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Amplitude mode formalism for conjugated polymers and collective coordinate method for non-linear excitations

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Abstract. The collective coordinate method is introduced to the amplitude mode formalism for *trans*-polyacetylene in order to describe the motions of non-linear excitations, such as a soliton or a polaron. Using the explicit normal-mode solutions of lattice vibrations around the excitations, we define the Lagrangian coordinates of the excitations and the normal modes. The Hamiltonian is rewritten in terms of these coordinates and conjugate momenta. The result is a straightforward generalisation of single-component non-linear models.

1. Introduction

Ever since it was found that some non-linear models have stable and localised particular solutions, extensive studies were carried out to find what meanings these solutions have and how they can be used in quantum theory. In the arguments, it was realised that an excitation always arises without any additional energy. It is associated with the breakdown of the translational invariance due to the localised solution and is called the Goldstone mode. The Goldstone mode is sometimes cumbersome, particularly in statistical mechanics. To overcome this, the collective coordinate method was introduced (Gervais and Sakita 1975; Tomboulis 1975; Gervais and Jevicki 1976). Instead of the Goldstone mode, the coordinate of the non-linear excitation is defined. Since it increases the total degrees of freedom, there should be a constraint. This is met by the requirement that the fluctuation around the excitation is orthogonal to the Goldstone mode. This requirement, in turn, determines the collective coordinate. The collective coordinate method works particularly well when the excitation moves slowly. When it moves quickly, we have to take account of other effects, such as Lorentz contraction and so on, which make discussions less perspicuous. It was remarkable that Tomboulis showed that these new variables are obtainable by means of a canonical transformation from the original field variables (Tomboulis 1975, Tomboulis and Woo 1976). This was of great help in establishing the statistical mechanics.

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The collective coordinate method was first developed for the simple mathematical models such as sine–Gordon and φ^4 models. On the other hand, we now have several materials which would have non-linear excitations as solitons, polarons, and breathers. Each of them corresponds to the stable and localised particular solution. *Trans*-polyacetylene is the material most likely to have such excitations today. It has more complicated structures than the simple mathematical models. It is composed of both electrons and lattice. The lattice is dimerised, since it is predominantly one dimensional. The dimerisation has two patterns which give doubly degenerate ground states. When the two patterns arise at the same time, the boundary between the two gives the soliton. In addition, we can have the polaron which modulates the pattern locally. A simple but quite effective model was proposed by Su, Schrieffer and Heeger (SSH), in which the electrons interact with one type of lattice vibrations (Su *et al* 1979, 1980). It was immediately pointed out by Takayama *et al* (1980) that the SSH model could be reduced to a continuum model, since the soliton extends over a region of many lattice constants. This continuum (TLM) model has made an analytical approach more feasible. Since then, the physics of polyacetylene has been extensively studied experimentally as well as theoretically.

Optical studies have given one of the most interesting results. Particularly, the infrared absorption and the Raman scattering have shown that polyacetylene has more complicated lattice vibrations than the SSH model. Horovitz (1982) pointed out that we can understand the experimental facts with the help of the SSH model, if three types of lattice vibrations are taken into account, instead of only one. His theory is called 'amplitude mode formalism'. Melé and Hicks (1985) later showed that the amplitude mode formalism can be incorporated into the TLM model, if the latter is slightly generalised. The generalisation is indispensable in quantitative discussions of relevant properties of polyacetylene.

It has been realised that the collective coordinate method is straightforwardly applicable to the TLM model (Ogata *et al* 1986, 1987, Kunz 1986). The application needs no change from the simple mathematical models, if we can use an adiabatic approximation for the electrons. The electrons instantaneously follow the motions of the lattice. This is the case in polyacetylene, since the electronic energy gap is much larger than the phonon frequencies. With the help of the collective coordinate method, soliton–phonon interactions have been studied, as have the possible diffusive motions of the soliton.

