

Chapter 2

The Structural and Electronic Properties of Carbon Nanotubes

Carbon has a rich and varied chemistry, forming compounds with almost every other known element of the periodic table. It is also the compounds that it forms with itself, however, that are of great technological interest. Bulk carbon materials, such as diamond and graphite, have been known for centuries; more recently, quasi-low-dimensional allotropes of carbon have been discovered: the two-dimensional graphene [1, 2], zero-dimensional fullerenes [3], and one-dimensional nanotubes [4]. The excitement that arises from these newly discovered materials comes from their physical properties which offer unparalleled improvements over conventional materials. For instance, many remarkable properties of carbon nanotubes have been identified including a mechanical strength greater than most other materials [5] and thermal conductivity an order of magnitude greater than that of copper [6].

It is the electronic properties of carbon nanotubes that form the focus of this thesis. Very high conductivities have been observed in CNTs, with ballistic conductance occurring over very large length-scales or order microns (see Sect. 3.2). The maximum current densities obtainable in carbon nanotubes is found to be very high, up to 10^9 – 10^{10} A/cm², which considerably exceeds the 10^6 A/cm² current found to destroy copper nanowires [7], and even exceeds the critical current densities of superconductors (10^8 – 10^9 A/cm²) [8]. Applications for high-frequency electronics may also prove fruitful as the impact of the skin effect is reduced [9]. In a wire made from a conventional material, the skin effect makes high frequency current flow at the surface of a wire reducing the effective cross-sectional area of a wire and increasing the resistance; in carbon nanotubes, the tubular structure already makes the current flow at the nanotube surface minimising the impact of the skin effect. Coupled with the low mass density of carbon nanotubes, 1.3–2.1 g/cm³ [10, 11] compared to 9 g/cm³ for copper, carbon nanotubes are promising candidates for light-weight high-performance electrical wires.

In this chapter, we introduce the fundamental structural and electronic properties of carbon nanotubes (CNTs). The theoretical electronic structure is derived within a tight-binding framework, and a discussion is made on how these results are modified

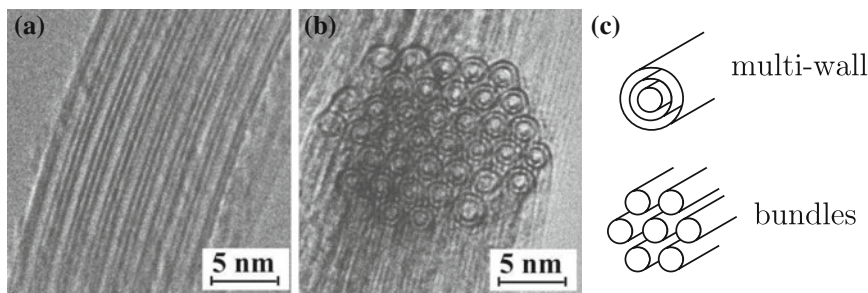


Fig. 2.1 Bundles of double walled CNTs imaged under transmission electron microscopy. **a** bulk-like region; **b** a cross-sectional view demonstrating the hexagonal packing within the bundle and the double walls of the CNTs; **c** the schematic geometry of multi-walled CNTs and CNT bundles. Adapted from Ref. [14] with permission from The Royal Society of Chemistry.

by more sophisticated calculations. The aim of this chapter is to introduce this background and define relevant quantities in sufficient detail that are then used throughout the remainder of this dissertation. For a comprehensive review of the electronic and structural properties of carbon nanotubes see [4, 12].

2.1 The Structure of Carbon Nanotubes

Carbon nanotubes (CNTs) are tubules of carbon with walls made from a single layer of carbon atoms arranged in a hexagonal structure. As structures, they can have remarkably high aspect ratios, defined as the ratio of the tube diameter to the length of the tube, on the order of $1 : 10^6$ —typical diameters are on the order of nanometres, and maximum length on the order of microns up to centimetres [13]—and can therefore be considered as a realisation of ideal atomic wires of carbon.

Along with individual single-walled CNTs, multiple CNTs can be combined to form composite structures. A CNT inside another CNT with larger diameter forms a double-walled CNT, shown in Fig. 2.1; further CNTs contained within this double-walled CNT forms multi-walled CNTs¹ with a spacing between the concentric shells of individual CNTs around $3.4 \text{ \AA}$ as in graphite.

These single- or multi-walled CNTs may also conglomerate together to form bundles. The axes of the constituent CNTs are aligned and the individual CNTs have a hexagonal packing arrangement as shown in Fig. 2.1, with a similar inter-tube separation.

¹Note that double-walled CNTs are often referred to as multi-walled CNTs.

