Adiabatic self-trapped states in carbon nanotubes

L. Brizhik∗, A. Eremko†, Bogolyubov Institute for Theoretical Physics, 03143 Kyiv, Ukraine
B. Piette‡, M. Watson§ and W. Zakrzewski¶
Department of Mathematical Sciences, University of Durham,
Durham DH1 3LE, UK

Abstract

We study here polaron (soliton) states of electrons or holes in a model describing carbon-type nanotubes. In the Hamiltonian of the system we take into account the electron-phonon interaction that arises from the deformation dependencies of both the on-site and the hopping interaction energies. Using an adiabatic approximation, we derive the equations for self-trapped electron states in zigzag nanotubes. We find the ground states of an electron in such a system and show that the polaron states can have different symmetries depending on the strength of the electron-phonon coupling. Namely, at relatively weak coupling the polarons possess quasi-one-dimensional (quasi-1D) properties and have an azimuthal symmetry. When the coupling constant exceeds some critical value, the azimuthal symmetry breaks down and the polaron spreads out in more than one dimension.

We also study polarons that are formed by the electrons in the conducting band (or by holes in the valence band) in semiconducting carbon nanotubes. We show that their properties are more complex than those of quasi-1D ground state polarons. In particular, polarons in semiconducting carbon nanotubes possess an inner structure: being self-trapped along the nanotube axis they exhibit some modulations around the nanotube.

1 Introduction

Over the last few years much work has been done on studying physical properties of carbon nanotubes [1, 2, 3], and boron nitride nanotubes [4]. The experimental studies of such nanosystems have revealed their peculiar properties that are important for practical applications [5].

Not surprisingly, carbon and boron nitride nanotubes are quite complex systems. Their geometry is based on a deformable hexagonal lattice of atoms which is wrapped into a cylinder. Experimental and theoretical studies show the important role of the nanotube geometry: many properties of nanotubes can be modified in a controllable way by either varying the nanotube diameter and chirality, \textit{i.e.} the way the lattice is wrapped into a cylinder, [1, 2], or by doping them with impurity atoms, molecules and/or compounds [6]. Theoretical studies of single wall carbon nanotubes (SWNT) [7, 8] have demonstrated the importance of the interaction of electrons with lattice vibrations [9, 10, 11, 12, 13, 7, 14, 15]. Note that sufficiently long SWNTs can be considered as one-dimensional (1D) metals or semiconductors depending on their diameter and chirality [1, 2]. The nanotubes possess a series of electron bands, which can be determined by 1D energy dispersion relations for the wave vector \( k \) along the axis of the nanotube.

In 1D systems the electron-phonon coupling can lead to the formation of self-trapped soliton-like states (large polarons) which can move with a constant momentum \[^{16}\]. In 1D metals, due

∗ e-mail address: brizhik@bitp.kiev.ua
† e-mail address: eremko@bitp.kiev.ua
‡ e-mail address: B.M.A.G.Piette@durham.ac.uk
§ e-mail address: m.j.watson@durham.ac.uk
¶ e-mail address: W.J.Zakrzewski@durham.ac.uk
to the Peierls instability [17], the energy gap appears at the Fermi level and the Fröhlich charge-density wave is formed [18] instead of a soliton. Recent experiments [19, 20] have shown that even long channel semiconductor SWNTs may have very high mobilities at a high doping level. The possibility for the formation of states which spontaneously break symmetry in carbon nanotubes has been discussed in [10, 11, 12]. In particular, large polarons (solitons) in nanotubes have recently been studied in [13, 21] where the long-wave approximation has been used for the states close to the Fermi level. However, such a description, equivalent to the continuum approximation, does not take into account some important aspects of the crystallographic structure of the system.

In this paper, first, we consider the ground states of a quasiparticle (electron, hole or exciton) in the zigzag nanotube system and, second, we study the polaron states of an electron in the lowest unfilled (conducting) band or an extra hole (an electron deficiency) in the highest filled (valence) band in carbon nanotubes. For this we use the semi-empirical tight-binding model with nearest-neighbour hopping approximation [1]. The advantages of this method for some 1D systems, like polyacetylene and carbon nanotubes, have been demonstrated in [22] and [1, 9, 10], respectively. We study a quantum system involving a hexagonal lattice of atoms and electrons and then perform an adiabatic approximation. Then we derive the system of discrete nonlinear equations, which as such, can possess localised soliton-like solutions. We perform an analytical study of these equations and show that, indeed, this is the case, and various polaron states can be formed in the system. In fact, these equations were used in [23] to determine numerically the conditions for the formation of such polaron states. Our analytical results on self-trapped states of a quasiparticle are in good agreement with the results obtained in [23]. We also study polarons that are formed by the electrons in the conducting band (or by holes in the valence band) in semiconducting carbon nanotubes.

The paper is organised as follows. The next section presents the model of the nanotube. The phonon Hamiltonian is discussed in Sect. 3, electron in Sect. 4 and in Sect. 5 we discuss the electron-phonon interactions. The details of the diagonalization of the electron Hamiltonian are presented in Appendix 1. In Section 6 we determine the adiabatic and non-adiabatic terms of the Hamiltonian. The corresponding zero-order adiabatic approximation then leads to the equations for the self-trapped electron states while the non-adiabatic term of the Hamiltonian provides a self-consistent test to determine the conditions of applicability of the adiabatic approximation. The system of equations in the zero-order adiabatic approximation is derived in Appendix 2. In Sect. 7 we derive some analytical solutions for the large polaron ground state, and in Sect. 8 we discuss the transition to the states with broken axial symmetry. In Section 9 we study large polaron states in semiconducting carbon nanotubes. The paper ends with conclusions.

2 Model of a Nanotube

In this section we define the variables to describe a nanotube. Let $d$ be the length of the side of the hexagons of the nanotube, $R$ its radius and let $N$ be the number of hexagonal cells wrapped around the nanotube. Then we have

$$\alpha = \frac{2\pi}{N}, \quad a = d\sqrt{3}, \quad b = d/2, \quad a = 4R\sin\left(\frac{\alpha}{4}\right),$$

(1)

where $a$ is the distance between two next to nearest neighbour sites.

To label all sites on the nanotube one can use two different schemes. They involve having 2 or 4 lattice sites as a basic unit. The first one, used in [23], is closely connected with a unit cell of a graphene sheet and is based on nonorthogonal basic vectors. The corresponding labelling, $(i, j, \rho)$, involves index $i$ numerating the sites around the nanotube, spiral index $j$ and index $\rho = 0, 1$ that describes sites that have the nearest neighbours ‘down’ ($\rho = 0$) or ‘up’ ($\rho = 1$), as shown in Fig.1.
Note further that a hexagonal nanotube possesses two symmetries: the translation along the axis of the nanotube by $3d$ and the rotation by an angle $\alpha$ around the nanotube axis. Given this, one can use an alternative labelling scheme in which the basic unit cell is rectangular and contains four atoms. This scheme, also shown in Fig. 1, involves using the labelling $(m, n, \varrho)$ where $m$ is the axial index, $n$ is the azimuthal index and the index $\varrho = 1, 2, 3, 4$ enumerates the atoms in the unit cell.

The position of any nanotube lattice site, at its equilibrium, can be described by $\vec{R}_0^{(m,n,\varrho)}$ given by

$$\vec{R}_0^{(m,n,\varrho)} = R_e \sin \Theta_{m,n,\varrho} + e_x^c \cos \Theta_{m,n,\varrho} + e_z \zeta_{m,n,\varrho},$$  \hspace{1cm} (2)$$

where the three-component index $\varrho = \{\varrho_1, \varrho_2, \varrho_3\}$ indicates the nanotube atoms, and the coordinates $\Theta$, being an azimuthal angle and $z$, being a coordinate along the tube, describe positions of atoms on the cylindrical surface of the nanotube. In the first scheme $\varrho = \{i,j,\rho\}$ and in the second one $\varrho = \{m,n,\varrho\}$. In a zigzag nanotube the azimuthal and longitudinal positions of atoms are:

$$\Theta_{i,j,\rho} = (i + \frac{j + \rho}{2})\alpha; \hspace{1cm} \Theta_{m,n,1} = \Theta_{m,n,4} = n\alpha; \hspace{1cm} \Theta_{m,n,2} = \Theta_{m,n,3} = (n + \frac{1}{2})\alpha;$$

$$z_{i,j,\rho} = \frac{3j + \rho}{2}d; \hspace{1cm} z_{m,n,\varrho=1,2} = (3m - 1 + \frac{\rho-1}{2})d, \hspace{1cm} z_{m,n,\varrho=3,4} = (3m + 1 + \frac{\varrho-4}{2})d. \hspace{1cm} (3)$$

Although in the numerical work reported in [23], we have used the first description, the second one is more convenient when taking into account the boundary conditions. The azimuthal periodic condition $f(n + N) = f(n)$ is natural because going from $n$ to $n + N$ corresponds to a rotation by $2\pi$. In the $m$ direction, however, for a long enough nanotube, we can use the Born-Karman periodic conditions for electron and phonon states in a nanotube. Thus, nanotubes can be considered as 1D systems with a complex inner structure.

Next, we consider displacements from the equilibrium positions of the all sites of the nanotube:

$$\vec{R}_\varrho = \vec{R}_0^{(m,n,\varrho)} + \vec{U}_\varrho,$$  \hspace{1cm} (4)$$

where the local displacement vector can be represented as the three orthogonal local vectors:

$$\vec{U}_\varrho = \vec{u}_\varrho + \vec{s}_\varrho + \vec{v}_\varrho. \hspace{1cm} (5)$$
Here $\vec{u}_\alpha$ is tangent to the surface of the undeformed nanotube and perpendicular to the nanotube axis, $\vec{s}_\alpha$ is tangent to this surface and parallel to the nanotube axis, and $\vec{z}_\alpha$ is normal to the surface of the nanotube. Then, using Cartesian coordinates, we have

$$
\vec{u}_\alpha = u_\alpha (\vec{e}_x \cos \Theta_\alpha - \vec{e}_y \sin \Theta_\alpha),
\vec{s}_\alpha = s_\alpha (\vec{e}_x \sin \Theta_\alpha + \vec{e}_y \cos \Theta_\alpha),
\vec{z}_\alpha = v_\alpha \vec{e}_z.
$$

(6)

To write down the Hamiltonian in a compact form, it is convenient to define the formal index operators of lattice translations: $r()$, $l()$ and $d()$, which when applied to any lattice site index, translate the index to one of the three nearest sites. Applying these operators to the lattice site which has the nearest neighbour down, i.e. which in the first formulation have the index $\rho = 0$, they translate the index respectively to the right, left and down from that site. For the lattice sites which have an upper nearest neighbour, i.e. which in the first formulation have the index $\rho = 1$, one has to turn the lattice upside down before applying these definitions. Notice that the square of each of these three operators is equivalent to the identity operator. So, for example, moving from a lattice site to the right once and then moving to the right again, after flipping the lattice upside down, one returns to the starting site. In particular, we have for the first lattice parametrisation

$$
r(i, j, 0) = (i, j, 1), \quad r(i, j, 1) = (i, j, 0),
\quad l(i, j, 0) = (i - 1, j, 1), \quad l(i, j, 1) = (i + 1, j, 0),
\quad d(i, j, 0) = (i, j - 1, 1), \quad d(i, j, 1) = (i, j + 1, 0),
$$

(7)

while for the second one, which we will use below, we have

$$
r(m, n, 1) = (m, n, 2), \quad r(m, n, 2) = (m, n, 1),
\quad r(m, n, 3) = (m, n + 1, 4), \quad r(m, n, 4) = (m, n - 1, 3),
\quad l(m, n, 1) = (m, n - 1, 2), \quad l(m, n, 2) = (m, n + 1, 1),
\quad l(m, n, 3) = (m, n, 4), \quad l(m, n, 4) = (m, n, 3),
\quad d(m, n, 1) = (m - 1, n, 4), \quad d(m, n, 2) = (m, n, 3),
\quad d(m, n, 3) = (m, n, 2), \quad d(m, n, 4) = (m + 1, n, 1).
$$

(8)

Some physical quantities, e.g. the potential energy of the lattice distortion, include central forces, which depend on the distance between two sites. Let us define the following lattice vectors connecting the atom $\{\alpha\}$ with its three nearest neighbours $\delta(\alpha)$ with $\delta = r, l, d$ for the right ($r$), left ($l$) and down or up (d) neighbours:

$$
\vec{D}_{\delta(\alpha)} = \vec{R}_{\delta(\alpha)} - \vec{R}_\alpha = \vec{D}_{\delta(\alpha)}^0 + (\vec{U}_{\delta(\alpha)} - \vec{U}_\alpha).
$$

(9)

When $\vec{U}_\alpha = 0$ we add the upper index 0 to all quantities to indicate their values at the equilibrium position. Note that $|\vec{D}_{\delta(\alpha)}^0| = |\vec{D}_{\delta(\alpha)}^0| = |\vec{D}_{\delta(\alpha)}^0| = d$. In the case of small displacements, i.e when $|\vec{U}_{\delta(\alpha)} - \vec{U}_\alpha| \ll d$, the distance between the lattice sites is approximately given by:

$$
|\vec{D}_{\delta(\alpha)}| \approx d + W_{\delta(\alpha)}
$$

(10)

where

$$
W_{\delta(\alpha)} = \frac{(\vec{U}_{\delta(\alpha)} - \vec{U}_\alpha) \cdot \vec{D}_{\delta(\alpha)}^0}{d}
$$

