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Theory of libron effects on the electron spectrum of one-dimensional conductors

G. Gumbs and C. Mavroyannis
Division of Chemistry, National Research Council of Canada, Ottawa K1A OR6, Canada

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The Peierls instability has been studied for a one-dimensional conductor in which the rotational degree of freedom of the molecules plays a role. The rotational motion is described in terms of a pseudospin $S = 1$ Hamiltonian in which the electrostatic quadrupole-quadrupole and dipole-dipole interactions are included. The Hamiltonian also takes account of the conduction-electron-band motion as well as the coupling of the conduction band to the rotation of the molecules. The electron Green's function is evaluated in the mean-field approximation and the libron Green's function in a self-consistent field theory. It is found that the derived expressions for both the electron and libron Green's functions give a simple recursion formula for the Peierls transition temperature T_c which is driven by the loss of librons from the Peierls condensate through thermal excitation. The recursion formula is solved numerically for a half-filled tight-binding conduction band and the dependence of T_c on the values of the different parameters involved in the problem is studied. An expression for the electrical conductivity is derived which describes the collective contribution arising from the phase oscillations of the lattice distortion. This expression is compared with the corresponding one for the Fröhlich Hamiltonian which describes the translational degree of freedom of the molecules but ignores their rotational motion.

I. INTRODUCTION

One-dimensional organic conductors such as the tetracyanoquinodimethan (TCNQ) salts have received considerable attention because of their interesting structural and electronic properties.[1-6] One of the structural problems of prime concern is the periodic modulation of the molecules which may occur in these crystals and the relation of these displacements to charge-density waves, Peierls distortion, and electrical conduction. In many studies of modulated structures, it has been assumed that the modulation arises from the effective coupling of the longitudinal acoustic phonons with the conduction electrons. However, Morawitz[7] has suggested that in some molecular crystals with segregated stacks of molecules the orientational degree of freedom couples more effectively to the conduction band, since the charge density at the ends of the radical ions has the largest spatial displacement. Following this suggestion, the possibility of an orientational Peierls distortion due to the coupling of the conduction electrons with librons (the small torsional oscillations about the equilibrium orientations of the molecules) has since received much attention.[8-15] It has been proposed that the large pressure dependence of tetrathiafulvalene- (TTF) TCNQ is due to the role of librons[10-13] while the diffuse x-ray scattering in tetraselenafulvalene- (TSeF) TCNQ (Ref. 14) and TTF_7-I_5 (Ref. 15) has been attributed to the orientational rather than translational motion of the molecules, but these conclusions need further investigation.

For simplicity, Morawitz[7] assumed that at low temperatures a one-dimensional metal is unstable against a lattice distortion of wave vector $2k_F$ (where k_F is the Fermi wave vector) which creates a gap in the excitation spectrum at the Fermi energy. The presence of the lattice distortion causes the electrons to scatter from states k to $k \pm 2k_F$ and the libron mode of wave vector $2k_F$ goes soft at the metal-insulator transition temperature. In a recent article,[16] we also assumed that the wave vector of the distortion is equal to twice the Fermi wave vector and discussed the possibility of an orientational Peierls metal-insulator transition in a linear strand. In Ref. 16, the rotational degree of freedom was described by spin $S=1$ quadrupoles and the translational motion of their centers of mass was neglected. That calculation[16] was for a simple model of a quasi-one-dimensional conductor with intrastack forces only in a parameter space spanned by electronic bandwidth, electron-quadrupole coupling constant, and quadrupole-quadrupole coupling constant. In this paper, we use a model Hamiltonian which generalizes the electron-quadrupole Hamiltonian of Ref. 16 so as to include dipolar effects on a one-dimensional strand. Also a more systematic derivation of the results is presented. There appears to be much in common between some of the quasi-one-dimensional and quasi-two-dimensional charge-density structures.[17-19] However, we shall confine our attention to the one-dimensional problem although the algebraic analysis is for arbitrary dimensions d.

In general, the interaction energy between two molecules with nonoverlapping charge distributions at lattice sites i and j may be written as a sum of terms representing the interaction of the multipoles at these two sites.[20] The terms of the expansion are a product of spherical harmonics whose arguments depend on the orientation of the molecules and whose coefficients depend on the details of the charge distributions. Treating the molecules as rotating about the centers of their electrical charge distributions with angular momentum S, we may write the Hamiltonian describing the spin-spin interaction for a d-dimensional lattice in the form

$$\mathcal{H}_r=-\tfrac{1}{2}\sum_{ij}\sum_{ll'>0}\sum_{mm'} V_{ll'}^{mm'}(i,j)L_l^m(i)L_{l'}^{m'}(j) + \sum_{ij}\sum_{l} U_l(i,j)L_l^0(i)\rho(j)\,, \tag{1.1}$$

where V is a generalized interaction between spins at lattice sites R_i^0 and R_j^0 and is a function only of the intermolecular distance R_{ij}. Also, V is zero if the magnitude of m or m' is bigger than the smaller of l and l'. U is the interaction between the 2^l pole at the lattice site i and the charge density $\rho(j)$, assuming that the molecule at j has a net charge. The spherical tensor operator[21] $L_l^m(i)$ of rank l associated with the site i $(l=0,1,\ldots,2S)$ transforms under rotations like a spherical harmonic and, for $l=1,2$, is given by

$$\begin{aligned} &L_1^0(i)=S_i^z/\sqrt{f_1}\,,\quad L_1^1(i)=S_i^+/\sqrt{2f_1}\,,\\ &L_2^0(i)=[(S_i^z)^2-\tfrac{1}{3}S(S+1)]/\sqrt{f_2}\,,\\ &L_2^1(i)=(S_i^z,S_i^+)_+/\sqrt{6f_2}\,,\\ &L_2^2(i)=(S_i^+)^2/\sqrt{6f_2}\,, \end{aligned} \tag{1.2}$$

where $(L_l^m)^\dagger=L_l^{-m}$ and the normalizing factors f_1 and f_2 are defined to be

$$f_1=S(S+1),\quad f_2=S(S+1)(2S+3)(2S-1)/15\,. \tag{1.3}$$

We note that these definitions for f_l differ by a factor from those of Barma[22] and Fedders and Myles.[23]

The interaction V is in general anisotropic (dependent on m and m'). For molecular hydrogen in which the electric quadrupole-quadrupole (EQQ) interaction is dominant, it has become clear that this anisotropy should be included in a realistic calculation of its thermodynamic properties.[24] However, in our model calculation we shall assume, for simplicity, that the quadrupole-quadrupole term in Eq. (1.1) is isotropic with nearest-neighbor interactions and write

$$\mathcal{H}_{\mathrm{EQQ}}=-\tfrac{1}{2}\sum_{\langle ij\rangle}\sum_{m=-2}^{2} J(i,j)L_2^m(i)L_2^{-m}(j) \tag{1.4a}$$

$$=-\frac{1}{6f_2}\sum_{\langle ij\rangle} J(i,j)[2(\vec{S}_i\cdot\vec{S}_j)^2+\vec{S}_i\cdot\vec{S}_j] + \frac{N}{9}\,\frac{f_1^2}{f_2}\mathcal{J}_0\,, \tag{1.4b}$$

where J is the isotropic coupling between nearest neighbors $\langle ij\rangle$, N is the number of lattice sites, and $\mathcal{J}_0$ is the zero wave-vector Fourier transform of $J(i,j)$. Written as an inner product of spin operators, the EQQ interaction in Eq. (1.4b) is clearly rotationally invariant in spin space. By applying an operator inequality of Bogoliubov,[25] Thorpe[26] has shown that for $d=1$ and $d=2$, the biquadratic-spin Hamiltonian in Eq. (1.4) cannot have rotational ordering. Therefore it is crucial to use anisotropic EQQ interactions in order to get the ordered phases of hydrogen molecules on the surface of graphoil.[27,28] The proof given in the literature[26] also applies to the isotropic electric dipole-dipole (EDD) part of the Hamiltonian in Eq. (1.1):

$$\mathcal{H}_{\mathrm{EDD}}=-\tfrac{1}{2}\sum_{\langle ij\rangle}\sum_{m=-1}^{1}\Gamma(i,j)L_1^m(i)L_1^{-m}(j) \tag{1.5a}$$

$$=-\frac{1}{2f_1}\sum_{\langle ij\rangle}\Gamma(i,j)\vec{S}_i\cdot\vec{S}_j\,, \tag{1.5b}$$

where $\Gamma(i,j)$ is the nearest-neighbor interaction energy for two dipoles at i and j. The strict absence of long-range order (spontaneous magnetization) for the two-dimensional Heisenberg Hamiltonian (1.5) was first shown by Mermin and Wagner.[29] The charge-quadrupole (CQ) interaction

$$\mathcal{H}_{\mathrm{CQ}}=(\tfrac{2}{3})^{1/2}\sum_{ij} g(i,j)L_2^0(i)\rho(j) \tag{1.6a}$$

$$=\left(\frac{2}{3f_2}\right)^{1/2}\sum_{ij} g(i,j)[(S_i^z)^2-\tfrac{1}{3}f_1]\rho(j) \tag{1.6b}$$

and charge-dipole (CD) interaction

$$\mathcal{H}_{\mathrm{CD}}=\sqrt{2}\sum_{ij}\lambda(i,j)L_1^0(i)\rho(j) \tag{1.7a}$$

$$=\left(\frac{2}{f_1}\right)^{1/2}\sum_{ij}\lambda(i,j)S_i^z\rho(j) \tag{1.7b}$$

break the rotational symmetry of our model and play important roles in the problem. Here g and λ are the CQ and CD parameters, respectively.

