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Magnetic properties of alternate nonclassical polymers: The elementary excitation spectrum

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The magnetic properties of a new class of extended organic compounds, alternate nonclassical polymers, are studied. The most conspicuous feature of their band-structure pattern is the occurrence of a narrow (nonbonding) band, originating from the topological structure of the hydrocarbon networks considered. To analyze the stability of the ferromagnetically aligned state, wherein the nonbonding band is occupied only by spin-down electrons, the spectrum of the elementary magnetic excitations and the expressions for the corresponding wave functions are calculated analytically, utilizing a generalized Hubbard-type Hamiltonian. The lowest (magnon) excited state is found to be separated from the quasicontinuum of the magnetic excitation spectrum by a gap of the order of the on-site Coulomb repulsion. Stability of the ferromagnetic state with respect to magnon excitation is shown to depend on the competition between the transfer energy and the Coulomb exchange interaction which enter the model as parameters.

I. INTRODUCTION

Magnetic properties of alternate hydrocarbons with conjugated bonds have been an active area of research during the past few years. By definition, an alternate system is characterized by a partitioning of its atoms into two disjoint subsets of N^* starred and N^0 unstarred atoms, such that every starred atom is linked to unstarred ones and vice versa. A particularly interesting class of hydrocarbons is comprised by conjugated networks with $|N^*-N^0|>0$, as depicted in Fig. 1. Since no Kekule formula[1] can be attributed to such organic π-electron systems, the latter have been termed alternate nonclassical (ANC) hydrocarbons.

Several theoretical investigations on the ground-state spin multiplicity of finite hydrocarbon systems (oligomers) have been carried out. In a study, based on the exact solution of the Pariser-Paar-Pople (PPP) Hamiltonian, Koutecky *et al.*[2] furnished theoretical support for the existence of hydrocarbon molecules with a high-spin ground-state configuration. In a related work, utilizing configuration interaction calculations for small alternate oligomers, such as biallyl, triallyl, etc., Klein *et al.*[3] showed within the Hubbard and the PPP models that the ground-state spin amounts to

$$S=|N^*-N^0|/2\ , \tag{1.1}$$

a conjecture made earlier by Ovchinnikov.[4]

In 1983 Teki *et al.*[5] detected, by electron spin resonance (ESR) spectroscopy, an aromatic hydrocarbon *m*-phenylenebis [(diphenylmethylen-3-yl) methylene], with a nonet spin multiplicity ($S=4$) in the electronic ground state—the highest spin multiplicity observed in alternate hydrocarbons so far. (See Fig. 2.)

Very recently, attention has been drawn to the possible existence of high-spin ground-state configurations in extended hydrocarbon networks, a question which still remains an important challenge, both for theorists and synthetists. Klein *et al.*[3] applied a cluster expansion method for constructing a degenerate-perturbation-theory effective Hamiltonian for polyallyl compounds. Using exact results for the monomer and dimer units they found a ground-state solution of spin $n/2$, with n the number of monomer units, in agreement with the predictions of valence-bond theory.[4] Utilizing an analogous approach, as in Ref. 3, Durand *et al.*[6] constructed effective spin Hamiltonians for large systems starting from Hamiltonians for small pattern molecules. In a series of studies, Tyutyulkov *et al.*[7–9] investigated the band structure of a number of quasi-one-dimensional (1D) ANC polymers by taking into account electron

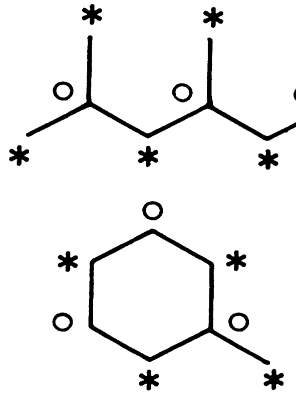

FIG. 1. Examples of hydrocarbon networks with a different number of starred (N^*) and unstarred (N^0) atoms: (a) triallyl, (b) benzylradical.

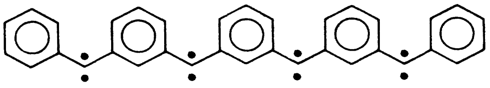

FIG. 2. *m*-phenylenebis [(diphenylmethylen-3-yl)methylene] exhibting a nonet spin multiplicity ($S=4$) in the electronic ground state.