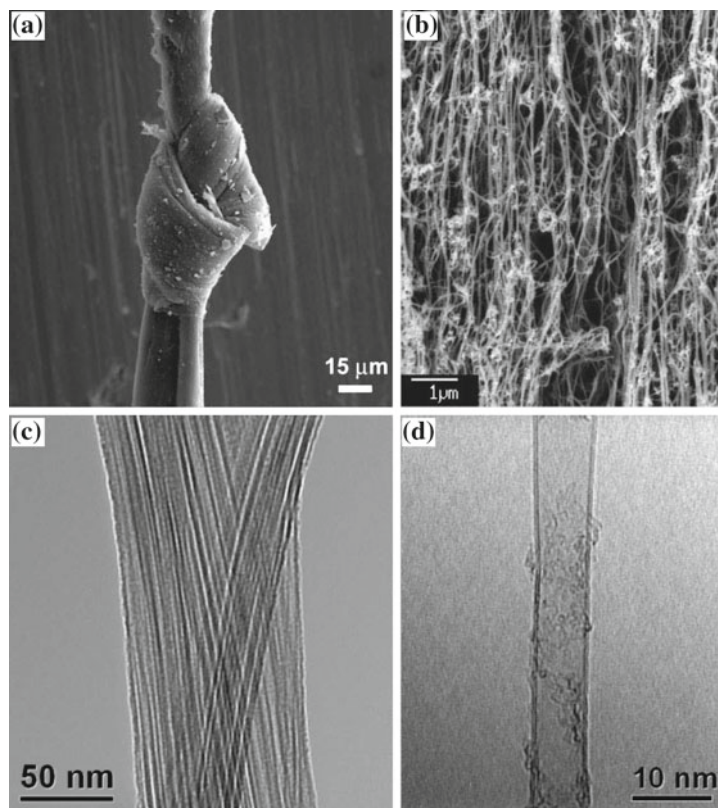


Fig. 2.2 The hierarchical structure of carbon nanotubes: **a** a macroscopic nanotube fibre with knot; **b** a disordered nanotube bundle network; **c** bundles of single and multiwall carbon nanotubes; **d** an individual (double wall) nanotube. From [15], copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

2.1.1 Carbon Nanotube Wires, Fibres and Networks

As a result of the impressive electronic properties of individual CNTs on the atomic scale, considerable effort has been made to construct macroscopic materials that reproduce these desirable quantities. It is currently impractical to grow perfect CNTs that are macroscopic in length, and so alternative approaches have been investigated. One approach is to spin the individual CNTs into bundles and then into fibres and wires [16–18]. Figure 2.2a shows such a CNT fibre.

In this material, a conducting network of CNTs is formed and, as no individual CNT traverses the length of the wire, electrons must percolate through paths involving many CNTs. The conductivities of these wires is orders of magnitude lower than expected based on the conductances of the individual CNTs. To date, the highest

specific conductivity² obtained for a CNT fibre is $20 \text{ S m}^{-1}/(\text{g cm}^{-3})$ [19] which is somewhat better than the same quantity for copper ($6.5 \text{ S m}^{-1}/(\text{g cm}^{-3})$) and aluminium ($14 \text{ S m}^{-1}/(\text{g cm}^{-3})$). The theoretical maximum specific conductivity for CNTs can be estimated to be of order $10^3\text{--}10^4 \text{ S m}^{-1}/(\text{g cm}^{-3})$, however, indicating that significant improvement could still be made.³ The additional resistance found in experiment is attributed to a range of factors, including the relative contributions from metallic/semiconducting CNTs (see Sect. 2.3), the morphology of the network and the presence of defects and impurities. An additional significant contribution to the resistance is believed to come from poor tunnelling between CNTs in the network. Understanding the factors that affect this *inter-tube* tunnelling rate and how it may be improved forms a significant focus of this thesis. To achieve this goal, however, an understanding of the electronic structure of individual CNTs is required.

2.2 The Geometry of Individual Carbon Nanotubes

The structure of an individual CNT can be considered to be derived from the graphene lattice, an infinite hexagonal planar network of carbon atoms, which is rolled up to form a cylinder. Depending on how this rolling performed, CNTs of different structure, diameter and indeed electronic properties (see Sect. 2.3) can be made.

To uniquely determine the type of CNT, it is sufficient to specify the circumferential vector ($\mathbf{C}_h$) that defines the chiral vector (AA' in Fig. 2.3) between two sites of the graphene lattice (A and A') that are equivalent once the sheet is rolled. This chiral vector can be defined simply in terms of a pair of indices (n, m) which define the vector in terms of the graphene lattice vectors ($\mathbf{a}_1, \mathbf{a}_2$):

²Specific conductivity, defined as the conductivity normalised by the density, is used to allow comparison of CNT networks with different morphologies and densities.