(11)
are the changes of the distances between the nearest neighbours due to site displacements. The explicit expressions for \(W_\delta\) in the first scheme are

\[
W_{i,j,0} = \frac{\sqrt{3}}{2}\left(\cos\left(\frac{\alpha}{4}\right)(u_{i,j,1} - u_{i,j,0}) + \sin\left(\frac{\alpha}{4}\right)(s_{i,j,1} + s_{i,j,0})\right) + \frac{1}{2}(v_{i,j,1} - v_{i,j,0})
\]

\[
W_{i,j,0} = \frac{\sqrt{3}}{2}\left(\cos\left(\frac{\alpha}{4}\right)(u_{i,j,0} - u_{i-1,j,1}) + \sin\left(\frac{\alpha}{4}\right)(s_{i-1,j,1} + s_{i,j,0})\right) + \frac{1}{2}(v_{i-1,j,1} - v_{i,j,0})
\]

\[
W_{i,j,1} = W_{i,j,0}, \quad W_{i,j,1} = W_{i+1,j,0}, \quad W_{d_{i,j,1}} = W_{d_{i,j+1,0}}.
\]

(12)

Because the central forces between neighbouring sites do not provide lattice stability, in addition to \(W_\delta\), which are invariant under translations, we need also the quantities \(\Omega_\delta\) which describe relative shifts of neighbouring sites. The corresponding explicit expressions are:

\[
\Omega_{i,j,0} = \frac{1}{2}\left(\cos\left(\frac{\alpha}{4}\right)(u_{i,j,1} - u_{i,j,0}) + \sin\left(\frac{\alpha}{4}\right)(s_{i,j,1} + s_{i,j,0})\right) - \frac{\sqrt{3}}{2}(v_{i,j,1} - v_{i,j,0}),
\]

\[
\Omega_{i,j,0} = \frac{1}{2}\left(\cos\left(\frac{\alpha}{4}\right)(u_{i,j,0} - u_{i-1,j,1}) + \sin\left(\frac{\alpha}{4}\right)(s_{i-1,j,1} + s_{i,j,0})\right) - \frac{\sqrt{3}}{2}(v_{i-1,j,1} - v_{i,j,0}),
\]

\[
\Omega_{d_{i,j,0}} = -u_{i,j-1,1} + u_{i,j,0}, \quad \Omega_{r_{i,j,1}} = \Omega_{r_{i,j,0}},
\]

\[
\Omega_{l_{i,j,1}} = \Omega_{l_{i+1,j,0}}, \quad \Omega_{d_{i,j,1}} = \Omega_{d_{i,j+1,0}}.
\]

(13)

Note, the curvature of the lattice and corresponding bond-bending in nanotubes is an important factor for the lattice stability \([7]\) and electron-phonon interaction \([24]\). To take into account this factor we choose to base our discussion on the solid angle spanned by the 3 lattice vectors

\[
S = \frac{(\vec{D}_{l_\alpha} \times \vec{D}_{r_\alpha}) \cdot \vec{D}_{d_\alpha}}{|\vec{D}_{l_\alpha}||\vec{D}_{r_\alpha}||\vec{D}_{d_\alpha}|} \approx S_0 + \frac{\sqrt{3}}{2d}C
\]

where \(S_0 = \frac{2}{4}\sin(\frac{\alpha}{2})\) and, in the case of small displacements,

\[
C_{i,j,0} = \frac{\sqrt{3}}{4}\sin\left(\frac{\alpha}{2}\right)(2v_{i,j,0} - v_{i,j,1} - v_{i-1,j,1})
\]

\[
- \cos\left(\frac{\alpha}{4}\right)s_{i,j-1,1} + 3\cos^3\left(\frac{\alpha}{4}\right)s_{i,j,0}
\]

\[
+ \left(\frac{3}{2}\cos\left(\frac{\alpha}{4}\right) - \frac{5}{2}\cos^3\left(\frac{\alpha}{4}\right)\right)(s_{i-1,j,1} + s_{i,j,1})
\]

\[
+ \sin\left(\frac{\alpha}{4}\right)\left(\frac{5}{2}\cos^2\left(\frac{\alpha}{4}\right) - 1\right)(u_{i,j,1} - u_{i-1,j,1}),
\]

\[
C_{i,j,1} = \frac{\sqrt{3}}{4}\sin\left(\frac{\alpha}{2}\right)(v_{i,j,0} + v_{i+1,j,0} - 2v_{i,j,1})
\]

\[
- \cos\left(\frac{\alpha}{4}\right)s_{i,j+1,0} + 3\cos^3\left(\frac{\alpha}{4}\right)s_{i,j,1}
\]

\[
+ \left(\frac{3}{2}\cos\left(\frac{\alpha}{4}\right) - \frac{5}{2}\cos^3\left(\frac{\alpha}{4}\right)\right)(s_{i+1,j,0} + s_{i,j,0})
\]

\[
+ \sin\left(\frac{\alpha}{4}\right)\left(\frac{5}{2}\cos^2\left(\frac{\alpha}{4}\right) - 1\right)(u_{i+1,j,0} - u_{i,j,0}),
\]

(15)

It is easy to write down the corresponding expressions in the second labelling scheme. This time one has twice the number of the expressions as compared with the first scheme.
3 Phonon Hamiltonian

We define the phonon Hamiltonian in the nearest-neighbour interaction approximation and take into account the potential terms responsible for the central, $V_W$, non-central, $V_Q$, and the bond-bending, $V_C$ forces in the harmonic approximation:

$$H_{ph} = \frac{1}{2} \sum_w \left( \frac{\vec{P}_w^2}{M} + k \sum_{\delta} [\omega_{\delta w}^2 + \Omega_{\delta w}^2] + k_c \delta_{\delta w} \right), \tag{16}$$

where $M$ is the atom mass, $k$ is the elasticity constant for the relative atom displacements, $k_c$ is a characteristic constant of the bond-bending force while $\vec{P}_w$ is the momentum, canonically conjugate to the displacement $\vec{U}_w$.

According to the theory of lattice dynamics (see, e.g., [26]) the Hamiltonian (16) can be diagonalized by some unitary transformation. For the lattice labelling $\varphi = \{m, n, \vartheta\}$, this transformation has the form

$$u_{m,n,\vartheta} = \frac{1}{\sqrt{12MNL}} \sum_{k,\nu,\tau} e^{i(km+\nu n)}U_{\vartheta,\tau}(k,\nu)Q_{k,\nu,\tau},$$

$$s_{m,n,\vartheta} = \frac{1}{\sqrt{12MNL}} \sum_{k,\nu,\tau} e^{i(km+\nu n)}S_{\vartheta,\tau}(k,\nu)Q_{k,\nu,\tau},$$

$$v_{m,n,\vartheta} = \frac{1}{\sqrt{12MNL}} \sum_{k,\nu,\tau} e^{i(km+\nu n)}V_{\vartheta,\tau}(k,\nu)Q_{k,\nu,\tau}. \tag{17}$$

Then, introducing the operators of creation, $b_{k,\nu,\tau}^\dagger$, and annihilation, $b_{k,\nu,\tau}$, of phonons

$$Q_{k,\nu,\tau} = \sqrt{\frac{\hbar}{2\omega_\tau(k,\nu)}} \left( b_{k,\nu,\tau} + b_{-k,-\nu,\tau}^\dagger \right), \tag{18}$$

we can rewrite the phonon Hamiltonian (16) in the standard form

$$H_{ph} = \frac{1}{2} \sum_{k,\nu,\tau} \left( P_{k,\nu,\tau}^\dagger P_{k,\nu,\tau} + \omega_\tau^2(k,\nu)Q_{k,\nu,\tau}^\dagger Q_{k,\nu,\tau} \right) + \sum_{q,\nu,\tau} \hbar \omega_\tau(q,\nu) \left( b_{q,\nu,\tau}^\dagger b_{q,\nu,\tau} + \frac{1}{2} \right). \tag{19}$$

Here $\omega_\tau(k,\nu)$ is the frequency of the normal lattice vibrations of the mode $\tau$ ($\tau = 1, 2, \ldots, 12$) with the longitudinal wavenumber $k$ and the azimuthal quantum number $\nu$. The adimensional wavenumber (quasi-momentum) along the nanotube, $k = \frac{2\pi}{L} n_1$, takes quasi-continuum values (for $L \gg 1$) in the range $-\pi < k \leq \pi$. The azimuthal quantum number takes discrete values $\nu = \frac{2\pi}{N} n_2$ with $n_2 = 0, \pm 1, \ldots, \pm \frac{N-1}{2}$ if $N$ is odd and $n_2 = 0, \pm 1, \ldots, \pm \left( \frac{N}{2} - 1 \right)$, $\frac{N}{2}$ if $N$ is even.

The frequencies $\omega_\tau(q,\nu)$ and the coefficients of the transformation (17) can be found from the diagonalization condition of the potential energy of the lattice displacements in (16) with the orthonormalization conditions

$$\frac{1}{12} \sum_{\vartheta} \left( U_{\vartheta,\tau}(k,\nu)U_{\vartheta,\tau'}(k,\nu) + S_{\vartheta,\tau}(k,\nu)S_{\vartheta,\tau'}(k,\nu) + V_{\vartheta,\tau}(k,\nu)V_{\vartheta,\tau'}(k,\nu) \right) = \delta_{\tau,\tau'},$$

$$\frac{1}{12} \sum_{\tau} U_{\vartheta,\tau}(k,\nu)U_{\vartheta',\tau}(k,\nu) = \frac{1}{12} \sum_{\tau} S_{\vartheta,\tau}(k,\nu)S_{\vartheta',\tau}(k,\nu) = \frac{1}{12} \sum_{\tau} V_{\vartheta,\tau}(k,\nu)V_{\vartheta',\tau}(k,\nu) = \delta_{\vartheta,\vartheta'},$$

$$\sum_{\tau} U_{\vartheta,\tau}(k,\nu)S_{\vartheta,\tau}(k,\nu) = \sum_{\tau} S_{\vartheta,\tau}(k,\nu)V_{\vartheta,\tau}(k,\nu) = \sum_{\tau} V_{\vartheta,\tau}(k,\nu)U_{\vartheta,\tau}(k,\nu) = 0. \tag{20}$$
Note that any linear form of lattice displacements, such as $W_{m,n,\varrho}$, $\Omega_{m,n,\varrho}$ and $C_{m,n,\varrho}$, after applying the transformation (17) can be written as

$$F_{m,n,\varrho} = \frac{1}{\sqrt{12MN}} \sum_{k,\nu,\tau} e^{i(km+\nu n)} F_{\varrho}(k,\nu|\tau) Q_{k,\nu,\tau}$$

(21)

where $F_{\varrho}(k,\nu|\tau)$ is a linear form of the transformation coefficients $S_{\varrho,\tau}(k,\nu)$, $V_{\varrho,\tau}(k,\nu)$ and $U_{\varrho,\tau}(k,\nu)$.

Therefore, in general, the frequencies $\omega_{\tau}(k,\nu)$ of the normal vibrations of the lattice can be represented as

$$\omega_{\tau}^2(k,\nu) = \frac{1}{12} \sum_{\varrho} \left( \frac{k}{M} \sum_{\delta} \left[ |W_{\delta}(k,\nu|\tau)|^2 + |\Omega_{\delta}(k,\nu|\tau)|^2 \right] + \frac{k_c}{M} |C_{\delta}(k,\nu|\tau)|^2 \right).$$

(22)

The equations for the normal modes of lattice vibrations are too complicated to be solved analytically in the general case. For carbon nanotubes the phonon modes were calculated numerically (see, e.g., [1, 28] and references therein). Here we do not calculate the phonon spectrum explicitly, instead we use the general relations (20), (22) to get some estimates which only depend on the parameters $k$, $k_c$ and $M$. Meanwhile, the explicit expressions for the electron dispersions are more important for us and will be derived below.

4 Electron Hamiltonian

The electron eigenstates are found from the tight-binding model using the nearest-neighbour hopping approximation. In this approximation the Hamiltonian which describes electron states is given by

$$H_e = \sum_{\alpha,\sigma} \left( \mathcal{E}_0 a_{\alpha,\sigma}^\dagger a_{\alpha,\sigma} - J \sum_{\delta} a_{\alpha,\sigma}^\dagger a_{\delta(\alpha),\sigma} \right).$$

(23)

Here $a_{\alpha,\sigma}^\dagger(a_{\alpha,\sigma})$ are creation (annihilation) operators of a $\pi$-electron with the spin $\sigma$ on the site $\alpha$, $\mathcal{E}_0$ is the $\pi$-electron energy, $J$ is the energy of the hopping interaction between the nearest neighbours and the summation over $\delta$ denotes the summation over the three nearest neighbour sites.

