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ORIGINAL ARTICLES

Ab-initio Calculation of the Ground State of a Truncated Single-Walled Carbon Nanotube

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ABSTRACT

An *ab-initio* calculation of the ground state of a truncated single-walled carbon nanotube was performed. For this calculation, we adopted Density Functional Theory approach which significantly reduced computational requirements through converting the problem of many-electron system with a very large dimensional configuration space into the problem of one electron moving in an effective potential in the three-dimensional real-space. We modeled a truncated signle-walled carbon nanotube by first developing a computer model of graphen and then rolling it into an arm-chair nanotube. Through successful numerical simulation, we obtained a converged ground state of the nanotube.

Key words: Single-Walled Carbon Nanotube, Density Functional Theory, Electron Density.

Introduction

Since discovery in the last decade, Single-Walled carbon nanotubes (SWCNT) have drawn considerable attention of researchers from relevant communities (Lüer, L., 2009; Lefebvre, J., 2004; Qian, H., 2008; Ando, T., 2004; Maultzsch, J., 2006). The physics of these nanotubes have been intensively investigated both theoretically and experimentally at different academic and professional organizations. Also, many potential applications of these nanotubes have been proposed in the areas of electronics, photonics and material science.

As the diameter of a SWCNT is very small, typically of the order of few nanometers, quantum effects become dominant factors in their physical properties. Thus study of quantum behaviors of the SWCNT is important for proper understanding of nanotube physics. Also, SWCNTs can be excellent test-beds for studying principles of quantum theory.

A number of research articles appear in the literature on the quantum mechanical aspects of different kinds of nanotubes. Among them, Roy and Maksym (2010) calculated 3- and 4-electron states of a carbon nanotube quantum dot by exact diagonisation of a modified effective mass Hamiltonian. Chkhartishvi (2009) estimated ground state parameters of boron nanotube. There parameters included bond lengths and intersite distances and these were calculated using a quasi-classical estimation. On the other hand, Ohara and Yamamoto 2009 investigated ground state properties of a Peierls-Hubbard nanotube using a group theoretical analysis. Carbon nanotube, in particular SWCNT, being a very active area of research, more efforts are required to come up with a in-depth understanding of the quantum mechanical aspects of nanotubes.

In this paper, we describe ab-initio estimation of the ground state of a truncated SWCNT using Density Functional Theory (DFT). The next section describes a computer model of a truncated SWCNT. Section 3 focuses on the quantum state of the SWCNT. Theory behind the ground state estimation using DFT is presented in section 4. Then section 5 presents numerical simulation while section 6 describes the simulation results. Finally section 7 concludes the paper.

2. Modeling of Truncated SWCNT:

In order to derive a computer model of a carbon nanotube, we first constructed a computer model of a graphen sheet with lattice vectors $\vec{a}$ and $\vec{b}$ as depicted in figure 1 (a). Then the graphen sheet was rolled into a nanotube as shown in figure 1(b).

For the present research, we chose arm-chair chiral configuration. Also, the nanotube, which is ideally infinite in one dimention, was truncated and carbon atoms at the both ends were replaced by hydrogen atoms. We modeled the nanotube in the real-space, which made the numerical calculations quite intuitive. The real-space was divided into grids with granularity sufficiently smaller than the distance between nearest neighbor carbon atoms in the nanotube.

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(a) (b)

Fig. 1: (a) Graphen sheet (b) Nanotube obtained by rolling the graphen sheet.

3. Quantum State of Truncated SWCNT:

The fundamental concept behind the quantum physics of SWCNT is the many-body non-relativistic Schrödinger equation for the electrons moving in the potential produced by nuclei of the carbon atoms and the other electrons. Under the approximation that much heavier nuclei can be considered fixed in space (Born-Oppenheimer approximation (Atkins, P. and R. Friedman, 2005)), this many-electron wavefunction Ψ is given by (Kohn, W., 1999).

$$\left\{-\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_{j,l}\frac{Z_l e^2}{|r_j - R_l|} + \frac{1}{2}\sum_{j=j'}\frac{e^2}{|r_j - r_{j'}|}\right\}\Psi = E\,\Psi \tag{1}$$

where, r_j are positions of the electrons, R_l and Z_l are positions and charges of nuclei respectively. Also, *E* is the energy eigenvalue and $\hbar$, *m* and *e* are respectively reduced Planck constant, mass and charge of an election. However, this many particle wavefunction is defined in a large dimensional configuration space and finding solution for Ψ is generally impractical except for only few ($\approx O(10)$) chemically active electrons (Kohn, W., 1999). Since the number of active electrons in a typical carbon nanotube is much greater than 10, this traditional method of solving Schrödinger equation for nanotube is inadequate for present day computers.

