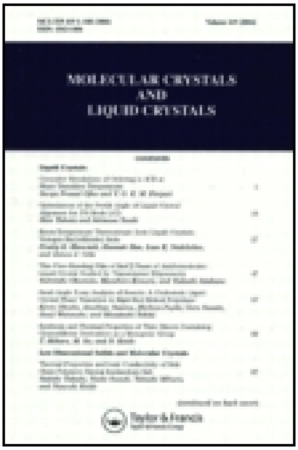

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A MODEL FOR SOLITON EXCITATIONS IN $(CH)_x$

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We present a simple model for those properties of $(CH)_x$ which are associated with the concept of solitons. We propose an "ab initio" calculation of the wave function and energy of the soliton within an "Unrestricted Hartree-Fock" scheme. Electron-electron interactions are capable to originate an organization into domains and walls when described in terms of the so-called alternant orbitals of LÖWDIN. The essential features of the treatment are reviewed and numerical results are reported. Then a connection is made between the model and some other formalisms. Finally we discuss a tentative interpretation of electron spin resonance experiments. Specially emphasized are numerical simulations of spectra and analysis of diffusive motions of solitons.

1. INTRODUCTION

During the last few years the importance of solitons in polyacetylene has been stressed many times[1,4]. It is generally assumed that, because of "kinks" in bond alternation, excitations can exist under the form of a moving wall carrying an unpaired spin.

The idea that bond alternation is essential[5,6] for the understanding of $(CH)_x$ implies that the conventional band theory is always suitable for describing polymers having conjugated bonds. This problem has been widely discussed by Mott[7] and leads to the hypothesis that the gap could be a correlation gap, bond alternation acting only to stabilize the system[8].

Our purpose is to present a model of soliton with this hypothesis and within the framework of a method specially deviced to account for correlation effects[9]. We shall also attempt to connect this description with more conventional ones.

2. MODEL

2-1. A Special Choice Of Wave Functions

Because of inter-electron correlations the true behaviour of a polyene chain is intermediate between Molecular Orbital (MO) and Valence Bond (VB) descriptions. In his quest for the best compromise, Löwdin suggests to use Alternant Molecular Orbitals (AMO).

Electrons with different spins are alloted to different orbitals and thus kept apart, the two sets of orbitals having their respective maxima of amplitude on the nodes of two imterpenetrating sublattices.

Let a_k be the orbitals associated with α spins and $\bar{a}_k$ those for β spins

$$<a_k|a_\ell>=<\bar{a}_k|\bar{a}_\ell>=\delta_k^\ell \text{ and } <a_k|\bar{a}_\ell>=<\bar{a}_k|a_\ell>=\lambda_k.\delta_k^\ell \qquad (1)$$

The set of λ_k 's is the set of Löwdin's correlation parameters. For practical conveniency we shall set $\lambda_k = \lambda$ for all k.

More precisely each AMO is a combination of Bloch waves ψ_k and $\psi_{\bar{k}}$ with wave vectors k and $\bar{k}$ differing by twice the Fermi vector[10,11].

$$a_k = \cos\theta\psi_k+\sin\theta\psi_{\bar{k}} \; ; \; \bar{a}_k =\cos\theta\psi_k-\sin\theta\psi_{\bar{k}} \; ; \; \lambda=\cos2\theta \quad (2)$$

With the two sets $\{a\}$ and $\{\bar{a}\}$ we construct a Slater determinant which is not an eigenstate ot the total spin operator. If the variation of energy (which determines optimal λ) is made on a component with a definite spin multiplicity the method is called Extended Hartree-Fock (EHF) method. If one does not select any component one enters Unrestricted Hartree-Fock (UHF) scheme.

2-2. Derivation Of An Energy Expression

A particularly tractable expression for the total energy can be derived in terms of density matrices[12]. Let us define

$$\rho_+(1,2)=\sum_k a_k^*(\vec{r}_1)\,a_k(\vec{r}_2) \text{ and } \rho_-(1,2)=\sum_k \bar{a}_k^*(\vec{r}_1)\,\bar{a}_k(\vec{r}_2) \qquad (3)$$

The total energy in the sum of three terms (kinetic, classical coulombian, exchange). Only the third one plays a role in the soliton problem. It can be written as

$$E_3=-\frac{e^2}{8\pi\varepsilon_o}\iint \frac{\rho_+(1,2)\rho_+(2,1)+\rho_-(1,2)\rho_-(2,1)}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1 d\vec{r}_2 \qquad (4)$$

The spin density ($\rho_+-\rho_-$) alternates as if the system were an antiferromagnet. Actually this magnetic structure is spurious[13] and does not persist when using the correct EHF singlet groundstate. Nevertheless we can use directly the AMO basis to get the self consistent-energy-band structure since for a very large number of electron the UHF- and singlet EHF- energies tend to the same limit[14].