By the unitary transformation

$$a_{m,n,\varrho,\sigma} = \frac{1}{2\sqrt{LN}} \sum_{k,\nu,\lambda} e^{ikm+\nu n} u_{\varrho,\lambda}(k,\nu)c_{k,\nu,\lambda,\sigma},$$

(24)

with

$$\frac{1}{4} \sum_{\varrho} u_{\varrho,\lambda}^*(k,\nu) u_{\varrho,\lambda'}(k,\nu) = \delta_{\lambda,\lambda'}$$

(25)

the Hamiltonian (23) is transformed into a diagonal form (see Appendix 1):

$$H_e = \sum_{k,\nu,\lambda,\sigma} E_{\lambda}(k,\nu) c_{k,\nu,\lambda,\sigma}^\dagger c_{k,\nu,\lambda,\sigma}.$$

(26)

Here $k$ is an adimensional quasi-momentum along the nanotube, $\nu$ is an azimuthal quantum number, and $\lambda = 1, 2, 3, 4$ labels the four series (due to the four atoms in each cell), of $1D$ electronic bands with the dispersion laws

$$E_{\lambda}(k,\nu) = \mathcal{E}_0 \pm \mathcal{E}_\pm(k,\nu),$$

(27)
where
\[ \mathcal{E}_\pm(k, \nu) = J \sqrt{1 + 4 \cos^2\left(\frac{\nu}{2}\right) \pm 4 \cos\left(\frac{\nu}{2}\right) \cos\left(\frac{k}{2}\right)}. \] (28)

In (26) the operators \( c_{k,\nu,\lambda,\sigma}^\dagger(c_{k,\nu,\lambda,\sigma}) \) are creation (annihilation) operators of electrons with the quasi-momentum \( k \) and spin \( \sigma \) in the band \((\nu,\lambda)\). If we label the electronic bands as
\[ E_1(k, \nu) = \mathcal{E}_0 - \mathcal{E}_+(k, \nu), \quad E_2(k, \nu) = \mathcal{E}_0 - \mathcal{E}_-(k, \nu), \]
\[ E_3(k, \nu) = \mathcal{E}_0 + \mathcal{E}_-(k, \nu), \quad E_4(k, \nu) = \mathcal{E}_0 + \mathcal{E}_+(k, \nu), \] (29)

then the matrix of the unitary transformation coefficients \( \mathbf{u}(24) \) is given by
\[ \mathbf{u}(k, \nu) = \begin{pmatrix} e^{-i\frac{k-\nu}{4}+\theta_+} & e^{-i\frac{k-\nu}{4}-\theta_-} & e^{-i\frac{k+\nu}{4}+\theta_-} & e^{-i\frac{k+\nu}{4}-\theta_+} \\ e^{-i\frac{k+\nu}{4}-\theta_+} & e^{-i\frac{k+\nu}{4}+\theta_-} & -e^{-i\frac{k-\nu}{4}+\theta_-} & -e^{-i\frac{k-\nu}{4}-\theta_+} \\ e^{-i\frac{k+\nu}{4}+\theta_-} & e^{-i\frac{k-\nu}{4}-\theta_+} & e^{-i\frac{k+\nu}{4}+\theta_-} & e^{-i\frac{k-\nu}{4}-\theta_+} \\ e^{-i\frac{k-\nu}{4}-\theta_-} & e^{-i\frac{k+\nu}{4}+\theta_+} & e^{-i\frac{k-\nu}{4}-\theta_-} & e^{-i\frac{k+\nu}{4}+\theta_+} \end{pmatrix}, \] (30)

where the phases \( \theta \) satisfy the relation (148), given in Appendix 1.

5 Electron-Phonon Hamiltonian

The electron-phonon interaction originates from different mechanisms [10, 14, 11, 7, 8]. Usually, the dependence of the hopping interaction between the nearest neighbours \( J_{(\omega),\delta(\omega)} \) on their separation is considered and in the linear approximation with respect to the displacements one has
\[ J_{(\omega),\delta(\omega)} = J - G_2 W \delta_\omega. \] (31)

In general, neighbouring atoms also alter the energy of the \( \pi \)-electrons on each site and so, in the same linear approximation, we can write
\[ \mathcal{E}_\omega = \mathcal{E}_0 + \chi_1 \sum_\delta W \delta_\omega + \chi_2 C_\omega. \] (32)

Thus, the total electron-phonon interaction Hamiltonian should be taken in the following form
\[ H_{int} = \sum_{\omega,\sigma} \left( a_{\omega,\sigma}^\dagger a_{\omega,\sigma} \left[ \chi_1 \sum_\delta W \delta_\omega + \chi_2 C_\omega \right] + G_2 \sum_\delta a_{\omega,\sigma}^\dagger a_{\delta(\omega),\sigma} W \delta_\omega \right), \] (33)

where we have used the translation index operator \( \delta(\omega) \) defined in (8).

The unitary transformations (24) and (17), transform the interaction Hamiltonian into
\[ H_{int} = \frac{1}{2\sqrt{3}L_N} \sum_{k,\nu,\lambda,q,\mu,\tau,\sigma} F^{(\tau)}_{\lambda,\nu}(k, \nu; q, \mu; c_{k+q,\nu+\mu,\lambda,\sigma}^\dagger Q_{q,\mu,\tau}) \] (34)

where \( Q_{q,\mu,\tau} \) was determined in (18) and
\[ F^{(\tau)}_{\lambda,\nu}(k, \nu; q, \mu) = \frac{1}{4} \sum_{\rho' \rho} u_{\rho',\lambda}(k+q, \nu+\mu; c_{k+q,\nu+\mu,\lambda,\rho'}^\dagger c_{k,\nu,\lambda,\rho} Q_{q,\mu,\tau}) \] (35)

Note that \( T_{\rho' \rho}(k, \nu; q, \mu; \tau) = T_{\rho' \rho}(k+q, \nu+\mu; -q, -\mu; \tau) \) and that \( T_{1,3} = T_{3,1} = T_{2,4} = T_{4,2} = 0 \). The diagonal elements, at \( \rho' = \rho \), are
\[ T_{\rho,\rho}(q, \mu; \tau) = \frac{\chi_1}{\sqrt{M}} W_\rho(q, \mu; \tau) + \frac{\chi_2}{\sqrt{M}} C_\rho(q, \mu; \tau), \] (36)
and the nonzero off-diagonal elements, \( q \neq q' \), are given by

\[
T_{q', q}(k, \nu; q, \mu|\tau) = \frac{G_2}{\sqrt{M}} W_{q', q}(k, \nu; q, \mu|\tau),
\]

(37)

where \( W_{q}(q, \mu|\tau) \), \( C_{q}(q, \mu|\tau) \) and \( W_{q', q}(k, \nu; q, \mu|\tau) \) are determined only by the coefficients of the phonon unitary transformation (17). In particular,

\[
W_1(q, \mu|\tau) = \sqrt{3} \sin(\frac{\alpha}{4}) \left( S_{1, \tau} + e^{-i\frac{\mu}{2}} \cos(\frac{\mu}{2}) S_{2, \tau} \right) + i \sqrt{3} \cos(\frac{\alpha}{4}) \sin(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} U_{2, \tau} + \cos(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} V_{2, \tau} - e^{-i\nu} V_{4, \tau},
\]

\[
W_2(q, \mu|\tau) = \sqrt{3} \sin(\frac{\alpha}{4}) \left( S_{2, \tau} + \cos(\frac{\mu}{2}) e^{i\frac{\mu}{2}} S_{1, \tau} \right) + i \sqrt{3} \cos(\frac{\alpha}{4}) \sin(\frac{\mu}{2}) e^{i\frac{\mu}{2}} U_{1, \tau} - \cos(\frac{\mu}{2}) e^{i\frac{\mu}{2}} V_{1, \tau} + V_{3, \tau},
\]

\[
W_3(q, \mu|\tau) = \sqrt{3} \sin(\frac{\alpha}{4}) \left( S_{3, \tau} + \cos(\frac{\mu}{2}) e^{i\frac{\mu}{2}} S_{4, \tau} \right) + i \sqrt{3} \cos(\frac{\alpha}{4}) \sin(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} U_{4, \tau} + \cos(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} V_{4, \tau} - V_{2, \tau},
\]

\[
W_4(q, \mu|\tau) = \sqrt{3} \sin(\frac{\alpha}{4}) \left( S_{4, \tau} + \cos(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} S_{3, \tau} \right) + i \sqrt{3} \cos(\frac{\alpha}{4}) \sin(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} U_{3, \tau} - \cos(\frac{\mu}{2}) e^{-i\frac{\mu}{2}} V_{3, \tau} + e^{i\nu} V_{1, \tau},
\]

(38)

and

\[
W_{12}(\nu; q, \mu|\tau) = e^{-i\frac{\mu}{2}} \left( \sqrt{3} \sin(\frac{\alpha}{4}) \left( \cos(\frac{\nu}{2}) S_{1, \tau} + \cos(\frac{\mu}{2}) \sin(\frac{\nu + \mu}{2}) U_{2, \tau} \right) - i \sqrt{3} \cos(\frac{\alpha}{4}) \left( \sin(\frac{\nu}{2}) U_{1, \tau} - \cos(\frac{\nu + \mu}{2}) V_{2, \tau} \right) \right) + e^{-i\frac{\mu}{2}} \cos(\frac{\nu + \mu}{2}) V_{2, \tau} - \cos(\frac{\nu}{2}) V_{1, \tau},
\]

\[
W_{14}(k; q, \mu|\tau) = e^{-ik} \left( V_{1, \tau} - e^{-i\nu} V_{4, \tau} \right), \quad W_{23}(q, \mu|\tau) = V_{3, \tau} - V_{2, \tau},
\]

\[
W_{34}(\nu; q, \mu|\tau) = e^{i\frac{\mu}{2}} \left( \sqrt{3} \sin(\frac{\alpha}{4}) \left( \cos(\frac{\nu}{2}) S_{3, \tau} + \cos(\frac{\mu}{2}) U_{4, \tau} \right) - i \sqrt{3} \cos(\frac{\alpha}{4}) \left( \sin(\frac{\nu}{2}) U_{3, \tau} - \cos(\frac{\nu + \mu}{2}) V_{4, \tau} \right) \right) + e^{i\frac{\mu}{2}} \cos(\frac{\nu + \mu}{2}) V_{4, \tau} - \cos(\frac{\nu}{2}) V_{3, \tau},
\]

(39)

where \( S_{q, \tau} = S_{q, \tau}(q, \mu) \), \( V_{q, \tau} = V_{q, \tau}(q, \mu) \), and \( U_{q, \tau} = U_{q, \tau}(q, \mu) \).

Thus, the functions \( F_{q, \lambda, \nu}(k; q, \nu; \mu, \lambda) \) are determined by the interaction parameters \( \chi_1, \chi_2, G_2 \) and the coefficients of the unitary transformations (24) and (17). Note that, in (34), the azimuthal numbers satisfy the relation \( \nu_1 = \nu + \mu \), for which the following rule should be applied: if \( |\nu + \mu| > 2\pi \), then \( \nu_1 \rightarrow \nu_1' = \nu_1 \pm 2\pi \) in such a way that \( |\nu_1'| < 2\pi \).

6 Adiabatic approximation

The total Hamiltonian of the system is then given by

\[
H = H_e + H_{ph} + H_{int},
\]

(40)

where \( H_e, H_{ph} \) and \( H_{int} \) are given by (26), (19) and (34), respectively.
Below we consider only one-particle states in a carbon nanotube taking into account the interaction of the particle with the lattice distortions. When the coupling constant of this interaction is strong enough, this interaction can lead to the self-trapping of the particle. The self-trapped states are usually described in the adiabatic approximation. In this approximation the wavefunction of the system is represented as

$$|\Psi\rangle = U |\psi_e\rangle,$$

(41)

where $U$ is a unitary operator of the coherent atom displacements induced by the presence of the quasiparticle and so is given by an expression of the form

$$U = \exp\left[\sum_{\mu,q,\tau} (\beta_\tau(q,\mu)b^\dagger_{q,\mu,\tau} - \beta^*_\tau(q,\mu)b_{q,\mu,\tau})\right]$$

(42)

and $|\psi_e\rangle$ is the wavefunction of the quasiparticle itself. Moreover we require that it satisfies $\langle \psi_e | \psi_e \rangle = 1$.

In (42) the coefficients $\beta_{\mu,\tau}(q)$ depend on the state of the quasiparticle which, in turn, is determined by the lattice configuration. Using (41) in the Schrödinger equation $H |\Psi\rangle = E |\Psi\rangle$, we find the equation for the electronic part $|\psi_e\rangle$ of the total function (41)

$$\tilde{H} |\psi_e\rangle = E |\psi_e\rangle,$$

(43)

where

$$\tilde{H} = U^\dagger H U = W + \tilde{H}_e + H_{\text{int}} + H_{\text{ph}} + H_d.$$  

(44)

Here

$$W = \sum_{q,\mu,\tau} \hbar\omega_\tau(q,\mu)|\beta_\tau(q,\mu)|^2$$

(45)

is the energy of the lattice deformation,

$$\tilde{H}_e = \sum_{k,\nu,\lambda,\sigma} E_{\lambda}(k,\nu) c^\dagger_{k,\nu,\lambda,\sigma} c_{k,\nu,\lambda,\sigma} +$$

$$+ \frac{1}{2\sqrt{3LN}} \sum_{k,q,\lambda,\chi,\tau,\sigma} F^{(\tau)}_{\lambda,\chi}(k, q; \nu, \mu) Q_\tau(q, \mu)c^\dagger_{k+q,\nu+\mu,\chi,\sigma} c_{k,\nu,\chi,\sigma}$$

(46)

is the Hamiltonian of quasiparticles in the deformed lattice with the deformation potential given by

$$Q_\tau(q, \mu) = \left(\frac{\hbar}{2\omega_\tau(q, \mu)}\right)^{\frac{1}{2}} (\beta_\tau(q, \mu) + \beta^*_\tau(-q, -\mu)),$$

(47)

and

$$H_d = \sum_{q,\mu,\tau} \hbar\omega_\tau(q,\mu)(\beta_\tau(q,\mu)b^\dagger_{q,\mu,\tau} + \beta^*_\tau(q,\mu)b_{q,\mu,\tau})$$

(48)

is the displacement term of the phonon Hamiltonian. The latter term, $H_d$, is linear with respect to the phonon operators and appears here as a result of the action of the unitary operator (42).

