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Effects of boundary conditions on the stability of one-dimensional Peierls–Hubbard systems

Shi-Jie Xie[†], Jian-Hua Wei[†], Liang-Mo Mei[†], Sheng-Hao Han^{†‡} and Shu-Shen Lai[§]

[†] Department of Physics, Shandong University, Jinan, Shandong 250100, People's Republic of China

[‡] Institute of Photoelectricity, Shandong University, Jinan, Shandong 250100, People's Republic of China

[§] Hua-Fan College of Humanities and Technology, Taipei, Taiwan

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Abstract. Several boundary conditions have been proposed to stabilize the dimerized structures of finite-length Peierls–Hubbard chains. The effects of different boundary conditions on the lattice structures and the electronic energy spectra have been analysed. It was found that the natural or the fixed-end boundary conditions are more suitable to describe polymer chains with very short lengths than the periodic boundary condition. The competition of electron–electron interactions with electron–phonon interactions in finite-length chains has also been studied.

1. Introduction

Since the beginning of the 1970s, intense research work has been undertaken in the study of the physical properties of system of restricted dimensionality. Many chainlike compounds, such as conjugated polymers and platinum compounds, have been synthesized in which the electrical conductivity along the chains is much larger than that perpendicular to the chains. In the treatment of conjugated polymers, if only electron–phonon (e–ph) couplings are explicitly included, the well known Su–Schrieffer–Heeger (SSH) model [1] is obtained, while if electron–electron (e–e) interactions are also included, then the Peierls–Hubbard [2, 3] and Pariser–Parr–Pople (PPP) [4, 5] models are widely adopted. These models have achieved great success in studying the static and dynamical properties of quasi-one-dimensional conjugated polymers. For example, these models predicted, as has indeed been observed, a ground state consisting of alternating bonds with an associated Peierls gap of about 1.6 eV. Moreover, because of the reduced dimensionality of the lattice, a variety of nonlinear excitations could be supported, such as solitons, polarons and bipolarons depending upon whether the polymer has a degenerate ground state or a nondegenerate ground state [6].

Due to the complex treatment of the SSH, PPP and Peierls–Hubbard Hamiltonians, most works have been carried out in numerical computation methods in a finite chain or in the continuous version of the models in an infinite-length chain. In the case of a finite chain, the periodic boundary condition is generally imposed, while the effect of the ends of the chain is totally neglected [1–5, 7].

However, some recent research has revealed that the conjugated lengths of polymer chains may be very short. So the ends of chains may be fatal to some properties of materials. In actual polymer samples, there are chain breaks and various conjugation

defects, such as sp^3 bonds, cross-links, inclusion of catalyst or precursor polymers, which act as chain breaks. For *t*-PA, analysis of Raman scattering results has provided good evidence that a sizable proportion of chains has 40 CHs or fewer [8]. Photoluminescence studies of thermally isomerized *t*-PA samples have also led to the conclusion that the mean lengths of *t*-PA segments are probably less than 26 CHs [9]. Mulazzi *et al* have indicated that in real materials the polymer chains are always broken by the chain defects into conjugated fragments of finite lengths. Copolymers with $(CH)_x$ sequences have been prepared in a controlled manner, with expected various lengths ranging from 10 to 100 or more C=C bonds [10]. In these cases, the role of the ends of the short chains should become apparent. Lanzani *et al* has reported typical linear electronic absorption spectra of samples with different average conjugation length and found that the blue shift of the absorption maximum occurring on shortening the conjugation length is striking [11]. Study of electroluminescent polymers (LEDs [12] or LECs [13]) also showed that polymers with short lengths have a wide $\pi-\pi^*$ energy gap. The photon/electron quantum efficiency of LEDs can be significantly improved by using short-length conducting polymers as an electron-injection layer [14].

In this paper, finite-length *t*-PA chains characterized with the Peierls–Hubbard model were studied. Three kinds of boundary condition were proposed for the short chains. The lattice structure and the electronic energy band gap were calculated in each boundary condition separately. Then the results were compared with the possible experimental data.

2. The SSH model in finite-length *t*-PA chains

Neglecting the electron–electron interactions and the interchain couplings of conjugated polymers, in the framework of the tight-binding approximation, the SSH model is proposed [1],

$$H = - \sum_{n,s} [t_0 - \alpha(u_{n+1} - u_n)] (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}) + 1/2 \sum_n K(u_{n+1} - u_n)^2 + 1/2 \sum_n M u_n^2. \quad (1)$$

All the notations have the conventional meaning.

