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An Alternative Approach to the Problem of CNT Electron Energy Band Structure

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1. Introduction

We intended to discuss in this chapter, TBM (tight binding method), APW (augmented-plane-wave), OPW (orthogonalized -plane-wave) methods and corresponding theoretical concepts. In particulars, we pay a great attention to the theory of CNT (Carbon Nano Tube), but discuss in less details some conventional band structure models, unless nearly electron approximation (NFA), TBM, APW and OPW models have been used for determining the electron energy band structure of solids. In fact, this chapter is partly based on the many – electron description of nano transistor – CNTFET (carbon nano tube field effect transistor), which was done with a number of MSC and PhD students for a number of years at university of Mazandaran in Iran (See our published papers [1-7] for more details). We hope this chapter can complete the present book and be of interest for researchers whom work in the nano technology and for beginners. Some part of the material may be used in lection course for students.

There are actually two different approaches for studying the band spectrum of CNT. In the first view, some researchers believe that carbon atoms are as isolated atoms and consider the CNT potential of neighbor's atoms as a perturbation and neglect the intra atomic potential. The second approach is about the density functional theory (DFT), in that the exact exchange energy (EXX) instead of the exchange energy given by the local – density approximation (LDA). The EXX energy, which corresponds to the Fock term in the Hartree-Fock scheme, is treated as a function of electron densities via the eigenfunctions of the Kohn-Sham KS equations [8]. This approach cannot satisfy the electron behavior in CNT due to its self-interaction-free in its construction.

Indeed, this chapter discusses about electronic band energy. It is an energy interval in which electronic states exist in the CNT. This energy structure has been usually obtained by solving the Schrödinger equation for electrons in the CNT. As usual, the electronic wave functions depend on both the wave vector and the spatial coordinates. The eigenvalues and eigenvectors have been determined by Fourier – transforming the differential equation into an algebraic equation. The solution of this equation can be used for some special cases with some reasonable approximation, such as NFE and TB methods. However, these approaches cannot be used for samples with critical dimensions of less than 100 nm due to overlap integrals in nano scale samples.

The reason is that carbon atoms are not in fact stationary, but continually undergo vibrations (like thermal vibrations of ions in a crystal) about their positions, in where, the

overlapping between carbon atom functions is of importance, in particularly while the nearest neighbor atoms come close together. In principle a many – electron problem, for the full Hamiltonian of the CNT should be taken into account. It means Hamiltonian should contain not only the one – electron potentials describing the interactions of the electrons with the massive carbon atomic nuclei, but also pair potentials describing the electron – electron interactions in CNTs. But this idea should be included both the exchange and correlation effects into the interaction phenomena due to nearly free electrons. The Schrödinger equation for a many-electron system can be then reduced to the effective one-particle problem for an electron in a self-consistent field.

We therefore need to develop a method of band structure spectrum; because in the conventional method of solution, the unknown functions of Schrödinger equation has usually been expanded in some bases set. The search for the unknown expansion coefficients will be necessarily reduced to the solution of a secular equation which is usually of large dimension and provide high speed of expansion convergence, in order to doing less effort for finding band structure spectrum.

As stated above, in second view, a large majority of the electronic structures and band plots are calculated using DFT [9], which is not a model but rather a theory. It involves the electron-electron many-body problem via the introduction of an exchange-correlation term in the functional of the electronic density. Although, the band shape is typically well reproduced by DFT, there are also systematic errors in DFT bands due to shrinking the CNT size.

In addition, some researchers [10 and references therein] believe OPW can solve this problem, but some critical technological barriers and fundamental limitations to size reduction are threatening the use of OPW method for calculation of band energy. It means that there are some difficulties with current crystalline potentials which reside quite simply in considering, for example, electrons of carbon atoms as independent particles.

Furthermore, the OPW expansion converges poorly for a CNT even when modified by the addition of an atomic like function to the basis set. The APW expansion also converges rapidly, but requires the crystal potential to be approximated by an unphysical spherical muffin-tin potential. However, in many of above methods you need to an ingenious the choice of CNT potential, which is not so easy due to the enormously complicating effects of the interactions between atoms (and electrons). Henceforth, a more accurate calculation of the electronic properties of a CNT should start with modifying of above approaches, in particularly, NFA, TB and OPW methods. We should thus develop a modified APW/OPW expansion and compare its convergence with the other methods.

An alternative approach to the problem of CNT band energy and of constructing exchange – correlation potential uses the calculation of the total energy. However, after describing the conventional methods and/or models, we will see that these models cannot sufficiently describe the electron behaviors in CNT. A new method is presented for finding the band structure of a lattice of potentials which individually are spherically symmetric, but with overlap's functions. The method does not necessitate a division of space into non-overlapping spherical regions. It exploits the properties of the complete set of functions associated with the individual potentials. An expansion of the wave function of the crystal in this set yields a relatively simple determinant secular equation. The present method can be employed to introduce a matrix of CNT band energy.