It is, therefore, desirable to write the amplitude mode formalism in terms of the language of the collective coordinate method. This is the purpose of the present paper. Since we know the complete sets of eigenfunctions for the lattice vibrations either around the soliton or the polaron, we make use of them. The constraint, that compensates for the increased degree of freedom, is easily satisfied. The discussions, then, follow the most elementary way of introducing Lagrangian coordinates. The commutation relations and the Hamiltonian are given in forms free from the eigenfunctions of the lattice vibrations. The results turn out to be the straightforward generalisation of the single-component TLM model.

We review the amplitude mode formalism in § 2, in the terminology of Melé and Hicks (1985). In § 3, the collective coordinate is introduced as one of the Lagrangian coordinates. The conjugate momenta are defined. The Hamiltonian is written in terms of them. In § 4, the discussions are summarised and possible applications are pointed out.

2. Amplitude mode formalism

The single-component TLM model has the Hamiltonian (Takayama *et al* 1980)

$$H_{\mathrm{TLM}} = \frac{1}{2\pi v_{\mathrm{F}}\lambda}\int \mathrm{d}x \left[\frac{1}{\omega_{\mathrm{Q}}^2}\dot{\Delta}(x)^2 + \Delta^2(x)\right] + \sum_s \int \mathrm{d}x\, \psi_s^+(x)[-\mathrm{i}v_{\mathrm{F}}\sigma_3\partial_x + \sigma_1\Delta(x)]\psi_s(x) \tag{2.1}$$

where v_{F} is the Fermi velocity, λ the electron–phonon coupling constant, $\Delta(x)$ is the order parameter which represents the degree of dimerisation, ω_{Q} the bare optical phonon frequency. The electron fields, ψ_s^+ and ψ_s, are in the form of spinors, the first and second components being associated with the right-and left-going waves, respectively. The suffix s indicates the spin. The quantities σ_3 and σ_1 are the Pauli matrices. Here, we have a single field $\Delta(x)$ for the optical phonons.

In order to have the amplitude mode formalism, Melé and Hicks (1985) generalised H_{TLM} into

$$H = \sum_{\alpha=1}^{3} \frac{1}{2\pi v_{\mathrm{F}}\lambda_\alpha}\int \mathrm{d}x\left(\frac{1}{\omega_\alpha^2}\dot{\Delta}_\alpha^2(x) + \Delta_\alpha^2(x)\right) + \sum_s \int \mathrm{d}x\, \psi_s^+(x)[-\mathrm{i}v_{\mathrm{F}}\sigma_3\partial_x + \sigma_1\Delta(x)]\psi_s(x) \tag{2.2}$$

where the three types of phonon fields $\Delta_\alpha(x)$ are taken into account, λ_α being the coupling constant of the αth phonon with the bare frequency ω_α, and $\Delta(x)$ is defined by

$$\Delta(x) = \sum_{\alpha=1}^{3} \Delta_\alpha(x). \tag{2.3}$$

It is well known that the TLM model, (2.1), has a static soliton solution

$$\Delta_s(x) = \Delta_0 \tanh(x/\xi_0) \tag{2.4}$$

with $\xi_0 = v_{\mathrm{F}}/\Delta_0$. Then, the Hamiltonian (2.2) gives a static solution

$$\bar{\Delta}_\alpha(x) = (\lambda_\alpha/\lambda)\Delta_s(x) \tag{2.5}$$

where

$$\lambda = \sum_{\alpha=1}^{3} \lambda_\alpha. \tag{2.6}$$

In the TLM model phonons around the soliton are introduced as small deviations from the static solution

$$\delta\Delta(x) = \Delta(x) - \Delta_s(x). \tag{2.7}$$

Linearisations of equations of motion with respect to $\delta\Delta(x)$ and small deviations of

electronic wavefunctions give an eigenvalue equation which determines phonon normal modes. It takes the form (Ito *et al* 1984, Terai *et al* 1985, Hicks and Blaisdell 1985)

$$\left(1 - \frac{\Omega_i^2}{\omega_Q^2}\right) g_i(x) = \frac{\lambda}{2} \int \mathrm{d}y\, K(x, y) g_i(y) \tag{2.8}$$

