Calculation of the band structure of a non-chiral semiconductor and metallic carbon nanotubes

S M Ridha Hussain¹, S I Kharitonov¹,² and V S Pavelyev¹,²

¹Samara National Research University, Moskovskoe Shosse 34, Samara, Russia, 443086
²Image Processing Systems Institute - Branch of the Federal Scientific Research Centre “Crystallography and Photonics” of Russian Academy of Sciences, Molodogvardeyskaya str. 151, Samara, Russia, 443001

e-mail: prognoz2007@gmail.com

Abstract. A new form of the linear augmented cylindrical wave method is proposed. For the construction of basis functions, the electron potential is taken to be spherically symmetric in atomic regions, constant in the intermediate region and cylindrically symmetric in the vacuum regions. The basis functions of the method, obtained from the solution of the Schrodinger equation in the corresponding domains, are sewn on the boundaries of the MT-spheres and the cylindrical surfaces of the tube, forming everywhere continuous and differentiable functions. In order to approve a method, the band structure of the non-chiral semiconductor and metallic single-wall carbon nanotubes was calculated.

1. Introduction
Carbon nanotubes were discovered by Iijima in 1991 as by-products of the synthesis of fullerenes [1]. Nanotubes demonstrate a whole range of the most unexpected physical properties that open up great possibilities for their application in engineering. Investigation of the electronic structure (band structure) of nanotubes makes it possible to determine the type of conductivity and optical properties, and, respectively, the band structure of semiconductor tubes determines the band gap and a number of other electrophysical properties.

To calculate the electronic structure of carbon nanotubes with allowance for translational symmetry, the linear augmented cylindrical wave (LACW) methods were developed by authors [1–3]. The LACW method is just a reformulation of the linear augmented plane wave theory, well known and one of the most accurate in the theory of the band structure of crystals, for cylindrical multi-atomic systems [4–6]. The main argument for using cylindrical waves is to account for the cylindrical geometry of the nanotubes in an explicit form that offers obvious advantages in terms of rapid algorithm convergence. However, all previous calculations of single-walled and double-walled carbon and non-carbon nanotubes by the LACW method were limited to non-chiral tubes \( (n,n) \) of the armchair type and \( (n,0) \) zigzag type with small atomic numbers per translational unit cell [1–3, 7–12]. Even for small-diameter chiral nanotubes, the number of atoms in the translational unit cell can be very large. For example, the translational cell of the chiral \( (10,10) \) nanotube comprises 40 atoms, whereas the translational cell of the chiral \( (10,9) \) tube of somewhat smaller diameter comprises 1084 atoms.

Produced test calculations (with varying parameters) confirm this assumption: the best result (in the sense of the equivalence of the nanotube and graphite valence bands, as well as the similarity of the calculated band structure with the results obtained using the tight-binding (TB) method [8, 9]) was
achieved with \( a - b = 2r_i \), that is with the above-indicated choice of the outer and inner radii of the nanotube.

2. Calculation method
To construct the basis functions of the LACW method and to solve the Schrödinger equation, the assumption that the electron potential has a so-called cylindrical muffin-tin (MT) shape is made. The MT approximation implies that each atom of the nanotube is surrounded by a sphere (MT-sphere), and the space is partitioned into three regions: region \( \Omega_s \), inside the muffin-tin sphere of radius \( r_i \) around the atom of the variety \( s \); the region \( \Omega_l \) outside the MT-sphere between the inner and outer cylindrical surfaces of the tube, which called the interstitial region; two vacuum regions \( \Omega_v \) outside the cylindrical surfaces of the tube (internal \( \Omega_i \) and external \( \Omega_o \)).

