj}(k) = & \frac{1}{2} \sum_{mj'} o_{j'} (o_j - \delta_{jj'}) |c_{nj}|^2 \sum_{k'} \hbar \omega_{k'} B_{mk'} (b_{nk'j} + b_{nk'j}^*) (b_{mkj'} - b_{m+1,kj'}) \\
 & \times [c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} \\
 & - c_{mj'} c_{m+1,j'}^* D_{m+1,m,j'} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j}^*] \quad (C53)
 \end{aligned}$$

$$\omega'_{nj,mj'}(k) = -\frac{1}{2} o_j (o_{j'} - \delta_{jj'}) |c_{mj'}|^2 \sum_{k'} \hbar \omega_{k'} (b_{mk'j'} + b_{mk'j'}^*) \Upsilon_{nm,jj'}^k. \quad (C54)$$

It remains to determine  $T(4)$ , which results from differentiation of the factors  $P_{nj}$  and  $P_{njj'}$ . For this purpose  $T(4)$  is split into two terms. First of all we have

$$T'(4) = - \left[ \sum_{mj'} o_{j'} c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} \Upsilon_{mj'} \frac{\partial P_{mj'}}{\partial b_{nkj}^*} + \sum_{mj'} o_{j'} c_{mj'} c_{m+1,j'}^* D_{m+1,mj'} \Upsilon_{mj'}^* \frac{\partial P_{mj'}^*}{\partial b_{nkj}} \right] \quad (C55a)$$

where  $\Upsilon_{mj'}$  is defined in equation (C17). This leads to

$$\begin{aligned}
 \frac{\partial P_{mj'}}{\partial b_{nkj}^*} = & \frac{\partial}{\partial b_{nkj}^*} \prod_{j''} \left[ \sum_{m'} |c_{m'j''}|^2 D_{mj'}^{m'j''} (D_{m+1,j'}^{m'j''})^* \right]^{o_{j''} - \delta_{jj''}} \\
 = & \frac{1}{2} \sum_{j''} (o_{j''} - \delta_{jj''}) \sum_{m'} b_{m'k'j''} |c_{m'j''}|^2 [D_{nj}^{m'j''} (D_{n+1,j}^{m'j''})^* P_{njj''} \delta_{nm} \\
 & - D_{n-1,j}^{m'j''} (D_{nj}^{m'j''})^* P_{n-1,jj''} \delta_{m+1,n}] \delta_{jj''} \\
 & + \frac{1}{2} (o_j - \delta_{jj'}) D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} (b_{mkj} - b_{m+1,k,j}) \quad (C55b)
 \end{aligned}$$

$$T'(4) = -\lambda''_{nj}(k) - \sum_{mj'} \omega''_{nj,mj'}(k) b_{mkj'} \quad (C56)$$

with

$$\begin{aligned} \lambda''_{nj} &= \frac{1}{2} \sum_{mj'} o_{j'} (o_j - \delta_{jj'}) (b_{mkj'} - b_{m+1,kj'}) [c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} \gamma_{mj'} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j}^* \\ &\quad - c_{mj'} c_{m+1,j'}^* D_{m+1,mj'} \gamma_{mj'}^* (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j}^*] \\ \omega''_{nj,mj'} &= \frac{1}{2} o_j (o_{j'} - \delta_{jj'}) [c_{nj}^* c_{n+1,j} D_{n,n+1,j} \gamma_{nj} D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* P_{njj'} \\ &\quad - c_{nj} c_{n+1,j}^* D_{n+1,nj} \gamma_{nj}^* (D_{nj}^{mj'})^* D_{n+1,j}^{mj'} P_{njj'}^* \\ &\quad - c_{n-1,j}^* c_{nj} D_{n-1,nj} \gamma_{n-1,j} D_{n-1,j}^{mj'} (D_{nj}^{mj'})^* P_{n-1,jj'} \\ &\quad + c_{n-1,j} c_{nj}^* D_{n,n-1,j} \gamma_{n-1,j}^* (D_{n-1,j}^{mj'})^* D_{nj}^{mj'} P_{n-1,jj'}^*]. \end{aligned} \quad (C57)$$

The last term is

$$\begin{aligned} T''(4) &= - \sum_{mj'} o_{j'} \sum_{k'} \hbar \omega_{k'} B_{mk'} \sum_{m'j''} (o_{j''} - \delta_{j'j''}) |c_{m'j''}|^2 (b_{m'k'j''}^* + b_{m'k'j''}) \\ &\quad \times \left[ c_{mj'}^* c_{m+1,j'} D_{mj'}^{m'j''} (D_{m+1,j'}^{m'j''})^* \frac{\partial P_{mj'j''}}{\partial B_{nkj}^*} + c_{mj'} c_{m+1,j'}^* (D_{mj'}^{m'j''})^* D_{m+1,j'}^{m'j''} \frac{\partial P_{mj'j''}^*}{\partial b_{nkj}^*} \right] \end{aligned} \quad (C58)$$

where

$$\begin{aligned} \frac{\partial P_{mj'j''}}{\partial b_{nkj}^*} &= \frac{1}{2} \sum_{j''} (o_{j''} - \delta_{j'j''} - \delta_{j''j''}) \sum_{m''} |c_{m''j''}|^2 [b_{m''kj''} (\delta_{m+1,n} - \delta_{mn}) \delta_{j'j''} \\ &\quad + (b_{mkj'} - b_{m+1,kj'}) \delta_{m''n} \delta_{j'j''}] D_{mj'}^{m''j''} (D_{m+1,j'}^{m''j''})^* P_{mj'j''}^{m''j''}. \end{aligned} \quad (C59)$$