For a finite-length *t*-PA chain with open ends, if the ends were allowed to be flexible and if the SSH Hamiltonian could still be used to describe the open-end chain, then with a small deviation from the equilibrium configuration, a static condition could be derived by minimizing the total energy of the system through the second-order perturbation theory,

$$\phi_n + \phi_{n+1} = \pi \lambda (-1)^n \sum_{\mu,s}' Z_{\mu,n,s} Z_{\mu,n+1,s} \quad (2)$$

where $\phi_n = (-1)^n (\alpha/t_0) u_n$ and $\lambda = 2\alpha^2/\pi K t_0$ are the dimensionless order parameter and the e–ph coupling strength. The prime means the sum over the occupied electronic states. The eigenstate $Z_{\mu,n,s}$ and the eigenvalue ε_μ are determined by the following eigenequation,

$$-(1 - \delta_{n,1}) [1 + (-1)^{n-1} (\phi_{n-1} + \phi_n)] Z_{\mu,n-1,s} - (1 - \delta_{n,N}) [1 + (-1)^n (\phi_n + \phi_{n+1})] Z_{\mu,n+1,s} \varepsilon_\mu Z_{\mu,n,s}. \quad (3)$$

$\delta_{m,n}$ is the Kronecker delta function.

The iterative equation (2) and (3) can be solved self-consistently. It can be proved that a uniform dimerized solution cannot be obtained from the equations, which means that the SSH Hamiltonian is unstable for the dimerized lattice structure of an *open t*-PA chain.

Moreover, it can be proved that, without a suitable boundary condition, from the SSH Hamiltonian one cannot obtain the stable soliton and polaron in a finite-length t -PA chain. This is apparently inconsistent with the well known experimental observations that t -PA has an alternating lattice structure and solitons and polarons are the stable excitations. So for a finite-length chain, suitable boundary conditions are necessary to obtain the theoretical results that are consistent with the experimental observation.

3. Boundary conditions of finite chains

In the real materials, each chain is surrounded by the others. The weak interchain couplings make the conjugated chain a stable structure. So the conjugated polymer can be regarded as a quasi-one-dimensional system. For a finite-length chain, three kinds of boundary condition are proposed here.

(1) *The periodic boundary condition.* The periodic boundary condition has been widely adopted to describe the finite t -PA chain. It eliminates the end effects.

$$u_{N+1} = u_1 \quad Z_{\mu,N+1,s} = Z_{\mu,1,s}. \quad (4)$$

In this case the static condition is derived as [15]

$$\phi_n + \phi_{n+1} = (-1)^n \pi \lambda \left[\sum'_{\mu,s} Z_{\mu,n,s} Z_{\mu,n+1,s} - \frac{1}{N} \sum_{m=1}^N \sum'_{\mu,s} Z_{\mu,m+1} Z_{\mu,m} \right]. \quad (5)$$

(2) *The fixed-end boundary condition.* Supposing that the length of the chain keeps unchanged under the Peierls transition, a fixed-end boundary condition is obtained,

$$u_1 = 0 \quad u_N = 0. \quad (6)$$

Then the static condition is

$$\phi_n + \phi_{n+1} = (-1)^n \pi \lambda \left[\sum'_{\mu,s} Z_{\mu,n,s} Z_{\mu,n+1,s} - \frac{1}{N-1} \sum_{m=1}^{N-1} \sum'_{\mu,s} Z_{\mu,m+1} Z_{\mu,m} \right]. \quad (7)$$

(3) *The free-end boundary condition.* Comparing the fixed-end boundary condition, another situation is that the chain can expand and contract freely, Su has indicated that, in this case, an extra constraint must be applied to stabilize the dimerized structure [16, 17],

$$H' = \sum_n^{N-1} K'(u_{n+1} - u_n) \quad (8)$$

where K' can be considered as an effective field caused by the surrounding environment.

