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Continuum Hartree Fock scheme for 1-d organic polymers

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Résumé. — Nous établissons la version continue du modèle des polymères organiques à une dimension en prenant en compte la déformation du réseau par une formulation du type SSH et la corrélation électronique par une interaction du type Hubbard. L'hamiltonien obtenu rentre dans la catégorie des théories des champs à symétrie interne. Nous le traitons par une méthode du type Hartree-Fock et nous obtenons de manière simple les résultats préalablement déduits par le calcul direct sur le réseau. Ceci nous permet de préciser la validité des modèles continus.

Abstract. — We establish the continuum version for the model of 1-d organic polymers by taking into account within a SSH type formulation the lattice deformation, and within a Hubbard interaction, the electronic correlation. The deduced Hamiltonian belongs to the category of field theories with internal symmetry. We treat it by a self-consistent field method and we obtain in a simple way the results already deduced by direct calculation on the lattice model. This allows for a discussion of the validity of continuum models.

1. Introduction.

Within a few exceptions, the study of conducting 1-d organic polymers rests on the so-called SSH model [1]. Essentially this model assumes that the polymer can be described by non interacting electrons moving on a dimerizable one dimensional lattice, the electrons being characterized by a tight-binding band with a transfer integral modulated *via* the chain deformation. Therefore a competition results between the gain in electron energy due to dimerization (a gap opens at $k = k_F$: Peierls instability) and the loss of elastic energy of the lattice. SSH concluded that in, e.g. polyacetylene, the ground state is indeed an alternate succession of « simple » and « double » bonds. Recent experiments support this description [2].

A question however arises : does Peierls instability subsist in the presence of correlation between electrons ? To be sure no definite answer is known on theoretical grounds [3]. On the other hand, polymers with analogous properties, e.g. polyparaphenylene, do not show up the doubly degenerate configuration required by the SSH treatment, which therefore does not apply.

In order to take into account the electron cor-

relation, a simple way is to add a Hubbard repulsion term to the SSH Hamiltonian. Equivalently this amounts to allow for a modulation of the transfer integral in the famous exact calculation by Lieb and Wu [4]. To our knowledge the exact solution of this new problem is not known so that approximate treatments have to be used.

Several authors have tackled the question by using a Hartree-Fock approximation for the Hubbard term [5]. The most recent work is Kivelson and Heim's [5]. They conclude that there exists an upper critical value U_{cr} for the Hubbard parameter below which the stablest phase is dimerized. If one retains the values of the parameters used in the SSH model, one obtains $U_{cr} \sim 4.6$ eV, a rather low value as compared to 10, 15 eV the « bare » value ordinarily retained. Kivelson and Heim estimate that for polyacetylene $U \sim 4.5$ a value which is rather close, if below, to U_{cr} . Moreover if one compare two exact models, namely the SSH ground state (dimerization, one electron per site and the repulsion U), and the Lieb and Wu state (no-dimerization) it is found that U_{cr} is reduced by a factor ~ 3 [6].

Furthermore, another statement of Kivelson and Heim is surprising. They have tried to improve the Hartree-Fock treatment by a perturbation calculation, and they reach the conclusion that the dimeriza-

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tion is enhanced when U is increased in the limit $U/t_0 \ll 1$, a result which has also been obtained recently by a Monte-Carlo calculation [7]. Clearly, on physical grounds, for $U \rightarrow \infty$ the system must be uniform, a fact that all models exhibit.

In this paper we present a continuous version of the Lieb and Wu problem in the presence of dimerization, which seems to us a better starting point for reaching an exact solution. However we have not been able to diagonalize exactly the corresponding Hamiltonian, and we give an Hartree-Fock treatment which recovers most of the Kivelson and Heim results.

To our opinion the interest is threefold :

1) It is a way to test the continuum approximation and it shed light on various aspects of the solutions of exact models (in particular on the problem of cut-off determination).

2) It details and illustrates our paper on solitons in the spin density wave (SDW) phase and shows clearly the symmetric rôle played by the two order parameters : chain distortion amplitude, and SDW amplitude [8].

