

## Spin-polarization effects in $(AB_2)_n$ polymeric chains

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The techniques of renormalization of interactions and transfer matrices are used to investigate spin-polarization effects in  $(AB)_2$  polymeric chains, within a Hartree-Fock solution to a diagonal Hubbard Hamiltonian approximation. The electronic structure of the infinite chain is obtained and the corresponding magnetization is examined for different values of the one-center repulsion integrals  $J$ . It is observed that one-third of the total electronic states available are associated to nondispersive states localized on the  $B$  sites; for half-filled systems the conductive and magnetic properties of the chain are obtained as a function of  $J$ . The damped spin density wave resulting from a substitutional impurity on an  $A$  center is also calculated. [S0163-1829(96)03823-4]

### I. INTRODUCTION

After an earlier suggestion that odd-alternant radicals would be likely candidates to present organic ferromagnetic interactions,<sup>1</sup> in his 1978 pioneering work Ovchinnikov<sup>2</sup> has examined the existence conditions for ferromagnetism in large alternant hydrocarbon molecules. By definition, alternant molecules are those in which one could identify two classes of atoms,  $C$  and  $C^*$ , such that each atom of one given kind would only have atoms of the other type as first neighbors, and vice versa. Classical alternant molecules have an equal number of  $C$  and  $C^*$  carbon sites and obey the Coulson-Rushbrooke<sup>3</sup> (CR) theorem, which states that in such systems there will be a well-defined unoccupied molecular orbital (MO) corresponding to each occupied MO. Ovchinnikov<sup>2,4</sup> has also considered the case of nonclassical alternant molecules<sup>5,6</sup> in which one type of atom is in excess: it can be expected that the ground state of these molecules would display a high multiplicity and a total spin

$$S = \frac{|n_C - n_{C^*}|}{2}, \quad (1)$$

where  $n_C$  and  $n_{C^*}$  are the numbers of atoms of each kind. By the same reasoning, nonclassical alternant polymeric chains would have a nonvanishing magnetization per unit cell ( $S_{uc}$ ) and an extremely high total spin.

The field experienced a renaissance<sup>7-11</sup> in the second part of the 1980's. Since then, the search for organic ferromagnets of increasingly high Curie temperature has continued at a steady pace,<sup>12,13</sup> and a promising development was the relatively recent identification of all-organic magnetism in the family of nitroxide crystals.<sup>14,15</sup>

From the conceptual point of view, the study of the magnetism in polymers is akin to the investigation of the behavior of one-dimensional Heisenberg chains,<sup>16,17</sup> for which a series of theorems have been established within the Hubbard model<sup>18-20</sup> [as a matter of fact, Eq. (1) has been rederived in this context by Lieb<sup>20</sup>]. To analyze the existence of ferromagnetism in these systems, the electron-electron repulsion is usually described within a Hubbard approximation,<sup>21</sup> for

which Nagaoka has demonstrated an important theorem valid for the almost half-filled band case.<sup>22</sup>

In the present work we will use the renormalization of interactions technique<sup>23,24</sup> to examine the electronic structure of  $(AB_2)_n$  chains [Fig. 1(a)], described by a diagonal Hubbard Hamiltonian.<sup>25</sup> This polymeric structure represents the simplest case of the type of nonclassical system with odd-membered rings analyzed by Tyutyulkov and collaborators,<sup>6,26,27</sup> for which no alternant structure can be assigned (and hence the CR theorem cannot be applied.) For these systems the unpaired molecular orbitals in excess are of nonbonding nature and will collapse into an infinitely narrow band that could lead to a high-spin ground-state configuration.<sup>26</sup> This system was first discussed for the case of identical ( $A \equiv B$ ) atoms by Coutinho-Filho and collaborators,<sup>28</sup> who have obtained results through direct diagonalization and quantum Monte Carlo simulation. We will show in Sec. II how the use of renormalization techniques will permit the investigation of the characteristics of the non-dispersive states of the  $(AB_2)_n$  chains in a simple and analytical manner. In Sec. III, these techniques will be used to study the effects of the introduction of a substitutional impurity in an  $A$ -type site upon the electronic structure of the system. A preliminary account of this work can be found in Ref. 29.