In the same way, the static condition is derived ($k' = (-\pi/4\alpha)K'$),

$$\phi_n + \phi_{n+1} = (-1)^n \pi \lambda \left[\sum'_{\mu,s} Z_{\mu,n,s} Z_{\mu,n+1,s} - \frac{2}{\pi} k' \right]. \quad (9)$$

Multiplying by $(-1)^n$ on both sides of the above equation, one obtains

$$k' = \frac{1}{2\lambda(N-1)} \left[\pi \lambda \sum'_{\mu,m,s} Z_{\mu,m,s} Z_{\mu,m+1,s} - \sum_m^{N-1} (-1)^m (\phi_m + \phi_{m+1}) \right]. \quad (10)$$

4. Comparison of the boundary conditions

The following calculations show that, from all the three boundary conditions (BCs), one can give stable structures of a finite-length chain. But the dimerization may not be identical to different boundary conditions. Comparing the static equilibrium equations obtained in different boundary conditions, one can find that the main difference lies in the second term of each equation, the stability correction, which is defined as $B_i(\lambda, N)$,

$$\text{periodic BC: } B_1(\lambda, N) = \frac{1}{N} \sum'_{\mu, m, s} Z_{\mu, m, s} Z_{\mu, m+1, s} \quad (11a)$$

$$\text{fixed-end BC: } B_2(\lambda, N) = \frac{1}{N-1} \sum'_{\mu, m, s} Z_{\mu, m, s} Z_{\mu, m+1, s} \quad (11b)$$

$$\begin{aligned} \text{free-end BC: } B_3(\lambda, N) &= \frac{1}{N-1} \sum'_{\mu, m, s} Z_{\mu, m, s} Z_{\mu, m+1, s} \\ &- \frac{1}{\pi \lambda (N-1)} \sum'_m (-1)^m (\phi_m + \phi_{m+1}). \end{aligned} \quad (11c)$$

In the limit $N \rightarrow \infty$, it can be found,

$$B_1 = B_2 = B_3 = \lim_{n \rightarrow \infty} \frac{1}{N} \sum'_{\mu, m, s} Z_{\mu, m, s} Z_{\mu, m+1, s}. \quad (12)$$

The three kinds of boundary condition tend to unanimity. For a uniform dimerized structure $\phi_n = \phi_0$, the eigenstate and the eigenvalue can be obtained analytically. Then

$$B_1 = B_2 = B_3 = \frac{2}{\pi} \int_0^{\pi/2} \frac{\cos^2 \theta}{\sqrt{\cos^2 \theta + 4\phi_0^2 \sin^2 \theta}} d\theta \quad (13)$$

and the relation of dimerized parameter ϕ_0 to the e-ph coupling λ can also be obtained,

$$\frac{1}{2\pi} = \int_0^{\pi/2} \frac{\sin^2 \theta}{\sqrt{\cos^2 \theta + 4\phi_0^2 \sin^2 \theta}} d\theta. \quad (14)$$

For t -PA, $T_0 = 2.5$ eV, $\alpha = 4.2$ eV \AA^{-1} , $K = 18.7$ eV \AA^{-2} , this gives $\lambda = 0.24$. From (14) is obtained $\phi_0 = 0.096$ or $u_0 = 0.04$ \AA , which is consistent with the experimental data [5]. For the undimerized uniform structure, $\phi_0 = 0$, (10) gives out $k' = 1$ or $K' = -4\alpha/\pi$, which is the same as what [16] and [17] took. Actually K' is related to the lattice structure λ and N of the chains. Figure 1 shows the dependence of k' is related to the lattice structure λ and N of the chains. Figure 1 shows the dependence of k' on λ in an infinite t -PA chain with a dimerized lattice structure. It can be seen that $k' = 1$ is the value at the limit of weak coupling. With increasing e-ph coupling, k' decreases.

For a finite-length t -PA chain, it was found that for stable structure the ends of the chain tend to be double bonds. If the chain consists of an even number of CH groups, a uniformly dimerized structure is obtained, but if the chain consists of an odd number of CH groups, a kink or a soliton excitation will be formed. Here we focused on a t -PA chain consisting of an even number of CH groups. The dependences of B , dimerized parameter $\langle \phi \rangle$ and the electronic energy gap Δ on chain lengths are calculated separately for each boundary condition. The results are shown in figures 2, 3 and 4 separately. It was found that the final calculated results are identical for the fixed-end and the free-end boundary

