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# New quantum Monte Carlo formulation for modeling *trans*-polyacetylene properties: specific heat calculation

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## Abstract

In this paper we propose a new hybridization scheme for numerical simulation based on the determinantal quantum Monte Carlo and analytical model to treat the vibration mode of one-dimensional *trans*-polyacetylene chain. We use both of the extended Hubbard model (EHM) and Peierls–Hubbard model to compute the specific heat for different assumptions. For both the two models, our results indicate that the behavior of the specific heat is characterized by a maximum. We also introduce the effect of dimerization through Peierls–Hubbard model. In this case it is found that the specific heat magnitude is slightly more important when compared to specific heat value found with the EHM case. Moreover the inclusion of electron–phonon interaction, the bond alternation and dimerization give an explication to the existence of quantum fluctuations, which may be associated to the existence of soliton solutions of the lattice vibration. The important result of this study is that the analytical ground state preserves size consistency and can be generalized for other geometries (e.g. *cis*-polyacetylene, polyacene, etc.), while still being both easy to interpret and to evaluate accurately.
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## 1. Introduction

The richness of organic chemistry data, which was devoted originally to develop the idea of 'the plastics that conduct', has been used widely to develop several experimental and theoretical considerations to treat polymers. The theory of conjugated polymers, developed for exploring properties of the recent interest in these materials and the related synthetic metals [1,2] has achieved an important step in the area of the debate between electron–electron (e–e) and electron–phonon (e–ph) interactions in the behavior of polymers [3]. Among theoretical works, the model Hamiltonians [4]. The primary simplifications given by these Hamiltonians vis-a-vis the ab-initio methods, when one consider only some of the degrees of freedom, leading to a reduced set of parameters which cannot be reliable to describe the reality of the considered systems. A panoply of model Hamiltonians, describing the interactions, was proposed in aims to overcome the difficulty of deriving the form of the interactions parameters from the underlying microscopic theory. Two approaches were adopted: first, for small systems, the ground state and low lying excitation states are calculated for the parametrized model Hamiltonians by adjusting the parameters of the model so as to reproduce the ab-initio results. The second approach is based on the phenomenological method to calculate physical quantities such as electronic energies [5,6] or optical absorption spectrum. Adjustable parameters are determined by comparing the calculated quantities with experiments [7]. The importance of this problem is granted by the fact that this kind of interactions is the most probable process leading to the formation of excited states which recombine radiatively to the ground state, explaining many macroscopical behaviors (e.g. the electroluminescence observed in the conjugated polymers) [8].

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In this work, we detail a new approach based on the hybridization of an analytical model given by Jia-xin Xiao [9] and the efficient determinantal Monte Carlo (dQMC) technique, which has been applied to fermionic systems by Blakenbecler, Scalapino, Sugar and Hirsch (BSSH algorithm) [10]. As a first application, we calculate the ground state properties of the extended Hubbard model (EHM). With the present scheme we are particularly, interested in the calculation of the specific heat observable. The specific heat exhibit an anomalous contribution which confirm the validity of the proposed hybridization approach.

The paper is organized as follows: in Section 2 we describe the model and the numerical method used in the present study. Section 3 is devoted to discussion of our main results. A general summary and conclusions are given in Section 4.

## 2. Model and calculation

### 2.1. The one dimensional extended Hubbard model (EHM)

The Hamiltonian is taken as in Ref. [11]:

$$H = H_{ph} + H_e + H_{int} \tag{1}$$

where $H_{ph}$ is the contribution of the lattice motion:

$$H_{ph} = \frac{M}{2} \sum_i \dot{R}_i^2 + \frac{K}{2} \sum_i (R_{i+1} - R_i)^2 \tag{2}$$

in which $M$ is the mass of the lattice atom, $K$ the elastic constant of the lattice, $R_i$ the position of the $i$th lattice site is given by $R_i = \bar{R}_i(t) + u_i(t)$, where $\bar{R}_i$ and $u_i$ are the equilibrium position and displacement, respectively.

$H_e$ is the contribution of the electrons subsystem, which includes the electron transfer at adjacent sites, the interaction between electrons at the same lattice site, and the chemical potential of electrons $\mu$ as follows:

$$H_e = \sum_{i\lambda\sigma} E_\lambda n_{i\sigma}^\lambda + \sum_{ij\lambda\eta\sigma} t_{ij}^{\lambda\eta} c_{j\sigma}^{\lambda+} c_{j\sigma}^\eta + \sum_{i\lambda} U_\lambda n_{i\uparrow}^\lambda n_{i\downarrow}^\lambda$$
$$- \mu \sum_{i\lambda\sigma} n_{i\sigma}^\lambda \tag{3}$$

where the indices $i, j$ label the spatial sites.

$\lambda, \eta$ label the different atoms in a given site, and $\sigma$ is a spin index ($\sigma = \uparrow\downarrow$); $c_{j\sigma}^{\lambda+}(c_{j\sigma}^\lambda)$ are creation (annihilation) operators and $n_{i\sigma}^\lambda = c_{j\sigma}^{\lambda+} c_{j\sigma}^\lambda$; $E_\lambda$, represents the repulsive interaction between electrons within an elementary cell; $t_{ij}^{\lambda\eta}$, is the transition matrix, which is introduced from the Hückel theory representing the degree to which the $\pi$-orbitals on adjacent atoms in a chain overlap [12]. In the nearest-neighbor approximation we take:

$$t_{ij}^{\lambda\eta} = t_{ij}^{\eta\lambda} \quad \forall i, j, \lambda, \eta \tag{4}$$

and the transitional invariance:

$$t_{ij}^{\lambda\eta} = t_{ij}^{\eta\lambda}(R_i - R_j) \tag{5}$$

$U_\lambda$ are the on-site Coulomb coupling between fermions.