![Figure 1. Nanotube (5, 5) in a potential well limited by cylindrical potential barriers. (In calculations, atomic spheres are considered contiguous).](image)

Each of these regions is characterized by its own kind of one-electron potential. In the MT-spheres the potential is spherically symmetric; in the interstitial region the potential is constant; in vacuum regions the potential is cylindrically symmetric. Thus, the potential has the form:

\[
V(r) = V(|r - \tau|), \quad r \in \Omega_s,
\]

\[
V(r) = V(\rho), \quad r \in \Omega_l,
\]

\[
V(r) = V', \quad r \in \Omega_v,
\]

where \( \tau \) is the basis vector indicating the position of the atom in the unit cell. Note that the electron potential in the cylindrical MT approximation is used only for construction of basis functions. Having determined the system of basis functions, we can use the potential of a general form in constructing the matrix elements of Hamiltonian. Let us consider the form of the basis function in each of the three areas indicated above. Then, the construction of basis functions is completed, it is possible to use one-electron function included matrix elements of Hamiltonian. Let us consider the form of the basis function in each of the three regions indicated above.

3. Basis functions
In the interspherical region, the basis functions are the solutions of the Schrödinger equation for free movement of electrons. Inside the MT-spheres and in vacuum regions, by analogy with the linearized augmented plane-wave method (LAPW) \([5, 6]\), the basis function is taken as a linear combination of the Schrödinger equation solution and its energy derivative. The Schrödinger equation inside the MT-spheres and in the vacuum regions is solved for fixed values of the energy.
3.1. Interspherical region

In the interspherical region, where the potential is constant and is taken as the energy zero point, the basis function satisfies the Schrödinger equation for free space, which in the cylindrical coordinate system has the form:

\[-\left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(\rho, \phi, z) = E \Psi(\rho, \phi, z). \tag{2}\]

The general solution of this equation can be written as:

\[\Psi = \Psi_{\mu N}(\rho, \phi, z) = \varphi_\mu(z) \varphi_M(\rho) R_{MN}(\rho), \tag{3}\]

where \(\varphi_\mu(z)\) and \(\varphi_M(\rho)\) the functions describe free movement of an electron along the translational symmetry axis of the nanotube and free rotation about the axis of symmetry, respectively:

\[\varphi_\mu(z) = \frac{1}{\sqrt{\pi}} e^{ikzc}, \quad -\frac{\pi}{c} \leq k \leq \frac{\pi}{c}, \quad k_\mu = k + \frac{2\pi}{c} \mu, \quad \mu = 0, \pm 1, \ldots, \tag{4}\]

\[\varphi_M(\rho) = \frac{1}{\sqrt{2\pi}} e^{ik_M \rho} = 0, \pm 1, \ldots. \tag{5}\]

Here \(c\) is the lattice spacing along the translational symmetry axis; the wave vector \(k\) belongs to the first one-dimensional Brillouin zone.

The function \(R_{MN}(\rho)\) describes the radial movement of the free electron in the interspherical region, \(N\) is the radial quantum number. Substituting the expansion (3) into (2), taking into account (4) and (5), we obtain an equation for the function \(R_{MN}(\rho)\):

\[-\left(\frac{1}{\rho} \frac{d}{d \rho} \left( \rho \frac{d}{d \rho} \right) + \frac{M^2}{\rho^2} - \left( E - k_\mu^2 \right) \right) R_{MN}(\rho) = 0. \tag{6}\]

It can be reduced to the Bessel equation [7]. Any solution of the Bessel equation can be represented as a linear combination of Bessel functions of the first and second kinds:

\[R_{MN}(\rho) = c^{J}_{MN} J_M(k_{MN} \rho) + c^{Y}_{MN} Y_M(k_{MN} \rho), \tag{7}\]

Here the notation is introduced:

\[k_{MN} = \sqrt{E - k_\mu^2}. \tag{8}\]

We determine the value of \(k_{MN}\) (and thus the value of energy) and the coefficients \(c^{J}_{MN}\) and \(c^{Y}_{MN}\), equating \(R_{MN}(\rho)\) to zero at points \(a'\) and \(b'\) \((a' > a)\) and \(b' > b\), where \(a\) and \(b\) are the outer and inner radii of the nanotube, respectively:

\[c^{J}_{MN} J_M(k_{MN} b \cdot ) + c^{Y}_{MN} Y_M(k_{MN} b \cdot ) = 0, \tag{9}\]

\[c^{J}_{MN} J_M(k_{MN} a \cdot ) + c^{Y}_{MN} Y_M(k_{MN} a \cdot ) = 0.\]