2. Summary of some band structure models

Several efficient methods have been developed in last four decades: Korringa, Kohn and Rostocker (KKR) model [11], indicates the initials of Korringa (in 1947), Kohn, and Rostoker (in 1954), DFT, Green function methods [12] and *ab intitio* approximation [13] have been used for studying the electronic band structure of CNT, because they lend themselves very well in reproducing the band shape. In this area, we naturally prefer to consider the simplest form of the approximation centers non-overlapping spheres (referred to as muffin tins) on the atomic positions. In one hand, within these regions, the potential experienced by an electron is approximated to be spherically symmetric about the given carbon atoms. In the remaining interstitial region, the potential is approximated as a constant. Continuity of the potential between the atom-centered spheres and interstitial region is enforced. On the other hand, The KKR method is one of the popular methods of electronic structure calculation and is also called Green's function method. Therefore, KKR is actually referred to multiple scattering theory of solving the Schrödinger equation, in where the problem is broken up into two parts: solving the scattering problem of a single potential in free space and then solving the multiple scattering problems by demanding that the incident wave to each scattering centre should be the sum of the outgoing waves from all other scattering centers. The scheme has met great success as a Green function method, within DFT. To calculate the bands including electron-electron interaction many-body effects, one can resort to so-called Green's function methods.

Indeed, knowledge of the Green's function of a system provides both ground (the total energy) and also excited state observables of the system. The poles of the Green's function are the quasiparticle energies, the bands of a solid. Sometimes spurious modes appear. Large problems scaled as $O(n^3)$, with the number of the plane waves (n) used in the problem. This is both time consuming and complex in memory requirements. Its applications range from the full potential *ab initio* treatment of bulk, surfaces, interfaces and layered systems with O(N) scaling to the embedding of impurities and clusters in bulk and on surfaces. In this way, after the single particle Hamiltonian (H) is generated either by empirical pseudo potential method or the charge patching method, it needs to be solved in an order N scaling [14].

As we know, the band plot can obviously show the excitation energies of electrons injected or removed from the system. It can say nothing about energies of a fictive non-interacting system, the Kohn-Sham system, which has no physical interpretation at all. The Kohn-Sham electronic structure must not be confused with the real, quasi particle electronic structure of a system, and there is no Koopman's theorem holding for Kohn-Sham energies, as there is for Hartree-Fock energies, which can be truly considered as an approximation for quasi particle energies. Hence, in principle, DFT is not a band theory, i.e., not a theory suitable for calculating bands and band-plots.

The self-energy can also in principle be introduced variationally [14]. A variational derivation of the self-energies for the electron-electron and electron-phonon interactions are presented in [36].Due to the presence of the strong Coulomb interaction between electrons in the CNT atoms, the differential equations for the single- electron Green functions contain the multi-electron Green functions and all these coupled equations form an infinite system of differential equations for an infinite number of Green functions. In order to find some approximate finite closed system of equations one can either to apply the perturbation theory and retain only some appropriate chain of ladder diagrams or to assume some

approximation to decouple the infinite system of equations and obtain a finite closed system. For CNT, the self-energy is a very complex quantity and usually approximations are needed to solve the problem.

In addition to DFT and KKR methods, one of the other popular methods which has been usually used to all band structure calculations and studies, is NFA model. It is a method of approximating the energy levels of electrons in a CNT by considering the potential energy resulting from carbon atomic nuclei and from other electrons in the CNT as a perturbation on free electron states. Although the NFA is able to describe many properties of electron band structures, it can only predict the same number of electrons in each unit cell, which conflict with this result as for materials require inclusion of detailed electron-electron interactions (treated only as an averaged effect on the crystal potential in band theory) known as Mott insulators [15]. The Hubbard model is an approximate theory that can include these interactions and contains a large number of closely spaced molecular orbitals, which appear as a band.

Anyway, we cannot here explain all band structure's model, but they are based on some elementary theory as reflected in Bloch, NFA or NFE and TB idea, which well models useful for illustration of band formation need these idea. The main is that each model describes some types of solids very well and others poorly. The NFE model works well for metals, but poorly for non-metals. The NFE model works particularly well in materials like metals where distances between neighboring atoms are small. In such materials the overlap of atomic orbitals and potentials on neighboring atoms are relatively large. In that case the wave function of the electron can be approximated by a modified plane wave. The TB model is extremely accurate for ionic insulators, such as metal halide salts (e.g. NaCl), but cannot be used for free electrons in a solid, e.g. CNT.

The main difficulty with current graphite potentials resides quite simply in considering electrons of carbon atoms as independent particles. The reason is due to neglecting the wave function's overlapping, i.e., in the independent electron approximation the electron – electron interactions are just represented by an effective one – electron potential.

