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On-site repulsion as the source of pairing in carbon nanotubes and intercalated graphite

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Abstract. We show that different non-conventional superconductors have one fundamental feature in common: pair eigenstates of the Hamiltonian are repulsion-free, the $W = 0$ pairs. In extended Hubbard models, pairing can occur for reasonable parameter values. For (N, N) nanotubes the binding energy of the pair depends strongly on the filling and decreases towards a reduced but nonzero value for the graphite sheet $N \to \infty$.

PACS. 74.20.Mn Nonconventional mechanisms (spin fluctuations, polarons and bipolarons, resonating valence bond model, anyon mechanism, marginal Fermi liquid, Luttinger liquid, etc.) – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 73.63.Fg Nanotubes

Rapid Note

There is experimental evidence that the critical temperature T_c in alkali-graphite intercalation compounds (GIC) C_xM (where M is a given alkali metal) grows as x decreases [1]. Under high-pressure, high metal concentration samples such as C_6K, C_3K, C_4Na, C_3Na, C_2Na, C_2Li have been synthesized; for C_2Na the value of T_c is 5 K while for C_2Li, T_c=1.9 K; quite recently potassium [2] and lithium [3] have been intercalated also in single- and multi-wall carbon nanotubes [4] up to high concentration (the highest metal concentration was obtained with lithium in C_2Li) and a net charge transfer was observed between the alkali-metals and the carbon atoms. The alkali-metals cause little structural deformation, but increase the filling of the original bands. Nanotubes close to half filling are deemed to be Luttinger liquids down to milli-kelvin temperatures [5,6]. In this letter we use the Hubbard Hamiltonian H on the honeycomb lattice to represent the valence bands of carbon single-wall (N, N) nanotubes and propose a symmetry-driven configuration interaction pairing mechanism which works away from half-filling. We present analytic expressions for the effective interaction and obtain the binding energy for (N, N) armchair nanotubes; in the case $N = 1$ we verify these analytic results by exact diagonalization and get high-precision agreement. Starting from the undoped system we find that the pair binding energy grows as the number of electrons per C atom increases. Furthermore, we obtain stronger binding in nanotubes than in graphite sheets and this suggests a higher critical temperature for the former. This is also supported by the measurements of a $T_c \approx 15$ K in the 4 angstrom single-wall nanotube (SWNT) by Tang *et al.* [7].

Using standard notation, the full Hamiltonian reads

$$H = H_0 + W = t \sum_{\langle \mathbf{r},\mathbf{r}' \rangle} \sum_{\sigma} \left(c^{\dagger}_{\mathbf{r},\sigma} c_{\mathbf{r}',\sigma} + \text{h.c.} \right) + U \sum_{\mathbf{r}} \hat{n}_{\mathbf{r},\uparrow} \hat{n}_{\mathbf{r},\downarrow}, \quad (1)$$

where $\mathbf{r}$ denotes the honeycomb site, the sum runs over the pairs $\langle \mathbf{r}, \mathbf{r}' \rangle$ of nearest neighbour carbon atoms and t is the hopping parameter. The one-body eigenvalues $\varepsilon^{\pm}(\mathbf{k})$, (– for the bonding and + for the antibonding bands) are readily obtained, and the Fermi line has C_{2v} symmetry for the nanotubes (C_{6v} for the graphite sheet). Here, we assume that the Fermi level ε_F lies in the + band. The Hamiltonian in equation (1) admits *two-body* singlet eigenstates with no double occupancy and we shall refer to them as $W = 0$ pairs. 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 already used for the cuprates [8–10]. We note that such states are also building bricks of the ground state of Hubbard and related models at half filling [11–13].

