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Quasiparticle Band Structure of Carbon Nanotubes

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Electronic structure of single-wall carbon nanotubes is investigated in detail by means of the local-density approximation (LDA) in the framework of density-functional theory. The many-body correction to the LDA is also studied within the GW approximation. The LDA band gap of semiconducting nanotube is roughly proportional to the inverse of diameter (d) for d>0.8 nm. This suggests that the electoronic properties of large-diameter nanotubes can be understood from zone folding of graphene band structure. The band structure is influenced only slightly by the many-body effect, which indicates that the LDA band is reasonable for large-diameter tubes. As d is decreased, the LDA gap turns to decrease at d~0.8 nm. The GW calculation for the (7,0) tube shows a sizable opening of band gap compared to the LDA, indicating important role of many-body correction in small-diameter semiconducting tubes. On the other hand, the thinner (6,0) and (5,0) tubes are found to be metallic in both LDA and GW calculation. The many-body correction is found to be minor in these metallic tubes.

Key words: carbon nanotube, electronic structure, first-principles calculation

1. INTRODUCTION

Ever since carbon nanotube has been discovered a decade ago [1], a lot of experimental and theoretical works have been reported. Carbon nanotube consists of one-dimensional network of carbon bonds, and it can be regarded as a new class of carbon network materials other than zero-dimensional fullerenes, two-dimensional graphite, and three-dimensional diamond. It possesses a couple of fascinating properties that make carbon nanotube as a promising material in nanotechnology. In addition to peculiar shape, nanotube is physically strong and thermal conductivity is very high. Of particular interest is the electronic property. Early theoretical works using tight-binding methods concluded that the nanotube could be both metallic and semiconducting depending on topology [2,3], which has been confirmed experimentally later.

Carbon nanotube is made up by rolled-up graphite sheet (graphene). Therefore, the starting point of understanding its electronic properties is the electronic states of graphene. Starting from graphene band structure and supposing an appropriate boundary condition along the circumference direction, one finds that the (n,m) tube is metallic when n-m is a multiple of three, whereas it is semiconducting otherwise [3]. Considering that the graphene band structure has linear dispersion around the Fermi level, the band gap of semiconducting tubes is expected to be inversely proportional to diameter [4,5]. When we go one step further and include hybridization between π and σ orbitals by curvature effect, "metallic" nanotubes are not metallic but narrow-gap semiconducting except armchair nanotubes [2]. This tells us that we need to be careful when discussing thin nanotubes, since curvature effect should be greater in small-diameter tubes. Lattice relaxation effect is another important factor in thin tubes.

Local-density approximation (LDA) in the framework of density-functional theory (DFT) [6,7] is a standard scheme these days for investigating detail of both geometric and electronic structure. It fully includes both curvature effect and geometry optimization effect. Another advantage of LDA is that it contains no adjustable, thus LDA can be used for quantitative prediction. However, there is one serious problem. The LDA underestimates band gap of semiconductors considerably.

In the present work, we study the electronic structure of single-wall carbon nanotubes in detail theoretically with parameter-free methods. We start with LDA calculation, and discuss lattice-relaxation effect with this scheme. We also discuss many-body correction to LDA within the GW approximation [8] based on the many-body Green's function theory, which has been applied to wide range of materials so far, and turned to reproduce band gap of semiconductors accurately [9-12]. We find that the many-body correction is small in graphene. It suggests LDA band structure is reasonable in large nanotubes. On the other hand, the electronic structure of the (7,0) nanotube is modified a lot by both lattice relaxation and many-body correction. We also discuss (6,0) and (5,0) tubes. Both tubes are confirmed to be metallic.

2. COMPUTATIONAL METHOD

The lattice relaxation is performed within LDA of DFT. The core electrons are frozen in norm-conserving pseudopotential [13] in the Kleinman-Bylander approximation [14]. The valence electron orbitals are expanded by plane wave basis set with the cutoff energy of 50 Ry. The Perdew-Zunger formula is adopted for the exchange-correlation functional [15,16]. Supercell scheme is applied. The unit cell size in the perpendicular direction to the tube axis is fixed to be 20.0, 21.5, and 23.0 angs. in the (5,0), (6,0), and (7,0) tube, respectively.