3) It is a starting point for a subsequent paper in which we show that if one uses a naive description for the electronic correlation (i.e. of the Luttinger type) no dimerization is to be expected.

2. Continuum approximation and SCF equations.

The starting Hamiltonian for 1-d polymers in the

presence of Hubbard repulsion reads :

$$H_L = - \sum_{n,s} [t_0 - \alpha(u_{n+1} - u_n)] (C_{n+1s}^+ C_{ns} + hc) + \frac{1}{2} U \sum_{n,s} N_{ns} N_{n-s} + \frac{1}{2} \sum K (u_{n+1} - u_n)^2 \quad (2.1)$$

where the notations are standard and may be found in Kivelson and Heim's paper. A part from the last term which represents the elastic energy due to the lattice deformation, the Hamiltonian is Lieb and Wu's Hamiltonian except for the modulation term $\alpha(u_{n+1} - u_n)$.

The basic step in deriving the continuum version is to exhibit the assumed rapid spatial variation of the $C_{n,s}$'s. We set :

$$a^{-1/2} C_{ns} = \psi_{1s}(n) e^{ink_F a} - i\psi_{2s}(n) e^{-ink_F a} \quad (2.2)$$

Where $k_F a = \pi/2$. The ψ 's are assumed to be slowly varying functions on the scale of the lattice spacing a .

Equation (2.2) introduces a two component quasi-spinor $\psi_s = \begin{bmatrix} \psi_{1s} \\ \psi_{2s} \end{bmatrix}$. When rewriting (2.1) in terms of these new operators we remark that sums like

$$\sum_n \psi_{1s}^+(n) \psi_{\mu s'}(n) e^{\pm 2ink_F a}$$

are negligible. After a small algebra the Hamiltonian is transformed into :

$$H = \sum_s \int dx \left\{ \psi_s^+ \left(-i\hbar v_F \tau_3 \frac{\partial}{\partial x} + m\tau_1 \right) \psi_s + a \frac{U}{2} [(\psi_s^+ \psi_s)(\psi_{-s}^+ \psi_{-s}) + (\psi_s^+ \tau_2 \psi_s)(\psi_{-s}^+ \tau_2 \psi_{-s})] \right\} + 2NKu^2 \quad (2.3)$$

When writing (2.3) we have, as usual (see Takayama, Lin-Liu and Maki [9]) linearized the spectrum around $k = k_F$ and assumed a uniform dimerization of the lattice, i.e. :

$$u_n = (-)^n u.$$

The τ 's are the isotopic (Pauli) matrices, $\hbar v_F = 2at_0$, $m = 4au$ and N is the number of carbon atoms in the quantization « box ». One immediately remarks the analogy between the Hamiltonian (2.3) and the so-called « massive Thirring model » which has been recently diagonalized by Bergknoff and Thacker [10]. However the interaction term is much more complicated and actually (2.3) belongs to the class of « field theories with internal symmetry ».

Ordinarily problems of this kind are handled by a Bethe *Ansatz*, but no one can *a priori* be sure that the procedure will be successful. Indeed Belavin (11) has diagonalized a Hamiltonian with internal symmetry. But the interaction term is much simpler than (2.3) and moreover Belavin states, that even for his Hamiltonian, the Bethe *Ansatz* fails when a « mass term » (i.e. $m \neq 0$) is present.

We have nevertheless tried to diagonalize (2.3) exactly by a Bethe *Ansatz*, following the method of Bergknoff and Thacker [10], but with no success. We therefore resort to an approximate treatment which will be developed below.

We first write down the equation of motion :

$$\left[-i\hbar v_F \tau_3 \frac{\partial}{\partial x} + m\tau_1 - Ua(\psi_{-s}^+ \psi_{-s} + \psi_{-s}^+ \tau_2 \psi_{-s} \tau_2) \right] \psi_s = E\psi_s \quad (2.4)$$

and make the self consistent field approximation (SCF) by setting :

$$\langle C_{ns}^+ C_{ns} \rangle = \frac{1}{2} + (-)^n 2 s \delta. \quad (2.5)$$