Evaluation of (C58) with the help of (C59) leads to

$$T''(4) = -\lambda'''_{nj}(k) - \sum_{mj'} \omega'''_{nj,mj'}(k) b_{mkj} \quad (C60)$$

with

$$\begin{aligned} \lambda'''_{nj}(k) &= \frac{1}{2} \sum_{mj'} \sum_{m'j''} o_{j'} (o_{j''} - \delta_{j'j''}) (o_{j''} - \delta_{j'j''} - \delta_{j''j''}) |c_{mj'}|^2 |c_{m'j''}|^2 \\ &\quad \times \sum_{k'} \hbar \omega_{k'} B_{mk'} (b_{m'k'j''}^* + b_{m'k'j''}) (b_{mkj'} - b_{m+1,kj'}) \\ &\quad \times [c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} D_{mj'}^{m'j''} (D_{m+1,j'}^{m'j''})^* D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j''}^* \\ &\quad - c_{mj'} c_{m+1,j'}^* D_{m+1,m,j'} (D_{mj'}^{m'j''})^* D_{m+1,j'}^{m'j''} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j''}^*] \end{aligned} \quad (C61)$$

and

$$\begin{aligned} \omega'''_{nj,mj'} &= \frac{1}{2} \sum_{m'j''} o_j (o_{j''} - \delta_{j'j''}) (o_{j''} - \delta_{j'j''} - \delta_{j''j''}) |c_{mj'}|^2 |c_{m'j''}|^2 \\ &\quad \times \sum_{k'} \hbar \omega_{k'} (b_{m'k'j''}^* + b_{m'k'j''}) [B_{n-1,k'} c_{n-1,j}^* c_{nj} D_{n-1,nj} D_{n-1,j}^{m'j''} (D_{nj}^{m'j''})^* D_{n-1,j}^{m'j''} \\ &\quad \times (D_{nj}^{mj'})^* P_{n-1,jj''j'} - B_{nk'} c_{nj}^* c_{n+1,j} D_{n,n+1,j} D_{nj}^{m'j''} (D_{n+1,j}^{m'j''})^* D_{nj}^{mj'} (D_{n+1,j}^{mj'})^* \\ &\quad \times P_{njj''j'} - B_{n-1,k'} c_{n-1,j}^* c_{nj}^* D_{n,n-1,j} (D_{n-1,j}^{m'j''})^* D_{nj}^{m'j''} (D_{n-1,j}^{mj'})^* D_{nj}^{mj'} P_{n-1,jj''j'}^* \\ &\quad + B_{nk'} c_{nj} c_{n+1,j}^* D_{n+1,nj} (D_{nj}^{m'j''})^* D_{n+1,j}^{m'j''} (D_{nj}^{mj'})^* D_{n+1,j}^{mj'} P_{njj''j'}^*]. \end{aligned} \quad (C62)$$

Therefore we can write finally

$$T(3) + T'(4) + T''(4) = -\lambda_{nj}(k) - \sum_{mj'} \omega_{nj,mj'}(k) b_{mkj'}$$

$$\lambda_{nj}(k) = \lambda'_{nj}(k) + \lambda''_{nj}(k) + \lambda'''_{nj}(k) \tag{C63}$$

$$\omega_{nj,mj'}(k) = \omega'_{nj,mj'}(k) + \omega''_{nj,mj'}(k) + \omega'''_{nj,mj'}(k).$$

Now all terms in the equations of motion are defined. They are collected to a closed form in appendix D.

Finally we would like to note that equation (C25) can also be obtained from

$$i\hbar \dot{c}_{nj} = \frac{i\hbar N_j}{2 N_j} c_{nj} + N_j \sum_m K_{nmj}(t) c_{mj} \tag{C64}$$

by the normalization transformation

$$c_{nj} = \sqrt{N_j} a_{nj} \Rightarrow \dot{c}_{nj} = \sqrt{N_j} \dot{a}_{nj} + \frac{1}{2} \frac{\dot{N}_j}{\sqrt{N_j}} a_{nj}. \tag{C65}$$

Substitution of (C65) into (C64) leads to

$$i\hbar \sqrt{N_j} \dot{a}_{nj} + \frac{i\hbar N_j}{2 \sqrt{N_j}} a_{nj} = \frac{i\hbar N_j}{2 N_j} \sqrt{N_j} a_{nj} + N_j \sqrt{N_j} \sum_m K_{nmj} a_{mj} \tag{C66}$$

where  $K_{nmj}$  contains now some additional normalization factors, which in the end are equal to unity, and finally to

$$i\hbar \dot{a}_{nj} = N_j \sum_m K_{nmj} a_{mj} \tag{C67}$$

which is identical to (C25).

### Appendix D. Closed form of the equations of motion

One can split the equations of motion for the electrons (C21) and (C41), into terms which contain time derivatives of the unknown functions and those which do not. For this purpose we define

$$O_{nmj} \equiv -H'_{nj} \delta_{nm} - G_{nj} \delta_{m,n+1} (1 - \delta_{nN}) - G_{n-1,j}^* \delta_{m,n-1} (1 - \delta_{n1}) \tag{D1}$$

and

$$T_{jj'} \equiv -\frac{o_{j'}}{o_j + o_{j'}} \sum_m \{ (H'_{mj'} - H'_{mj}) c_{mj} c_{mj'}^* + (G_{mj'} - G_{mj}) c_{m+1,j} c_{mj'}^* (1 - \delta_{mN}) + (G_{m-1,j'}^* - G_{m-1,j}^*) c_{m-1,j} c_{mj'}^* (1 - \delta_{m1}) \} \tag{D2}$$

where we have the matrix

$$H'_{nj} \equiv D_{nj} + E_j + F_{nj}. \tag{D3}$$

Matrix  $\mathbf{D}$  and vector  $\mathbf{E}$  are defined in equation (C14), matrix  $\mathbf{G}$  in equation (C18b) and (C19) and  $\mathbf{F}$  in equation (C17) and (C18d). Thus our equations of motion are

$$\begin{aligned} i\hbar\dot{c}_{nj} + \frac{i\hbar}{2}(A_j + B_{nj} + C_j)c_{nj} + \frac{i\hbar}{2} \sum_{j'} \frac{o_{j'}c_{nj'}}{o_j + o_{j'}} \\ \times \sum_m (A_{j'} + B_{mj'} + C_{j'} - A_j - B_{mj} - C_j)c_{mj}c_{mj}^* \\ = \sum_{mj'} W_{nj,mj'}c_{mj'} \end{aligned} \quad (\text{D4})$$

where  $\mathbf{A}$  is defined in equation (C8),  $\mathbf{B}$  in equation (C11),  $\mathbf{C}$  in equation (C13), and

$$W_{nj,mj'} \equiv O_{nmj}\delta_{jj'} + T_{jj'}\delta_{nm}. \quad (\text{D5})$$