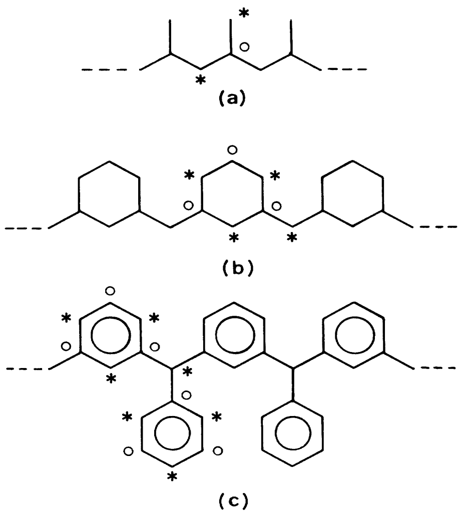

FIG. 3. Alternate nonclassical (ANC) polymers with $(N^* - N^0)/N = 1$, where N is the number of units.

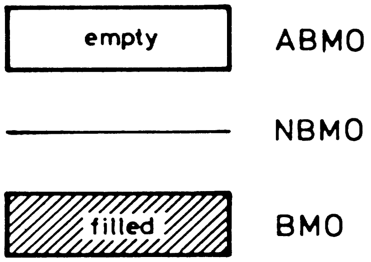

FIG. 4. Band-structure pattern of the ANC polymers.

correlation within the alternate molecular orbitals (AMO) version of the extended Hartree-Fock method. In Fig. 3, three of the investigated polymers are shown.[8] Some additional extended 1D and 2D and ANC π-electron systems are suggested in Refs. 4 and 8. Since, in the examples shown, the number of electrons per unit cell is odd, one of the π electrons remains unpaired. All studied polymers[8] exhibit the same characteristic band-structure scheme comprising filled bonding molecular-orbital (MO) bands (BMO's) empty antibonding MO bands (ABMO's), and an infinitely narrow half-filled nonbonding MO band (NBMO). A pictorial representation of the band pattern of ANC polymers is displayed in Fig. 4. It has been pointed out that the occurrence of the NBMO band is a consequence of the topological structure of the ANC polymers (as reflected by the Coulson-Rushbrooke theorem)[10] and it has become clear[8,9] that the strong mutual correlation of the electrons in the degenerate band may give rise to the creation of magnetic order.

It should be noted that the infinite degeneracy of the NBMO band is an idealization based on the one-electron picture, the assumption of equivalence of the Coulomb, and resonance integrals pertaining to different sites. In a genuine polymer the influence of the σ-electron core and the fully occupied BMO bands will inevitably bring about a broadening of the NBMO band. Different substituents might have a similar effect towards removing the degeneracy and hence enhancing the itineracy of the unpaired electrons. However, the calculations[8] carried out for polymer Fig. 3, (b), show that the band width remains small, being of the order of magnitude 0.2 eV. This implies an effective resonance transfer integral, β_{NBMO}, which is comparable in size to the exchange interactions in the NBMO band.[11] Hence, the competition between the nearest-neighbor Coulomb exchange term J_{NBMO} and the hopping term β_{NBMO} will be of crucial importance for the type of magnetic correlation in the ANC polymers under consideration.

In a recent work, Nasu[12] was concerned with the magnetic properties of *m*-polydiphenylcarbene (see Fig. 2) which differs from polymer (b) in Fig. 3 insofar as the carbon atoms bridging the benzene rings have a localized nonbonding electron in addition to the (unpaired) π electron. Nasu finds the same band-structure scheme as presented in Ref. 8 and reaffirms the importance of the topological structure of the polymer for the occurrence of magnetic correlation between the unpaired π electrons. On taking into account the additional Hund correlation between the π electron and the σ electron at the bridging atoms, the author shows, within mean-field theory, that the ferromagnetic ground state is stabilized.

In the present paper we take a different approach to study the stability of the saturated ferromagnetic state. To form as complete a picture as possible of the itinerant spin correlations within the narrow π-electron band of ANC polymers, we omit in the following additional stabilization effects on the magnetic alignment due to cooperation between the π-electron network and the localized (nonbonding) σ electron. Thus proceeding from a fully aligned NBMO band we calculate the spectrum of the elementary excitations and study its dependence on the physical parameters entering the model.