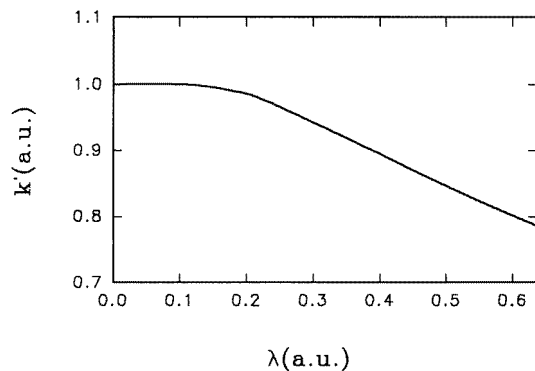


Figure 1. Dependence of the end correction k' on the e–ph coupling λ in the free-end boundary condition.

conditions although the initial physical intentions are different. The reason may be that the requirement of the lowest energy of the system in our calculation, the extra constraint of the free-boundary condition, in fact results in fixing of the ends. So only B_2 is shown in the figures.

In the case of short chains, it was found that the role of boundary conditions becomes apparent. With the shortening of the chain, the stability correction B_1 of the periodic boundary condition decreases, while B_2 of the fixed- or free-end boundary condition increases. When the chain is longer than $24a$, there is no obvious difference between the periodic boundary and the fixed- (or free-) end boundary condition.

Lanzani *et al* [11] have used cw photomodulation spectroscopy to probe the effects of the finite chain lengths on the optical transition. The behaviour has been carefully checked using absorption spectroscopy in polyenes with a known number of conjugated bonds up to $N = 12$ [18]. According to the Kuhn model [19], which introduces a periodic sinusoidal potential on the electron gas to account for the bond alternation, the transition Δ corresponding to the absorption maximum of the π – π^* optical transition in polyenes is a linear function of the inverse chain length N

$$\Delta = A_1 + \frac{A_2}{N} \quad (15)$$

where A_1 and A_2 are the fitting parameters. Various estimates of the parameters have been given by different groups. As a matter of fact an unambiguous choice of A_i is hampered by the lack of data for large N and by the fact that short polyenes with different substitutions yield different scaling laws with N^{-1} .

In our calculations presented in the periodic boundary conditions, it is found that in the case of weak e–ph coupling, the transition Δ basically fits the inverse law (15), while in the strong e–ph coupling, the transition keeps unchanged until the chain length decreases below 10, then a sharp increase appears. The scaling law with N^{-1} does not hold well.

In the fixed- or free-end boundary condition, our calculations showed that in the whole e–ph coupling range, the transition Δ accords with the scaling law (15) quite well. This indicates that the fixed- or free-end boundary condition is more suitable for the short conjugated chains than the periodic boundary condition.

To understand the role of the boundary conditions in more detail, the dimerization $\langle\phi\rangle$ is calculated in each boundary condition. For an infinite chain, the transition Δ is proportional to the dimerization $\langle\phi\rangle$ [17]. For a finite chain, it was found that, as shown

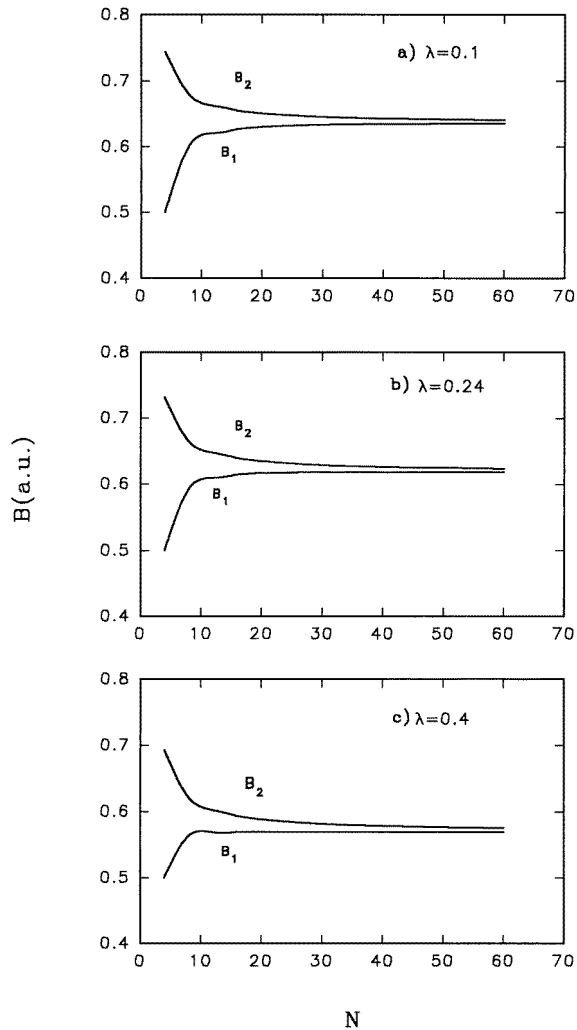


Figure 2. Dependence of stability correction B on chain lengths. $\lambda = 0.1, 0.24$ and 0.4 express the weak, intermediate and strong e–ph coupling separately.