This allows to treat on an equal footing the two features : spin polarization and lattice distortion. In terms of the ψ 's (2.5) reads :

$$a \langle \psi_s^+ \tau_2 \psi_s \rangle = (-)^n 2 s \delta \quad (2.6)$$

and the electronic part of the Hamiltonian is now approximated by the SCF Hamiltonian :

$$\bar{H}_{el} = \sum_s \int dx \psi_s^+ \left\{ U \left[\frac{1}{2} - \left(\frac{1}{4} - \delta^2 \right) \right] - i \hbar v_F \tau_3 \frac{\partial}{\partial x} + m \tau_1 + 2 s U \delta \tau_2 \right\} \psi_s. \quad (2.7)$$

Defining ρ and θ by

$$m + i U \delta \equiv \rho e^{i\theta} \quad (2.8a)$$

and setting :

$$\tilde{\psi}_s = e^{is\theta\tau_3} \psi_s \quad (2.8b)$$

the complete Hamiltonian takes the form :

$$\bar{H} = \sum_s \int dx \tilde{\psi}_s^+ \left(- i \hbar v_F \tau_3 \frac{\partial}{\partial x} + \rho \tau_1 \right) \tilde{\psi}_s + N \left[\left(\frac{1}{4} + \delta^2 \right) U + 2 K u^2 \right]. \quad (2.9)$$

3. Solution of the SCF equations.

The electronic part of \bar{H} is readily diagonalized by setting :

$$\tilde{\psi}_s(x) = \sum_v \begin{bmatrix} \alpha_v(x) & -\beta_v(x) \\ \beta_v(x) & \alpha_v(x) \end{bmatrix} \begin{bmatrix} A_{vs} \\ B_{vs} \end{bmatrix}$$

where A_{vs} and B_{vs} obey the equations of motion :

$$[\bar{H}_{el}, A_{vs}] = -\epsilon_v^A A_{vs}; \quad [\bar{H}_{el}, B_{vs}] = -\epsilon_v^B B_{vs}.$$

One checks easily that $\epsilon_v^A = -\epsilon_v^B$ and that the solutions of these equations are :

$$\begin{aligned} \alpha_{vs} &= M_s e^{ikx}; & \beta_{vs} &= N_s e^{ikx} \\ \epsilon_v^A &= -\rho \cosh \phi; & \sinh \phi &= \rho^{-1} \hbar k v_F \end{aligned}$$

or in terms of the $\tilde{\psi}$'s :

$$\begin{aligned} \tilde{\psi}_{1s} &= c \left[\sum_k (1 + e^{2\phi})^{-1/2} e^{ikx} A_{ks} + (1 + e^{-2\phi})^{-1/2} e^{ikx} B_{ks} \right] \\ \tilde{\psi}_{2s} &= c \left[\sum_k - (1 + e^{-2\phi})^{-1/2} e^{ikx} A_{ks} + (1 + e^{2\phi})^{-1/2} e^{ikx} B_{ks} \right] \end{aligned} \quad (3.1)$$

where c is the normation constant.

The ground state is now written as :

$$\prod_{\substack{k,s \\ |k| < k_c}} A_{ks}^+ |0\rangle$$

where k_c is some cut-off to be specified later on.

Using equations (2.8b) and (2.5) one derives the self consistent equation. Let us first note that for N particles on a line of length L ($L/N = \text{Cte}$ $N \rightarrow \infty$) the density of state is determined *via* the usual cyclic boundary conditions. In the SCF approximation the quasiparticles are actually independent so that there is no phase shift in the wave function. The boundary condition is therefore $e^{ikL} = 1$ and the density of states is a constant, namely $L/2\pi$. In other words the cut-off momentum equals k_F i.e. $k_c = k_F = \pi/2a$.