³This estimate is obtained by assuming that conductance within a CNT can be considered ballistic over the electron mean free path of carbon nanotubes $\ell_{\text{m.f.p.}} \sim 1 \mu\text{m}$ (see Chap. 3 for a discussion of ballistic conductance and mean free paths). This defines a conductivity of $\sigma \sim G\ell_{\text{m.f.p.}}/A$ where the conductance G is of order the quantum conductance $G_0 = 7.75 \times 10^{-5} \text{ S}$ and A is the CNT cross-sectional area. Assuming that each CNT within the network contributes independently to the conductivity, the specific conductivity of the network as a whole is equal to the specific conductivity of an individual CNT. The mass density of an individual CNT is obtained as $\rho = Nm_C/Ad$ where d is the unit length of the tube, $m_C \sim 10^{-26} \text{ kg}$ is the atomic mass of a carbon atom and $N = 2\pi Dd/3\sqrt{3}a_{CC}^2$ is the number of carbon atoms per unit length d with $D \sim 1 \text{ nm}$ the CNT diameter and $a_{CC} = 1.4 \text{ \AA}$ the carbon-carbon bond length. The resulting expression for the specific conductivity is

$$\sigma' = \frac{\sigma}{\rho} = \frac{3\sqrt{3}G_0\ell_{\text{m.f.p.}}a_{CC}^2}{2\pi Dm_C}. \quad (2.1)$$

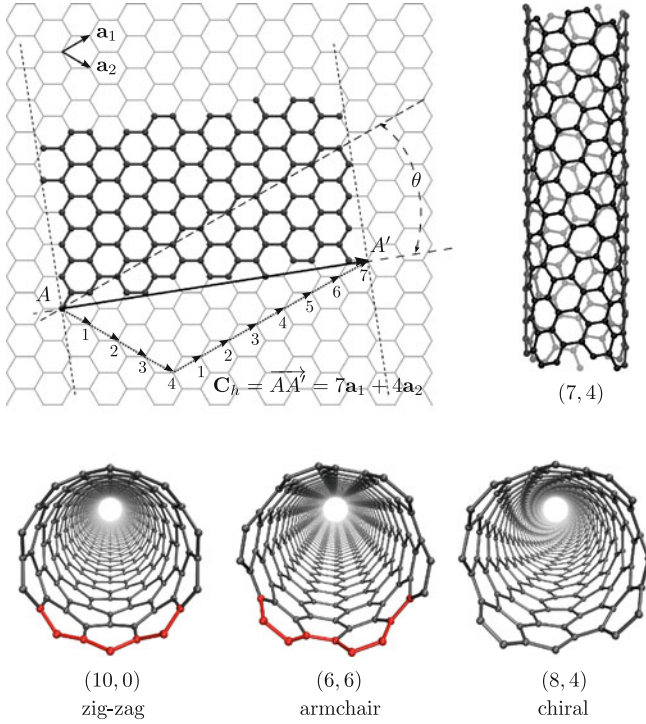


Fig. 2.3 *Top panel* the graphene hexagonal lattice with lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$. The chiral vector $\mathbf{C}_h = 7\mathbf{a}_1 + 4\mathbf{a}_2$ represents one wrapping of the graphene lattice to form the (7, 4) CNT which is shown on the right; rolling into a tube joins the two *dashed lines*. The shaded atoms represent the periodic repeating unit of this CNT. The chiral angle θ is defined as the angle between $\mathbf{C}_h$ and the $\mathbf{a}_1$ vector defining the zig-zag ($n, 0$) direction. *Bottom panel* the atomic structures of the zig-zag (10, 0), armchair (6, 6), and chiral (8, 4) CNTs; the zig-zag and armchair edges are indicated in *red*. Adapted from [12]

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2. \quad (2.2)$$

A vector within the graphene plane that is perpendicular to $\mathbf{C}_h$ defines the direction of the CNT axis. In addition to $\mathbf{C}_h$, a chiral angle θ can be defined as the angle between the chiral vector and the $\mathbf{a}_1$ graphene lattice vector

$$\cos \theta = \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{|\mathbf{C}_h||\mathbf{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}}. \quad (2.3)$$

Due to the hexagonal symmetry of the graphene lattice, the chiral angle can always be defined within the range $0^\circ \leq \theta \leq 30^\circ$. In general, CNTs are chiral and have a left- or right-handed screw direction (Fig. 2.2 bottom right). There are two exceptions, however, where the CNTs are achiral: for either $n = 0$ or $m = 0$, $\theta = 0^\circ$ and the CNT is said to be *zig-zag*; for $n = m$, $\theta = 30^\circ$, the CNT is said to be *armchair*.