Recently we obtained [10,14] a general 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 that justifies the degeneracy of the single particle energy levels. We may say that an irreducible representation (irrep) η is *represented* in the one-body spectrum of H if at least one of the one-body levels belongs to η. Let $\mathcal{E}$ be the set of the irreps of $\mathcal{G}$ which are represented in the one-body spectrum of H ($\mathcal{E}$ includes all the

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irreps when $\mathcal{G}$ is Abelian). Let $|\psi\rangle$ be a two-body eigenstate of the kinetic energy H_0 with vanishing z component of the spin. Then, it holds the *W=0 Theorem*:

$$\eta \notin \mathcal{E} \Leftrightarrow W P^{(\eta)} |\psi\rangle = 0 \tag{2}$$

where $P^{(\eta)}$ is the projection operator on the irrep η. In other terms, any nonvanishing projection of $|\psi\rangle$ on an irrep *not* contained in $\mathcal{E}$, is an eigenstate of H_0 with no double occupancy. The singlet component of this state is a $W = 0$ pair. Conversely, any pair belonging to an irrep represented in the one-body spectrum must have positive W expectation value. If a subgroup of $\mathcal{G}$ is available, the $\Rightarrow$ implication still holds. Using the space group, we find that in the vanishing quasi-momentum sector the only $W = 0$ pairs belong to the pseudoscalar irrep A_2. Let (a, b) denote the basis of the Bravais lattice and $u(\mathbf{k}, \zeta)$ the periodic part of the Bloch function of quasi-momentum $\mathbf{k}$, with $\zeta = a, b$. The pair wavefunction reads [15]

$$\psi^{[A_2]}_{\zeta_1,\zeta_2}(\mathbf{k}, \mathbf{R}_1, \mathbf{R}_2) = \sin(k_x(X_1 - X_2)) \times \frac{1}{\sqrt{2}} \Big[u^*(\mathbf{k}, \zeta_1)\, u^*(-\mathbf{k}, \zeta_2)\, \mathrm{e}^{\mathrm{i}k_y(Y_1 - Y_2)} - u^*(\mathbf{k}, \zeta_2)\, u^*(-\mathbf{k}, \zeta_1)\, \mathrm{e}^{-\mathrm{i}k_y(Y_1 - Y_2)} \Big] \chi_0, \tag{3}$$

with $\mathbf{R}_i = (X_i, Y_i)$ the origin of the cell where the particle i lies. We can verify by direct inspection that $\psi^{[A_2]}_{\zeta_1,\zeta_2}(\mathbf{k}, \mathbf{R}_1, \mathbf{R}_2)$ vanishes for $X_1 = X_2$, that is the two-body singlet wavefunction vanishes if the particles lie on the same annulus of the (N, N) tube. As a consequence $\psi^{[A_2]}_{\zeta_1,\zeta_2}(\mathbf{k}, \mathbf{R}_1, \mathbf{R}_2)$ is an eigenstate of the kinetic energy H_0 [with eigenvalue $2\varepsilon(\mathbf{k})$] and of the on-site Hubbard repulsion W with vanishing eigenvalue of the latter, that is $\psi^{[A_2]}_{\zeta_1,\zeta_2}(\mathbf{k}, \mathbf{R}_1, \mathbf{R}_2)$ is a $W = 0$ pair. Remarkably, $\psi^{[A_2]} = 0$ when the *transverse* component $k_y = 0$.

The effective interaction W_{eff} between the particles of a $W = 0$ pair can be obtained analytically by a canonical transformation in the spirit of reference [9]. Letting $n^{(0)}_\nu(\mathbf{p})$ denote the non-interacting occupation number in band ν with wavevector $\mathbf{p}$, we find