where Ω_i^2 is the eigenvalue and $K(x, y)$ is defined in terms of electronic wavefunctions $\psi_n^{(0)}(x)$ with eigenvalues ε_n in the TLM model. It is given by

$$K(x, y) = -2\pi v_F \sum_{n,s}{}' \sum_{m}{}'' \frac{\psi_n^{(0)+}(x)\sigma_1 \psi_m^{(0)}(x)\psi_m^{(0)+}(y)\sigma_1 \psi_n(y)}{\varepsilon_n - \varepsilon_m} + \text{CC} \qquad \text{etc} \tag{2.9}$$

where the prime and double prime indicate summations over the occupied and unoccupied states, respectively. The eigenvalue problem (2.8) is solved numerically. We have detailed knowledge of Ω_i and $g_i(x)$ (Ono *et al* 1986, Terai and Ono 1986, Sun *et al* 1985, Chao and Wang 1985).

For convenience later on, we change the notation, introducing

$$\tilde{\Delta}_\alpha(x) = (\lambda/\lambda_\alpha)^{1/2}(\omega_0/\omega_\alpha)\Delta_\alpha(x) \tag{2.10}$$

where

$$\omega_0^2 = 2\lambda\omega_Q^2. \tag{2.11}$$

The Hamiltonian (2.2) becomes

$$H = \sum_{\alpha=1}^{3} (2\pi v_F \lambda \omega_0^2)^{-1} \int \mathrm{d}x (\dot{\tilde{\Delta}}_\alpha^2(x) + \omega_\alpha^2 \tilde{\Delta}_\alpha^2(x)) + \sum_s \int \mathrm{d}x\, \psi_s^+(x)[-\mathrm{i}v_F\sigma_3\partial_x + \sigma_1\Delta(x)]\psi_s(x) \tag{2.12}$$

while equation (2.3) gives

$$\Delta(x) = \sum_{\alpha=1}^{3} \left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2} \left(\frac{\omega_\alpha}{\omega_0}\right) \tilde{\Delta}_\alpha(x). \tag{2.13}$$

3. Collective coordinate method

The Hamiltonian (2.12) can be obtained, if a corresponding Lagrangian is given. It is written

$$L = \sum_{\alpha=1}^{3} \frac{m}{2} \int \mathrm{d}x [\dot{\tilde{\Delta}}_\alpha^2(x) - \omega_\alpha^2 \tilde{\Delta}_\alpha^2(x)] + \sum_s \int \mathrm{d}x \{\mathrm{i}\psi_s^+(x)\dot{\psi}_s(x) + \psi_s^+(x)[\mathrm{i}v_F\sigma_3\partial_x - \sigma_1\Delta(x)]\psi_s(x)\} \tag{3.1}$$

where $m = (\pi v_F \lambda \omega_0^2)^{-1}$. The collective coordinate method begins in writing

$$\begin{aligned}\tilde{\Delta}_\alpha(x, t) &= (\lambda/\lambda_\alpha)^{1/2}(\omega_0/\omega_\alpha)\bar{\Delta}_\alpha(x - Q_0(t)) + \chi_\alpha(x - Q_0(t), t) \\ &= \left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2} (\omega_0/\omega_\alpha)\Delta_s(x - Q_0(t)) + \chi_\alpha(x - Q_0(t), t)\end{aligned} \tag{3.2}$$

where the first term is due to the slowly moving soliton. It is at location $Q_0(t)$ at time t. The second term χ_α is any deviation from the soliton. The variable $Q_0(t)$ is the soliton coordinate. It is called the collective coordinate.