II. THE EIGENVALUE PROBLEM

In the Wannier representation the effective NBMO band Hamiltonian reads

$$H = \sum_{\sigma} \sum_{m,n} \beta_{mn} a^{\dagger}_{m\sigma} a_{n\sigma} + \tfrac{1}{2} \sum_{\sigma,\sigma'} \sum_{m,n} U(n-m) a^{\dagger}_{m\sigma} a^{\dagger}_{n\sigma'} a_{n\sigma'} a_{m\sigma} + \tfrac{1}{2} \sum_{\sigma,\sigma'} \sum_{m \neq n} J(n-m) a^{\dagger}_{m\sigma} a^{\dagger}_{n\sigma'} a_{m\sigma'} a_{n\sigma} , \tag{2.1}$$

where $a^{\dagger}_{n\sigma}$ ($a_{n\sigma}$) is the creation (annihilation) operator for an electron at lattice site R_n and β_{mn} are the corresponding Coulomb ($m = n$) and resonance ($m \neq n$) one-electron integrals. The hopping matrix element β_{mn}, $m \neq n$, reflects the electron transfer between the mth and nth unit sites, and $U(n)$ and $J(n)$ are the two center Coulomb and exchange integrals, respectively. In the following we adopt the tight-binding (Hückel) approximation for the one-electron part of (2.1),

$$\beta_{mn}=\begin{cases}\alpha=0, \text{ for } m=n\ ,\\ \beta, \text{ for } m,n \text{ nearest neighbors},\\ 0, \text{ elsehwere}\ .\end{cases} \tag{2.2}$$

Before passing to the Bloch representation by means of the Fourier transform

$$a_{n\sigma}^{\dagger}=N^{-1/2}\sum_{k}\exp(-ikR_n)a_{k\sigma}^{\dagger}\ , \tag{2.3}$$

it is expedient to introduce the electron-hole operators $\rho_k^{\dagger}(q)$ by

$$\rho_k^{\dagger}(q)=a_{k\uparrow}^{\dagger}a_{k+q\downarrow}\ . \tag{2.4}$$

In view of the fact that the number density operators $N_\sigma=\sum_n a_{n\sigma}^{\dagger}a_{n\sigma}$, $\sigma=\uparrow,\downarrow$, are constants of motion, we introduce at this stage the subspace X_M of the complete Hilbert space as follows. X_M is the space spanned by the simultaneous eigenvectors of H and $N_\uparrow$ for a fixed eigenvalue M of $N_\uparrow$. Thus for any $|\Psi_M\rangle\in X_M$ it holds that

$$S_z\,|\Psi_M\rangle=\hbar(M-N/2)\,|\Psi_M\rangle\ .$$

In the subspace X_M the Hamiltonian (2.1) is easily rewritten in terms of the electron-hole operators (2.4),

$$H_M=V_0+\sum_{k,k'}\sum_{q}[M^{-1}\omega_k(q)\delta_{kk'}-\Omega_{k-k'}(q)]\rho_k^{\dagger}(q)\rho_{k'}(q)+\tfrac{1}{2}\sum_{q}\tilde{U}(q)\sum_{i=1}^{2}\Gamma_i^{\dagger}(q)\Gamma_i(q)\ , \tag{2.5}$$

where

$$\omega_k(q)=U+\sum_{n(\neq 0)}J(n)+\varepsilon_k(q)\ , \tag{2.6}$$

with $U=U(0)$ the on-site Coulomb repulsion. The electron-hole energies $\varepsilon_k(q)$ read

$$\varepsilon_k(q)=\varepsilon_k-\varepsilon_{k+q}\ , \tag{2.7}$$

where the Bloch energies ε_k are given by

$$\varepsilon_k=\beta\sum_{\langle n,0\rangle}\cos(kR_n)\ , \tag{2.8}$$

and $\langle n,0\rangle$ pertains to summation over the nearest neighbors of a fixed site (e.g., $R_1=0$). In the 1D case (2.8) goes into

$$\varepsilon_k=2\beta\cos(ka)\ , \tag{2.9}$$

with a the lattice spacing of the polymer. The quantity $\Omega_k(q)$ is given by

$$\Omega_k(q)=U(k)+J(q)\ , \tag{2.10}$$

where $U(k)$ and $J(q)$ are the Fourier transforms of the two-electron Coulomb and exchange integrals, respectively. The last term in Eq. (2.5) describes the interactions between different e-h pairs and

$$\Gamma_1^{\dagger}(q)=M^{-1}\sum_{k,k'}\rho_{k'}^{\dagger}(k+q)\rho_{k'}(k)\ , \tag{2.11a}$$

$$\Gamma_2^{\dagger}(q)=M^{-1}\sum_{k,k'}\rho_{k'}^{\dagger}(k+q)\rho_{k'+q}(k)\ . \tag{2.11b}$$