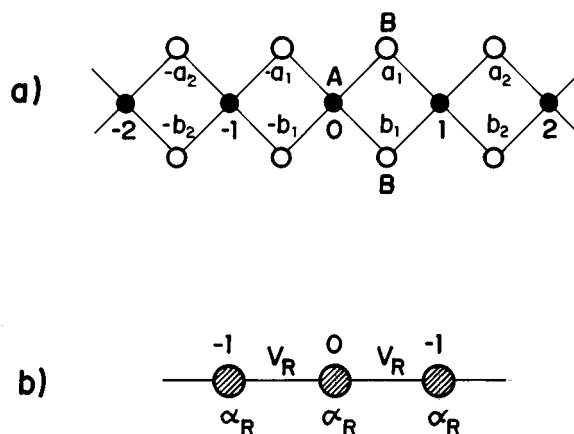


FIG. 1. (a) Regular  $(AB_2)_n$  chain and (b) its renormalized equivalent.

## II. PERFECT CHAIN

### A. General expressions

Let us consider first a perfect chain with no impurities or defects present [Fig. 1(a)]. Following the general idea of renormalization of interactions,<sup>23,24</sup> we will identify two different kinds of sites in the  $(AB_2)_n$  chain: ‘‘knot’’ ( $\dots, -2, -1, 0, 1, 2, \dots$ ) and ‘‘angle’’ ( $\dots, -a_2, -a_1, a_1, a_2, \dots$ ) sites. The former will be preserved, while any explicit reference to the latter will be eliminated in the renormalization process.

In a Wannier orthogonal basis, the generic equation for the Green function can be written as

$$EG_{i,j} = \delta_{i,j} + \sum_k H_{i,k} G_{k,j}, \quad (2)$$

where, within the diagonal Hubbard approximation adopted, only intrasite

$$H_{A,A}^{\uparrow(\downarrow)} = -(\alpha_A + J_A \langle n_A^{\uparrow(\downarrow)} \rangle) \equiv -(\alpha_A + f_A^{\uparrow(\downarrow)}), \quad (3)$$

$$H_{B,B}^{\uparrow(\downarrow)} = -(\alpha_B + J_B \langle n_B^{\uparrow(\downarrow)} \rangle) \equiv -(\alpha_B + f_B^{\uparrow(\downarrow)}),$$

and first-neighbor  $\langle \Psi_k | H^{\uparrow(\downarrow)} | \Psi_{j=k\pm 1} \rangle = -V$  interactions are considered. [As usual, the superscripts  $\uparrow(\downarrow)$  indicate the spin orientation.] The self-consistent nature of this simple Hamiltonian is such that the ‘‘self-energy’’ of an electron of a given spin orientation at any atom will depend on the electronic density of electrons with opposite spin orientation already present at that site. If we take 0 to represent a typical A-type of site of the perfect chain, we have (for the  $\uparrow$  electrons, for instance)

$$EG_{0,0}^{\uparrow} = 1 - VG_{0,-a_1}^{\uparrow} - VG_{0,a_1}^{\uparrow} - (\alpha_A + f_A^{\uparrow})G_{0,0}^{\uparrow} - VG_{0,-b_1}^{\uparrow} - VG_{0,b_1}^{\uparrow}, \quad (4)$$

or, using the symmetry of the chain,

$$(E + \alpha_A + f_A^{\uparrow})G_{0,0}^{\uparrow} = 1 - 4VG_{a_1,0}^{\uparrow}. \quad (5)$$

It is convenient to divide the above equation by  $2\sqrt{2}V$ , so that the set of parameters  $(\alpha_A, f_A, E)$  could be replaced by the corresponding dimensionless quantities  $(\bar{\alpha}_A, \delta_A, \varepsilon)$ . Accordingly, the dimensionless Green function  $\mathcal{G}_{i,j} = 2\sqrt{2}VG_{i,j}$  is introduced and one can write finally

$$(\varepsilon + p_A^{\uparrow})\mathcal{G}_{0,0}^{\uparrow} = 1 - \sqrt{2}\mathcal{G}_{a_1,0}^{\uparrow}, \quad (6)$$

where  $p_A^{\uparrow} \equiv \bar{\alpha}_A + \delta_A \langle n_A^{\uparrow} \rangle$  is a parameter to be self-consistently determined, after the amount of electronic charge at any individual site is correctly adjusted. Due to the first-neighbor coupling approximation, the equivalent expression for  $\mathcal{G}_{a_1,0}^{\uparrow}$  only involves  $\mathcal{G}_{0,0}^{\uparrow}$  and  $\mathcal{G}_{1,1}^{\uparrow}$ , and therefore we can eliminate any explicit reference to the  $a_1$  site (of the B-type) and write

$$(\varepsilon + \alpha_R)\mathcal{G}_{0,0}^{\uparrow} = -2V_R\mathcal{G}_{1,0}^{\uparrow}, \quad (7)$$

where only the renormalized interactions

$$\alpha_R^{\uparrow} = p_A^{\uparrow} - \frac{1}{2(\varepsilon + p_B^{\uparrow})} \quad \text{and} \quad V_R^{\uparrow} = -\frac{1}{4(\varepsilon + p_B^{\uparrow})} \quad (8)$$

are present.