If we pay somewhat closer attention to the form of potential, recognizing that it will be made up of a sum of atomic potentials centered at carbon atoms, then we can draw some further conclusions that are important in studying the electronic structure of graphite as well as graphene structures. Suppose that the basis consists of identical atoms at positions d_j. Then the periodic potential $u_{nk}(r)$ will have the form

$$u_{nk}(\mathrm{r}) = \sum_{\mathrm{R}} \sum_{\mathrm{j}} \phi(r - R - d_j) \tag{1}$$

Where Φ(k) is the Fourier transform of the atomic potential,

$$\phi(\mathrm{k}) = \int \mathrm{e}^{-\mathrm{ik.\,R}}\ \phi(r)\ \mathrm{dr} \tag{2}$$

One can see that it has the form of a traveling plane wave, as represented by the factor $e^{\mathrm{ik.r}}$, which implies that the electron propagates through the crystal like a free particle. The effect of the function $u_{\mathrm{k}}(\mathbf{r})$ is to modulate this wave so that the amplitude oscillates periodically from one cell to the next. However, it cannot affect the basic character of the state function, which is that of a traveling wave. But the electron in CNT is not completely free. Since electrons in CNT can interact with the other of CNT atom's electrons, the special character of

the periodic function u_k will be varied. Moreover, Ψ_{nk} may be delocalized throughout the CNT atoms and not localized around any particular atom, meaning it may be as NFE wave functions (As an example graphene structure in figure 1. A graphene structure has been considered for determining of CNT band structure. It only includes four nearest neighbors and can be expanded to the other neighbors as well.).

To these notifications, researchers [16 and references therein] have considered some special form of crystalline potentials in calculating of the electronic band energy of the CNT . They have tried to construct Bloch waves from appropriately defined functions (Known as Wannier functions) localized at each lattice site and used **K.P** approximation method. In this view the dispersion around the external points of an energy band can be found, but within these models, the spatial derivatives in the Schrödinger equation of the CNT, are carried out only for the plane wave component of the Bloch function, given by [2];

$$\{\frac{|p|^2}{2m}+\frac{\hbar\, k.p}{m} + \frac{\hbar\,|k|^2}{2m} + V(r)\}\, u_{n,k}(r) = E_n(k)\, u_{n,k}(r) \tag{3}$$

Here, n denotes the band index, V and E_n are lattice potential and eigen state, respectively. For k = 0, it simplifies significantly, and an approximate solution can be found for all band involved. A non – vanishing but small wave vector can then be treated as a perturbation. The term $\propto k^2$ produces an energy shift that depends on k, but does not couple the bands. The term containing **k.p**, however, must be treated with degenerate perturbation theory.

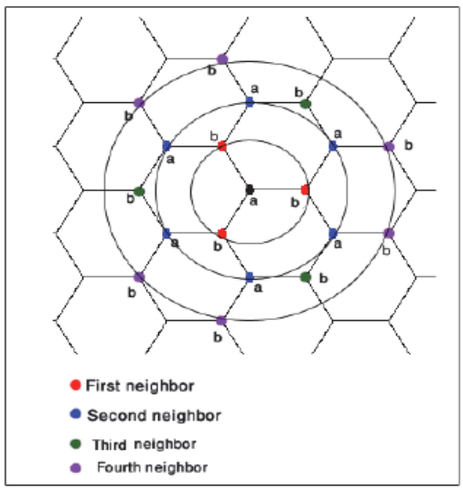

Fig. 1. Graphene structure. There are two different carbon shape atoms in the graphene sheet, where each 'a' atom has 3 'b' atom as the first neighbor's atoms, 6 'a' atom in the second neighborhood and 3 'b' atom as the third neighbor atoms and finally 6 'b' atom in its 4'th neighbors.

However, these wave functions represent a type of plane wave throughout space – a graphene as well as CNT crystal actually has infinite size based on the definition of a lattice (Note: the wave function must be normalized on a finite region of space with volume CNT that usually comes from periodic boundary conditions over the CNT circumference, so that with the definition of;

$$\phi_{nk}(\mathrm{r}) = \frac{\mathrm{e}^{\mathrm{ik.\,R}}}{\sqrt{V_{CNT}}}\,\mathrm{u}_{nk}(r) \tag{4}$$

And explicitly demonstrate the normalization for u_{nk} (r). As we know, NFE method starts from a free electron gas in a CNT and treats a weak periodic crystal potential within perturbation theory. There is also a different approach TBM, which constructs the electronic eigenstates from those of the individual atoms that form the CNT, which belongs in the independent-electrons framework. Within TB picture, the energy bands and the band gaps are reminders of the discrete atoms. Contrary to the free-electron picture, TB model describes the electronic states starting from the limit of isolated-atom orbitals. It is based on the assumption that the atomic orbitals belonging to an energy eigenvalue are good starting point for constructing Bloch waves. The CNT wave function in this view is usually expanded in the Bloch functions. But there are some assumptions: the energy level is non degenerate and there is no other energy level nearly. In that case, it yields to an approximation of the Bloch waves that emerges from the atomic wave functions.
A more accurate approach using this idea employs Wannier functions, defined by [20]. The Wannier functions are localized near atomic sites, like atomic orbitals, but being defined in terms of Bloch functions they are accurately related to solutions based upon the CNT potential. Wannier functions on different atomic sites are orthogonal. The Wannier functions can be used to form the Schrödinger solution for the *n*-th energy band . The width of the energy bands is determined by the overlap of atomic wave functions at neighbor lattice sites and decreases rapidly for inner shells. As a rule, the bands, which originate from different levels, overlap considerably. This simple model gives good quantitative results for bands derived from strongly localized atomic orbitals, which decay to essentially zero on a radius much smaller than the next neighbor half-distance in the solid.
The size of this matrix eigenvalue problem is clearly as large as the number of eigenstates of the atomic problem, i.e. infinite. It is therefore necessary to do some approximation. In particular, one could hope that all the off-diagonal matrix elements of the matrices could be neglected for some given level. This cannot work for atomic degenerate levels. Due to the exponential decay of the atomic wave functions at large distance, both the overlap integrals and the energy integrals become exponentially small for large distance **R** between the centers of the atoms. It therefore makes sense to ignore all the integrals outside some $\mathbf{R}_{max}$, which would bring in only negligible corrections to the band structure. One may obtain a band structure depending on a minimal number of parameters by making further rather radical approximations [20].