Finally $\tilde{U}(k)=U(k)-J(k)$ and V_0 is defined by

$$V_0=(N/2)\sum_{n\neq 0}[U(n)-J(n)]\ . \tag{2.12}$$

The state of full magnetic saturation,

$$|\Psi_0\rangle=\prod_{\substack{k\in\text{first}\\ \text{Brillouin zone}}}a_{k\downarrow}^{\dagger}\,|\text{vac}\rangle\ , \tag{2.13}$$

now plays the role of a new vacuum state, and V_0 is immediately revealed as the eigenvalue of H corresponding to (2.13). In the study of the elementary excitations from the fully aligned band, we deal with the dynamics in the subspace $X_{M=1}$, where (2.5) has the following simple form:

$$H_1=V_0+\sum_{k,k'}\sum_{q}[\omega_k(q)\delta_{kk'}-\Omega_{k-k'}(q)]\rho_k^{\dagger}(q)\rho_{k'}(q)\ . \tag{2.14}$$

By virtue of the hermiticity of the matrix

$$W_{kk'}(q)=\omega_k(q)\delta_{kk'}-\Omega_{k-k'}(q)\ , \tag{2.15}$$

H_1 is easily diagonalized by means of the $N\times N$ unitary matrix $u_{kp}(q)$, leading to the (collective) excitations

$$R_p^{\dagger}(q)=\sum_{k}u_{kp}(q)\rho_k^{\dagger}(q)\ . \tag{2.16}$$

Equation (2.16) represents coherent linear combinations of pair states with quasimomentum $\hbar q$. The pair wave functions and the spectrum of the elementary excitations are determined by the Schrödinger equation

$$[\omega_k(q)-E_p(q)]u_{kp}(q)=\sum_{k'}\Omega_{k-k'}(q)u_{k'p}(q)\ . \tag{2.17}$$

Although the eigenvalue problem (2.17) is amenable to numerical treatment, this will be deferred to a later calculation. Instead, in the present work, we strive to obtain an analytical solution which provides a means of analyzing the interplay between the significant parameters incorporated in the model. To this end we introduce some simplifications which do not impair the essence of the Hamiltonian but which facilitate the mathematical treatment of the final equation. In accordance with the Hubbard model[13] we consider only on-site e-e repulsion $[U=U(0)]$, thus maintaining the competition between the parameter U, tending towards covalent configurations, and the transfer integral β, which tends to destroy the single-site correlation. However, our model improves upon the Hubbard approximation by taking into account nearest-neighbor exchange matrix elements J, which in turn compete with the hopping parameter β in favor of magnetic alignment. A discussion on the anticipated effects of the long-range Coulomb repulsion will be given in the concluding section. Under these conditions the eigenvalue equation (2.17) takes the following form:

$$[\omega_k(q)-E]u_{kp}(q)=[U+NJ(q)]N_p(q)\ , \tag{2.18}$$

where

$$J(q)=N^{-1}\sum_{\langle n,0\rangle} J(n)\cos(qR_n)\ , \tag{2.19}$$

and the normalization factor $N_p(q)$ is introduced by

$$N_p(q)=N^{-1}\sum_k u_{kp}(q)\ . \tag{2.20}$$

III. THE ELEMENTARY EXCITATION SPECTRUM

The total number of solutions of Eq. (2.18) is equal to N^2, where N is the number of lattice sites. Since solutions corresponding to various q values are independent, for every value of q there should exist N corresponding solutions of the eigenvalue equation. We will distinguish two different types of solutions.

The first type of solutions of (2.18) satisfy the condition $N_p(q)=0$, with $u_{kp}(q)\neq 0$ if

$$E^{(1)}(q)=U+\sum_{\langle n,0\rangle} J(n)+\varepsilon_k(q)\ ; \tag{3.1}$$

see Eqs. (2.20) and (2.6). For a fixed value of q and k running over the entire first Brillouin zone, the *e-h* energy $\omega_k(q)$ takes $n_q\leq N$ different values: $\omega_p(q)$, $p=1,2,\ldots,n_q$. Consequently, there are n_q different classes of solutions corresponding to the different energy eigenvalues $E_p^{(1)}(q)=\omega_p(q)$. However, because of the condition $N_p(q)=0$, in each class there is a solution which is not independent, and hence the total number of linearly independent solutions of the first type is $N-n_q$.

