W=0 pairing in \((N,N)\) carbon nanotubes away from half filling

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(Received 12 July 2002; published 30 October 2002)

We use the Hubbard Hamiltonian \(H\) on the honeycomb lattice to represent the valence bands of carbon single-wall \((N,N)\) nanotubes. A detailed symmetry analysis shows that the model allows \(W=0\) pairs which we define as two-body singlet eigenstates of \(H\) with vanishing on-site repulsion. By means of a nonperturbative canonical transformation we calculate the effective interaction between the electrons of a \(W=0\) pair added to the interacting ground state. We show that the dressed \(W=0\) pair is a bound state for a reasonable parameter values away from half filling. Exact diagonalization results for the \((1,1)\) nanotube confirm the expectations. For \((N,N)\) nanotubes of length \(l\), the binding energy of the pair depends strongly on the filling and decreases towards a small but nonzero value as \(l\to\infty\). We observe the existence of an optimal doping when the number of electrons per C atom is in the range 1.2–1.3, and the binding energy is of the order of 0.1–1 meV.

DOI: 10.1103/PhysRevB.66.165434

PACS number(s): 73.63.Fg, 71.27.+a, 74.20.Mn, 73.22.-f

I. INTRODUCTION

After the discovery of carbon nanotubes\(^1\) the interest in such systems has been stimulated by their anomalous normal properties\(^2\) and by the recently reported superconductivity.\(^3\) Indeed there has been growing evidence of superconducting fluctuations in single-wall carbon nanotubes placed between superconducting contacts\(^4\)\(^–\)\(^6\) up to the transition temperature of \(\approx 0.5\) K.\(^3\)

A single-wall carbon nanotube (SWNT) is a graphite sheet wrapped onto a cylinder. The carbon atoms are arranged on the sites of a honeycomb lattice. The two primitive Bravais lattice vectors are \(a_\pm = (d/2)(\pm 1,\sqrt{3})\), where \(d/\sqrt{3}\) is the nearest neighbor carbon separation, see Fig. 1. A SWNT is characterized by a pair of integers \((N,M)\) which specifies the wrapping: the cylinder has the axis running perpendicular to \(Na_\pm + Ma_\mp\), so that atoms separated by \(Na_\pm + Ma_\mp\) are identified. Only in recent years, it was possible to study the electronic properties of atomically resolved SWNT’s; it was found\(^7\) that they are strongly dependent on the integers \(N\) and \(M\).

From band-structure calculations\(^8\)\(^,\)\(^9\) one predicts that the “armchair” \((N,N)\) tubes are metals while the “zig-zag” \((N,−N)\) ones [which are the same as the \((N,0)\) tubes] are insulators or semiconductors. However, the Coulomb interaction cannot be neglected.\(^10\)\(^,\)\(^11\) Due to the quasi-one-dimensional structure, the SWNT’s are believed to exhibit non-Fermi-liquid behavior.\(^12\) The band structure of the armchair nanotubes suggests\(^13\)\(^,\)\(^14\) that near half filling the low-energy effective Hamiltonian should be a four-component Luttinger model. This theory was developed by the perturbative renormalization group\(^13\)\(^,\)\(^15\) and by the bosonization technique\(^16\)\(^,\)\(^17\) in the weakly doped case, revealing the presence of a superconducting instability for short-ranged interactions. Still in a one-dimensional scheme, phonon induced pairing mechanisms have also been reported.\(^18\)\(^,\)\(^19\)

On the other hand, in this exploratory paper we consider a different scenario in which the electron density is so far from half-filling that any one-dimensional free-fermion model with a linear spectrum fails to describe the noninteracting Hamiltonian. This is motivated by the expectation\(^5\) that an increased doping by chemical manipulations and/or external fields could enhance the superconducting transition temperature. In recent years, we proposed a pairing mechanism\(^20\)\(^,\)\(^21\) in the two-dimensional (one-band and three-bands) repulsive Hubbard model for the cuprates. Here we show that the same idea extends to the case at hand. In our approach bound electron pairs in SWNT are obtained by a symmetry-driven configuration interaction mechanism in which the transverse direction plays a crucial role.

In this paper, we do not (yet) include phonons even if we acknowledge that their contribution could be relevant. However, on one hand, we wish to explore an electronic mechanism which \textit{per se} leads to bound pairs. On the other hand, any mechanism in low-dimensional systems such as the cuprates and nanotubes, must overcome somehow the problem of the repulsion between confined charges. This is an obvious difference compared to the traditional superconductors where pairs have hundreds of Å of space to delocalize. The notion that pairing can arise by a purely electronic mechanism, i.e., from purely repulsive electron-electron interactions, was put forth by Kohn and Luttinger long ago.\(^22\) They suggested that for large odd values of the relative angular momentum two electrons could stay enough far apart from each other to take advantage of the Friedel oscillations of the screened Coulomb potential. In our approach, based on a \(2d\) Hubbard model, the first-order Coulomb repulsion is removed by symmetry.

The plan of the paper is the following. In Sec. II we define the Hubbard model Hamiltonian \(H\) for the armchair \((N,N)\) SWNT and we introduce some useful notations. In Sec. III we use a general theorem to obtain all the two-body singlet eigenstates of \(H\) with vanishing Hubbard repulsion \((W=0\) pairs\). We exploit the space group symmetry of the system to get all the \(W=0\) pairs with zero total momentum. Remarkably, we find that their wave function vanishes if the particles...
have the same \( x \) value. In Sec. IV we propose a nonperturbative canonical transformation to deal with the effective interaction between the electrons of a \( W = 0 \) pair added to the many-body ground state. Since the two extra particles cannot interact directly by definition of \( W = 0 \) pair, their effective interaction comes out from virtual electron-hole excitation exchange with the Fermi sea and in principle can be attractive. In Sec. V we consider the \((1,1)\) nanotube, with length \( l = 2d \). This system has eight sites and is the smallest nanotubelike cluster showing the superconducting \( W = 0 \) pairing. Therefore, it represents a very good probe to test the pairing mechanism described in Sec. IV, since we can compare exact diagonalization results with the analytic ones. In Sec. VI we apply the canonical transformation approach to study the \((N,N)\) nanotubes of finite length and periodic boundary conditions. We obtain a Cooper-like equation for the binding energy \(-\Delta\) of the \( W = 0 \) pair which is numerically solved for \( 2 \leq N \leq 6 \) and length \( l \) up to \( 32d \); the results are then extrapolated to study the dependence of \( \Delta \) on the radius of the tube and on the Fermi energy in the limit of infinite length. Finally the conclusion are drawn in Sec. VII.