Since we have increased the degrees of freedom by introducing $Q_0(t)$, the function χ_α has to satisfy a constraint. The constraint is the requirement that χ_α does not involve the Goldstone mode. The Goldstone mode is a phonon normal mode with zero frequency. Since the translational invariance is broken by the soliton, there is such a zero-frequency mode. Excitation of the Goldstone mode leads to a translation of the soliton, which needs no extra energy. In the collective coordinate method, however, the soliton translation is given by the change in $Q_0(t)$. Thus, the Goldstone mode should not be included in χ_α. We shall show that the constraint is given by

$$\sum_\alpha \int \mathrm{d}x \left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2} \left(\frac{\omega_0}{\omega_\alpha}\right) \frac{\partial \Delta_s(x - Q_0(t))}{\partial x} \chi_\alpha(x - Q_0(t), t) = 0. \tag{3.3}$$

Phonon normal modes are studied in the amplitude mode formalism with the help of (2.8) and (2.9) (Terai *et al* 1986b, Hicks and Melé 1986). The two parameters ω_Q^2 and λ are replaced by ω_α^2 and λ_α, and there is a summation over α on the right hand side of (2.8). We immediately obtain an equation for $\chi_\alpha(x, t) \sim \mathrm{e}^{-\mathrm{i}\omega t}\chi_\alpha(x, \omega)$

$$(\omega_\alpha^2 - \omega^2)\chi_\alpha(x, \omega) = \sum_{\alpha'} [(\lambda_\alpha \lambda_{\alpha'})^{1/2}/2]\omega_\alpha \omega_{\alpha'} \int \mathrm{d}y\, K(x, y)\chi_{\alpha'}(y, \omega). \tag{3.4}$$

Here, the soliton is assumed to be static and at $Q_0(t) = 0$. The eigenvalue ω^2 depends on two indices i and j, i being an index classifying x-dependence and j classifying α-dependence. If we write the eigenfunction with the eigenvalue $\omega^2 = \omega_{ij}^2$ as $\varphi_\alpha(x, \omega_{ij})$, it is given by

$$\varphi_\alpha(x, \omega_{ij}) = c_\alpha(\omega_{ij}) g_i(x) \tag{3.5}$$

where $c_\alpha(\omega_{ij})$ is defined by

$$c_\alpha(\omega_{ij}) = \left(\sum_{\alpha=1}^{3} \frac{\lambda_\alpha \omega_\alpha^2}{(\omega_\alpha^2 - \omega_{ij}^2)^2}\right)^{-1/2} \frac{\lambda_\alpha^{1/2}\omega_\alpha}{\omega_\alpha^2 - \omega_{ij}^2}. \tag{3.6}$$

Substitution of (3.5) into (3.4) gives

$$1 = \left(1 - \frac{\Omega_i^2}{\omega_Q^2}\right) \sum_{\alpha=1}^{3} \frac{\lambda_\alpha}{\lambda} \frac{\omega_\alpha^2}{(\omega_\alpha^2 - \omega_{ij}^2)}. \tag{3.7}$$

For each Ω_i^2, equation (3.7) gives ω_{i0}^2, ω_{i1}^2, and ω_{i2}^2. With the help of (3.4), we obtain

$$(\omega_{ij}^2 - \omega_{ik}^2) \sum_\alpha \int \mathrm{d}x\, \varphi_\alpha^*(x, \omega_{ij})\varphi_\alpha(x, \omega_{ik}) = 0 \tag{3.8}$$

where φ_α^* is the complex conjugate of φ_α. Since the functions $g_i(x)$ form a complete orthonormal set, the orthonormalisation condition is given by

$$\sum_\alpha \int \mathrm{d}x\, \varphi_\alpha^*(x, \omega_{ij})\varphi_\alpha(x, \omega_{kl}) = \delta_{ik}\delta_{jl}. \tag{3.9}$$

It is known that equation (2.8) has a normal mode with zero frequency $\Omega_0 = 0$. Equation (3.7), then, gives an eigenvalue which vanishes

$$\omega_{00} = 0. \tag{3.10}$$

The corresponding eigenfunction is given, with the help of (3.5),

$$\varphi_\alpha(x, \omega_{00}) = (\lambda_\alpha^{1/2}/\omega_\alpha)cg_0(x) = (\sqrt{3}\lambda_\alpha^{1/2}\xi_0^{1/2}c/2\omega_\alpha\Delta_0)\partial\Delta_s(x)/\partial x \tag{3.11}$$

where $c = (\sum_{\alpha=1}^{3} \lambda_\alpha/\omega_\alpha^2)^{-1/2}$. Equations (3.9) and (3.11) show that equation (3.3) is the constraint that χ_α has to satisfy.