This renormalization scheme allows the formal reduction of the original lozenge-shaped chain to the simpler structure of Fig. 1(b), where only knotlike (A-type) sites are retained. The general expression for the Green function of this latter chain,

$$(\varepsilon + \alpha_R^{\uparrow})\mathcal{G}_{n,0}^{\uparrow} = -V_R^{\uparrow}\mathcal{G}_{n-1,0}^{\uparrow} - V_R^{\uparrow}\mathcal{G}_{n+1,0}^{\uparrow}, \quad (9)$$

can be solved for any particular element of interest after the introduction of the transfer matrix<sup>30</sup>  $T^{\uparrow} = \mathcal{G}_{n+1,0}^{\uparrow}/\mathcal{G}_{n,0}^{\uparrow}$ . The resulting equation for  $T^{\uparrow}$  can be solved analytically, and in terms of the self-consistent parameters  $p_A$  and  $p_B$  one can write

$$T^{\uparrow} = [2(\varepsilon + p_A^{\uparrow})(\varepsilon + p_B^{\uparrow}) - 1] \pm [4(\varepsilon + p_A^{\uparrow})(\varepsilon + p_B^{\uparrow})]^{1/2} \sqrt{(\varepsilon + p_A^{\uparrow})(\varepsilon + p_B^{\uparrow}) - 1}. \quad (10)$$

Since  $\mathcal{G}_{1,0}^{\uparrow} = T^{\uparrow}\mathcal{G}_{0,0}^{\uparrow}$ , we can now solve for the diagonal element of the Green function for site 0:

$$\mathcal{G}_{0,0}^{\uparrow} = \pm \left( \frac{\varepsilon + p_A^{\uparrow}}{\varepsilon + p_B^{\uparrow}} \right)^{1/2} \frac{1}{\sqrt{(\varepsilon + p_A^{\uparrow})(\varepsilon + p_B^{\uparrow}) - 1}}. \quad (11)$$

An essential feature of the renormalization process is that there is no loss of physical content associated with it; rather, all necessary information about the angle sites can be recovered from the new expressions for the renormalized knot sites. For the original chain, one can write, for example,

$$(\varepsilon + p_A^{\uparrow})\mathcal{G}_{a_1,a_1}^{\uparrow} = 1 - \frac{1}{2\sqrt{2}}\mathcal{G}_{0,a_1}^{\uparrow} - \frac{1}{2\sqrt{2}}\mathcal{G}_{1,a_1}^{\uparrow}. \quad (12)$$

Using Eq. (6), and the fact that by symmetry  $\mathcal{G}_{0,a_1}^{\uparrow} = \mathcal{G}_{1,a_1}^{\uparrow}$  we obtain

$$\mathcal{G}_{a_1,a_1}^{\uparrow} = \frac{1 + (\varepsilon + p_A^{\uparrow})\mathcal{G}_{0,0}^{\uparrow}}{2(\varepsilon + p_B^{\uparrow})}, \quad (13)$$

or, finally,

$$\mathcal{G}_{a_1,a_1}^{\uparrow} = \frac{1}{2(\varepsilon + p_B^{\uparrow})} \pm \frac{1}{2} \left( \frac{\varepsilon + p_A^{\uparrow}}{\varepsilon + p_B^{\uparrow}} \right)^{1/2} \frac{1}{\sqrt{(\varepsilon + p_A^{\uparrow})(\varepsilon + p_B^{\uparrow}) - 1}}. \quad (14)$$

Equations (11) and (14) will provide all information required for the knowledge of the electronic structure of the  $(AB_2)_n$  unit cell. The band edges for the spin-up electrons can be analytically found as

$$\begin{aligned} \varepsilon_1^{\uparrow} &= -p_A^{\uparrow}, \\ \varepsilon_2^{\uparrow} &= -p_B^{\uparrow}, \\ \varepsilon_3^{\uparrow} &= -\frac{(p_A^{\uparrow} + p_B^{\uparrow})}{2} + \sqrt{\frac{(p_A^{\uparrow} - p_B^{\uparrow})^2}{4} + 1}, \end{aligned} \quad (15)$$

and

$$\varepsilon_4^\uparrow = -\frac{(p_A^\uparrow + p_B^\uparrow)}{2} - \sqrt{\frac{(p_A^\uparrow - p_B^\uparrow)^2}{4} + 1},$$

with similar expressions for the other spin orientation.

