Soliton dynamics in a formamide stack using a Taylor-series expansion for the potential surface. II. The Pariser-Parr-Pople Hamiltonian

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The effects of explicit electron-electron interactions described by the semiempirical Pariser-Parr-Pople Hamiltonian on soliton dynamics in formamide stacks as a model system are investigated. It is shown that explicit treatment of electron-electron interactions does not influence the properties of solitary waves in the model system. Possibilities that solitary waves might serve as charge carriers in stacked systems after doping are discussed.

I. INTRODUCTION

For the explanation of the long-range effects of carcinogen binding and release in DNA,[1-6] Ladik and Čížek[7,8] suggested a mechanism which invokes the concept of conformational solitons. Solitons are used for the interpretation of a wide range of physical and chemical phenomena (see Ref. 9 for a review and Refs. 10 and 11 for a short list of phenomena explained by solitons). The existence of such solitary waves in a formamide stack has been shown numerically,[10] using a Hückel-type Hamiltonian similar to that formulated by Ladik and Čížek.[7,8] Formamide has been chosen as simple model system since the molecule contains the same sequence of heavy atoms as the nucleotide base cytosine.

The present series of papers deals with the numerical study of the details of this simple model system. We feel that only after a full understanding of the model system is it reasonable to attack the formidable problem of realistic DNA models. In Ref. 11 (an earlier paper in this series) it was shown that explicit treatment of the π electrons of the system on the Hückel level is not necessary. In Ref. 11 the Hartree-Fock (HF) potential surface of a formamide dimer was expanded into a sixth-order Taylor series in three geometrical degrees of freedom. Then the potential energy of the system is taken as the sum of such pair potentials. It was possible to reproduce the results given in Ref. 10. In the preceding paper, referred to as paper I, the exact equations of motion had been derived and applied. Qualitative differences in the behavior of the system compared to the approximate equations of motion used in Refs. 7, 8, 10, and 11 had been found. Also in paper I the intermolecular dispersion energy was introduced into the model, using London's formula. It turned out that the dispersion energy has considerable influence on the properties of solitary waves within the system. In Ref. 13 we have studied in addition the effects of impurities on the soliton.

However, our model is based on the assumption that in stacked systems of this kind only first-neighbors interactions are of importance. Long-range interactions, if present, should have their origin in the π electrons of the system. For a Hückel-type model we have already shown that there are no long-range interactions present. However, in *trans*-polyacetylene it turned out that electron-electron interactions, which are included only indirectly via the parameters in Hückel-type models, have a strong influence on the properties of solitons.[14] Therefore in this work we want to study the influence of electron-electron interactions using the Pariser-Parr-Pople (PPP) model for the π electrons on soliton dynamics in a formamide stack.

II. METHOD

The model system consists of a stack of N planar formamide molecules with parallel molecular planes (see Fig. 1 of the preceding paper). The z axis is perpendicular to the molecular planes. The stack is described by three geometrical degrees of freedom per molecule n: z_n, ϑ_n, and φ_n; z_n is the negative difference between the actual position of the plane on the z axis (Z_n) and its equilibrium position $Z_n^{(e)} = -(n-1)Z_0$, where $Z_1^{(e)} = 0$. Z_0 is chosen to be 3.36 Å, as in B-DNA (B conformation). ϑ_n is the angle between the C—H bond and its projection onto the plane perpendicular to the z axis containing the hydrogen. ϑ_n is defined as negative if the rotation occurs in the positive z direction. φ_n is the rotation around the z axis relative to the equilibrium position $\phi_n^{(e)} = -(n-1)\phi_0$, with ϕ_0 being 36° as in B-DNA.

In the quantum-chemical treatment of planar molecular systems one can distinguish between three different kinds of molecular orbitals (MO's). First of all there are the so-called core or inner-shell orbitals. These are localized near the nuclei and their contributions to chemical bonding are negligible. The second kind of orbitals are the σ orbitals which, in planar molecules, are symmetric with respect to the molecular planes. These orbitals form so-called lone pairs and chemical bonds. They are local-

ized mainly between two atoms (bonds) or at one atom (lone pairs). The third kind are called π orbitals. They are antisymmetric with respect to the molecular planes and are usually delocalized over the entire molecule. In *ab initio* Hartree-Fock calculations, if the molecular plane is perpendicular to the z axes of the coordinate system, the π MO's are linear combinations of the p_z atomic orbitals only.