From the conditions for the existence of nontrivial solutions of system (9) we obtain an equation for finding \(k_{MN}\):

\[J_M(k_{MN} b \cdot ) Y_M(k_{MN} a \cdot ) - J_M(k_{MN} a \cdot ) Y_M(k_{MN} b \cdot ) = 0, \tag{10}\]

which has a numerical solution. Next, we define the coefficients \(c^{J}_{MN}\) and \(c^{Y}_{MN}\). Finally, the basic function in the interspherical region takes the form:

\[\Psi_1(r) = -\frac{1}{2\pi c} [c^{J}_{MN} J_M(k_{MN} \rho) + c^{Y}_{MN} Y_M(k_{MN} \rho)] e^{i(k_{MN} \rho + \phi)}. \tag{11}\]

3.2. Vacuum regions

In the inner and outer vacuum regions, where the electron potential has cylindrical symmetry, the Schrödinger equation has the form:
Due to the cylindrical symmetry of the electron potential, the solution of this equation has the form:
\[ \Psi = \Psi_{\mu l}(\rho, \varphi, z) = \varphi_{\mu}(z) \varphi_{l}(\varphi) R_{\mu l}(\rho), \]
(13)

The functions \( \varphi_{\mu}(z) \) and \( \varphi_{l}(\varphi) \) are determined by the expressions (4) and (5), respectively. And for the function \( R_{\mu l}(\rho) \) describing the radial movement of the electron in the vacuum region, using the substitution of (13), (4) and (5) into (12), we obtain the equation:
\[ \left( -\frac{1}{\rho d\rho} \left( \rho \frac{d}{d\rho} \right) + \frac{M^2}{\rho^2} + k_{\mu}^2 + V(\rho) \right) \times R_{\mu l}(\rho) = E R_{\mu l}(\rho). \]
(14)

Equation (14) is numerically integrated for a fixed value of the energy, which is the parameter of calculation.

When equation (14) is differentiated with respect to the energy, we obtain the corresponding equation for the energy derivative:
\[ \left( -\frac{1}{\rho d\rho} \left( \rho \frac{d}{d\rho} \right) + \frac{M^2}{\rho^2} + k_{\mu}^2 - E_{E} + V(\rho) \right) \times R_{\mu E}(\rho) = E_{E} R_{\mu E}(\rho). \]
(15)

The basis function for the vacuum regions can be written in a form similar to the linearized augmented plane-wave method (LAPW) [6]:
\[ \Psi_{i}(r) = -\frac{1}{\sqrt{2\pi c}} \left[ A_{\mu MN} R_{\mu MN}(E_{E}, \rho) + B_{\mu MN} R_{\mu MN}^{*}(E_{E}, \rho) e^{i(k_{E}z+\lambda(\varphi))} \right]. \]
(16)

3.3. Regions of MT-spheres

Inside the MT-sphere of the s-th atom the electron potential is spherically symmetric and the basis function is written in the form similar to the linearized augmented plane-wave method (LAPW) [5]:
\[ \Psi_{i}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left[ A_{LMN} R_{LMN}(E_{i}, r) + B_{LMN} R_{LMN}^{*}(E_{i}, r) \right] \times Y_{LMN}(\theta, \varphi), \]
(17)

where \( Y_{LMN}(\theta, \varphi) \) is the spherical harmonic, \( N_{LMN} \) is the normalization factor, \( P_{LMN}(x) \) is the associated Legendre function, \( R_{LMN}(E_{i}, r) \) is the solution of the radial Schrödinger equation inside the MT-sphere of the s-th atom for energy \( E_{i} \), a \( \hat{R}_{LMN}(E_{i}, r) \) is its energy derivative.