$$W_{\text{eff}}(\mathbf{k}, \mathbf{k}', E) = 2 \sum_{\hat{O} \in C_{2v}} \chi^{(A_2)}(\hat{O}) \sum_{\mathbf{p},\nu} \Big[1 - n^{(0)}_+(\hat{O}\mathbf{k}' + \mathbf{k} + \mathbf{p}) \Big]\, n^{(0)}_\nu(\mathbf{p}) \times \frac{U_\nu(\hat{O}\mathbf{k}' + \mathbf{k} + \mathbf{p}, -\mathbf{k}, \hat{O}\mathbf{k}', \mathbf{p})}{\varepsilon^+(\hat{O}\mathbf{k}' + \mathbf{k} + \mathbf{p}) - \varepsilon^\nu(\mathbf{p}) + \varepsilon^+(\mathbf{k}') + \varepsilon^+(\mathbf{k}) - E} \times U_\nu(\mathbf{k}, \mathbf{p}, \hat{O}\mathbf{k}' + \mathbf{k} + \mathbf{p}, -\hat{O}\mathbf{k}') \tag{4}$$

where $\chi^{(\eta)}(\hat{O})$ is the character in η of the operation $\hat{O}$ of C_{2v}, E is the interacting pair energy and $U_\nu(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)$ is the interaction vertex, with incoming legs $\mathbf{k}_3$ and $\mathbf{k}_4$ in band + and outgoing $\mathbf{k}_1$ in band + and $\mathbf{k}_2$ legs in band ν. The effective Schrödinger equation for the pair reads

$$[2\varepsilon(\mathbf{k}) + W_F + F(\mathbf{k}, E)]\, a_{\mathbf{k}} + \sum_{\mathbf{k}' \in \mathcal{D}/4} W_{\text{eff}}(\mathbf{k}, \mathbf{k}', E) a_{\mathbf{k}'} = E a_{\mathbf{k}}, \tag{5}$$

where W_F is the first-order self-energy shift and

$$F(\mathbf{k}, E) = -2\delta(\mathbf{k} - \mathbf{k}') \times \sum_{\mathbf{p},\nu} \sum_{\mathbf{q}} \frac{[1 - n^{(0)}_+(\mathbf{k} + \mathbf{p} - \mathbf{q})]\, [1 - n^{(0)}_+(\mathbf{q})]\, n^{(0)}_\nu(\mathbf{p})}{\varepsilon^+(\mathbf{k} + \mathbf{p} + \mathbf{q}) - \varepsilon^\nu(\mathbf{p}) + \varepsilon^+(\mathbf{q}) + \varepsilon^+(\mathbf{k}) - E} \times |U_\nu(\mathbf{k}, \mathbf{p}, \mathbf{k} + \mathbf{p} - \mathbf{q}, \mathbf{q})|^2 \tag{6}$$

is the *forward scattering* term which does not contains any direct interaction between the particles of the pair. Equation (5) requires a self-consistent calculation of E (since W_{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 $\mathcal{D}/4$. We show below that $E = 2\varepsilon_F + W_F + F_{\min}(\mathbf{k}_F) + \Delta$, with a positive binding energy $-\Delta$ of the $W = 0$ pair; here $F_{\min}(\mathbf{k}_F)$ is the minimum value of $F(\mathbf{k}, E)$ among the k_F-wavevectors on the Fermi line.

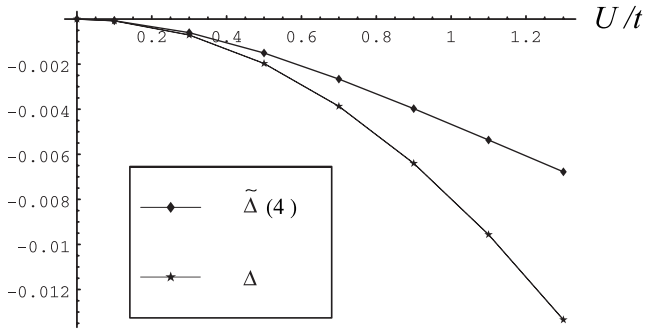

Fig. 1. Comparison between Δ and $\tilde{\Delta}(4)$ in units of t *versus* U/t.