The unit-cell size along the tube axis is optimized. The Brillouine zone integration is carried out by summation over the 1x1x8 mesh. Some of the results using the same technique are found somewhere else [17].

The GW calculation is done starting from the LDA wavefunctions and eigenvalues obtained by the full-potential linear-muffin-tin-orbital (FP-LMTO) method. The Coulomb interaction and polaraizability are expanded by mixed basis, which consists of plane waves in the interstitial region and products of two atomic orbitals in the muffin-tin region [18,19]. The 1x1x8 k-point mesh is used, and 13 unoccupied orbitals per atom are included. Frequency dependence of the polarizability is calculated directry based on the random-phase-approximation. The k^{-2} divergence of the Coulomb matrix $v(k)$ at k=0 is avoided by the offset gamma method [20]. In this method, the k=0 point is shifted slightly to $(0,0,k_0)$ and $(0,0,-k_0)$ such that the integral $\int \exp(-k^2)/k^2 d^3k = 2\pi^{3/2}$ is calculated exactly by the descrete k-point mesh. More technical detail is found in Ref.[21]. We calculated the band gap of diamond as a test, and obtained the value of 5.4 eV, which is to be compared with the LDA value of 4.1 eV, and previous GW results of 5.6 eV [9], 5.33 eV[10].

3. RESULTS AND DISCUSSIONS

In Fig.1, the band gap (Eg) of the $(n,0)$ nanotube is plotted as a function of tube diameter (d). Geometry of the nanotubes is prepared by rolling up a graphene with the C-C distance (a) of 1.42 angs. and no lattice relaxation effect is included in this calculation. Crosses are the tight-binding results with π orbitals only (π-only TB) in which the nearest-neighbor transfer-integral $\gamma 0$ is set to 2.5 eV. We see that the band gap closes when n is a multiple of three ("1/3 rule"). The gap value of semiconducting tubes decreases as the diameter increases, and it follows the line of $Eg = \gamma 0\ a\ /\ d$ ("1/d rule"). As the diameter decreases, on the other hand, the curvature increases. Accordingly, hybridization between π and σ orbitals is expected to be stronger, hence, the π-only TB would be invalid. Squares in the figure are results by the tight-binding method including both π and σ orbitals as a basis set, proposed by Hamada and Sawada (π–σ TB) [2,22]. The results are indeed affected by the σ orbitals. The band gap is significantly reduced compared to the π-only TB for the (5,0) tube.

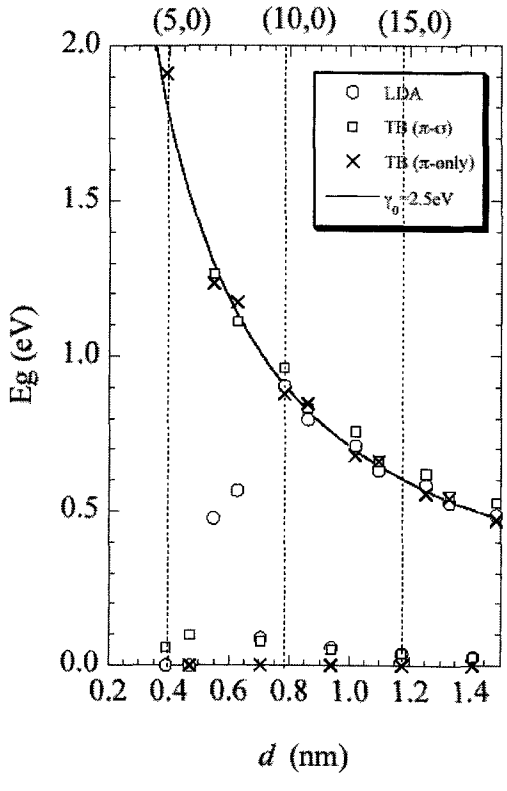

Fig.1: Band gap versus tube diameter. Circles are LDA results, squares are tight-binding calculation including π and σ orbitals, and crosses are tight-binding calculation with π orbitals only. Solid line is the 1/d line.