In addition to the electrostatic interaction between the molecules, there is a term that takes account of the motion of the electrons on the lattice:

$$\mathcal{H}_e=\sum_{\langle ij\rangle\sigma} t(i,j)\alpha_{i\sigma}^\dagger\alpha_{j\sigma}\,. \tag{1.8}$$

Here $t(i,j)$ is the intermolecular electron-transfer integral which takes an electron between a pair of nearest-neighbor sites $\langle ij\rangle$ and $\alpha_{i\sigma}^\dagger$ $(\alpha_{i\sigma})$ creates (destroys) an electron of spin σ on the lattice site i. Therefore, our total anisotropic Hamiltonian is given by

$$\mathcal{H}=\mathcal{H}_e+\mathcal{H}_{\mathrm{EQQ}}+\mathcal{H}_{\mathrm{EDD}}+\mathcal{H}_{\mathrm{CQ}}+\mathcal{H}_{\mathrm{CD}}\,, \tag{1.9}$$

where $\mathcal{H}_{\mathrm{CQ}}$ and $\mathcal{H}_{\mathrm{CD}}$ may be viewed as describing the anisotropy of our system. While the use of isotropic EQQ and EDD interactions is not justified from first principles, the simple Hamiltonian in Eq. (1.9) nevertheless gives some interesting results which might be further studied by more sophisticated models. It is interesting to note that in the spin-one case ($S_i^z = -1, 0, 1$) the $m = 0$ term of the quadrupolar Hamiltonian $\mathcal{H}_{\mathrm{EQQ}}$ in Eq. (1.5) corresponds to the $\sigma_i = \pm 1$ Ising model where $(S_i^z)^2 = \frac{1}{2}(1 + \sigma_i)$.[30] The classical analog of the total Hamiltonian $\mathcal{H}_{\mathrm{EQQ}}$ with the fluctuation $m = \pm 1$ terms is the biquadratic Blume-Emery-Griffiths-Rys model which has been used to study multicritical phenomena by a variety of methods such as mean-field theory (MFT), the modern renormalization group method, Monte Carlo techniques, as well as high- and low-temperature series expansions.[31] In Eq. (1.9), the term $\mathcal{H}_{\mathrm{EQD}}$ describing electrostatic quadrupole-dipole interaction has been discarded as a result of symmetry considerations.

We shall assume that the angular momentum distribution is axially symmetric about the z axis, parallel to the chain, and therefore the averages $\langle L_2^m \rangle$ for $m \neq 0$ vanish. If $\langle L_2^0 \rangle$ is nonzero, then the angular momentum distribution is not isotropic and the molecular axis has a degree of order depending on the value of $\langle L_2^0 \rangle$. We shall show, within an MFT, that if the molecules are in an ordered state, the electron-libron interaction may induce a gap in the energy band of the conduction electrons. Furthermore, it will become clear that within the MFT and the $S = 1$ manifold the CQ and not the CD interaction produces the metal-insulator transition. The theory makes use of temperature-dependent Green's functions, and standard decoupling procedures are used as well. We make use of these Green's functions to study the effect of the collective motion of the molecules on the frequency-dependent electrical conductivity $\sigma(\omega)$ in the Peierls distorted state and we compare this contribution with that from single-particle excitations.

In this paper, we consider spin-one molecules only. In Sec. II, we transform the Hamiltonian in Eq. (1.9) in the $S = 1$ manifold to pseudospin creation and destruction operators, using a transformation due to the work of Raich and Etters.[32] The equations of motion of the electronic Green's functions and explicit expressions for these functions in the MFT are given in Sec. III. The equations of motion of the pseudospin Green's functions are derived in Sec. IV. By approximating the self-energy by its frequency-independent part in Sec. V, we obtain approximations for the pseudospin Green's functions. In Sec. VI, we show how the molecular field results in Ref. 16 are related to the new results in Sec. V. The electrical conductivity is calculated in Sec. VII. The results of our calculation are summarized and discussed in Sec. VIII.

II. TRANSFORMATION TO PSEUDOSPIN OPERATORS

Raich and Etters[32] have shown that for molecules of spin $S = 1$, one may express the operator components S^+, S^-, and S^z in terms of pseudospin operators which cause transitions from the excited states to the ground state:

$$a_i = (1/\sqrt{2})[L_1^{-1}(i) + L_2^{-1}(i)], \tag{2.1}$$

$$b_i = (1/\sqrt{2})[L_1^{1}(i) - L_2^{1}(i)]. \tag{2.2}$$

The creation operators $a_i^\dagger, b_i^\dagger$ are given by the Hermitian conjugates of Eqs. (2.1) and (2.2), respectively. In terms of these operators, we have

$$L_1^0(i) = (1/\sqrt{2})(n_i - m_i) = (1/\sqrt{2})S_i^z, \tag{2.3}$$

$$L_2^0(i) = (\tfrac{3}{2})^{1/2}(n_i + m_i - \tfrac{2}{3}), \tag{2.4}$$

$$L_2^2(i) = a_i^\dagger b_i, \tag{2.5}$$

where the number operators n_i and m_i are defined to be

$$n_i = a_i^\dagger a_i, \quad m_i = b_i^\dagger b_i. \tag{2.6}$$

Since we are assuming that the charge is distributed with cylindrical symmetry about the z axis, the averages of the number operators are equal:

$$\langle n_i \rangle = \langle m_i \rangle. \tag{2.7}$$

The commutation relations for a_i, b_i and their Hermitian conjugates are well known.[32,33] For completeness, we list them:

$$[a_i, a_j^\dagger] = (1 - 2n_i - m_i)\delta_{ij}, \tag{2.8}$$

$$[b_i, b_j^\dagger] = (1 - n_i - 2m_i)\delta_{ij}, \tag{2.9}$$

$$[a_i, b_j^\dagger] = -b_i^\dagger a_i \delta_{ij}, \tag{2.10}$$

$$[b_i, a_j^\dagger] = -a_i^\dagger b_i \delta_{ij}, \tag{2.11}$$

$$[a_i, b_j] = [a_i^\dagger, b_j^\dagger] = 0. \tag{2.12}$$

From these relations, we may evaluate the commutators of a_i, b_i with L_1^m and L_2^m. We also have

$$a_i a_i = b_i b_i = a_i b_i = b_i a_i = a_i b_i^\dagger = 0 \tag{2.13}$$

in the $S = 1$ manifold.

Substituting Eqs. (2.1)–(2.5) into Eqs. (1.4) and (1.5), we have for the isotropic quadrupolar Hamiltonian[34]

$$\mathcal{H}_{\mathrm{EQQ}} = -\sum_{\langle ij \rangle} J(i,j)[a_i^\dagger b_i b_j^\dagger a_j + \tfrac{3}{4}(n_i + m_i - \tfrac{2}{3})(n_j + m_j - \tfrac{2}{3}) + \tfrac{1}{2}(a_i^\dagger - b_i)(a_j - b_j^\dagger)], \tag{2.14}$$

and for the isotropic dipolar interaction

$$\mathcal{H}_{\mathrm{EDD}} = -\sum_{\langle ij\rangle} \Gamma(i,j)\left[\tfrac{1}{2}(a_i^\dagger - b_i)(a_j - b_j^\dagger) + \tfrac{1}{4}(n_i - m_i)(n_j - m_j)\right]. \quad (2.15)$$

The CQ and CD interactions in Eqs. (1.6) and (1.7) are given by

$$\mathcal{H}_{\mathrm{CQ}} = \sum_{ij} g(i,j)(n_i + m_i - \tfrac{2}{3})\rho(j) \quad (2.16)$$

and

$$\mathcal{H}_{\mathrm{CD}} = \sum_{ij} \lambda(i,j)(n_i - m_i)\rho(j) \quad (2.17)$$

in terms of the pseudospin operators. We shall make use of these transformations in evaluating the Green's functions.

III. SINGLE-PARTICLE ELECTRON GREEN'S FUNCTIONS

We now form the equations of motion of the single-particle electron Green's functions. Since $i\dot{\alpha}_{i\sigma} = [\alpha_{i\sigma}, \mathcal{H}]$ (we shall set $\hbar = 1$), the equations of motion are obtained by commuting $\alpha_{i\sigma}$ with the Hamiltonian (1.9) whose terms are given by Eqs. (1.8) and (2.14)–(2.17). Using the usual Fermi commutation relations for the electron creation and destruction operators, and assuming that the electron and pseudospin operators commute, one can show that the CQ and CD interactions induce changes in the electron operators which, in Fourier space, are given by

$$i\dot{\alpha}_{k\sigma} = \epsilon_k \alpha_{k\sigma} + \sum_p g_p \alpha_{k-p\sigma}(n_p + \tfrac{2}{3}\delta_{p,0}) + \sum_p \lambda_p \alpha_{k-p\sigma}(n_p - m_p). \quad (3.1)$$

Here δ is the Kronecker delta, k and p are vectors in the first Brillouin zone, and

$$\alpha_{k\sigma} = \frac{1}{\sqrt{N}} \sum_i e^{-ikR_i^0} \alpha_{i\sigma}, \quad (3.2)$$

$$\epsilon_k = \sum_j e^{-ikR_{ij}} t(i,j), \quad (3.3)$$

$$n_k = \frac{1}{N} \sum_i e^{-ikR_i^0} n_i. \quad (3.4)$$

The definition of the Fourier transform of $g(i,j)$ and $\lambda(i,j)$ is similar to that of $t(i,j)$ in Eq. (3.3).