The constraint is easily satisfied, if we make use of the phonon eigenmodes (3.5). The function χ_α is written

$$\chi_\alpha(x - Q_0(t), t) = \sum_{ij}{}' Q_{ij}(t)\varphi_\alpha(x - Q_0(t), \omega_{ij}) \tag{3.12}$$

where the prime indicates that the sum does *not* include the term with $i = j = 0$. The variables $Q_0(t)$ and $Q_{ij}(t)$ are the Lagrangian coordinates.

Substitution into (3.1) gives

$$\begin{aligned} L = \frac{m}{2}\sum_{\alpha=1}^{3}\int \mathrm{d}x \Bigg\{ \Bigg[-\dot{Q}_0\left(\left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2}\frac{\omega_0}{\omega_\alpha}\frac{\partial\Delta_s}{\partial x} + \frac{\partial\chi_\alpha}{\partial x}\right) + \sum_{ij}{}' \dot{Q}_{ij}\varphi_\alpha(\omega_{ij}) \Bigg]^2 \\ - \omega_\alpha^2\left[\left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2}\frac{\omega_0}{\omega_\alpha}\Delta_s + \chi_\alpha\right]^2 \Bigg\} \\ + \sum_s \int \mathrm{d}x \left(-\mathrm{i}\dot{Q}_0\psi_s^+\frac{\partial\psi_s}{\partial x} + \mathrm{i}\psi_s^+\frac{\partial\psi_s}{\partial t} + \psi_s^+(\mathrm{i}v_F\sigma_3\partial_x - \sigma_1\Delta)\psi_s \right). \end{aligned} \tag{3.13}$$

The electron fields also depend on the collective coordinate as $\psi_s(x - Q_0(t), t)$.

Conjugate momenta are found to be

$$\begin{aligned} P_0 = \frac{\partial L}{\partial \dot{Q}_0} = \dot{Q}_0\left(M + 2\xi + m\sum_\alpha \int \mathrm{d}x \left(\frac{\partial\chi_\alpha}{\partial x}\right)^2\right) \\ - m\sum_\alpha \int \mathrm{d}x \frac{\partial\chi_\alpha(x,t)}{\partial x}\sum_{ij}{}' \dot{Q}_{ij}\varphi_\alpha(x, \omega_{ij}) \\ - \mathrm{i}\sum_s \int \mathrm{d}x\, \psi_s^+\frac{\partial\psi_s}{\partial x} \end{aligned} \tag{3.14}$$

$$P_{ij} = \frac{\partial L}{\partial \dot{Q}_{ij}} = m\dot{Q}_{-ij} - \dot{Q}_0\sum_{kl}{}' c_{kl}^{ij}Q_{kl} \tag{3.15}$$

where we have introduced

$$M = m\sum_\alpha \int \mathrm{d}x \frac{\lambda_\alpha}{\lambda}\frac{\omega_0^2}{\omega_\alpha^2}\left(\frac{\partial\Delta_s}{\partial x}\right)^2 \tag{3.16}$$

$$\xi = m\sum_\alpha \int \mathrm{d}x \left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2}\frac{\omega_0}{\omega_\alpha}\frac{\partial\Delta_s}{\partial x}\frac{\partial\chi_\alpha}{\partial x} \tag{3.17}$$

$$c_{kl}^{ij} = m\sum_\alpha \int \mathrm{d}x\, c_\alpha(\omega_{ij})c_\alpha(\omega_{kl})g_i(x)\frac{\mathrm{d}g_k(x)}{\mathrm{d}x}. \tag{3.18}$$

Here, we have made use of the notation that the phonon normal mode $g_{-i}(x)$ means the mode with the opposite wavenumber to $g_i(x)$ and it is the complex conjugate of $g_i(x)$. For the localised modes, $g_{-i} = g_i$. The quantity ξ is still a dynamic quantity.