Circles are the LDA results. They also show turnover, even at larger diameter of d~0.8 nm. The LDA data can be fitted to the 1/d line at large-diameter region with $\gamma 0$=2.5 eV. Very recent work for larger-diameter nanotubes, including chiral tubes, gives a slightly larger transfer-integral of $\gamma 0$=2.67 eV [23]. Experimentally, a couple of measurements have been reported for $\gamma 0$. The STM-STS measurement concluded 2.7 eV [24], and 2.45 eV [25]. On the other hand, the resonant Raman scattering measurement reported $\gamma 0$=2.9 eV [26]. These values are apparently in agreement with the LDA value. However, the experimental data are for the mixture of tubes with various size and chirality. In addition, the data contain sizable uncertainty. Exciton effect [27,28] is also to be considered in the case of the Raman measurement. These factors make it difficult to compare the theoretical value directly with available experimental data, and more careful analysis is needed in the future.

The above results indicate that the electronic structure of nanotubes at $d > 0.8$ nm are well described by zone

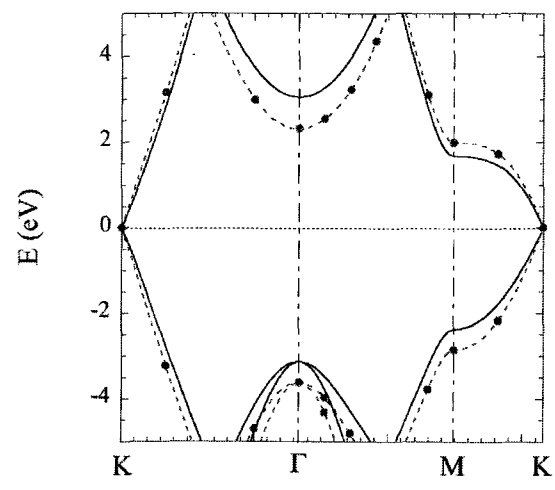

Fig.2: Electronic structure of graphene. Solid line: LDA, circles: GW calculation. Dashed lines are guides for the eye. The Fermi level is set to zero.

folding of graphene band structure. Then, we study graphene in detail on behalf of large-diameter tubes. Figure 2 shows the band dispersion of graphene. The solid lines represent the LDA results. The unoccupied π^* band touches the occupied π band at the K point, and dispersion is linear in the vicinity of the Fermi level, which is the origin of the 1/d rule. The GW quasiparticle band structure is plotted by circles. The GW dispersion near the Fermi level is similar with the LDA one. It indicates that the electronic properties of large-diameter tubes are well described by the LDA. When we look at the dispersion more in detail, however, the dispersion is steeper when the GW correction is included. The Fermi velocity increases by 9 % for the π^* band, 16 % for the π band, and 13 % in average. This implies the band gap of large-diameter tubes is a little underestimated by the LDA.

About 3 eV above the Fermi level is there a parabolic band with the minimum at the gamma point. Analysis reveal that the wavefunction of the state has low density at the graphene plane and is distributed away from the plane. This corresponds to the state known as the interlayer state in graphite. Carbon nanotube also has a corresponding state, which is called "nearly-free-electron" (NFE) state [29,30]. The NFE state is about 3-4 eV above the Fermi level in the LDA band structure of pristine nanotubes. However, in certain doped systems [31-33], the NFE state is pulled down to the Fermi level by coupling with the orbital of dopant, so that it contributes to conductivity. Since the state is away from the carbon wall, it may be free from the effect of impurities. Thus the NFE could be a key state for technical application. Figure 2 shows that the NFE state is closer to the Fermi level when the GW correction is included.

Now we move on to small-diameter tubes. In Fig.3, the electronic structures of the (5,0) nanotube obtained by various methods are shown. Figure (a) is the result of the π-only TB method with $\gamma 0$=2.5 eV. The π-only TB (without taking nonorthogonality of the basis into account) gives symmetric dispersion with respect to the Fermi level. This symmetry is found for carbon nanotubes in genetal, not specific to the (5,0) tube. The (5,0) tube is a semiconductor following the 1/3 rule in the π-only TB. The theoretical work based on the effective mass approximation predicts that photoabsorption is active for the transition from a valence band to the conduction band symmetric with respect to the Fermi level [34], as the first and second lowest transitions are indicated by arrows in the figure. The first transition corresponds to the band gap, which is 1.9 eV.