From Eq. (3.1), we find that the electron Green's function $\langle\langle \alpha_{k\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle \equiv \langle\langle \alpha_{k\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle_\omega$ defined to be the Fourier transform of

$$\langle\langle \alpha_{k\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle_{t,t'} = -i\langle \hat{T} \alpha_{k\sigma}(t) \alpha_{k'\sigma'}^\dagger(t') \rangle, \quad (3.5)$$

where $\hat{T}$ is the time-ordering operator, satisfies the equation

$$(\omega - \epsilon_k)\langle\langle \alpha_{k\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle = \delta_{kk'}\delta_{\sigma\sigma'} + \sum_p g_p \langle\langle \alpha_{k-p\sigma}(n_p + m_p - \tfrac{2}{3}\delta_{p,0}); \alpha_{k'\sigma'}^\dagger \rangle\rangle + \sum_p \lambda_p \langle\langle \alpha_{k-p}(n_p - m_p); \alpha_{k'\sigma'}^\dagger \rangle\rangle. \quad (3.6)$$

This equation involves higher-order Green's functions on the right-hand side. These higher-order terms are decoupled with the following two approximations:

$$\langle\langle \alpha_{k-p\sigma}(n_p + m_p - \tfrac{2}{3}\delta_{p,0}); \alpha_{k'\sigma'}^\dagger \rangle\rangle \approx \langle n_p + m_p - \tfrac{2}{3}\delta_{p,0}\rangle \langle\langle \alpha_{k-p\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle, \quad (3.7)$$

$$\langle\langle \alpha_{k-p\sigma}(n_p - m_p); \alpha_{k'\sigma'}^\dagger \rangle\rangle \approx \langle n_p - m_p\rangle \langle\langle \alpha_{k-p\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle = 0, \quad (3.8)$$

where use is made of Eq. (2.7) in order to get the result in Eq. (3.8). The approximation in Eq. (3.7) means that all dynamic effects arising from the interactions of the electrons with the quadrupoles are neglected and that an electron sees only the average (static) field produced by this interaction. Similarly, Eq. (3.8) implies that in the static approximation the number densities of the pseudospin operators may be decoupled from the electron Green's function $\langle\langle \alpha_{k-p\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle$ but because of the cylindrical symmetry of the molecules the average field arising from the charge-dipole interaction is zero. Making use of the relations (3.7) and (3.8), we rewrite Eq. (3.6) in the form

$$(\omega - \epsilon_k)\langle\langle \alpha_{k\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle = \delta_{kk'}\delta_{\sigma\sigma'} + \sum_p g_p \langle n_p + m_p - \tfrac{2}{3}\delta_{p,0}\rangle \langle\langle \alpha_{k-p\sigma}; \alpha_{k'\sigma'}^\dagger \rangle\rangle. \quad (3.9)$$

The electron Green's functions which we use form a 2×2 matrix:

$$\mathcal{G}(k,\omega) = \langle\langle X_{k\sigma}; X_{k\sigma}^\dagger \rangle\rangle = \begin{pmatrix} \langle\langle \alpha_{k\sigma}; \alpha_{k\sigma}^\dagger \rangle\rangle & \langle\langle \alpha_{k\sigma}; \alpha_{k+q\sigma}^\dagger \rangle\rangle \\ \langle\langle \alpha_{k+q\sigma}; \alpha_{k\sigma}^\dagger \rangle\rangle & \langle\langle \alpha_{k+q\sigma}; \alpha_{k+q\sigma}^\dagger \rangle\rangle \end{pmatrix}, \quad (3.10)$$

where $X_{k\sigma}$ is a column vector defined by

$$X_{k\sigma} = \begin{pmatrix} \alpha_{k\sigma} \\ \alpha_{k+q\sigma} \end{pmatrix}. \quad (3.11)$$

Only the Green's functions in Eq. (3.10) are needed, since we assume that only the libron modes of wave vector $k = 0, \pm q$ are coupled to the conduction electrons in a half-filled band. $2q$ is a reciprocal-lattice vector so that q and $-q$ are equivalent. Therefore, in the case considered here, we include only the correlation between the electron states of wave vector k and $k \pm q$. As a result, we obtain the complete Green's function $\mathcal{G}$ whose inverse is

$$\mathcal{G}^{-1}(k,\omega)=\begin{pmatrix}\omega-\epsilon_k & -\Delta \\ -\Delta & \omega-\epsilon_{k+q}\end{pmatrix}. \tag{3.12}$$

The poles of $\mathcal{G}$ are

$$E_k^{\pm}=\tfrac{1}{2}\{\epsilon_k+\epsilon_{k+q}\pm[(\epsilon_k-\epsilon_{k+q})^2+4\Delta^2]^{1/2}\}, \tag{3.13}$$

with the sign corresponding to the appropriate superscript. Thus the energy levels of the electrons are split for wave vector $k=\pm q/2$ and the lattice potential has created a gap of size 2Δ in the conduction band. For the Peierls distortion, the potential acting on the electrons has a period π/k_F and is due to the librons. The energy gap occurs at the Fermi energy and is given by

$$\Delta=2g_q\langle n_q\rangle=-2g_q T\sum_{k\omega_n}\langle\langle a_{k+q};a_k^\dagger\rangle\rangle, \tag{3.14}$$

where a_k is the Fourier transform of a_i and $\omega_n = 2n\pi T$ $(n=0,1,2,\ldots)$ are Matsubara frequencies.

From the definition of the gap parameter in Eq. (3.14), it is clear that in order to determine the complete temperature dependence of Δ one has to evaluate the double-time Green's function $\langle\langle a_{k+q};a_k^\dagger\rangle\rangle$ which is the subject of the next section.

IV. SINGLE-PARTICLE LIBRON GREEN'S FUNCTIONS

The equations of motion of the libron Green's functions are obtained by commuting the operators a_i and b_i with the Hamiltonian (1.9). On inspection of these equations, one finds that a_i on lattice site R_i^0 is coupled to a_j, b_j and their Hermitian conjugates $a_j^\dagger, b_j^\dagger$ for different sites R_j^0. A description of these results is given by the following two equations which are written in momentum space:

$$i\dot{a}_k=\nu_0(k)a_k+\omega_0(k)b_{-k}^\dagger+A_k, \tag{4.1}$$

$$-i\dot{b}_{-k}^\dagger=\omega_0(k)a_k+\nu_0(k)b_{-k}^\dagger+B_k. \tag{4.2}$$

The first two terms in Eqs. (4.1) and (4.2) are linear in a_k and $b_{-k}^\dagger$ and the coefficients $\nu_0(k)$ and $\omega_0(k)$ are defined by

$$\nu_0(k)=\mathcal{J}_0-\tfrac{1}{2}\mathcal{J}_k, \tag{4.3}$$

$$\omega_0(k)=\tfrac{1}{2}\mathcal{J}_k, \tag{4.4}$$

where $\mathcal{J}_k$ is the Fourier transform of the EQQ interaction $J(i,j)$. The terms A_k, B_k are nonlinear in the pseudospin operators. In direct space, these are given by

$$A_i=A_i^Q+A_i^D, \tag{4.5}$$

$$B_i=B_i^Q+B_i^D, \tag{4.6}$$

where

$$A_i^Q=-\sum_j J(i,j)\left(\tfrac{3}{2}a_i(n_j+m_j)-\frac{1}{\sqrt{2}}(2n_i+m_i)L_2^{-1}(j)+b_iL_2^{-2}(j)+\frac{1}{\sqrt{2}}L_2^{-2}(i)L_2^{1}(j)\right)+\sum_j g(i,j)\rho(j)a_i, \tag{4.7}$$

$$A_i^D=-\sum_j \Gamma(i,j)\left(\frac{1}{\sqrt{2}}a_iL_1^0(j)-\frac{1}{\sqrt{2}}L_2^{-2}(i)L_1^1(j)+\frac{1}{\sqrt{2}}(1-2n_i-m_i)L_1^{-1}(j)\right)+\sum_j \lambda(i,j)\rho(j)a_i, \tag{4.8}$$

$$B_i^Q=-\sum_j J(i,j)\left(\tfrac{3}{2}b_i^\dagger(n_j+m_j)+\frac{1}{\sqrt{2}}(n_i+2m_i)L_2^{-1}(j)+a_i^\dagger L_2^{-2}(j)-\frac{1}{\sqrt{2}}L_2^{-2}(i)L_2^{1}(j)\right)+\sum_j g(i,j)\rho(j)b_i^\dagger, \tag{4.9}$$

$$B_i^D=-\sum_j \Gamma(i,j)\left(-\frac{1}{\sqrt{2}}b_i^\dagger L_1^0(j)-\frac{1}{\sqrt{2}}L_2^{-2}(i)L_1^1(j)+\frac{1}{\sqrt{2}}(1-n_i-2m_i)L_1^{-1}(j)\right)-\sum_j \lambda(i,j)\rho(j)b_i^\dagger, \tag{4.10}$$

are the contributions to A_i and B_i from the quadrupoles (superscript Q) and dipoles (superscript D).

The libron Green's functions which arise in this problem from a 4×4 matrix. In the notation of Eq. (3.10), this matrix is conveniently written as

$$K(k,\omega)=\langle\langle Y_k;Y_k^\dagger\rangle\rangle, \tag{4.11}$$

where the row vector $Y_k^\dagger$ is given by

$$Y_k^\dagger=(a_k^\dagger, b_{-k}, a_{k+q}^\dagger, b_{-k+q}). \tag{4.12}$$

From Eqs. (4.1) and (4.2), it is straightforward to show that the libron Green's functions in Eq. (4.11) satisfy the equation

$$K_0^{-1}(k,\omega)K(k,\omega)=I_4+\phi(k,\omega), \tag{4.13}$$

where I_4 is the unit 4×4 matrix and $K_0^{-1}(k,\omega)$ is given by

$$K_0^{-1}(k,\omega)=\begin{pmatrix}M(k,\omega) & 0_2 \\ 0_2 & M(k+q,\omega)\end{pmatrix}, \tag{4.14}$$

with 0_2 the null 2×2 matrix and $M(k,\omega)$ defined to be

$$M(k,\omega)=\frac{1}{\bar{\eta}}\begin{pmatrix}\omega-\nu_0(k) & -\omega_0(k) \\ -\omega_0(k) & -\omega-\nu_0(k)\end{pmatrix}. \tag{4.15}$$

$\bar{\eta}$ is an order parameter which is given by

$$\bar{\eta} = 1 - 3\langle n_0 \rangle = \frac{1}{N}\sum_i \bar{\eta}_i \,, \tag{4.16}$$

where

$$\bar{\eta}_i = -\left(\frac{3}{2}\right)^{1/2} \langle L_2^0(i) \rangle \,, \tag{4.17}$$

and

$$\langle n_0 \rangle = \frac{1}{N}\sum_k \langle a_k^\dagger a_k \rangle = \frac{1}{N}\sum_k \langle b_k^\dagger b_k \rangle \tag{4.18}$$

is the average number of librons in the $k=0$ wave-vector state. $\phi(k,\omega)$ in Eq. (4.13) is a 4×4 matrix Green's function which is given by

$$\phi(k,\omega) = \frac{1}{\bar{\eta}} \langle\langle Z_k ; Y_k^\dagger \rangle\rangle \,, \tag{4.19}$$

where Z_k is the column vector

$$Z_k = \begin{pmatrix} C_k \\ C_{k+q} \end{pmatrix}, \quad C_k = \begin{pmatrix} A_k \\ B_k \end{pmatrix}. \tag{4.20}$$

Clearly, K_0 is the approximation for K if all fluctuation (nonlinear) effects arising from ϕ are ignored. We shall refer to K_0 as the *linear approximation* of K. $\bar{\eta}$ is a measure of the rotational ordering of the molecules and we have assumed that it is nonzero. Thus our theory is not applicable to cases in which there is a band gap in the presence of static disorder.