With the help of the unitary transformation

$$c_{k,\nu,\lambda,\sigma} = \sum_\eta \psi_{\eta,\lambda}(k,\nu) C_{\eta,\sigma},$$

(49)

we can introduce the new Fermi operators $C_{\eta,\sigma}$ for which, in the general case, the quantum number $\eta$ is a multicomponent index. The coefficients $\psi_{\eta,\lambda}(k,\nu)$ are to be chosen from the condition that the electron Hamiltonian (46) can be transformed into a diagonal form:

$$\tilde{H}_e = \sum_{\eta,\sigma} E_{\eta} C^\dagger_{\eta,\sigma} C_{\eta,\sigma}.$$  

(50)
This requirement leads to the following equations for the transformation coefficients:

\[
E_\eta \psi_{\eta;\lambda}(k, \nu) = E_\lambda(k, \nu) \psi_{\eta;\lambda}(k, \nu) + \frac{1}{2\sqrt{3L}} \sum_{q, \lambda', \tau} F^{(\tau)}_{\lambda,\lambda'}(k - q, q; \nu - \mu, \mu) Q_\tau(q, \mu) \psi_{\eta;\lambda'}(k - q, \nu - \mu).
\]  
(51)

Solutions of this system of equations, with the orthonormalization condition

\[
\sum_{\lambda, \nu, k} \psi_{\eta;\lambda}^*(k, \nu) \psi_{\eta';\lambda}(k, \nu) = \delta_{\eta, \eta'}
\]  
(52)

then give us the coefficients \( \psi_{\eta;\lambda}(k, \nu) \) as well as the eigenvalues \( E_\eta \) of the electron energy levels.

After the transformation (49) the interaction Hamiltonian becomes

\[
\tilde{H} = H_0 + H_{\text{na}}
\]  
(55)

where

\[
H_0 = W + \tilde{H}_e + H_{\text{ad}} + H_{\text{ph}} + H_d
\]  
(56)

describes the system in the adiabatic approximation and \( H_{\text{na}} \) is the nonadiabaticity operator.

At large enough electron-phonon coupling, the nonadiabaticity is less important and the operator \( H_{\text{na}} \) can be considered as a perturbation. In the zero-order adiabatic approximation the quasiparticle wavefunction \( |\psi_e^{(0)}\rangle \) does not depend on phonon variables. In the case of a system with \( N_e \) electrons it can be represented as a product of \( N_e \) electron creation operators which act on the quasiparticle vacuum state.

In particular, the one-particle states are described by the function

\[
|\psi_e^{(0)}\rangle = C_{\eta, \sigma}^\dagger |0\rangle,
\]  
(57)

where \( |0\rangle \) is the quasiparticle and phonons’ vacuum state, the index \( \eta \) labels the adiabatic state which is occupied by the quasiparticle. For the ground state we put \( \eta = g \). The total wavefunction of the system (41) describes the self-trapped states of a large polaron in the zero-order adiabatic approximation.

Note that the function (57) is an eigenstate of the zero-order adiabatic Hamiltonian \( H_0 \):

\[
H_0 |\psi_e^{(0)}\rangle = \left[ W + E_g + \sum_{q, \mu, \tau} \left( \hbar \omega_{\tau}(q, \mu) \beta_{\mu, \tau}(q) + \frac{1}{2} \frac{\hbar}{6L} \Gamma^{(\tau)}_{g,g}(q, \mu) \psi_{q, \mu, \tau}^\dagger + h.c. \right) \right] |\psi_e^{(0)}\rangle
\]  
(58)
with the energy $E_g = W + E_g$ provided that the coefficients $\beta_\tau(q, \mu)$ in (42) satisfy:

$$\hbar \omega_\tau(q, \mu) \beta_\mu,\tau(q) = -\frac{1}{2} \sqrt{\frac{\hbar}{6LN \omega_\tau(q, \mu)}} \gamma_{g\eta}(q, \mu) =$$

$$-\frac{1}{2} \sqrt{\frac{\hbar}{6LN \omega_\tau(q, \mu)}} \sum_{k,\nu,\lambda\lambda'} F_{\lambda,\lambda'}^{(\tau)}(q, \nu, \mu) \psi_{\eta;\lambda'}^*(k, \nu; k, \nu) \psi_{\eta;\lambda}(k + q, \nu + \mu). \quad (59)$$

The adiabatic electron states are determined by (51) in which the lattice distortion $Q_\tau(q, \mu)$, according to Eqs.(47,59), is self-consistently determined by the electron state:

$$Q_\tau(q, \mu) = -\frac{1}{2\sqrt{3LN}} \sum_{k,\nu,\lambda\lambda'} F_{\lambda,\lambda'}^{(\tau)}(q, \nu, \mu) \psi_{\eta;\lambda}^*(k, \nu) \psi_{\eta;\lambda}(k + q, \nu + \mu). \quad (60)$$

Substituting (60) into equations (51) for the occupied electron state, we obtain a nonlinear equation for $\psi_{\eta;\lambda}(k, \nu)$ whose solution, satisfying the normalization condition (52), gives the wavefunction and eigenenergy $E_g$ of the electron ground state and, therefore, the self-consistent lattice distortion. All other unoccupied excited electron states with $\eta \neq g$ can be found from the linear equations (51) with the given deformational potential.

Using the inverse unitary transformations (49) and (24), we can rewrite the eigenfunction (57) in the following form:

$$|\psi_e^{(0)}\rangle = \sum_{\lambda,\nu,\eta} \psi_{\eta;\lambda}(k, \nu) c_{k,\nu,\lambda,\eta}^\dagger |0\rangle = \sum_\omega \psi_{\eta,\omega} a_{\alpha,\omega}^\dagger |0\rangle,$$

where

$$\psi_{\eta,\omega} = \frac{1}{2\sqrt{LN}} \sum_{\lambda,\nu,\eta} e^{i(km + \nu n)} u_{\eta,\lambda}(k, \nu) \psi_{\eta;\lambda}(k, \nu). \quad (62)$$

Here $\psi_{\eta,\omega}$ is the polaron wave function, i.e., the probability amplitude of the distribution of a quasiparticle over the nanotube sites: $P(\omega) = |\psi_{\eta,\omega}|^2$.

### 7 Large polaron state

Putting Eqs (60) into (51) gives us the nonlinear equations

$$\left( E_{\lambda}(k, \nu) - E \right) \psi_{\lambda}(k, \nu) =$$

$$\frac{1}{LN} \sum_{\lambda',\lambda_1,k_1,\nu_1,\mu} G_{\lambda,\lambda'}^{\lambda_1,\lambda_1} \left( k, k_1, q, \nu, \nu_1, \mu \right) \psi_{\lambda_1}^*(k_1, \nu_1) \psi_{\lambda_1'}(k_1 + q, \nu_1 + \mu) \psi_{\lambda'}(k - q, \nu - \mu) \quad (63)$$

for the one-electron ground state. Here, and from now onwards, we have omitted the index $\eta = g$ and introduced the notation

$$G_{\lambda,\lambda'}^{\lambda_1,\lambda_1} \left( k, k_1, q, \nu, \nu_1, \mu \right) = \frac{1}{12} \sum_\tau F_{\lambda,\lambda'}^{(\tau)}(k - q, \nu - \mu; q, \mu) F_{\lambda_1,\lambda_1'}^{(\tau)}(k_1, \nu_1; q, \mu) \psi_{\lambda'}^*(k - q, \nu - \mu) \quad (64)$$

We see that all sub-levels of all sub-bands participate in the formation of the self-trapped electron states and, in general, there are many solutions of Eq.(63). Among these solutions there are ‘one-band’ solutions in which only the function $\psi_{\lambda}(k, \nu)$ with quantum numbers $\lambda = \lambda_0$ and $\nu = \nu_0$ is nonzero and all other functions $\psi_{\lambda}(k, \nu) = 0$ with $\lambda \neq \lambda_0$ and $\nu \neq \nu_0$. But not all of these solutions are stable.
Next we consider the ‘one-band’ self-trapped state which is stable and is split off from the lowest energy subband in (29), namely from $E_1(k, 0)$ with $\lambda_0 = 1$ and $\nu_0 = 0$. In this case Eq. (63) becomes

$$0 = \left( E - E_1(k, 0) \right) \psi_1(k, 0)$$

$$+ \frac{1}{LN} \sum_{k_1, q} G(k, k_1, q) \psi_1(k_1, 0) \psi_1(k_1 + q, 0) \psi_1(k - q, 0),$$

(65)

where

$$G(k, k_1, q) = G^{1,1}_{1,1} \left( \begin{array}{ccc} k & k_1 & q \\ 0 & 0 & 0 \end{array} \right).$$

(66)

To solve (65), we introduce the function

$$\varphi(\zeta) = \frac{1}{\sqrt{L}} \sum_k e^{ikx} \psi_1(k, 0)$$

(67)

which depends on the continuous variable $\zeta$, that is a dimensionless coordinate along the nanotube axis related to $z$ by $\zeta = z/3d$.

Then we assume that in the site representation a solution of (65) is given by a wave packet broad enough so that it is sufficiently narrow in the $k$- representation. This means that $\psi_1(k, 0)$ is essentially nonzero only in a small region of $k$-values in the vicinity of $k = 0$. Therefore, we can use the long-wave approximation

$$E_1(k, 0) = \mathcal{E}_0 - J \sqrt{5 + 4 \cos\left(\frac{k}{2}\right)} \approx \mathcal{E}_1(0) + \frac{1}{12} Jk^2,$$

$$G(k, k_1, q) \approx G_0(0, 0, 0) = G,$$

(68)

where

$$\mathcal{E}_1(0) = \mathcal{E}_0 - 3J$$

(69)

is the energy bottom of the subband $E_1(k, 0)$.

Using Eqs. (35) - (39) and (19) for $\nu = \mu = 0$ in the long-wave approximation, we can represent the nonlinearity parameter $G$ as

$$G = \frac{(\chi_1 + G_2)^2 a_1^2 + \chi_2 b_1^2 + b_2(\chi_1 + G_2) \chi_2}{k + c^2 k_c}$$

(70)

where $a_1$ is a constant of the order of unity, while the constants $b_1, b_2, c$ are less than 1. Introducing

$$\Lambda = E - \mathcal{E}_1(0),$$

(71)

we can transform Eq.(65) into a differential equation for $\varphi(\zeta)$:

$$\Lambda \varphi(\zeta) + \frac{J}{12} \frac{d^2 \varphi(\zeta)}{d\zeta^2} + \frac{G}{N} |\varphi(\zeta)|^2 \varphi(\zeta) = 0,$$

(72)

which is the well-known stationary nonlinear Schrödinger equation (NLSE). Its normalized solution is given by

$$\varphi(\zeta) = \sqrt{\frac{g_0}{2 \cosh(g_0(\zeta - \zeta_0))}},$$

(73)

with the eigenvalue

$$\Lambda_0 = -\frac{J g_0^2}{12},$$

(74)
where
\[ g_0 = \frac{3G}{NJ}. \] (75)
Thus, the eigenenergy of this state is
\[ E_0 = E_1(0) - \frac{3G^2}{4NJ^2}. \] (76)

The probability amplitude (62) of a quasiparticle distribution over the nanotube sites, in this state, is given by
\[ \psi_{m,n,\varrho} = \frac{1}{2\sqrt{LN}} \sum_k e^{ikm} u_{\varrho,1}(k,0) \psi_1(k,0). \] (77)

The explicit expressions for \( u_{\varrho,1}(k,0) \) are given in (30). In the long-wave approximation for the phase \( \theta_{\pm}(k,0) \) we find from (148) that \( \theta_{\pm}(k,0) \approx k/12 \). Then, using the expressions for \( u_{\varrho,1}(k,0) \) and taking into account the definition (67), we obtain
\[ \psi_{m,n,\varrho} = \frac{1}{2\sqrt{N}} \varphi(z_{m,\varrho}), \] (78)
where \( z_{m,\varrho} \) are the atom positions along the nanotube axis (2):
\[
\begin{align*}
    z_{m,1} &= (m - \frac{1}{3})3d, & z_{m,2} &= (m - \frac{1}{6})3d, \\
    z_{m,3} &= (m + \frac{1}{6})3d, & z_{m,4} &= (m + \frac{1}{3})3d.
\end{align*}
\] (79)

Therefore, according to our solution (73), the probability distribution of a quasiparticle over the nanotube sites is given by
\[ P_{\varrho}(m,n) = \frac{1}{4N} |\varphi(z_{m,\varrho})|^2 = \frac{g_0}{8N} \frac{1}{\cosh^2(\frac{g_0}{3d} z_{m,\varrho})}. \] (80)
Thus, the quasiparticle is localized along the tube axis and distributed uniformly over the tube azimuthal angle. Therefore, (80) describes a quasi-1D large polaron. In this state, as well as in other one-band states, according to (60), only the total symmetrical distortion of the nanotube takes place, i.e. \( Q_x(q,0) \neq 0 \) with \( \mu = 0 \) and \( Q_x(q,\mu) = 0 \) for \( \mu \neq 0 \). The total energy of the polaron state according to (58), is
\[ \mathcal{E}_0 = W + E_0 = E_1(0) - \frac{G^2}{4NJ^2}, \] (81)
and, thus, depends on the diameter of the nanotube.