One can easily verify that parts of the second term in equation (D4) can be rewritten as

$$\frac{i\hbar}{2}c_{nj}(B_{nj} + C_j) = i\hbar c_{nj} \sum_k \sum_{mj'} [A_{nj,mj'}(k)\dot{b}_{mkj'} - A_{nj,mj'}^*(k)\dot{b}_{mkj'}^*] \quad (\text{D6})$$

where

$$\begin{aligned} A_{nj,mj'}(k) \equiv \frac{1}{2} \left\{ \left[ \dot{b}_{mkj'}^* + \sum_{m'j''} (o_{j''} - \delta_{jj''}) |c_{m'j''}|^2 \dot{b}_{m'kj''}^* \right] \delta_{nm} \delta_{jj'} \right. \\ \left. + |c_{mj'}|^2 \left[ (o_{j'} - \delta_{jj'}) (\dot{b}_{nkj}^* + \dot{b}_{mkj'}) \right. \right. \\ \left. \left. + \sum_{m'j''} (o_{j''} - \delta_{jj''})(o_{j'} - \delta_{j'j} - \delta_{j'j''}) |c_{m'j''}|^2 \dot{b}_{m'kj''}^* \right] \right\}. \end{aligned} \quad (\text{D7})$$

Although, as shown below for the  $A_j$ , the parts of the third term in equation (D4) containing the  $C_j$  vanish, we keep them here, because it is easy to rewrite that term with the above-defined  $\mathbf{A}(k)$ , which in the course of a calculation has to be computed anyway. Thus with the help of this matrix we obtain from the third term in equation (D4)

$$\begin{aligned} \frac{i\hbar}{2} \sum_{m'j''} \frac{o_{j''}c_{nj''}}{o_j + o_{j''}} [(B_{m'j''} + C_{j''}) - (B_{m'j} + C_j)] c_{m'j} c_{m'j''}^* \\ = -i\hbar \sum_k \sum_{mj'} \sum_{m'j''} \frac{o_{j''}c_{nj''}}{o_j + o_{j''}} c_{m'j''}^* c_{m'j} \{ -[A_{m'j,mj'}(k) - A_{m'j'',mj'}(k)] \dot{b}_{mkj'} \\ + [A_{m'j,mj'}^*(k) - A_{m'j'',mj'}^*(k)] \dot{b}_{mkj'}^* \}. \end{aligned} \quad (\text{D8})$$

Together with

$$\sum_m c_{mj} c_{mj'}^* = S_{j'j} = \delta_{jj'} \Rightarrow \frac{i\hbar}{2} \sum_{j'} \frac{o_{j'}c_{nj'}}{o_j + o_{j'}} (A_{j'} - A_j) \sum_m c_{mj} c_{mj'}^* = 0 \quad (\text{D9a})$$

we obtain the equations

$$i\hbar\dot{c}_{nj} + \frac{i\hbar}{2}A_jc_{nj} + i\hbar \sum_k \sum_{mj'} [U_{nj,mj'}(k)\dot{b}_{mkj'} + V_{nj,mj'}(k)\dot{b}_{mkj'}^*] = \sum_{mj'} W_{nj,mj'}c_{mj'} \quad (\text{D9b})$$

where we have the definitions

$$\begin{aligned}
 U_{nj,mj'}(k) &\equiv c_{nj} A_{nj,mj'}(k) + \sum_{m'j''} \frac{o_{j''} c_{nj''}}{o_j + o_{j''}} c_{m'j} c_{m'j''}^* [A_{m'j'',mj'}(k) - A_{m'j,mj'}(k)] \\
 V_{nj,mj'}(k) &\equiv -c_{nj} A_{nj,mj'}^*(k) - \sum_{m'j''} \frac{o_{j''} c_{nj''}}{o_j + o_{j''}} c_{m'j} c_{m'j''}^* [A_{m'j'',mj'}^*(k) - A_{m'j,mj'}^*(k)].
 \end{aligned}
 \tag{D10}$$

Further we obtain from

$$\frac{i\hbar}{2} A_j c_{nj} = \frac{i\hbar}{2} c_{nj} \sum_{mj'} (o_{j'} - \delta_{jj'}) (c_{mj'}^* \dot{c}_{mj'} - c_{mj'} \dot{c}_{mj'}^*)
 \tag{D11}$$

the equation

$$i\hbar \dot{c}_{nj} + \frac{i\hbar}{2} A_j c_{nj} = i\hbar \sum_{mj'} [P_{nj,mj'} \dot{c}_{mj'} + Q_{nj,mj'} \dot{c}_{mj'}^*]
 \tag{D12}$$

with the definitions

$$\begin{aligned}
 P_{nj,mj'} &\equiv \delta_{nm} \delta_{jj'} + \frac{1}{2} c_{nj} (o_{j'} - \delta_{jj'}) c_{mj'}^* \\
 Q_{nj,mj'} &\equiv -\frac{1}{2} c_{nj} (o_{j'} - \delta_{jj'}) c_{mj'}.
 \end{aligned}
 \tag{D13}$$

With this we can write the equations of motion in the simple form

$$i\hbar \sum_{mj'} \left\{ P_{nj,mj'} \dot{c}_{mj'} + Q_{nj,mj'} \dot{c}_{mj'}^* + \sum_k [U_{nj,mj'}(k) \dot{b}_{mkj'} + V_{nj,mj'}(k) \dot{b}_{mkj'}^*] \right\} = \sum_{mj'} W_{nj,mj'} c_{mj'}
 \tag{D14}$$

or if we consider  $\{nj\}$  as one combined index we obtain

$$i\hbar \left[ \mathbf{P} \dot{\mathbf{c}} + \mathbf{Q} \dot{\mathbf{c}}^* + \sum_k (\mathbf{U}(k) \dot{\mathbf{b}}_k + \mathbf{V}(k) \dot{\mathbf{b}}_k^*) \right] = \mathbf{W} \mathbf{c}.
 \tag{D15}$$