The solutions of the second type are characterized by $N_p(q)\neq 0$ and the pair functions $u_{kp}(q)$ are represented as

$$u_{kp}(q)=[U+NJ(q)]N_p(q)[\omega_k(q)-E_p^{(2)}(q)]^{-1}\ , \tag{3.2}$$

and the corresponding energy eigenvalues are determined as the zeros of the characteristic function

$$F(q,E)=1+[U/N+J(q)]\sum_k[E-\omega_k(q)]^{-1}\ . \tag{3.3}$$

$F(q,E)$ has n_q poles of first order, which are exactly the excitation energies belonging to the solutions of the first type. Differentiation of Eq. (3.3) yields

$$\left[\frac{U}{N}+J(q)\right]\frac{\partial F(q,E)}{\partial E}\bigg|_{E_p^{(2)}(q)}=-N^{-2}\,|N_p(q)|^{-2}\ , \tag{3.4}$$

which shows that the slopes of $F(q,E)$ at the points $E_p^{(2)}(q)$ are negative. The qualitative behavior of $F(q,E)$ is displayed in Fig. 5. A closer look at the graphical solution in Fig. 5 shows that the n_q energy eigenvalues pertaining to the solutions of the second type split up into two subsets. There is one isolated root $E_0(q)$, lying below the quasicontinuum $\omega_p(q)$, whereas the second subset consists of n_q-1 solutions $E_p^{(2)}(q)$, $p=2,3,\ldots,n_q$, which are regularly interspersed between the n_q poles $\omega_p(q)$. The quasiparticle energy $E_0(q)$ can be obtained by direct integration, cf. Eq. (3.3),

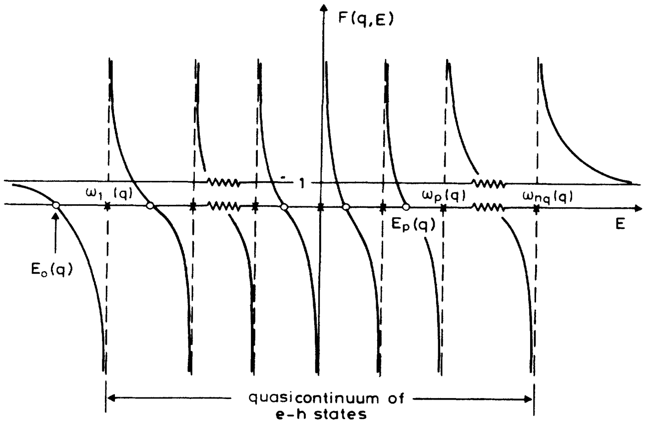

FIG. 5. Graphical representation of the solutions of Eq. (3.3). The crosses mark the positions of the poles $\omega_p(q)$ of $F(q,E)$, pertaining to the solutions of the first type. The positions of the excitation energies belonging to the solutions of the second type are marked by circles. $E_0(q)$ denotes the quasiparticle (magnon) excitation energy.

$$1=[U+NJ(q)]\frac{v}{(2\pi)^d}\times\int_{\text{Brillouin zone}} dk[\omega_k(q)-E_0(q)]^{-1}\ . \tag{3.5}$$

Here v is the volume of the Wigner-Seitz unit and d denotes the number of dimensions. To obtain the roots $E_p^{(2)}(q)$ for $p\geq 2$ more care is required in evaluating Eq. (3.3) because of the divergences occurring. Nevertheless, the problem can be exactly solved by considering the analytic continuation of $F(q,E)$ into the complex plane and applying a contour integration technique suggested by Wentzel.[14] This yields the relation

$$E_p^{(2)}(q)=\omega_p(q)+\frac{1}{2\pi i}\int_\Gamma dz\,\ln F(q,z)\ , \tag{3.6}$$

where Γ is a rectangular contour defined in the complex plane as shown in Fig. 6. On performing the limit $\varepsilon\rightarrow 0+$ we arrive at

$$E_p^{(2)}(q)=\omega_p(q)-\frac{1}{\pi}\Delta_p(q)\arctan[G(q,E_p^{(2)})/D(q,E_p^{(2)})]\ , \tag{3.7}$$

with Δ_p the spacing between two successive poles

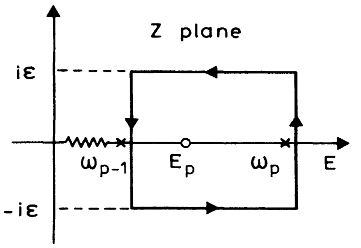

FIG. 6. Integration contour Γ in the complex plane. Δ_p denotes the spacing between two successive poles ω_{p-1} and ω_p.