### 8 Transition to states with broken axial symmetry

As we see from (78),(73) and (80), our solution, obtained in the long-wave (continuum) approximation, possesses the azimuthal symmetry and describes a quasi-1D large polaron state which is localized along the nanotube axis in the region \( \Delta z = \frac{3m}{g_0} \). Moreover, (75) shows that as the electron-phonon coupling increases the region of the localization gets smaller. Consequently, the wave packet in the quasimomentum representation becomes broader and the electron states with higher energies participate in the formation of the polaron state. At strong enough coupling the long-wave (continuum) approximation is not valid. Moreover, the electron states from the upper bands can also contribute to the polaron formation. To consider the transition from the large
polaron state to the small one, it is convenient to transform Eqs.(63) into the site representation.

As a first step, let us introduce the functions

$$\phi_0(k, \nu) = \frac{1}{2} \sum_{\lambda} u_{\phi, \lambda}(k, \nu) \psi_{\lambda}(k, \nu).$$  \hspace{1cm} (82)

Then Eqs.(63) can be rewritten as the following system of equations

$$E\phi_1(k, \nu) = E_0\phi_1(k, \nu) - 2J \cos\left(\frac{\nu}{2}\right) e^{-i\frac{\mu}{2}} \phi_2(k, \nu) - J e^{-ik} \phi_4(k, \nu) -$$

$$- \frac{1}{LN} \sum_{k_1, \nu_1 q, \mu} \sum_{\ell_1, \ell_1, \ell'} T_{1, \ell, \ell'} \phi_1(k, \nu; k_1, \nu_1; \mu, \nu_1) \phi_{\ell_1}(k_1 + q, \nu_1 + \mu) \phi_{\ell'}(k - q, \nu - \mu),$$

$$E\phi_2(k, \nu) = E_0\phi_2(k, \nu) - 2J \cos\left(\frac{\nu}{2}\right) e^{i\frac{\mu}{2}} \phi_1(k, \nu) - J \phi_3(k, \nu) -$$

$$- \frac{1}{LN} \sum_{k_1, \nu_1 q, \mu} \sum_{\ell_1, \ell_1, \ell'} T_{2, \ell, \ell'} \phi_2(k, \nu; k_1, \nu_1; \mu, \nu_1) \phi_{\ell_1}(k_1 + q, \nu_1 + \mu) \phi_{\ell'}(k - q, \nu - \mu),$$

$$E\phi_3(k, \nu) = E_0\phi_3(k, \nu) - 2J \cos\left(\frac{\nu}{2}\right) e^{-i\frac{\mu}{2}} \phi_4(k, \nu) - J \phi_2(k, \nu) -$$

$$- \frac{1}{LN} \sum_{k_1, \nu_1 q, \mu} \sum_{\ell_1, \ell_1, \ell'} T_{3, \ell, \ell'} \phi_3(k, \nu; k_1, \nu_1; \mu, \nu_1) \phi_{\ell_1}(k_1 + q, \nu_1 + \mu) \phi_{\ell'}(k - q, \nu - \mu)$$

$$E\phi_4(k, \nu) = E_0\phi_4(k, \nu) - 2J \cos\left(\frac{\nu}{2}\right) e^{i\frac{\mu}{2}} \phi_3(k, \nu) - J e^{ik} \phi_1(k, \nu) -$$

$$- \frac{1}{LN} \sum_{k_1, \nu_1 q, \mu} \sum_{\ell_1, \ell_1, \ell'} T_{4, \ell, \ell'} \phi_4(k, \nu; k_1, \nu_1; \mu, \nu_1) \phi_{\ell_1}(k_1 + q, \nu_1 + \mu) \phi_{\ell'}(k - q, \nu - \mu)$$

(83)

where

$$T_{\ell_1, \ell'}(k, \nu; k_1, \nu_1; \mu, \rho) = \frac{1}{12} \sum_{\tau} T_{\ell, \ell'}(k - q, \nu - \mu; \rho, \mu | \tau) T_{\phi, \phi}(k_1, \nu_1; \mu | \tau) \omega_{\ell}(q, \mu).$$  \hspace{1cm} (84)

In the derivation of these equations we have used the explicit expressions (64) and (35), the orthonormalization conditions (52) and the following expressions for $E_{\pm}(k, \nu)$

$$E_{\pm}(k, \nu) = J \left(2 \cos\left(\frac{\nu}{2}\right) e^\pm i\frac{\mu}{2}\right) e^{\pm 2i\phi_{\pm}(k, \nu)}.$$  \hspace{1cm} (85)

To describe the system in the site representation, we introduce

$$\phi_{0,m}(\nu) = \frac{1}{L} \sum_k e^{ikm} \phi_0(k, \nu),$$  \hspace{1cm} (86)

and obtain

$$E\phi_{1,m}(\nu) = E_0\phi_{1,m}(\nu) - 2J \cos\left(\frac{\nu}{2}\right) e^{-i\frac{\mu}{2}} \phi_{2,m}(\nu) - J \phi_{4,m-1}(\nu) - \frac{a^2}{N} \sum_{\nu_1, \mu} \left(2 \chi^2 \phi_{1,m}(\nu_1) \phi_{1,m}(\nu_1 + \mu) + \chi G_{2} e^{i\phi_{2,m}(\nu_1)} \phi_{1,m}(\nu_1 + \mu) + \cos\left(\frac{\nu_1 + \mu}{2}\right) e^{-i\frac{\mu}{2}} \phi_{1,m}(\nu_1) \phi_{1,m}(\nu_1 + \mu) \right.$$ 

$$+ \phi_{1,m-1}(\nu_1) \phi_{1,m}(\nu_1 + \mu) \right) \phi_{1,m}(k - q, \nu - \mu) -$$

$$- \frac{a^2}{N} \sum_{\nu_1, \mu} \left( \chi G_{2} \phi_{1,m}(\nu_1) \phi_{1,m}(\nu_1 + \mu) + \ chi \right.$$.  \hspace{1cm} (86)
\[ + \cos(\frac{\nu_1 + \mu}{2})e^{-i\frac{\nu_1 + \mu}{2}} \cos(\frac{\nu_1}{2})e^{i\frac{\nu_1}{2}} \phi_{2,m}(\nu_1)\phi_{2,m}(\nu_1 + \mu) + \\
+ 2G_2^2[\cos(\frac{\nu_1}{2})e^{i\frac{\nu_1}{2}} \phi_{2,m}(\nu_1)\phi_{1,m}(\nu_1 + \mu) + \\
+ \cos(\frac{\nu_1 + \mu}{2})e^{-i\frac{\nu_1 + \mu}{2}} \phi_{1,m}(\nu_1)\phi_{2,m}(\nu_1 + \mu)]e^{-i\frac{\nu_1 + \mu}{2}} \phi_{2,m}(k - q, \nu - \mu) - \\
- \frac{a_0^2}{N} \sum_{\nu_1,\mu} \left( \chi_1 G_2[\phi_{1,m}(\nu_1)\phi_{1,m}(\nu_1 + \mu) + \phi_{4,m-1}(\nu_1)\phi_{4,m-1}(\nu_1 + \mu)] + \\
+ 2G_2^2[\phi_{4,m-1}(\nu_1)\phi_{1,m}(\nu_1 + \mu) + \phi_{1,m}(\nu_1)\phi_{4,m-1}(\nu_1 + \mu)]\phi_{4,m-1}(k - q, \nu - \mu) \right). \tag{87} \]

with similar equations for \( q = 2, 3, 4. \)

When deriving equations (87) we have made a qualitative estimate of the expressions of the form

\[ \frac{1}{12} \sum_{\tau} \frac{W_{0,\tau}(k - q, \nu - \mu; q, \mu|\tau)W_{\tau,\tau}(k_1, \nu_1; q, \mu|\tau)}{\omega_\tau^2(q, \mu)} \tag{88} \]

by assuming that the main contribution to these quantities comes from the lattice variables with small \( q \) and \( \mu \). This gives us an estimate of \( a_1 \) in Eq.(87).

In zigzag nanotubes, one can identify zigzag chains of carbon atoms which encircle the nanotube. Let the ring chain \( j \) consists of atoms enumerated as \((m, n, 1)\) and \((m, n, 2)\), the zigzag chain of atoms \((m, n, 3)\) and \((m, n, 4)\) corresponds to the ring \( j + 1 \), and the chain of atoms \((m - 1, n, 3)\) and \((m - 1, n, 4)\), respectively, to the ring with number \( j - 1 \). Then we can enumerate atoms as \((j, n, \rho)\) where \( \rho = 0, 1 \). Note that the indices \((j, \rho)\) coincide with the ones used in the numerical calculations [23].

A circle around the nanotube is a zigzag ring chain, with two atoms per unit cell, which contains \( 2N \) atoms. The atoms of the \( j \)-th chain are equivalent except that atoms with \( \rho = 0 \) are coupled to the \((j - 1)\)-th chain and those with \( \rho = 1 \) to the \((j + 1)\)-th chain, and these two sets of atoms are shifted with respect to each other in the opposite directions from some central line, \( z_j \), (symmetry axes). Thus, we can put

\[ \psi_j(\nu) = \frac{1}{\sqrt{2}} \left( \phi_{1,m}(\nu) + e^{-i\frac{\pi}{2n}} \phi_{2,m}(\nu) \right) = \frac{1}{\sqrt{2N}} \left( \sum_{n=1}^{N-1} e^{-i\frac{\pi}{2n}} \phi_{1,m,n} + \sum_{n=1}^{N-1} e^{-i\frac{\pi}{2n}(2n+1)} \phi_{2,m,n} \right) = \frac{1}{\sqrt{2N}} \sum_{l=1}^{2N-1} e^{-i\frac{\pi}{2n}} \phi_{m,l}. \tag{89} \]

We see that \( \psi_j(\nu) \) is a \( k \)-representation for a simple chain with \( 2N \) atoms with \( k = \nu/2 = \pi \nu_1/n \). Therefore, this zigzag ring chain is equivalent to an isolated nanocircle, studied in [25].

Introducing the notation: \( \phi_{1,m}(\nu) = \phi_{0,j}(\nu), \ e^{-i\frac{\pi}{2n}} \phi_{2,m}(\nu) = \phi_{1,j}(\nu) \) and neglecting \( \chi_2 \) we can rewrite Eq.(87) as follows:

\[ E\phi_{0,j}(\nu) = E_0\phi_{0,j}(\nu) - 2J \cos(\frac{\nu}{2})\phi_{1,j}(\nu) - J\phi_{1,j-1}(\nu) - \frac{G}{N} \sum_{\nu_1,\mu} \phi_{0,j}(\nu_1)\phi_{0,j}(\nu_1 + \mu)\phi_{0,j}(\nu - \mu), \tag{90} \]

where \( G \) is given by Eq. (70).

For the azimuthal symmetric solution the only nonzero functions are those with zero argument, \( \nu = 0 \). In this case we can use the continuum approximation:

\[ \phi_{0,j} = \phi(\zeta_0,j), \ \phi_{1,j} = \phi(\zeta_0,j + \frac{1}{6}) = \phi(\zeta_0,j) + \frac{1}{6} \phi'(\zeta_0,j) + \frac{1}{72} \phi''(\zeta_0,j), \]

\[ \phi_{1,j-1} = \phi(\zeta_0,j - \frac{1}{3}) = \phi(\zeta_0,j) - \frac{1}{3} \phi'(\zeta_0,j) + \frac{1}{18} \phi''(\zeta_0,j). \tag{91} \]

As a result Eq. (90) transforms into the continuum NLSE (72). The azimuthally symmetric solution of this equation does not always correspond to the state of the lowest energy. To find
the lowest energy state, we consider Eq. (90) assuming that the electron is localized mainly on one chain (for simplicity we label it by \( j = 0 \)) and we look for a solution of the form

\[
\phi_{\rho,j}(\nu) = A_{\rho,j} \phi(\nu),
\]

(92)

where \( A_{\rho,j} \) are given by Eq. (73) with \( \zeta_0 \) describing the position of the considered chain.

