

From Graphene to Nanotubes

Zone Folding and Quantum Confinement at the Example of the Electronic Band Structure

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Zone folding represents a powerful tool for investigating the spectra of quasi particles of carbon nanotubes (CNTs) on the basis of the corresponding spectrum in graphene. We introduce the zone folding scheme by considering the electronic band structure of CNTs and thus investigate the electronic properties of CNTs depending on their chirality.

1 Introduction

The first numerical predictions for the electronic band structure of carbon nanotubes (CNTs) were published in 1992 [1, 2] only a few months after the discovery of CNTs [3]. Hamada et. al. discussed firstly in Ref. [2] the existence of metallic and semiconducting CNTs and found within a heuristic picture that 1/3 of all possible tubes are metallic which depends only on the chirality of the corresponding CNT. The used heuristic picture corresponds to the zone folding approximation which can be applied to approximate the spectrum of any quasi particle in CNTs on the basis of the corresponding spectrum in graphene.

This scheme has proven to be useful as the direct numerical calculation of physical properties of general CNTs represents a hard problem, due to the fact that the unit cell of a common chiral CNT contains usually several hundreds of carbon atoms.

2 Going from Graphene to Nanotubes in Real and k-space

In real space, graphene shows a honeycomb-like lattice structure which can be described with a two atomic unit cell with lattice basis vectors \mathbf{a}_1 and \mathbf{a}_2 where $\|\mathbf{a}_i\| = a_0 = 2.461 \text{ \AA}$ and $\angle(\mathbf{a}_1, \mathbf{a}_2) = 60^\circ$, i. e. \mathbf{a}_1 and \mathbf{a}_2 are not orthogonal.

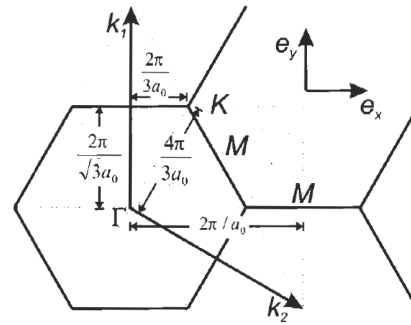


Figure 1: Image of the first Brillouin zone of graphene with indicated reciprocal lattice basis vectors \mathbf{k}_1 and \mathbf{k}_2 and points of high symmetry, K and M. [4]

The k-space of graphene can be easily introduced by using that the reciprocal lattice basis vectors \mathbf{k}_1 and \mathbf{k}_2 are defined by the relation $\mathbf{a}_i \mathbf{k}_j = 2\pi \delta_{ij}$ which leads to, written in the basis $\{\mathbf{a}_1, \mathbf{a}_2\}$, $\mathbf{k}_1 = \frac{1}{a_0^2} (\frac{8\pi}{3}, -\frac{4\pi}{3})_a$ and $\mathbf{k}_2 = \frac{1}{a_0^2} (-\frac{4\pi}{3}, \frac{8\pi}{3})_a$ where $(\dots)_a$ emphasises the chosen basis $((x_1, x_2)_a \equiv x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2)$. Drawing the first Brillouin zone yields a hexagon as shown in Fig. 1 with the K- and M-point as points of high symmetry with $\mathbf{K} = \frac{1}{3}(\mathbf{k}_1 - \mathbf{k}_2)$. It is useful in several cases to work with the inverted relation between the \mathbf{a}_i and \mathbf{k}_j which reads $\mathbf{a}_1 = \frac{a_0^2}{4\pi} (2\mathbf{k}_1 + \mathbf{k}_2)$ and $\mathbf{a}_2 = \frac{a_0^2}{4\pi} (\mathbf{k}_1 + 2\mathbf{k}_2)$.

As a CNT can be described by rolling up a strip of graphene, its unit cell can be constructed on basis of the real space of graphene. The basic structure of the tube is given by the chiral vector

$$\mathbf{c} = (n_1, n_2)_a$$

along which the tube is rolled up, i. e. $\|\mathbf{c}\|$ corresponds to the circumference of the tube and $\frac{\|\mathbf{c}\|}{\pi}$ to its diameter. Tubes with chiral indices (n,n) are denoted as armchair tubes, CNTs with indices $(n,0)$ as zig-zag tubes, where both kinds represent tubes with high symmetry and are therefore the favored examples for numerical calculations.