Semiempirical π-electron methods assume that the electrons occupying π MO's can be separated from the core and σ electrons. Since in our system we are interested in the interactions of stacked planar molecules which are rather far away from each other (3.36 Å) one can safely assume that mainly the delocalized π electrons contribute to these interactions. To justify our previous assumption (Ref. 11 and paper I) that the potential energy of our system can be computed as the sum of first-neighbor pair interaction energies, one has to study the behavior of the π electrons. Namely, one has to show that they do not give rise to long-range or nonpairwise additive interaction contributions. This was already done for the case of a Hückel-type model for the π electrons.[10] The comparison of the results of Refs. 10 and 11 confirms the assumption made in Ref. 11 and paper I.

However, in case of *trans*-polyacetylene we have shown that the explicit inclusion of electron-electron interactions into a Hückel-type model can change even the qualitative properties of a system considerably.[14] Therefore one has to apply the Pariser-Parr-Pople model Hamiltoni-

an[15] also to our system and compare the results to those of a Hückel model and of paper I. In case of the PPP model the total potential energy of the system is given by

$$V = E_\pi + V_\sigma + V_B \ . \tag{1}$$

Here E_π contains all effects due to the π electrons only, while V_σ contains all energy terms due to σ-electrons (also σ-π interactions), while V_B is a term due to a backbone which is necessary to stabilize a stack like nucleotide base stacks. V_B is described in detail in paper I.

The π electrons are described by the PPP-RHF (restricted HF for closed-shell systems) eigenvalue equations:

$$\underline{F}\mathbf{c}_i = \varepsilon_i \mathbf{c}_i \ . \tag{2}$$

Here c_{ir} is the coefficient of the atomic p_z orbitals at atom r in the MO i and ε_i is the energy eigenvalue of this MO. $\underline{F}$ is the PPP-RHF Fock matrix. Since each atom contributes one p_z orbital to the system, $\underline{F}$ is of dimension $mN \times mN$, if our stack consists of N molecules with m π centers (atoms having p_z orbitals). In a formamide stack the dimension of $\underline{F}$ is therefore $3N \times 3N$, for a cytosine stack it would be $8N \times 8N$. The overlap matrix is assumed to be the unit matrix due to the zero differential overlap (ZDO) approximation (all products $\chi_r\chi_s$ are assumed to vanish if the p_z orbitals χ_r and χ_s are not at the same atom).

The Fock-matrix elements are given by

$$F_{rs} = \left[-I_r + \tfrac{1}{2}\gamma_{rr}P_{rr} + \sum_{t=1}^{mN}(P_{tt}-Z_t)\gamma_{rt}(1-\delta_{r,t}) \right]\delta_{r,s} + (\beta_{rs} - \tfrac{1}{2}\gamma_{rs}P_{rs})(1-\delta_{r,s}) \ , \tag{3}$$

where $\delta_{r,s}$ is the Kronecker δ. The quantities I_r, γ_{rs}, and β_{rs} are parameters and will be discussed in Sec. III. Here we only want to mention that γ_{rs} represents a two-electron integral

$$\left\langle \chi_r(1)\chi_s(2) \left| \frac{1}{r_{12}} \right| \chi_r(1)\chi_s(2) \right\rangle \ .$$

All other two-electron integral types vanish due to the ZDO approximation. Z_t is the net charge of atom t after all its π electrons are removed ($+1$ for C,O and $+2$ for N in formamide). The indices r,s,t run over all π centers of the system. $\underline{P}$ is the charge-density-bond order matrix and is given by

$$P_{rs} = \sum_i O_i c_{ir}c_{is} \ , \tag{4}$$

where O_i is the occupation number of MO i. Finally the one-electron part $\underline{H}^N$ of (3) is given by

$$H_{rs}^N = \left[-I_r - \sum_{t=1}^{mN} Z_t\gamma_{rt}(1-\delta_{r,t}) \right]\delta_{r,s}$$

$$+ \beta_{rs}(1-\delta_{r,s}) \equiv \alpha_r\delta_{r,s} + \beta_{rs}(1-\delta_{r,s}) \ . \tag{5}$$

Then starting from a guess on $\underline{P}$ one can construct $\underline{F}$, di-

agonalize it, compute a new $\underline{P}$ and iterate until self-consistency is reached. In the first time step of a simulation the guess on $\underline{P}$ can be obtained from the $\underline{P}$ matrices of the free molecules. In all consecutive time steps as guess the converged P of the preceding step is taken.

