**Quasiparticle band structure of carbon nanotubes**

Takashi Miyake and Susumu Saito  
*Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan*  
(Received 11 August 2003; published 23 October 2003)

We study the electronic structure of carbon nanotubes theoretically by first-principles techniques. Geometry is optimized with the local-density approximation (LDA) in density functional theory, and many-body effects between electrons are taken into account within the GW approximation. We find that the (5,0) tube is metallic even at the GW level, being different from the tight-binding result. The (6,0) tube is also confirmed to be metallic. The GW correction to LDA is found to be small in metallic tubes. The (7,0) tube is semiconducting, in which the GW correction considerably increases the gap. On the other hand, the GW correction is small in graphene, suggesting that the density functional theory gives a reasonable description of large nanotubes.

DOI: 10.1103/PhysRevB.68.155424  
PACS number(s): 73.22.-f, 71.20.Mq

Carbon nanotube is a needle-like one-dimensional material composed entirely of carbon atoms. Its topology is characterized by a set of two numbers \((n,m)\) called chiral indices. According to the early studies by the tight-binding models, the \((n,m)\) tube is a metal or a narrow-gap semiconductor when \(n-m\) is a multiple of three, whereas otherwise it is moderate-gap semiconductor ("1/3 rule"). This property has triggered extensive research because it would be utilized as a new electronic device. The band gap \(E_g\) of moderate-gap semiconducting tubes is predicted by the \(k\cdot p\) theory and the tight-binding method to be inversely proportional to the tube diameter \(d\) as \(E_g = 2a_{\sigma,\pi}\gamma_0/d\), where \(a_{\sigma,\pi}\) and \(\gamma_0\) are the distance and \(\pi\)-orbital transfer integral between adjacent carbon sites, respectively. This "1/d rule" suggests a possibility of controlling electronic and optical properties by changing the size of nanotubes.

The gap has been measured by a couple of methods thus far. One is the scanning-tunneling-spectroscopy (STS) measurement. The gap value as a function of diameter was reported by combining the STS results with the geometry determined by the scanning-tunneling-microscopy (STM). Fitting the data to the 1/d rule gave \(\gamma_0 = 2.7\pm0.1\) eV (Ref. 6) or 2.45 eV (Ref. 7). There is also an experiment by the resonant Raman scattering, which reported \(\gamma_0 = 2.9\) eV (Ref. 8). However, it is difficult to identify \((n,m)\) precisely since the samples are mixture of various chiral indices. Added to this is the exciton effect which is to be considered in the case of the Raman spectra measurement. These factors, as well as sizable experimental uncertainties in these reports, prevent us from getting accurate band gap of individual nanotube.

Theoretically, tight-binding method is a convenient tool for electronic structure. However, it contains empirical parameters to be determined in some other ways, so that one cannot use tight-binding method to predict the band gap. Local-density approximation (LDA) calculation based on density functional theory (DFT) is a parameter-free and powerful technique. It has been successfully applied to many materials to describe a variety of electronic properties. As far as band gap is concerned, however, LDA tends to underestimate the gap of semiconductors; the LDA gap is typically half to two-third of the experimental gap. Therefore, the gap of carbon nanotubes is still an open question in spite of its importance.

In this work, we study the electronic structure of carbon nanotubes using the GW approximation (GWA). GWA takes account of dynamical screening effect of electrons within the random-phase approximation and has been applied to a wide range of semiconductors, and turned out to improve the band gap significantly to LDA. Here (5,0), (6,0), and, (7,0) tubes with fully relaxed geometries are studied. It is found that neither the 1/3 rule nor the 1/d rule holds in these small tubes. We also study graphene in order to obtain insight into large-diameter nanotubes. We see that the many-body correction plays a minor role in them.

We begin with density functional calculation. The exchange-correlation energy is approximated by the LDA in the Perdew-Zunger formula. Influence of core electrons are included in the Troullier-Martins type pseudopotential and valence electrons are expanded by the plane-waves up to 50 Ry. We adopt the supercell method. Nanotubes form the two-dimensional triangular lattice. The wall-to-wall distance between adjacent tubes is set to 7 Å, which is large enough to neglect intertube interaction. Brillouine zone integration in the tube direction is replaced by summation over \(8k\) points. Some results using the same scheme have been reported before, and the importance of geometry relaxation in the electronic-structure study has been revealed.