The lattice vector of the CNT is given by the smallest graphene lattice vector perpendicular to \mathbf{c} , which can be found to be

$$\mathbf{a} = \left(-\frac{2n_2 + n_1}{p}, \frac{2n_1 + n_2}{p} \right)_a,$$

with p as the greatest common divisor (gcd) of $2n_2 + n_1$ and $2n_1 + n_2$; note that it is convenient to split p into $p = nR$ with n gcd of n_1 and n_2 and $R = 3$ if 3 divides $\frac{n_1 - n_2}{n}$ or $R = 1$ else. Comparing the area of the unit cell of the tube and graphene yields the number of graphene unit cells in one tube unit cell $q = \frac{2}{nR}(n_1^2 + n_2^2 + n_1 n_2)$. In Fig. 2 the unit cell of the (2,1) tube is shown as example.

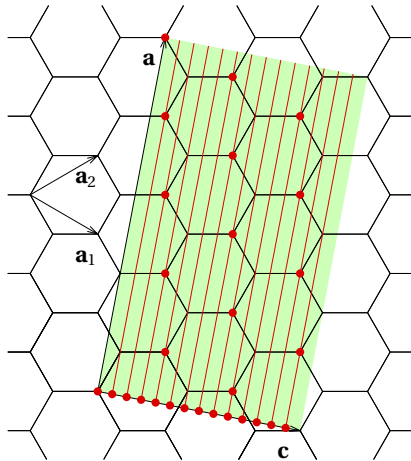


Figure 2: Unit cell of the (2,1) tube (green area) with indicated graphene basis lattice vectors \mathbf{a}_1 and \mathbf{a}_2 . Projecting the unit cell of the (2,1) tube on the \mathbf{c} axis yields $q = 14$ projected origins of graphene unit cells which yields the smallest physical real space period in \mathbf{c} direction to be $\frac{\|\mathbf{c}\|}{q}$.

CNTs are one dimensional lattices as only along the \mathbf{a} axis a translational invariance exists, which yields that their reciprocal space is also one dimensional and can be introduced via $\mathbf{a}\mathbf{k}_{\parallel} = 2\pi$, which yields $\mathbf{k}_{\parallel} = \frac{2\pi}{\|\mathbf{a}\|}\hat{\mathbf{a}}$, where the first Brillouin zone is given by the interval $\left] -\frac{\pi}{\|\mathbf{a}\|}, \frac{\pi}{\|\mathbf{a}\|} \right]$. Nevertheless, as the tube corresponds to a rolled up graphene sheet, periodic boundary conditions have to be imposed to any real-space function living on the tube. Due to the finite circumference of the tube, the momentum representation of any such function is given by a Fourier series with discrete modes \mathbf{k}_{\perp} as $e^{i\mathbf{k}_{\perp}\mathbf{c}} = 1$, which directly yields $\mathbf{k}_{\perp, m} = \frac{2\pi}{\|\mathbf{c}\|}m\hat{\mathbf{c}}$ with $m \in \mathbb{Z}$. The number of modes is given by the smallest physical real-space period in $\hat{\mathbf{c}}$ -direction which can be found to be $\frac{\|\mathbf{c}\|}{q}$ by projecting the whole tube unit cell on the \mathbf{c} -axis as illustrated in Fig. 2 which yields q equidistant projections of the q contained origins of graphene unit cells. Therefore, the $q = m$ mode corresponds to the $q = 0$ mode and, as q is even, we find $m = -q/2 + 1, -q/2 + 2, \dots, q/2$. Note that we could also have used that $\frac{2\pi}{\|\mathbf{c}\|}q\hat{\mathbf{c}} = \frac{2n_1 + n_2}{nR}\mathbf{k}_1 + \frac{2n_2 + n_1}{nR}\mathbf{k}_2$ which is obviously the smallest possible reciprocal graphene lattice vector in the corresponding direction, as nR was defined as the gcd of $2n_1 + n_2$ and $2n_2 + n_1$, which yields with the periodicity of the graphene lattice again the existence of maximal q different modes.