The equations of motion for the  $b$  values are given in matrix form by

$$i\hbar \sum_{mj'} [\Delta_{nj,mj'}(k) \dot{c}_{mj'} + \Lambda_{nj,mj'}(k) \dot{c}_{mj'}^* + \Theta_{nj,mj'}(k) \dot{b}_{mkj'}] = \sum_{mj'} \Omega_{nj,mj'}(k) b_{mkj'} + J_{nj}(k)
 \tag{D16}$$

where the matrices on the left-hand side are defined as

$$\begin{aligned}
 \Delta_{nj,mj'}(k) &\equiv \frac{1}{2} o_j c_{nj}^* \left\{ \left[ b_{nkj} + \sum_{m'j''} (o_{j''} - \delta_{jj''}) |c_{m'j''}|^2 b_{m'kj''} \right] \delta_{nm} \delta_{jj'} \right. \\
 &\quad \left. + c_{nj} (o_{j'} - \delta_{jj'}) c_{mj'}^* b_{mkj'} \right\} \\
 \Lambda_{nj,mj'}(k) &\equiv \frac{1}{2} o_j c_{nj} \left\{ \left[ b_{nkj} + \sum_{m'j''} (o_{j''} - \delta_{jj''}) |c_{m'j''}|^2 b_{m'kj''} \right] \delta_{nm} \delta_{jj'} \right. \\
 &\quad \left. + c_{nj}^* (o_{j'} - \delta_{jj'}) c_{mj'} b_{mkj'} \right\} \\
 \Theta_{nj,mj'}(k) &\equiv o_j |c_{nj}|^2 [\delta_{nm} \delta_{jj'} + (o_{j'} - \delta_{jj'}) |c_{mj'}|^2]
 \end{aligned}
 \tag{D17}$$



as can be verified from equations (C43) and (C44).

On the right-hand side we have from equations (C44) and (C47) first of all

$$\begin{aligned} \Omega_{nj,mj'}(k) = & \hbar\omega_k o_j |c_{nj}|^2 [\delta_{nm} \delta_{jj'} + (o_j - \delta_{jj'}) |c_{mj'}|^2] \\ & + o_j \delta_{jj'} \{ c_{nj}^* c_{n+1,j} D_{n,n+1,j} \Gamma_{n,n+1,j} \delta_{m,n+1} \\ & - \frac{1}{2} [c_{nj}^* c_{n+1,j} D_{n,n+1,j} \Gamma_{n,n+1,j} + c_{n-1,j}^* c_{nj} D_{n-1,n,j} \Gamma_{n-1,n,j} \\ & + c_{nj}^* c_{n-1,j} D_{n,n-1,j} \Gamma_{n-1,n,j}^* + c_{n+1,j}^* c_{nj} D_{n+1,n,j} \Gamma_{n,n+1,j}^*] \delta_{nm} \\ & + c_{nj}^* c_{n-1,j} D_{n,n-1,j} \Gamma_{n-1,n,j} \delta_{m,n-1} \} + \omega_{nj,mj'}(k) \end{aligned} \tag{D18}$$

where matrix  $\Gamma$  is defined in equation (C48), while  $\omega$  is defined in equations (C54), (C57), (C62), and (C63). Finally we have

$$\begin{aligned} J_{nj}(k) = & \hbar\omega_k o_j c_{nj}^* (B_{nk} c_{n+1,j} D_{n,n+1,j} P_{nj} + B_{n-1,k} c_{n-1,j} D_{n,n-1,j} P_{n-1,j}) \\ & + \sum_{mj'} (o_j - \delta_{jj'}) o_{j'} |c_{nj}|^2 \hbar\omega_k B_{mk} [c_{mj'}^* c_{m+1,j'} D_{m,m+1,j'} D_{mj'}^{nj} (D_{m+1,j'}^{nj})^* P_{mj'j} \\ & + c_{mj'}^* c_{m+1,j'} D_{m+1,m,j'} (D_{mj'}^{nj})^* D_{m+1,j'}^{nj} P_{mj'j}^*] + \lambda_{nj}(k) \end{aligned} \tag{D19}$$

where matrix  $\lambda$  is defined in equations (C53), (C57), (C61), and (C63). Using again  $\{nj\}$  as one index and together with equation (D15) we have the following system of equations for the determination of the time derivatives of  $c$  and the  $b_k$  from their actual values at a given time:

$$i\hbar \left[ \mathbf{P}\dot{c} + \mathbf{Q}\dot{c}^* + \sum_k \mathbf{U}(k)\dot{b}_k + \sum_k \mathbf{V}(k)\dot{b}_k^* \right] = \mathbf{W}c \tag{D20a}$$

$$i\hbar [\Delta(k)\dot{c} + \Lambda(k)\dot{c}^* + \Theta(k)\dot{b}_k] = \Omega(k)b_k + J(k). \tag{D20b}$$

### Appendix E. The Lagrangian and the time-dependent variational principle

In the Lagrangian method we have the variational principle

$$\delta \int_{t_1}^{t_2} L dt = \delta \int_{t_1}^{t_2} \left[ \frac{i\hbar}{2} \left( \left\langle \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \varphi \right\rangle \right) - \langle \varphi | \hat{H} \varphi \rangle \right] dt = 0. \tag{E1}$$

The part containing the time derivatives leads to

$$\int_{t_1}^{t_2} \left( \left\langle \delta \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle + \left\langle \varphi \left| \frac{\partial}{\partial t} \delta \varphi \right\rangle - \left\langle \frac{\partial}{\partial t} \delta \varphi \left| \varphi \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \delta \varphi \right\rangle \right) dt. \tag{E2}$$

In the parts where the variation occurs under the time derivative, partial integration leads to

$$\int_{t_1}^{t_2} \left( \left\langle \delta \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \delta \varphi \right\rangle \right) dt + \langle \varphi | \delta \varphi \rangle \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \left\langle \frac{\partial \varphi}{\partial t} \left| \delta \varphi \right\rangle dt - \langle \delta \varphi | \varphi \rangle \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \left\langle \delta \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle dt. \tag{E3}$$