II. HUBBARD MODEL ON THE SWNT

The four outer-shell electrons of each carbon atom form three \( \sigma \) \( sp_2 \) bonds and a resonant \( \pi \) bond with the remaining \( p_z \) electron. A simple description consists of a tight-binding Hamiltonian where only the \( p_z \) orbital is taken into account

\[
H_0 = t \sum_{(r,r')} \sum_\sigma \left( c_{r,\sigma}^{\dagger} c_{r',\sigma} + H.c. \right),
\]

where \( c_{r,\sigma} \) is the creation operator of an electron of spin \( \sigma \) on the honeycomb site \( r \), the sum runs over the pairs \((r,r')\) of nearest-neighbor carbon atoms and \( t \) is the hopping parameter. The on-site Coulomb repulsion is

\[
W = U \sum_r \hat{n}_{r,\uparrow} \hat{n}_{r,\downarrow},
\]

where \( \hat{n}_{r,\sigma} = c_{r,\sigma}^{\dagger} c_{r,\sigma} \) is the number operator referred to the site \( r \) and to the spin \( \sigma \). The full Hamiltonian reads

\[
H = H_0 + W.
\]

Although the point symmetry Group of the graphite layer is \( D_{6h} \), the simplified Hubbard Hamiltonian in Eq. (3) has \( C_{6v} \) symmetry since the fermionic operators are taken to be even under reflection with respect to the plane; for a SWNT only \( C_{2v} \) point symmetry remains, due to the wrapping. The \( C_{2v} \) Group is Abelian and its table of characters is shown in Table I.

Below, we shall diagonalize the kinetic term \( H_0 \) and introduce some useful notation. Let us write the position \( \mathbf{R} \) of the cells in terms of a pair of integers \((n,m)\), \( \mathbf{R} = n \mathbf{a}_x + m \mathbf{a}_y \). As illustrated in Fig. 1, we set the origin at an \( a \) site, and therefore any \( \mathbf{R} \) translation will take us to another \( a \) site; to get a \( b \) site one must translate by \( \mathbf{R} = (0,d/2 \sqrt{3}) \). It is convenient to rename the creation operators on the site \( r \) by distinguishing the \( a \) sites from the \( b \) sites:

\[
c_R^{\dagger} = \begin{cases} c_R^{(a)} & \text{if } \mathbf{R} = \mathbf{R}_a, \\ c_R^{(b)} & \text{if } \mathbf{R} = (0,d/2 \sqrt{3}) \end{cases}
\]

where the spin index is omitted for the sake of simplicity. Let us introduce the Bloch creation operators

\[
c_k^{(v)} = \sum_{\mathbf{R}} \left[ u(v)^{\ast}(\mathbf{k},a)c_{\mathbf{R}}^{(a)} + u(v)^{\ast}(\mathbf{k},b)c_{\mathbf{R}}^{(b)} \right] e^{-i\mathbf{k} \cdot \mathbf{R}},
\]

with

\[
\begin{align*}
\frac{u^+(\mathbf{k},a)}{u^-(\mathbf{k},b)} &= \frac{1}{\sqrt{4Nl}} \left( \pm \frac{|A(\mathbf{k})|}{A(\mathbf{k})} \right) \\
A(\mathbf{k}) &= \left( 1 + 2 e^{-i(d/2)\sqrt{3}k_y} \cos \frac{dk_x}{2} \right) 
\end{align*}
\]

The kinetic term \( H_0 \) can be written in a diagonal form as

\[
H_0 = \sum_{\mathbf{k}} \sum_{\sigma} \varepsilon_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma}^{\dagger} c_{\mathbf{k},\sigma},
\]

where

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( 1 )</th>
<th>( C_2 )</th>
<th>( \sigma_x )</th>
<th>( \sigma_y )</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( x^2 + y^2 )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( xy - yx )</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>( x )</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( y )</td>
</tr>
</tbody>
</table>

TABLE I. Character table ot the \( C_{2v} \) symmetry group. Here \( 1 \) denotes the identity, \( C_2 \) the 180 degrees rotation, \( \sigma_x \) and \( \sigma_y \) the reflections with respect to the \( x = 0 \) and \( y = 0 \) axes respectively. The \( C_{2v} \) symmetry group is Abelian and hence has four one-dimensional irreducible representations (irreps) denoted by \( A_1, A_2, B_1, B_2 \). In the last column simple basis functions for each irrep are shown.
\[ e^{\mp}(\mathbf{k}) = \pm t \sqrt{1 + 4 \cos^2 \left( \frac{k_x d}{2} \right) + 4 \cos \left( \frac{k_y d}{2} \right) \cos \left( \frac{k_z \sqrt{3} d}{2} \right)}, \]

are the bonding (−) and antibonding (+) bands.

The Hubbard interaction becomes

\[ W = 2NL \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} \sum_{\nu_1, \nu_2, \nu_3, \nu_4} U_{\nu_1, \nu_2, \nu_3, \nu_4} \left( \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4 \right) c_{\mathbf{k}_1, \nu_1}{\dagger} c_{\mathbf{k}_2, \nu_2} c_{\mathbf{k}_3, \nu_3} c_{\mathbf{k}_4, \nu_4} \delta_{\mathbf{G}}(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \]

where

\[ U_{\nu_1, \nu_2, \nu_3, \nu_4} \left( \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4 \right) = U \sum_{\xi = a, b} u^{(\nu_1, \xi)}(\mathbf{k}_1, \xi) u^{(\nu_2, \xi)}(\mathbf{k}_2, \xi) u^{(\nu_3, \xi)}(\mathbf{k}_3, \xi) u^{(\nu_4, \xi)}(\mathbf{k}_4, \xi) \delta_{\mathbf{G}}(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \]

and \( \delta_{\mathbf{G}}(\mathbf{k}) = 1 \) if \( \mathbf{k} \) is a reciprocal lattice vector \( \mathbf{G} \) and zero otherwise; in the \((N, N)\) nanotubes \( \mathbf{G} = n \mathbf{G}_z + m \mathbf{G}_x \), with \( n \) and \( m \) integers, and \( \mathbf{G}_z = (2 \pi / d)(1, \pm 1 / \sqrt{3}) \). For the \((N, N)\) nanotubes of length \( L = Nd \) and periodic boundary conditions along the \( \hat{x} \) direction the \( \mathbf{k} \) vectors are quantized as

\[ k_x = \frac{2 \pi}{Ld} m_x, \quad m_x = 0, 1, \ldots, L - 1, \]

\[ k_y = \frac{2 \pi}{\sqrt{3}Nd} m_y, \quad m_y = 0, 1, \ldots, 2N - 1. \]

For \( \mathbf{k} = [(2 / 3d) \pi, (2 / \sqrt{3}d) \pi] = \mathbf{k}_z \) the bonding and antibonding bands touch each other and \( e^{\mp}(\mathbf{k}_z) = 0 \) linearly.

In the next section we show that the Hamiltonian in Eq. (3) admits two-body singlet eigenstates with no double occupancy on the honeycomb sites and we shall refer to them as \( W = 0 \) pairs. \( W = 0 \) pairs are therefore eigenstates of the kinetic energy operator in Eq. (8) and of the Hubbard repulsion \( W \) of Eq. (10) with vanishing eigenvalue of the latter. The particles forming a \( W = 0 \) pair have no direct interaction and are the main candidates to achieve bound states in purely repulsive Hubbard models.\(^{20,21,23}\) Incidentally, we note that such states are involved in the antiferromagnetic ground state of Hubbard and related models at half filling.\(^{24-27}\)

### III. \( W = 0 \) Pairs in the Armchair \((N, N)\) SWNT

We obtained\(^{20,28}\) a powerful and elegant criterion to get all the \( W = 0 \) pairs. We can do that in terms of the optimal group \( \mathcal{G} \) of the Hamiltonian, that we define as a symmetry group which is big enough to justify the degeneracy of the single particle energy levels. By definition, every one-body eigenstate of \( H \) can be classified as belonging to one of the irreducible representations (irreps) of \( \mathcal{G} \). We may say that an irrep \( \eta \) is represented in the one-body spectrum of \( H \) if at least one of the one-body levels belongs to \( \eta \). Let \( \mathcal{E} \) be the set of the irreps of \( \mathcal{G} \) which are represented in the one-body spectrum of \( H \). Let \( | \psi \rangle \) be a two-body eigenstate of the kinetic energy \( H_0 \) with spin \( S_z = 0 \).