2-3. Possible Existence Of Solitons

Considering that the spin is a label to distinguish the nodes of the two sublattices that interpenetrate each other to produce what quantum chemists name an alternant structure[15], we wonder whether the two degenerate forms ($a\alpha,\bar{a}\beta$) and ($a\beta$, $\bar{a}\alpha$) of the AMO groundstate can coexist as two domains separated by a wall.

ρ_+ and ρ_- have twice the crystal period. 2N being the total number of electrons and calling magnetic cell the unit formed by two adjacent crystallographic cells, E_3 is N times the integral in (4) $\vec{r}_1$ ranging over one magnetic cell and $\vec{r}_2$ over the whole crystal. We put

$$E_3 \text{ (monodomain)} = N\, e_3 \qquad (5)$$

When an organization into domains occurs, a "cluster" covering n magnetic cells is included between to regions where spin labels are interchanged from one to the other. This cluster contributing to E_3 as a quantity δ,

$$E_3 \text{ (with a wall)} = (N-n)\, e_3 + \delta \qquad (6)$$

The wall is then analogous to that in a uniaxial antiferromagnet. Associated with it is a soliton excitation[16] with energy

$$E_{sol} = E_3 \text{ (wall)} - E_3\text{(mono)} = \delta - ne_3 \qquad (7)$$

3. RESULTS AND DISCUSSION

3-1. Results

e_3 is determined within a conventional AMO treatment[17]. Alternant orbitals are generated from a gaussian representation of the π-orbitals of carbon atoms[18]. To get δ we adopt a phenomenological description of the kink : a localized state in the middle of the gap[19] compensates for a lack in the density of states[2]. Otherwise the band-structure is the same as that of the regular system[19]. The mixtures

$$u=Aa+(1-A)\bar{a} \text{ and } v=(1-A)a+A\bar{a} \text{ vith } \lim_{r\to-\infty}A=1 \text{ and } \lim_{r\to+\infty}A=0 \quad (8)$$

give matrices that match ρ_+ and ρ_- on one end of the chain and interchange their rôles on the other. Moreover $\rho_+ + \rho_-$ does not normalize to 2N and what is missing simulates the squared modulus of the soliton wave function

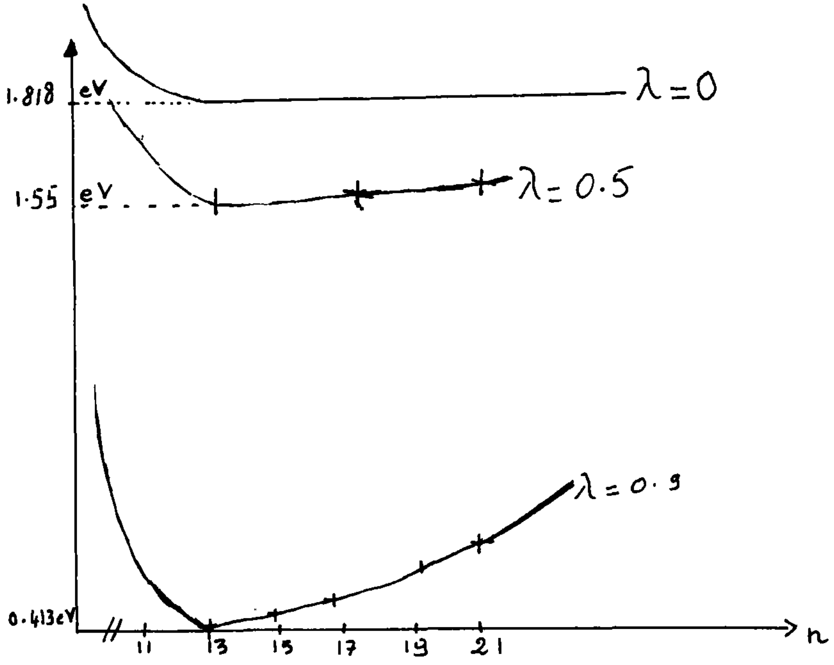

FIGURE 1 Soliton wave function versus its spatial extension

For conveniency results are gathered in figures 1 and 2 and table 1.

Figure 1 shows the variations of E soliton versus its size for different values of λ.