The $\pi\sigma$-TB result for the fixed geometry before lattice relaxation is shown in (b). The gap is significantly reduced compared to the π-only TB result, and the tube is a narrow-gap semiconductor. This clearly shows the importance of the π–σ hybridization in thin nanotubes. Comparing (a) and (b), we see that the reduction of the gap is not due to shift of all conduction bands but attributed to descent of a band indicated by * in the figure. The descent has been pointed out previously by Blasé et al. for the (6,0) nanotube [35]. The LDA band (for the fixed geometry) is shown in (c). The * band is pulled down further and it crosses the Fermi level. Consequently, the material is metallic in contrast with the TB results [36,37]. When lattice is relaxed, the tube is compressed in the tube direction by 1%, whereas the diameter increases by 1 %. The internal lattice coordinates also changes, which are discussed in detail in Ref.[17]. The electronic band structure for the relaxed geometry is shown in (d). The * band crosses the Fermi level and the (5,0) tube remains to be metallic. One characteristic feature in the LDA band is the presence of a parabolic band about 4 eV above the Fermi level, which is not observed in the TB results in (a) and (b). Analysis on spatial distribution of the wavefunction clarifies that the state is distributed away from the carbon wall [38]. This is the NFE state mentioned

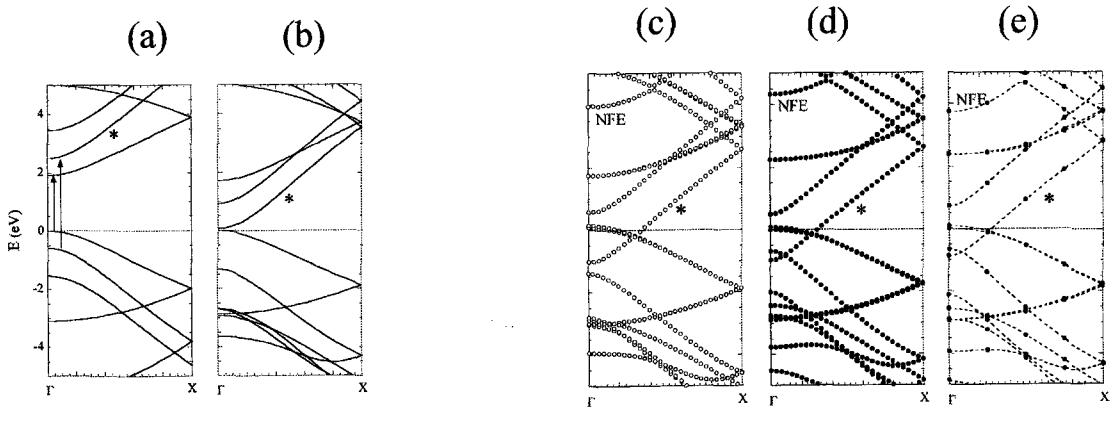

Fig.3: Electronic structure of the (5,0) nanotube. (a) π-only TB, (b) $\pi\sigma$-TB, (c) LDA for fixed geometry, (d) LDA for relaxed geometry, and (e) GW results. The energy is measured from the top of the valence band in (a) and (b), and from the Fermi level in (c)-(e). Arrows in (a) indicate optically active transitions. Dashed lines in (e) are guides for the eye.