We can now consider the equation for the chain \( j = 0 \) only. For \( \phi(\nu) \) we obtain the equation:

\[
(E - \mathcal{E}(\nu))\phi(\nu) + \frac{GA_{\rho,0}^2}{N} \sum_{\nu_1,\mu} \phi^*(\nu_1)\phi(\nu_1 + \mu)\phi(\nu - \mu),
\]

(93)

where

\[
\mathcal{E}(\nu) = \mathcal{E}_0 - J \frac{A_{1,-1}}{A_{0,0}} - 2J \cos \frac{\nu}{2}.
\]

(94)

Moreover, from (73) we find that

\[
A_{0,0} = A_{1,0} = \sqrt{\frac{g_0}{2} \frac{1}{\cosh(g_0/12)}}, \quad A_{1,-1} = \sqrt{\frac{g_0}{2} \frac{1}{\cosh(5g_0/12)}}.
\]

(95)

Assuming that the function \( \phi(\nu) \) is essentially nonzero in the vicinity of the zero values of \( \nu \), the energy dispersion can be written in the long-wave approximation as

\[
\mathcal{E}(k) = \mathcal{E}(0) + J \left( \frac{\nu}{2} \right)^2 + \ldots,
\]

(96)

where

\[
\mathcal{E}(0) = \mathcal{E}_0 - J \left( 2 + \frac{A_{1,-1}}{A_{0,0}} \right).
\]

(97)

To solve Eq.(93) we introduce the function

\[
\varphi(x) = \frac{1}{\sqrt{2N}} \sum_k e^{ikx}\psi(k)
\]

(98)

of the continuum variable \( x \) with \( k = \nu/2 \) being the quasimomentum of the nanotube circle with one atom per unit cell. Therefore, the quasimomentum representation should be studied in the extended band scheme and \( -\pi < k < \pi \). Note that \( \varphi(x) \) is a periodic function, \( \varphi(x+2N) = \varphi(x) \), and that the discrete values of \( x = n, n = 1, 2, \ldots 2N - 1 \), correspond to the atom positions in the zigzag ring.

Using the approximation (96) one can transform (93) into a nonlinear differential equation for \( \varphi(x) \) (stationary NLSE):

\[
J \frac{d^2\varphi(x)}{dx^2} + GA_{0,0}^2|\varphi(x)|^2\varphi(x) + \Lambda \varphi(x) = 0,
\]

(99)

where \( \Lambda = E - \mathcal{E}(0) \).

As it has been shown in [25], the solution of Eq. (93), satisfying the normalization condition

\[
\int_0^{2N} |\varphi(x)|^2 dx = 1,
\]

(100)

is expressed via the elliptic Jacobi functions:

\[
\varphi(x) = \frac{\sqrt{g}}{2\mathbf{E}(k)} dn \left[ \frac{2K(k)x}{2N}, k \right].
\]

(101)
Here \( g = GA_0^2/(2J) \), and \( K(k) \) and \( E(k) \) are complete elliptic integrals of the first and second kind, respectively [29]. The modulus of the elliptic Jacobi function, \( k \), is determined from the relation

\[
E(k)K(k) = \frac{gN}{2}. \tag{102}
\]

The eigenvalue of the solution (101) is

\[
\Lambda = -J \frac{g^2}{4} \frac{(2 - k^2)}{E^2(k)}. \tag{103}
\]

According to [25], the azimuthally symmetric solution exists (relation (102) admits solution) only when \( g \) exceeds the critical value of the nonlinearity constant

\[
g > g_{cr} = \frac{\pi^2}{2N}, \tag{104}
\]

or, in an explicit form,

\[
3 \frac{\sigma^2}{2\pi^2 \cosh^2(\sigma/(4N))} > 1, \tag{105}
\]

where \( \sigma = G/J \) is the adimensional electron-phonon coupling constant.

From (105) we find the critical value of the coupling constant, \( g_{cr} \approx 6 \) for \( N = 8 \). According to the numerical solution [23], the critical value of the coupling constant \((\chi_1 + G_2)^2/(kJ) \approx 3.2 \) for this value of \( N \). Comparing this result with the analytical prediction, we conclude, that the parameter \( a_1 \) in (70) is \( a_1 \approx 0.9 \). Therefore, the estimation \( a_1 \approx 1 \) made above is indeed valid, which justifies our analytical results. Of course, the applicability of this approach far from the transition breaks down because the continuum approximation itself is not valid anymore.

9 Large polaron states in semiconducting nanotubes

In zigzag nanotubes, when \( N \) is not a multiple of 3, there is an energy gap in the electron spectrum (29). In the carbon SWNT this energy gap, \( \Delta \), separates the 1D electron sub-bands \( E_0 - E_\pm(k, \nu) \), which are fully occupied, from the empty ones with energy \( E_0 + E_\pm(k, \nu) \). Such nanotubes are semiconducting [1]. Their charge carriers are either electrons (in the conducting band) or holes (in the valence band). For semiconducting zigzag nanotubes \( N \) can be represented as \( N = 3n_0 + 1 \) or \( N = 3n_0 - 1 \). The lowest conducting subband above the energy gap is

\[
E_3(k, \nu_0) = E_0 + E_-(k, \nu_0), \tag{106}
\]

and the highest valence subband below the gap is

\[
E_2(k, \nu_0) = E_0 - E_-(k, \nu_0) \tag{107}
\]

with \( \nu_0 = 2\pi n_0/N \). So, the energy gap in semiconducting carbon nanotubes is given by

\[
\Delta = E_3(0, \nu_0) - E_2(0, \nu_0) = 2E_-(0, \nu_0) = 2J[1 - 2\cos(\nu_0/2)]. \tag{108}
\]

Next, we consider a self-trapped state of electrons in the lowest conducting band \( E_3(k, \nu) \). Because \( E_\pm(k, -\nu) = E_\pm(k, \nu) \), this subband is doubly degenerate. In this case we look for a solution in which only the functions \( \psi_3(k, \nu) \) with \( \nu = \pm \nu_0 \) are nonzero. Then Eqs. (63) become

\[
E\psi_3(k, \nu) = E_3(k, \nu_0)\psi_3(k, \nu) - \frac{1}{LN} \sum_{k', q, \nu'} \left( \sum_{\nu''} G^{(1)}_{\nu', \nu''}(k, k', q) \psi_3^*(k', \nu')\psi_3(k' + q, \nu')\psi_3(k - q, \nu) + G^{(2)}_{\nu, -\nu}(k, k', q) \psi_3(k', -\nu)\psi_3(k' + q, \nu)\psi_3(k - q, -\nu) \right), \tag{109}
\]
where $\nu, \nu' = \pm \nu_0$ and

\[
G^{(1)}_{\nu,\nu'}(k, k', q) = G^{3,3}_{3,3} \left( k, k', \nu, \nu', q, 0 \right), \quad (110)
\]

\[
G^{(2)}_{\nu,-\nu}(k, k', q) = G^{3,3}_{3,3} \left( k, k', \nu, -\nu, q, 2\nu \right). \quad (111)
\]

Here the equivalence of the azimuthal numbers $\mu$ and $\mu \pm 2\pi$ should be taken into account.

To solve (109), we introduce functions of the continuum variable $x$ using the relation (67)

\[
\varphi_{\nu,3}(x) = \frac{1}{\sqrt{L}} \sum_k e^{ikx} \psi_3(k, \nu)
\]

and use the long-wave approximation

\[
E_3(k, \nu_0) \approx E_3(0, \nu_0) + \frac{\hbar^2 k^2}{2m},
\]

\[
G^{(1)}_{\nu,\nu}(k, k', q) \approx G^{(1)}_{\nu,\nu}(0,0,0) = G_1,
\]

\[
G^{(2)}_{\nu,-\nu}(k, k', q) \approx G^{(2)}_{\nu,-\nu}(0,0,0) = G_2. \quad (113)
\]

Note that

\[
E_3(0, \nu_0) = \varepsilon_0 + \frac{1}{2}\Delta
\]

is the energy bottom of the subband $E_3(k, \nu_0)$ and

\[
m = \frac{2|1 - 2\cos(\frac{\nu_0}{2})|\hbar^2}{J\cos(\frac{\nu_0}{2})}
\]

is the quasiparticle effective mass in the subband $E_3(k, \nu_0)$.

In this case Eqs.(109) are transformed into a differential equations for $\varphi_{\nu,3}(x)$:

\[
\Lambda \varphi_{\nu,3}(x) + \frac{\hbar^2}{2m} \frac{d^2\varphi_{\nu,3}(x)}{dx^2} + \frac{1}{N} \left( G_1|\varphi_{\nu,3}(x)|^2 + (G_1 + G_2)|\varphi_{-\nu,3}(x)|^2 \right) \varphi_{\nu,3}(x) = 0,
\]

where

\[
\Lambda = E - E_3(0, \nu_0),
\]

(117)

and $\nu = \pm \nu_0$.

We observe that equations (116) admit two types of soliton-like ground state solutions. The first type corresponds to the given azimuthal quantum number: $\nu = \nu_0$ or $\nu = -\nu_0$. Such solutions describe solitons with a fixed value of the azimuthal number and are formed by the electron sublevels with $\nu$ from the doubly degenerate band, i.e., only one function $\varphi_{\nu} \neq 0$ is nonzero and the other one vanishes: $\varphi_{-\nu} = 0$. These types of solitons are described by the NLSE:

\[
\Lambda \varphi_{\nu,3}(x) + \frac{\hbar^2}{2m} \frac{d^2\varphi_{\nu,3}(x)}{dx^2} + \frac{G_1}{N} |\varphi_{\nu,3}(x)|^2 \varphi_{\nu,3}(x) = 0.
\]

(118)

A normalised solution of this equation is given by

\[
\varphi_{3,\nu}(x) = \sqrt{\frac{g_1}{2\cosh(g_1 x)}}
\]

(119)

with the eigenvalue

\[
\Lambda_1 = -\frac{\hbar^2 g_1^2}{2m},
\]

(120)
where

\[ g_1 = \frac{mG_1}{2\hbar^2 N} = \frac{G_1\left[1 - 2\cos\left(\frac{\nu k}{2}\right)\right]}{JN\cos\left(\frac{\nu k}{2}\right)}. \]  

(121)

Thus, the eigenenergy of these states is

\[ E_1 = \mathcal{E}_0 + \frac{1}{2}\Delta - \frac{G_1^2\left[1 - 2\cos\left(\frac{\nu k}{2}\right)\right]}{4JN^2\cos\left(\frac{\nu k}{2}\right)}. \]  

(122)

The energy levels of the two solitons with different azimuthal numbers (\(\nu = \nu_0\) and \(\nu = -\nu_0\)) are degenerate, similarly to the levels of the corresponding bands. However, according to Jan-Teller theorem, this degeneracy can be broken by the distortions of the lattice resulting in the hybridization of these two states.

Next we consider a case when both these functions are nonzero, \(\varphi_\pm \neq 0\). In this case \(\varphi_\pm\) are determined by the system of nonlinear equations (116). A normalised solution of these equations is given by

\[ \varphi_{\pm \nu_0} = \frac{1}{\sqrt{2}}e^{i\phi_{\pm}}\varphi_{h,3}, \]  

(123)

where \(\phi_{\pm}\) are arbitrary phases and where \(\varphi_{h,3}\) satisfies the NLSE (118) in which the nonlinearity parameter \(G_1\) is replaced by \(G_1 \rightarrow (2G_1 + G_2)/2\). Therefore, this solution is given by (119) with

\[ g_0 = \frac{m(2G_1 + G_2)}{4\hbar^2 N} = \frac{(2G_1 + G_2)\left[1 - 2\cos\left(\frac{\nu k}{2}\right)\right]}{2JN\cos\left(\frac{\nu k}{2}\right)}. \]  

(124)

Its eigenenergy is

\[ E_h = \mathcal{E}_0 + \frac{1}{2}\Delta - \frac{(2G_1 + G_2)^2\left[1 - 2\cos\left(\frac{\nu k}{2}\right)\right]}{16JN^2\cos\left(\frac{\nu k}{2}\right)}. \]  

(125)

This hybrid soliton possesses a zero azimuthal number while solitons (119) have a nonvanishing one: \(\nu = \nu_0\) or \(\nu = -\nu_0\). The energy level of the hybrid soliton state, \(E_h\), is lower than the level of a soliton with the fixed azimuthal number, \(E_1\), because \((2G_1 + G_2)/2 > G_1\). Note also that the deformation of the nanotube in this state is more complicated due to the fact that the components \(Q_{\pm 2\nu_0}\) of the lattice distortion, as well as the \(Q_0\)-component, are non-zero. Moreover, the probability distributions of a quasiparticle over the nanotube sites in the state of a hybrid polaron and in the state of polaron with a fixed azimuthal number, are different.

For a polaron state with a fixed azimuthal quantum number (e.g. \(\nu = \nu_0\)), the probability amplitude (62) is

\[ \psi_{m,n,\nu} = \frac{1}{2\sqrt{LN}} \sum_k e^{i(km + i\nu_0n)}u_{\varphi,3}(k, \nu_0)|\psi_3(k, \nu_0). \]  

(126)

The explicit expressions for \(u_{j,3}(k, \nu)\) are given in (30). In the long-wave approximation for the phase \(\theta_{\nu}(k, \nu_0)\) we find from (148) that

\[ \tan 2\theta_{\nu}(k, 0) \approx \frac{k}{4(2\cos\left(\frac{\nu k}{2}\right) - 1)}. \]  

(127)

Then, using the expressions for \(u_{j,3}(k, \nu)\) and taking into account the definition (67), we obtain

\[
\begin{align*}
\psi_{m, n, 1} &= \frac{1}{2\sqrt{N}} e^{i\nu_0(n - \frac{1}{2})} \varphi_{\nu, 3}(m - \frac{1}{3} + \frac{1}{2} \delta), \\
\psi_{m, n, 2} &= -\frac{1}{2\sqrt{N}} e^{i\nu_0(n + \frac{1}{4})} \varphi_{\nu, 3}(m - \frac{1}{6} - \frac{1}{2} \delta), \\
\psi_{m, n, 3} &= -\frac{1}{2\sqrt{N}} e^{i\nu_0(n + \frac{1}{4})} \varphi_{\nu, 3}(m + \frac{1}{6} + \frac{1}{2} \delta), \\
\psi_{m, n, 4} &= \frac{1}{2\sqrt{N}} e^{i\nu_0(n - \frac{1}{4})} \varphi_{\nu, 3}(m + \frac{1}{3} - \frac{1}{2} \delta),
\end{align*}
\]  

(128)
where
\[ \delta = \delta(\nu_0) = \frac{\cos\left(\frac{\nu_0}{2}\right) + 1}{3(2\cos\left(\frac{\nu_0}{2}\right) - 1)}. \] (129)

Therefore, according to (128) and (119), the quasiparticle distribution over the nanotube sites in this state is
\[ P_e(m, n) = P(z_{m,\varrho}) = \frac{g_1}{8N \cosh^2\left(\frac{g_1}{2}(z_{m,\varrho} \pm \frac{1}{2} 3d\delta)\right)}, \] (130)
where \( z_{m,\varrho} \) are the atom positions along the nanotube axis (2), the “+” and “−” signs correspond respectively to atoms with an odd \((\varrho = 1, 3)\) and even \((\varrho = 2, 4)\) index \(\varrho\). Usually these two types of atoms are labelled as \(A\) and \(B\) atoms.