We got a direct verification that pairing actually occours by exact diagonalization for the $(1, 1)$ nanotube of length $L = 2$ (in units of the lattice spacing) and periodic boundary conditions. We define, following references [8,16],

$$\tilde{\Delta}(\mathcal{N} + 2) = E(\mathcal{N} + 2) + E(\mathcal{N}) - 2E(\mathcal{N} + 1), \tag{7}$$

where $E(\mathcal{N})$ is the ground state energy with $\mathcal{N}$ electrons (referenced to the electron vacuum); $|\tilde{\Delta}(\mathcal{N} + 2)|$ is one definition of the pairing energy. In previous studies of $W = 0$ pairing in finite systems we found [8,10,17] that at least at weak coupling $\tilde{\Delta}$ agrees well with Δ as obtained by the canonical transformation. For the $(1, 1)$ nanotube with $\mathcal{N} = 2$, we can see in Figure 1 that the agreement between $\tilde{\Delta}(4)$ and Δ is again very good up to $U/t \approx 1$. However, we emphasize that $\tilde{\Delta}(4)$ decreases up to a characteristic value of $U/t \sim 4 \div 5$, where a minimum is reached [15]; at the minimum $\tilde{\Delta}(4) \sim -0.018\ t$. The ratio of the second

Table 1. Pair binding energy $-\Delta$ (in units of $10^{-3}t$) and average effective interaction V (in units of t) for (N,N) nanotubes of various lengths L, as a function of the Fermi energy ε_F (in units of t). Numerical values were computed $U/t = 2.5$ for illustration.

L	$N=2$					$N=4$					$N=6$				
	ε_F	0.8	0.9	1.0	1.1	ε_F	0.8	0.9	1.0	1.1	ε_F	0.8	0.9	1.0	1.1
10	$-\Delta$	86	86	82	84	$-\Delta$	44	47	47	37	$-\Delta$	22	23	29	22
	$-V$	2.5	2.5	2.4	2.8	$-V$	2.2	1.5	1.5	1.7	$-V$	1.4	1.7	1.8	1.7
	ε_F	0.8	0.9	1.0	1.1	ε_F	0.8	0.9	1.0	1.1	ε_F	0.8	0.9	1.0	1.1
15	$-\Delta$	62	62	61	61	$-\Delta$	29	28	35	27	$-\Delta$	16	19	21	21
	$-V$	2.7	2.7	2.7	2.9	$-V$	2.1	2.1	2.5	1.2	$-V$	1.7	1.6	1.8	2.0
	ε_F	0.8	0.9	1.0	1.1	ε_F	0.8	0.9	1.0	1.1	ε_F	0.8	0.9	1.0	1.1
25	$-\Delta$	35	38	38	38	$-\Delta$	17	17	21	16	$-\Delta$	12	10	15	11
	$-V$	2.3	2.4	2.4	2.8	$-V$	1.7	1.7	2.0	1.8	$-V$	1.2	1.7	1.8	1.4