One may check quite easily from Eq. (4.13) that if K is approximated by K_0 the band gap defined by Eq. (3.14) vanishes since the off-diagonal matrices of K_0 are equal to the null matrix. Therefore, in order to obtain a Peierls transition, fluctuations in the libron motion have to be included. The procedure we shall follow in order to systematically incorporate the nonlinear effects is to determine the equation of motion of $\phi(k,\omega)$. This leads to Dyson's equation with a self-energy. A suitable approximation of the self-energy enables one to go beyond the linear approximation.

Taking the time derivative of $\phi(k, t-t')$ with respect to the time argument t' and using the commutation relations for the pseudospin operators, we have the following result for the Fourier transform $\phi(k,\omega)$:

$$\phi(k,\omega) K_0^{-1}(k,\omega) = \Pi(k,\omega) \,. \tag{4.21}$$

The quantity $\Pi(k,\omega)$, defined by

$$\Pi(k,\omega) = \bar{\Pi}(k) + \tilde{\Pi}(k,\omega) \,, \tag{4.22}$$

is the sum of a frequency-independent part

$$\bar{\Pi}(k) = \frac{1}{\bar{\eta}^2} \begin{bmatrix} \langle [A_k, a_k^\dagger] \rangle & -\langle [A_k, b_{-k}] \rangle & \langle [A_k, a_{k+q}^\dagger] \rangle & -\langle [A_k, b_{-k+q}] \rangle \\ \langle [B_k, a_k^\dagger] \rangle & -\langle [B_k, b_{-k}] \rangle & \langle [B_k, a_{k+q}^\dagger] \rangle & -\langle [B_k, b_{-k+q}] \rangle \\ \langle [A_{k+q}, a_k^\dagger] \rangle & -\langle [A_{k+q}, b_{-k}] \rangle & \langle [A_{k+q}, a_{k+q}^\dagger] \rangle & -\langle [A_{k+q}, b_{-k+q}] \rangle \\ \langle [B_{k+q}, a_k^\dagger] \rangle & -\langle [B_{k+q}, b_{-k}] \rangle & \langle [B_{k+q}, a_{k+q}^\dagger] \rangle & -\langle [B_{k+q}, b_{-k+q}] \rangle \end{bmatrix} , \tag{4.23}$$

which involves commutators of the components of the vectors Z_k and $Y_k^\dagger$ and a frequency-dependent part

$$\tilde{\Pi}(k,\omega) = \frac{1}{\bar{\eta}^2} \langle\langle Z_k ; Z_k^\dagger \rangle\rangle \,, \tag{4.24}$$

using the same notation as in Eq. (3.10).

Eliminating $\phi(k,\omega)$ from Eqs. (4.13) and (4.21), we obtain the following matrix equation for $K(k,\omega)$ in terms of $\Pi(k,\omega)$:

$$K(k,\omega) = K_0(k,\omega) + K_0(k,\omega)\Pi(k,\omega)K_0(k,\omega) \,. \tag{4.25}$$

We now rewrite this equation as Dyson's equation

$$K(k,\omega) = K_0(k,\omega) + K_0(k,\omega)\Sigma(k,\omega)K(k,\omega) \,, \tag{4.26}$$

where $\Sigma(k,\omega)$ is the proper self-energy. Substituting Eq. (4.25) for $K(k,\omega)$ into the right-hand side of Eq. (4.26) and then equating this result for $K(k,\omega)$ to its value in Eq. (4.25), we obtain the self-energy $\Sigma(k,\omega)$ in terms of Π and K_0:

$$\Sigma(k,\omega) = \Pi(k,\omega)[I_4 + K_0(k,\omega)\Pi(k,\omega)]^{-1} \,, \tag{4.27}$$

where we have assumed that the determinant of the matrix in the square brackets on the right-hand side of Eq. (4.27) is nonzero. Assuming that we are not in a region of nonanalyticity, we now proceed to obtain complete expressions for K.

V. $K(k,\omega)$ IN THE STATIC APPROXIMATION

In this section, we obtain a complete expression for the single-particle libron Green's functions $K(k,\omega)$ when $\Sigma(k,\omega)$ is not neglected. Assuming that the matrix in square brackets on the right-hand side of Eq. (4.27) has an inverse, we may take the self-energy to be given by the first factor $\Pi(k,\omega)$. In this approximation, some dynamic effects arising from the fluctuations in the self-energy would be ignored. We shall neglect all dynamic contributions to the self-energy and thus approximate $\Sigma(k,\omega)$ by the first term in Eq.

(4.22):

$$\Sigma(k)=\overline{\Pi}(k)\,. \tag{5.1}$$

The lowest-order approximation for the self-, energy (a) modifies the excitation energies of the libron modes and (b) gives a nontrivial temperature-dependent value for the band gap.

The calculation of $\overline{\Pi}(k)$ in Eq. (4.23) requires the evaluation of the commutators of Z_k with $Y_k^\dagger$. Using the commutation relations for the pseudospin operators in configuration space, we obtain the following results:

$$\begin{aligned}[][A_i^Q, a_l^\dagger] = -\Big(&\delta_{il}\sum_j \big(\tfrac{1}{2}J(l,j)\{3(n_j+m_j)+\sqrt{2}\,[b_l^\dagger L_2^1(j)-2a_l^\dagger L_2^{-1}(j)]\}-g(l,j)\rho(j)\big)\\ &+\tfrac{1}{2}J(i,l)(3a_l^\dagger a_i+2b_l^\dagger b_i-2n_i-m_i)\Big)(1-2n_l-m_l)+\sum_j J(l,j)(\delta_{il}-\delta_{ij})L_2^2(l)L_2^{-2}(j)\,,\end{aligned} \tag{5.2}$$

$$\begin{aligned}[][A_i^D, a_l^\dagger] = -\Big(&\delta_{il}\sum_j \{\tfrac{1}{2}\Gamma(l,j)[(n_j-m_j)-\sqrt{2}\,b_l^\dagger L_1^1(j)-2\sqrt{2}\,a_l^\dagger L_1^{-1}(j)]-\lambda(l,j)\rho(j)\}\\ &+\tfrac{1}{2}\Gamma(i,l)[a_ia_l^\dagger+(1-2n_i-m_i)]\Big)(1-2n_l-m_l)-\tfrac{1}{2}\Gamma(i,l)L_2^{-2}(i)L_2^2(l)\,,\end{aligned} \tag{5.3}$$

$$\begin{aligned}[][A_i^Q, b_l] = (1-n_l-2m_l)\Big(&\delta_{il}\sum_j \frac{1}{\sqrt{2}}J(l,j)[a_l^\dagger L_2^{-1}(j)-b_l^\dagger L_2^1(j)]+\tfrac{1}{2}J(i,l)(3b_la_i+2a_lb_i+2n_i+m_i)\Big)\\ &-\tfrac{1}{2}J(i,l)L_2^2(l)L_2^{-2}(i)\,,\end{aligned} \tag{5.4}$$

$$\begin{aligned}[][A_i^D, b_l] = -(1-n_l-2m_l)\Big(&\delta_{il}\sum_j \frac{1}{\sqrt{2}}\Gamma(l,j)[a_lL_1^1(j)+b_lL_1^{-1}(j)]+\tfrac{1}{2}\Gamma(i,l)\\ &\times[a_ib_l-(1-2n_i-m_i)]\Big)-\tfrac{1}{2}J(i,l)L_2^2(l)L_2^{-2}(i)\,.\end{aligned} \tag{5.5}$$

The commutators of B_i with $a_l^\dagger$ and b_l are also obtained by making use of the commutation relations in Eqs. (2.8)–(2.12). However, we do not need to write the answers down because of the symmetry of the matrix in Eq. (4.23).

Taking the ensemble average of Eqs. (5.2)–(5.5) and making use of the relation (2.7), we have

$$\langle[A_i^Q, a_l^\dagger]\rangle \simeq -\overline{\eta}_l\Big(\delta_{il}\sum_j [J(l,j)(3\langle n_j\rangle+\tfrac{3}{2}\langle a_l^\dagger b_j^\dagger\rangle-\tfrac{3}{2}\langle a_l^\dagger a_j\rangle)-g(l,j)\langle\rho(j)\rangle]+\tfrac{1}{2}J(i,l)(5\langle a_l^\dagger a_i\rangle-3\langle n_i\rangle)\Big)\,, \tag{5.6}$$

$$\langle[A_i^D, a_l^\dagger]\rangle \simeq \overline{\eta}_l\Big(\delta_{il}\sum_j [\Gamma(l,j)(\tfrac{3}{2}\langle a_l^\dagger a_j\rangle+\tfrac{3}{2}\langle a_l^\dagger b_j^\dagger\rangle)+\lambda(l,j)\langle\rho(j)\rangle]-\tfrac{1}{2}\Gamma(i,l)(\langle a_l^\dagger a_i\rangle+1-3\langle n_i\rangle)\Big)\,, \tag{5.7}$$

$$\langle[A_i^Q, b_l]\rangle \simeq \overline{\eta}_l\Big(\delta_{il}\sum_j J(l,j)(\langle a_l^\dagger a_j\rangle-\langle a_l^\dagger b_j^\dagger\rangle)+\tfrac{1}{2}J(i,l)(5\langle a_lb_i\rangle+3\langle n_i\rangle)\Big)\,, \tag{5.8}$$

$$\langle[A_i^D, b_l]\rangle \simeq -\overline{\eta}_l\Big(\delta_{il}\sum_j \Gamma(l,j)(\langle a_la_j^\dagger\rangle+\langle a_lb_j\rangle)+\tfrac{1}{2}\Gamma(i,l)(\langle a_ib_l\rangle-1+3\langle n_i\rangle)\Big)\,. \tag{5.9}$$

Here we have decoupled the factors $1-n_l-2m_l$ and $1-2n_l-m_l$ from the factors in large parentheses in Eqs. (5.2)–(5.5). We have also ignored the quadratic terms involving the product of $L_2^2(i)$ with $L_2^{-2}(j)$, since these terms lead to higher-order Green's functions which are assumed negligible in this approximation.