Since at the end points of the integration interval we have  $\delta\varphi(t_1) = \delta\varphi(t_2) = 0$ , we have together with an additional partial integration

$$\begin{aligned} \frac{i\hbar}{2} \delta \int_{t_1}^{t_2} \left( \left\langle \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \varphi \right\rangle \right) dt &= i\hbar \int_{t_1}^{t_2} \left( \left\langle \delta\varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \delta\varphi \right\rangle \right) dt \\ &= i\hbar \int_{t_1}^{t_2} \left\langle \delta\varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle dt - \langle \varphi | \delta\varphi \rangle \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \left\langle \varphi \left| \frac{\partial}{\partial t} \delta\varphi \right\rangle dt \\ &= i\hbar \int_{t_1}^{t_2} \left( \left\langle \delta\varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle + \left\langle \varphi \left| \frac{\partial}{\partial t} \delta\varphi \right\rangle \right) dt = i\hbar \delta \int_{t_1}^{t_2} \left\langle \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle dt. \end{aligned} \tag{E4}$$

Thus we have shown that

$$\delta \int_{t_1}^{t_2} \langle \varphi | \hat{L} | \varphi \rangle dt \equiv \delta \int_{t_1}^{t_2} \left\langle \varphi \left| \frac{i\hbar}{2} \frac{\partial^{\leftrightarrow}}{\partial t} - \hat{H} \right| \varphi \right\rangle dt = \delta \int_{t_1}^{t_2} \left\langle \varphi \left| i\hbar \frac{\partial}{\partial t} - \hat{H} \right| \varphi \right\rangle dt \tag{E5}$$

where

$$\left\langle \varphi \left| \frac{\partial^{\leftrightarrow}}{\partial t} \right| \varphi \right\rangle \equiv \left\langle \varphi \left| \frac{\partial \varphi}{\partial t} \right\rangle - \left\langle \frac{\partial \varphi}{\partial t} \left| \varphi \right\rangle. \tag{E6}$$

Therefore the solution of our Euler-Lagrange equations

$$\frac{d}{dt} \frac{\partial L}{\partial \langle \dot{\varphi} |} - \frac{\partial L}{\partial \langle \varphi |} = 0 \quad \frac{d}{dt} \frac{\partial L}{\partial |\dot{\varphi} \rangle} - \frac{\partial L}{\partial |\varphi \rangle} = 0 \tag{E7}$$

is equivalent with the application of the time-dependent variational principle. This is meant when we speak about 'correct' equations of motion in contrast to those derived with the method of Davydov who used the Hamiltonian principle but not the correct canonical conjugate variables [29]. The Euler-Lagrange equations finally follow directly from the variational principle:

$$\delta \int_{t_1}^{t_2} L(\varphi, \varphi^*, \dot{\varphi}, \dot{\varphi}^*) dt = \int_{t_1}^{t_2} \left[ \frac{\partial L}{\partial \varphi} \delta\varphi + \frac{\partial L}{\partial \dot{\varphi}} \delta\dot{\varphi} + \frac{\partial L}{\partial \varphi^*} \delta\varphi^* + \frac{\partial L}{\partial \dot{\varphi}^*} \delta\dot{\varphi}^* \right] dt = 0 \tag{E8}$$

by partial integration and using  $\delta\varphi(t_1) = \delta\varphi(t_2) = \delta\varphi^*(t_1) = \delta\varphi^*(t_2) = 0$ :

$$\begin{aligned} \int_{t_1}^{t_2} \left[ \frac{\partial L}{\partial \dot{\varphi}} \delta\dot{\varphi} + \frac{\partial L}{\partial \dot{\varphi}^*} \delta\dot{\varphi}^* \right] dt &= \frac{\partial L}{\partial \dot{\varphi}} \delta\varphi \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \delta\varphi \frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}} dt + \frac{\partial L}{\partial \dot{\varphi}^*} \delta\varphi^* \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \delta\varphi^* \frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}^*} dt \\ &= \int_{t_1}^{t_2} \left[ \delta\varphi \frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}} + \delta\varphi^* \frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}^*} \right] dt. \end{aligned} \tag{E9}$$

Therefore our variational principle

$$\begin{aligned} \delta \int_{t_1}^{t_2} L(\varphi, \varphi^*, \dot{\varphi}, \dot{\varphi}^*) dt &= \int_{t_1}^{t_2} \delta\varphi \left[ -\frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}} + \frac{\partial L}{\partial \varphi} \right] dt \\ &+ \int_{t_1}^{t_2} \delta\varphi^* \left[ -\frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}^*} + \frac{\partial L}{\partial \varphi^*} \right] dt = 0 \end{aligned} \tag{E10}$$

can be fulfilled for arbitrary variations only if the Euler-Lagrange equations

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}} - \frac{\partial L}{\partial \varphi} = 0 \quad \frac{d}{dt} \frac{\partial L}{\partial \dot{\varphi}^*} - \frac{\partial L}{\partial \varphi^*} = 0 \tag{E11}$$

are fulfilled.

### Appendix F. Adiabatic dynamics with classical lattice

In this model which is usually applied in simulations of the dynamics of polyacetylene the ionic  $\text{CH}^+$  cores are assumed to move as classical particles in a potential created by the  $\pi$ -electrons, which are treated within a Hückel-type model, and by the  $\sigma$ -electrons. However, the  $\sigma$ -electron potential and the  $\sigma$ - $\pi$  interactions are assumed to be included in the lattice potential. Also the dynamics of the  $\pi$ -electrons are not computed explicitly, but the electrons are assumed to follow the ionic cores immediately. Thus we have

$$V = E_\pi + \frac{K}{2} \sum_n (u_n - u_{n+1})^2 - A(u_1 - u_N). \quad (\text{F1})$$

The coordinates  $u_n$  are usually transformed to the so-called staggered coordinates  $\psi_n = (-1)^{n+1}u_n$ , leading to the form

$$V = E_\pi + \frac{K}{2} \sum_n (\psi_n + \psi_{n+1}) - A(\psi_1 + (-1)^N \psi_N). \quad (\text{F2})$$