in figure 3, the dimerization $\langle\phi\rangle$ increases with the shortening of the chain in the case of weak e–ph coupling. However, the increase in the fixed- or free-end boundary condition is slower than that in the periodic boundary condition. In the intermediate and the strong e–ph coupling, the dimerization $\langle\phi\rangle$ obtained in the fixed- or free-end boundary condition keeps basically unchanged, although it still increases with the shortening of the chain in the periodic boundary condition.

5. The Peierls–Hubbard model in finite-length t -PA chains

In the above calculations, the effect of electron–electron (e–e) interactions has been totally neglected. There is accumulating experimental evidence of the importance of the Coulomb

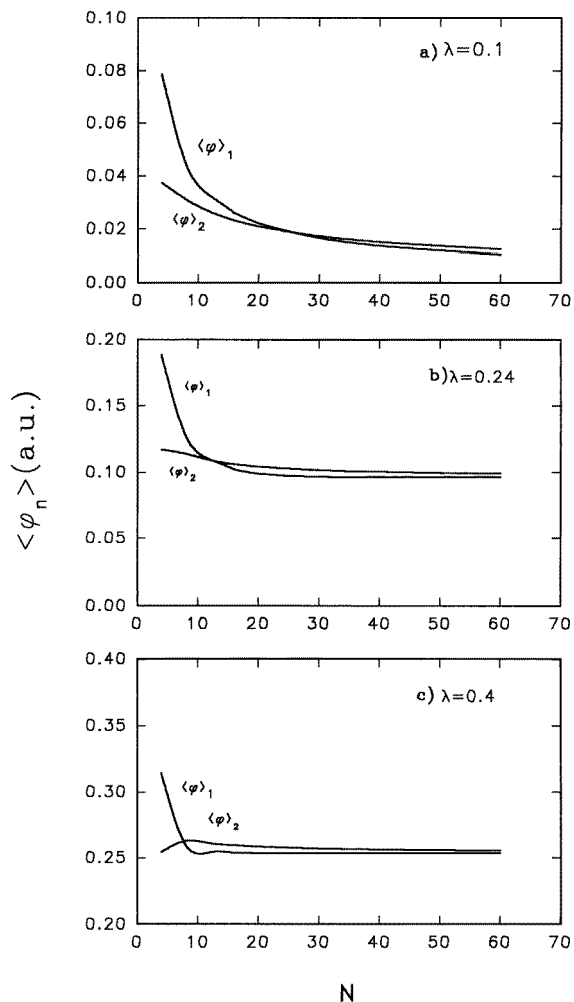


Figure 3. Dependence of the average dimerization $\langle \phi \rangle$ on chain lengths.

e–e interactions in polymers. For example, extensive photo-luminescence data [18] indicate that in polyene the lowest excited state is the dipole-forbidden single state (A_g symmetry) which lies 0.1–0.6 eV below the lowest dipole-allowed excited state (B_g symmetry) due to the e–e interactions. It has been pointed out that, based on the Peierls–Hubbard model, the dimerization disappears for strong e–e interaction, but the e–e interactions have no effect on the dimerization at the on-site term $U/4t_0 \leq \pi\lambda(1+2\lambda)$ [20]. Kivelson *et al* reconsidered this question by adding an important e–e interaction term, the on-bond interaction, to the Hubbard model. They concluded that e–e interactions always restrain the dimerization [21]. A more detailed study was later presented by Wu *et al* and Zie *et al* on the screening Coulomb potential of e–e interactions [22,23]. However, all of the calculations were performed in an infinite or closed ring. The effect of boundary conditions was totally