\( W = 0 \) theorem:

\[ \eta \notin \mathcal{E} \Rightarrow WP^{(\eta)}|\psi\rangle = 0, \]
where $\chi^{(\eta)}(\hat{O})$ is the character in $\eta$ of the operation $\hat{O}$ of $C_{2\eta}$. While $\psi^{B_1}=0$, after some algebra one finds

$$
\psi^{[A_2]}_{\xi_1, \xi_2}(\mathbf{k}, \mathbf{R}_1, \mathbf{R}_2) = \frac{1}{2} \sum_{\mathbf{R}_3} \chi^{(\eta)}(\hat{O}) \psi_{\xi_1, \xi_2}(\hat{O} \mathbf{k}, \mathbf{R}_1, \mathbf{R}_2),
$$

(15)

and set up the Schrödinger equation

$$
H|\Psi_0(n+2)\rangle = E(n+2)|\Psi_0(n+2)\rangle.
$$

(18)

We stress that Eq. (17) is configuration interaction, not a perturbative expansion. When the number $n$ of electrons in the system is such that $|\Phi_0(n)\rangle$ is a single nondegenerate determinant (the Fermi surface is totally filled), we can easily and unambiguously define and calculate the effective interaction between the two extra electrons since the expansion in Eq. (17) for the interacting ground state is unique: this is done by a canonical transformation from the many-body Hamiltonian of Eq. (3). We consider the effects of the operators $H_0$ and $W$ on the terms of $|\Psi_0(n+2)\rangle$. Choosing the $m$, $\alpha$, $\beta$, ... states to be eigenstates of the kinetic energy $H_0$ we have

$$
H_0|m\rangle = E_m|m\rangle, \quad H_0|\alpha\rangle = E_\alpha|\alpha\rangle, \quad H_0|\beta\rangle = E_\beta|\beta\rangle, \ldots.
$$

(19)

Since $W$ can create or destroy up to 2 $e$-$h$ pairs, its action on an $m$ state yields

$$
W|m\rangle = \sum_{m'} W_{m',m'}|m'\rangle + \sum_{\alpha} W_{\alpha,m}|\alpha\rangle + \sum_{\beta} W_{\beta,m}|\beta\rangle.
$$

(20)

The action of $W$ on the $\alpha$ states yields

$$
W|\alpha\rangle = \sum_{m} W_{\alpha,m}|m\rangle + \sum_{\alpha'} W_{\alpha',\alpha}|\alpha'\rangle + \sum_{\beta} W_{\beta,\alpha}|\beta\rangle + \sum_{\gamma} W_{\gamma,\alpha}|\gamma\rangle.
$$

(21)

where scattering between four-body states is allowed by the second term, and so on. In this way we obtain an algebraic system for the coefficients of the configuration interaction of Eq. (17). However, to test the instability of the Fermi liquid pairing it is sufficient to study the amplitudes of $E_\alpha$. Hence we have shown, the inclusion of the $\beta, \gamma, \ldots$ states produces a $E$-dependent renormalization of the matrix elements of higher order in $W$, leaving the structure of the equations unaltered.

By taking a linear combination of the $\alpha$ states in such a way that

$$
(H_0 + W)|\alpha, \alpha'\rangle = \delta_\alpha \alpha' E_\alpha
$$

(22)

the algebraic system reduces to

$$
[E_m - E(n+2)] a_m + \sum_{m'} a_{m'} W_{m,m'} + \sum_{\alpha} a_\alpha W_{m,\alpha} = 0,
$$

(23)

$$
[E'_\alpha - E(n+2)] a_\alpha + \sum_{m} a_m W_{\alpha,m} = 0.
$$

(24)

Solving for $a_\alpha$ and substituting in Eq. (23) we exactly decouple the four-body states as well, ending up with an equation for the dressed pair $|\psi\rangle = \sum_{m} a_m|m\rangle$. The effective
The ground state energy \( E \) which contains all the pairwise interactions except those be-
some term \( E \). This way of looking at Eq. (25) is perfectly consistent, de-

to the electron vacuum.

\( E \) is of the form of a Schrödinger equation with
eigenvalue \( E(n+2) \) for the added pair with the interaction
\( W^{(d)} + W^{(f)} \). Here the \( W=0 \) pairs are special because \( W^{(d)} \)
 chosen. We interpret \( a_m \) as the wave function of the dressed
pair, which is acted upon by an effective Hamiltonian \( H_{\text{pair}} \).

\[
E_m \rightarrow E^{(R)}_m = E_m + W_m + F_m.
\]

Equation (25) is of the form of a Schrödinger equation with
eigenvalue \( E(n+2) \) for the added pair with the interaction
\( W^{(d)} + W^{(f)} \). Here the \( W=0 \) pairs are special because \( W^{(d)} \)
vanishes. We interpret \( a_m \) as the wave function of the dressed
pair, which is acted upon by an effective Hamiltonian \( H_{\text{pair}} \).
This way of looking at Eq. (25) is perfectly consistent, de-
spite the presence of the many-body eigenvalue \( E(n+2) \).

Indeed, if the interaction is attractive and produces bound
states the spectrum of Eq. (25) contains discrete states below
the threshold of the continuum (two-electron Fermi energy).
This is a clear-cut criterion for pairing, which is exact in
principle. The threshold is given by

\[
E^{(R)}_F = \min_{m} [E^{(R)}_m(E)],
\]

which contains all the pairwise interactions except those be-
tween the particles in the pair; it must be determined once
Eq. (25) has been solved (since \( F \) depends on the solution).

The ground state energy \( E \) may be conveniently written as

\[
F^{(R)} + \Delta, \quad \Delta < 0 \text{ indicates a Cooper-like instability of the nor-
mal Fermi liquid and its magnitude represents the binding}
energy of the pair. We emphasize the fact that in principle the canonical
transformation is exact because in this way our framework
does not require \( U/t \) to be small. The next problem is how to
find a practical estimate of the renormalized Fermi energy. In
the numerical calculations, some approximation is needed. In
Secs. V and VI, we shall compute the bare quantities; that is,
we shall neglect the six-body and higher excitations in the
calculation of \( W^{(f)} \) and \( F \). This is a reasonable approximation
if we compute small corrections to a Fermi liquid back-
ground and the exact numerical results in the (1,1) nanotube
suggestion that this is the case, see Sec. V. We want to stress that
once the expansion of \( |\Psi_0(n+2)\rangle \) in Eq. (17) is truncated as
specified above we do not need to construct a good approxi-
mation of the interacting ground state wave function in order
to get the \( a_m \) amplitudes at weak coupling; in this way we
obtain information about pairing.