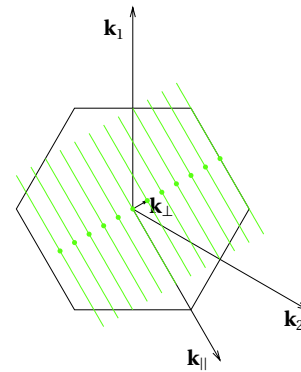


Figure 3: Connection between graphene and the (6,6) tube in reciprocal space. The Γ -point of the CNT is indicated by a dot on every allowed \mathbf{k} -state line. Note that the area of the rectangle spanned by the allowed lines (including the not drawn $m=-q$ mode) agrees with the area of the first Brillouin zone of graphene.

The connection between graphene and a CNT

in k -space is therefore given by drawing all k -states of the tube in the reciprocal space of graphene by using \mathbf{k}_{\parallel} and \mathbf{k}_{\perp} , where one always has to remember that the bare reciprocal space of the tube is only one dimensional and corresponds to the interval mentioned above; this yields especially that the Γ -point of the tube appears on every allowed tube k -state line as shown in Fig. 3.

3 Zone Folding

Using the connection between CNTs and graphene and the spectrum of a certain quasi particle, like a lattice electron or a phonon, in graphene yields the possibility to approximate the spectrum of the corresponding quasi particle in the tube by slicing the band structure in k -space with the allowed k -states, as illustrated in Fig. 4, and reading out the dispersion along these lines.

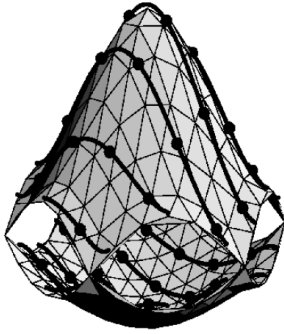


Figure 4: Illustration of the slicing of the graphene band structure with the allowed k -states of a CNT. [5]

The terminology of zone folding refers here in general to the spreading of allowed tube k -states over the considered band structure (zone unfolding) and the corresponding collection of the dispersion along the allowed lines (zone folding). By applying the zone folding approximation, we reduce the problem of calculating the band structure of every tube by its own to the determination of the allowed k -states for a certain CNT and once to the calculation of the graphene band structure.

This is, as mentioned, a general procedure, which can be applied for different quasi particles. In the following we want to examine the electronic band structure of CNTs based on the zone folding approximation; an additional similar dis-

cussion for the phonon spectrum and a general comprehensive introduction to the zone folding scheme can be found for example in Ref. [5].

4 Electronic Band Structure of Nanotubes

In order to apply the zone folding approximation for a general tube, the graphene band structure is needed. For a qualitative discussion of the electronic properties of a CNT, whether a tube is metallic or semiconducting, the tight binding description of graphene within the nearest neighbor approximation is sufficient as it captures the correct behavior of the electronic band structure around the Fermi energy, the crossing of the π bands at the K point. Defining the energy scale by $E_F = 0$ yields for graphene $E_{\text{TB}}^{\text{nn}}(\mathbf{k}) \propto \pm \left\{ 3 + 2 \cos(\mathbf{k}\mathbf{a}_1) + 2 \cos(\mathbf{k}\mathbf{a}_2) + 2 \cos[\mathbf{k}(\mathbf{a}_1 - \mathbf{a}_2)] \right\}$ [4].

Restricting $E_{\text{TB}}^{\text{nn}}(\mathbf{k})$ only to allowed k -states of the CNT by writing $\mathbf{k} = \mathbf{k}_t + \mathbf{k}_{\perp,m}$ where $\mathbf{k}_t = k\mathbf{k}_{\parallel}$ with $k \in]-\frac{1}{2}, \frac{1}{2}]$ yields as general expression for the allowed k -states $\mathbf{k} = \left[-\frac{n_2 k}{q} + \frac{(2n_1 + n_2)m}{nRq} \right] \mathbf{k}_1 + \left[\frac{n_1 k}{q} + \frac{(2n_2 + n_1)m}{nRq} \right] \mathbf{k}_2$ and therefore $E_{\text{TB}}^{\text{nn}}(k, m) \propto \pm \left[3 + c_{k,m}(2n_1 + n_2, -n_2) + c_{k,m}(2n_2 + n_1, n_1) + c_{k,m}(n_1 - n_2, -n_1 - n_2) \right]$ with $c_{k,m}(x, y) = 2 \cos\left(\frac{2\pi mx}{nRq} + \frac{2\pi ky}{q}\right)$ as closed expression for the electronic band structure of a general CNT in the nearest neighbor tight binding approximation which is also discussed in Ref. [6].