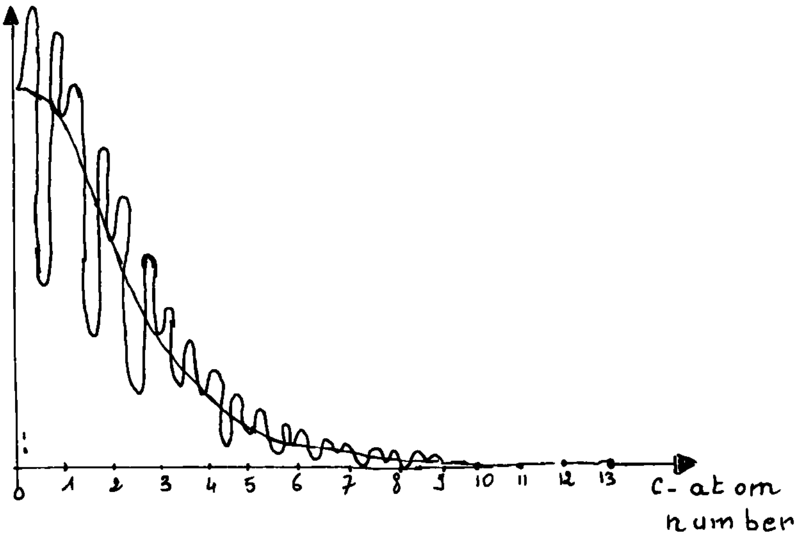

FIGURE 2 Soliton wave function

The coefficient A of equation (8) is taken equal to

$$A(r) = (1 - \tanh(r/pa))/2 \qquad (9)$$

p characterizes (by analogy with spectroscopy vocabulary) a soliton half-width and is directly related to n.

Figure 2 shows the shape of the soliton wave function for $\lambda = 0.9$. This value of the correlation parameter provides the best fit of the gap to the experimental value of 1.4 eV. The numerical values of the spin densities are listed in table 1.

3-2. Comments

We see that for $\lambda = 0.9$ the wall has an optimal extension. The results p=7 and n=13 must be compared to those of reference 2 : half-width of 7 CH units, soliton covering about 15 units on each side of the central atom. Apparently the fact that we find almost the same soliton energy checks

Table 1 Spin Densities On Atoms Of The Wall

atom number	spin density	atom number	spin density
0	.1641	± 7	.0077
± 1	.1506	± 8	.0058
± 2	.0965	± 9	.0048
± 3	.0618	±10	.0029
± 4	.0540	±11	.0019
± 5	.0193	±12	.0010
± 6	.0116	±13	.0001

the validity of Rice's prediction[1]. Whatever might be the origin of the gap, a correct adjustment of the latter leads to the same soliton excitations.

3-3. Connection With Other Formalisms

While Rice[1] investigated only lattice distorsions within a Lagrangian formalism, Su-Schrieffer-Heeger[2] have deviced a complete microscopic theory of solitons, later extended to the continuous limit[3]. Our model, when compared to the preceding ones, remains rather semi-phenomenological and tributary of a certain degree of roughness. Nevertheless, with some tedious algebraic manipulations, the hamiltonian of ref. 17 used throughout the present paper gives exactly the electronic term of ref. 2 when interactions are restricted to next neighbours. What we have presented could be a trick to avoid handling of Green functions.

4. SOLITONS AND EPR EXPERIMENTS IN $(CH)_x$

4-1. EPR Spectra Of Trans-$(CH)_x$

Within the hypothesis that hyperfine interactions are responsible for the observed linewidths and from the spin densities on the CH groups concerned by the wall, we have attempted to fit the experimental EPR signal by numerical simulations of the unnarrowed hyperfine spectrum of a soliton.

The hyperfine coupling constant a_o^H for an electronic spin on a CH proton is handled by our computer program as a flexible parameter. Each individual line of the composite spectrum is assumed to be lorentzian in shape, with a linewidth (peak-to-peak distance of the derivated curve) of .45 Gauss. This value corresponds to the high-temperature asymptotic width obtained by most authors[20].

The best fit to experimental spectrum is obtained for a_o^H = 22 Gauss. A larger a_o^H leads to a partial appearance of hyperfine structure. This also occurs with a_o^H = 22 G for a smaller soliton, that is for $n < 11$. Thus we get a confirmation of the fact that the domain wall spreads out in order to minimize its energy and that there exists a lower bond to its size.

4-2. Diffusive Motion Of The Soliton

Due to interactions with phonons the wall is subjected to a brownian motion the fundamental parameter of which is the diffusion coefficient D.

For an ab initio estimation of D we add to the electron hamiltonian a phonon term and attempt to solve the time-dependent Schrödinger equation by means of a trial function describing "birth" or "death" of spin labels.

Combining Heisenberg evolution equations together with Hamilton equations we are able to get the displacement $\delta(t)$ of the wall, from which D follows via

$$D = \langle (\delta\ (t)\ )^2 \rangle\ /t \qquad (10)$$

Despite the fact that our calculations are only at their preliminary phase we can give an order of magnitude $D \sim 10^{13}$ rad/s per unit of lattice parameter.

4-3. Conclusions

We find the best fit for a value of a_o^H close to that of a free spin in a $2p_z$ carbon orbital (23.4 G) successfully used for interpretation of NMR experiments in $(CH)_x$.[21] Nevertheless a simulation on the basis of ref.2 leads to a higher a_o^H (31 G) which is also claimed to be in good agreement with experiments[22]. However to enhance a_o^H from 23 to 31 G it is necessary to assume deformation of orbitals. We think that such deformations are not very likely in $(CH)_x$.

Concerning D, we find a result in agreement with NMR experiments[21] and which could be the "intrinsic" diffusion coefficient of the soliton. The D-coefficient measured by EPR is two orders of magnitude smaller. This is probably the consequence of fixed centers that interrupt the motion.

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