For each geometry  $\{\psi_n\}$  the energy  $E_\pi$  is computed by diagonalization of the Hückel matrix

$$H_{nm} = [\beta^0 - (-1)^{n+1}(\psi_n + \psi_{n+1})\alpha]\delta_{m,n+1}(1 - \delta_{nN}) \\ + [\beta^0 + (-1)^{n+1}(\psi_n + \psi_{n-1})\alpha]\delta_{m,n-1}(1 - \delta_{n1}) \quad (\text{F3})$$

i.e. the eigenvalue problem

$$Hc_i = \varepsilon_i c_i \quad (\text{F4})$$

has to be solved. The  $\pi$ -electron energy can now be obtained by summation of the eigenenergies multiplied with the occupation numbers of the orbitals:

$$E_\pi = \sum_i o_i \varepsilon_i. \quad (\text{F5})$$

It can be shown that the derivatives of  $E_\pi$  with respect to the displacements can be obtained analytically by [13]

$$\frac{\partial E_\pi}{\partial \psi_n} = 2\alpha(-1)^n [P_{n,n+1}(1 - \delta_{nN}) - P_{n,n-1}(1 - \delta_{n1})] \quad (\text{F6})$$

where the density matrix is given as usual by

$$P_{nm} = \sum_i o_i c_{ni} c_{mi}. \quad (\text{F7})$$

Note that the MO coefficients are real numbers in this case. The constants  $K$  and  $A$  are determined by the requirement that a geometry

$$\psi_n = u + (-1)^n(n - 1)a \quad (\text{F8})$$

corresponds to a minimum of the total potential for  $u = u_0$  and  $a = 0$ . In this way a regular geometry with dimerization  $u_0$  and chain length  $(N - 1)a_0$  is the equilibrium geometry. Thus

one performs a Hückel calculation on this equilibrium geometry, computes the derivatives of  $E_\pi$  with respect to the  $\psi_r$  and from this

$$\frac{\partial E_\pi}{\partial u} = \sum_n \frac{\partial E_\pi}{\partial \psi_n} \quad \frac{\partial E_\pi}{\partial a} = \sum_n (-1)^n (n-1) \frac{\partial E_\pi}{\partial \psi_n}. \quad (\text{F9})$$

From this the constants can be computed by [26]

$$K = \left[ -\frac{\partial E_\pi}{\partial u} + 2 \frac{\Theta(N)}{N-1} \frac{\partial E_\pi}{\partial a} \right] / \left\{ 4u_0 \left[ (N-1) - \frac{\Theta(N)}{(N-1)} \right] \right\}$$

$$A = \frac{1}{N-1} \frac{\partial E_\pi}{\partial a} - \Theta(N) \left( \frac{1}{2} \frac{\partial E_\pi}{\partial u} - \frac{1}{N-1} \frac{\partial E_\pi}{\partial a} \right) / [N(N-2)] \quad (\text{F10})$$

$$\Theta(N) = \frac{1}{2}(1 + (-1)^N).$$

Newton's equations of motion are then

$$\chi_n = \frac{d\psi_n}{dt}$$

$$M \frac{d\chi_n}{dt} = -\frac{\partial V}{\partial \psi_n} = -\frac{\partial E_\pi}{\partial \psi_n} - K[(\psi_n + \psi_{n+1})(1 - \delta_{nN})$$

$$+ (\psi_{n-1} + \psi_n)(1 - \delta_{n1})] + A(\delta_{n1} + (-1)^N \delta_{nN}) \quad (\text{F11})$$

or in the physical displacement coordinates

$$p_n = M\dot{u}_n$$

$$F_n \equiv \dot{p}_n = -\frac{\partial E_\pi}{\partial u_n} - K[(u_n - u_{n+1})(1 - \delta_{nN}) - (u_{n-1} - u_n)(1 - \delta_{n1})] + A(\delta_{n1} - \delta_{nN}). \quad (\text{F12})$$

Temperature effects can be included in our calculations as described in the main text via the initial conditions; however, one can also add random forces  $R_n$  and a friction term to equation (F12), leading to the Langevin equations

$$\dot{p}_n = F_n(t) + R_n(t) - \Gamma p_n. \quad (\text{F13})$$

$\Gamma$  is the time constant of the heat bath. The correlation function for the random forces is (assuming for the moment a continuum limit):

$$\langle R(x, t) R(0, 0) \rangle = 2Mk_B T \Gamma a_0 \delta(x) \delta(t) \quad (\text{F14})$$

where  $T$  is the temperature and  $a_0$  the lattice constant. The random forces are assumed to follow a normal distribution with standard deviation  $\sqrt{\sigma}$ :

$$w(R_n) = (1/\sqrt{2\pi\sigma}) \exp[-R_n^2/(2\sigma)] \quad (\text{F15})$$

where in the normalization factor for  $\sigma$  just its value in the actually used units has to be inserted. In actual computations we usually [12] calculate a series of  $L = 12$  uniformly

distributed random numbers  $X_{ns}(t)$  ( $0 \leq X_{ns}(t) \leq 1$ ) for each site  $n$  in each time step  $t$  and generate the forces as

$$R_n(t) = \sqrt{\sigma} \sum_{s=1}^L [X_{ns}(t) - \frac{1}{2}]. \quad (\text{F16})$$

Thus the variance of  $[X_{ns}(t) - 0.5]$  is  $\frac{1}{2}$  and the standard deviation of  $R_n(t)$  is  $\sqrt{\sigma}$  with the mean value zero as required. The interval for the forces is  $|R_n(t)| \leq 6\sqrt{\sigma}$ . Thus we obtain an approximate Gaussian distribution which would be exact if  $L$  would go to infinity. To get a feeling for to what extent the Gaussian distribution is realized, we computed random forces for a value of  $\sigma$  as obtained for a chain of 100 units,  $\Gamma = 0.0413 \text{ ps}^{-1}$  and  $T = 310 \text{ K}$ ,  $M = 114m_p$  ( $m_p$  is the proton mass),  $K = 13 \text{ N m}^{-1}$ , and  $L = 12$ . We computed  $10^6$  values and divided the total range of  $\pm 6\sqrt{\sigma}$  into 200 equidistant intervals. Then we counted the number of  $R$  values occurring in each of the intervals. These numbers were normalized such that for the interval around zero the value  $(2\pi\sigma)^{-1/2}$  is obtained. In figure F1 this histogram is plotted together with the exact Gaussian distribution function and we see that the agreement is satisfactory.