The interaction between an electron and the phonon is given by:

$$H_{int} = I \sum_{i,\sigma} [(u_{i,\sigma} - u_{i+1,\sigma})(c_{i\sigma}^{\lambda+})c_{i+1\sigma}^\eta + (c_{i+1,\sigma}^\eta)^+ c_{i\sigma}^\lambda$$
$$+ (c_{i+1,\sigma}^\lambda)^+ c_{i,\sigma}^\eta + (c_{i,\sigma}^\eta)^+ c_{i+1,\sigma}^\lambda] \tag{6}$$

where $I$ denotes the coupling constant.

For background we will first deal with the vibration model of the Hubbard chain and then the contribution to the specific heat due to this vibration. As a first hypothesis, we suppose that the ground state is antiferromagnetic [13] and the lattice is divided into equivalent ferromagnetic sub-lattices A and B, then the resulting magnetic moment is zero in the absence of an external magnetic field.

If the ground state of the system is the antiferromagnetic with spin zero, the wave function of the low excitation state can be taken as [9]:

$$|\Psi\rangle = |\Psi_1\rangle + |\Psi_2\rangle \tag{7}$$

where $|\Psi_1\rangle$ denotes the excitation state of a single electron and take the following form:

$$|\Psi_1\rangle = \sum_{n,\sigma} \alpha_{n,\sigma}(t) C_{n,\sigma}^+ |\Psi_0\rangle \tag{8}$$

where $\alpha_{n,\sigma}(t)$ is the probability amplitude of an electron excitation with spin $\sigma$ at the $n$th site. $|\Psi_0\rangle$ is the antiferromagnetic ground state.

The basic idea is to start with a state $|\Psi_0\rangle$, that is a first approximation to the full ground state $|\Psi\rangle$. So, we can write the wave function of a double electron excitation in the lattice chain as follows:

$$|\Psi_2\rangle = \sum_{m,n,\sigma_1,\sigma_2} \beta_{m,\sigma_1;n,\sigma_2}(t) C_{m,\sigma_1}^+ C_{n,\sigma_2}^+ |\Psi_0\rangle \tag{9}$$

where $\beta_{m,\sigma_1;n,\sigma_2}$ corresponds to the probability amplitude of the excitation state in which there is one electron with spin $\sigma_1$ at the $m$th lattice site and another electron with spin $\sigma_2$ at the $n$th lattice site.

Substituting Eqs. (1) and (7) into the Schrödinger equation, we get the following expression:

$$i \frac{\partial}{\partial t} |\Psi\rangle = H |\Psi\rangle \tag{10}$$

### 2.2. The quasi-continuous approximation

Let us consider $a_0$ to be the lattice constant. By taking the quasi-continuous approximation, we can introduce the new

set of variables:

$$n \to \xi$$

$$m \to \eta$$

$$u_n(t) = R_n(t) - \bar{R}_n \to u(\xi, t), \; \alpha_{n,\sigma}(t) \to \alpha(\xi, t), \text{ and } \beta_{m,\sigma_1;n,\sigma_2}$$

$$\to \beta_{\sigma_1,\sigma_2}(\xi, \eta, t)$$

We have

$$R_n = a_0[u(\xi, t) \pm u_\xi + \tfrac{1}{2} u_{\xi\xi} + \cdots]$$

$$\alpha_{n+1,\sigma} \to \alpha_{n,-\sigma} \pm \alpha'_{n,-\sigma} + \tfrac{1}{2}\alpha'_{n,-\sigma} + \cdots \to \alpha_{-\sigma}(\xi, t)$$

$$\pm \alpha'_{-\sigma}(\xi, t) + \tfrac{1}{2}\alpha'_{-\sigma}(\xi, t) + \cdots$$

$$\beta_{n\pm1,\sigma,m,\sigma'} \to \beta_{-\sigma,\sigma'}(\xi, \eta, t) \pm \frac{\partial}{\partial\xi}\beta_{-\sigma,\sigma'}(\xi, \eta, t) + \frac{1}{2}\frac{\partial^2}{\partial\xi^2}$$

$$\times \beta_{-\sigma,\sigma'}(\xi, \eta, t) + \cdots$$

$$\beta_{n,\sigma,m\pm,\sigma'} \to \beta_{-\sigma,\sigma'}(\xi, \eta, t) \pm \frac{\partial}{\partial\eta}\beta_{-\sigma,\sigma'}(\xi, \eta, t) + \frac{1}{2}\frac{\partial^2}{\partial\eta^2}$$

$$\times \beta_{-\sigma,\sigma'}(\xi, \eta, t) + \cdots$$

If we assume that occupied number of the electron at every site $n = |\alpha_\uparrow|^2 + |\alpha_\downarrow|^2 = \text{const}$, we obtain the equation of motion of $\alpha_\sigma(\xi, t)$ and $\beta_{\sigma,\sigma'}(\xi, \eta, t)$ from Eq. (10), respectively,

$$i\hbar\dot{\alpha}_\sigma(\xi, t) = (W - \mu)\alpha_\sigma(\xi, t) + \frac{V}{2}|\alpha_{-\sigma}|^2\alpha_\sigma$$

$$+ \left[\bar{t} - I\frac{\partial u(\xi, t)}{\partial\xi}\right]$$

$$\times \left[2\alpha_{-\sigma}(\xi, t) + \frac{\partial^2}{\partial\xi^2}\alpha_{-\sigma}(\xi, t)\right] \quad (11)$$

