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Strain induced correlation gaps in carbon nanotubes

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Abstract. We calculate the change in the correlation gap of armchair carbon nanotubes with uniaxial elastic strain. We predict that such a stretching will enlarge the correlation gap for all carbon nanotubes by a change that could be as large as several meV per percent of applied strain, in contrast with pure band structure calculations where no change for armchair carbon nanotubes is predicted. The correlation effects are considered within a self-consistent Hartree-Fock approximation to the Hubbard model with on-site repulsion only.

PACS. 62.25.+g Mechanical properties of nanoscale materials – 71.10.Pm Fermions in reduced dimensions (anyons, composite fermions, Luttinger liquid, etc.) – 71.20.Tx Fullerenes and related materials; intercalation compounds

Carbon nanotubes (CNT) have many extraordinary electronic and mechanical properties [1]. In particular, band theory predicts that CNT are either metallic or semiconducting depending on chirality, i.e. in which direction a graphite monolayer is "rolled up" into a cylinder forming the tube [2]. Probing CNT with a scanning tunneling microscope, this metallic or semiconducting behaviour could be tested experimentally [3,4]. In addition, CNT can sustain large mechanical strains and can be deformed elastically up to bendings of order 19° which corresponds to a strain along the tube of 5.5% [5]. Experiments and numerical calculations indicate a large Young modulus of order 1TPa [6]. The interaction of mechanical and electronic properties has been studied at room temperature in two experiments [5,7] where it has been shown that uniaxial stress can change dramatically the electronic structure of CNT. In these experiments CNT have been suspended between two metal electrodes on SiO_2/Si substrates. To apply uniaxial stress along the tube the tip of an atomic force microscope (AFM) was used. The tip was lowered to push at the center of the CNT. The AFM allows to measure simultaneously the deflection and the conductance of the CNT. The strain can be defined as $\sigma = \left[\sqrt{4\delta^2 + l^2} - l\right]/l$ where l is the suspended length of the tube and δ is its vertical deflection. In the first experiment [5] it was shown that changing the strain from 0% to 3.2% let the conductance of a metallic CNT drop by two orders of magnitude. Both the mechanical and the electronic properties were observed to be completely reversible. More recently it was demonstrated [7] that not only metallic CNT become less conducting when applying stress but also inversely that some samples modified their behaviour from semiconducting to metallic. These experiments show convincingly that uniaxial stress applied to CNT changes their electronic properties.

Theoretically, the effect of strain on the electronic properties of CNT has been studied in band structure calculations, either analytically, using a tight-binding approach, or numerically by density functional theory [8–13]. In particular it has been shown that, depending on chirality, uniaxial stress can increase, decrease or not alter the band gap.

In this paper we include the effect of electron-electron correlations in these calculations. We compute in detail the gap as a function of applied strain and we compare our results to the one-electron band structure calculations in the literature. The calculations are carried out within a Hubbard tight-binding model using the self-consistent Hartree-Fock (H-F) approximation. It has been argued by the authors [14] that the charge gap of CNT at half-filling is well described within this approximation.

In this work we consider single-walled CNT at half-filling. In a first approximation, single walled CNT can be thought to be a rectangular graphite monolayer with the appropriate boundary conditions (Fig. 1). They can be classified by their chirality vector $\boldsymbol{C_h} = n\boldsymbol{a_1} + m\boldsymbol{a_2}$, where $\boldsymbol{a_1}$ and $\boldsymbol{a_2}$ are the basis vectors of the honeycomb lattice, while n and m are integers with $m \leq n$ [2]. $\boldsymbol{C_h}$ determines into which direction the graphene layer is rolled up. We describe CNT by a Hubbard model at half-filling with

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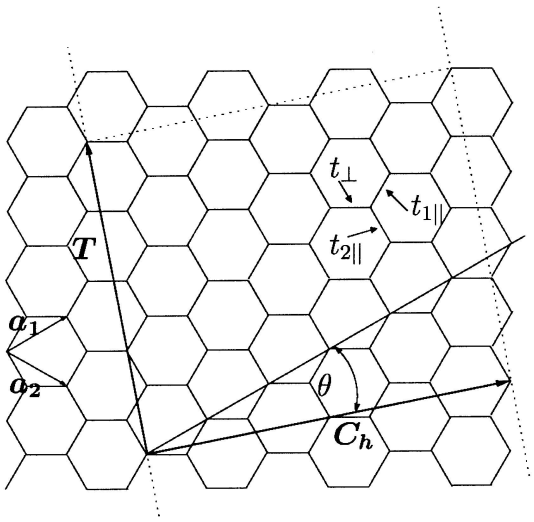