We see that the quasiparticle is localised along the tube axis and is uniformly distributed over the tube azimuthal angle like a quasi-1D large polaron. But the distributions of the quasiparticle among \(A\) and \(B\) sites are shifted relatively to each other by the value \(3d\delta(\nu_0)\).

For a hybrid polaron state which possesses zero azimuthal number, the probability amplitudes (62) are
\[ \psi_{m,n,1} = \cos\left(\nu_0(n - \frac{1}{4}) + \phi_0\right) \frac{\varphi_{h,3}(m - \frac{1}{3} + \frac{1}{2}\delta)}{\sqrt{2N}}, \]
\[ \psi_{m,n,2} = -\cos\left(\nu_0(n + \frac{1}{4}) + \phi_0\right) \frac{\varphi_{h,3}(m - \frac{1}{6} - \frac{1}{2}\delta)}{\sqrt{2N}}, \]
\[ \psi_{m,n,3} = -\cos\left(\nu_0(n + \frac{1}{4}) + \phi_0\right) \frac{\varphi_{h,3}(m + \frac{1}{6} + \frac{1}{2}\delta)}{\sqrt{2N}}, \]
\[ \psi_{m,n,4} = \cos\left(\nu_0(n - \frac{1}{4}) + \phi_0\right) \frac{\varphi_{h,3}(m + \frac{1}{3} - \frac{1}{2}\delta)}{\sqrt{2N}}, \] (131)

Therefore, the quasiparticle distribution over the nanotube sites in this state is given by
\[ P_e(m, n) = P(z_{m,\varrho}, \phi_{n,\varrho}) = \frac{g_h \cos^2(n_0\phi_{n,\varrho} + \phi_0)}{4N \cosh^2\left(\frac{g_1}{2}(z_{m,\varrho} \pm \frac{1}{2} 3d\delta)\right)}, \] (132)
where \(\phi_{n,\varrho}\) is the angle for the atoms position in the nanotube (2), \(\phi_{n,\varrho} = n\alpha\) for \(\varrho = 1, 4\) and \(\phi_{n,\varrho} = (n + \frac{1}{2})\alpha\) for \(\varrho = 2, 3\); \(n_0\) is a number which determines the azimuthal number \(\nu_0\) \((\nu_0 = 2\pi n_0/N)\), and the “+” and “−” signs correspond to the odd and even values of \(\varrho\) as above.

We see, that in this polaron state the quasiparticle is localised along the tube axis and is modulated over the tube azimuthal angle with the angle modulation \(2\pi/n_0\). The longitudinal distributions of the quasiparticle among \(A\) and \(B\) sites are shifted relatively to each other by the value \(3d\delta(\nu_0)\).

10 Conclusions

In this paper we have derived the equations describing self-trapped states in zigzag nanotubes taking into account the electron-phonon coupling. We defined the electron and phonon Hamiltonians using the tight-binding model and derived the electron-phonon interaction arising due to the dependence of both the on-site and hopping interaction energies on lattice distortions. Next we performed the adiabatic approximation and we obtained the basic equations of the model. These are the equations in the site representation that were used by us in [23] to compute numerical solutions of nanotubes states and to determine the ranges of parameters for which the lowest states were soliton or polaron in nature.
In this paper we have studied this problem analytically. We have shown that the electrons in low lying states of the electronic Hamiltonian form polaron-like states. We have also looked at the sets of parameters for which the continuum approximation holds and the system is described by the nonlinear Schrödinger equation. This has given us good approximate solutions of the full equations (thus giving us good starting configurations for numerical simulations) and has also allowed us to compare our predictions with the numerical results [23].

Our results demonstrate the richness of the spectrum of polaron states. They include quasi-1D states with azimuthal symmetry for not too strong coupling constant, and, at relatively high coupling, states with broken azimuthal symmetry which are spread in more than one dimension. Theoretical estimates of the critical value of the coupling constants between the two regimes of self-trapping (with or without axial symmetry) are in good agreement with our numerical results [23].

We have also found that for the values of the parameters corresponding to carbon nanotubes, the lowest energy states are ring-like in nature with their profiles resembling a NLS soliton, ie similar to a Davydov soliton as was claimed in [23].

We have considered the polaron state of an electron (or a hole) in semiconducting carbon nanotubes and have shown that the degeneracy of the conducting (or valence) band with respect to the azimuthal quantum number plays an important role. The polarons with lowest energy spontaneously break down the azimuthal symmetry as well as the translational one and possess an inner structure: they are self-trapped along the nanotube axis and are modulated around the nanotube.

Next we plan to look in more detail at some higher lying states and study their properties. We are also planning to study the electric conduction properties of our system.

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12 Appendix 1. Diagonalization of the polaron Hamiltonian

Due to the fact that the diagonal expression

$$H_{e,0} = E_0 \sum_{a,\sigma} a^\dagger_{a,\sigma} a_{a,\sigma}$$  \hspace{1cm} (133)

remains diagonal under any unitary transformation, we consider only $H_J$. Omitting the multiplier $J$ and the spin index we note that $H_J$ is given by, in an explicit form ,

$$H_J = - \sum_{m,n} \left[ a^\dagger_{m,n,1} (a_{m,n-1,2} + a_{m,n,2} + a_{m-1,n,4}) \\
+ a^\dagger_{m,n,2} (a_{m,n,1} + a_{m,n,3} + a_{m,n+1,1}) \\
+ a^\dagger_{m,n,3} (a_{m,n,4} + a_{m,n+1,4} + a_{m,n,2}) \\
+ a^\dagger_{m,n,4} (a_{m,n-1,3} + a_{m+1,n,1} + a_{m,n,3}) \right].$$  \hspace{1cm} (134)

Due to the translational invariance (with respect to shifting the index $m$) and the rotational invariance (changing $n$) we can perform the transformation

$$a_{m,n,e} = \frac{1}{\sqrt{LN}} \sum_{k,\nu} e^{ikm+ivn} a_{k,\nu,e},$$  \hspace{1cm} (135)
which transforms the Hamiltonian (134) into a diagonal form with respect to the indices \( k \) and \( \nu \) and we get

\[
H_J = - \sum_{k,\nu} \left[ a_{k,\nu}^\dagger a_{k,\nu,3} + a_{k,\nu,3}^\dagger a_{k,\nu,2} + e^{-ik} a_{k,\nu,1}^\dagger a_{k,\nu,4} + e^{ik} a_{k,\nu,4}^\dagger a_{k,\nu,1} + 2 \cos \frac{\nu}{2} \left( e^{i\frac{\pi}{4}} a_{k,\nu,3}^\dagger a_{k,\nu,4} + e^{-i\frac{\pi}{4}} a_{k,\nu,4}^\dagger a_{k,\nu,3} \right) + 2 \cos \frac{\nu}{2} \left( e^{-i\frac{\pi}{4}} a_{k,\nu,1}^\dagger a_{k,\nu,2} + e^{i\frac{\pi}{4}} a_{k,\nu,2}^\dagger a_{k,\nu,1} \right) \right].
\]  

(136)

Note that a direct way to diagonalise (136) is to use the unitary transformation

\[
a_{k,\nu,\ell} = \frac{1}{2} \sum_{\lambda} u_{\varrho,\lambda}(k, \nu) c_{k,\nu,\lambda}
\]

with

\[
\frac{1}{4} \sum_{\lambda} u_{\varrho,\lambda}(k, \nu) u_{\varrho',\lambda}(k, \nu) = \delta_{\varrho,\varrho'}, \quad \frac{1}{4} \sum_{j} u_{\varrho,\lambda}(k, \nu) u_{\varrho,\lambda'}(k, \nu) = \delta_{\lambda,\lambda'}
\]

which leads to a system of equations (four in our case) for the coefficients \( u_{\varrho,\lambda}(k, \nu) \) which diagonalise the Hamiltonian. A solution of these equations would give us the coefficients of the transformation as well as the eigenvalues \( E_{\lambda}(k, \nu) \) \( (\lambda = 1, 2, 3, 4) \). Instead, we prefer to use a sequential diagonalization.

To do this we choose any two different pairs of operators \( a_{k,\nu,\varrho} \) and \( a_{k,\nu,\varrho'} \) and using unitary transformations we first diagonalise two of the four lines in (136). Taking the following two pairs: \( \{ a_{k,\nu,1,1}, a_{k,\nu,2} \} \) and \( \{ a_{k,\nu,3,1}, a_{k,\nu,4} \} \), and diagonalising the last two lines in (136) by the unitary transformations, we get

\[
a_{k,\nu,1} = \frac{1}{\sqrt{2}} \left( e^{-i\frac{\pi}{4}} b_{k,\nu,1} + e^{-i\frac{\pi}{4}} b_{k,\nu,2} \right),
\]

\[
a_{k,\nu,2} = \frac{1}{\sqrt{2}} \left( e^{i\frac{\pi}{4}} b_{k,\nu,1} - e^{i\frac{\pi}{4}} b_{k,\nu,2} \right),
\]

(139)

and

\[
a_{k,\nu,3} = \frac{1}{\sqrt{2}} \left( e^{i\frac{\pi}{4}} b_{k,\nu,3} + e^{i\frac{\pi}{4}} b_{k,\nu,4} \right),
\]

\[
a_{k,\nu,4} = \frac{1}{\sqrt{2}} \left( e^{-i\frac{\pi}{4}} b_{k,\nu,3} - e^{-i\frac{\pi}{4}} b_{k,\nu,4} \right).
\]

(140)

Substituting (139) and (140) into (136), we obtain

\[
H_J = - \sum_{k,\nu} \left[ 2 \cos \frac{\nu}{2} \left( b_{k,\nu,1}^\dagger b_{k,\nu,1} + b_{k,\nu,3}^\dagger b_{k,\nu,3} \right) + \cos \frac{k}{2} \left( e^{-i\frac{\pi}{4}} b_{k,\nu,1}^\dagger b_{k,\nu,3} + e^{i\frac{\pi}{4}} b_{k,\nu,3}^\dagger b_{k,\nu,1} \right) \right] - \\
\left[ 2 \cos \frac{\nu}{2} \left( b_{k,\nu,2}^\dagger b_{k,\nu,2} + b_{k,\nu,4}^\dagger b_{k,\nu,4} \right) + \cos \frac{k}{2} \left( e^{-i\frac{\pi}{4}} b_{k,\nu,2}^\dagger b_{k,\nu,4} + e^{i\frac{\pi}{4}} b_{k,\nu,4}^\dagger b_{k,\nu,2} \right) \right] + \\
i \sin \frac{k}{2} \left( e^{-i\frac{\pi}{4}} b_{k,\nu,4}^\dagger b_{k,\nu,1} - e^{i\frac{\pi}{4}} b_{k,\nu,1}^\dagger b_{k,\nu,4} - e^{-i\frac{\pi}{4}} b_{k,\nu,2}^\dagger b_{k,\nu,3} - e^{i\frac{\pi}{4}} b_{k,\nu,3}^\dagger b_{k,\nu,2} \right). \]

(141)

Here we have combined the two pairs of operators: \( \{ b_{k,\nu,1}, b_{k,\nu,3} \} \) with energies \( 2 \cos \frac{\nu}{2} \), and \( \{ b_{k,\nu,2}, b_{k,\nu,4} \} \) with energies \( -2 \cos \frac{\nu}{2} \). Next we observe that the diagonalization of the first two lines in (141) reduces to the diagonalization of only the non-diagonal parts (the second terms in the square brackets) which is achieved by the transformations similar to (139)-(140):

\[
b_{k,\nu,1} = \frac{1}{\sqrt{2}} \left( e^{-i\frac{\pi}{4}} d_{k,\nu,1} + e^{-i\frac{\pi}{4}} d_{k,\nu,2} \right),
\]

\[
b_{k,\nu,3} = \frac{1}{\sqrt{2}} \left( e^{i\frac{\pi}{4}} d_{k,\nu,1} - e^{i\frac{\pi}{4}} d_{k,\nu,2} \right),
\]