The self-consistent equation now reads :

$$\sin \theta \frac{a}{2\pi} \int_{-k_F}^{k_F} \frac{dk}{\cosh \phi} = \delta$$

or :

$$\frac{U\delta}{\sqrt{m^2 + U^2 \delta^2}} \frac{a}{\pi} \int_0^{k_F} \left[1 + \frac{(\hbar k v_F)^2}{m^2 + U^2 \delta^2} \right]^{-1/2} dk = \delta. \quad (3.2)$$

The integration is straightforward and yields :

$$\delta \frac{\gamma}{\pi} \sinh^{-1} \frac{\pi/2}{[(\gamma\delta)^2 + y^2]^{1/2}} = \delta \quad (3.3)$$

where

$$\gamma = \frac{U}{2t_0} \quad y = \frac{m}{2t_0}.$$

The total energy is computed with the help of equation (2.9) and reads :

$$\begin{aligned} (2Nt_0)^{-1} E &= -\frac{2a}{\pi} \int_0^{k_F} [a^2 k^2 + y^2 + \gamma^2 \delta^2]^{1/2} dk + \gamma \left(\frac{1}{4} + \delta^2 \right) + \frac{Ku^2}{t_0} = \\ &= -\frac{1}{\pi} (y^2 + \gamma^2 \delta^2) \left(\Lambda + \frac{1}{2} \sinh 2\Lambda \right) + \gamma \left(\frac{1}{4} + \delta^2 \right) + \frac{2}{\eta} y^2 \end{aligned} \quad (3.4)$$

where :

$$\sinh \Lambda(\delta) = \frac{\hbar k_F v_F}{\rho}; \quad \eta = \frac{8\alpha^2}{Kt_0}$$

δ is to be determined by solving equation (3.3). Two solutions are available :

1) $\delta = 0$. This is the dimerized SSH-like solution for which the energy is (it corresponds to TLM results [9] with $\delta = 0$) :

$$(2Nt_0)^{-1} E_1 = \frac{\gamma}{4} + \left[\frac{2}{\eta} - \frac{1}{\pi} \left(\Lambda(0) + \frac{1}{2} \sinh 2\Lambda(0) \right) \right] y^2. \quad (3.5)$$

As expected E_1 display two minima at $y_0 = \pm \frac{ak_F}{\sinh \Lambda_0}$; $\Lambda_0 = \frac{2\pi}{\eta}$. We designate by E^D the corresponding energy :

$$E^D = \frac{\gamma}{4} - \frac{1}{\pi} a^2 k_F^2 \coth \frac{2\pi}{\eta}. \quad (3.5a)$$

2) $\delta = \delta_0$ where

$$\delta_0 = \gamma^{-1} \left[\left(\frac{ak_F}{\sinh \frac{\pi}{\gamma}} \right)^2 - y^2 \right]^{1/2}. \quad (3.6)$$

The corresponding energy is :

$$[2Nt_0]^{-1} E_2 = \frac{\gamma}{4} - \frac{1}{\pi} \frac{a^2 k_F^2}{\tanh \frac{\pi}{\gamma}} + \left(\frac{2}{\eta} - \frac{1}{\gamma} \right) y^2. \quad (3.7)$$

This energy is extremum for $y = 0$. We designate it by E^{SDW} . For $\gamma < \frac{\eta}{2}$ this extremum is a maximum and the corresponding solution is unstable. For $\gamma > \frac{\eta}{2}$ the extremum is a minimum, the corresponding solution is stable. Physically it represents a spin density wave (SDW) of amplitude δ_0 on a non-dimerized lattice .

Notice that we do not find a coexistence of SDW and dimerized lattice, as was obtained by Kivelson and Heim. The «mixed state» has been washed out by the continuum approximation.

Comparing the energies of the two solutions, it is readily seen that the SSH-like state is the stablest for $\gamma < \frac{\eta}{2}$, and the SDW state for $\gamma > \frac{\eta}{2}$. For $\gamma = \frac{\eta}{2}$, the energies of the two states coincide.

It is interesting to plot E_1 and E_2 as functions of the parameter y for various values of γ . This is represented on figure 1.

Note that the two curves are tangent for $y = y_{\text{int}} = \frac{\pi}{2} \sinh \frac{\pi}{\gamma}$. For $y > y_{\text{int}}$ the self consistency equation (3.3) exhibits an imaginary solution for δ , which cannot correspond to a physical situation. This is pictured by the dashed parts in figure 1.