In the GW calculation, Green’s function is constructed from the one-body wave functions and eigenvalues obtained by LDA with full-potential linear-muffin-tin-orbital (FPLMTO) scheme. Valence orbitals are expanded by 20 muffin-tin-orbitals per carbon atom, and \(8k\) points are sampled in the tube direction. We use mixed basis for Green’s function approach, products of two atomic orbitals in the muffin-tin region, and plane waves up to 7.29 Ry in the interstitial region. Test calculation for diamond with the same basis set and \(8^3\) \(k\)-point mesh gives the band gap of 5.4 eV, which is to be compared with the LDA value 4.1 eV, previous GW values 5.6 eV Ref. 12 and 5.33 eV Ref. 13, and experimental value, 5.48 eV. Further numerical techniques are found elsewhere.

The fundamental gap of zigzag nanotubes is plotted in Fig. 1 against the tube diameter. In this calculation, atomic coordinates are fixed at the positions which are generated by rolling up a graphene sheet with the C—C bond length of...
The LDA results (circles) follow the $1/d$ rule when tube is equal to or larger than the $(10,0)$ tube. They can be fitted to the $1/d$ rule with $\gamma_0=2.5$ eV (solid line). The crosses are obtained by the tight-binding method including $\pi$ orbitals only ($\pi$-only TB) with the same $\gamma_0$, and the squares are from the tight-binding model by Hamada et al.\textsuperscript{2} which takes account of both $\pi$ and $\sigma$ orbitals ($\pi$-$\sigma$ TB). Both TB methods give gap values close to LDA in large-diameter region, because the TB parameters were determined so as to reproduce the LDA results. Gap value itself was fitted in the $\pi$-only TB, and the band structures of graphite and $C_{60}$ were fitted in the $\pi$-$\sigma$ TB. The $\pi$-only TB data follow the $1/d$ rule in the whole region, while the $\pi$-$\sigma$ TB gap deviates downward at $d<0.5$ nm. The LDA results also turn to decrease even at larger diameter of $d=0.8$ nm. These show that $\pi$ orbitals alone are not sufficient to describe the electronic structure of small nanotubes.

The $(7,0)$ tube has a diameter of 0.55 nm, which is smaller than the LDA crossover diameter. The LDA gap is 0.5 eV and is less than half the $\pi$-only TB value, 1.2 eV. In order to see how the gap is reduced, the electronic band structure is shown in Fig. 2. Comparing the $\pi$-only TB band structure in (a) with the LDA result plotted by dashed line in (b), it turns out that the small LDA gap is due to descent of a state marked by "*" rather than all conduction bands being shifted down. In the $\pi$-only TB, the "*" state is located at 2.6 eV above the top of the valence band and is not even the lowest conduction-band state. We also performed the $\pi$-$\sigma$ TB calculation (figure not shown), and found that the * state is pulled down to the lowest conduction-band state. This clearly indicates the importance of hybridization between $\pi$ and $\sigma$ orbitals.

One factor to be considered is the lattice relaxation effect, which could be considerable in small tubes. In order to look into this effect, we optimized geometry within LDA of DFT. The optimized geometry is compressed in the tube direction by 1% and the diameter is increased by 1%. The electronic structure for the relaxed geometry is shown by solid lines in Fig. 2(b). Lattice relaxation is actually important in this system. The * state is pulled down by the relaxation so that the gap is reduced to 0.2 eV from 0.5 eV. The second highest valence-band state is also lowered by 0.3 eV.

Another issue is the many-body correction to LDA. The $GW$ band structure (with the above relaxed geometry) is plotted by circles in Fig. 2(c), where the LDA results are also shown by solid lines for comparison. We can see that the gap increases from 0.2 eV (LDA) to 0.6 eV ($GW$). Thus, as far as the fundamental gap is concerned, the many-body correction cancels the lattice relaxation effect. Consequently, the $GW$ gap for the relaxed geometry is accidentally close to the LDA gap for the fixed geometry before relaxation.