4. Sewing of basic functions

4.1. The surface of MT-spheres

Due to the representation of the basis function for the interspherical region (11) in the local spherical coordinate system and equating its value and the value of the normal derivative on the surface of the MT-sphere to the corresponding values for the basis function inside the MT-sphere (17), we obtain a system of linear algebraic equations for finding the coefficients \( A_{LMN} \) and \( B_{LMN}^{*} \):
\[ A_{LMN} R_{LMN}(E_{i}, r_{1}) + B_{LMN}^{*} R_{LMN}^{*}(E_{i}, r_{2}) = D_{LMN, MN} \times I_{i}^{1}(\mu MN, lms), \]
\[ A_{LMN}^{*} \frac{\partial}{\partial r} R_{LMN}(E_{i}, r_{1}) + B_{LMN}^{*} \frac{\partial}{\partial r} R_{LMN}^{*}(E_{i}, r_{2}) = D_{LMN, MN} \times I_{i}^{2}(\mu MN, lms). \]

The expressions for \( D_{LMN, MN} \), \( I_{i}^{1}(\mu MN, lms) \), \( I_{i}^{2}(\mu MN, lms) \) are given in the paper [6]. The main determinant of this system [6]:
\[ \Delta = R_{i}(E_{i}, r_{1}) \frac{\partial}{\partial r} \hat{R}_{i}(E_{i}, r_{2}) - \hat{R}_{i}(E_{i}, r_{1}) \frac{\partial}{\partial r} \hat{R}_{i}(E_{i}, r_{2}) = -\frac{1}{r_{i}^{2}}. \]

Then:
5. Inner and outer cylindrical surfaces of the nanotube

To determine the coefficients in expression (16) for the basis function of the internal and external vacuum regions, it is necessary to equate the basis functions and their radial derivatives in the interspherical region (formula (11)) and in the corresponding vacuum region (formula (16)) on the surface of the nanotube. We obtain a system of algebraic equations:

\[
A_{m}^{(E, \rho_{E})} + B_{m}^{(E, \rho_{E})} = c_{MN}^{J_{M}}(k_{MN} \rho_{E}) + c_{MN}^{Y_{M}}(k_{MN} \rho_{E}),
\]

\[
A_{m}^{(E, \rho_{E})} = \frac{\partial}{\partial \rho} R_{m}^{(E, \rho_{E})} = k_{MN}(c_{MN}^{J_{M}}(k_{MN} \rho_{E}) + c_{MN}^{Y_{M}}(k_{MN} \rho_{E})).
\]

Here the prime mark of the Bessel function means differentiation with respect to the whole argument \( k_{MN} \rho \). Solving the system, we get:

\[A_{m}^{(E, \rho_{E})} = \frac{1}{\Delta^{(E)}} \left\{ \frac{\partial}{\partial \rho} R_{m}^{(E, \rho_{E})} \times \left[ c_{MN}^{J_{M}}(k_{MN} \rho_{E}) + c_{MN}^{Y_{M}}(k_{MN} \rho_{E}) \right] - R_{m}^{(E, \rho_{E})} \right\},\]

\[B_{m}^{(E, \rho_{E})} = \frac{1}{\Delta^{(E)}} \left\{ R_{m}^{(E, \rho_{E})} \times \left[ c_{MN}^{J_{M}}(k_{MN} \rho_{E}) + c_{MN}^{Y_{M}}(k_{MN} \rho_{E}) \right] - \frac{\partial}{\partial \rho} R_{m}^{(E, \rho_{E})} \left[ c_{MN}^{J_{M}}(k_{MN} \rho_{E}) + c_{MN}^{Y_{M}}(k_{MN} \rho_{E}) \right] \right\}.\]

Here \( \Delta^{(E)} \) is the principal determinant of the system. On the outer surface \( (v = 0) \): \( \rho_{E}^{v} = a, \sqrt{\nu} = 1/a \).

On the inner surface \( (v = i) \): \( \rho_{E}^{v} = b, \sqrt{\nu} = -1/b \).