$$i\hbar\dot{\beta}_\sigma(\xi, \eta, t) = (W - 2\mu + V\delta_{m,n}\delta_{\sigma_1,\sigma_2})\beta_{\sigma_1,\sigma_2}(\xi, \eta, t)$$

$$+ \left[2\bar{t} - 2I\frac{\partial u}{\partial\xi}\right]$$

$$\times \left[2\beta_{-\sigma_1,\sigma_2}(\xi, \eta, t) + \frac{\partial^2}{\partial\xi^2}\beta_{-\sigma_1,\sigma_2}(\xi, \eta, t)\right] \quad (12)$$

where $W$ is the average value of the lattice vibration energy. The motion equation of the lattice vibration can be obtained from the average energy of the system by the canonical equations of the classical mechanics. $\delta$ is Kronecker function.

$$\bar{H} = \langle\Psi|H|\Psi\rangle \quad (13)$$

From:

$$M\ddot{u}_j = \dot{P}_j = \frac{\partial\bar{H}}{\partial u_j} \quad (14)$$

We have:

$$M\ddot{u}(\xi, t) = Ku_{\xi\xi} - 2I\sum_\sigma\frac{\partial}{\partial\xi}(\alpha_\sigma^*\alpha_\sigma) - 8I\sum_{\sigma,\sigma'}\int d\eta\frac{\partial}{\partial\xi}$$

$$\times(\beta_{-\sigma,\sigma'}^*\beta_{-\sigma,\sigma'}) \quad (15)$$

By taking the travel wave solution $u(\xi, t) = (\xi - vt)$ and letting $v_0^2 = K/M$. Then we have:

$$\ddot{u} = v_0^2 u_{\xi\xi} - \frac{2I}{\alpha_0 M}$$

$$\times \left[\sum_{\sigma,\sigma'}\frac{\partial}{\partial\xi}(\alpha_\sigma^*\alpha_\sigma) + 4\sum_{\sigma,\sigma'}\int d\eta\frac{\partial}{\partial\xi}(\beta_{-\sigma,\sigma'}^*\beta_{-\sigma,\sigma'})\right] \quad (16)$$

By integrating the above equation with respect to $\xi$, we obtain the following expression:

$$u_\xi(\xi, t) = -\frac{2I}{\alpha_0 M(v^2 - v_0^2)}$$

$$\times \left[\sum_\sigma(\alpha_\sigma^*\alpha_\sigma) + 4\sum_{\sigma,\sigma'}\int d\eta\frac{\partial}{\partial\xi}(\beta_{-\sigma,\sigma'}^*\beta_{-\sigma,\sigma'})\right]$$

$$+ C \quad (17)$$

$C$ is a constant associated with the initial condition.

Eqs. (11), (12) and (17) are the motion equations of the electron state and the lattice. The single-electron excitation approximation allow us to write [14]:

$$|\Psi\rangle = |\Psi_1\rangle \quad (18)$$

If the average occupation number $n$ is a constant [15], then the solution can be written as:

$$\alpha_\uparrow = \tfrac{1}{2}(\Psi^{(1)} + \Psi^{(2)}) \quad (19)$$

$$\alpha_\downarrow = \tfrac{1}{2}(\Psi^{(1)} - \Psi^{(2)}) \quad (20)$$

where:

$$\Psi^{(1)} = \sqrt{2n}\text{sech}\left[\frac{n(V - I')^{1/2}}{T}(\xi - vt)\right]$$

$$\exp\left[\frac{iv\xi}{2T} - i\omega_1 t\right] \quad (21)$$

$$\Psi^{(2)} = \sqrt{2n}\tanh\left[\frac{n(V - I')^{1/2}}{T}(\xi - vt)\right]$$

$$\exp\left[\frac{iv\xi}{2T} - i\omega_2 t\right] \quad (22)$$

In which:

$$I' = -\frac{2I}{\alpha_0 M(v^2 - v_0^2)}, \quad T = \bar{t} - a_0 IA \quad (23)$$

$$\omega_1 = 2T + W - \mu - \frac{v^2}{4T} \quad \text{and} \quad \omega_2$$

$$= -2T + W - \mu - (V - I') + \frac{v^2}{4T}$$

Using the above expressions one can find $\sum_\sigma \alpha_\sigma^* \alpha_\sigma$. Substituting it into Eq. (16) we obtain the motion equation of the lattice vibration in the excitation state of the single electron:

$$\ddot{u} - v_0^2 u_{\xi\xi} + \omega_0^2 \frac{d}{du} V_1 = 0 \tag{24}$$

where:

$$V_1 = \frac{b}{4}\left[u^2 - \frac{1}{b}\right]^2 - \frac{1}{4b}, \quad \gamma^2 = \frac{n(V - I')}{T}, \quad b$$

$$= \frac{a_0^2 M^2 (v_0^2 - v^2)\gamma^2}{16 n^2 I^2} = \frac{1}{C^2}, \quad \omega_0^2 = 2\gamma^2(v_0^2 - v^2) \tag{25}$$

We notice that $u$ satisfies the equations of $\phi^4$-field, and hence it should have the well-known soliton solution as:

$$u = C \tanh[\gamma(\xi - vt)] \tag{26}$$

### 2.3. Determination of the anharmonic vibration by dQMC technique

It is well known that the anharmonic vibration contributes to the specific heat [16]. Next we investigate this contribution using dQMC simulation method.