In the Hückel approximation used in Ref. 10 only $\underline{H}^N$ is taken as the Hamiltonian matrix. Thus no iterations are necessary. The α's and β's have been assumed as (converged) *ab initio* Fock-matrix elements between corresponding p_z atomic orbitals. The α's and intramolecular β's have been taken from a calculation on the monomer, the intermolecular ones from dimer calculations. They had been expanded as a Taylor series of sixth order in the three geometrical degrees of freedom.[10]

Having obtained a converged $\underline{P}$ one can calculate E_π as

$$E_\pi = \tfrac{1}{2}\sum_{r,s=1}^{mN}(H_{rs}^N + F_{rs})P_{rs} + \tfrac{1}{2}\sum_{r,s=1}^{mN}Z_rZ_s\gamma_{rs}(1-\delta_{r,s}) \ . \tag{6}$$

The second term represents the nuclear repulsion energy between the ionic cores. In dynamic simulations one needs also the derivatives of E_π with respect to the geometrical degrees of freedom $q_{\mu n}$ [$\mathbf{q}_n^+ = (z_n, \vartheta_n, \varphi_n)$; $\mu = 1,2,3$). They are given by[16]

$$\frac{\partial E_{\pi}}{\partial q_{\mu n}} = \sum_{r,s=1}^{mN} (1-\delta_{r,s}) \left[\frac{\partial \beta_{rs}}{\partial q_{\mu n}} P_{rs} + \frac{1}{2} \frac{\partial \gamma_{rs}}{\partial q_{\mu n}} (Z_r Z_s - \tfrac{1}{2} P_{rs}^2 + P_{rr} P_{ss} - P_{rr} Z_s - P_{ss} Z_r] \right] .$$ (7)

It was shown[16] that terms containing $\partial P_{rs}/\partial q_{\mu n}$ which arise from differentiation of (6) cancel each other exactly. The derivatives of β_{rs} and γ_{rs} depend on the parametrization and will be discussed below (Sec. III).

To obtain V_σ we have computed E_π^D and the *ab initio* HF energy V_{HF}^D of dimers (see Fig. 1 of the preceding paper) for 400 different geometries in a range $|\Delta Z| \le 0.5$ Å, $|\Delta \vartheta| \le 15°$, and $|\Delta \varphi| \le 15°$ (for details see Ref. 11). Then $V_\sigma^{D'}$ of a dimer is defined as

$$V_\sigma^{D'} = V_{HF}^D - E_\pi^D .$$ (8)

V_σ^D is expanded in a Taylor series

$$V_\sigma^D = \sum_{i,j,k \ge 0}^{(i+j+k) \le 6} K_{ijk} \Delta z^i \Delta \vartheta^j \Delta \varphi^k ,$$ (9)

where $\Delta q = q_2 - q_1$, and the total V_σ is obtained by summation of the pair potentials

$$V_\sigma = \sum_{i,j,k=1}^{(i+j+k) \le 6} K_{ijk} \sum_{n=1}^{N-1} \Delta z_n^i \Delta \vartheta_n^j \Delta \varphi_n^k ,$$ (10)

where $\Delta q_n = q_{n+1} - q_n$. The potential constants K_{ijk} have been computed by a least-square fitting of V_σ^D to the 400 values of $V_\sigma^{D'}$. As in Ref. 11 where simply the complete HF potential was fitted with a series of the type of Eq. (9),the values of $V_\sigma^{D'}$ could be reproduced to an accuracy of ≈ 9 μhartree with the ansatz (9). The derivatives of V_σ with respect to $q_{\mu n}$ can be calculated in a straightforward way from (9).

The explicit expression for the kinetic energy T, the equations of motion, and the time simulation procedure are described in detail in paper I.

III. RESULTS AND DISCUSSION

First of all, we have to specify the parameters entering the PPP model. One can think to use *ab initio* Hartree-Fock one-electron matrix elements for the α's and β's, and the HF integrals $\langle rs|rs \rangle$ for the γ's. If one does that and computes a simple formamide molecule one obtains unreasonable results. For instance, the energy spacings between the one-electron levels ε_i are greater than 100 eV and excitation energies are greater than 70 eV. The reason for this is that the electron-nuclear attraction terms in the one-electron HF matrix elements are computed with the naked nuclear charge and thus are far too large in absolute values. For π-electron calculations the nuclear charges must be shielded by the σ electrons. Therefore the use of semiempirical parameters seems to be reasonable, at least for the intramolecular terms.