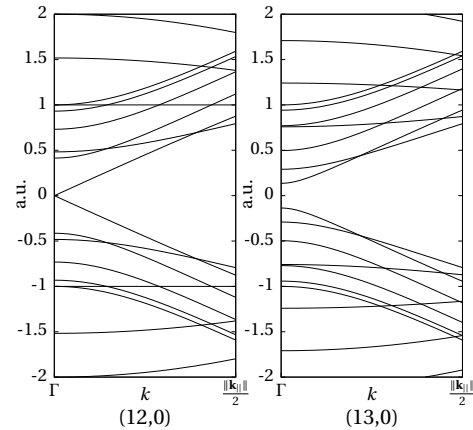


Figure 5: Band structure of the (12,0) and (13,0) tube obtained from the closed expression for $E_{\text{TB}}^{\text{nn}}$. The shown bands agree well with the results obtained in Ref. [2]. In accordance with Fig. 6 the (12,0) tube is metallic and the (13,0) tube semiconducting.

Plotting for example the band structure of the

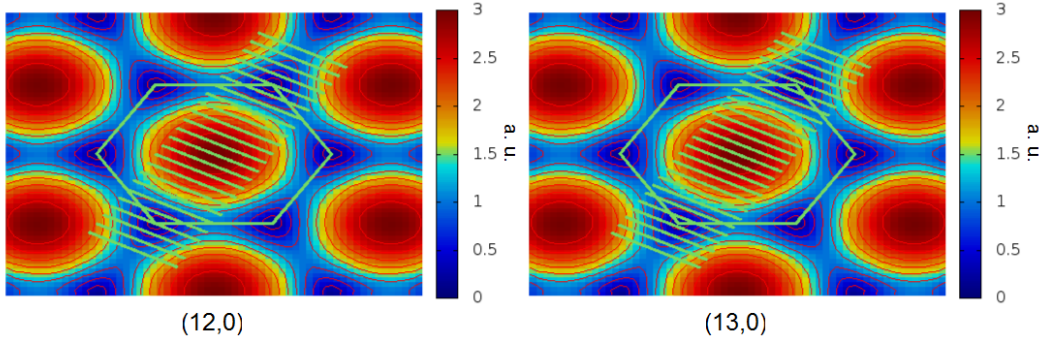


Figure 6: Contour plot of the electronic band structure of graphene (in arbitrary units) above the Fermi level in nearest neighbour tight binding approximation sliced by the allowed k-states for the (12,0) and (13,0) tube. Note that for the (12,0) tube the K point belongs to the allowed states, for the (13,0) tube it is forbidden.

(12,0) and (13,0) tube, as they were investigated by Hamada et. al. in Ref. [2], in an usual E-k-diagram and a contour plot in Fig. 5 and 6 reveals that the (12,0) tube is metallic, as two bands cross at the Fermi level, and the (13,0) tube is semiconducting; inserting the correct prefactors for $E_{\text{TB}}^{\text{nn}}$ of about 2.7 eV would lead to a gap of about 0.7 eV.

The contour plot reveals the reason for this behavior, for the (12,0) tube the K-point of graphene is allowed whereas for the (13,0) tube the K-point is forbidden. We conclude that as graphene, at half filling, has only a 0-dimensional Fermi surface, CNTs can be either metallic or semiconducting which depends on the inclusion or exclusion of the Fermi point, the point of crossing bands at the Fermi level, in the allowed tube k-states.

In order to relate this to the chiral indices n_1 and n_2 , we can use the zone folding approximation and assume that the Fermi point is located at the K-point. Using the quantization condition yields that the K-point is among the allowed states if $\exists m \in \mathbb{Z} : \mathbf{Kc} = 2\pi m$. Inserting the expression for \mathbf{K} leads to the condition $2\pi m = \frac{2\pi}{3}(n_1 - n_2)$, so that 3 has to divide $n_1 - n_2$ in order to have a general CNT to be metallic. From this condition we easily conclude that all armchair tubes are expected to be metallic, where zig-zag tubes are only metallic if 3 divides n which agrees with the finding of Hamada et. al. for the (12,0) and (13,0) tube. The same result can be obtained by considering the real space image of the graphene wave function at the K point, which is shown in Fig. 7, where this wave function can only live on a certain tube if it respects the periodic boundary conditions, which is again fulfilled for all arm-

chair tubes but only for those zig-zag tubes where n is a multiple of 3.