For the vibration system of the $\phi^4$-field due to the single-electron excitation $|\Psi_1\rangle$ the Hamiltonian can be written as:

$$H = \int d\xi \left[\frac{1}{2}\dot{u}^2 + \frac{1}{2}v_0^2 u_{\xi\xi} - \omega_0^2 V_1(u)\right] \tag{27}$$

where $V_1(u)$ is given by Eq. (24). We can use the method of standard statistical physics to study of thermodynamics properties given by the above equation. In other words, we can write the partition function [15] of the part of the lattice vibration from Eq. (27) as:

$$Z = \int \prod_{i=1}^{N} dP_i \int \prod_{i=1}^{N} du_i \exp(-\beta H) \tag{28}$$

However, the novelty in our work, will be in using of the BSSH algorithm [10] for computing the partition function $Z$.

It is well known that a large variety of methods have been developed for treating the many body problem defined by Eq. (1). Here we shall use the determinantal version of quantum Monte Carlo method [17]. Using Trotter approximation in separating the one-particle and two-particle terms and dividing the imaginary time interval $[0, \beta]$ into $L$ subintervals of width $\Delta\tau = \beta/L$, the partition function may

be written as:

$$Z = \text{Tr}(e^{-\beta \hat{H}}) = \text{Tr} \prod_{i=1}^{L} e^{-\Delta\tau \hat{H}} \approx \text{Tr} \prod_{i=1}^{L} e^{-\Delta\tau \hat{H}_0} e^{-\Delta\tau \hat{H}_1} \tag{29}$$

To eliminate the two-body interaction term, we use the discrete Hubbard–Stratonovich transformation [14] using the identity:

$$\text{Tr} \exp(-c_i^+ A_{ij} c_j) \exp(-c_i^+ B_{ij} c_j) = \det(1 + e^{-A} e^{-B}) \tag{30}$$

for arbitrary matrices $A$ and $B$ and taking the trace over fermions [15], one obtains the following expression:

$$Z = \text{Tr}_\sigma \prod_{\alpha = \pm 1} \prod_{l=1}^{L} [1 + B_L(\alpha) B_{L-1}(L) \cdots B_1(\alpha)] \tag{31}$$

$$= \text{Tr}_\sigma \det O_\uparrow \det O_\downarrow \tag{32}$$

where $O_\sigma$ is an $NL \times NL$ matrix

$$O_\sigma = 1 + \prod_{l=1}^{L} B_l^\sigma(\alpha) \tag{33}$$

$$B_l(\alpha) = \exp[-\Delta\tau K] \exp[V^\alpha(l)] \tag{34}$$

where:

$$K_{i,j} = \begin{cases} -t(>0) & \text{for } i, j \text{ nearest neighbor} \\ 0 & \text{otherwise} \end{cases}$$

$$V_{ij}^\alpha(l) = \delta_{ij}\left[\lambda\alpha\sigma_i(l) + \Delta\tau(\mu - \frac{U}{2})\right] \tag{35}$$

$$\lambda = \cosh^{-1}(\Delta\tau \frac{U}{2}) \tag{36}$$

To perform the Monte Carlo simulation, we can take the determinant in Eq. (4) as the Boltzmann weight. For the case of half-filled band, the product in Eq. (4) is positive for arbitrary $\sigma$ configurations [18]. In this case the heat-bath algorithm is used to perform the sum over Ising spins. Suppose, $R_\alpha$ is the ratio of new to old determinant for fermion spin $\alpha$ on flipping a given Ising spin, the flipping probability for this is given by:

$$P = \frac{R_\uparrow R_\downarrow}{1 + R_\uparrow R_\downarrow} \tag{37}$$

$R_\alpha$ can be computed by using the procedure introduced by Blakenbecler, Scalapino and Sugar [19], which involves updating the Green's function when a move is accepted. Therefore, measurements of statistical averages of many observable can be performed.

### 2.4. Statistical averages of the ground state properties of a t-PA chain

In the following section we describe in detail how to evaluate the ground state energies, for the t-PA chain. We must recall, that all the physical observables are calculated for a chain consisting of 64 sites (see Fig. 1). Therefore, the
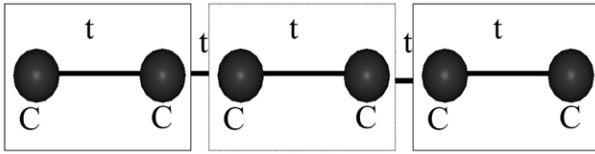
Fig. 1. Schematic illustration of the unit cell of *trans*-polyacetylene used in simulation (first assumption).

calculations are done for the half-filled case (i.e. $\mu = U/2$). For explicit calculations the following typical set of values for the parameters involved in Eq. (1) will be used [20], the selected set of parameters are: $t = 2.5$(eV), and the value of the bandwidth is taken as $\Delta = 4t = 10$(eV) [21,22]. We note that in this work we have treated three regimes (i.e. $U > 4t$, $U < 4t$ and $U \approx 4t$) and for all these cases we are interested to the specific values of $E$: ($E \approx U$, $E \approx U/2$, $E > U/2$, $E < U/2$), respectively.