Fig. 1. A rectangular honeycomb lattice of a $(4,2)$ CNT, i.e. $\boldsymbol{C_h} = 4\boldsymbol{a_1} + 2\boldsymbol{a_2}$. The basis vectors are chosen to be $\boldsymbol{a_1} = a/2(\sqrt{3},1)$ and $\boldsymbol{a_2} = a/2(\sqrt{3},-1)$. $a = 2.49\mathring{A}$ is the lattice constant for CNT. The chirality vector $\boldsymbol{C_h}$ and the vector $\boldsymbol{T}$ define the quasi-one-dimensional unit cell. $\boldsymbol{C_h}$ describes the circumference and $\boldsymbol{T}$ is oriented parallel to the tube.

nearest neighbour hopping between π orbitals, and on-site interaction:

$$H = \sum_{\langle i,j\rangle\sigma} \left(t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow} \qquad (1)$$

σ is the spin index and i, j sum over the sites of a rectangular honeycomb lattice with periodic boundary conditions. $c^\dagger_{i\sigma}$ ($c_{i\sigma}$) are the fermion creation (annihilation) operators and $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$. The hopping integrals t_{ij} are restricted to nearest neighbors and in general they can have different values in every hopping direction, say $t_\perp$, $t_{1\|}$ and $t_{2\|}$ (cf. Fig. 1). These three hopping amplitudes and the one-site interaction strength U are the four parameters entering into the model. Choosing some values for those parameters we can determine the charge gap through a H-F calculation for a given (n,m) CNT. All the details of the H-F approximation can be found in reference [14] where also its validity has been discussed.

If there is no applied strain we set in our calculation all the hopping amplitudes equal to a certain value t_0. This is of course only an approximation. Forming a CNT from a graphite sheet, where this is true, we change the hopping integrals due to effects of curvature. It has been shown [10,15] that there is a curvature induced gap due to σ-π hybridization for all CNT except armchair CNT. This gap is at least of order 10 meV. Thus armchair CNT are the only CNT where band structure calculations predict a metallic gapless behaviour. They correspond to chiralities with $n = m$ or equivalently to a chiral angle $\theta = \pi/6$ (cf. Fig. 1). For armchair CNT the curvature induces only two different hopping amplitudes, namely $t_\perp$ and $t_\| \equiv t_{1\|} = t_{2\|}$. Due to this symmetry, no gap is opened from the band point of view. However we will show that there will be a gap induced from electron-electron correlation effects for all CNT, even if they are of armchair type. We concentrate our discussion on armchair CNT. The same effects are apparent in CNT of other chiralities but in that case these effects are less visible as there is already a gap in the one-electron band structure.

Following references [8,9] we use Harrison's phenomenological law to relate the hopping parameter t_0 of the undeformed CNT to the ones of the elastically deformed CNT [16] $t_i = t_0 \left(r'_i/r_i\right)^2$ where $\boldsymbol{r'_i}$ and $\boldsymbol{r_i}$ respectively, are the bond vectors before and after the deformation and $i = \perp, 1_\|, 2_\|$. Projecting these vectors along the directions of $\boldsymbol{T}$ and $\boldsymbol{C_h}$, we can write for an elastic uniaxial strain along the tube: $r_{iT} = (1+\sigma) r'_{iT}$ and $r_{iC_h} = (1-\nu\sigma) r'_{iC_h}$ where ν is the Poisson ratio. t_0 can be estimated from ab initio calculations to be 2.4 eV [17] and the Poisson ratio has been computed numerically [1] and measured experimentally for graphite to be about $\nu = 0.2$ [18]. It is difficult to get an estimate for the on-site repulsion U of atomic carbon. In the literature values between 5 and 12 eV are suggested [19–21].

To study now the correlation effects in the situation described above, i.e. stretching the tube by application of uniaxial strain, we rely as in previous work [14] on the H-F approximation. Based on the observation that the H-F calculations reproduce correctly the functional dependence of the energy gap in the one-dimensional Hubbard model at half-filling, we believe that it gives also reliable results for the gap of CNT.