If one keeps only the terms involving the average values of the libron number density $\langle n_j\rangle$ and the electron number density $\langle\rho(j)\rangle$ in Eqs. (5.6) and (5.8), then each spin precesses in the uncorrelated field produced by the interactions. This leads to the results in Ref. 16 where the dipolar effects have been ignored. However, keeping all the terms in Eqs. (5.6)–(5.9) and Fourier transforming to momentum space, we obtain the following results for the matrix elements of $\overline{\Pi}(k)$:

$$\overline{\Pi}_{11}^Q(k) = -\overline{\eta}^{-1}\{3\nu_0(k)\langle n_0\rangle-g_0\langle\rho_0\rangle-3[\overline{\mathcal{R}}(0)-\hat{\mathcal{R}}(0)]+5\overline{\mathcal{R}}(k;0)\}\,, \tag{5.10}$$

$$\overline{\Pi}_{11}^D(k) = \overline{\eta}^{-1}\{\tfrac{3}{2}\gamma_k\langle n_0\rangle-\tfrac{1}{2}\gamma_0+\lambda_0\langle\rho_0\rangle+3[\overline{\mathcal{P}}(0)+\hat{\mathcal{P}}(0)]-\overline{\mathcal{P}}(k;0)\}\,, \tag{5.11}$$

$$\overline{\Pi}_{12}^Q(k) = -\overline{\eta}^{-1}\{3\omega_0(k)\langle n_0\rangle+2[\overline{\mathcal{R}}(0)-\hat{\mathcal{R}}(0)]+5\hat{\mathcal{R}}(k;0)\}\,, \tag{5.12}$$

$$\overline{\Pi}_{12}^D(k) = \overline{\eta}^{-1}\{\tfrac{3}{2}\gamma_k\langle n_0\rangle-\tfrac{1}{2}\gamma_0+2[\overline{\mathcal{P}}(0)+\hat{\mathcal{P}}(0)]+\hat{\mathcal{P}}(k;0)\}\,, \tag{5.13}$$

$$\overline{\Pi}_{13}^{Q}(k)=-\overline{\eta}^{-1}\{6\omega_0(q)\langle n_q\rangle-3\omega_0(k+q)\langle n_q\rangle-g_q\langle\rho_q\rangle-3[\overline{\mathcal{R}}(0;q)-\hat{\mathcal{R}}(0;q)]+5\overline{\mathcal{R}}(k;q)\}\,, \tag{5.14}$$

$$\overline{\Pi}_{13}^{D}(k)=\overline{\eta}^{-1}\{\tfrac{3}{2}\gamma_{k+q}\langle n_q\rangle+\tfrac{3}{2}\gamma_q\langle n_q\rangle\overline{\eta}^{-1}+\lambda_q\langle\rho_q\rangle+3[\overline{\mathcal{P}}(0;q)+\hat{\mathcal{P}}(0;q)]-\overline{\mathcal{P}}(k;q)\}\,, \tag{5.15}$$

$$\overline{\Pi}_{14}^{Q}(k)=-\overline{\eta}^{-1}\{3\omega_0(k+q)\langle n_q\rangle+2[\overline{\mathcal{R}}(0;q)-\hat{\mathcal{R}}(0;q)]+5\hat{\mathcal{R}}(k;q)\}\,, \tag{5.16}$$

and

$$\overline{\Pi}_{14}^{D}(k)=\overline{\eta}^{-1}\{\tfrac{3}{2}\gamma_{k+q}\langle n_q\rangle+\tfrac{3}{2}\gamma_q\langle n_q\rangle\overline{\eta}^{-1}+2[\overline{\mathcal{P}}(0;q)+\hat{\mathcal{P}}(0;q)]+\hat{\mathcal{P}}(k;q)\}\,, \tag{5.17}$$

where $\overline{\mathcal{R}}$ and $\hat{\mathcal{R}}$ are defined by

$$\overline{\mathcal{R}}(k;k')=\frac{1}{N}\sum_p\omega_0(p)\langle a^\dagger_{k+k'+p}a_{k+p}\rangle\,, \tag{5.18}$$

$$\hat{\mathcal{R}}(k;k')=\frac{1}{N}\sum_p\omega_0(p)\langle a^\dagger_{k+k'-p}b^\dagger_{p-k}\rangle\,. \tag{5.19}$$

$\overline{\mathcal{P}}$ and $\hat{\mathcal{P}}$ are defined in a similar way with $\omega_0(p)$ replaced by $\frac{1}{2}\gamma_p$ where γ_p is the Fourier transform of $\Gamma(i,j)$. For convenience, we have written $\overline{\mathcal{R}}(0;0)=\overline{\mathcal{R}}(0)$, $\hat{\mathcal{R}}(0)=\hat{\mathcal{R}}(0;0)$, and similarly for $\overline{\mathcal{P}}(0)$ and $\hat{\mathcal{P}}(0)$. The second-row matrix elements are obtained from those in the first row by making use of the symmetry properties: $\overline{\Pi}_{21}(k)=\overline{\Pi}_{12}(k)$, $\overline{\Pi}_{22}(k)=\overline{\Pi}_{11}(k)$, $\overline{\Pi}_{23}(k)=\overline{\Pi}_{14}(k)$, and $\overline{\Pi}_{24}(k)=\overline{\Pi}_{13}(k)$. The elements in the third row are obtained from those in the first row, since we have $\overline{\Pi}_{31}(k)=\overline{\Pi}_{13}(k+q)$, $\overline{\Pi}_{32}(k)=\overline{\Pi}_{14}(k+q)$, $\overline{\Pi}_{33}(k)=\overline{\Pi}_{11}(k+q)$, and $\overline{\Pi}_{34}(k)=\overline{\Pi}_{12}(k+q)$. In a similar way one can obtain the fourth-row elements from those in the second row. The self-energy is thus completely determined in the approximation we have made in Eq. (5.1).

Substituting these results for $\Sigma(k)$ into Dyson's equation (4.26) which we rewrite as

$$K^{-1}(k,\omega)=K_0^{-1}(k,\omega)-\Sigma(k)\,, \tag{5.20}$$

we have an explicit expression for $K(k,\omega)$ which ignores the dynamic correlations of the precessions of the spins about their equilibrium positions. The eigenfrequencies of the libron modes are renormalized from their values in the linear approximation and correspond to the poles of $K(k,\omega)$ in Eq. (5.20). Since $K(k,\omega)$ depends on $\overline{\mathcal{R}},\hat{\mathcal{R}}$ and $\overline{\mathcal{P}},\hat{\mathcal{P}}$ which in turn involve sums over the matrix elements of $K(k,\omega)$, Δ and $\overline{\eta}$ have to be determined iteratively and self-consistently. In order to get more insight into our model calculation some numerical results are presented in the next section.

VI. NUMERICAL RESULTS IN THE MEAN-FIELD APPROXIMATION

If the correlations between the spins are neglected so that each spin precesses in the mean field produced by its neighbors, the numerical calculation of Δ and $\overline{\eta}$ is considerably simplified. In this MFT, only the terms in Eqs. (5.6)–(5.9) which involve the libron or electron density operators are included. This means that we ignore the *correlation sums* $\overline{\mathcal{R}},\hat{\mathcal{R}}$ and $\overline{\mathcal{P}},\hat{\mathcal{P}}$. Therefore in the MFT the single-particle libron Green's function is given by[16]

$$K^{-1}(k,\omega)=\frac{1}{\overline{\eta}}\begin{pmatrix}\overline{\Lambda}(k,\omega) & -\hat{\Lambda}(k)\\ -\hat{\Lambda}(k+q) & \overline{\Lambda}(k+q,\omega)\end{pmatrix}, \tag{6.1}$$

where

$$\overline{\Lambda}(k,\omega)=\begin{pmatrix}\omega-\nu_k & -\omega_k\\ -\omega_k & -\omega-\nu_k\end{pmatrix}, \tag{6.2}$$

$$\hat{\Lambda}(k)=\begin{pmatrix}\tilde{\Omega}_k & \hat{\Omega}_k\\ \hat{\Omega}_k & \tilde{\Omega}_k\end{pmatrix}. \tag{6.3}$$

The frequencies ν_k, ω_k, $\tilde{\Omega}_k$, and $\hat{\Omega}_k$ are defined by

$$\begin{aligned}\nu_k&\equiv\nu_0(k)+\overline{\eta}\overline{\Pi}_{11}^{\mathrm{MFT}}(k)\\ &=\overline{\eta}\nu_0(k)+(g_0+\lambda_0)\langle\rho_0\rangle+\tfrac{3}{2}\gamma_k\langle n_0\rangle\,,\end{aligned} \tag{6.4}$$

$$\omega_k\equiv\omega_0(k)+\overline{\eta}\,\overline{\Pi}_{12}^{\mathrm{MFT}}(k)=\overline{\eta}\omega_0(k)+\tfrac{3}{2}\gamma_k\langle n_0\rangle\,, \tag{6.5}$$

$$\begin{aligned}\tilde{\Omega}_k&\equiv\overline{\eta}\,\overline{\Pi}_{13}^{\mathrm{MFT}}(k)\\ &=3[\omega_0(k+q)-2\omega_0(q)+\tfrac{1}{2}\gamma_{k+q}]\langle n_q\rangle+(g_q+\lambda_q)\langle\rho_q\rangle\,,\end{aligned} \tag{6.6}$$

$$\hat{\Omega}_k\equiv\overline{\eta}\,\overline{\Pi}_{14}^{\mathrm{MFT}}(k)=-3[\omega_0(k+q)-\tfrac{1}{2}\gamma_{k+q}]\langle n_q\rangle\,. \tag{6.7}$$

The expression for K^{-1} in Eq. (6.1) has the same form as the libron Green's function in Ref. 16. The frequencies in Eqs. (6.4)–(6.7), however, are different from our earlier results,[16] since they contain the dipolar coupling parameters λ and γ.