The problem of finding quantum state of many-particle system has been seriously addressed by the researchers form relevant communities and a number of alternative solutions have been proposed. A successful alternative is to consider an effective charge density in the three dimensional real space instead of electron wave functions in the configuration space. One particurly successful method in this line is the Density Functional Theory put forward by Hohenberg and Kohn and extended by (Kohn, W., 1999; Fakuda, R., 1994; Kohn, W. and L.J. Sham, 1965), as briefly expained in the next section.

4. Estimation of the Ground State using Density Functional Theeory:

We calculated the ground state of the truncated SWCNT using Density Functional Theory (DFT) (Kohn, W., 1999). This theory is based on the hypothesis that knowledge of the ground state electron density $n(r)$ for any electronic system uniquely determines the system. Also, in the Kohn-Sham extension (Kohn, W., 1999; Kohn, W. and L.J. Sham, 1965) of this thoery, the many-electron problem is converted into a single-electron one, where the single electron moves in an effective external potential v_{eff} given by,

$$v_{eff}(r) = v(r) + \int \frac{n(r')}{|r - r'|}dr' + v_{xc}(r) \tag{2}$$

where, r is the single electron position, r' other electron position and *v(r)* the *external* potential due to nuclei. The potential $v_h(r) = v(r) + \int \frac{n(r')}{|r - r'|}dr'$ is called the Hartree potential. The term v_{xc}, called local exchange-correlation potential, depends on the electron density as follows,

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$$v_{xc}(r) = \frac{\delta}{\delta \tilde{n}(r)} E_{xc}[\tilde{n}(r)]\Big|_{\tilde{n}(r)=n(r)} \tag{3}$$

Here, E_{xc} is the so called exchange-correlation energy functional and $\tilde{n}(r)$ is a trial function for electron density. With this definition of v_{eff}, the ground state of the system is given by the following coupled equations called Kohn-Shan equations (Kohn, W., 1999; Kohn, W. and L.J. Sham, 1965).

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(r)\right)\varphi_j(r) = \varepsilon_j \varphi_j(r) \tag{4}$$

$$n(r) = \sum_{j=1}^{N} \left|\varphi_j(r)\right|^2 \tag{5}$$

$$v_{eff}(r) = v(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}(r) \tag{6}$$

Where, $\varphi_j(r)$'s are the eigenfunctions representing ground state and ε_j's are the corresponding eigenvalues. These self-consistent equations can be solved iteratively through computer programs. At every iteration step, the ground state energy of the SWCNT is estimated as,

$$E = \sum_j \varepsilon_j + E_{xc}[n(r)] - \int v_{xc}(r) n(r) dv - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|} \tag{7}$$

5. Numerical Simulation:

We used a first principle DFT package 'Octopus' (Marques, M.A.L., 2003; Castro, A., 2006) for computation of the ground state. As mentioned, an arm-chair (4, 4) SWCNT was modeled in a cylindrical shape real-space simulation box represented in a Cartesian coordinate system. The potentials produced by carbon and hydrogen atoms together with core electrons were approximated by pseudo-potentials provided the 'Octopus' package (Marques, M.A.L., 2003; Castro, A., 2006). Adopted units system was *ev-angstrom* where electron-volt was the unit for energy and angstrom for length. We adopted Dirichlet boundary conditions and set the value of the electron wavefunction at the boundaries of the simulation box to zero.

As mentioned before, the Kohn-Sham equitations (Eq. 10, 11 and 12) were solved iteratively. Out of these equitations, Eq. 4 represents an eigen-equation. At each iteration, Eigenfunctions $\varphi_j(r)$ and eigenvalues e_j of the Hamiltonian operator $-\frac{1}{2}\nabla^2 + v_{eff}(r)$ were computed. In our ground state calculation, 71 eigenfunctions and corresponding eigenvalues of the Hamiltonian were computed. These eigenfunctions represent the Kohn-Sham wavefunctions and the eigenvalues represent corresponding energies. Electron density was computed from the eigenfunctions using Eq. 5. Then effective external potential v_{eff} was computed using Eq. 6. With this newly estimated v_{eff}, the next iteration of computation started and so on. The iterations continued until the solution converged.