V. THE (1,1) NANOTUBE:

EXACT DIAGONALIZATION AND PAIRING MECHANISM

There is evidence from cluster calculations that pairing
can arise in the repulsive Hubbard model.\(^{23,30,31}\) In this sec-
tion we shall consider the (1,1) nanotube, with \( l=2d \) and
periodic boundary conditions, see Fig 2(a). This system has
eight sites and is the smallest nanotubelike cluster showing
the superconducting \( W=0 \) pairing. Therefore, it represents a
very good probe to test the pairing mechanism shown in Sec.
IV, since we can compare exact diagonalization results with
the analytic approximations of the canonical transformation.

We define, following Refs. 32,33,

\[
\bar{\Delta}(n+2) = E(n+2) + E(n) - 2E(n+1),
\]

where \( E(n) \) is the ground state energy with \( n \) electrons (re-
ferrered to the electron vacuum). \( |\bar{\Delta}(n+2)\rangle \) is one definition
of the pairing energy. This definition is simple, but requires
computing the eigenvalues with great accuracy, and has se-
veral drawbacks. It says nothing about the dynamics which
leads to pairing. Moreover, generally a negative \( \bar{\Delta} \) does not
unambiguously imply pairing, and further problems arise
since the above definition depends on the comparison of sys-
tems with different \( n \).

However, in several studies of \( W=0 \) pairing in finite sys-
tems when it was possible to compute \( \bar{\Delta} \) by exact diagonal-
ization we pointed out\(^{21,25,34}\) that at least at weak coupling it
Table II: Top row: symbols of the 10 classes \( C \) of \( G \); bottom row: one typical operation for each of the classes; the others can be obtained by conjugation. The operations are: the identity \( I \), the translation \( t_{0,m} \) of \( n \) steps along \( a_{x} \) and \( m \) along \( a_{x} \); \( d \) is the dynamical symmetry. The other operations \( C_{2}, \, C_{4}, \, \sigma_{x}, \, \sigma_{y} \) are those of the group of the rectangle and are referenced to the center \( c \) of Fig. 2(a).

\[
\begin{array}{cccccccccc}
C_{1} & C_{2} & C_{3} & C_{4} & C_{5} & C_{6} & C_{7} & C_{8} & C_{9} & C_{10} \\
I & C_{2} & \sigma_{x} & \sigma_{y} & \sigma_{d} t_{1,0} & \sigma_{d} t_{1,0} & t_{1,0} & d & C_{2} d & \sigma_{d} d \\
\end{array}
\]

agrees well with \( \Delta \) as obtained by the canonical transformation. This supports the application of Eq. (31).

Below we perform a group-theoretical analysis and obtain \( W=0 \) pairs by exploiting the \( W=0 \) theorem. Next, we compute the interacting ground state energy with two, three, and four electrons by exact numerical diagonalization in order to get \( \Delta(4) \). Finally the canonical transformation is applied to evaluate \( \Delta(4) \) which will be compared with \( \tilde{\Delta}(4) \).

A. Symmetry properties and \( W=0 \) pairs

The first Brillouin zone (FBZ) consists of four points and since there are two atoms in the unit cell, two bands result. The symmetry properties of this system are intriguing: it is not invariant under the operations of the space group (translations and \( C_{2v} \) operations), but also under the dynamical operation \( d \) shown in Fig. 2(b). The dynamical operation \( d \) is reminiscent of a similar symmetry which must be taken into account to understand the degeneracies in the \( 4 \times 4 \) Hubbard model.21

Including \( d \) and closing the multiplication table we obtain a symmetry group \( G \) with 48 elements in 10 classes as shown in Table II.

In Table III we report the character table of the full symmetry group \( G \) of the \((1,1)\) nanotube of length \( l=2d \). The one-body eigenenergies for \( t=1 \) eV are shown in Table IV together with the irreps of the associated eigenvectors. From Tables III and IV we see that \( G \) is an optimal group as defined above. In Sec. III we have shown how to

Table III: Character table of the optimal group \( G \). The irreps \( A_{1}, \, A_{2}, \, B_{1}, \) and \( B_{2} \) reduce to the corresponding ones of the subgroup \( C_{2v} \); if \( G \) is broken.

\[
\begin{array}{cccccccccc}
G & C_{1} & C_{2} & C_{3} & C_{4} & C_{5} & C_{6} & C_{7} & C_{8} & C_{9} & C_{10} \\
A_{1} & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
A_{2} & 1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\
B_{1} & 1 & -1 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 \\
B_{2} & 1 & -1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & 1 \\
E_{1} & 2 & 0 & 2 & 0 & 2 & 2 & 0 & 0 & -1 & 1 \\
E_{2} & 2 & 0 & -2 & 0 & -2 & -2 & 0 & 0 & -1 & 1 \\
T_{1} & 3 & 1 & -1 & 1 & 3 & -1 & 1 & 0 & -1 & 0 \\
T_{2} & 3 & -1 & -1 & 3 & -1 & 1 & 1 & 0 & 0 & 0 \\
T_{3} & 3 & -1 & 1 & -3 & -1 & -1 & 0 & 0 & 0 & 0 \\
T_{4} & 3 & 1 & 1 & -3 & 1 & -1 & 1 & 0 & 0 & 0 \\
\end{array}
\]

Table IV: One-body spectrum for \( t=1 \) eV. The energies are in eV.

\[
\begin{array}{cccc}
\text{Quasimomentum} & \text{Energy (}\nu=-\text{)} & \text{Irrep} (\nu=-) & \text{Irrep} (\nu=+) \\
\hline
k_{1}=(0,0) & -3 & B_{2} & 3 & A_{1} \\
k_{2}=(0,2\pi/3) & -1 & T_{1} & 1 & T_{3} \\
k_{3}=(\pi,0) & -1 & T_{1} & 1 & T_{3} \\
k_{4}=(0,0) & -1 & T_{1} & 1 & T_{3} \\
\end{array}
\]

get all the \( W=0 \) pairs of vanishing momentum and belonging to the irrep \( A_{2} \) of \( C_{2v} \). However, the \((1,1)\) nanotube is too small to achieve this kind of \( W=0 \) pair states and the projection on the irrep \( A_{2} \) of \( c_{k_{1},c_{k_{2}},c_{k_{3}},c_{k_{4}}} \) is identically zero. Nevertheless, this cluster admits \( W=0 \) pair solutions of different type and they may be obtained by applying the \( W=0 \) theorem,28 which contains a very general prescription to determine all the \( W=0 \) pairs, see Sec. III.