As in usual PPP parametrizations we neglect all β_{rs} if atoms r and s are not covalently bound, thus all intermolecular β's and the intramolecular β_{O-N} are neglected. γ_{rr} is chosen as usual as the difference $\gamma_{rr} = \mathcal{I}_r - \mathcal{E}_r$,

where $\mathcal{I}_r$ is the ionization potential and $\mathcal{E}_r$ the electron affinity of the valence state of atom r. The values chosen are given in Table I together with the β's. For $\mathcal{I}_r$ usually $\mathcal{I}_r$ is used. However, if one computes a formamide molecule using the $\mathcal{I}$ values from Table I, the charge distribution especially at the N atom differs strongly from the *ab initio* (net charge of $> +1$ on N) one. The reason for this is that N contributes two π electrons to the system and thus the use of the first ionization potential (which is correct for the γ_{rr} where valence state ionization potentials are necessary) is not appropriate. Therefore we use the second ionization potential for N which is 29.2 eV.[20] Calculation of the formamide molecule with this set of parameters leads to a lowest one-electron level being 5.58 eV below the corresponding *ab initio* HF level. Therefore we have subtracted 5.58 eV from all $\mathcal{I}$'s to obtain the $\mathcal{I}_r$. This final set of parameters together with the intramolecular parts of α_r and the intramolecular γ's is given in Table II.

The intramolecular γ's are computed with the well-known Ohno formula[21]

$$\gamma_{rs} = e^2 \left[\left[\frac{e^2}{0.5(\gamma_{rr} + \gamma_{ss})} \right]^2 + R_{rs}^2 \right]^{-1/2} .$$ (11)

With this parametrization we obtain an electronic energy of $-3.389\,395$ hartree, a nuclear repulsion energy of $1.277\,066$ hartree, and $E_\pi = -2.112\,329$ hartree $= -57.48$ eV for the formamide molecule. The energy levels ε_i and net atomic charges q_r for the molecule obtained with different methods are given in Table III. Obviously the agreement for the two occupied levels is very good between HF and PPP while in the Hückel model the level spacing is ≈ 3 eV too large. The virtual level occurs in both semiempirical models lower in energy than in HF. However, virtual levels are in general too high in HF calculations. The net charges are in moderate agreement between HF and PPP, while the Hückel method gives the charge at carbon far too low.

For the intermolecular γ's we use the first-neighbor HF integrals $\langle rs|rs \rangle$ fitted in the same way as V_σ^D. The

TABLE I. Values used for the ionization potentials $\mathcal{I}$ and electron affinities $\mathcal{E}$ of the valence states of the atoms occurring, the γ_{rr} values computed from them, and the β values used (all values in eV).

Atom	$\mathcal{I}$[a]	$\mathcal{E}$[b]	γ_{rr}	Bond	β_{rs}[c]
C	11.24	1.27	9.97	C—N	−2.39
N	12.25	−0.10	12.35	C—O	−3.11
O	17.25	1.46	15.79	N—O	0.0

[a]Experimental, from Ref. 17.
[b]Experimental, from Ref. 18.
[c]Following Ref. 19.

TABLE II. Intramolecular γ values (in eV) as used in the calculations together with the intramolecular contributions to α_r and the final values of I_r (in eV).

Atom	N	C	O
N	12.3500		
C	7.3655	9.9700	
O	5.6582	8.7016	15.7900
α_r (eV)	−36.6437	−29.1125	−31.6880
I_r (eV)	23.62	5.68	11.67

Ohno parametrization cannot be used for this purpose because it is specially fitted to a planar arrangement of p_z AO's not to a stacked one, as occurring in the intermolecular γ's of our system. Also simulations of soliton dynamics using Ohno integrals and one-electron *ab initio* Fock-matrix elements for $\underline{H}^N$ lead to unreasonable results.[22]

In Table IV the interaction energies in a formamide dimer and trimer (in equilibrium geometry) are given. For the trimer also the nonpairwise additive term together with the second-neighbor contribution is given. The energies are calculated with the HF method, with the direct potential fit used in Ref. 11 and paper I, with the Hückel method of Ref. 10, and finally with the PPP method. Obviously in the case of the Hückel method the assumption that most of the intermolecular interaction energy is due to π electrons is not fulfilled. In the Hückel method E_π is attractive and only the large repulsive σ potential corrects it to the correct repulsive HF value. On the other hand, in case of PPP the electronic energy E_π is somewhat too repulsive and is corrected by a rather small attractive σ term. Therefore we conclude that our parametrization leads to a consistent model of the HF interactions in formamide stacks. Second-neighbor HF integrals are two orders of magnitude smaller than the first-neighbor ones and can be neglected.