From Eqs. (6.1)–(6.3), the matrix element $\langle\langle a_{k+q};a_k^\dagger\rangle\rangle$ is given by

$$\langle\langle a_{k+q};a_k^\dagger\rangle\rangle=\overline{\eta}\,\mathfrak{D}(k,\omega)^{-1}\begin{vmatrix}-\omega_k & -\omega-\nu_k & -\tilde{\Omega}_k\\ -\tilde{\Omega}_{k+q} & -\hat{\Omega}_{k+q} & -\omega_{k+q}\\ -\hat{\Omega}_{k+q} & -\tilde{\Omega}_{k+q} & -\omega-\nu_{k+q}\end{vmatrix}, \tag{6.8}$$

where $\mathfrak{D}(k,\omega)$ is the determinant of the matrix on the right-hand side of Eq. (6.1). From Eqs. (3.14) and (6.8), one may determine the half-width Δ of the conduction-band gap. When the gap is small, we may expand the determinants in Eq. (6.8) to order Δ and we have

$$\langle\langle a_{k+q}\,;a_k^\dagger\rangle\rangle$$

$$\simeq \frac{\bar{\eta}}{\mathfrak{D}(k,\omega)}\{(\omega+\nu_k)(\omega+\nu_{k+q})\tilde{\Omega}_{k+q} - \omega_{k+q}[\hat{\Omega}_{k+q}(\omega+\nu_k)-\tilde{\Omega}_{k+q}\omega_k] - \hat{\Omega}_{k+q}\omega_k[\omega+\nu_{k+q}]\}\,, \tag{6.9}$$

where

$$\mathfrak{D}(k,\omega)\simeq(\omega^2-\Omega_k^2)(\omega^2-\Omega_{k+q}^2) \tag{6.10}$$

and

$$\Omega_k=(\nu_k^2-\omega_k^2)^{1/2} \tag{6.11}$$

is the eigenfrequency of the libron mode in the absence of a conduction-electron band gap.

Doing the frequency sums analytically and integrating over the wave vector, Eq. (6.9) gives[16] the following equation:

$$\frac{\bar{\eta}}{N}\sum_k(\Omega_k^2-\Omega_{k+q}^2)^{-1}\left[F(k,\Omega_k)\coth\left(\frac{\Omega_k}{2T_c}\right)-F(k,\Omega_{k+q})\coth\left(\frac{\Omega_{k+q}}{2T_c}\right)\right]=1\,, \tag{6.12}$$

which determines the mean-field Peierls transition temperature T_c. Here

$$F(k,z)=z^{-1}[(z^2+\nu_k\nu_{k+q}+\omega_k\omega_{k+q})\tilde{\theta}_{k+Q} - (\nu_k\omega_{K+q}+\omega_k\nu_{k+q})\hat{\theta}_{k+q}]\,, \tag{6.13}$$

where

$$\tilde{\theta}_k=\tfrac{3}{2}[\omega_0(k+q)-2\omega_0(q)+\tfrac{1}{2}\gamma_{k+q}] - g_q(g_q+\lambda_q)\sum_{k'}\epsilon_{k'}^{-1}\ \tanh\left(\frac{\epsilon_{k'}}{2T_c}\right) \tag{6.14}$$

and

$$\hat{\theta}_k=-\tfrac{3}{2}[\omega_0(k+q)-\tfrac{1}{2}\gamma_{k+q}]\,. \tag{6.15}$$

From Eq. (6.1), one can show that the matrix element $\langle\langle a_k\,;a_k^\dagger\rangle\rangle$ is given by

$$\langle\langle a_k\,;a_k^\dagger\rangle\rangle=\bar{\eta}\,\mathfrak{D}(k,\omega)^{-1}\begin{vmatrix} -\omega-\nu_k & -\hat{\Omega}_k & -\tilde{\Omega}_k \\ -\hat{\Omega}_{k+q} & \omega-\nu_{k+q} & -\omega_{k+q} \\ -\tilde{\Omega}_{k+q} & -\omega_{k+q} & -\omega-\nu_{k+q} \end{vmatrix}\,. \tag{6.16}$$

At T_c, $\Delta=0$ and (6.16) gives

$$\langle\langle a_k\,;a_k^\dagger\rangle\rangle=\bar{\eta}(\omega+\nu_k)/(\omega^2-\Omega_k^2)\,. \tag{6.17}$$

Doing the frequency sums analytically and integrating over k, Eq. (6.17) gives

$$\frac{3\bar{\eta}}{2N}\sum_k\left[\left(\frac{\nu_k}{\Omega_k}\right)\coth\left(\frac{\Omega_k}{2T_c}\right)-1\right]=1-\bar{\eta}\,, \tag{6.18}$$

where we have made use of $\langle n_0\rangle=(1-\bar{\eta})/3$ from Eq. (4.16). Thus $\bar{\eta}$ in Eq. (6.12) must satisfy Eq. (6.18). The essential factors which determine T_c are contained in the expressions (6.12) and (6.18). These are the effective libron-libron interaction, the electron-libron coupling parameters, the libron energy Ω_k, the band structure of the electrons which determines ϵ_k, and the occupation number of the $k=0$ libron modes. One should note that the hyperbolic cotangent rather than tangent enters into the formulas (6.12) and (6.18) because of the bosonlike nature of the libron modes. The coth factors arise from the loss of librons from the Peierls *condensate* through thermal excitation.

We have solved Eqs. (6.12) and (6.18) for T_c and $\bar{\eta}$. We have assumed nearest-neighbor EQQ and EDD interactions on a strand with $\mathcal{J}_k=\mathcal{J}\cos(kc)$ and $\gamma_k=\gamma\cos(kc)$ where c is the lattice spacing. We have also assumed nearest-neighbor hopping of the electrons between the molecules, such that $\epsilon_k=-(W/2)\cos(kc)$ where W is the bandwidth. In Fig. 1, we have plotted T_c as a function of $\mathcal{J}$, W, g_q, and g_0. In these plots, we have set both the dipole-dipole interaction γ and the electron-dipole interaction λ equal to zero so as to isolate the contributions from the quadrupoles. We have done calculations with finite values of γ and λ and found that their effect is to reduce the Peierls critical temperature. In Fig. 2, we have plotted T_c and $\bar{\eta}$ as a function of $\mathcal{J}$; in Fig. 2(b), the effect of increasing λ_0 is illustrated. Calculation shows that T_c is more sensitive to changes in λ_0 than it is to λ_q and γ.

The Peierls condensate is formed from the macroscopic occupancy of the states of vectors k and $k\pm q$. The gap parameter comes from the interaction of the electrons with the librons and it is this interaction which distorts the lattice. At low temperatures, most of the librons are in the condensate. As the temperature increases, some of them are thermally excited from the condensate. The dependence of T_c on g_q is like the exponential variation of the Peierls transition temperature with the electron-phonon coupling in Fröhlich's Hamiltonian with only two (zone-boundary) phonon modes. Figure 1(c) shows that there is an upper and a lower *cutoff* limit in the range of values of g_q for which there is a T_c. Comparing Fig. 1(c) with Fig. 1(d), we find that T_c depends quite differently on the Fourier components g_0 and g_q.

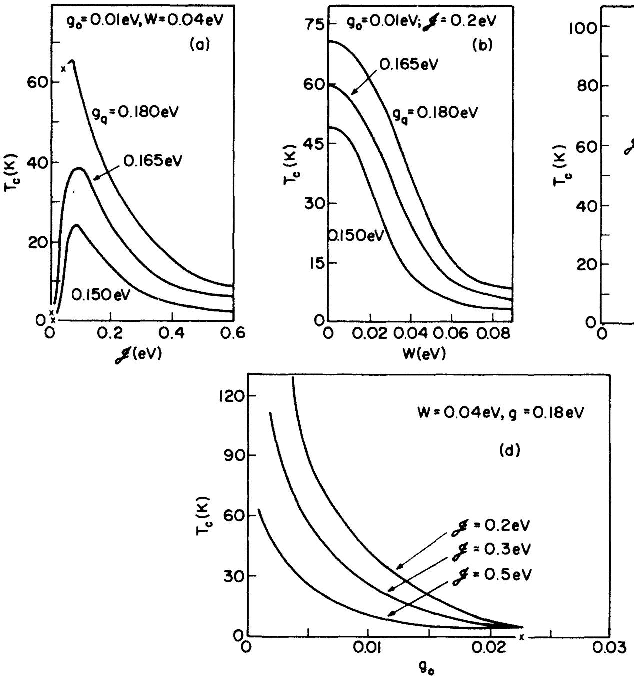

FIG. 1. Mean-field Peierls transition temperature T_c as a function of (a) the isotropic quadrupole-quadrupole coupling $\mathcal{J}$, (b) the conduction electron bandwidth W and the Fourier components, (c) g_q and (d) g_0 of the coupling of the conduction band to the quadrupole moments. The dipole-dipole and electron-dipole interaction parameters are equal to zero.