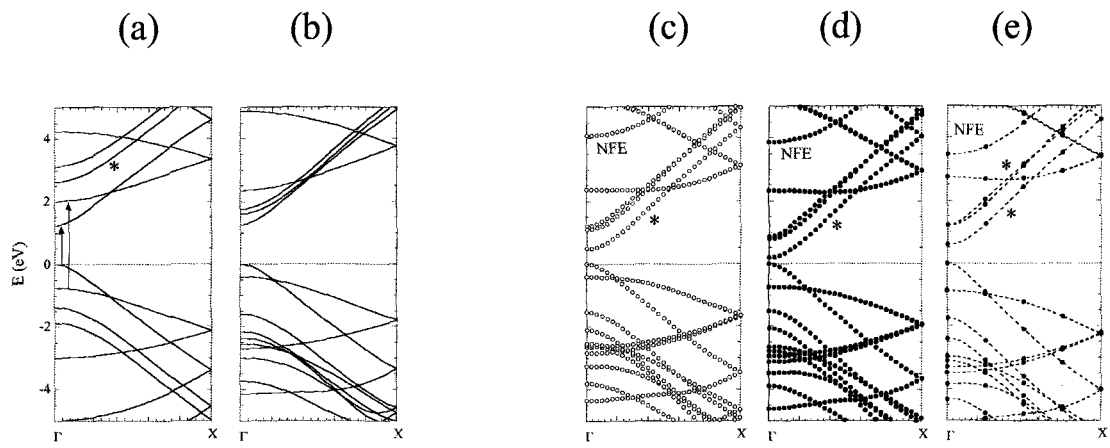

Fig.4: Electronic structure of the (7,0) nanotube. (a) π-only TB, (b) $\pi\sigma$-TB, (c) LDA for fixed geometry, (d) LDA for relaxed geometry, and (e) GW results. The energy is measured from the top of the valence band. Arrows in (a) are the first and second lowest optically allowd transitions.

above. Figure (d) shows that the NFE state is raised up by lattice relaxation.

In order to see whether the metallic character is an artifact of LDA which tends to underestimate the band gap, we estimate the many-body effect due to electron-correlations within the GW approximation. The band dispersion with the GW many-body correction is shown in (e). We see that the many-body correction is small, except for the NFE state which is pulled down. We also performed calculation for the (6,0) nanotube. In this tube, the * state crosses the Fermi level in the LDA band dispersion, hence the tube is metallic in contradict with the π-σ TB result, in which the (6,0) tube is a narrow-gap semiconductor. We found the GW correction is minor again and the (6,0) tube is metallic also in the GW calculation. These GW calculations for the two metallic tubes imply that the LDA gives accurate band dispersion for thin metallic nanotubes. On the other hand, as described above, the many-body correction is also not remarkable in graphene. Combining these facts, we can expect that the LDA gives reasonable band structure of metallic tubes in the whole diameter region.

Finally, we discuss the (7,0) nanotube. The electronic structures by (a) the π-only TB, (b) $\pi\sigma$-TB for fixed geometry, (c) LDA for fixed geometry, (d) LDA for relaxed geometry, and (e) GW approximation for relaxed geometry are shown in Fig.4. As we move from the π-only TB to π-σ TB, LDA, i.e. the number of the basis is increased, the * band is pulled down. However, the band does not cross the Fermi level and the (7,0) tube is a semiconductor even at the LDA level, following the 1/3 rule. The LDA gap is 0.5 eV for the fixed geometry. We note that the fundamental gap in the LDA band dispersion is not optically allowed, because the lowest unoccupied band is the * band which is not the "symmetric" band to the highest occupied band.

The electronic structure is modified when the geometry is optimized. The gap is reduced considerably to 0.2 eV. The LDA predicts the (7,0) tube is narrow-gap semiconductor. When the many-body correction is included in the GW approximation, on the other hand, the gap is increased to 0.6 eV. Thus, both lattice relaxation and many-body correction are crucial in discussing thin semiconducting nanotubes. This is in contrast with metallic cases. The NFE state is shifted down again by inclusion of the many-body correction.

4. CONCLUDING REMARKS

We have investigated the electronic structure of carbon nanotubes. The lattice relaxation is performed with the LDA in the framework of DFT, and many-body correction to LDA is estimated within the GW approximation. In the thin nanotubes, the * band is pulled down partly because of hybridization between the π and σ otbitals. As a result, neither 1/3 nor 1/d rules hold in the small-diameter tubes. The (7,0) tube is a semiconductor, whereas the (5,0) and (6,0) tubes are confirmed to be metallic. On the other hand, the band gap follows 1/d rule for d>0.8 nm, for which the band folding analysis starting from graphene band would work.

The GW many-body correction to the LDA band dispersion is found to be significant in the (7,0) nanotube, while it is small in the (5,0), (6,0) tubes, and graphene. This suggests the LDA electronic structure is reasonable except for thin semiconducting nanotubes, for which the band gap is underestimated considerably. We also found that the effect of geometry optimization on the band dispersion is sizable for the (7,0) nanotube. Therefore, we need to be careful when discussing thin semiconducting tubes. Our GW results can be compared with the STM-STS data or photoemission spectra. Precise measurements of individual tubes are desirable. On the other hand, direct comparison with the optical data needs to include exciton effects, which is still an open question.

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