(142)
and
\[ b_{k,\nu,2} = \frac{1}{\sqrt{2}} (e^{-i\frac{k}{4}} d_{k,\nu,3} + e^{-i\frac{k}{4}} d_{k,\nu,4}), \]
\[ b_{k,\nu,4} = \frac{1}{\sqrt{2}} (e^{i\frac{k}{4}} d_{k,\nu,3} - e^{i\frac{k}{4}} d_{k,\nu,4}). \] (143)

After such transformations, the Hamiltonian (141) becomes
\[
H_J = - \sum_{k,\nu} \left\{ \varepsilon_+ d_{k,\nu,1}^\dagger d_{k,\nu,1} - \varepsilon_+ d_{k,\nu,3}^\dagger d_{k,\nu,3} + i \sin \frac{k}{2} \left( d_{k,\nu,1}^\dagger d_{k,\nu,3} - d_{k,\nu,3}^\dagger d_{k,\nu,1} \right) \right\} + \\
+ \left\{ \varepsilon_- d_{k,\nu,2}^\dagger d_{k,\nu,2} - \varepsilon_- d_{k,\nu,4}^\dagger d_{k,\nu,4} - i \sin \frac{k}{2} \left( d_{k,\nu,2}^\dagger d_{k,\nu,4} - d_{k,\nu,4}^\dagger d_{k,\nu,2} \right) \right\} 
\] (144)

where
\[
\varepsilon_+ = \varepsilon_+ (k, \nu) = 2 \cos \frac{\nu}{2} + \cos \frac{k}{2}, \quad \varepsilon_- = \varepsilon_- (k, \nu) = 2 \cos \frac{\nu}{2} - \cos \frac{k}{2}. \] (145)

Thus we have obtained two independent pairs of operators: \{\(d_{k,\nu,1}, d_{k,\nu,3}\}\) with energies \(\varepsilon_+\) and \(-\varepsilon_+\), and \{\(d_{k,\nu,2}, d_{k,\nu,4}\)\}, with energies \(\varepsilon_-\) and \(-\varepsilon_-\). So, the diagonalization of the Hamiltonian (134) is reduced to the diagonalization of two independent quadratic forms. The first and second lines in (144) are diagonalised respectively by the unitary transformation
\[
d_{k,\nu,1} = \cos \theta_+ c_{k,\nu,1} - i \sin \theta_+ c_{k,\nu,4}, \\
d_{k,\nu,3} = -i \sin \theta_+ c_{k,\nu,1} + \cos \theta_+ c_{k,\nu,4} 
\] (146)
and
\[
d_{k,\nu,2} = \cos \theta_- c_{k,\nu,2} + i \sin \theta_- c_{k,\nu,3}, \\
d_{k,\nu,4} = i \sin \theta_- c_{k,\nu,2} + \cos \theta_- c_{k,\nu,3} 
\] (147)

Here \(\theta_\pm = \theta_\pm (k, \nu)\) are determined from the relations
\[
\tan 2\theta_\pm = \frac{\sin \frac{k}{2}}{2 \cos \frac{\nu}{2} \pm \cos \frac{k}{2}}. 
\] (148)

After this we obtain the final expression for the Hamiltonian (134) in the diagonal representation:
\[
H_J = \sum_{k,\nu} \left[ -\mathcal{E}_+ c_{k,\nu,1}^\dagger c_{k,\nu,1} - \mathcal{E}_- c_{k,\nu,2}^\dagger c_{k,\nu,2} + \mathcal{E}_- c_{k,\nu,3}^\dagger c_{k,\nu,3} + \mathcal{E}_+ c_{k,\nu,4}^\dagger c_{k,\nu,4} \right], 
\] (149)

where
\[
\mathcal{E}_\pm = \mathcal{E}_\pm (k, \nu) = \varepsilon_\pm \cos 2\theta_\pm + \sin \frac{k}{2} \sin 2\theta_\pm = \\
= \sqrt{\varepsilon_\pm^2 + \sin^2 \frac{k}{2}} = \sqrt{1 + 4 \cos^2 \frac{\nu}{2} \pm 4 \cos \frac{k}{2} \cos \frac{\nu}{2}}. 
\] (150)

Thus, the electron Hamiltonian (23) has been transformed into the diagonalised form (26)
\[
H_e = H_{e,0} + H_J = \sum_{k,\nu,\lambda,\sigma} E_{\lambda}(k, \nu) c_{k,\nu,\lambda,\sigma}^\dagger c_{k,\nu,\lambda,\sigma} 
\] (151)

with the energy bands (29).
Combining all the transformations together, we can write down the resulting unitary transformation:

\[
\begin{align*}
    a_{k,\nu,1} &= \frac{1}{2} e^{-i\frac{k+\nu}{4}} \left( e^{-i\theta_k} a_{k,\nu,1} + e^{i\theta_k} a_{k,\nu,2} + e^{i\theta_k} a_{k,\nu,3} + e^{-i\theta_k} a_{k,\nu,4} \right), \\
    a_{k,\nu,2} &= \frac{1}{2} e^{-i\frac{k-\nu}{4}} \left( e^{i\theta_k} a_{k,\nu,1} + e^{-i\theta_k} a_{k,\nu,2} - e^{i\theta_k} a_{k,\nu,3} - e^{-i\theta_k} a_{k,\nu,4} \right), \\
    a_{k,\nu,3} &= \frac{1}{2} e^{i\frac{k+\nu}{4}} \left( e^{-i\theta_k} a_{k,\nu,1} - e^{i\theta_k} a_{k,\nu,2} - e^{i\theta_k} a_{k,\nu,3} + e^{-i\theta_k} a_{k,\nu,4} \right), \\
    a_{k,\nu,4} &= \frac{1}{2} e^{i\frac{k-\nu}{4}} \left( e^{i\theta_k} a_{k,\nu,1} - e^{-i\theta_k} a_{k,\nu,2} + e^{-i\theta_k} a_{k,\nu,3} - e^{i\theta_k} a_{k,\nu,4} \right)
\end{align*}
\]

which can be written in the general form (137).

The inverse transformation is

\[
\begin{align*}
    c_{k,\nu,1} &= \frac{1}{2} \left( e^{i\frac{k+\nu}{4}+\theta_k} a_{k,\nu,1} + e^{i\frac{k-\nu}{4}+\theta_k} a_{k,\nu,2} + e^{-i\frac{k-\nu}{4}-\theta_k} a_{k,\nu,3} + e^{-i\frac{k+\nu}{4}-\theta_k} a_{k,\nu,4} \right), \\
    c_{k,\nu,2} &= \frac{1}{2} \left( e^{i\frac{k+\nu}{4}-\theta_k} a_{k,\nu,1} + e^{i\frac{k-\nu}{4}-\theta_k} a_{k,\nu,2} - e^{-i\frac{k-\nu}{4}+\theta_k} a_{k,\nu,3} - e^{-i\frac{k+\nu}{4}+\theta_k} a_{k,\nu,4} \right), \\
    c_{k,\nu,3} &= \frac{1}{2} \left( e^{i\frac{k+\nu}{4}+\theta_k} a_{k,\nu,1} - e^{i\frac{k-\nu}{4}+\theta_k} a_{k,\nu,2} - e^{-i\frac{k-\nu}{4}-\theta_k} a_{k,\nu,3} + e^{-i\frac{k+\nu}{4}-\theta_k} a_{k,\nu,4} \right), \\
    c_{k,\nu,4} &= \frac{1}{2} \left( e^{i\frac{k+\nu}{4}+\theta_k} a_{k,\nu,1} - e^{i\frac{k-\nu}{4}+\theta_k} a_{k,\nu,2} + e^{-i\frac{k-\nu}{4}-\theta_k} a_{k,\nu,3} - e^{-i\frac{k+\nu}{4}-\theta_k} a_{k,\nu,4} \right)
\end{align*}
\]

which can be written in the general form as

\[
    c_{k,\nu,\lambda} = \frac{1}{2} \sum_\varphi u_{\varphi,\lambda}^{\ast}(k,\nu) a_{k,\nu,j}.
\]

13 Appendix 2. Semi-Classical Equations

Due to the fact that \( H_{na} \) (55) is nondiagonal, its average value on the wavefunctions (41) vanishes: \( \langle \Psi | H_{na} | \Psi \rangle = 0 \). The average value of the total Hamiltonian, \( \mathcal{H} = \langle \Psi | H | \Psi \rangle = E \), gives us the energy in the zero adiabatic approximation. The calculation of \( \mathcal{H} \) with (42) and (41) gives us the Hamiltonian functional of classical displacements \( \bar{U}_s \) and the quasiparticle wavefunction \( \varphi_{i,j,p} \). So we see that the zero adiabatic approximation leads to the semiclassical approach which is often used in the description of self-trapped states.

Calculating \( \mathcal{H} \), we get the Hamiltonian functional,

\[
\mathcal{H} = H_{ph} + \sum_\varphi \left( \mathcal{E}_\varphi | \varphi_\varphi \rangle^2 - J \sum_\delta \varphi_\varphi^\ast \varphi_\delta \varphi_\delta (\varphi) + \chi_1 | \varphi_\varphi \rangle^2 \sum_\delta W \delta_\varphi \right) + \chi_2 | \varphi_\varphi \rangle^2 C_\varphi + G_2 \sum_\delta \varphi_\varphi^\ast \varphi_\delta (\varphi) W \delta_\varphi.
\]

Here \( H_{ph} \) is given by (16), where the displacements and the canonically conjugate momenta are classical variables. The site labelling in (155) corresponds to the elementary cell with two atoms, based on the non-orthogonal basis vectors, and index \( \varphi \) labels sites \( i,j,p \).

From (155) we derive the following static equations for the functions \( u, v, s \) and \( \varphi_\varphi \):

\[
\begin{align*}
    0 &= (W + \mathcal{E}) \varphi - J (\varphi + \varphi_l + \varphi_d) + \chi_1 \varphi (W_r + W_l + W_d) + \chi_2 \varphi C \\
    &+ G_2 [\varphi_r W_r + \varphi_l W_l + \varphi_d W_d],
\end{align*}
\]
0 = k\left[\sqrt{3} \cos\left(\frac{\alpha}{4}\right)(W_l - W_r) + \cos\left(\frac{\alpha}{4}\right)(\Omega_l - \Omega_r) + 2\Omega_d\right] + k_c\left[\sin\left(\frac{\alpha}{4}\right)(\frac{5}{2} \cos^2\left(\frac{\alpha}{4}\right) - 1)(C_l - C_r)\right]
+ \chi_1(|\varphi_l|^2 - |\varphi_r|^2)(\sqrt{3} \cos\left(\frac{\alpha}{4}\right)) + \chi_2(|\varphi_l|^2 - |\varphi_r|^2)\sin\left(\frac{\alpha}{4}\right)(\frac{5}{2} \cos^2\left(\frac{\alpha}{4}\right) - 1)
+ \frac{\sqrt{3}}{2} \cos\left(\frac{\alpha}{4}\right)G_2(\varphi^* \varphi_l + \varphi^*_l \varphi - \varphi^* \varphi_r + \varphi^*_r \varphi),
\hspace{1cm} (157)

0 = k\left[(2W_d - W_r - W_l) + \sqrt{3}(\Omega_r + \Omega_l)\right] + k_c\left[\frac{\sqrt{3}}{4} \sin\left(\frac{\alpha}{4}\right)(2C + C_r + C_l)\right]
+ \chi_1\frac{1}{2}(2|\varphi_d|^2 - |\varphi_r|^2 - |\varphi_l|^2) + \chi_2(2|\varphi|^2 + |\varphi_r|^2 + |\varphi_l|^2)\left(\frac{\sqrt{3}}{4} \sin\left(\frac{\alpha}{2}\right)\right)
+ \frac{1}{2}G_2(-\varphi^* \varphi_r - \varphi^*_r \varphi - \varphi^* \varphi_l - \varphi^*_l \varphi + 2\varphi^* \varphi_d + 2\varphi_d^* \varphi),
\hspace{1cm} (158)

0 = k\left[\sqrt{3} \sin\left(\frac{\alpha}{4}\right)(W_r + W_l) + \sin\left(\frac{\alpha}{4}\right)(\Omega_r + \Omega_l)\right]
+ k_c\left[\left\{\frac{3}{2} \cos\left(\frac{\alpha}{4}\right) - \frac{5}{2} \cos^3\left(\frac{\alpha}{4}\right)\right\}(C_r + C_l) - \cos\left(\frac{\alpha}{4}\right)C_d + 3 \cos^3\left(\frac{\alpha}{4}\right)C\right]
+ \chi_1\frac{3}{2} \sin\left(\frac{\alpha}{4}\right)(2|\varphi|^2 + |\varphi_r|^2 + |\varphi_l|^2)
+ \chi_2\left(\left\{\frac{3}{2} \cos\left(\frac{\alpha}{4}\right) - \frac{5}{2} \cos^3\left(\frac{\alpha}{4}\right)\right\}(|\varphi_r|^2 + |\varphi_l|^2) - \cos\left(\frac{\alpha}{4}\right)|\varphi_d|^2 + 3 \cos^3\left(\frac{\alpha}{4}\right)|\varphi|^2\right)
+ \frac{3}{2}G_2\sin\left(\frac{\alpha}{4}\right)(\varphi^* \varphi_r + \varphi^*_r \varphi + \varphi^* \varphi_l + \varphi^*_l \varphi).
\hspace{1cm} (159)

These equations were used in [23] to determine numerically the conditions for the existence of polaron/soliton states.

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