VII. THE ELECTRICAL CONDUCTIVITY FOR A STRAND

The results of Secs. III and VI enable us to obtain the electrical conductivity of a one-dimensional conductor which we describe by the simple but nontrivial Hamiltonian in Secs. I and II. The conductivity is obtained from the single-particle electron and libron Green's functions as we discuss in this section.

We begin by quoting Kubo's formula for the complex dc-conductivity tensor in the absence of a magnetic field[35]:

$$\sigma_{\mu\nu}(k,\omega)=\int_0^\infty dt\, e^{i\omega t}\int_0^{1/T} d\lambda\langle j_\nu(k,-i\lambda)j_\mu(-k,t)\rangle\,. \tag{7.1}$$

Here k is the wave vector of the electromagnetic field, ω its frequency, and j is the current-density operator. One can show quite easily that Eq. (7.1) may be rewritten as

$$\sigma_{\mu\nu}(k,\omega)=\left(\frac{e}{m}\right)^2\sum_{pp'} p_\nu p'_\mu D^{\sigma\sigma'}_{p'p}(k,\omega)\ , \tag{7.2}$$

where $-e$ and m are the charge and mass of the electron, p and p' are the momenta of the electrons, and

$$D^{\sigma\sigma'}_{p'p}(k,\omega)=\int_0^\infty dt\, e^{i(\omega+io^+)t}D^{\sigma\sigma'}_{p'p}(k,t)\,, \tag{7.3}$$

with

$$D^{\sigma\sigma'}_{p'p}(k,t)=\int_0^{1/T} d\lambda\langle\rho_{p\sigma}(k,-t-i\lambda)\rho_{p'\sigma'}(-k,0)\rangle\,. \tag{7.4}$$

In Eq. (7.4), we have defined

$$\rho_{p\sigma}(k,t)=e^{i\mathcal{H}t}\alpha^\dagger_{p-k\sigma/2}\alpha_{p+k\sigma/2}e^{-i\mathcal{H}t}\ . \tag{7.5}$$

But, after integrating Eq. (7.3) by parts, we have

$$D^{\sigma\sigma'}_{pp'}(k,\omega)=[\mathcal{a}^R_{pp'}(k,\omega)-\mathcal{a}_{pp'}(k,0)]/i\omega, \tag{7.6}$$

where

$$\mathcal{a}^R_{pp'}(k,\omega)=\int_{-\infty}^\infty dt\, e^{i\omega t}\,\hat{\mathcal{a}}^R_{pp'}(k,t) \tag{7.7}$$

and

$$\hat{\mathcal{a}}^R_{pp'}(k,t)=-\theta(t)\frac{\partial}{\partial t}D^{\sigma\sigma'}_{pp'}(k,t)\ . \tag{7.8}$$

$\mathcal{a}_{pp'}(k,0)$ is the zero-frequency component of

$$\mathcal{a}_{pp'}(k,\omega_n)=\int_0^{1/T} d\lambda\, e^{i\omega_n\lambda}\,\hat{\mathcal{a}}_{pp'}(k,\lambda), \tag{7.9}$$

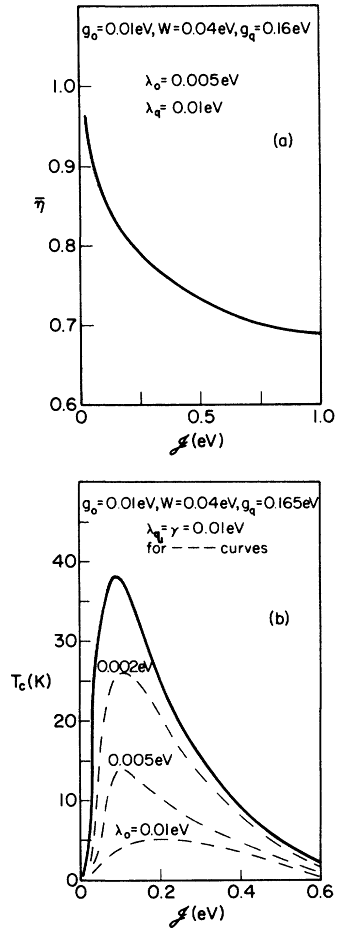

FIG. 2. (a) The alignment parameter $\bar{\eta}$ and (b) Peierls transition temperature T_c as a function of the isotropic quadrupole-quadrupole interaction $\mathcal{J}$ within the mean-field approximation. The broken curves in (b) show the effect of the electron-dipole and dipole-dipole interactions on the solid curve for which γ and λ are equal to zero.

where $\omega_n = 2n\pi T$, $n = 0, \pm 1, \pm 2, \ldots,$

$$\hat{\mathfrak{a}}_{pp'}(k,\lambda) = \langle \hat{T}[\rho_{p'\sigma'}(k)]_\lambda [\rho_{p\sigma}(-k,0)]_0 \rangle , \tag{7.10}$$

and $[\rho]_\lambda = e^{\lambda \mathcal{K}} \rho e^{-\lambda \mathcal{K}}$. One can show that $\hat{\mathfrak{a}}^R_{pp'}(k,t)$ in Eq. (7.8) can be expressed as a retarded Green's function:

$$\hat{\mathfrak{a}}^R_{pp'}(k,t) = i\theta(t)\langle [\rho_{p'\sigma'}(k,-t), \rho_{p\sigma}(-k,0)]\rangle , \tag{7.11}$$

whose Fourier transform $\mathfrak{a}^R_{pp'}(k,\omega)$ is the analytic continuation of $\mathfrak{a}_{pp'}(k,\omega)$ from the imaginary- to the real-frequency axis.

We have thus cast the expression for the electrical conductivity in Eq. (7.1) into a form which is suitable for evaluation using diagrammatic methods. The Eqs. (7.2)–(7.11) were derived by

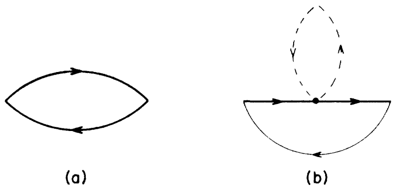

FIG. 3. Diagrams giving (a) the single-particle and (b) the collective parts of the conductivity. An electron Green's function is denoted by a continuous line and a libron Green's function by a broken line.

Perel' and Éliashberg,[36] but are rederived here so as to establish the notation. In the long-wavelength limit, we have for $\sigma(\omega) \equiv \sigma(\omega, k=0)$ in the case of a linear conductor with a half-filled tight-binding band

$$\sigma(\omega) = \frac{e^2 v_F^2}{i\omega} [\mathfrak{a}^R(\omega) - \mathfrak{a}(0)] , \tag{7.12}$$

where

$$\mathfrak{a}^R(\omega) = \sum_{pp'\sigma\sigma'} \mathfrak{a}^R_{pp'}(0,\omega) . \tag{7.13}$$

$\mathfrak{a}(0)$ is obtained from $\mathfrak{a}_{pp'}(0,0)$ by summing over p, p' and σ, σ'. In Eq. (7.12), the unperturbed electron energy near the Fermi level is approximated by $\epsilon_k = v_F(|k| - k_F)$ where v_F and k_F are the Fermi velocity and wave vector, respectively.

The single-particle contribution to $\mathfrak{a}^R(\omega)$ corresponds to the diagram in Fig. 3(a). This contribution, which we denote by $\mathfrak{a}^{0,R}(\omega)$, is given by

$$\begin{aligned} \mathfrak{a}^{0,R}(\omega) = \frac{1}{N} \sum_{k\nu} [& \mathcal{G}_{11}(k,\nu)\mathcal{G}_{11}(k,\nu+\omega) \\ & + \mathcal{G}_{22}(k,\nu)\mathcal{G}_{22}(k,\nu+\omega) \\ & + \mathcal{G}_{12}(k,\nu)\mathcal{G}_{21}(k,\nu+\omega)] , \end{aligned} \tag{7.14}$$

where $\mathcal{G}_{ij}(k,\omega)$ are the matrix elements of the single-particle electron Green's function in Eq. (3.10). Substituting the mean-field results from Eq. (3.12) into Eq. (7.14) and doing the frequency sum over ν, we obtain

$$\mathfrak{a}^{0,R}(\omega) = \frac{1}{N} \sum_k \tanh\left(\frac{\xi_k}{2T}\right) \left(\frac{\Delta^2/\xi_k}{\omega^2 - 4\xi_k^2}\right) , \tag{7.15}$$

where $\xi_k = \mathrm{sgn}(\epsilon_k)(\epsilon_k^2 + \Delta^2)^{1/2}$. As expected, the single-particle contribution to $\sigma(\omega)$ has the same form at $T = 0$ K as that obtained by Lee, Rice, and Anderson[37] using Fröhlich's Hamiltonian.