3. CNT band structure

According to the definition of SWCNT (single walled carbon nano tube), the energy bands of a SWCNT consist of a set of one-dimensional energy dispersion relations which are cross sections of those of graphene. When graphene sheet is rolled to make a CNT, $K_\perp$ is rolled too. So by using periodic boundary conditions in the circumference direction denoted by the chiral vector C_h, the wave vector associated with the C_h direction becomes quantized, while the wave vector associated with the direction of the translational vector T (or along the nanotube axis) remains continuous for a nanotube of infinite length. Since N $K_\perp$ corresponds to a reciprocal lattice vector, two wave vectors which differ by N $K_\perp$ are equivalent. In this view, the wave vector of CNT is a continuum component along tube axis and a discrete value of $K_\perp$, as found before [1,2] and shown in figures 2, 3 (for details see ref. [2]).

$$K_{\nu}^{CNT} = (k\frac{K_{II}}{|K_{II}|} + \nu K_{\perp}),$$
$$\nu = 0, ..., N\text{-}1. \quad , \quad k = -\frac{\pi}{|T|}, ..., \frac{\pi}{|T|} \tag{5}$$

Therefore, the band structure of CNT can be determined via;

$$E = \frac{\pm\beta|f(K)|}{1 \pm s|f(K)|} \tag{6}$$

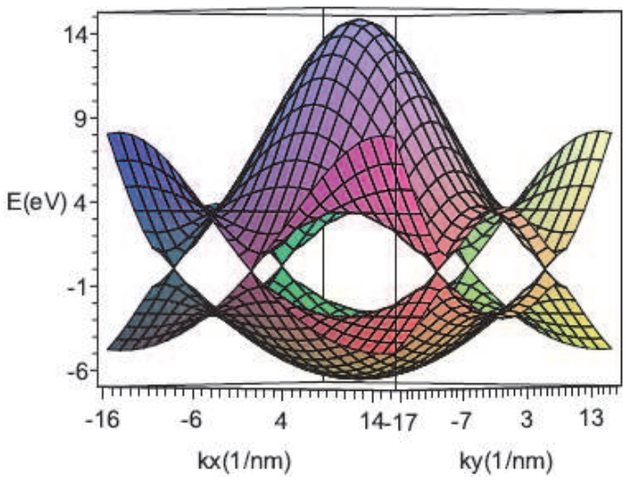

Fig. 2. Graphene band structure.

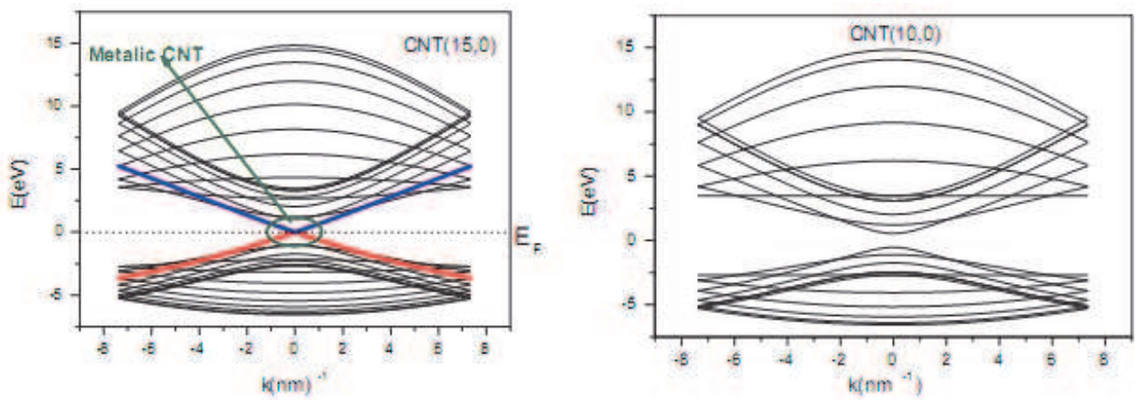

Fig. 3. Electronic band structure of some CNTs based on TB model. The banding energy of π orbital is equal to -3.03 eV and its overlap matrix is equal to 0.129. This figure clearly show that CNT (15,0) is a metallic CNT. We will drive an important relation between the geometry of CNT and its conduction. There is an important note. There are (N/2) + 1 degenerate levels in Zig-Zag CNT (n, 0).