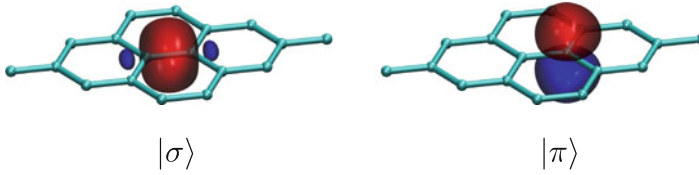


Fig. 2.4 A $|\sigma\rangle$ bond and $|\pi\rangle$ orbital of the graphene sheet

These names arise from the profile of the CNT cross-sections as shown in Fig. 2.2. The diameter of the CNT can also be defined from the chiral vector ($a = |\mathbf{a}_1|$)

$$d = \frac{|\mathbf{C}_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2}. \quad (2.4)$$

2.3 The Electronic Properties of Carbon Nanotubes

As a result of the relationship between the structure of CNTs and graphene, it is useful to describe the CNT bonding structure in terms of the electronic structure of graphene. In the following discussion, we follow the review of Ref. [12].

The electronic structure within graphene can be described using hybridisation theory. Of the four valence orbitals of the carbon atom ($2s$, $2p_x$, $2p_y$ and $2p_z$ with the z -axis perpendicular to the atomic-plane), the s , p_x and p_y orbitals are combined together into a planar sp^2 hybridisation scheme. These sp^2 orbitals are symmetric with respect to the planar symmetry and hybridise with equivalent orbitals on adjacent carbon atoms producing strong, covalent σ/σ^* bonds that are responsible for the majority of the binding energy and elastic properties of the graphene sheet. The remaining p_z orbitals are out-of-plane and, for a flat graphene lattice, cannot couple with the σ/σ^* bonds due to symmetry. Interactions between neighbouring p_z orbitals, however, are strong creating a manifold of delocalised π/π^* orbitals which exist in the planes above and below the atomic sheet. In Fig. 2.4 we show the relative shapes of the σ bonds and p_z orbitals.

The energy of the σ/σ^* bonds lie far from the Fermi energy (see Fig. 2.5), and therefore contribute little to conduction. In contrast, the Fermi energy is located within the π/π^* bands making these states the dominant contributor to conduction within the material.

2.3.1 Tight-Binding Model of Graphene

A simple but efficient description of the electronic band structure of graphene can be obtained using a straightforward tight-binding model which we now describe. The

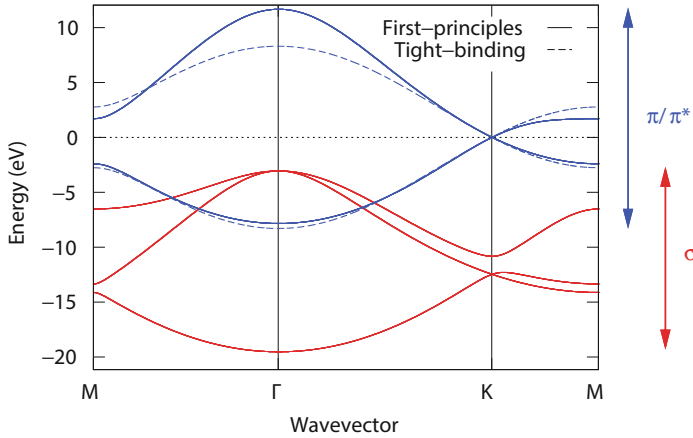


Fig. 2.5 The band structure of graphene. The *solid lines* are calculated from first-principles calculations (see Chap. 4), and coloured by the symmetry of the orbitals: σ in *red*, π in *blue*. The *dashed line* gives band structure calculated using the π/π^* tight-binding model (Sect. 2.3.1)

primitive unit cell of graphene is hexagonal and contains two carbon atoms, each of which form hexagonal sublattices which are conventionally denoted the A and B sublattices. Each atom contributes four electrons for a total of eight electrons per unit cell. The interactions between the six sp^2 hybrid orbitals within the primitive unit cell (three per carbon atom) produce three bonding σ bands and three anti-bonding σ^* bands. The three bonding σ bands are occupied by six of the eight electrons per unit cell, but as these bands lie far below the Fermi energy their contribution to the transport properties is negligible. The anti-bonding σ^* bands lie high in energy and are unoccupied. The remaining two electrons per unit cell are placed within the π/π^* bands which are formed from the interactions between the p_z orbitals only. The Fermi energy is found to lie within these bands and therefore a tight-binding model that describes only this band is sufficient to describe the electronic transport properties of graphene. A suitable basis for this tight-binding calculation is therefore a single $p_z(\mathbf{r} - \mathbf{r}_{A,B})$ orbital located on each atom site $\mathbf{r}_{A,B}$ of the A/B sublattice.