In Fig. 1 we show the time evolution of the local kinetic energy of a stack of 30 units after an excitation of $z_2 = -0.3$ Å. The first and last unit of the stack has been kept fixed. The three plots have been computed with the potential fit method (a), the Hückel method (b), and the PPP method (c). Obviously there is no visible difference between the three methods. The initial excitation energies are 25.76 meV (potential fit), 27.64 meV (Hückel),
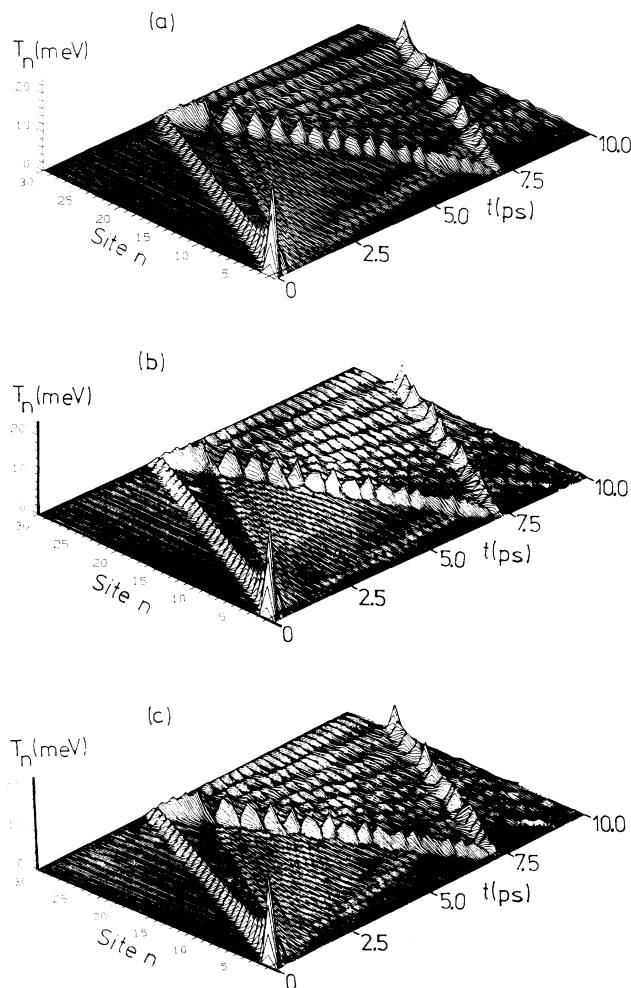

FIG. 1. Local kinetic energy T_n as function of site (n) and time (t) in a stack of 30 units after an initial excitation of $z_2 = -0.3$ Å. (a) Direct HF-potential fit; (b) Hückel model; (c) PPP model.

and 26.06 meV (PPP). The mean kinetic energies are 14.61 meV (potential fit), 15.29 meV (Hückel), and 14.56 meV (PPP). As Fig. 1 shows the velocities and shapes of the solitons are identical. Thus one concludes that the applicability of the potential fit method can be fully proven numerically with the help of these results. In the cal-

TABLE III. Energy levels ε_i and net atomic charges q_r for the formamide molecule obtained with the *ab initio* HF, the Hückel, and the PPP method (energies in eV).

Method	ε_i Level No.			q_r Atom		
	1	2	3	N	C	O
HF[a]	−12.94	−8.35	8.62	−0.051	+0.304	−0.253
Hückel[b]	−16.32	−8.18	6.47	+0.123	+0.080	−0.204
PPP	−12.94	−8.51	6.23	+0.056	+0.285	−0.341

[a]Minimal atomic basis set applied.
[b]Parameters from Ref. 10.

TABLE IV. Interaction energies for the formamide dimer $[E(D)]$, trimer $[E(T)]$, and the nonadditive plus second-neighbor term $[E'(T)]$ for the trimer, computed with the HF method, the potential fit of Ref. 11 and paper I (Fit), the Hückel method of Ref. 10 and the PPP method (all in meV, equilibrium geometries).