Furthermore, density of State (DOS) of a one dimensional lattice with a lattice vector T and for one level is given by [2]

$$g_i(\varepsilon) = \frac{|T|}{\pi} \cdot \frac{1}{\left|\frac{\partial E_i}{\partial k}\right|_{E_i=\varepsilon}} \tag{7}$$

$$\text{DOS}(\varepsilon) = \sum_i g_i(\varepsilon) \tag{8}$$

Figure 4 Shows DOS of some CNT's. As we see in this figure semiconducting Zig-Zag CNT's have not any density of state at the Fermi level but armchair CNT's have a little density of state at Fermi level. If we focused to the armchair CNTs at around Fermi level, we find that the DOS has not treat as a constant value and treat as a parabola curvature.

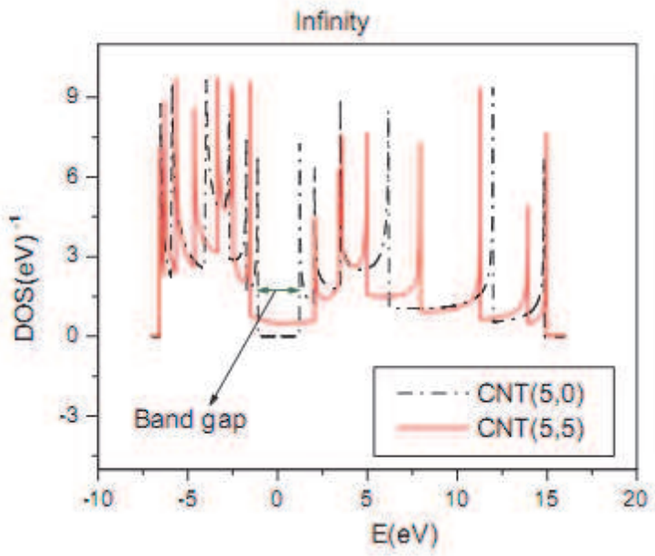

Fig. 4. This figure compares density of state of a Zig-Zag CNT via as an armchair CNT. As you see the Zig-Zag CNT has not any DOS near the Fermi level.

4. Augmented Plane Wave (APW) method

Slater introduced the APW method in 1937. Shortly after that researchers have used it for determining the electronic band structure of the rocksalt lattice structure. Although APW method is a sound one for calculating the band structure in metals, it has a great deal in the past few years. In this method the influence of potentials from non – nearest neighbors is taken into account.

As one can see in a schematic view in figure 5, the effective crystal potential is constant in most of the open spaces between the cores. Therefore, we can begin by assuming such a potential, which is referred to as the muffin-tin potential (because the potential is constant there). The potential is that of a free ion at the core, and a plane wave outside the core. Inside the core the function is atom-like, and is found by solving the appropriate free-atom Schrödinger equation. Also, the atomic function is chosen such that it joins continuously to the plane wave at the surface of the sphere forming the core; this is the boundary condition. The wave function does not have the Bloch form, but this can be remedied by forming the linear combination.

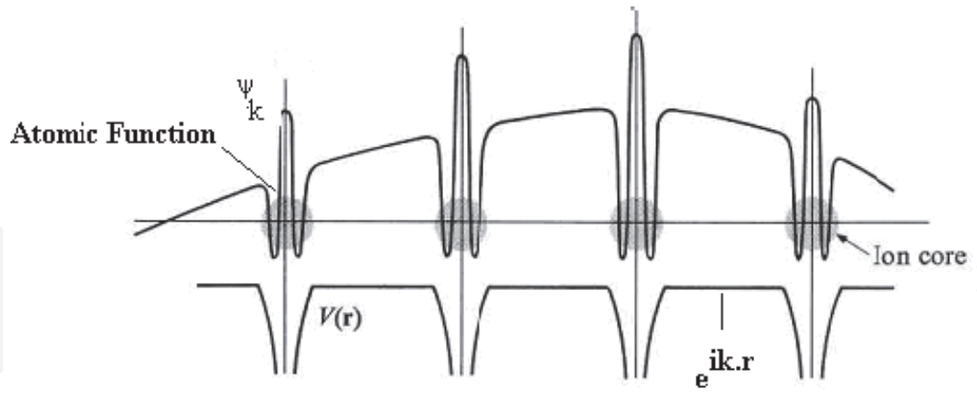

Fig. 5. The potential and wave function in the APW method.

From the point of APW method view, the overlap of the wave functions centered, on the six contact sites cannot be neglected, indicating that the atomic levels should be essentially altered in a CNT. We thus assume that the bound levels of the atomic Hamiltonian are not well localized, meaning the wave function is not small when **r** (like the core radius) exceeds a distance of the order of the lattice constant.