In the \((1,1)\) nanotube \( W=0 \) pairs formed by particles of the same kinetic energy may be obtained in the three-fold degenerate one-body levels with energies \( \pm 1 \) eV by projecting \( c_{k_{1},c_{k_{2}},c_{k_{3}},c_{k_{4}}} \) with \( i,j=2,3,4 \), onto the irreps which are not represented in the one-body spectrum. In this way we find two singlets

\[
\left| \psi_{1}^{1+E} \right| = \frac{1}{\sqrt{2}}(c_{k_{1},1}c_{k_{2},1} - c_{k_{1},1}c_{k_{2},1})|0\rangle, \\
\left| \psi_{2}^{1+E} \right| = \frac{1}{\sqrt{6}}(2c_{k_{2},1}c_{k_{2},1} - c_{k_{1},1}c_{k_{2},1} - c_{k_{2},1}c_{k_{2},1})|0\rangle, \\
\]

and three triplets

\[
\left| \psi_{1}^{3+T} \right| = \frac{1}{\sqrt{2}}(c_{k_{1},1}c_{k_{2},1} - c_{k_{1},1}c_{k_{2},1})|0\rangle, \\
\left| \psi_{2}^{3+T} \right| = \frac{1}{\sqrt{2}}(c_{k_{2},1}c_{k_{2},1} - c_{k_{2},1}c_{k_{2},1})|0\rangle, \\
\left| \psi_{3}^{3+T} \right| = \frac{1}{\sqrt{2}}(c_{k_{1},1}c_{k_{2},1} - c_{k_{2},1}c_{k_{2},1})|0\rangle, \\
\]

while all the other projections yield nothing.

In the above expressions the Bloch states \( c_{k_{1},c_{k_{2}}} \) can be taken both in the bonding and the antibonding bands (\( e= \mp 1 \) eV, respectively). In conclusions we found that the \((1,1)\) nanotube with eight sites has two \( W=0 \) pairs in each band. As already observed, such pairs have a nonvanishing total momentum, contrarily to the \( W=0 \) pairs of Sec. III.

B. Exact diagonalization data

We have performed the numerical diagonalization of the Hamiltonian in Eq. (3) for the \((1,1)\) nanotube of length \( 2d \) and periodic boundary conditions, filled with 2, 3, and 4 electrons. The interesting case arises when the number of
electrons is \( n + 2 = 4 \), since the noninteracting ground state \( |\Phi_0(2)\rangle \) is a nondegenerate singlet with vanishing momentum containing two electrons in the lowest energy level. Therefore, the two added electrons may form a \( W = 0 \) pair according to the result of Sec. V A.

We found that the interacting ground state \( |\Psi_0(2)\rangle \) with two electrons is a totally symmetric singlet with vanishing momentum for any value of the ratio \( U/t \). On the other hand, \( |\Psi_0(3)\rangle \) is threefold degenerate in the sector \( S_z = 1 \), with momenta \((0,2\pi/\sqrt{3})\), \((\pi,0)\), and \((-\pi,0)\), for \( U/t < 10^2 \). It belongs to the irrep \( T_1 \) in the weak coupling regime. With four electrons (784 configurations) the ground state is a doubly degenerate singlet, with momenta \((0,0)\) and \((0,2\pi/\sqrt{3})\), and belongs to the irrep \( 1^E_1 \). This is the symmetry of the \( W = 0 \) pair; our approach predicts the correct symmetry of the ground state. The first excited state with four electrons is a threefold degenerate triplet with momenta \((0,0)\), \((\pi,0)\), and \((-\pi,0)\), and belongs to \( T_2 \). We show below that we are able to predict the symmetry of this state as well. We found that there is no level crossing up to \( U/t < 10^2 \).

In order to study the pairing between the two added electrons, we must compute the quantity \( \tilde{\Delta}(4) = E(4) + E(2) - 2E(3) \), which is related to the effective interaction according to the discussion made at the beginning of Sec. V. \( \tilde{\Delta}(4) \) has been computed in a large range of \( U/t \) values, and its trend is shown in Fig. 3.

For arbitrary small values of \( U/t \), \( \tilde{\Delta}(4) \) is negative and decreases up to a characteristic value of \( U/t \sim 4 - 5 \), where a minimum is reached; at the minimum \( \tilde{\Delta}(4) \sim -0.018 \) eV. Thus, as in the model Cu-O clusters, \( \tilde{\Delta}(4) \) is a new energy scale of the system, widely different from any of the input parameters. For larger \( U/t \), \( \tilde{\Delta}(4) \) increases until \( \tilde{\Delta}(4) = 0 \) for \( U/t \sim 14 \). As far as \( U/t \to \infty \), \( \tilde{\Delta}(4) \) increases monotonically up to the asymptotic positive value of \( \sim 0.063 \) eV. We emphasize that \( \tilde{\Delta}(4) \) becomes positive for large values of \( U/t \) and hence pairing disappears in the strong coupling regime. Therefore, the above pairing mechanism cannot be related to the ones considered within the framework of the \( t-J \)-like models, where an infinite \( U \) is required to forbid double occupation on the same site and pairing is achieved by means of residual attractive interactions.

### C. Analytical canonical transformation: Pairing mechanism

In this section we study the (1,1) nanotube with eight sites by implementing the canonical transformation described in Sec. IV but truncated to the \( \alpha \)-states. We shall compare the analytic results with the numerical data obtained previously. The noninteracting Fermi sphere \( |\Phi_0(2)\rangle = c_{k_1}^\dagger c_{k_1}^\dagger |0\rangle \) has two electrons in the lowest level. Since the one-body levels are widely separated the intrashell interaction is much more important than the intershell one. Therefore, we consider only the \( |m\rangle \) states having the added pair of electrons in the lowest unoccupied level of energy \( -1 \) eV, neglecting the higher-energy orbitals. We recall that in the threefold degenerate level with energy \( -1 \) eV we can write five two-body states (two singlets and three triplets) without double occupancy, see Eqs. (32)–(36). Hence, we may further reduce the set of the \( m \) states in the expansion of the interacting ground state \( |\Psi_0(4)\rangle \) [see Eq. (17)] by dropping the ones with nonzero direct interaction (which are expected to have wrong symmetries to be the ground state). A convenient basis for the analytic evaluation of the matrix elements \( W_{m,m'} \) and \( \langle S[E]\rangle_{m,m'} \) (see below) is obtained in terms of the creation operators

\[
\hat{f}_{1,\sigma}^\dagger = \frac{1}{\sqrt{2}} (c_{k_1,\sigma}^\dagger + c_{k_1,\sigma}^\dagger), \quad \hat{f}_{2,\sigma}^\dagger = \frac{1}{\sqrt{2}} (c_{k_2,\sigma}^\dagger - c_{k_2,\sigma}^\dagger).
\]