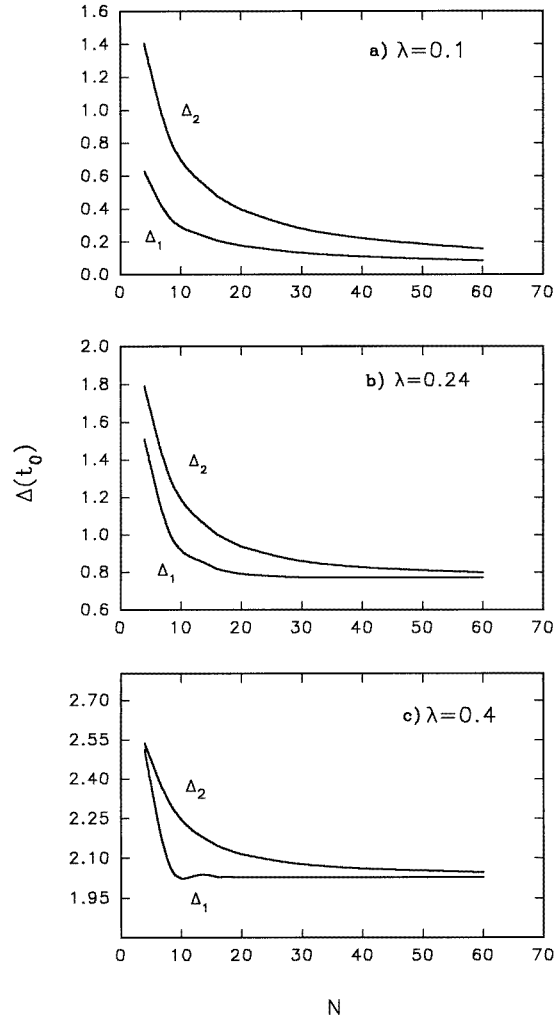


Figure 4. Dependence of electronic band gap Δ on chain lengths.

neglected. Here we considered the e–e interactions in an open chain,

$$\begin{aligned}
 H_{e-e} = & U/2 \sum_{i,s}^N n_{i,s} n_{i,-s} + V/2 \sum_{i,s,\sigma}^{N-2} n_{i,s} n_{i+1,\sigma} + X/2 \sum_{i,s}^{N-1} (n_{i,s} + n_{i+1,s}) G_{i,i+1,-s} \\
 & + W/2 \sum_{i,s}^{N-1} G_{i,i+1,s} G_{i,i+1,-s}
 \end{aligned} \quad (16)$$

where $n_{i,s} = C_{i,s}^+ C_{i,s}$ is the charge density operator on site i and $G_{i,i+1,s} = C_{i,s}^+ C_{i+1,s} + C_{i+1,s}^+ C_{i,s}$ the charge density operator between bond i and $i + 1$. It includes four e–e interaction terms: on-site, site–site, site–bond and on-bond. The Hubbard model is recovered by neglecting the site–bond term X and on-bond W .

(16) was treated in the self-consistent field Hartree–Fock approximation. A group of parameters $(U, V, X, W) = (0.6, 0.3, 0.15, 0.1)t_0$ [23, 24] was chosen to make the numerical