We have shown in reference [14] that the H-F calculations for the charge gap of armchair CNT give the following scaling law

$$E_g/t_\| = c/n \, \exp\left\{-\alpha n (t_\|/U - t_\|/U^{HF}_{cr})\right\} \qquad (2)$$

with $c = 1.01$, $\alpha = 5.44$ and $U^{HF}_{cr} = 2.23 t_0$, the critical value to open a gap in the two-dimensional honeycomb lattice. In H-F theory U^{HF}_{cr} is given by the inverse of the bare static susceptibility

$$\frac{1}{U^{HF}_{cr}} = \chi_0 = \int_{\epsilon<0} \mathrm{d}\epsilon \frac{\rho(\epsilon)}{2\,|\epsilon|}. \qquad (3)$$

Since graphite is a semi-metal U is expected to be smaller, but close to this value, i.e. $U \lesssim U^{HF}_{cr}$. For such values a correlation gap of order 10 meV is present for CNT of small diameter. We verified that for (n,n) CNT with $n = 5, \ldots, 30$ and for an on-site repulsion in the interval $\left[U^{HF}_{cr} - 0.7t_0, U^{HF}_{cr}\right]$ the scaling law (2) is still valid when uniaxial stress σ is applied, which produces a change of the ratio $t_\perp/t_\|$ in the Hamiltonian (1) from 1 to larger values. $t_\perp/t_\|$ and σ are related by Harrison's formula in a non-linear way. The prefactor c depends only slightly on the change in $t_\perp/t_\|$. The variation of α and U^{HF}_{cr} on the applied strain is much more significant and it is shown in Figure 2. We observe that U^{HF}_{cr} increases with applied strain. From equation (2) we can see that this would imply that the charge gap diminishes since a U far from the critical value disfavours a large gap. However the simultaneous decrease of the parameter α overcomes this

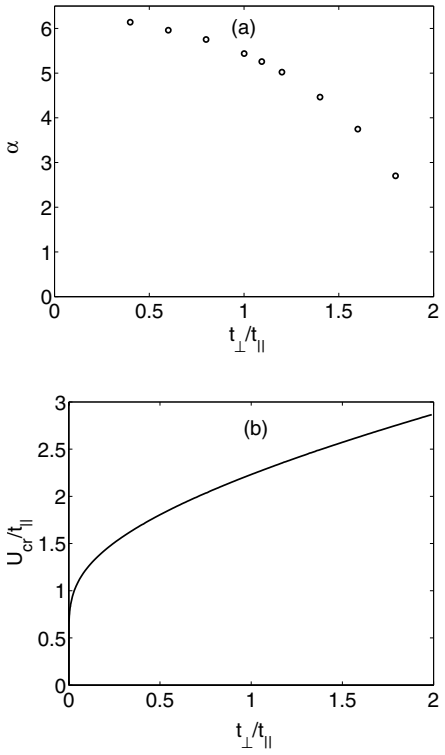

Fig. 2. Numerical results for the dependence of the parameters α and U_{cr}^{HF} in equation (2) on $t_\perp/t_\parallel$: (a) α is extracted from fitting the H-F results to the scaling law (2). (b) U_{cr}^{HF} is calculated by evaluating $\chi_0 = \int_{\epsilon<0} \mathrm{d}\epsilon \frac{\rho(\epsilon)}{2|\epsilon|}$, the bare staggered static susceptibility, and where $\rho(\epsilon)$ is the tight-binding density of states of the honeycomb lattice. In H-F theory we have $U_{cr}^{HF} = \chi_0^{-1}$.

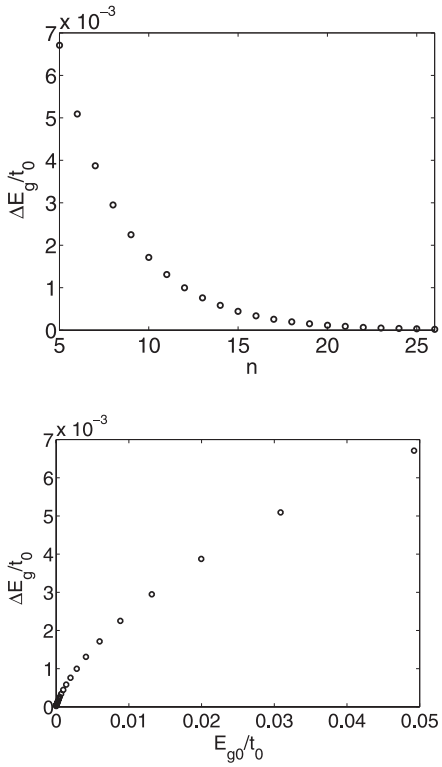

Fig. 3. The variation of the correlation gap for different (n, n) armchair CNT is plotted when a strain of 1% is applied ($U = 2t_0$). The upper plot shows the variation of the gap $E_g(\sigma = 1\%) - E_g(\sigma = 0)$ as a function of n. n is proportional to the tube diameter. The lower plot shows the same variation as a function of the original correlation gap at zero applied strain $E_{g0} \equiv E_g(\sigma = 0)$. E_{g0} is calculated for different armchair CNT, $n = 5, \ldots, 26$.