Method	$E(D)$	$E(T)$	$E'(T)$
HF	$+40.63$	$+82.31$	$+1.05$
Fit	$+40.49$	$+80.98$	
Hückel E_π	-9.09	-18.17	-0.01
$E_\pi + V_\sigma$	$+40.47$	$+80.93$	-0.01
PPP E_π	$+48.69$	$+95.66$	-1.72
$E_\pi + V_\sigma$	$+40.49$	$+79.26$	-1.72

culations presented 2000 time steps of 0.005 ps were used. For this the PPP method needs 4.4 h CPU time, the Hückel method 3.1 h, and the potential fit method of Ref. 11 and paper I 6.5 min on a Control Data Corporation CYBER 995E computer.

In Fig. 2 we plot the squares of the coefficients (intramolecular contributions summed up) of the wave functions of the highest occupied molecular orbital [HOMO, Fig. 2(a)] and the lowest unoccupied molecular orbital [LUMO; Fig. 3(b)], as obtained from the Hückel calculation. Obviously the results suggest that in case of p or n doping the excess charge would remain localized at the soliton and travel with it through the chain. However, in the PPP calculations HOMO and LUMO remain localized at the first (LUMO) and last (HOMO) site of the stack. In explicit calculations with an additional electron or hole the PPP–self-consistent-field (PPP-SCF) iteration does not converge. This is probably due to the fact that an RHF-PPP formalism with half-filled frontier orbital was used. On would need an unrestricted HF (UHF)-PPP formalism to obtain a decisive answer whether or not conformational solitons in stacked systems are related to charge transport in doped systems. For these doublet states also a method to avoid spin contaminations has to be introduced. Investigations along these lines are in progress.

IV. CONCLUSION

We have shown by numerical comparison that explicit treatment of π electrons is not necessary for the description of soliton dynamics in stacked systems, at least in undoped ground states. This statement holds both for strictly one-electron models of Hückel type as well as for explicit inclusion of electron-electron interactions in PPP-type models. However, the Hückel model suggests that upon doping charge transport in stacked systems may be related to soliton movement. This question remains an open one since RHF-PPP suggests the opposite. For a detailed study of these phenomena a UHF-PPP model is necessary. Investigations along this line are in progress.
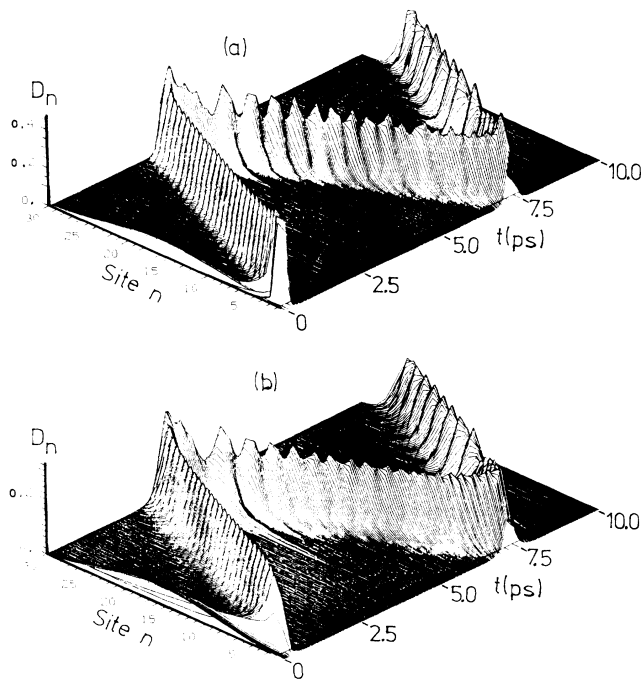

FIG. 2. The squares D_n of the MO coefficients [intramolecular contributions summed up to D_n as function of site (n) and time (t) for the system of Fig. 1] computed with the Hückel model. (a) Highest occupied molecular orbital $(i = 60)$; (b) Lowest unoccupied molecular orbital $(i = 61)$.

Finally, our potential fit model is now in a state that application to realistic nucleotide base stacks seems to be reasonable. Then also comparisons to experiments should be possible. Calculations on nucleotide base stacks are already in progress. Also effects of impurities of aperiodicity and of environment are under investigation. The introduction of quantum equations of motion seems not to be necessary for two reasons. First of all in contrast to solitons in trans-polyacetylene and proteins the solitons in our system have an extremely high kinetic mass of $> 100m_e$ up to $> 1000m_e$ depending on the kinetic energy carried by them. Secondly the moving units especially in nucleotide base stacks also possess a very high mass. Both facts make the existence of important quantum effects highly improbable. However, to prove this assumption numerical calculations would be necessary.

ACKNOWLEDGMENTS

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