The determinantal states

\[
|m_1\rangle = \hat{f}_{1,1}^\dagger \hat{f}_{2,1}^\dagger |\Phi_0(2)\rangle, \quad |m_2\rangle = \hat{f}_{1,2}^\dagger \hat{f}_{2,1}^\dagger |\Phi_0(2)\rangle
\]

have projection only on the first component of \( E_1 \) and on the first component of \( T_2 \), and are mixed by the operators \( W \) and \( S[E] \) in Eq. (25). Indeed, the symmetric combination of \( |m_1\rangle \) and \( |m_2\rangle \) yields \( |\psi_{1E_1}\rangle \) of Eq. (32), while the antisymmetric combination yields \( |\psi_{1T_2}\rangle \) defined in Eq. (34). Hence, the eigenvalue Eq. (25) reduces to

\[
\begin{pmatrix}
E_{m_1} + W_{m_1} + F_{m_1} \\
(W_{\text{eff}})_{m_2,m_1} \\
E_{m_2} + W_{m_2} + F_{m_2}
\end{pmatrix}
\begin{pmatrix}
am_{m_1} \\
(W_{\text{eff}})_{m_2,m_1} a_{m_2} \\
am_{m_2}
\end{pmatrix} = E \begin{pmatrix}
am_{m_1} \\
am_{m_2}
\end{pmatrix},
\]

where we have taken into account that \( W^{(d)} = 0 \) since \( |m_1\rangle \) and \( |m_2\rangle \) have no-direct interaction and that the diagonal part of the effective interaction \( W_{\text{eff}} \) vanishes due to the Pauli principle [More generally, \( (W_{\text{eff}})_{m,m} = 0 \) if the \( m \) state is a determinant state. Let \( m = (\varphi_{1,1}, \varphi_{2,1}) \) be a pair index containing two spin orbitals; drawing the diagram for the effective interaction \( W_{\text{eff}} \) with incoming \( \varphi_{1,1} \) and \( \varphi_{2,1} \) and outgoing \( \varphi_{1,1} \) and \( \varphi_{2,1} \) one realizes that one of the two spin orbitals must be occupied twice.]. We performed the sum in Eq. (26) over the \( \alpha \) states analytically using non renormalized \( \alpha \)-state energies, which is justified at least in the weak-
coupling regime. As a consequence of the fact that \((W_{\text{eff}})_{m,m}=0\) the forward scattering term turns out to be given by

\[
F_m = (S[E])_{m,m} = \frac{U^2}{8} \left( \frac{1}{2E} + \frac{1}{E+4t} \right) = f(E),
\]

and it is independent of the pair index \(m\). The first-order self-energy \(W_1\) is equal to \(W_2\) and we defer the reader to Sec. VI for the proof in a more general case; here we limit to write the final result

\[
W_F = W_1 = W_2 = \frac{3U}{32}. \tag{41}
\]

The off-diagonal matrix elements \((W_{\text{eff}})_{m_1,m_2}=(W_{\text{eff}})_{m_2,m_1} = w_{\text{eff}}[E]\) are responsible for a spin-flip-like effective interaction due to the structure of the states \(m_1\) and \(m_2\). Performing the sum over the \(\alpha\) states and taking the bare energies \(E_\alpha\) we get

\[
w_{\text{eff}}[E] = \frac{U^2}{32} \frac{1}{E+4t}. \tag{42}
\]

Hence, the eigenvectors of Eq. (39) are \((1/\sqrt{2})(1,1)\) and \((1/\sqrt{2})(1,-1)\) and correspond to the states

\[
|\Psi^{1E_1}_1\rangle = \frac{1}{\sqrt{2}}(|m_1\rangle + |m_2\rangle) = |\phi^1_{E_1}\rangle \otimes |\Phi_0(2)\rangle, \tag{43}
\]

\[
|\Psi^{3T_2}_1\rangle = \frac{1}{\sqrt{2}}(|m_1\rangle - |m_2\rangle) = |\phi^{3T_2}_{E_1}\rangle \otimes |\Phi_0(2)\rangle. \tag{44}
\]

From the symmetric combination we get the singlet belonging to the irrep \(^1E_1\) and the lowest energy \(E_S\) satisfies the equation

\[-8t + W_F + f(E_S) + w_{\text{eff}}[E_S] = E_S. \tag{45}\]

According to the treatment described in Sec. IV we write \(E_S = -8t + W_F + f(E_S) + \Delta[E_S]\) so that

\[
\Delta[E_S] = w_{\text{eff}}[E_S]. \tag{46}\]

The antisymmetric combination corresponds to the triplet belonging to the irrep \(^3T_2\) and the lowest energy \(E_T\) satisfies the equation

\[-8t + W_F + f(E_T) - w_{\text{eff}}[E_T] = E_T. \tag{47}\]

In this case \(-\Delta[E_T] = w_{\text{eff}}[E_T]\) and it coincides with the modulus of \(w_{\text{eff}}[E_S]\) in standard second-order perturbation theory, see Fig. 4(a).

In Fig. 4(b) it is reported the comparison between \(\Delta(4)\), as defined in Eq. (31), and \(\Delta[E_S]\) obtained from the canonical transformation. We have exactly fitted the eight points for \(\Delta(4)\) and \(\Delta[E_S]\) by using a polynomial of order 7 in \(U/t\). The ratio \(r\) between the quadratic coefficient of \(\Delta[E_S]\) and the quadratic coefficient of \(\Delta(4)\) is \(r = 1.00003\), while the linear coefficients are essentially zero in both cases. We observe that the analytical value \(|\Delta[E_S]|\) is \(\sim 2\) times greater than \(\Delta(4)\) for \(U/t = 1\). This means that the inter-shell interactions and the renormalizations of the \(\alpha\)-state energies have an important weight in determining the right value of \(\Delta[E_S]\). However, what is comfortable is that the analytical approach predicts the right trend of the binding energy: the singlets feel attraction, while triplet repulsion. This is the result we need to apply the canonical transformation to larger and more physical systems.

VI. PAIRING IN NANOTUBE SUPERCELLS

A. Canonical transformation and pairing mechanism for \((N,N)\) nanotubes

Recently, potassium\(^35\) and lithium\(^36\) have been intercalated in single-wall and multiwall carbon nanotubes and a net charge transfer was observed between the alkali metals and the carbon atoms. Since the intercalation causes a very small structural deformation, we may say that the alkali-metal electrons fill the original bands of the nanotube carrying the system away from half filling. In this section we apply the canonical transformation to study the pairing mechanism in the electron-doped \((e_F>0)\) armchair nanotubes of length \(L = Ld\) and periodic boundary conditions. Omitting the band index we choose the \(m\) states as determinantal eigenstates of the kinetic energy \(H_0\);
virtual hole. The vertex
the same limit.
second-order self-energy of the one-particle propagator in
energy
acting Fermi
over the occupied states and we used the fact that
\[ W = \sum_{\xi,\tau,\nu} \left[ \sum_{\mathbf{k},\mathbf{k}'} \left| u(\mathbf{k},\xi) \right|^2 \left| u(\mathbf{k}',\xi) \right|^2 \right] \]
where \(|m\rangle = c_{\mathbf{k}_1,\xi}^\dagger c_{\mathbf{k}_2,\xi}^\dagger |\Phi_0(n)\rangle\), the sums over \(\mathbf{k}\) and \(\mathbf{k}'\) run over the occupied states and we used the fact that
\[ |u(\mathbf{k},\xi)|^2 = 1/(4N\xi) \] for any \(\mathbf{k}\) and \(\xi\).

We truncate the expansion of the interacting ground state
\[ |\Psi_0(n+2)\rangle \] of Eq. (17) to the \(\alpha\) states and a basis for them looks similar to
\[ c_{\mathbf{k}_1,\xi}^\dagger c_{\mathbf{k}_2,\xi}^\dagger c_{\mathbf{k}_3,\xi}^\dagger c_{\mathbf{k}_4,\xi}^\dagger |\Phi_0(n)\rangle, \]
where \(\alpha = \uparrow, \downarrow\).