We define the π_α field by

$$\pi_\alpha(x,t) = \sum_{ij}{}' P_{-ij}(t)\varphi_\alpha(x,\omega_{ij}). \tag{3.19}$$

Eliminating $\dot{Q}_{ij}$ in (3.14) with the help of (3.15), we obtain

$$P_0 = \dot{Q}_0\left[M + 2\xi + m\sum_\alpha \int \mathrm{d}x \left(\frac{\partial \chi_\alpha}{\partial x}\right)^2 - \sum_{\substack{ijk\\lmn}}{}' \frac{1}{m} c^{ij}_{mn} c^{-ij}_{kl} Q_{mn} Q_{kl}\right]$$
$$- \sum_\alpha \int \mathrm{d}x \frac{\partial \chi_\alpha}{\partial x}\pi_\alpha - \mathrm{i}\sum_s \int \mathrm{d}x\, \psi_s^+ \frac{\partial \psi_s}{\partial x}. \tag{3.20}$$

Making use of the completeness relation

$$\sum_{ij} \varphi^*_\alpha(x,\omega_{ij})\varphi_\beta(y,\omega_{ij}) = \sum_{ij} c_\alpha(\omega_{ij}) c_\beta(\omega_{ij}) g_{-i}(x) g_i(y)$$
$$= \delta_{\alpha\beta}\delta(x-y) \tag{3.21}$$

we find

$$m\sum_\alpha \int \mathrm{d}x \left(\frac{\partial \chi_\alpha}{\partial x}\right)^2 = \frac{1}{m}\sum_{ijkl}{}' \sum_{mn} c^{-mn}_{ij} c^{mn}_{kl} Q_{ij} Q_{kl}. \tag{3.22}$$

Substitution into (3.20) gives

$$P_0 = \dot{Q}_0\left(M + 2\xi + \frac{1}{m}\sum_{ijkl}{}' c^{00}_{ij} c^{00}_{kl} Q_{ij} Q_{kl}\right)$$
$$- \sum_\alpha \int \mathrm{d}x \frac{\partial \chi_\alpha}{\partial x}\pi_\alpha - \mathrm{i}\sum_s \int \mathrm{d}x\, \psi_s^+ \frac{\partial \psi_s}{\partial x}. \tag{3.23}$$

Since equation (3.17) is rewritten

$$\xi = \left(\frac{M}{m}\right)^{1/2} \sum_{ij}{}' c^{00}_{ij} Q_{ij} \tag{3.24}$$

equation (3.23) finally becomes

$$\dot{Q}_0 = \left(P_0 + \sum_\alpha \int \mathrm{d}x \frac{\partial \chi_\alpha}{\partial x}\pi_\alpha + \mathrm{i}\sum_s \int \mathrm{d}x\, \psi_s^+ \frac{\partial \psi_s}{\partial x}\right) \Big/ M(1+\xi/M)^2. \tag{3.25}$$

Equation (3.15) is also rewritten

$$\dot{Q}_{ij} = \frac{1}{m}\left[P_{-ij} + \frac{1}{M(1+\xi/M)^2}\left(P_0 + \sum_\alpha \int \mathrm{d}x \frac{\partial \chi_\alpha}{\partial x}\pi_\alpha \right.\right.$$
$$\left.\left. + \mathrm{i}\sum_s \int \mathrm{d}x\, \psi_s^+ \frac{\partial \psi}{\partial x}\right)\sum_{kl}{}' c^{-ij}_{kl} Q_{kl}\right]. \tag{3.26}$$