$\omega_{p-1}(q)$ and $\omega_p(q)$. Furthermore,

$$D(q,E)=1+[U+NJ(q)]\frac{v}{(2\pi)^d}\times P\int_{\text{Brillouin zone}} dk[E-\omega_k(q)]^{-1}\ , \tag{3.8}$$

and

$$G(q,E)=[U+NJ(q)]\frac{\pi v}{(2\pi)^d}\times \int_{\text{Brillouin zone}} dk\,\delta[E-\omega_k(q)]\ . \tag{3.9}$$

In (3.7) the variable E has been replaced by the root $E_p^{(2)}\in\Delta_p$ and because of $\Delta_p\sim 1/N$ relation (3.7) becomes exact in the limit $N\gg 1$.

All results obtained so far hold for an arbitrary number of dimensions d. However, we confine the following to the treatment of quasi-1D ANC systems and thus specify the calculations to the case $d=1$. Since, in one dimension it holds that

$$\omega_k(q)=U+2J+2\beta[\cos(ka)-\cos(ka+qa)]\ , \tag{3.10}$$

one infers immediately, that for a fixed quasimomentum $\hbar q$, the $N/2$ mutually different e-h energies (3.10) are exhausted for k running within the reduced zone $[(-\pi/a-q)/2,(\pi/a-q)/2]$. By (3.10) it is easy to see that the spacing $\Delta_p(q)$ amounts to

$$\Delta_p(q)=-(8\pi\beta/N)\,|\sin(qa/2)\cos(pa+qa/2)|\ . \tag{3.11}$$

Taking into account that for $d=1$ Eq. (3.9) takes the form

$$G(q,E)=[U+2J\cos(qa)]\times\{[4\beta\sin(qa/2)]^2-(E-U-2J)^2\}^{-1/2}\ , \tag{3.12}$$

while $D(q,E)=1$, insertion of (3.10) and (3.11) into (3.7) yields

$$E_p^{(2)}(q)=U+2J+4\beta\sin(qa/2)\sin(pa+qa/2)+(8\beta/N)\,|\sin(qa/2)\cos(pa+qa/2)|\times\arctan((U+2J\cos qa)\{[4\beta\sin(qa/2)]^2-[E_p^{(2)}(q)-U-2J]^2\}^{-1/2})\ . \tag{3.13}$$

Thus up to terms of the order $1/N$ the excitation energies, belonging to the second type of solutions, can be expressed in the concise form

$$E_p^{(2)}(q)=U+2J+2\beta[\cos(Q_pa)-\cos(Q_pa+qa)]\ , \tag{3.14}$$

where the pseudo-wave-vectors Q_p have been introduced by

$$Q_p=p-(2/Na)\arctan\frac{U+2J\cos(qa)}{4\beta\sin(qa/2)\cos(pa+qa/2)}\ . \tag{3.15}$$

Equation (3.14) shows, by reference to Eqs. (3.1) and (3.10), that in the strong correlation limit the eigenvalues $E_p^{(2)}(q)$ differ from their counterpart $E_p^{(1)}(q)$ merely by a shift of the arguments in the dispersion relation.

Integration of Eq. (3.5) leads to the following dispersion relation for the bound-state energy:

$$E_0(q)=U+2J-\{[U+2J\cos(qa)]^2+[4\beta\sin(qa/2)]^2\}^{1/2}\ . \tag{3.16}$$

Comparison of Eqs. (3.1), (3.14), and (3.16) reveals that in the case of a narrow NBMO band, $|U/\beta|\gg 1$, the collective mode $R_0^\dagger(q)\,|\Psi_0\rangle$ [see Eqs. (2.13) and (2.16)] is separated from the bottom of the quasicontinuum by a gap of the order of U. This is accounted for by the ionic (mixed valence) structure of the quasicontinuum states, which are to be contrasted with the bound-state solution, representing coherent superposition of covalent (Ising) states. In the concluding section we show that the quasiparticle state, pertaining to $E_0(q)$, involves in fact only configurations with singly occupied lattice sites.

Equations (3.14) and (3.15) represent a generalization of the expressions obtained by one of us[15] in the study of nonalternate systems (where the set of solutions of the first type is empty) within the Hubbard approximation.