The poles of  $\mathcal{G}_{0,0}^{\uparrow(\downarrow)}$  correspond to the band edge singularities and have vanishing residue. Therefore all states associated to knot sites are of a delocalized nature and can be described by the local density of states (LDS)

$$\rho_{A,A}^{\uparrow(\downarrow)}(\varepsilon) = -\frac{1}{\pi} \text{Im}[\mathcal{G}_{0,0}^{\uparrow(\downarrow)}(\varepsilon)]. \quad (16)$$

A different situation occurs for the  $B$ -type sites, since a pole for  $\mathcal{G}_{a_1,a_1}^\uparrow$  with a residue equal to  $1/2$  is found to exist at  $\varepsilon_2^\uparrow$ . After introducing the corresponding LDS

$$\rho_{B,B}^{\uparrow(\downarrow)}(\varepsilon) = -\frac{1}{\pi} \text{Im}[\mathcal{G}_{a_1,a_1}^{\uparrow(\downarrow)}(\varepsilon)], \quad (17)$$

the total electronic charge per unit cell and spin orientation  $q_{\text{uc}}^{\uparrow(\downarrow)} = q_A^{\uparrow(\downarrow)} + 2q_B^{\uparrow(\downarrow)}$  can be written as

$$q_{\text{uc}}^{\uparrow(\downarrow)} = \int_{-\infty}^{E_F^{\uparrow(\downarrow)}} \rho_{A,A}^{\uparrow(\downarrow)}(\varepsilon) d\varepsilon + 2 \left[ \int_{-\infty}^{E_F^{\uparrow(\downarrow)}} \rho_{B,B}^{\uparrow(\downarrow)}(\varepsilon) d\varepsilon + \frac{1}{2} \Theta(E_F^{\uparrow(\downarrow)} + p_B^{\uparrow(\downarrow)}) \right], \quad (18)$$

where  $\Theta(\varepsilon)$  is the Heaviside step function. The pattern of electronic distribution along the chain can then be derived from the total electronic charge and the net magnetization per unit cell obtained, respectively, as

$$q_{\text{uc}} = q_{\text{uc}}^\uparrow + q_{\text{uc}}^\downarrow \quad (19)$$

and

$$\mu_{\text{uc}} = q_{\text{uc}}^\uparrow - q_{\text{uc}}^\downarrow. \quad (20)$$

It is important to note that since the Hamiltonian used has no spin flipping terms, the total number of electrons of each given spin orientation must be independently preserved. This is consistent with the so-called ‘‘fixed spin moment’’ scheme,<sup>31–33</sup> so that the system naturally obeys Lieb’s theorem. Once the parameters are defined, the self-consistent procedure defined by Eq. (3) can be initialized by taking a guess at the up and down electronic charges for the  $A$  and  $B$  sites, and will proceed until the desired convergence is attained.

## B. Results and discussions

Let us consider initially the particular case of a homatomic chain with a half-filled band since this corresponds to the most important physical situation,<sup>22,28,34</sup> and examine the conditions for the existence of a gap just above the Fermi level. If  $J=J_A=J_B=0$  and  $\alpha_A=\alpha_B=0$  are taken in the general expressions above, one can observe that for all different values of  $V$  just a single band exists for the unit cell density of states (uc DOS) and hence the corresponding polymer would behave as a conductor. As previously found in the literature,<sup>28</sup> a localized state that contains  $1/3$  of the total

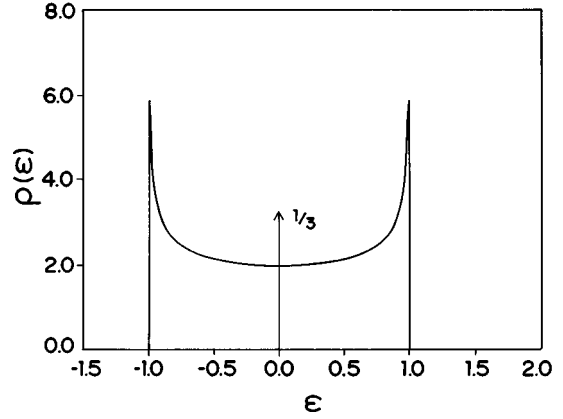


FIG. 2. The uc DOS for the case  $J=J_A=J_B=0$ ;  $1/3$  of the electronic states are associated to a dispersionless state at the middle of the band.

electronic states will be present at the middle of the band (Fig. 2); note that this dispersionless state, which occurs at any  $B$  site, has its origin associated to the lozenge topology of the chain.