The Hamiltonian is given by

$$H = P_0\dot{Q}_0 + \sum_{ij}{}' P_{ij}\dot{Q}_{ij} + \sum_s \int \mathrm{d}x\, \mathrm{i}\psi_s^+ \frac{\partial \psi_s}{\partial t} - L \tag{3.27}$$

which turns out to be

$$H = \left(P_0 + \sum_\alpha \int \mathrm{d}x \frac{\partial \chi_\alpha}{\partial x}\pi_\alpha + \mathrm{i}\sum_s \int \mathrm{d}x\, \psi_s^+ \frac{\partial \psi_s}{\partial x}\right)^2 \Big/ 2M(1+\xi/M)^2$$
$$+ \frac{1}{2m}\sum_\alpha \int \mathrm{d}x\, \pi_\alpha^2$$

$$+\frac{m}{2}\left[\left[\omega_0^2\int \mathrm{d}x\,\Delta_s^2+\sum_\alpha\int \mathrm{d}x\left[2\left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2}\omega_0\omega_\alpha\Delta_s\chi_\alpha+\omega_\alpha^2\chi_\alpha^2\right]\right]\right]$$

$$+\sum_s\int \mathrm{d}x\,\psi_s^+\left\{-\mathrm{i}v_\mathrm{F}\sigma_3\partial_x+\sigma_1\left[\Delta_s+\sum_\alpha\left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2}\frac{\omega_\alpha}{\omega_0}\chi_\alpha\right]\right\}\psi_s \tag{3.28}$$

where a relation

$$\sum_\alpha\int \mathrm{d}x\,\pi_\alpha\frac{\partial\chi_\alpha}{\partial x}=\frac{1}{m}\sum_{ijkl}{}'\,c_{kl}^{ij}P_{-ij}Q_{kl} \tag{3.29}$$

is used. The electronic states are represented by the TLM eigenfunctions. We can introduce the particle–hole representation. Electron creation operators above the Fermi level are particle creation operators, whereas electron creation operators below the Fermi level are hole annihilation operators. For a product of operators, the normal product is obtained when all the creation operators are transferred to the left-hand side of all the annihilation operators. The sign has to change, if the total transferences are performed by an odd number of transpositions of neighboring operators. The normal product is represented by colons. It is readily seen that

$$\sum_s\int \mathrm{d}x\,\psi_s^+(-\mathrm{i}v_\mathrm{F}\sigma_3\partial_x+\sigma_1\Delta_s)\psi_s$$

$$=:\sum_s\int \mathrm{d}x\,\psi_s^+(-\mathrm{i}v_\mathrm{F}\sigma_3\partial_x+\sigma_1\Delta_s)\psi_s:+\sum_{ns}{}'\,\varepsilon_n \tag{3.30}$$

and

$$\psi_s^+(x)\sigma_1\psi_s(x)=:\psi_s^+(x)\sigma_1\psi_s(x):+\sum_n{}'\,\psi_n^{(0)+}(x)\sigma_1\psi_n^{(0)}(x). \tag{3.31}$$

With the help of the self-consistency equation in the TLM model

$$\Delta_s(x)=-\pi v_\mathrm{F}\lambda\sum_{sn}{}'\,\psi_n^+(x)\sigma_1\psi_n(x) \tag{3.32}$$

we finally rewrite (3.28)

$$H=E_\mathrm{k}+\left(P_0+\sum_\alpha\int \mathrm{d}x\frac{\partial\chi_\alpha}{\partial x}\pi_\alpha+\mathrm{i}\sum_s\int \mathrm{d}x\,\psi_s^+\frac{\partial\psi_s}{\partial x}\right)^2\Big/2M(1+\xi/M)^2$$

$$+\frac{1}{2m}\sum_\alpha\int \mathrm{d}x\,(\pi_\alpha^2+m^2\omega_\alpha^2\chi_\alpha^2)$$

$$+:\sum_s\int \mathrm{d}x\,\psi_s^+\left\{-\mathrm{i}v_\mathrm{F}\sigma_3\partial_x+\sigma_1\left[\Delta_s+\sum_\alpha\left(\frac{\lambda_\alpha}{\lambda}\right)^{1/2}\frac{\omega_\alpha}{\omega_0}\chi_\alpha\right]\right\}\psi_s: \tag{3.33}$$

where

$$E_\mathrm{k}=\sum_{ns}{}'\,\varepsilon_n+(m\omega_0^2/2)\int \mathrm{d}x\,\Delta_s^2. \tag{3.34}$$