A crucial part of the calculation was to approximate E_{xc}. In our simulation, Local Density Approximation (LDA) approach was adopted.

6. Results:

During simulation, with progress of iterations, potentials (v_h, v_{xc} and v_{eff}) as well as wavefunctions and density of states (DOS) were converging from initial trial values to final converged values. Converged v_h and

v_{xc} are shown in figures 2 and 3 respectively, while converged effective potential veff is shown in figure 4.

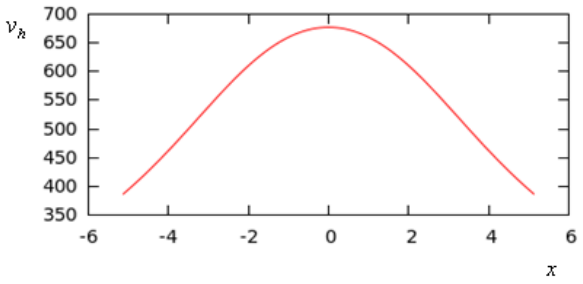

Fig. 2: Converged Hartree potential v_h.

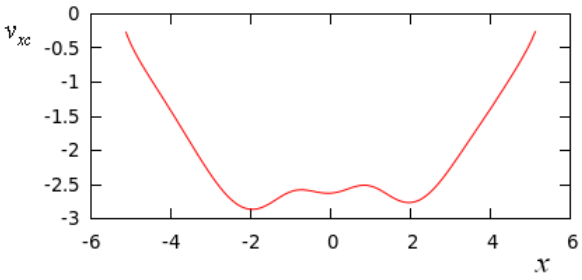

Fig. 3: Converged exchange-correlation potential v_{xc}

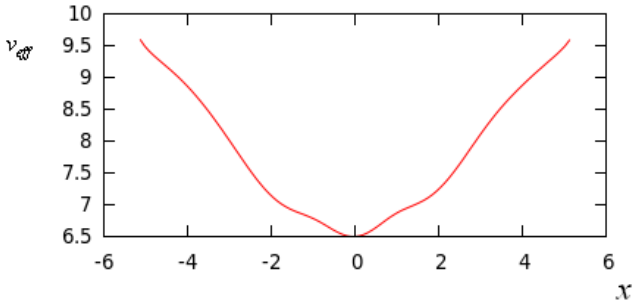

Fig. 4: Converged effective potential v_{eff}

Although, 71 eigenfunctions and corresponding eigenvalues were computed at every iteration step, for brevity, we report here four of the converged eigenfunctions along nanotube axis as shown in figure 5(a), 5(b), 5(c) and 5(d) below.

The first wavafunction in figure 5 (a) is a single-node, Gaussian shaped one symmetric about the x=0 plane. Wavefunctions shown in figure 5(b) and 5(c) are both double-node antisymmetric. However, the wavefunction in figure 5(b) positive node on the right side of the x=0 plane while that in figure 5(c) on the left side. Finally, the wavefunction in 5(d) has three node and is symmetric about the x=0 plane.

Out of the 71 band resolved density of states (DOS), we report four here corresponding to the above wavefunctions in figure 6 (a), 6(b), 6(c) and 6(d). As clearly seen in these figures, band resolved DOS profiles peak at -13, -10.5, -9.5 and -7.1 eV respectively.

Finally, estimated overall density of states (DOS) obtained by combining all 71 band resolved DOS profiles is shown in figure 7 below. As seen clearly, DOS has highest values between -3 eV to + 5 eV.

7. Conclusion:

We performed an *ab-initio* calculation of the ground state of a truncated SWCNT using DFT. We modelled the SWCNT in cylindrical real-space grid and performed numerical simulation for Kohn-Sham equation. From simulation, we obtained converged wavefunctions, DOS and various potentials namely Hartree potential, exchange-correlation potential and the effective potential. Simulation results clearly indicate a successful estimation of ground state of a truncated carbon nanotube.