In this scheme of approximation, we want to obtain the effective interaction between the electrons forming the \(W = 0\) pairs studied in Sec. III. Projecting on the irrep \(A_2\) the vanishing momentum pair \(|\psi(\mathbf{k})\rangle = c_{\mathbf{k}_1,\xi}^\dagger c_{-\mathbf{k}_1,\xi}^\dagger |\Phi_0(n)\rangle\) we get from Eq. (26)

\[
\langle \psi| A_2^\dagger (\mathbf{k}) |\hat{S}(E) | \psi| A_2 (\mathbf{k}') \rangle = -2 \delta(\mathbf{k} - \mathbf{k}') \sum_{\mathbf{p},\mathbf{q}} \sum_{\nu} \theta\left(\epsilon(\mathbf{k} + \mathbf{p} - \mathbf{q}) - \epsilon_F\right) \left[U_\nu(\mathbf{k},\mathbf{p},\mathbf{k} + \mathbf{p} - \mathbf{q},\mathbf{q})\right]^2 \\
+ 2 \sum_{\hat{\Omega} \in C_{2\nu}} \chi^{A_2}(\hat{\Omega}) \sum_{\mathbf{p},\mathbf{q}} \theta\left(\epsilon(\hat{\mathbf{O}} \mathbf{k}' + \mathbf{k} + \mathbf{p}) - \epsilon_F\right) \\
\times U_\nu(\hat{\mathbf{O}} \mathbf{k}' + \mathbf{k} + \mathbf{p}, \mathbf{k}, \mathbf{p}, \hat{\mathbf{O}} \mathbf{k}' + \mathbf{k} + \mathbf{p}) U_\nu(\hat{\mathbf{O}} \mathbf{k}' + \mathbf{k} + \mathbf{p}, \mathbf{k}, \mathbf{p}, -\hat{\mathbf{O}} \mathbf{k}') \\
\epsilon(\hat{\mathbf{O}} \mathbf{k}' + \mathbf{k} + \mathbf{p}) - \epsilon(\mathbf{k}') + \epsilon(\mathbf{k}) - E, \tag{51}
\]

where we have taken into account Eq. (50) for the \(\alpha\) states and we set \(E_{\mathbf{k}}^\prime = E_{\mathbf{k}},\) which is justified at least in the weak-coupling regime. The sums are over occupied \(\mathbf{p}\) and empty \(\mathbf{q}\). Since \(\epsilon_F > 0\), we omitted the band index \(\nu\) of the electron eigenenergies \(\epsilon\), while we sum over the band index \(\nu\) of the virtual hole. The vertex \(U_\nu\) is given by Eq. (11) where \(\nu\) refers to the Bloch function depending on \(\mathbf{p}\), while all the other band indices are intended to be \(+\). The first term on the right-hand side of Eq. (51) is the forward scattering contribution \(F(\mathbf{k})\), while the second term represents the effective interaction \(W_{\text{eff}}(\mathbf{k},\mathbf{k}')\). We may see that standard perturbation theory yields the arithmetic mean of the two unperturbed limits \(E - 2\epsilon(\mathbf{k})\) and \(E - 2\epsilon(\mathbf{k}')\). In particular, the forward scattering \(F\) in Eq. (51) coincides with the second-order self-energy of the one-particle propagator in the same limit.

We emphasize that Eq. (51) is characterized by a symmetry-induced quantum mechanical interference of several terms. This interference produces a partial cancellation, and the absolute value of the result is typically much smaller than individual contributions. This means that the interaction is dynamically small for \(W = 0\) pairs: they have no direct interactions [that is \(W(d)\), defined in Eq. (27), is zero for \(W = 0\) pairs], and because of the interference the effective interaction is reduced compared to what one could expect by a rough order-of-magnitude estimate. However, the presence of the theta functions and the anisotropy of the integrands prevent a total cancellation. Substituting Eqs. (49)–(51) into Eq. (25), we cast the result in the form of a Cooper-like Schrödinger equation

\[ 2 \epsilon(\mathbf{k}) + W_F + F(\mathbf{k}) |a_{\mathbf{k}}^+ + \sum_{\mathbf{k}' \in D/4} W_{\text{eff}}(\mathbf{k},\mathbf{k}') a_{\mathbf{k}'} = E a_{\mathbf{k}}, \tag{52} \]

for a self-consistent calculation of \(E\) (since \(W_{\text{eff}}\) and \(F\) are \(E\) dependent). The indices \(\mathbf{k}\) and \(\mathbf{k}'\) run over \(1/4\) of the empty part of the FBZ and we denoted such a set of wavevectors as \(D/4\). We are interested in the possibility that \(E = 2\epsilon_F + W_F + F_{\text{min}}(\mathbf{k}_F) + \Delta\), with a positive binding energy \(-\Delta\) of the \(W = 0\) pair; here \(F_{\text{min}}(\mathbf{k}_F)\) is the minimum value of \(F(\mathbf{k})\) among the \(\mathbf{k}_F\) wave vectors on the Fermi surface to be determined self-consistently with the eigenvalue \(E\).

We have performed numerical estimates of \(\Delta\) by working on supercells of \(2N \times L = N_C\) cells. Here we solved the Cooper-like equation in a virtually exact way for \(N\) up to 6 and \(L\) up to 32. The results have been reported in Tables V(a)–V(d) where the hopping parameter \(t = 1\) eV. As a reasonable value, we have taken \(U/t = 1.7\) which is of the correct order of magnitude for graphite. In line with our previous finding in the small \((1,1)\) cluster, \(W = 0\) \(A_2\) singlets show pairing. The calculations are performed with the Fermi
TABLE V. (a) Data at $\varepsilon_F=0.5$ eV. (b) Data at $\varepsilon_F=0.8$ eV. (c) Data at $\varepsilon_F=1.0$ eV. (d) Data at $\varepsilon_F=1.2$ eV. $\Delta$ is in meV; $V$ is in eV, $t=1$ eV and $U=1.7$ eV.

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<td>32</td>
<td>2</td>
<td>3.9</td>
<td>0.45</td>
<td>32</td>
<td>4</td>
<td>1.9</td>
<td>0.37</td>
<td>32</td>
<td>6</td>
<td>1.0</td>
<td>0.33</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Energy $\varepsilon_F$ varying between 0.5 and 1.2 eV (half filling corresponds to $\varepsilon_F=0$). We see that the binding energy $-\Delta$ of the pairs decreases monotonically both with the radius and the length of the tube. We need to work away from half filling in order to operate our mechanism; on the other hand, close to half filling the system is a Luttinger liquid down to extremely low temperatures where a gap could open.$^{14}$

**B. Extrapolation to Large $L$**

With supercell sizes $N_C>400$ numerical calculations become hard. Since we are concerned with the asymptotic behavior for fixed $N$ and $L \to \infty$ and $-\Delta(N,L)$ depends on $N$ and $L$ in a complicated way, we need a method to make reliable extrapolations of the numerical results. To this end, as in previous work,$^{20,31}$ we define the average effective interaction $V$. This is such that setting in Eq. (52) $W_{\text{eff}}= -V/N_C$, with a constant $V>0$ for all $k$ and $k'$ in $D$, one obtains the correct value of $\Delta$. In other terms, once the binding energy $-\Delta$ is known by solving Eq. (52), the constant $V$ must be chosen in such a way that

$$1/V = 1/N_C \times \sum_{k_{\infty}} \frac{1}{[2\varepsilon(k) + F(k)]} \left[2\varepsilon_F + F_{\min}(k_F)\right] - \Delta(N,L).$$