The knowledge of the excitation energies allows us to calculate the pair wave functions (3.2). For this purpose expression (3.4) for the normalization factors $N_p(q)$ is transformed to the following equivalent form:

$$N\,|N_p(q)|^2=\frac{1}{U+2J\cos(qa)}\times\left|U+2J+\beta\frac{\partial}{\partial\beta}E_p(q)-E_p(q)\right|\ . \tag{3.17}$$

Since throughout the rest of the paper we will be concerned with the collective mode $R_0^\dagger(q)\,|\Psi_0\rangle$, we confine ourselves to the explicit form of (3.17) for $p=0$,

$$|N_0(q)|^2=N^{-1}[U+2J\cos(qa)]\{[U+2J\cos(qa)]^2+[4\beta\sin(qa/2)]^2\}^{-1/2}, \tag{3.18}$$

which completes the determination of the pair functions $u_{k0}(q)$ [see Eq. (3.2)].

IV. DISCUSSION

The excitation energy (3.16), pertaining to the collective bound state, has been plotted in Fig. 7 for different values of the hopping parameter β and exchange interaction J, and for a fixed value of the on-site Coulomb repulsion U. The dashed line (0), which lies lower than the energy of the ferromagnetic configuration, refers to the (Hubbard) limiting case $J=0$. Thus, as pointed out by Herring[16] in the short-range (Hubbard) model the uniform ferromagnetic state is unstable relative to spin-density wave formation. Curves (1)–(3) indicate stabilization of the ferromagnetically aligned NBMO band. From Eq. (3.16) it is easily inferred that the excitation energy $E_0(q)$ lies below the state of magnetic saturation if the range of the parameters is such that the "kinetic" exchange $2\beta^2/U$ predominates over the so-called[17] "Coulomb" exchange term J: $2\beta^2/U > J$ [see curves (4) and (5)].

In the strong correlation limit $|\beta/U| \ll 1$ Eq. (3.16) goes into

$$E_0(q)=4J^{\text{eff}}(q)\sin^2(qa/2) , \tag{4.1}$$

where the effective exchange interaction $J^{\text{eff}}(q)$ has been introduced by

$$J^{\text{eff}}(q)=J-\frac{2\beta^2/U}{1+(2J/U)\cos(qa)} . \tag{4.2}$$

It is clear, by reference to Eqs. (3.16) and (4.2), that the effect of the elementary spin excitations on the ferromagnetic alignment of the nonbonding π electrons in a given ANC polymer will be determined by the specific values of its hopping and exchange interaction matrix elements. Previous calculations[11] have shown that ANC polymers are characterized by a nearest-neighbor exchange interaction J varying from 0.1 to 0.2 eV, while the next-nearest-neighbor exchange term is one or two orders of magnitude smaller than J. Thus for negligible ratios $2J/U$ the effective exchange (4.2) simplifies to $J^{\text{eff}}=J-2\beta^2/U$, a result well known in the valence-bond theory of magnetism.[17,18] Then for small values of q Eq. (4.1) yields a q^2 dependence of the bound-state energy, which is in accordance with Herring's theorem.[19] This result is not surprising because the q^2 dependence is characteristic of magnon-type excitations, and in the strong correlation limit Eq. (2.16) represents in fact a spin wave with translational momentum $\hbar q$. To show this, we write the expression for the pair functions $u_{k0}(q)$ up to terms of the order β/U:

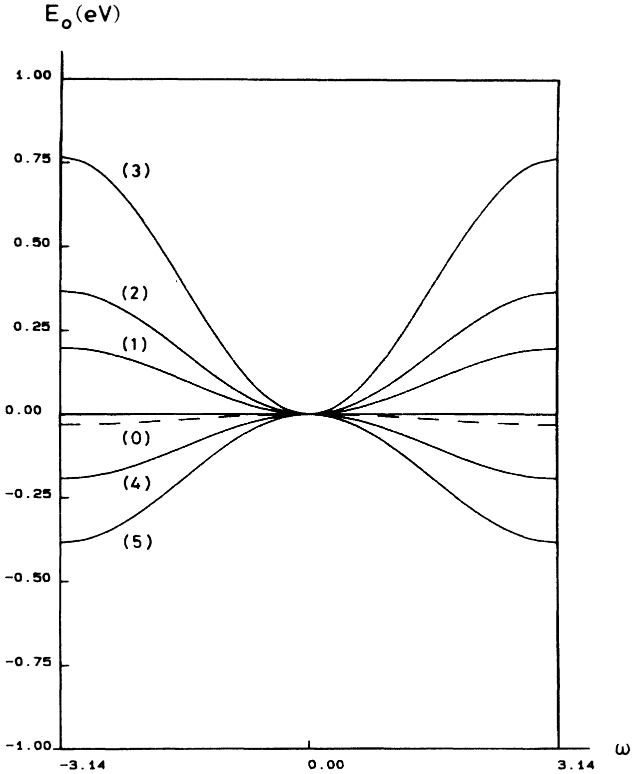

FIG. 7. The energy dispersion relation $E_0(\omega)$, with $\omega=qa$, for the lowest (magnon) excited state for $U=10$ eV and different values of $t=-\beta$ and J (all entries in eV): (0) $t=0.2$, $J=0.0$ (Hubbard case); (1) $t=0.5$, $J=0.1$; (2) $t=0.2$, $J=0.1$; (3) $t=0.2$, $J=0.2$; (4) $t=0.5$, $J=0.001$; (5) $t=1.0$, $J=0.1$.