To solve the Schrödinger equation for graphene, we apply Bloch's theorem [20] and write the wavefunctions⁴ as

$$\psi_{\mathbf{k}}(\mathbf{r}) = c_A(\mathbf{k})\tilde{p}_z^A(\mathbf{k}, \mathbf{r}) + c_B(\mathbf{k})\tilde{p}_z^B(\mathbf{k}, \mathbf{r}), \quad (2.5)$$

where

$$\tilde{p}_z^{A,B}(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} p_z(\mathbf{r} - \mathbf{r}_{A,B} - \mathbf{R}), \quad (2.6)$$

⁴For clarity, we omit the normalisation of the wavefunction.

$\mathbf{k}$ is the electron momentum within the plane and $\mathbf{R}$ is a lattice vector. In the basis of $\tilde{p}_z^{A,B}$, the Schrödinger equation is solved by the solutions to the secular equation

$$\begin{vmatrix} H_{AA} - E(\mathbf{k}) & H_{AB} \\ H_{BA} & H_{BB} - E(\mathbf{k}) \end{vmatrix} = 0, \quad (2.7)$$

with the matrix elements defined as

$$H_{AA}(\mathbf{k}) = \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \langle p_z^A(\mathbf{R}') | \hat{H} | p_z^A(\mathbf{R}) \rangle, \quad (2.8)$$

$$H_{AB}(\mathbf{k}) = \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \langle p_z^A(\mathbf{R}') | \hat{H} | p_z^B(\mathbf{R}) \rangle, \quad (2.9)$$

where $\hat{H}$ is the Hamiltonian operator. The state

$$\langle \mathbf{r} | p_z^{A/B}(\mathbf{R}) \rangle = p_z(\mathbf{r} - \mathbf{r}_{A,B} - \mathbf{R}) \quad (2.10)$$

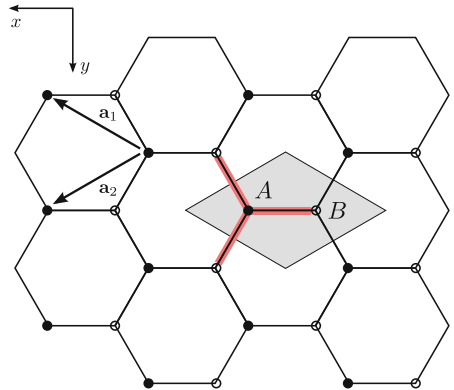
denotes a p_z orbital at position $\mathbf{r}_{A,B} + \mathbf{R}$ and we have assumed that the orbitals are orthogonal.

Under a nearest-neighbour approximation, shown schematically in Fig. 2.6, $H_{AA} = H_{BB}$ are independent of $\mathbf{k}$ and can be set to zero as an energy reference, and H_{AB} simplifies to

$$H_{AB} = \left[\langle p_z^A(\mathbf{0}) | \hat{H} | p_z^B(\mathbf{0}) \rangle + e^{i\mathbf{k} \cdot \mathbf{a}_1} \langle p_z^A(\mathbf{0}) | \hat{H} | p_z^B(\mathbf{a}_1) \rangle + e^{i\mathbf{k} \cdot \mathbf{a}_2} \langle p_z^A(\mathbf{0}) | \hat{H} | p_z^B(\mathbf{a}_2) \rangle \right] \quad (2.11)$$

$$= -t_0 \alpha(\mathbf{k}), \quad (2.12)$$

Fig. 2.6 The basis vectors and hexagonal lattice of graphene. The red bars indicate interactions between the three nearest-neighbour p_z orbitals. The shaded region indicates the graphene unit cell



where t_0 defines the transfer integral between first-nearest neighbours, typically of order 2.9 eV [21], and $\alpha(\mathbf{k}) = (1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2})$.

Upon solving Eq. 2.7 the dispersion relations become ($\mathbf{k} = (k_x, k_y)$, $a = |\mathbf{a}_1|$)⁵

$$E(\mathbf{k}) = |H_{AA}|^2 \pm |H_{AB}|^2 \quad (2.13)$$

$$= \pm t_0 |\alpha(\mathbf{k})| \quad (2.14)$$

$$= \pm t_0 \sqrt{1 + 4 \cos \frac{\sqrt{3}k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}}. \quad (2.15)$$

From the plot shown in Fig. 2.7, this dispersion relation is seen to consist of two sheets that touch at $E = 0$. These contacts occur at the corners of the first Brillouin zone and are denoted as the K and K' points. As the π/π^* manifold is to contain two electrons, both⁶ are placed within the lower sheet (the negative energy branch of (2.15)) which is fully occupied, the upper sheet is unoccupied and therefore the Fermi energy is the energy at which the two sheets touch which can be verified to be $E_F = H_{AA} = 0$ by our choice energy reference. As there are unoccupied states within the upper sheet that lie at infinitesimal energy away from the Fermi energy, graphene therefore displays metallic characteristics, although it is found that there is a low density of states in the vicinity of the Fermi energy and the term semi-metal is often used.