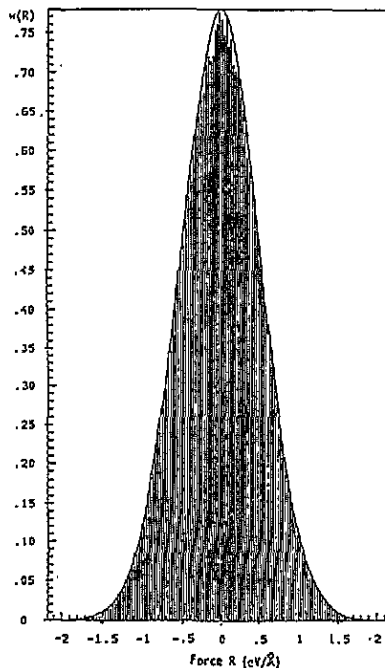


Figure F1. Plot of the numerically determined distribution of random forces  $w(R_n)$  as function of site  $n$  (vertical lines, see text for details) together with the exact Gaussian distribution function.

The effect of the two additional terms in the equations of motion is to drive the system into thermal equilibrium with the time constant  $\Gamma$ . Requiring the random forces to be constant within a time step  $\tau$  and in a lattice period  $a_0$  we obtain by averaging over  $\tau$  and

the lattice constant  $a_0$

$$\begin{aligned}\sigma &= \int_{-\tau/2}^{\tau/2} \frac{dt}{\tau} \int_{-a_0/2}^{a_0/2} \frac{dx}{a_0} \langle R(x, t) R(0, 0) \rangle \\ &= 2Mk_B T \frac{\Gamma}{\tau} \int_{-\tau/2}^{\tau/2} \delta(t) dt \int_{-a_0/2}^{a_0/2} \delta(x) dx = 2Mk_B T \frac{\Gamma}{\tau}.\end{aligned}\quad (\text{F17})$$

For the time constant we use the lower non-zero phonon frequency of the lattice:

$$\Gamma = \nu_{\min} = \frac{\omega_{\min}}{2\pi}.\quad (\text{F18})$$

Since the time constant is an additional parameter which can be chosen more or less arbitrarily, we recommend using the method of thermal lattice population as described in the main text. Further, the latter method can be used in all three methods applied, while the Langevin model is valid only for classical lattices. However, to study its validity, we applied it in this work.

### Appendix G. Numerical procedure for the solution of the equations of motion for the $|\Phi_2\rangle$ ansatz

The equations of motion for the electronic system in the  $|\Phi_2\rangle$  approximation are

$$i\hbar \dot{c}_{nj} = [\beta - \alpha(q_n - q_{n+1})]c_{n+1,j} + [\beta - \alpha(q_{n-1} - q_n)]c_{n-1,j}\quad (\text{G1})$$

where one has to take care for the boundary conditions in the cases  $n = 1$  and  $n = N$ . For the numerical solution of these equations neither a one-step nor a Runge-Kutta method was sufficient to obtain a constant overlap matrix and energy with a reasonably large time-step size. Thus at a given time  $t_0$  we solved the eigenvalue problem of the right-hand side of equation (G1):

$$\mathbf{H}\mathbf{V} = \mathbf{V}\boldsymbol{\varepsilon} \quad \varepsilon_{nm} = \varepsilon_n \delta_{nm} \quad \mathbf{V}^+ \mathbf{V} = \mathbf{V}\mathbf{V}^+ = \mathbf{1}\quad (\text{G2})$$

$$H_{nm}(t_0) = \{\beta - \alpha[q_n(t_0) - q_{n+1}(t_0)]\} \delta_{m,n+1} (1 - \delta_{nN}) + \{\beta - \alpha[q_{n-1}(t_0) - q_n(t_0)]\} \delta_{m,n-1} (1 - \delta_{n1}).\quad (\text{G3})$$

Then the equations of motion are written in matrix form

$$i\hbar \dot{c}_j(t) = \mathbf{H}(t_0) c_j(t).\quad (\text{G4})$$

Multiplication from the left with  $\mathbf{V}^+$ , insertion of the unity matrix in the form  $\mathbf{V}\mathbf{V}^+$  and transformation to  $d_j(t) = \mathbf{V}^+ c_j(t)$  yields the decoupled equations of motion

$$\begin{aligned}i\hbar \mathbf{V}^+ \dot{c}_j(t) &= \mathbf{V}^+ \mathbf{H}(t_0) \mathbf{V}\mathbf{V}^+ c_j(t) \Rightarrow i\hbar \dot{d}_j(t) = \boldsymbol{\varepsilon} d_j(t) \\ &\Rightarrow i\hbar \dot{d}_{nj}(t) = \varepsilon_n d_{nj}(t).\end{aligned}\quad (\text{G5})$$

Assuming  $\mathbf{H}$  to be constant during a reasonably small time step  $\tau$ , and thus also its eigenvectors and eigenvalues, the equations can be integrated:

$$d_{nj}(t_0 + \tau) = d_{nj}(t_0) e^{-(i/\hbar)\varepsilon_n \tau}\quad (\text{G6})$$

which yields the eigenvectors at  $t_0 + \tau$  after back transformation by multiplication with  $\mathbf{V}$  from the left

$$c_{nj}(t_0 + \tau) = \sum_m V_{nm} d_{mj}(t_0) e^{-(i/\hbar)\varepsilon_m \tau} = \sum_m V_{nm} \sum_k V_{km} c_{kj}(t_0) e^{-(i/\hbar)\varepsilon_m \tau} \quad (\text{G7})$$

Note that  $\mathbf{V}$  is real. The lattice variables are computed as usual:

$$p_n(t_0 + \tau) = p_n(t_0) + F_n(t_0)\tau \quad q_n(t_0 + \tau) = q_n(t_0) + p_n(t_0 + \tau) \frac{\tau}{M} \quad (\text{G8})$$

where one has to take care again for the boundary conditions in cases  $n = 1$  and  $N$ . The forces are given by

$$F_n(t_0) = K[q_{n+1}(t_0) - 2q_n(t_0) + q_{n-1}(t_0)] + 2\alpha \text{Re}[P_{n,n+1}(t_0) - P_{n,n-1}(t_0)]. \quad (\text{G9})$$