Therefore, we have to consider a many body system. The Schrödinger equation for a many-electron system can be reduced to the effective one-particle problem for an electron in a self-consistent field. Thus:

$$(-\frac{\nabla^2}{2m} + U(r))\ \psi_k(r) = E_k\psi_k(r) \tag{9}$$

where U(r) is the crystal self-consistent potential, and ψ_k and E_k are the wave function and the eigenvalue of the electron energy in k-state, correspondingly.

One of the main consequences of basis function over completeness is their linear dependence. This means

$$\sum_{G=0}^{G_m} |TPW_{k+G}\rangle\, C_G \rightarrow 0 \tag{10}$$

If $|G_m| \rightarrow 0$, C_G will indicate the numerical coefficients. Moreover, if $C_G \neq 0$, the transformed plane wave (OPW, APW) is denoted by the symbol $|TPW_{k+G}>$, the wave vector k belongs to the first Brillouin zone, and G are reciprocal lattice vectors. In the method of linearized augmented plane waves (LAPW) the linear dependence of the basis set $|APW_{k+G}>$ is manifested for $R_0\, G_{max} \geq 9$, which corresponds to accounting for 70-80 basis functions in APW, where R_0 is a muffin tin sphere radius. The OPW linear dependence begins to be manifested if the number of basis functions is more than 100 in (10) .

Although both APW and OPW, as two modern methods of band calculations, use combinations of atomic functions and plane waves, they cannot yet yield to exact results. In fact in the APW method, the wavefunction in general has discontinuous derivatives on the boundary between the interstitial and atomic regions. It means that we have to consider variational method in stead of Schrödinger equation. In this method, the augmenting

function corresponds to the exact muffin-tin potential eigenstates of eigenenergy. Because of this energy dependence of the augmenting function the eigenvalue problem will be non-linear in energy and has to be solved iteratively. This is, however, computationally very costly.
In addition, any eigenstate of a different eigenenergy will be poorly described without adapting. Hence, we need to linearized versions of the APW method with modifying the basis functions which gain extra flexibility to cover a larger energy region around their linearization energy. In this view, the linear combinations of energy-independent APW as a trial function and muffin-tin orbitals are inserted in the one-electron Hamiltonian. Then the secular equations are therefore eigenvalue equations, linear in energy in that the energy bands depend on the potential in the spheres through potential parameters which describe the energy dependence of the logarithmic derivatives. Keep in mind that the energy-independent APW inside the sphere is linear combination of an exact solution, which matches continuously and differentiable onto the plane-wave part in the interstitial region.

5. Orthogonalized Plane Waves (OPW) method

OPW method, as a simplified version of the pseudo potential method [17], has been used for the calculation of the electronic band structure of almost all types of solids with neglecting nonlocal effects. It has been especially determining the band structure of materials with covalent binding where the potential cannot be approximated by the conventional muffintin construction. Indeed, OPW method is rather practical and time-saving from the computational point of view since it leads to an eigenvalue problem involving matrix elements which do not depend on the eigenvalues, as in other methods of band theory. In contrast to above methods, in OPW method, the eigensolutions can be found easily by conventional methods of linear algebra . However, sometimes it cannot be used for calculating of nano scale materials due to the structure of the secular problem arising in the OPW formalism which can be related to a Born-series expansion, and it is known in scattering theory that resonances cannot be appropriately accounted for in any order of such an expansion.
Two main approaches based on expansion have been used: (i) basis set and (ii) trial wave function. Pseudo potential methods or OPW method use plane waves or modified plane waves as the basis set. The TBM are based on the second concept. There are also approaches which combine both delocalized and localized functions. In this approach the atomic-like functions are squeezed by an additional attractive potential. The extention of the basis functions is tuned by a parameter that can be found self-consistently [49]. The problem of APW and OPW methods for a CNT structure is an abundance of multi- center integrals, which must be performed to arrive at a reasonable accuracy of band structure calculations due to existence of a great number of neighbours within a given distance. To avoid these difficulties, we have tried to introduce an alternative method (see next section).
In our method we consider a lot of plane waves in the basis to decrease the spatial extent of localized valence orbitals in CNT. We could take a method far beyond usual pseudo potentials and improve our plane-wave basis set. The results show a good converged Bloch function for both valence electrons and excited states using a relatively small number of plane waves.
Two separated core orbital contributions and plane wave contributions, which are not OPWs at the outset have been involved in this approach, so that in the basis set three types

of functions are used: true core orbitals, squeezed local valence orbitals and plane waves. If a larger number of plane waves are included in the band structure calculations, there is usually the reason for the over-completeness breakdown of OPW expansions. The local basis function (both core and valence) can be constructed from radial functions, which are solutions of the radial Schrödinger equation. Our approach provides a full interpolation between the APW and OPW approaches adopting pseudo-potential features [18].
It is clear that there is an intense overlapping between electron wave functions of CNT when carbon atoms come close to each other, whilst in OPW method, each electron are imagined as a nearly free electron. Obviously, the above assumptions cannot explain behavior of the electron when carbon atoms come together like d-layer electrons.