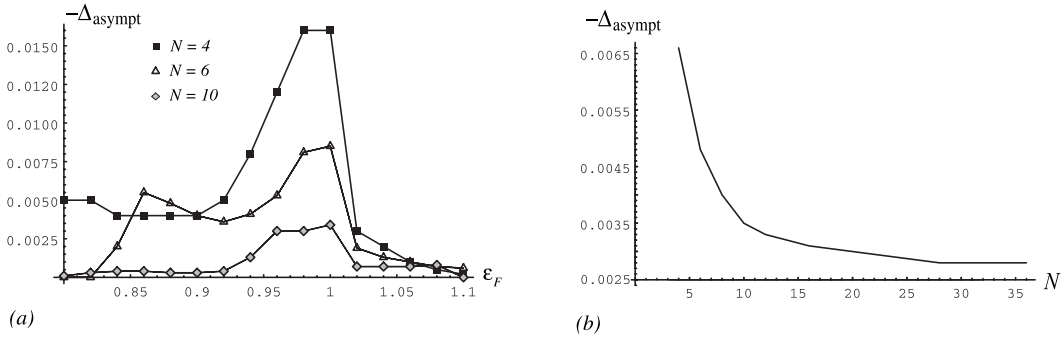

Fig. 2. (a) Results of the canonical transformation approach with $U/t = 2.5$. $-\Delta_{\rm asympt}$ as a function of the Fermi energy ε_F for $N = 4$ (black boxes), $N = 6$ (empty triangles) and $N = 10$ (grey diamonds). The Fermi energy varies in the range $0.8 \div 1.1$ t. (b) $-\Delta_{\rm asympt}$ as a function of N for N in the range $6 \div 36$ with $\varepsilon_F = t$ and average effective interaction $V = 1.5$ t. In both figures $-\Delta_{\rm asympt}$ is in units of t.

derivatives with respect to U/t at $U = 0$ was estimated by using best fits and turned out to be 1.00003, while the first derivative vanishes. The binding energy for $U \lesssim t$ is in the $10^{-3}t$ range and by analyzing the four-body ground-state wavefunction we assessed that the symmetry is ${}^1E_1$ as predicted by the canonical transformation. Here, E_1 is a twice degenerate irrep of the Optimal Group [15] $\mathcal{G}$ that breaks into $A_1 \oplus B_1$ in C_{2v}. This result encourages us to proceed with larger and more physical systems.

We considered supercells of $2\,N \times L = N_C$ cells, where L is the length of the (N,N) nanotube in units of the lattice spacing. We solved the Cooper-like equation in a virtually exact way for N up to 6 and L up to 25, using $U/t = 2.5$ (which is of the correct order of magnitude for graphite [18,19]). The canonical transformation overestimates $|\Delta|$ in this range of U/t, but remains qualitatively correct.

The calculations are performed with the Fermi energy ε_F varying between 0.8 t and 1.1 t (half filling corresponds to $\varepsilon_F = 0$). As in the $(1,1)$ cluster, the $W = 0$ singlets show pairing (see Tab. 1) albeit in general in ${}^1A_2$, as expected. The binding energy $-\Delta$ of the pairs decreases monotonically both with the radius and the length of the tube.

With supercell sizes $N_C > 300$ numerical calculations become hard. Since we are concerned with the asymptotic behaviour 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, like in previous work [9,20] we define the average effective interaction V. This is such that setting in equation (5) $W_{\rm eff} = -\frac{V}{N_C}$, with a constant $V > 0$ for all $\mathbf{k}$ and $\mathbf{k}'$ in $\mathcal{D}/4$, one obtains the correct value of Δ. In other terms, once the binding energy $-\Delta(N,L)$ is known, the constant V must be chosen in such a way that

$$\frac{1}{V} = \frac{1}{N_C} \sum_{\mathbf{k}\in\mathcal{D}/4} \frac{1}{[2\varepsilon(\mathbf{k}) + F(\mathbf{k})] - [2\varepsilon_F + F_{\min}(\mathbf{k}_F)] - \Delta(N,L)}. \tag{8}$$

In Table 1 we have reported V values; these remain fairly stable around $\approx 1.5 \div 2$ t for $N > 2$ with increasing L. Therefore V is largely independent on the Fermi energy and on the radius and this allows us to extrapolate to $\Delta_{\rm asympt}(N) = \lim_{L\to\infty} \Delta(N,L)$. For $N = 4$ and $N = 6$ we use for the average effective interaction V the arithmetical mean of the V values reported in Table 1 for $L = 10$, 15 and 25; the results are shown in Figure 2a together with $\Delta_{\rm asympt}(10)$ computed with $V = 1.5$ t. We found that $\Delta_{\rm asympt}$ is strongly dependent on the filling at fixed N; the sharp maximum at the *optimal doping* $\varepsilon_F \approx t$ (which

corresponds to a number of electrons per graphite atom of 1.25) can be understood in terms of a corresponding peak in the density of states. In the *optimally doped* case $-\Delta_{\rm asympt}(N)$ decreases monotonically as the radius of the tube increases, see Figure 2b. The decreasing of the binding energy with N is suggested by recent measurements on nanotubes with diameter of few angstrom [7]. However, in the limit of large N, $\Delta_{\rm asympt}(N)$ remains stable around 0.0028 t and may be interpreted as the binding energy of the $W = 0$ pair in an *optimally doped* graphite sheet.