Averaging over the MC samples a large number of observables can be calculated. We list here just the following quantities: kinetic, potential and total energy given by the following expressions:

Kinetic energy:

$$K = \sum_{ij\lambda\eta\sigma} t_{ij}^{\lambda\eta} \langle c_{i\sigma}^{\lambda+} c_{i\sigma}^{\eta} \rangle_{\text{MC}} \tag{38}$$

Potential energy:

$$V = \sum_{i\lambda} U_\lambda \langle n_{i\uparrow}^\lambda n_{i\downarrow}^\lambda \rangle_{\text{MC}} \tag{39}$$

Total energy:

$$\langle H \rangle = K + V + \sum_{i\lambda\sigma} E_\lambda \langle n_{i\sigma}^\lambda \rangle_{\text{MC}} \tag{40}$$

To study the variation of energy and their respective mean fluctuations versus both $\beta$ and specific sets of correlation parameters ($U$ and $E$), several results are reported in Figs. 2(a)–(c), 3(a)–(c), and 4(a)–(c), for ($U = 10$, $E = 5, 8, 10, 13$(eV)), ($U = 14, E = 5, 7, 9, 14$(eV)), and ($U = 6, E = 2, 3, 6$(eV)), respectively.

## 3. Numerical results and general discussion

In Section 2.4 we have described how to obtain ground state energies of some Hamiltonian parameters (regimes). In this section we describe a successful application of the approach to the EHM by calculation of the specific heat for both cases dimerized and undimerized polymeric chain.

### 3.1. Specific heat of an undimerized t-PA chain

We consider here the calculation of the specific heat for an undimerized polymer chain (see Fig. 1), which is proportional to the fluctuation of energy and may be obtained directly from the thermal fluctuations, using the following
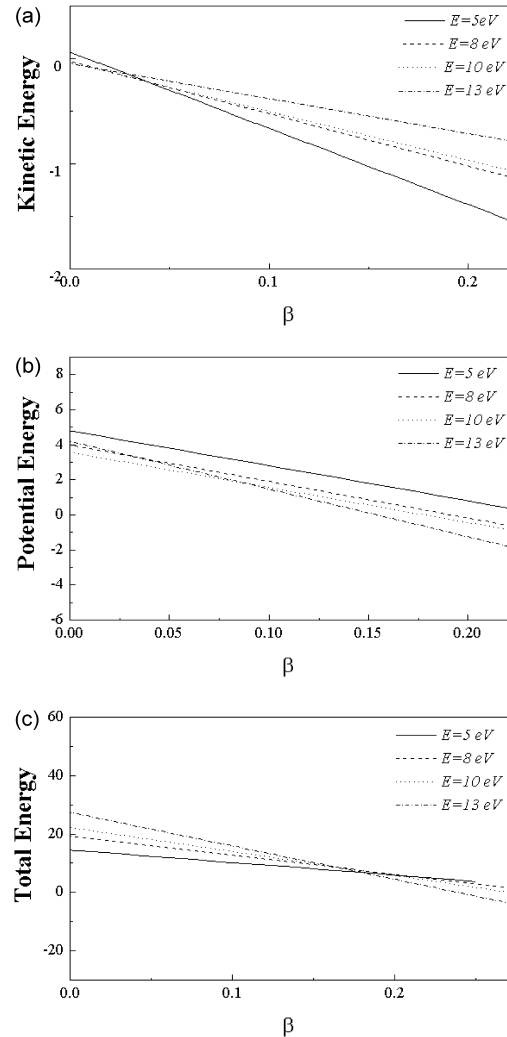


Fig. 2. (a)–(c) Kinetic, potential and total energy versus inverse temperature for ($U = 10, E = 5, 8, 10, 13$) (eV).

equation:

$$C = (k_B T^2)^{-1} (\langle E^2 \rangle - \langle E \rangle^2) \tag{41}$$

In this work, we have calculated the specific heat after evaluating the internal energy $E$ of the system [20]. The temperature dependence of the specific heat of a $t$-PA chain at typical values of $E$ can be observed in Fig. 5(a)–(c). Comparing these figures, one can easily notice how the features of the specific heat versus the inverse temperature varies with the relative magnitude of $U$ to $\Delta$.

The specific heat has a peak at a relative low temperature, suggesting a rearrangement of energy levels. It is also believed that the low temperature peak arises from the antiferromagnetic short-range ordering [23]. This conclusion is supported by the calculations of other thermal properties and correlation functions [24–26].

### 3.2. Dimerized t-PA chain
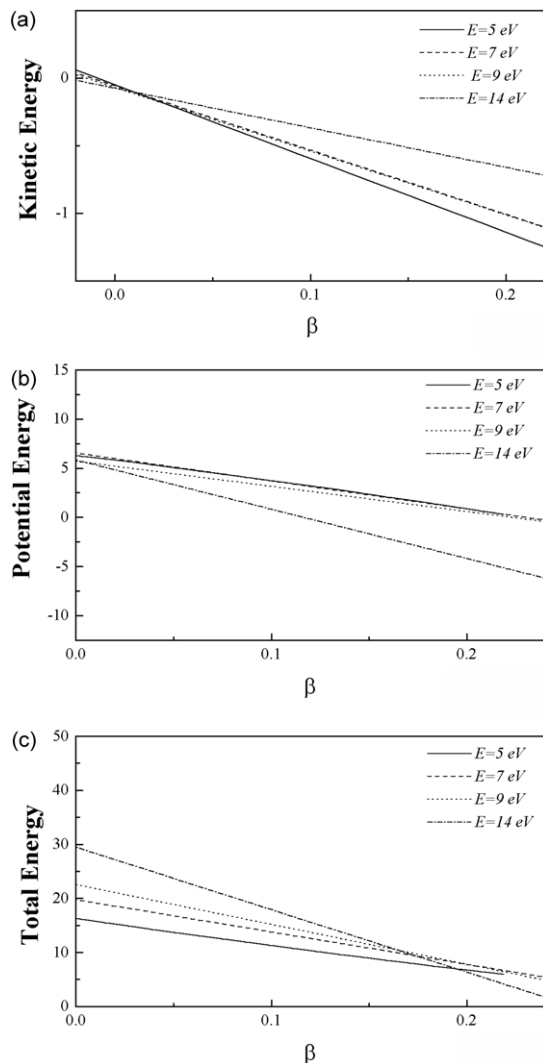
It is well known that the $t$-PA polymer is defined as a

Fig. 3. (a)–(c) Kinetic, potential and total energy versus inverse temperature for ($U = 14, E = 5, 7, 9, 14$) (eV).