6. A new method

One approach to overcoming these impending barriers involves finding on evaluating the potential of CNTs as the basis of a future nanoelectroncs technology. Single-walled CNT (SWCNTs) are materials with unique properties. They have several millimeters in length and are strongly bonded covalent materials. Because of their extremely small diameter, the OPW method should be modified and completed with TB method, with considering the overlapping of wave function of electrons. The procedure is to augment the basis set of present method by including wave functions which are OPWs between nuclei of carbon atoms but represent modified Bloch waves near the nuclei. It means that by scaling the CNT dimension, the carbon atoms come close to each other and change the band energy. Thus, by using Ritz variational method, we have modified the band energy.
Nothing said up to now has exploited any properties of the potential U(r) other than its periodicity, and, for convenience, inversion symmetry. If we pay somewhat closer attention to the form of U, recognizing that it will be made up of a sum of atomic potentials centered at the positions of the carbon atoms, then we can draw some further conclusions that are important in studying.
There is the other view, known the electron correlations. In fact, the existence of a unique density function which yields the exact ground state energy may not cause the possibility of reducing the many – electron problem to the one – electron one. This is due to at least the Coulomb interaction among electrons, in where at weaker electron correlations, it can involve a self – consistent potential which depends on electron density. In fact, the correlation effects near to carbon cores in where the strong intrasite Coulomb repulsion may lead to splitting of one – electron bands into many – electron subbands meaning TBM is inapplicable.
On one bands, nearest neighbor carbon atoms may share and/or transport electrons so that electrons become localized at carbon sites. In a such a situation of CNT, we need to modify the eigen functions and introduce a correction term by expressing them in terms of many – electron and/or overlapping functions of the atomic problem. It depends on many electron quantum numbers, s, L occurs in the full Hartree – Fock approximation [8].
Let us have a somewhat closer look at the band structures. The constructions reported so far, imply that there is just an electron as a localized particle (and completely free electron) if there are sufficiently many Bloch waves available. This is not necessarily the case in nano structures due to localization of electron with building a localized wave packet from the Bloch waves. It leads the sharply peaked character of the weight function and the spatial extension of such an electron wave packet which can be larger than the lattice constant.

In the Ritz method, the minimizing element in the n-th approximation is sought in the linear hull of the first n coordinate elements. The Ritz ansatz function is a linear combination of N orbitals. Based on linear combination of atomic orbital (LCAO) approximation, $\Psi(r)$ is

$$\Psi(\mathrm{r}) = \sum_{\mathrm{j}} \Phi_j(r) \tag{11}$$

The eigenvalues and eigenvectors can be found with finding a solution of the Ritz method. It is widely applied when solving eigenvalue problems, boundary value problems and OPW equations in general. The trial wave function will always give an expectation value larger than the ground energy (or at least, equal to it). It is known to be orthogonal to the ground state.

Further development of the OPW method led to the idea of introducing a weak pseudo potential which permits (unlike the real crystal potential) the use of perturbation theory. Because of strong core level potential within it, it may be represented in the form of a new Schrödinger equation where the non-local energy-dependent pseudo potential operator W is defined by

$$\mathrm{W} = \mathrm{V(r)} + \mathrm{V^R} \tag{12}$$

Although OPW method with pseudo potential principle a possibility to eliminate the difficulty pointed before, it is rather complicated and goes far beyond the original concept of the CNT band – structure methods due to requiring exact diagonalization of a matrix of the pseudo potential idea – applicability methods may not provide as a rule sufficiently satisfactory description of CNT.

To overcome of these difficulties, KKR method has been used. The advantage of the KKR method in comparison with the APW one is the decoupling of structural and atomic factors. For the same lattice potentials, the KKR and APW methods yield usually close results. However, the main difficulty of the KKR method is the energy dependence of the structural constants.

In the general APW, KKR and LCMTO (MT: Mofin Tin) methods, the matrix elements are functions of energy. Therefore, at calculating eigenvalues one has to compute the determinants in each point of k-space for large number values of E (of order of 100) which costs much time.

In the present work, according to Andersen theorem [2], we expand the radial wave functions at some energy value to linear terms in E, in which, both Hamiltonian and matrices do not depend on energy. We can get more accuracy by amount of higher – order terms in the expansion. Using this idea, we will be able to improve considerably the accuracy of CNT – band energy and achieve very good results.