tendency and when both effects are taken into account, the charge gap increases approximately linearly with the strain with a slope that depends on U. Note that $U_{cr}^{HF} > 0$ indicates that there is a metal-insulator transition in the infinite two-dimensional honeycomb lattice ($n \to \infty$) at a finite value $U = U_{cr}^{HF}$. This is due to the fact that the density of states in the honeycomb lattice is vanishing at the two Fermi points as $\rho(\epsilon) \propto |\epsilon|$. In the limit $t_\perp/t_\parallel \to 0$ we get the one-dimensional behaviour where any infinitesimal electron-electron interaction can open a gap and α takes its value known from the Bethe Ansatz solution, i.e. U_{cr}^{HF} tends towards zero and α to 2π. The other limiting point is $t_\perp/t_\parallel = 2$ where the two Fermi points collapse into one and a band gap appears for values $t_\perp/t_\parallel > 2$ which makes the system insulating already for $U = 0$.

To compare our results to experiments we plot the variation of the gap for armchair CNT as a function of its size when a strain of 1% is applied (cf. Fig. 3). The on-site interaction U is set to $2t_0$. As the hopping amplitude t_0 has a large value of 2.4 eV neither the correlation gap at $\sigma = 0$ of order 10 meV nor its variation of order meV per percent of applied strain can be neglected. As an example we look at the values for a $(10, 10)$ CNT. We can read off from Figure 3 that the energy gap at zero strain is 14 meV which corresponds to a temperature of 160 K and that a strain of 1% induces a rise of 4 meV in the gap.

How does this compare to the effect of strain to the band structure? For small strains the following formula has been derived from a tight-binding calculation [8]:

$$\frac{\mathrm{d}E_g}{\mathrm{d}\sigma} = \mathrm{sgn}\,(2p+1)\, 3t_0\,(1+\nu)\cos 3\theta \qquad (4)$$

where $p \in \{-1, 0, 1\}$ is defined by the equation $n - m = 3q + p$ (q is integer). This formula has been used to interpret the experimental results in reference [7]. It follows from it that the change of the band gap with applied stress can be either positive or negative, depending on the value of p, or in other words on the chirality. The maximum variation is achieved for zig-zag CNT (chiral angle zero) and is about ± 85 meV/%. The maximal variation of 85 meV/% is one or even two orders of magnitude larger then the variation of 4 meV/% which we derived from electron-electron correlation. However, for armchair CNT ($\theta = \pi/6$) equation (4) and ab initio calculations predict that no gap opens up with applied strain. Then correlation effects are the only reason why

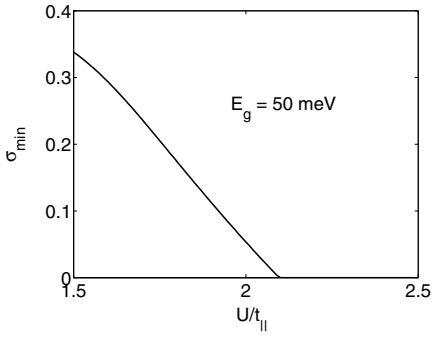

Fig. 4. Minimal strain σ_{min} necessary to open a gap of 50 meV as a function of the on-site repulsion U. The calculation was done for a $(10, 10)$ armchair CNT.

one should have a gap and this gap increases by applying uniaxial strain at a rate of several meV/%. In our previous example of the $(10, 10)$ CNT, we have seen that one percent of strain can change the correlation gap by about 30% of its original value.

To summarize, for semiconducting CNT with large band gaps the electronic structure at half filling is well described within band theory and correlation effects give only small corrections. But for CNT with a small gap (of several meV or less) correlation effects cannot be neglected. This is especially true for armchair CNT where no band gap at all is predicted but they should develop a measurable gap, induced from correlations alone, if sufficient pressure is applied. This conclusion is illustrated in Figure 4. We plot the strain which is necessary to open a gap of $E_g = 50\,\text{meV}$ as a function of the on-site repulsion U for a $(10, 10)$ armchair CNT. We see that if U is not too far from U_{cr} this quite large gap would be realisable experimentally and could be seen in low temperature data.

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