Collective contributions to the dc conductivity are associated with oscillations in the charge and lattice distortions about their equilibrium values. They are optically active along the chain direction since they involve a displacement of condensed charge. A diagram which arises from the phase oscillations is shown in Fig. 3(b). The sum of these diagrams gives $\sigma_c(\omega)$, the collective part of $\sigma(\omega)$. The electron lines are the elements of the Green's function matrix obtained by inverting Eq. (3.12) while the libron lines correspond to the averages $\overline{\eta}$ and Δ. Using the notation $\mathcal{G}_{ij}(k,\nu) = \mathcal{G}_{ij}(\nu)$, we find

$$\begin{aligned}\mathcal{A}^{c,R}(\omega) = g_0\overline{\eta}\sum_{k\nu}\{&\mathcal{G}_{11}(\nu)[\mathcal{G}_{11}(\nu)\mathcal{G}_{11}(\nu-\omega)+\mathcal{G}_{12}(\nu)\mathcal{G}_{21}(\nu-\omega)]+\mathcal{G}_{21}(\nu)[\mathcal{G}_{11}(\nu)\mathcal{G}_{12}(\nu-\omega)+\mathcal{G}_{12}(\nu)\mathcal{G}_{22}(\nu-\omega)]\}\\ +g_q\Delta\sum_{k\nu}\{&\mathcal{G}_{11}(\nu)[\mathcal{G}_{21}(\nu)\mathcal{G}_{11}(\nu-\omega)+\mathcal{G}_{22}(\nu)\mathcal{G}_{21}(\nu-\omega)]\\ &+\mathcal{G}_{21}(\nu)[\mathcal{G}_{21}(\nu)\mathcal{G}_{12}(\nu-\omega)+\mathcal{G}_{22}(\nu)\mathcal{G}_{22}(\nu-\omega)]\}.\end{aligned} \tag{7.16}$$

Simplifying Eq. (7.16), we obtain the collective part of $\mathcal{A}^R(\omega)$ to be

$$\mathcal{A}^{c,R}(\omega) = \frac{1}{T}\sum_k \frac{f(\xi_k)f(-\xi_k)}{\omega+2\xi_k}\left(g_0\overline{\eta}+\frac{\Delta^2}{\xi_k}\right), \tag{7.17}$$

where $f(\xi)$ is the Fermi-Dirac function. It is straightforward to show that $\mathcal{A}^{c,R}$ vanishes at zero temperature. But for the Fröhlich Hamiltonian with electron-phonon interactions the collective contribution to $\sigma(\omega)$ is not frozen out at $T=0$ K.[37,38] This result illustrates the quantitative difference between an orientational and translational Peierls instability for a one-dimensional stack of molecules. Substituting the results in Eqs. (7.15) and (7.17) into Eq. (7.12), we obtain as the total conductivity $\sigma(\omega)=\sigma_0(\omega)+\sigma_c(\omega)$:

$$\sigma(\omega) = e^2 v_F^2[\mathcal{C}(\omega)-\mathcal{C}(0)]/i\omega, \tag{7.18}$$

where

$$\begin{aligned}\mathcal{C}(\omega) = &\frac{1}{N}\sum_k \frac{\Delta^2/\xi_k}{\omega+2\xi_k}\left(\frac{\tanh(\xi_k/2T)}{\omega-2\xi_k}+\frac{1}{T}f(\xi_k)f(-\xi_k)\right)\\ &+\frac{g_0\overline{\eta}}{T}\frac{1}{N}\sum_k\frac{f(\xi_k)f(-\xi_k)}{\omega+2\xi_k}.\end{aligned} \tag{7.19}$$

It would be instructive to supplement this section with numerical calculations of $\sigma(\omega)$ for a one-dimensional conductor which undergoes a Peierls distortion commensurate with the lattice. Moreso, it would be interesting to see if $\sigma(\omega)$ is peaked or has broad maxima in our parameter space. We feel that because Eq. (7.17) involves a product of Fermi factors, $\sigma_c(\omega)$ might be more strongly temperature dependent for our model than for the one described by the Fröhlich Hamiltonian. However, because of the work involved in evaluating the gap and alignment parameters numerically, we shall report the results of this calculation separately.

VIII. CONCLUDING REMARKS

We have done calculations for a model of one-dimensional conductors, based on the multipole expansion of the electrostatic interaction between a pair of charge distributions. The isotropic EQQ and EDD interactions do not give rise to long-range order in one or two dimensions, as can be proven from general mathematical theorems.[26] However, the coupling of the conduction band of the electrons to the librational motion of the molecules gives rise to anisotropic effects which produce an orientational Peierls distortion. The numerical results of Sec. VI show the dependence of the Peierls transition temperature on the variables spanning the parameter space. These results suggest that for a one-dimensional conductor to have an orientational Peierls transition at finite temperature it is crucial that certain molecular features such as the strength of the electron coupling to the rotations of the molecules have to be carefully designed.

In our model with spin $S=1$ molecules, the quadrupolar coupling to the conduction band produces the band gap Δ. The dipolar terms just renormalize the value of T_c. For some solids where the intrinsic spin of the molecules is not $S=1$, the dipolar coupling to the conduction electrons is the dominant one and may produce the band gap. This calculation is being done and the results will be published later.

The cylindrical symmetry of the charge distribution was assumed for convenience so that there is only one parameter which describes the rotational ordering of the molecules. This is equivalent to the use of a diagonal density matrix. An interesting though complicated problem to follow up would be the use of a nondiagonal density matrix which takes account of the multiplicity of order-disorder phase transition in the conductor.

We may resolve Eq. (6.17) into partial fractions which we write as

$$\begin{aligned}\langle\langle a_k; a_k^\dagger\rangle\rangle = \overline{\eta}^2\Bigg(&\frac{u_k^{(1)2}}{\omega-\Omega_k^{(1)}}+\frac{v_k^{(1)2}}{\omega-\Omega_k^{(2)}}\\ &+\frac{r_k^{(1)2}}{\omega-\Omega_k^{(3)}}+\frac{s_k^{(1)2}}{\omega-\Omega_k^{(4)}}\Bigg),\end{aligned} \tag{8.1}$$

where $\Omega_k^{(i)}$ are the four roots of the equation $\mathfrak{D}(k,\omega)=0$. The Green's functions $\langle\langle b_k; b_k^\dagger\rangle\rangle$, $\langle\langle a_{k+q}; a_{k+q}^\dagger\rangle\rangle$, and $\langle\langle b_{k+q}; b_{k+q}^\dagger\rangle\rangle$ may also be written in terms of fractions with a set of coefficients $\{u_k^{(i)2}, v_k^{(i)2}, r_k^{(i)2}, s_k^{(i)2}\}$ where $i=2,3,4$, respectively, replacing those in Eq. (8.1). These coefficients satisfy the relation

$$u_k^{(i)2}+v_k^{(i)2}+r_k^{(i)2}+s_k^{(i)2}=1/\overline{\eta}\ . \tag{8.2}$$

We define a set of operators $\hat{\xi}_k^{(i)}$ in terms of the Peierls quadruplet $\{\psi_i\}\equiv\{a_k, b_k, a_{k+q}, b_{k+q}\}$ through the transformation

$$\psi_i=\overline{\eta}(u_k^{(i)}\hat{\xi}_k^{(1)}+v_k^{(i)}\hat{\xi}_k^{(2)}+r_k^{(i)}\hat{\xi}_k^{(3)}+s_k^{(i)}\hat{\xi}_k^{(4)})\ . \tag{8.3}$$

We also define a set of operators $c_{k\sigma}$ through the relation

$$c_{k\sigma}=\zeta_k^{(1)}\alpha_{k\sigma}+\zeta^{(2)}\alpha_{k+q\sigma}\ , \tag{8.4}$$

where

$$\zeta_k^{(1)2}=\frac{\epsilon_k-E_k^-}{E_k^+-E_k^-}\ ,\quad \zeta_k^{(2)2}=\frac{\epsilon_{k+q}-E_k^-}{E_k^+-E_k^-}\ , \tag{8.5}$$

with $E_k^\pm$ defined in Eq. (3.13). It is straightforward to show that $\hat{\xi}_k^{(i)}$ and $c_{k\sigma}$ diagonalize the effective Hamiltonian

$$\begin{aligned}\mathcal{H}_{\text{eff}}=&\sum_{k\sigma}\epsilon_k\alpha_{k\sigma}^\dagger\alpha_{k\sigma}+\Delta\sum_{k\sigma}\alpha_{k\sigma}^\dagger\alpha_{k+q\sigma}\\&+\sum_k[\nu_k(a_k^\dagger a_k+b_k^\dagger b_k)+\omega_k(a_{-k}b_k+a_k^\dagger b_{-k}^\dagger)+\tilde{\Omega}_k(b_k^\dagger b_{k+q}+a_{-k}a_{-k+q}^\dagger)+\tilde{\Omega}_k(b_k^\dagger a_{-k+q}^\dagger+a_{-k}b_{k+q})]\ ,\end{aligned} \tag{8.6}$$

provided

$$[\hat{\xi}_k^{(i)}, \hat{\xi}_{k'}^{(j)\dagger}]=\delta_{ij}\,\delta_{kk'}\ , \tag{8.7}$$

and the exact commutation relations for a_k and b_k are *approximated* by

$$[a_k, a_{k'}^\dagger]=[b_k, b_{k'}^\dagger]=\overline{\eta}\delta_{kk'}\ , \tag{8.8}$$

$$[a_k, b_{k'}^\dagger]=0\ . \tag{8.9}$$

From the Bogoliubov transformations, we can calculate the ground-state energy. We may also use them to include the frequency-dependent contribution to the self-energy.[34]

In conclusion, we would like to emphasize the following. Librons are quantum-mechanical elementary excitations which should not be confused with the classical rigid rotations of the molecules about their centers of mass. Each eigenstate of the molecules is determined by the two-body forces arising from the molecule-molecule and electron-molecule interactions. Basic to our calculation, like several others in the literature,[21,22,32] is that for weakly interacting systems $S=1$ can be taken as nearly a good quantum number.

The coupling between the rotations of the molecules and the conduction electrons, the $\mathcal{H}_{cQ}$ term of the Hamiltonian in Eq. (1.6a), is quadratic in the pseudospin operators a_i, b_i and their Hermitian conjugates. The Hamiltonian used by Gutfreund and Weger[10] is also quadratic in the displacement operators of the molecules from their equilibrium positions. However, while our Hamiltonian is applicable to systems in which the molecules can rotate freely about their centers of mass, the Hamiltonian used in Ref. 10 Taylor expands about a specific direction of the molecules. Our theory should apply to materials, like liquid crystals or some other solids, where free rotations are possible. If the Peierls transition temperature is close to its mean-field value, then the parameters entering the problem must satisfy the two equations (6.12) and (6.18). This is the criterion for the theory to be used in a particular case. With more calculations being done, we hope to find that our theory is suitable for some specific charge-transfer complexes or other related systems.

We feel that this paper gives interesting results for the effects of the rotations of the molecules on the conduction electron spectrum. We hope that these results will encourage experimental studies on quasi-one-dimensional conductors so as to shed some light on our understanding of these materials.

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