The low energy excitations can be obtained by expanding the dispersion relation about either the K or K' point⁷ resulting in linear dispersion relations

$$E(\mathbf{K} + \delta\mathbf{k}) = \pm \frac{\sqrt{3}a}{2} t_0 |\delta\mathbf{k}|, \quad (2.16)$$

where $\mathbf{K}$ is the co-ordinate vector of the K point with respect to the origin of the Brillouin zone.

2.3.2 Zone-Folding Approximation

To relate the band structure of graphene to the band structure of CNTs the periodicity around the CNT circumference must be imposed on the wavefunction

⁵We assume the graphene lattice vectors to be

$$\mathbf{a}_1 = (a_{1,x}, a_{1,y}) = \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right) a, \quad \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) a.$$

⁶Placed in each spin channel.

⁷These points are equivalent under time-reversal symmetry.

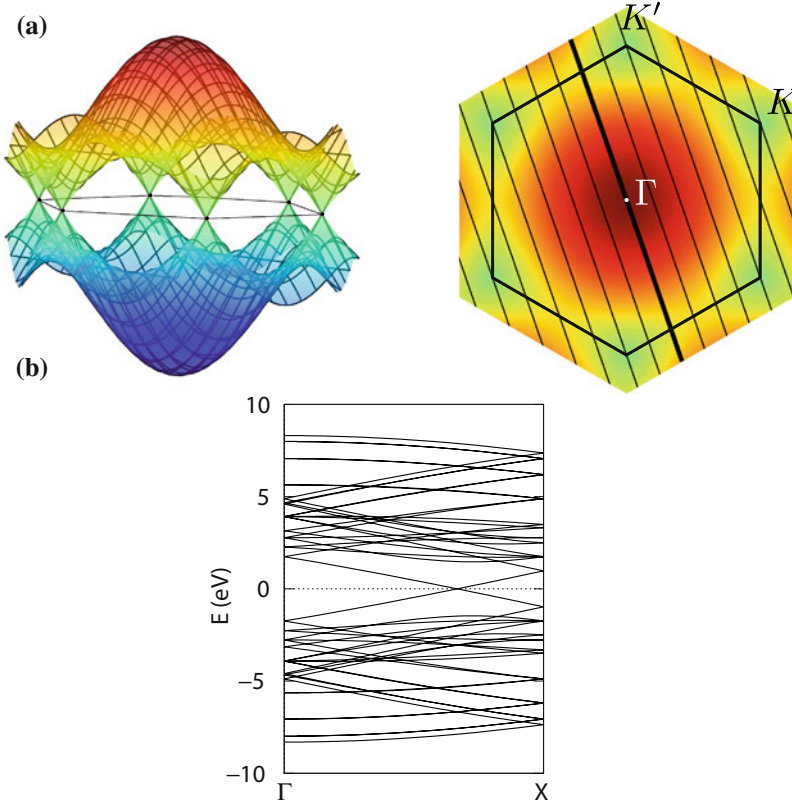


Fig. 2.7 Top panel the π/π^* band structure of graphene (2.15). In the right panel, the Brillouin zone is indicated by the hexagon; the lines indicate the states of the $(8,2)$ CNT that are allowed under the zone-folding approximation. The resulting $(8,2)$ one-dimensional band structure is shown in the lower panel. **a** Graphene band structure and Brillouin zone, **b** $(8,2)$ band structure

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{C}_h) = e^{i\mathbf{k} \cdot \mathbf{C}_h} \psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r}), \quad (2.17)$$

where the first equality is due to Bloch's theorem. Consequently, the imposed periodicity restricts the values that the electron momentum can take such that $\mathbf{k} \cdot \mathbf{C}_h = 2\pi\ell$ for integer ℓ , which corresponds to the allowed values of $\mathbf{k}$ being confined to discrete lines, termed subbands, within the graphene Brillouin zone. This is shown in Fig. 2.7 where we show these allowed lines for the $(8,2)$ CNT. The momentum along these subbands is the axial momentum and can take a continuous range of values; for each subband there is a single azimuthal momentum. Depending on the symmetry of the CNT, two distinct cases are possible: metallic and semiconducting CNTs, which we now describe in turn.