Fig. 4. (a)–(c) Kinetic, potential and total energy versus inverse temperature for ($U = 6, E = 2, 3, 6$) (eV).

quasi-one dimensional compound with a carbon backbone characterized by two types of bonds (single and double). Fig. 6, shows the calculation of the specific heat for dimerized polymeric chain in which we take two carbon atoms and two hydrogen atoms per unit cell. We consider also, the effect of bond alternation, and dimerization.

First the effect of interaction parameters ($U$ and $E$) on dimerization are examined. We investigate the regime of weak to strong coupling $U$, that is $U > 4t$.

We show in Fig. 7(a) and (b) the electronic energy gained at fixed dimerization parameter ($\delta = 0.035$ Å) (i.e. the bond order wave (BOW) condensate energy $\Delta E_g$) as a function of $E$ for different values of $U$ at fixed temperature ($\beta = 0.4$ and 1.0), respectively. Our results agree with calculations done by density-matrix renormalization group methods (DMRG) [27] and exact diagonalization [28]. These figures show that the only difference lies in the magnitude and the position of the peaks, which may be caused by the open boundary conditions and the effect of simulation parameters. As the
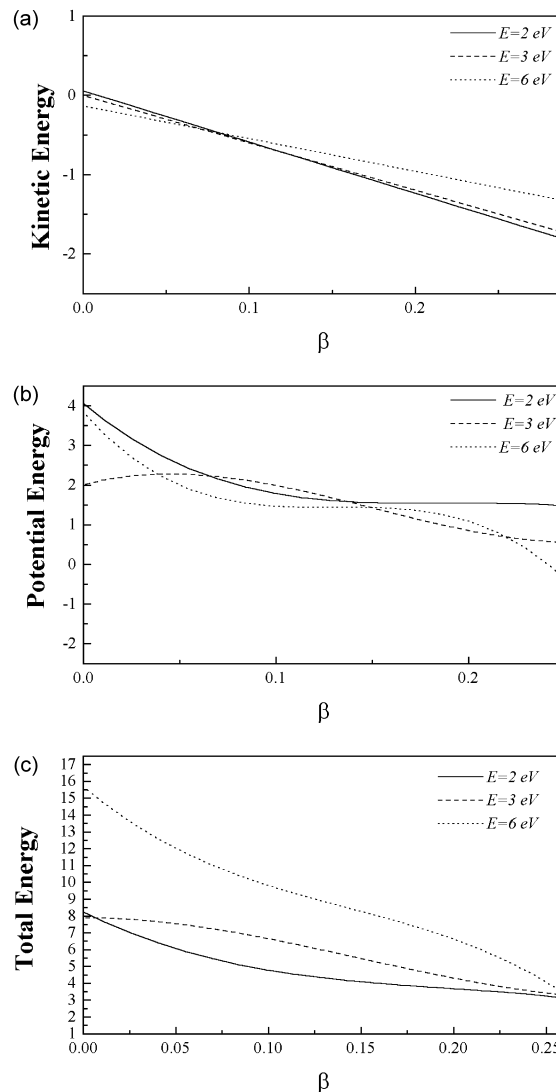
temperature decreases, energies gradually decrease. This feature can be explained by the gradual delocalization of electrons as the temperature decreases [16,24]. Note that the energy increases from $U = 0$ and reaches a maximum at 1.4s eV. The effect of $E$ is to increase $\Delta E_g$ at fixed values of $U$ for the relevant values of $\beta = 0.4$ and 1.0, respectively. This gain in BOW condensation energy is translated directly into an increasing tendency to dimerization [29].

The numerical calculation performed in this work supports the qualitative valence bond (VB) predictions [30,31]. Indeed, for the relevant ranges of parameters the bond-alternation is found to increase with the strength of the effective ($U$) Coulomb interactions in the Extended Peierls–Hubbard model.

This is also confirmed by the calculation of the total energy versus $E$ for different values of $U$ and $\beta$, respectively (see Fig. 8(a) and (b)). Therefore, we use Eq. (41) to calculate the specific heat, for the case of Hubbard (solid

(a)

(b)

(c)