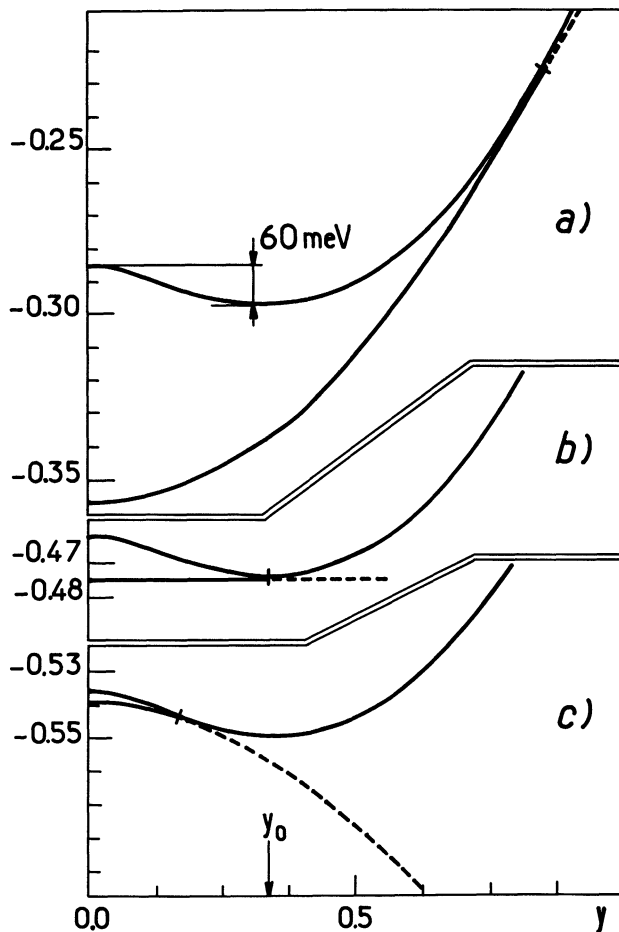


Fig. 1. — Variations of $(2 N t_0)^{-1} E_1$ (Eq. (3.5)) and of $(2 N t_0)^{-1} E_2$ (Eq. (3.7)) as functions of y for : a) $\gamma = 2$, b) $\gamma = \eta/2$, c) $\gamma = 1$, with $\eta = 2.56\dots$ as proposed by SSH. The dashed part of E_2 corresponds to the unphysical range where $\delta^2 < 0$. The arrow indicates the value y_0 where E_1 is minimal.

We can now easily draw a phase diagram in the γ, η plane (Fig. 2). The frontier is the straight line $\gamma = \eta/2$. In terms of U , it yields the critical value :

$$U_{\text{cr}} = \frac{8 \alpha^2}{K}.$$

Let us emphasize once again on the fact that there is no mixed state in this treatment. As a result, when crossing the boundary $\gamma = \eta/2$, the dimerization parameter drops abruptly from u_0 to 0 while the SDW parameter increases abruptly from 0 to δ_0 . This is to be compared with the results of the lattice version in which it is found that these parameters have an exponential variation in the mixed state.

It is also worth noting that the boundary in the continuum model is slightly above that of the lattice version.

It is interesting to compare the value of the dimerization parameter y_{0L} (resp. y_{0c}) and of the SDW amplitude parameter δ_{0L} (resp. δ_{0c}) in the lattice (resp. continuum) version.

$y_{0L} = \frac{2 \alpha u_{0L}}{t_0}$ is solution of the equation (Ref. [5] and [12]) :

$$K(1 - y_0^2) - E(1 - y_0^2) - \frac{2\pi}{\eta}(1 - y_0^2) = 0$$

where K and E are elliptic functions of the first and second kinds. For small values of $\eta \ll 2\pi$ this solution is