6. The secular equation

The finite expressions for the overlap integrals \( \langle \mu_{1} M_{1} N_{1} | \mu_{2} M_{2} N_{2} \rangle \) and the matrix elements of Hamiltonian \( \langle \mu_{1} M_{1} N_{1} | H | \mu_{2} M_{2} N_{2} \rangle \) are cumbersome and are not given here. It is worth noting that the overlap integrals and the matrix elements of Hamiltonian do not depend on energy, which makes it possible to significantly reduce the calculation time of the eigenvalues in the secular equation:

\[
\det \left[ \langle \mu_{1} M_{1} N_{1} | H | \mu_{2} M_{2} N_{2} \rangle - E \langle \mu_{1} M_{1} N_{1} | \mu_{2} M_{2} N_{2} \rangle \right] = 0.
\]

7. Results of calculations of the energy spectrum of nanotubes

The following parameters were used to calculate the band structure of carbon nanotubes: the distance between nanotube superlattices is 1.42 Å (as in graphene), the radius of the MT-sphere of the carbon atoms is \( r = 0.71 \) Å. The region inside the MT-spheres contains information about the atomic potential and, therefore, the choice of the maximum possible radius of MT-spheres, which corresponds to the tangency of the MT-spheres of neighboring atoms, is natural. The inner and outer radii of a nanotube (magnitudes and) should be chosen in such a way that the "interstitial" space is minimal. It corresponds to a zero gap between the surface of the MT-sphere and the walls of the nanotube, i.e. the distance from the nucleus of the atom to the inner and outer surfaces of the nanotube is equal to the radius of the MT-sphere. In the "interstitial" space outside the MT-spheres, the potential is assumed to be constant, while in the vacuum region it is taken to depend on the distance from the axis of the nanotube (i.e. it is determined more strictly), so it seems reasonable to minimize the constant potential region.
Produced test calculations (with varying parameters) confirm this assumption: the best result (in the sense of the equivalence of the nanotube and graphite valence bands, as well as the similarity of the calculated band structure with the results obtained using the tight-binding (TB) method [8, 9]) was achieved with $a - b = 2r$, that is with the above-indicated choice of the outer and inner radii of the nanotube.

![Figure 2. The band structure of the (6, 6) carbon armchair nanotubes.](image1)

![Figure 3. The band structure of the (12, 0) carbon zigzag nanotubes.](image2)

![Figure 4. The band structure of the (16, 0) carbon zigzag nanotubes.](image3)

The parameters $a'$ and $b'$ appearing in the system (9) were taken equal to: $a' = a + r$, $b' = b - r$, (18), where $r$ is the radius of the MT-sphere. The result of the calculation varies insignificantly with small changes in the parameters $a'$ and $b'$ (for a fixed number of basis functions) near the values of (18). This choice of parameters $a'$ and $b'$ is consistent with the LAPW method. In [10] they are chosen at a distance from the surface of the film equal to the unit radius of the MT-sphere. In [11] it is pointed out that the result of the band structure calculation changes insignificantly with distance values in the range from 0.5 to 1.5 of the radius of the MT-sphere. The energy parameters included in (17) were chosen near the center of the energy band, which corresponds to a given orbital quantum number. The energy of the regions in (16) was taken equal to 0.75 of the potential at infinity (if the potential in the interspherical region is taken as the energy origin). In order to validate the method we have been calculated the band structure of non-chiral single-walled carbon nanotubes of various types.

The Figure 2 shows the band structure of the (6, 6) carbon armchair nanotubes. The figure 3 shows the band structure of the (12, 0) carbon zigzag nanotubes. The figure 4 shows the band structure of the (16, 0) carbon zigzag nanotubes. The dashed line denotes the upper boundary of the valence band $E_v$.
in semiconductor structures or the Fermi level of EF in metallic structures. The results coincide with high accuracy with the results in [14]. In [15] the alternative approach to band structure calculation has been considered.

8. Conclusion
In the future, the results of calculations of the band structure can be used to calculate the electrical characteristics of carbon nanostructures and design various instruments based on them. In future we are planning to realize calculation of CNT band structure in the presence of electrical field [16]. It will give us opportunity to apply considered calculation methods for CNT sensor analysis.

9. References
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