For the case of a nonvanishing intrasite interaction, e.g.,  $J/V = -1.0$  and for the initial charges  $q_{\text{uc}}^\uparrow = 2e$  and  $q_{\text{uc}}^\downarrow = 1e$ , a different situation arises: for each spin orientation, a gap of width  $|p_A^{\uparrow(\downarrow)} - p_B^{\uparrow(\downarrow)}|$  now separates the valence and conduction bands (Fig. 3). We note that while for the DOS of site  $A$  there is no Van-Hove-type singularity at the top edge of the valence band, the position in energy of the localized state of the  $B$ -type sites will be distinct for different spin orientations: for example, this state will appear at the top of the valence band for the  $\uparrow$  electrons but at the bottom of the conduction band for the  $\downarrow$  electrons. Since the corresponding residue is  $1/2$  and there are two  $B$  atoms per unit cell,  $1/3$  of the total electronic states will continue to be associated to the corresponding energy position.

To determine the effect of the relative strength of the intrasite repulsion integral on the properties of the system, we have examined the evolution of both the gap width,  $\mathcal{E}_g$ , and of the unit cell magnetization with the variation of the parameter  $J$ . As shown in Fig. 4,  $\mathcal{E}_g$  grows monotonically

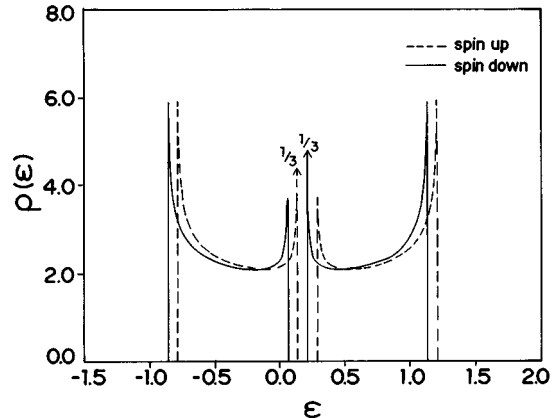


FIG. 3. DOS for the case  $J/V = -1.0$  and  $q_{\text{uc}}^\uparrow = 2e$ ,  $q_{\text{uc}}^\downarrow = 1e$ . The dispersionless state appears at different positions according to the spin orientation.

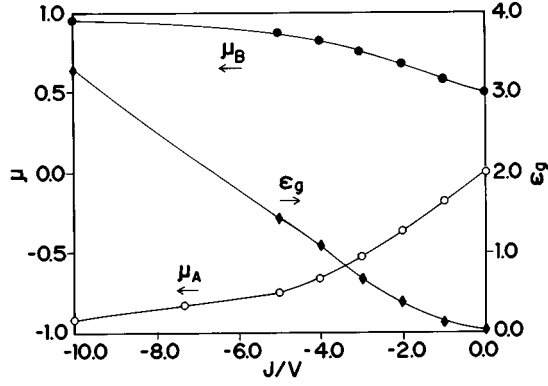


FIG. 4. Behavior of  $\epsilon_g$  ( $\blacklozenge$ ),  $\mu_A$  ( $\circ$ ), and  $\mu_B$  ( $\bullet$ ) and as a function of the ratio  $J/V$ .

with the increase of  $|J/V|$ , while  $\mu_{uc} \rightarrow 1e$  in the limit  $|J/V| \gg 1$ . Consistent with this behavior, we note that the pattern of electronic charge transfer along the chain is such that as  $|J/V|$  increases there is a net charge transfer of spin up (down) electrons to the angle- (knot) type sites. As could be expected, in the high intrasite repulsion limit the  $(AB_2)_n$  chain will behave as an antiferromagnet.

We can conclude that the ground state of the perfect homoatomic chain of lozenge topology corresponds to a spin density wave<sup>35–38</sup> of  $J$ -dependent magnitude (Fig. 5), with  $S_{uc} = 1/2$  in agreement with Lieb’s theorem.<sup>20</sup> Also, we can note that the asymmetry between the spin-up and spin-down DOS shown in Fig. 3 closely resembles the “covalent magnetism” model introduced by Williams *et al.*<sup>39</sup> to describe the itinerant magnetism in transition-metal systems.