In this case we deform new wave function based on OPW and TB methods, in that the carbon atoms cores are placed in the crystal lattice sites R. There are localized electrons and the lattice sites. Henceforth, the core electron wave functions can be assumed to be approximately equal to the corresponding Hartree-Fock functions of a free atom, that is,

$$\Psi_{\mathrm{i}}^{\mathrm{Cr}}(r-R) \approx \Psi_{\mathrm{i}}^{\mathrm{HF}}(r-R) \tag{13}$$

where I = n, I, m is a set of quantum numbers which characterize bound electron states. $\Psi_i^{HF}(r-R)$ are localized to such an extent and the overlap of $\Psi_i^{HF}(r-R)$ centered in different sites should be ignored, which leads:

$$\int \Psi_i^*(r-R)\Psi_{i'}(r-R')dr = \delta(R-R')\delta_{ii'} \tag{14}$$

On the other hand, for N unit cells in CNTs, u(k_i; r) can be written by the following expression:

$$u(k_i, r) = \frac{1}{\sqrt{N}} \sum_j e^{ik_i \cdot R_n} \Psi_{nlm}(r - R_n) \tag{15}$$

where R_n is the distance between two nearest neighbor carbon atoms. It yields new orthogonalized coefficients. We consider a correction term as L_{ij} ;

$$M_{ij} = (k_i \cdot k_j - E)\,\delta_{ij} + L_{ij} \tag{16}$$

By using separable variables method, the atomic wave functions, $\Psi_{nlm}(r)$, split into a set of radial $R_{nl}(r)$, azimuth angle part $\Phi_m(\varphi)$ and associated Legendre equation $P_{lm}(x)$, with x = cos ɵ. After doing some calculations on solving the above equation, the electronic band energy is determined by the following equation;

$$\det |H - EP| = 0 \tag{17}$$

Where

$$H = \begin{pmatrix} H_{ij}^{OPW} & H_{is} \\ H_{is}^{+} & H_{ss} \end{pmatrix} \tag{18}$$

And

$$P = \begin{pmatrix} P_{ij}^{OPW} & P_{is} \\ P_{is}^{+} & P_{ss} \end{pmatrix} \tag{19}$$

Finally, the overlapping wave functions of SWCNTs is demonstrated by H and P matrices,

$$H_{is} = \int_0^\infty \Phi_i(r) H\, u_s(k,r)\, d^3r - \sum_q E_q\, a_q\, b_{sq} \tag{20}$$

$$H_{ss'} = \int_0^\infty \Phi_i(r)\, u_s(k,r)\, H\, u_{s'}(k,r)\, d^3r - \sum_q E_q\, b_{sq}\, b_{s'q} \tag{21}$$

And

$$P_{is} = \int_0^\infty \Phi_i(r)\, u_s(k,r)\, d^3r - \sum_q C_q\, b_{sq} \tag{22}$$

$$P_{ss'} = \int_0^\infty \Phi_i(r)\, u_s(k,r)\, u_{s'}(k,r)\, d^3r - \sum_q b_{sq}\, b_{s'q} \tag{23}$$

Where

$$b_{sq} = \sum_{q} e^{ik.R_n} \int_0^{\infty} \Psi_q(r)\ \Phi_s(r - R_n)\, d^3r \qquad (24)$$

We found a reliable matrix which can describe the CNT electron behavior with doing the series of calculations based on the Ritz variational, OPW and TB methods. In this method, there is no limitation on crystalline potential of CNT structure, so it can be suggested for evaluating the electronic band energy of SWCNTs.

Therefore, the wave functions, which enter the Slater integrals, are based on self – consistent way from the corresponding integro – differential equations. It means the one – electron Hamiltonian of CNT in the many – electron representations, should take into account the electron transfer owing to matrix elements of electrostatic interaction, which will be more complicated in solving the CNT –atomic problem. Moreover, the general Hartree - Fock approximation may give us the radial one - electron wave functions which depend explicitly on atomic term, whilst these wave functions can not be factorized into one - electron ones, or, the interaction of different carbon electron on the other sites is sometimes required.

Thus we cannot describe unlocalized electron states in CNTs within above methods. In contrast to TBM, the strength of CNT potential can determine the widths of gaps rather than of electron bands (as addressed in TBM).

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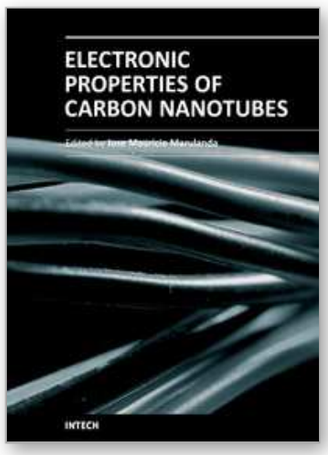

Electronic Properties of Carbon Nanotubes

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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. These one-dimensional (1D) graphene sheets rolled into a tubular form have been the target of many researchers around the world. This book concentrates on the semiconductor physics of carbon nanotubes, it brings unique insight into the phenomena encountered in the electronic structure when operating with carbon nanotubes. This book also presents to reader useful information on the fabrication and applications of these outstanding materials. The main objective of this book is to give in-depth understanding of the physics and electronic structure of carbon nanotubes. Readers of this book should have a strong background on physical electronics and semiconductor device physics. This book first discusses fabrication techniques followed by an analysis on the physical properties of carbon nanotubes, including density of states and electronic structures. Ultimately, the book pursues a significant amount of work in the industry applications of carbon nanotubes.

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