When we look at the whole band structure, the electronic bands by the $\pi$-only TB method form symmetric structure in energy with respect to the Fermi level. It has been shown theoretically that photoabsorption spectra have peaks at the transition energy between the top of a valence-band state to the bottom of the corresponding conduction-band state,\textsuperscript{25} as indicated by arrows in the figure for the lowest two transitions. The LDA bands have a similar structure. However, the fundamental gap does not correspond to this transition. The first active transition is that from the valence-band top to the second lowest conduction-band state, which is 1.1 eV in energy. The second transition is 2.8 eV. Conduction-band dispersion corresponding to this transition is smaller than that in the $\pi$-only TB. This indicates large density of states, which may lead to sharp peak in photoabsorption spectra. The first (second) transition energy changes to 0.8 eV (3.1 eV) after lattice relaxation, and further to 1.2 eV (3.6 eV) by inclusion of many-body correction. Hence, as is observed in the fundamental gap, the many-body correction cancels the lattice relaxation effect in the first transition energy, whereas both effects increase the second transition energy. We note that the $GW$ value for the first transition energy 1.2 eV is close to the value expected from the $1/d$ rule (see Fig. 1). (Although...
these arguments give an insight into the optical spectra, the exciton effect as well as the oscillator strength should be considered to discuss this issue in full detail.\textsuperscript{26,27}

The many-body correction pushes up most conduction bands. However, there is a state which approaches the Fermi level in the LDA calculation. It is the state marked by “NFE” in Fig. 2(c). Its dispersion is parabolic with the minimum at \( \Gamma \) point. The minimum is at 3.9 eV above the valence band top in LDA (for the relaxed geometry) and is reduced to 3.5 eV in \( GW \) (for the relaxed geometry). The state is distributed away from the carbon sites and is delocalized in the tube direction, thereby called nearly-free-electron (NFE) state.\textsuperscript{28}

As the tube becomes thinner, the * state comes lower. A previous LDA work reported it would cross the Fermi level in the \( (6,0) \) [Ref. 29] and \( (5,0) \) [Refs. 30,31] nanotubes. We checked instability of this metallicity against geometry relaxation in the \( (6,0) \) tube, and found that geometry optimization is of minor importance [Fig. 3(b)]. We then performed the \( GW \) calculation in order to see if the band overlap is an artifact of LDA. In Fig. 3(c), the \( GW \) band structure (circles) is compared with the LDA results (solid line). We see that the * state does not change the energy level so much by the many-body correction and it remains to cross the Fermi level. The state has a maximum overlap of 0.8 eV at \( \Gamma \) point in both LDA and \( GW \). As a result, the first transition expected from the \( \pi \)-only TB is forbidden since the bottom of the * state is occupied.

The band overlap is also observed in the \( (5,0) \) nanotube. In Fig. 4, we see that the * state crosses the Fermi level in both LDA and \( GW \). Hence, the \( (5,0) \) nanotube becomes metallic breaking the 1/3 rule. The band overlap is 1.2 eV (LDA with the fixed geometry), 1.1 eV (LDA with the relaxed geometry), and 1.0 eV (\( GW \) with the relaxed geometry), respectively. The first transition energy in photoabsorption is 1.6 eV (LDA with the fixed geometry), 2.2 eV (LDA with the relaxed geometry), and 2.3 eV (\( GW \) with the relaxed geometry), respectively. On the other hand, as is the first transition in the \( (6,0) \) tube, the second transition expected from the \( \pi \)-only TB is inactive.

Comparing the results for above three different tubes, the many-body correction in the \( (5,0) \) and \( (6,0) \) tubes is smaller than that in the \( (7,0) \) tube. This difference may be ascribed to the difference between metal and semiconductor. An exception is the NFE state. It is pulled down by 0.6 eV in the \( (5,0) \) tube and 0.7 eV in the \( (6,0) \) tube. These values are larger than the shift in the \( (7,0) \) tube, 0.4 eV.