(53)

In Tables V(a)–V(d), we have reported the value of $V$ which remains fairly stable around $\approx 0.4$ eV and does not drop to 0 in the limit of large $L$. Therefore $V$ must be interpreted as a characteristic energy scale of the system which is largely independent on the Fermi energy and on the radius. We have numerically observed that $|F(k) - F_{\min}(k_F)| \ll -\Delta$; hence we may extrapolate the asymptotic value of $-\Delta$ from Eq. (53) by dropping the difference $F(k) - F_{\min}(k_F)$ and taking the limit $L \to \infty$. The domain is extended to $D$ and the result is divided by 4. Since $k_x$ is the component along the tube axis, we convert the summation into an integral

$$1/V = \frac{1}{8N} \int d\kappa \int \sum_{\kappa} \frac{\theta[\varepsilon(k_x, k_y) - \varepsilon_F]}{2[\varepsilon(k_x, k_y) - \varepsilon_F] - \Delta_{\text{asympt}}(N,L)}. \tag{54}$$

with $\Delta_{\text{asympt}}(N) = \lim_{L \to \infty} \Delta(N,L)$. We solved the above equation for the unknown $\Delta_{\text{asympt}}(N)$ for several values of $N$ and $\varepsilon_F$, using a typical value $V \approx 0.4$ eV obtained from the calculations in supercells. We found that $\Delta_{\text{asympt}}$ is strongly dependent on the filling at fixed $N$. Remarkably, there exists an optimal doping at the Fermi energy $\varepsilon_F=1$ eV where $\Delta_{\text{asympt}}(N)$ is appreciably different from zero, while $\Delta_{\text{asympt}}$ is strongly suppressed far from it for $N>4$, see Fig. 5(a).

**FIG. 5.** Results of the canonical transformation approach with $t=1$ eV and $U=1.7$ eV. (a) $-\Delta_{\text{asympt}}$ as a function of the Fermi energy $\varepsilon_F$ for $N=4$ (empty triangles), $N=8$ (black boxes), and $N=16$ (gray diamonds). The Fermi energy varies in the range $0.6–1.2$. (b) $-\Delta_{\text{asympt}}$ as a function of $N$ for $N$ in the range $4–36$ and $\varepsilon_F=1$ eV.
The existence of an *optimal doping* can be understood by looking at the density of states \( \rho(\varepsilon) \) and at the integrand
\[
1/[2(\varepsilon - \varepsilon_F - \Delta_{\text{asympt}})] = g(\varepsilon) \text{ in Eq. (54).}
\]
From Fig. 6 we see that \( \rho(\varepsilon) \) has an absolute maximum at \( \varepsilon = 1 \) eV, which is reminiscent of the Van Hove singularity in the graphite sheet, and exhibits well-defined oscillations as a function of the nanotube radius.

On the other hand, \( g(\varepsilon) \) is peaked at \( \varepsilon = \varepsilon_F \). Therefore, for \( \varepsilon_F = 1 \) eV we have a synergy which leads to an absolute maximum of \( -\Delta_{\text{asympt}} \). The prediction of an optimal doping follows from Eq. (54) and is therefore largely mechanism-independent. A trend similar to the one shown in Fig. 5(b) was reported by Benedict et al., although they considered a phonon-driven mechanism.

At the optimal doping we observe that \( -\Delta_{\text{asympt}}(N) \) decreases monotonically as the radius \( \sqrt{3}d/N/2\pi \) of the tube increases, see Fig. 5(b). However, in the limit of large \( N \), \( \Delta_{\text{asympt}}(N) \) remains stable around 1.7 meV and may be interpreted as the binding energy of the \( W=0 \) pair in an optimally doped graphite sheet. By a rough order of magnitude estimate, we may say that the superconducting critical Temperature predicted by our approach at \( \varepsilon_F = 1 \) eV (which corresponds to a number of electrons per graphite atom of 1.25) is \( T_c = \Delta_{\text{asympt}}(\infty) \approx 10-20 \) K. These results may be compared with the available experimental data on the alkali-graphite intercalation compounds (GIC’s). There is experimental evidence that the critical temperature \( T_c \) in alkali-GIC \( CsM \) (where \( M \) is a given alkali metal) grows as \( x \) decreases. The number of electrons per graphite atom \( f \) is related to \( x \) by an empirical formula \( f = \kappa/x \) where \( \kappa \) is the fractional charge transfer. A typical value for \( \kappa \) is 0.5–0.6 (Ref. 43) and hence the filling \( f = 1.25 \) corresponds to the alkali-GIC’s \( CsM \).

Under high-pressure, high metal concentration samples such as \( CsK \), \( CsK \), \( CsNa \), \( CsNa \), \( CsNa \), \( CsLi \) have been synthesized; for \( CsNa \) the value of \( T_c \) is 5 K while for \( CsLi \), \( T_c = 1.9 \) K; in both cases the superconducting critical temperature is of the same order of magnitude of \( \Delta_{\text{asympt}}(\infty) \). Quite recently potassium and lithium have been intercalated also in single-wall and multiwall carbon nanotubes up to high concentration (the highest metal concentration was obtained with lithium in \( CsLi \)).

Our mechanism predicts that the binding energy of the \( W=0 \) pairs is bigger in nanotubes than in graphite sheets and this suggests a higher critical temperature for the former, see Fig. 5(b). This is also supported by the measurements of a \( T_c \approx 15 \) K in the 4 Å SWNT by Tang et al.

**VII. CONCLUSIONS**

Currently, carbon nanotubes superconduct at much lower temperatures than high-\( T_c \) cuprates and the two kinds of materials are apparently quite different. However, symmetry arguments based on the \( W=0 \) theorem tell us that, despite the obvious differences, part of the story must be the same, i.e., by a suitable choice of Dirac’s characters the on-site Coulomb interaction is utterly turned off. This produces the singlet pairing and constrains the ground state spin-orbital symmetry of the interacting system. We presented analytic expressions for the effective interaction and obtained the binding energy for \( (N,N) \) armchair nanotubes; in the case \( N = 1 \) we verified these predictions numerically and got high-precision agreement.

Although the results presented in this paper cannot be quantitatively compared with the experimental data, the order of magnitude of the pair binding energy agrees with experiment. Furthermore, the decreasing of the binding energy with \( N \) is suggested by recent measurements on nanotubes with diameter of a few Å.

The paired state we have obtained here is essentially two-dimensional, that is the transverse direction is crucial to have a non-Abelian symmetry group and hence \( W=0 \) pairs; the pairing mechanism uses degenerate electronic states that exist in \( 2d \) away from half filling. This opens up the interesting possibility that two distinct superconducting order parameters appear in the phase diagram, if it turns out that close to half-filling there is another one due to a breakdown of the Luttinger liquid.

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Burghard, Science 284, 1508 (1999); see also A. Yu. Kasumov, in (unpublished).


14 Jenö Sólyom (unpublished).


Gianluca Stefanucci and Michele Cini, Phys. Rev. B (to be published).