$$y_0 = y_{0L} \simeq \frac{4}{\rho} e^{-2\pi/\eta}.$$

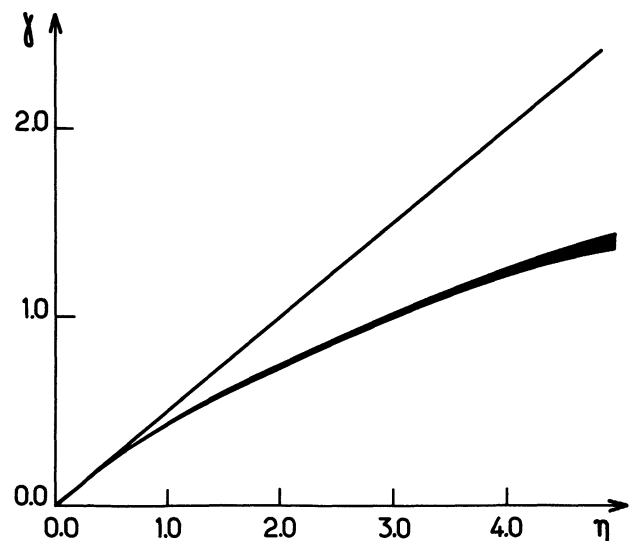


Fig. 2. — Phase diagram in the $(\eta - \gamma)$ plane. The bold line is the (narrow) domain found in the lattice version where coexist a spin density wave and a dimerization pattern.

This is to be compared with y_{0c} namely :

$$y_{0c} = \frac{\pi}{2 \sinh \frac{2\pi}{\eta}} \simeq \pi e^{-2\pi/\eta}. \quad (3.8)$$

The two expressions differ by the prefactor, but both exhibit the characteristic exponential dependency (see Fig. 3).

δ_{0L} is solution of the equation (Refs. [5] and [12]) :

$$\frac{\gamma}{\pi} \frac{1}{\sqrt{1 + \gamma^2 \delta_{0L}^2}} K\left(\frac{1}{1 + \gamma^2 \delta_{0L}^2}\right) = 0$$

which for $\gamma \ll 2\pi$ gives :

$$\delta_{0L} \simeq \frac{4}{\gamma} e^{-\pi/\gamma}.$$

This is to be compared with δ_{0c} namely :

$$\delta_{0c} = \frac{\pi}{2 \gamma \sinh \pi/\gamma} \simeq \frac{\pi}{\gamma} e^{-\pi/\gamma}.$$

Once again we find a different prefactor and the characteristic exponential dependency.

Finally let us remark that the optical gap is given in either phase by :

$$E_g^{SDW} = \frac{2 \pi t_0}{\sinh \frac{2 \pi t_0}{U}} ; \quad E_g^D = \frac{2 \pi t_0}{\sinh \frac{2 \pi}{\eta}}.$$

This shows that $\frac{U}{t_0}$ and $\eta = \frac{8 \alpha^2}{K t_0}$ play the same rôle as do m and $U\delta$ in the SCF Hamiltonian (see Eqs. (2.7) and (2.9)). This is the basic reason why it is possible to build bag and kink solitons in the SDW as well as in the dimerized phase [8].

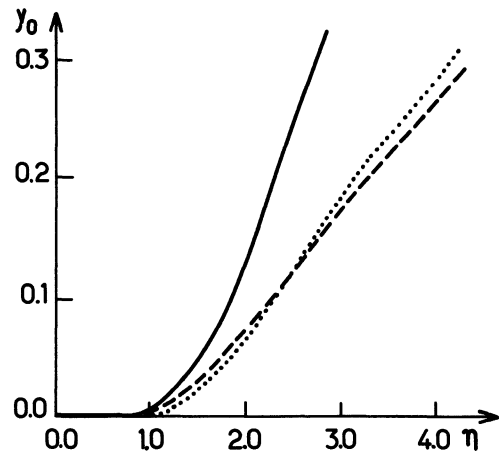


Fig. 3. — Variations of y_0 as a function of η . The dotted curve corresponds to the lattice version; the dashed one is $y_{0,c}$ with the right prefactor; the solid curve is $y_{0,c}$ as given by equation (3.8).

4. Conclusions.

In the above treatment we have obtained in a very simple way the essential features of the lattice model for the Hubbard type Hamiltonian in the presence of chain dimerization. The results are appealing because they appear in close form, in terms of elementary functions, on the one side, and because they allow to be confident in the continuum approximation, on the other side. As was shown by Campbell and Bishop, such treatment is attractive since it is equivalent to the Gross-Neveu model and as such is amenable to use well-known results of field theory, as we shall show in a subsequent paper.

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