Another dependence on chiral indices is seen in spatial distribution of orbitals. In Fig. 5, distribution of the * state of the \( (7,0) \) tube at \( \Gamma \) point is plotted. The distribution is asymmetric with respect to the tube wall and the maximum density is found outside the tube. The asymmetry is a consequence of hybridization between the \( \pi \) and \( \sigma \) orbitals, which is significant in thin tubes. Thus, it is found also in the thinner \( (5,0) \) tube, as shown in Fig. 6. The difference between the two tubes is observed in density inside of the tube. Although the inner space is low-density region in both tubes, the density does not decay even at the center in the \( (5,0) \) tube. This would be partly because of hybridization with the NFE state. It has the maximum density at 2.2 Å away from the carbon wall,\textsuperscript{28,32,33} which is around the center of the tube in the \( (5,0) \) tube. The importance of the NFE state is supported by the \( \pi-\sigma \) TB method, which takes account of \( \pi-\sigma \) hybridization but does not include the NFE state in the basis.\textsuperscript{2} The descent of the * state is smaller in the \( \pi-\sigma \) TB result than that in the LDA result. As a consequence, the * state does not cross the Fermi level in the \( (5,0) \) tube, and the tube is semiconductor in the TB calculation (Fig. 1).

Finally, we discuss large tubes. It is computationally too heavy to do \( GW \) calculations of large nanotubes. On the other hand, since downward shift of the * state is to take place only in small nanotubes,\textsuperscript{20} we can expect that the electronic structure of large nanotubes is similar to that obtained by simply folding the electronic structure of graphene with appropriate boundary condition in the circumference direction, as is assumed in the \( \pi \)-only tight binding method and \( k \cdot p \) theory. In fact, the LDA fundamental gap shows a simi-
lar behavior with the $\pi$-only TB gap and follows $1/d$ rule at $d > 0.8 \text{ nm}$ (Fig. 1). We then study graphene as an alternative to large nanotubes. In Fig. 7, the electronic structure of graphene by the $GW$ method (circles) is plotted together with the LDA results (solid line). Most states are pushed away from the Fermi level by the $GW$ correction, consequently the band is widened, while the NFE is again pulled down. An issue is the Fermi velocity $v_F$, since it determines the energy scale of low-lying electronic properties and is proportional to $\gamma_0$ in the $\pi$-only TB method. Estimating the Fermi velocity from the band dispersion along the K-$\Gamma$ line, we find $v_F^{GW}/v_F^{LDA}$ to be 1.16 for the occupied $\pi$ band and 1.09 for the unoccupied $\pi^*$ band. This suggests that band dispersion of large nanotubes, including the band gap, is underestimated by about 13% in LDA. This, in turn, means that the LDA electronic structure is expected to be reasonable in large nanotubes, given that the LDA usually underestimates the band gap of semiconductors significantly.

In summary, we have studied the electronic structure of the ($n,0$) tubes, ($n = 5,6,7$), and graphene by combining density-functional calculation and the $GW$ method. We found that a certain state comes downward as the diameter decreases. Since it is pulled down to the bottom of the conduction band, the gap breaks the $1/d$ rule and turns to decrease at $d \sim 0.8 \text{ nm}$. Consequently, the gap of the (7,0) tube is only 0.6 eV. The many-body correction is considerable in this system, though it is canceled by also a sizable lattice relaxation effect found in the fundamental-gap region. The lowered state crosses the Fermi level in the (5,0) and (6,0) tubes, so that both the tubes are metallic. Neither many-body correction nor lattice relaxation effect changes the electronic structure significantly in both tubes. On the other hand, the many-body correction is also only of minor importance in graphene. It suggests that the density-functional method gives a reasonable electronic structure of large nanotubes.

We wish to acknowledge Dr. T. Kotani, Prof. M. van Schilfgaarde, and Dr. F. Aryasetiawan for providing us with...
the GW code. We also thank Prof. A. Oshiyama, Prof. T. Nakayama, Dr. M. Saito, and Prof. O. Sugino for the pseudopotential program, and Prof. N. Hamada and Prof. S. Sawada for the tight-binding code. Numerical calculations were performed partly on Fujitsu VPP5000 at the Research Center for Computational Science, Okazaki National Institute. This work was supported by Grant-in-Aid from the Ministry of Education, Science and Culture of Japan.