### III. A-TYPE SUBSTITUTIONAL IMPURITY

#### A. General expressions

The role that impurities play on the electronic and optical properties of polymers is well known.<sup>40</sup> We will consider here how the electronic distribution of the  $(AB_2)_n$  chain will be affected by the presence of a substitutional impurity  $X$  in a knot ( $A$ -type) site [Fig. 6(a)]. The presence of the impurity represents a break in the translational symmetry of the system. As a consequence, the electronic distribution of the chain will be most affected in the immediate vicinity of the  $X$  site: as successive  $AB_2$  cells further away from the impurity are considered, the corresponding uc DOS should reveal a gradual “healing” to the regular chain pattern. Gen-

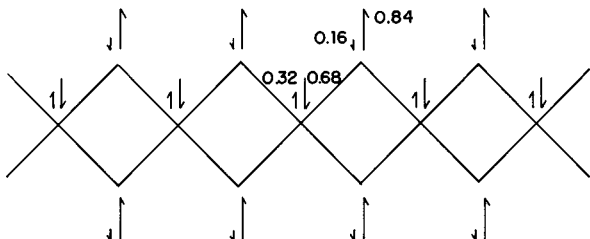


FIG. 5. Spin density wave associated to the regular  $(AB_2)_n$  chain, for the case  $J/V = -2.0$  and  $q_{uc}^\uparrow = 2e$ ,  $q_{uc}^\downarrow = 1e$ . Note that  $\mu_A = -0.36e$  and  $\mu_B = 0.68e$ , leading to  $\mu_T = 1.0e$  and  $S_{uc} = 1/2$ .

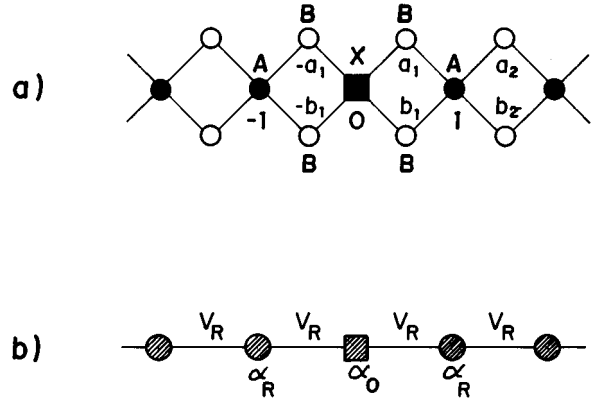


FIG. 6. (a)  $(AB_2)_n$  chain with an  $X$  substitutional impurity in an  $A$ -type site and (b) its renormalized equivalent.

eral expressions for the calculation of the Green’s-function elements for the different sites at varying distances from the impurity are then needed.

If the impurity is characterized by a different intrasite parameter  $J_X$ , the corresponding diagonal Hamiltonian element will be given by

$$H_{X,X}^{\uparrow(1)} = -(\alpha_X + J_X \langle n_X^{\uparrow(1)} \rangle) \equiv -(\alpha_X + f_X^{\uparrow(1)}). \quad (21)$$

We label the impurity site as 0 and use the remaining reflection symmetry of the chain to write

$$(\epsilon + p_X^\dagger) \mathcal{G}_{0,0}^\dagger = 1 - \sqrt{2} \mathcal{G}_{a_1,0}^\dagger \quad (22)$$

for the spin up electrons, where

$$p_X^\dagger = \frac{\alpha_X + f_X^\dagger}{2\sqrt{2}V}. \quad (23)$$

If one follows the same renormalization procedure as before, the following set of coupled equations,

$$\begin{aligned} (\epsilon + \alpha_0^\dagger) \mathcal{G}_{0,0}^\dagger &= 1 - 2V_R^\dagger \mathcal{G}_{1,0}^\dagger, \\ (\epsilon + \alpha_R^\dagger) \mathcal{G}_{1,0}^\dagger &= -V_R^\dagger \mathcal{G}_{0,0}^\dagger - V_R^\dagger \mathcal{G}_{2,0}^\dagger, \\ (\epsilon + \alpha_R^\dagger) \mathcal{G}_{2,0}^\dagger &= -V_R^\dagger \mathcal{G}_{1,0}^\dagger - V_R^\dagger \mathcal{G}_{3,0}^\dagger, \end{aligned} \quad (24)$$

etc., where

$$\alpha_0^\dagger = p_X^\dagger - \frac{1}{2(\epsilon + p_B^\dagger)}, \quad (25)$$

will be obtained. We then see that the  $(AB_2)_n X$  chain is equivalent to the renormalized chain of Fig. 6(b), and that for the periodic part of the system the transfer matrix given by Eq. (10) can be used. In this way, the dimensionless diagonal Green’s-function element for the impurity site can be found easily as

$$\mathcal{G}_{0,0}^\dagger = \frac{\epsilon + \alpha_R^\dagger + V_R^\dagger T^\dagger}{(\epsilon + \alpha_0^\dagger)(\epsilon + \alpha_R^\dagger + V_R^\dagger T^\dagger) - 2(V_R^\dagger)^2 T^\dagger}, \quad (26)$$

and successive use of the transfer matrix will allow the consecutive diagonal matrix elements to be obtained as