## References

- [1] Su W P, Schrieffer J R and Heeger A J 1979 *Phys. Rev. Lett.* **42** 1698  
Su W P 1980 *Solid State Commun.* **35** 899  
Su W P, Schrieffer J A and Heeger A J 1980 *Phys. Rev. B* **22** 2099  
Heeger A J, Kivelson S, Schrieffer J R and Su W P 1988 *Rev. Mod. Phys.* **60** 781
- [2] Thomann H, Dalton L R, Tomkiewicz Y, Shiren N S and Clarke T C 1983 *Phys. Rev. Lett.* **50** 533  
Thomson H, Kim H, Morrobel-Sosa A, Dalton L R, Jones M T, Robinson B H, Clarke T C and Tomkiewicz Y 1984 *Synth. Met.* **9** 255  
Thomann H, Cline J E, Hofmann B M, Kim H, Morrobel-Sosa A, Robinson B H and Dalton L R 1985 *J. Phys. Chem.* **89** 1994  
Heeger A J and Schrieffer J R 1983 *Solid State Commun.* **48** 207  
Soos Z G and Ramashesha S 1983 *Phys. Rev. Lett.* **51** 2374
- [3] Sasai M and Fukutome H 1984 *Synth. Met.* **9** 295
- [4] Orenstein J and Baker G L 1982 *Phys. Rev. Lett.* **49** 1043  
Weinberger B R 1983 *Phys. Rev. Lett.* **50** 1693  
Blanchet G B, Fincher C P and Heeger A J 1983 *Phys. Rev. Lett.* **51** 2132  
Blanchet G B, Fincher C P, Chung T C and Heeger A J 1983 *Phys. Rev. Lett.* **50** 1938
- [5] Bishop A R, Campbell D K, Lomdahl P S, Horowitz B and Phillpot S R 1984 *Phys. Rev. Lett.* **52** 671
- [6] Wang C L and Martino F 1986 *Phys. Rev. B* **34** 5540
- [7] Su W P 1986 *Phys. Rev. B* **34** 2988
- [8] Kivelson S and Wu W-K 1986 *Phys. Rev. B* **34** 5423
- [9] Su W P and Schrieffer J R 1980 *Proc. Natl Acad. Sci. USA* **77** 5626
- [10] Förner W, Seel M and Ladik J 1986 *Solid State Commun.* **57** 463
- [11] Förner W, Seel M and Ladik J 1986 *J. Chem. Phys.* **84** 5910
- [12] Liegener C-M, Förner W and Ladik J 1987 *Solid State Commun.* **61** 203  
Gozdik A, Seel M, Förner W and Ladik J 1986 *Solid State Commun.* **60** 609  
Orendi H, Förner W and Ladik J 1988 *Phys. Lett.* **150** 113
- [13] Förner W 1987 *Solid State Commun.* **63** 941
- [14] Gibson H W, Weagley R J, Mosher R A, Kaplan S, Prest W M and Epstein A J 1985 *Phys. Rev. B* **31** 2338
- [15] Förner W, Wang C-L, Martino F and Ladik J 1988 *Phys. Rev. B* **37** 4567
- [16] Boudreaux D S, Chance R R, Bredas J L and Silbey R 1983 *Phys. Rev. B* **28** 6927
- [17] Phillpot S R, Baeriswyl D, Bishop A R and Lomdahl P S 1987 *Phys. Rev. B* **35** 7533
- [18] Markus R, Förner W and Ladik J 1988 *Solid State Commun.* **68** 1
- [19] Förner W 1991 *Phys. Rev. B* **44** 11 743
- [20] Förner W 1992 *Chem. Phys.* **160** 173, 188
- [21] Nakahara M and Maki K 1982 *Phys. Rev. B* **25** 7789
- [22] Rukh R, Sigmund E and Eisele H 1989 *J. Chem. Phys.* **90** 6463
- [23] Davydov A S and Kislukha N I 1973 *Phys. Status Solidi* **b** 59 465

- Davydov A S 1979 *Phys. Scr.* **20** 387
- [24] Davydov A S 1980 *Zh. Eksp. Teor. Fiz.* **78** 789; 1980 *Sov. Phys.-JETP* **51** 397
- [25] Förner W 1992 *Habilitationthesis* University Erlangen-Nürnberg
- [26] Förner W 1989 *Synth. Met.* **30** 135
- [27] Förner W 1993 *J. Phys.: Condens. Matter* **5** 803
- [28] Skrinjar M J, Kapor D V and Stojanovic S D 1988 *Phys. Rev. A* **38** 6402
- [29] Mechtly B and Shaw P B 1988 *Phys. Rev. B* **38** 3075
- [30] Förner W 1992 *J. Phys.: Condens. Matter* **4** 1915
- [31] Förner W 1993 *J. Phys.: Condens. Matter* **5** 3883
- [32] Motschmann H, Förner W and Ladik J 1989 *J. Phys.: Condens. Matter* **1** 5083  
Förner W and Ladik J 1990 *Davydov's Soliton Revisited* ed P L Christiansen and A C Scott (New York: Plenum) p 267
- [33] Förner W 1991 *J. Phys.: Condens. Matter* **3** 4333; 1992 *J. Comput. Chem.* **13** 275; 1992 *Nanobiology* **1** 413
- [34] Förner W 1994 *Adv. Quantum Chem.* **25** 207
- [35] Davydov A S 1979 *Teor. Mat. Fiz.* **40** 408; 1988 *Phys. Status Solidi b* **146** 619; 1989 *Nonlinearity* **2** 383
- [36] Abramowitz M and Stegun I A 1970 *Handbook of Mathematical Functions* 9th edn (New York: Dover) pp 896, 897
- [37] Schinke R and Engel V 1990 *J. Chem. Phys.* **93** 3252
- [38] Majewski J A and Vogl P 1992 *Phys. Rev. B* **46** 12 219, 12 235