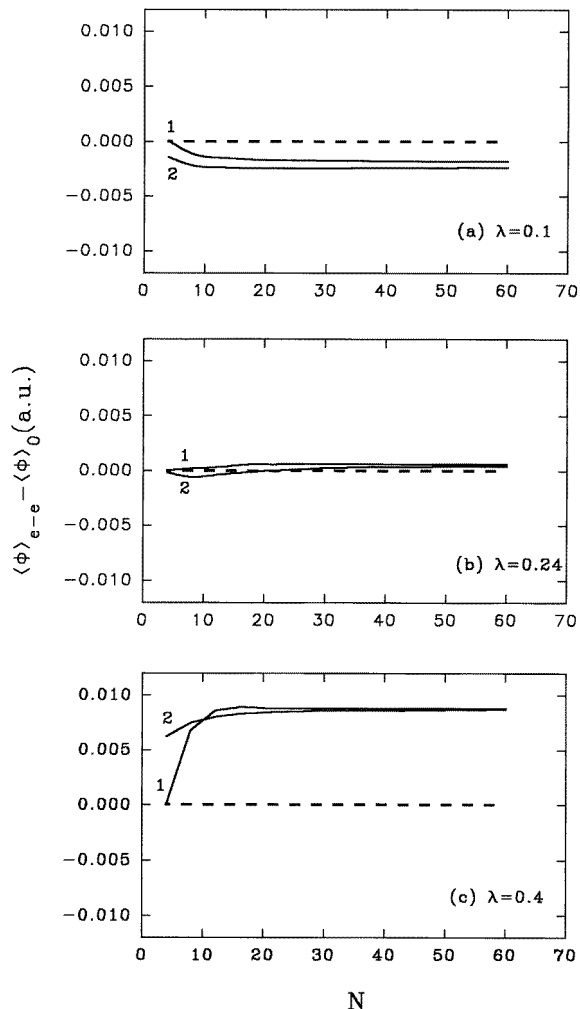


Figure 5. Dependence of the dimerization correction $\langle \phi \rangle_{e-e} - \langle \phi \rangle_0$ on chain lengths.

calculations. The results are shown in figures 5 and 6 for the dependence of the dimerization and the band gap on the chain length separately. The dashed lines in the figures are the results of the Hubbard model $(X, W) = (0, 0)$. It can be seen that the Hubbard model has no effect on either the dimerization or the band gap for any length of the chain with periodic or natural boundary conditions. The dimerization and the band gap will change as soon as the bond-related terms X and W are considered. Our results are consistent with [15] and [16]. But we found some new phenomena. First, as shown in figure 5, e – e interactions decrease the dimerization when the e – ph coupling is weak, while it will increase the dimerization when the e – ph coupling is strong. For a given e – e interaction, there exists a transition point of e – ph coupling (λ_c). $\lambda_c = 0.23$ was obtained in our calculations. Second, e – e interactions always decrease the band gap, as shown in figure 6. It is well known that in the Peierls model both the band gap Δ and dimerization ϕ will increase with the increasing of the e – ph coupling λ . When the e – e interactions are considered, it was found that although the

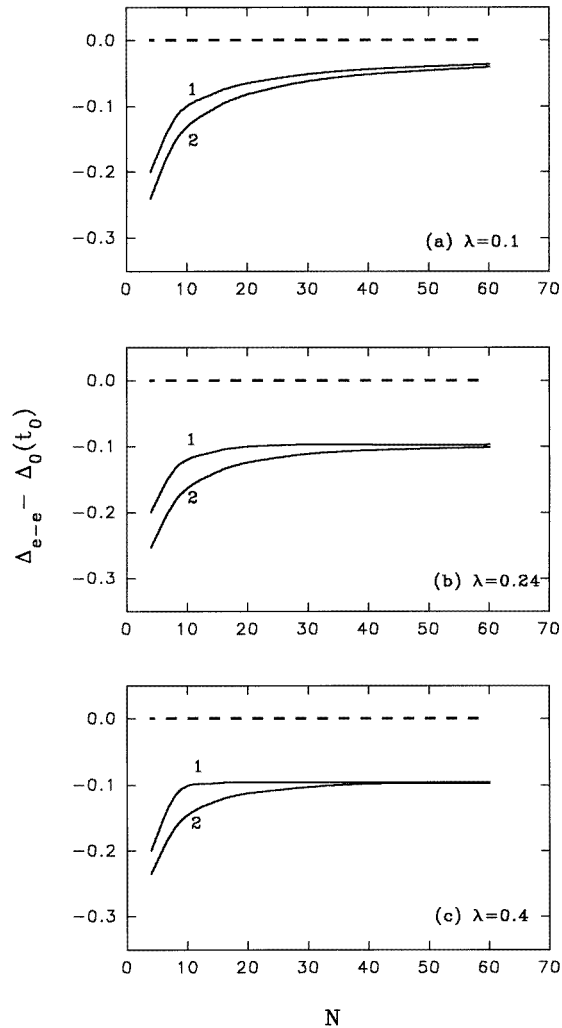


Figure 6. Dependence of the electronic band gap correction $\Delta_{e-e} - \Delta_0$ on chain lengths.

dimerization ϕ increases at strong e-ph couplings (for example, $\lambda = 0.4$), the band gap Δ always decreases. Third, the effect of e-e interactions on band gap becomes more apparent in a short chain than in a long chain. For example, at $\lambda = 0.24$, when the length of the chain decreases from $N = 20$ to $N = 8$, the difference $\Delta_{e-e} - \Delta$ of band gap decreases from -0.25 to -0.36 eV of the periodic boundary condition and -0.51 eV of the natural boundary condition. One can observe the same phenomenon in the dimerization when λ is larger than λ_c .

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