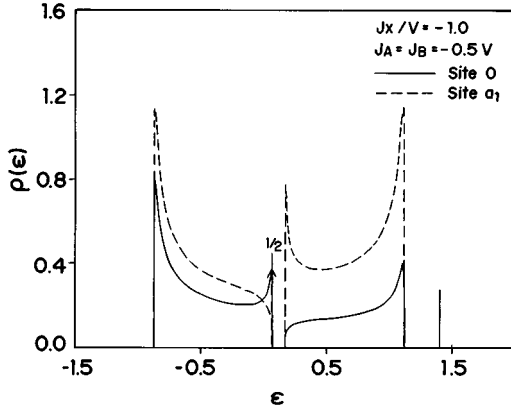


FIG. 7. LDS for the 0 and  $a_1$  sites in the case  $J_A = J_B = -0.5V$ ,  $J_X = -1.0V$ , and  $q_{uc}^\dagger = 2e$ ,  $q_{uc}^\ddagger = 1e$ . The localized state above the conduction band has a residue of 0.16 (0.05) at the 0 ( $a_1$ ) site.

$$\mathcal{G}_{n,n}^\dagger = \frac{1 - V_R^\dagger T^\dagger \mathcal{G}_{n-1,n-1}^\dagger}{\varepsilon + \alpha_R^\dagger + V_R^\dagger T^\dagger}. \quad (27)$$

The calculation of the electronic structure associated to any given site along the renormalized chain can be implemented from the general expression derived above. However, use of Eq. (27) is still not completely convenient since for any site considered the knowledge of the immediate neighbor diagonal matrix element is required. A more general expression can be obtained after repeated use of the identity

$$\varepsilon + \alpha_R^\dagger + V_R^\dagger T^\dagger = -\frac{V_R^\dagger}{T^\dagger}, \quad (28)$$

so that the intermediate expression

$$\mathcal{G}_{n,n}^\dagger = -\frac{1}{V_R^\dagger} \sum_{Rk=0}^{n-1} (T^\dagger)^{2k+1} + (T^\dagger)^{2n} \mathcal{G}_{0,0}^\dagger \quad (29)$$

can be simplified to

$$\mathcal{G}_{n,n}^\dagger = -\frac{1}{V_R^\dagger} \frac{T^\dagger [1 - (T^\dagger)^{2n}]}{1 - (T^\dagger)^2} + (T^\dagger)^{2n} \mathcal{G}_{0,0}^\dagger, \quad (30)$$

where  $n = 1, 2, 3, \dots$ . This permits then the direct calculation of the LDS associated to any knot site.

For any  $AB_2$  cell considered, the diagonal Green's-function elements for the angle sites can be directly found in terms of the diagonal elements for the nearest-neighbor knot sites. To do this one just has to relate the desired  $a_n$  site to the neighboring atoms of A type at the  $n-1$  and  $n$  sites, and use the reflection symmetry of the chain, so that

$$\mathcal{G}_{a_n, a_n}^\dagger = \frac{1}{\varepsilon + p_B^\dagger} \left\{ 1 - \frac{1}{4} [1 - (\varepsilon + p_A^\dagger) \mathcal{G}_{n-1, n-1}^\dagger] \right\} + \frac{1}{8(\varepsilon + p_B^\dagger)^2} (\mathcal{G}_{n,n}^\dagger + \mathcal{G}_{n-1, n-1}^\dagger). \quad (31)$$

To obtain the complete solution of the problem, one still needs to find the position of the localized states and the corresponding residues. The best way to accomplish that is to substitute the values of the parameters  $\alpha_R$ ,  $V_R$ , and  $\alpha_0$  into Eqs. (26) and (31). For the spin-up electrons, for instance, one gets

$$\mathcal{G}_{0,0}^\dagger = \frac{2(\varepsilon + p_B^\dagger)}{2(\varepsilon + \alpha_0^\dagger)(\varepsilon + p_B^\dagger) - \Delta(p_A^\dagger, p_B^\dagger)}, \quad (32)$$

where

$$\Delta(p_A^\dagger, p_B^\dagger) = 2(\varepsilon + p_A^\dagger)^{1/2} (\varepsilon + p_B^\dagger)^{1/2} \pm \sqrt{4(\varepsilon + p_A^\dagger)^2 (\varepsilon + p_B^\dagger)^2 - 1}.$$