It is important to point out that π_α and χ_α do not satisfy the usual commutation relations, when they are quantum operators. Since the P and Q satisfy

$$[P_0,Q_0]=-\mathrm{i},\ [P_{ij},Q_{kl}]=-\mathrm{i}\delta_{ik}\delta_{jl} \tag{3.35}$$

we get, with the help of (3.12) and (3.19)

$$[\pi_\alpha(x,t),\chi_\beta(y,t)]=-\mathrm{i}\sum_{ij}{}'\,\varphi_\alpha^*(x,\omega_{ij})\varphi_\beta(y,\omega_{ij})$$

$$=-\mathrm{i}\{\delta_{\alpha\beta}\delta(x-y)-[3(\lambda_\alpha\lambda_\beta)^{1/2}\xi_0c^2/4\omega_\alpha\omega_\beta\Delta_0^2]$$

$$\times(\partial\Delta_s(x)/\partial x)\partial\Delta_s(y)/\partial y\}. \tag{3.36}$$

4. Discussion

We have shown that the elementary application of the Lagrange method makes it possible to introduce the collective coordinate method into the amplitude mode formalism for *trans*-polyacetylene in which many types of lattice vibrations are taking part. We have extensively used the phonon eigenfunctions around the soliton. The final form for the Hamiltonian, however, does not involve them. It is a straightforward generalisation of the Hamiltonians which have been derived in the collective coordinate method for the single-component non-linear models and also for the TLM model.

Several authors have used the collective coordinate method for the TLM and SSH models. Their main purpose has been to study the interactions between the soliton and phonons, and to see how the motion of the soliton is modulated by the interactions. Sometimes, the method has unfortunately been misused. It is very important to realise that the collective coordinate Q_0 is a cyclic coordinate, if we do not take account of small soliton pinning effect by the discrete lattice of the SSH model. Its conjugate momentum P_0 is thus a constant of motion. These facts make it possible to disregard the Goldstone mode with zero frequency. In discussions of the soliton dynamics, however, it is sometimes tempting to think of a 'force' acting on the soliton. The easiest way to do so is to introduce some effective potential which depends on Q_0. This is clearly erroneous. The legitimate method is to derive the equation of motion for Q_0, with the help of the Hamiltonian (3.33) and the relevant commutation relations. We have been studying the diffusive motion of the solitons in the ϕ^4- and TLM models in this way (Ogata and Wada 1985, 1986, Ogata *et al* 1986, 1987).

The second misuse concerns the phonon eigenfunctions. Since it is demanding to use the exact eigenfunctions, they are very often substituted by plane waves. This presumably comes from the conception that, in discussing the soliton–phonon interaction with the help of perturbation theory, we could use unperturbed phonon functions which would be the plane waves. This is, however, a misconception. The soliton and phonons have the same origin: the lattice distortion. When the distortion is large, it gives rise to solitons; when it is small, to phonons. They are two parts of the lattice distortion. Interactions between the two parts may be weak, but the structure of one part is drastically modified by the emergence of the other. The modification cannot be taken into account by perturbation theory. It is necessary to use the knowledge of the structure of solitons, which cannot be obtained by a perturbation method. In addition, the weak interactions take place at the very region where the modification is most dominant. It is the region close to the soliton. It is, thus, clear that we have to use the correct phonon eigenfunctions to study the soliton–phonon interaction. Some examples of such discussions can be found in our previous works (Ogata and Wada 1985, 1986, Ogata *et al* 1986, 1987, Terai *et al* 1986a).

The Hamiltonian (3.33) makes it possible to study the soliton dynamics in the amplitude mode formalism. Furthermore, we can use it to investigate the effect of soliton–phonon interactions on the structure of the soliton itself. Results of such a study will be reported separately.

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