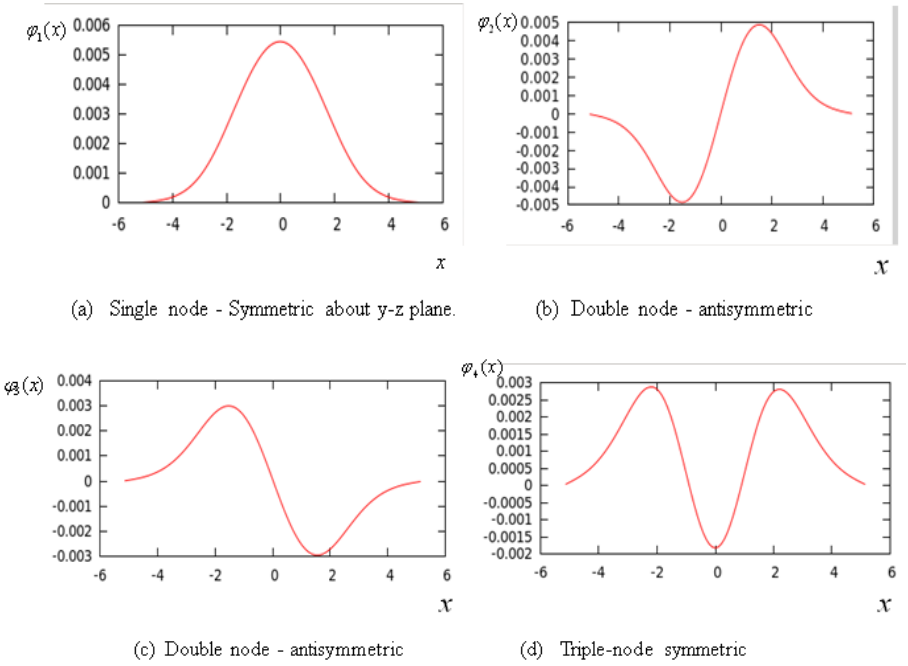

Fig. 5: Four converged wavefunctions with different symmetries and number of nodes.

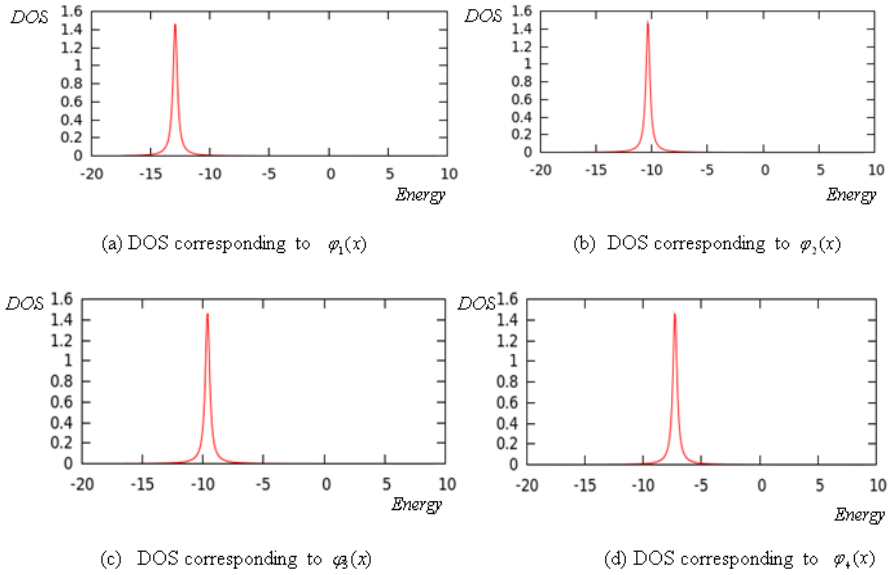

Fig. 6: Band resolved DOS corresponding to Kohn Sham wavefunctions.

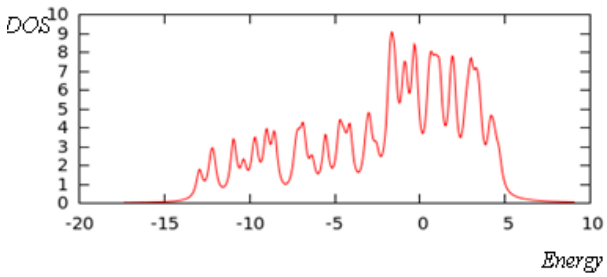

Fig. 7: Density of states (DOS) for the nanotube system.

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