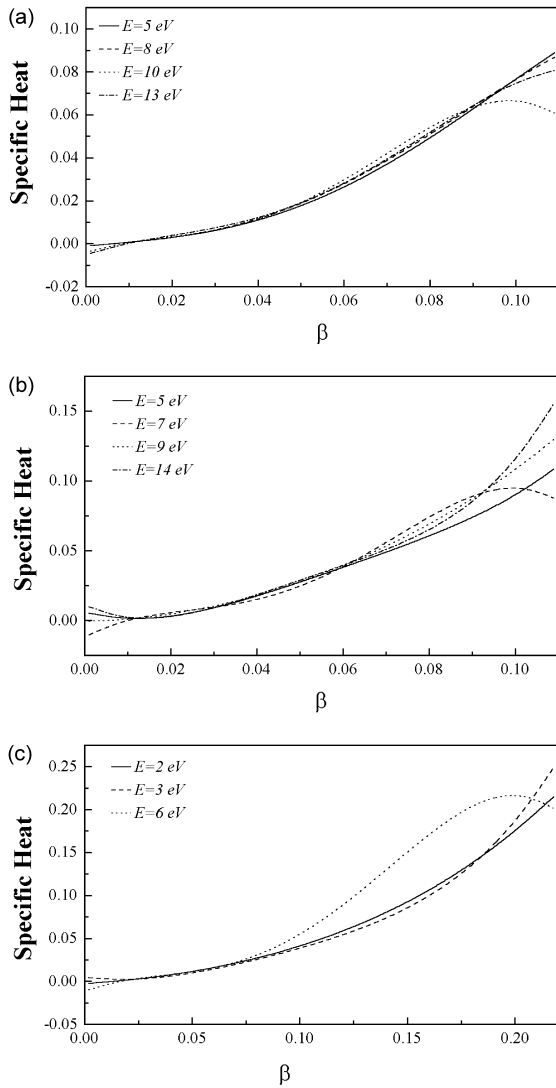Fig. 5. (a) The variation of the specific heat versus $\beta$ for ($U = 10, V = 5, 8, 10, 13$) (eV). (b) The variation of the specific heat versus $\beta$ for ($U = 14, V = 5, 7, 9, 14$) (eV). (c) The variation of the specific heat versus $\beta$ for ($U = 6, V = 2, 3, 6$) (eV).

lines) and Peierls–Hubbard (dot lines) models displayed in Fig. 9(a) and (b) for $\beta = 0.4$ and 1.0, respectively.

Our results show that the specific heat magnitude performed by the Peierls–Hubbard model calculation is more important compared to that computed by the Hubbard model. This may be explained by the fact that when both of e–ph interaction and bond alternation are included, an increase of quantum fluctuations is observed. Moreover for $\beta = 1.0$ the appearance of the peaks in specific heat curve may indicate an existence of a phase transition, which is also influenced by the variation of the parameters ($U, E$) as it is shown in Fig. 8(b), where the peak is more pronounced for $U/4t = 1.4$.

We can confirm these results by predictions through the analytical calculation based on Sine–Gordon model [32,33], for which the appearance of the peak in both energy
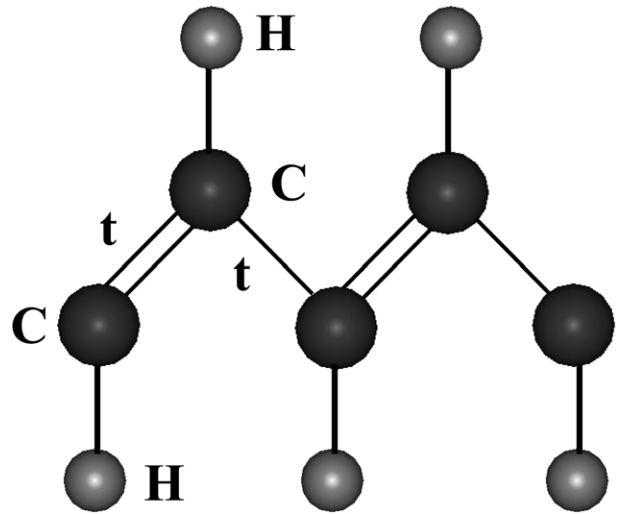


Fig. 6. Schematic illustration of the unit cell of *trans*-polyacetylene used in the simulation (second assumption).

fluctuations and specific heat, is due to the existence of non-linear excitations or more specifically solitons.

From the definition of solitary spin waves in a polymeric chain, we are able to give a definite interpretation of this behavior. The analytical theories relate the specific heat maximum to the structure of the spin-wave, but the validity
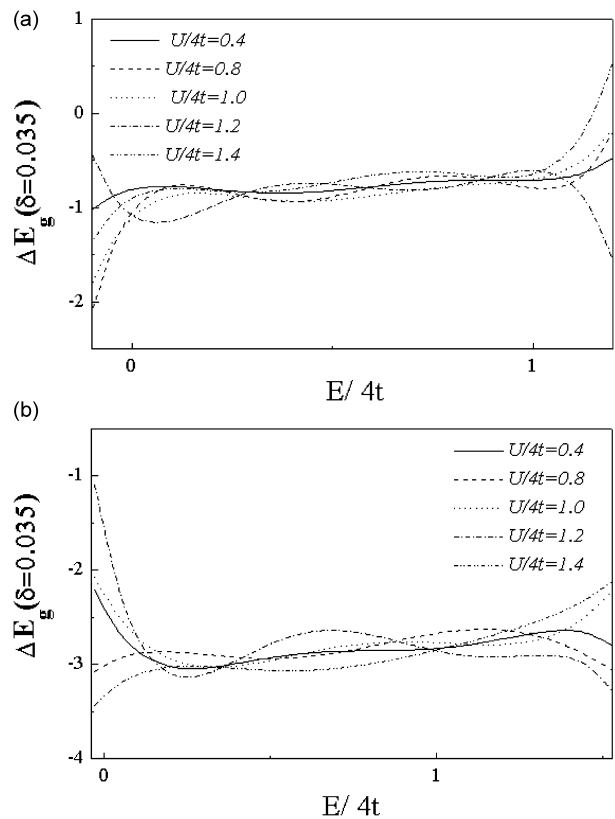


(a)

(b)