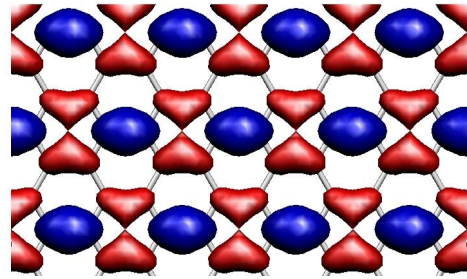


Figure 7: Plot of the real space image of the electron wave function of graphene for an electron with wave vector at the K-point (by courtesy of Prof. Dr. Reich).

5 Limits of the Zone Folding Approximation

Using the zone folding scheme yields in general two different kinds of approximations, one within the scheme and one due to its application. Within the zone folding scheme we approximated the electronic band structure of graphene by using only nearest neighbour tight binding results. However this does not affect the qualitative discussion made above, as the Fermi points are well described in this approximation. Nevertheless if we are interested in concrete numbers, in order to calculate for example optical transitions, more involved techniques like a 3rd nearest neighbour tight binding model or first principle calculations are required to determine the graphene band structure, see for example Ref. [4].

Certainly more important, as not that easy controllable, is the approximation done due to the application of zone folding. Using this scheme neglects all curvature effects, the change of bond lengths along the \mathbf{c} -direction and the rehybridization due to the non-orthogonality of the p_z and s , p_x , and p_y orbitals. Where the rehybridization in general only affects higher states above the Fermi level [4], the change in bond-length shifts the Fermi point in k -space. Therefore in tubes, which are metallic in the zone folding approximation, secondary gaps in the order of 10 meV to 100 meV can open and the tube becomes quasi metallic, which is for example discussed in Ref. [4, 7]; in fact only in case of armchair tubes the shift of the Fermi point happens to be along an allowed k -line so that only armchair CNTs are truly metallic.

The electronic properties of CNTs are for example accessible by scanning tunneling spectroscopy which can probe the density of states (DOS) around the Fermi level via the normalized conductance directly which shows for semiconducting tubes a vanishing DOS in the band gap [4, 8]. Even secondary gaps are detectable by this procedure and for instance their diameter dependence can be compared to theoretical predictions [9].

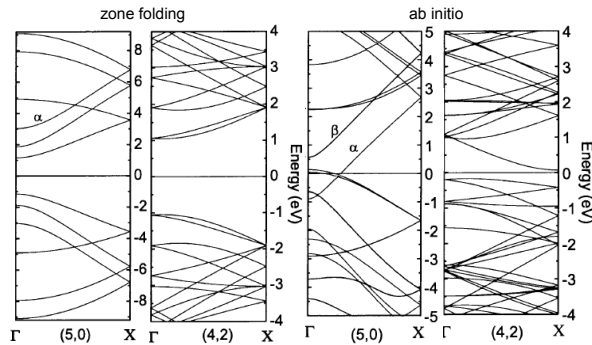


Figure 8: Comparison of the band structure of small diameter tubes, the (5,0) and (4,2) tube, obtained from zone folding and ab initio calculations. The zone folding scheme fails in describing the corresponding band structures as it predicts both tubes to be direct semiconductors where the (5,0) tube turns out to be metallic and the (4,2) tube a small gapped indirect semiconductor [10].

These curvature effects naturally increase with decreasing diameter of the tube. In case of 4Å-

diameter tubes we clearly see in Fig. 8 that a zone-folding description fails completely in even capturing the qualitative properties of the corresponding tubes. A further discussion of small diameter CNTs can be found in Ref. [10]. Nevertheless for larger tubes with diameters of about 1 nm, the zone folding approximation provides reasonable results.

6 Summary

By considering the zone folding scheme, we have implemented on basis of the example of the electronic band structure a powerful and efficient tool for calculating the spectrum of quasi particles in CNTs. Within the zone folding approximation we obtained that 1/3 of all possible CNTs are metallic or, if we take into account curvature effects, quasi metallic.

References

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