$$u_{k0}(q)=N^{-1/2}\left[1+\frac{4\beta\sin(qa/2)}{U+2J\cos(qa)}\sin(ka+qa/2)\right] , \tag{4.3}$$

and upon insertion into Eq. (2.16) this yields

$$\begin{aligned}|\varphi_0(q)\rangle &= R_0^{\dagger}(q)\,|\Psi_0\rangle \\ &= N^{-1/2}\sum_n \exp(-iqna)\rho_n^{\dagger}(n)\,|\Psi_0\rangle + N^{-1/2}\frac{4(\beta/U)\sin(qa/2)}{1+(2J/U)\cos(qa)}\sum_{m\neq n}\exp(-iqna)f_q(n-m)\rho_m^{\dagger}(n)\,|\Psi_0\rangle ,\end{aligned} \tag{4.4}$$

where

$$f_q(n-m)=N^{-1}\sum_k \exp[ika(m-n)]\sin(ka+qa/2) , \tag{4.5}$$

and $\rho_m^{\dagger}(n)=a_{m\uparrow}^{\dagger}a_{n\downarrow}$. Thus, in general, $|\varphi_0(q)\rangle$ represents a coherent linear combination of both covalent $(m=n)$ and ionic (doubly occupied) states $(m\neq n)$. However, in the narrow-band limit $|\beta/U| \ll 1$ the second term in Eq. (4.4) becomes negligible and $|\varphi_0(q)\rangle$ is well approximated by the magnon

$$|\varphi_0(q)\rangle \approx N^{-1/2}\sum_n \exp(-iqna)\rho_n^{\dagger}(n)\,|\Psi_0\rangle . \tag{4.6}$$

Thus, exploiting a generalized Hubbard-type Hamiltonian we have shown that the elementary (magnon) excitations from the fully saturated NBMO band do not give rise to destabilization of the ferromagnetic alignment, provided the inequality $2\beta^2/U < J$ is satisfied. It should be noted that in the present paper we have omitted nearest-neighbor electron repulsion. The effect of the latter on the electron spin correlation is the subject of a forthcoming study, where a numerical solution of the general Schrödinger equation (2.17) will be attempted. However, on the basis of qualitative arguments and some preliminary numerical calculations we anticipate enhancement of the kinetic exchange term due to renormalization of the on-site repulsion U. This is supported by an investigation of Linderberg and Öhrn,[20] carried out within the PPP model, i.e., under neglect of Coulomb exchange interactions. These authors arrived at an antiferromagnetic effective exchange of the form $J^{\mathrm{eff}}=-2\beta^2/(U-U_1)$, U_1 denoting the next-nearest-neighbor electron repulsion. This suggests that if the exchange interaction J is negligibly small, the long-range Coulomb repulsion will not be conducive to itinerant ferromagnetism within the single-band model under consideration. This is in line with the investigation carried out by Mattis.[21] A widening of the gap in the magnetic excitation spectrum is also to be expected. What is contemplated next is an extension of the numerical treatment of Eq. (2.17) to higher dimensions. This may be of importance in an attempt to shed some light on the existence of organic magnetism at finite temperature.

Finally, we would like to note that the investigated ANC polymers are polyradicals and, on general grounds, should be expected to be highly reactive. However, although radicals are less stable than hydorcarbons with closed-shell electronic configuration, their reactivity varies within a wide range. For example, comparison of Ziegler's radical,[22] tetra-phenyl-allylradical, with Koelsch's radical,[23] α-γ-bisphenylene-β-phenyl-allyl-radical, reveals that, while the former exhibits the usual reactivity of radicals, the latter does not undergo chemical changes when it is exposed to air. An assessment of the specific delocalization energy for a number of ANC polymers[8] shows that their delocalization energy exceeds in magnitude even that of the triphenylmethyl radical,[24] known as a stable chemical system. This indicates that nonclassical, but fully conjugated, polymers might turn out to be stable at room temperature or below.

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