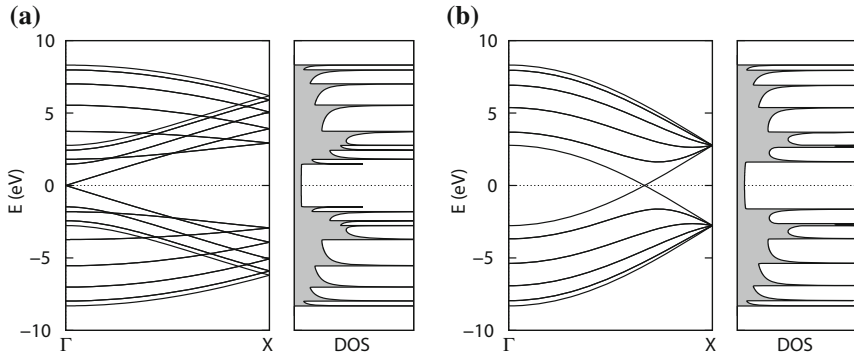


Fig. 2.8 The band structures and densities of states (DOS) of the achiral (9, 0) and (5, 5) metallic CNTs as calculated using the π/π^* tight-binding model under the zone-folding approximation. After [12]. **a** (9, 0), **b** (5, 5)

Metallic CNTs

If a subband includes the K point, the CNT will maintain the linear dispersion relations of the graphene Brillouin zone and will therefore be metallic. The condition to achieve this is $\mathbf{K} \cdot \mathbf{C}_h = 2\pi\ell$ which can be straightforwardly shown to be equivalent to $n - m = 3\ell$. All armchair (n, n) CNTs and subset of zig-zag $(n, 0)$ and chiral CNTs are therefore metallic. The low energy excitations retain the linear dispersion relations of the graphene excitations but the axial momentum where the bands cross, the Fermi momentum k_F , depends on the chirality

$$E(k) = \pm \hbar v_F |k - k_F|, \quad (2.18)$$

where k is the axial momentum and $v_F = \sqrt{3}at_0/2\hbar$ defines the Fermi velocity. In Figs. 2.7b and 2.8 we show the dispersion relations of the metallic (8, 2), (9, 0) and (5, 5) CNTs under the zone-folding approximation. In Fig. 2.8 we also plot the densities of states for the (9, 0) and (5, 5) CNTs. The divergences are called Van Hove singularities and are a result of the quasi one dimensional nature of CNTs and their functional dependence scales as the inverse of the energy difference to the band edge ($1/\sqrt{E - E_b}$).

2.3.2.1 Semiconducting CNTs

In the case that no subband includes the K point, i.e. when $n - m = 3\ell \pm 1$, the CNT will be semiconducting and there exists a band gap. Expanding the low energy excitations for the subband closest to the K point results in a dispersion relation [12]

$$E(k) \approx \pm \frac{\sqrt{3}a}{2} t_0 \sqrt{\left(\frac{2\pi}{3|C_h|}\right)^2 + k^2}, \quad (2.19)$$

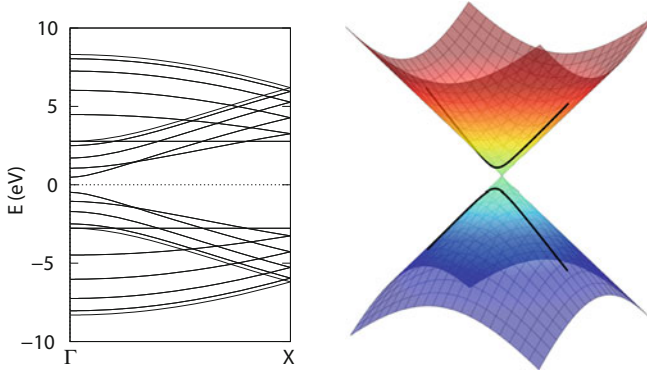


Fig. 2.9 The band structure of the achiral (10, 0) semiconducting CNT as calculated using the π/π^* tight-binding model under the zone-folding approximation. The *left panel* indicates the allowed subband closest to the K point of the graphene Brillouin zone

with a band gap opening at the Fermi energy

$$E_g = \frac{2\pi at_0}{\sqrt{3}|\mathbf{C}_h|}. \quad (2.20)$$

This is shown in the left panel of Fig. 2.8 where we plot the band structure of the semiconducting (10, 0) CNT; in the right panel we superimpose one of the lowest-energy CNT subband on the low-energy dispersion relation of graphene (Fig. 2.9). The size of the band gap is inversely proportional to the CNT diameter ($d = |\mathbf{C}_h|/\pi$) and is approximately 0.6 eV for CNTs with diameter of 1 nm [21, 22]. The effective mass of the charge carriers, given by the curvature at the band edges, can be derived to be

$$m^* = \frac{1}{\hbar} \left[\frac{\partial^2 E}{\partial k^2} \right]^{-1} = \frac{2\pi \hbar}{3|\mathbf{C}_h|v_F} \quad (2.21)$$

and therefore also depends on the inverse of the diameter.

The complex dependence of bandstructure character on the (n, m) indices in turn introduces a sensitive dependence on the tube diameter (Fig. 2.4), and CNTs with similar diameter but different (n, m) may have strikingly different electronic structures. A particular synthesis route will typically create CNTs with a range of diameters and therefore also a range of electronic characters. The ratio of metallic to semiconductor CNTs, which strongly affects the conductivity of a CNT network, is therefore not easy to control at synthesis.