Fig. 7. (a) The magnitude of the electronic energy difference between a dimerized and an undimerized chain for $\beta = 0.4$. (b) The magnitude of the electronic energy difference between a dimerized and an undimerized chain for $\beta = 1.0$.
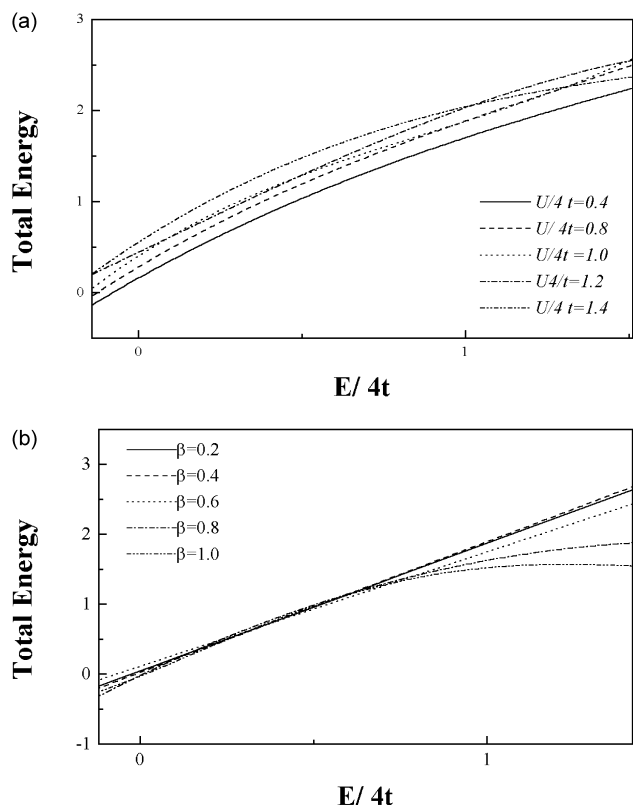
Fig. 8. (a) The total energy as a function of $E$, for different values of $U$ and $\beta = 1.0$. (b) The total energy as a function of $E$, for different values of $\beta$ and $U = 1.0$ eV.





Fig. 9. (a) The variation of the specific heat versus $E$ for Hubbard model calculation (solid line) and Peierls–Hubbard model (dot line) for $\beta = 0.4$. (b) The variation of the specific heat versus $E$ for Hubbard model calculation (solid line) and Peierls–Hubbard model (dot line) for $\beta = 1.0$.

of these theories is reliable only under certain conditions such as: temperature, correlation parameters, and other chemical consideration for example size of the system (number of monomers) and the nature of unit cell which depend on the isomerization.

## 4. Conclusion

We have described in detail a straightforward hybridization of the determinantal quantum Monte Carlo to the analytical treatment to study the vibration mode of a quasi-one dimensional *trans*-polyacetylene chain by the EHM.

We have paid attention to the soliton contribution to the specific heat for the lattice vibration. In the anharmonic vibration case, we have calculated the partition function using the BSSH algorithm without the need of the standard statistical method. Indeed the present algorithm works for the grand canonical ensemble and all the sources of systematic error can be controlled with a rigorous approach both for computing the ground state energies and for computing the specific heat observable. This may be a more efficient implementation of an analytical model, with a rather more powerful algorithm. We believe that the reported accuracy gives a very robust confirmation of the existence of antiferromagnetic short range order in the one-dimensional Hubbard model.
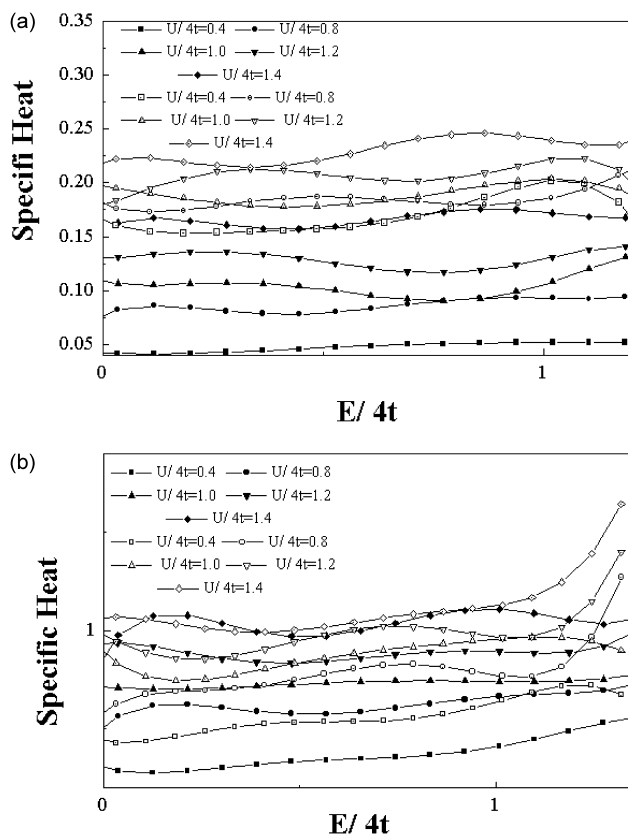
As a consequence, for a good comparison between theoretical works, one should conclude that the question about the influence of soliton on the behavior of correlation function on *t*-PA and/or polymeric chain remains still open because the specific heat maxima are not necessary unique feature of the existence of soliton, but it may also due to the different phase transitions which are not accessible by the analytical calculations.

We conclude that a detailed understanding of excitation properties of soliton containing systems can be obtained only when many-particles effects are taken into account. The calculations presented here are enough to obtain qualitative agreement with recent literature. In order to improve the results, one probably has to work with size-consistent methods, but still at the quantum level since it is essential for the accuracy and quality of the results that the calculations be performed on large systems. For comparison with experimental data on small model molecules of the polymer, however, ab-intio calculation will be of great importance.

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