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 $2d$ and works away from half filling. This opens up the interesting possibility that in nanotubes 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 [21].

Currently, intercalated graphite and 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.

References

1. J.T. Belash, O.V. Zharikov, A.V. Pal'nichenko, Solid State Comm. **63**, 153 (1987); J.T. Belash, A.D. Bronnikov, O.V. Zharikov, A.V. Pal'nichenko, Solid State Comm. **64**, 1445 (1987); J.T. Belash, A.D. Bronnikov, O.V. Zharikov, A.V. Pal'nichenko, Solid State Comm. **69**, 921 (1989)
2. M. Bockrath, J. Hone, H. Zettl, P.L. McEuen, A.G. Rinzler, R.E. Smalley, Phys. Rev. B **61**, R10606 (2000)
3. B. Gao, A. Kleinhammes, X.P. Tang, C. Bower, L. Fleming, Y. Wu, O. Zhou, Chem. Phys. Lett. **307**, 153 (1999); J. Zhao, A. Buldum, J. Han, J. Ping Lu, Phys. Rev. Lett. **85**, 1706 (2000)
4. S. Iijima, Nature (London) **354**, 56 (1991)
5. L. Balents, M.P.A. Fisher, Phys. Rev. B **55**, R 11973 (1997)
6. J. Sólyom, in *Proceedigs of the School and Workshop on Nanotubes and Nanostructures 2000, Santa Margherita di Pula (Ca), Italy*
7. Z.K. Tang, Lingyum Zhang, N. Wang, X.X. Zhang, G.H. Wen, G.D. Lee, J.N. Wang, C.T. Chan, Ping Sheng, Science **292**, 2462 (2001)
8. M. Cini, A. Balzarotti, Phys. Rev. B **56**, 14711 (1997)
9. M. Cini, G. Stefanucci, A. Balzarotti, Eur. Phys. J. B **10**, 293 (1999)
10. M. Cini, E. Perfetto, G. Stefanucci, Eur. Phys. J. B **20**, 91 (2001)
11. M. Cini, G. Stefanucci, Solid State Commun. **117**, 451 (2001)
12. G. Stefanucci, M. Cini, J. Phys. Cond. Matt. **14**, 2653 (2002)
13. G. Stefanucci, M. Cini, Phys. Rev. B **66**, 115108 (2002)
14. M. Cini, A. Balzarotti, R. Brunetti, M. Gimelli, G. Stefanucci, Int. J. Mod. Phys. B **14**, 2994 (2000)
15. E. Perfetto, G. Stefanucci, M. Cini, Phys. Rev. B **66**, 165434 (2002)
16. C.A. Balseiro, A.G. Rojo, E.R. Gagliano, A. Alascio, Phys. Rev. B **38**, 9315 (1988)
17. M. Cini, A. Balzarotti, G. Stefanucci, Eur. Phys. J. B **14**, 269 (2000)
18. M.P. Lopez Sancho, M.C. Munoz, L. Chico, Phys. Rev. B **63**, 165419 (2001)
19. A.L. Tchougreef, R. Hoffman, J. Phys. Chem. **96**, 8993 (1992)
20. W. Fettes, I. Morgenstern, Eur. Phys. J. B **9**, 9509 (1996)
21. Y.A. Krotov, D.H. Lee, S.G. Louie, Phys. Rev. Lett. **78**, 4245 (1997)