2.3.3 Beyond the π/π^* Zone-Folding Model

The successes of the π/π^* tight-binding model and zone-folding approximation arise from the resulting analytic expression that effectively captures the electronic structure of a wide range of CNTs. Some deficiencies are notable, however.

Firstly, it is assumed that the p_z orbitals do not interact with the σ bonds. Whilst for a perfectly flat graphene sheet this is true by symmetry, the introduction of curvature can allow for coupling between the σ bonds and the π/π^* manifold. For narrow diameter CNTs (< 1 nm), the strong curvature allows mixing of the σ and π bands and the π/π^* model can fail to describe the electronic structure. Calculations derived from first principles (see Chap. 4) have shown that hybridization between the π^* and σ^* can lower the energy of low-lying conduction bands considerably [23] reducing, or even closing, the band gaps of small-diameter CNTs that the zone-folding approximation predicts to be semiconducting [24, 25]. Further, high curvature reduces the Fermi wave-vector compared to the result derived from the zone-folding approximations [26].

Curvature effects are less prominent in larger diameter CNTs and do not significantly change the electronic character predicted by the zone-folding model for large diameter semiconductor or armchair metallic CNTs. In zig-zag and chiral metallic CNTs, the curvature creates a small (~ 20 meV) band gap, however this can be ignored at ambient temperatures due to thermal excitation of the electronic occupancies [27].

A second implicit assumption within the graphene tight-binding model is symmetry between the two sheets of the Brillouin zone (2.15), resulting in a symmetry between the valence and conduction bands describing the electrons and holes. First-principles calculations show that the symmetry of the valence and conduction bands is indeed broken, as shown in Fig. 2.5. Whilst this effect can be corrected by extending the π/π^* model to include non-orthogonal overlap elements between the p_z orbitals [28], in the vicinity of the K points first-principles calculations still predict the linear-dispersion relations showing that these corrections are largely unnecessary for studying conduction at low-bias.

2.3.4 Electronic Structure of Carbon Nanotube Bundles

Where CNTs bundle together, their electronic structure can be modified by the interactions between the tubes. Whilst this interaction is weak, arising from van der Waals interactions, the low-energy excitations can be strongly modified due to the lowering of symmetry which can open band gaps in the low energy dispersion relations. In bundles of (10, 10) CNTs, it was shown theoretically that the tube-tube interaction induces a pseudogap of around 0.1 eV at the Fermi energy [29], a result that was confirmed experimentally using low-temperature scanning tunnelling spectroscopy [30]. Where the bundles retain the symmetry of the individual CNTs, for example

in bundles of symmetrically aligned (6, 6) CNTs, no pseudogap is opened [31]. Similarly, pseudogaps were also predicted for CNTs bundles containing a range of metallic chiralities, however the reduction in densities of states is much smaller in magnitude and occurs over a wider range of energies around the Fermi level [32]. Equivalent modifications to the band structures are calculated in multi-walled CNTs [33, 34].

At ambient temperatures, however, these modifications to the electronic band structures have little impact on the bundle conductance. Whilst the opening of the pseudogap reduces the density of states precisely at the Fermi energy, the redistribution of the state energies ensures that the average density of states in the vicinity of the Fermi level remains constant. A finite electronic temperature comparable to the magnitude of the pseudogap ensures that the number of states that contribute to conductance is unchanged by the symmetry breaking. Furthermore, ambient thermal energies are also sufficient to overcome the weak inter-tube interaction, which is of order 8 meV/atom [35], allowing the significant contribution of lower-symmetry, pseudogapless configurations to the ensemble-averaged electronic properties.

Therefore, the electronic structure of bundles of CNTs at ambient temperatures can be well approximated by the superposition of the electronic structures of individual CNTs, [32] which itself can be well described by the π/π^* tight-binding model. The advantage of this model lies with the simple analytic expression for the band structure and its ability to capture well the low energy excitations.

2.4 Summary

In this chapter we have introduced the basic electronic properties of carbon nanotubes. Using a simple tight-binding model, we have reviewed the electronic properties of CNTs and have shown that their electronic structure can be metallic or semiconducting in character depending on their structure and chirality. For metallic CNTs, the low energy dispersion relations were demonstrated to depend linearly on the electron momentum. We discussed how this result is modified by the use of more sophisticated calculations, however we concluded that these corrections do not strongly modify the result determined by the simple tight-binding model.

We have also discussed the conductive properties of CNT wires, made from fibres of many individual CNTs, and noted that the electrical performance of this material is considerably lower than expected based on the conductances of the individual constituent CNTs. One approach for improving the conductivity of CNT fibres is to develop an understanding of the theoretical mechanisms that inhibit conductance. In the next chapter, we introduce a theoretical formalism to study the conductances of CNTs.

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