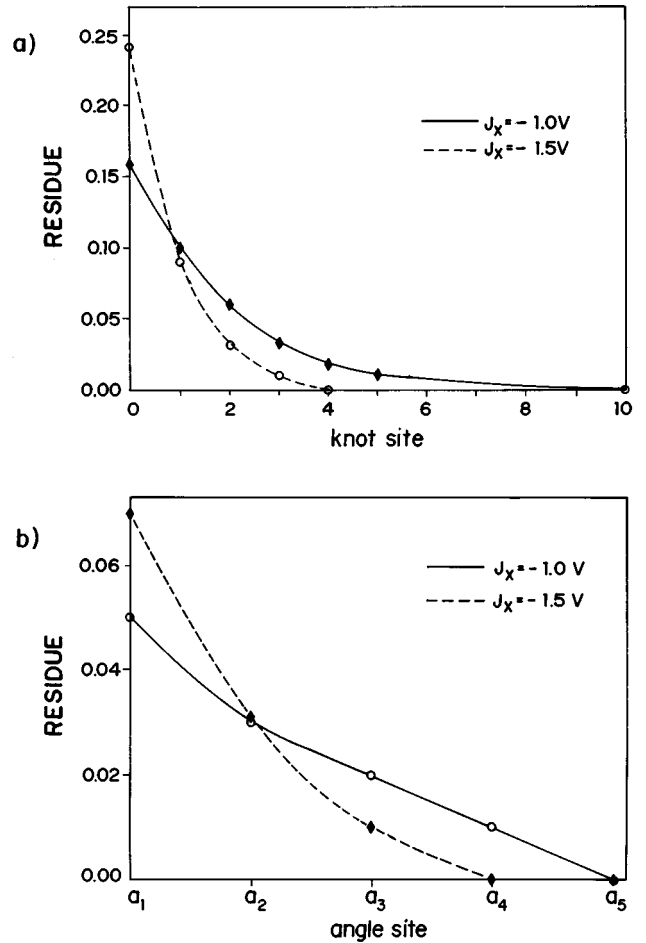


FIG. 8. Evolution of the residues of the localized state as a function to the distance from the impurity for the case  $J_A = J_B = -0.5V$  ( $q_{uc}^\dagger = 2e$ ,  $q_{uc}^\ddagger = 1e$ ) for different values of  $J_X$  along the knot (a) and angle (b) sites.

No analytical solution was found for the position of the poles of this expression, so that the corresponding residues were determined numerically.

### B. Results

Let us consider the initial set of parameters ( $\alpha_X = \alpha_A = \alpha_B = 0$ ;  $J_A/V = J_B/V = -0.5$ ;  $J_X/V = -1.0$ ). In Fig. 7 we depict the corresponding density of states for the sites 0 and  $a_1$ . One can note that a new localized state arises above the conduction band. The physical origin of this state is associated with the presence of the substitutional impurity and as a consequence its residue should decrease as we consider unit cells farther away from the  $X$  atom. For the values of parameters considered, this residue is essentially equal to zero for the seventh unit cell away from the impurity, although the corresponding LDS presents the oscillatory pattern characteristic of perturbed systems.<sup>41</sup> If the strength of the  $J_X$  parameter is increased, the damping of this localized state with the distance from the impurity is more noticeable (Fig. 8). In a similar way, the perturbation in the electronic distribution is mostly confined to the immediate vicinity of the impurity site.

For a real system of this kind, the local disruption of the electronic and magnetization wave pattern could be probed eventually by a magnetic hyperfine investigation. It must be noted that the above results were obtained for the case in which  $|J_X/J_A| > 1$ . If the impurity has an intrasite electronic repulsion term smaller than that of the original  $A$  atom it has substituted, the new localized state could be expected to appear below the valence band and, therefore, for a half-filled system it would be occupied.

### IV. CONCLUSION

In this paper we have examined the electronic structure of the lozenge-shaped  $(AB_2)_n$  polymeric chain, which was taken as a model of a nonclassical nonalternant system, and we have shown that the characteristic nondispersive state can lead to interesting magnetic properties in the half-filled band case. The use of the renormalization of interaction technique has allowed a simple and analytical treatment of the electronic structure of the problem, so that the description of the effects of the presence of an  $A$ -type substitutional impurity becomes possible.

Since a characteristic spin-density-wave pattern results from the introduction of a single impurity, the possibility of long-range ("through-bond") interaction<sup>42</sup> between disperse impurities along the chain can be imagined, with important consequences for the total magnetic properties of an appropriately doped polymer.

In spite of the simplicity of the polymeric chain considered, the present results indicate that other nonalternant nonclassical polymers of more complicated unit cells could be treated equally by the renormalization of interactions technique, which has already been applied to polymers of more complex structure.<sup>43</sup>

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