1. Introduction

Nano-carbon materials and hetero-materials including borons (B) and nitrogens (N) have been attracting much attention both in the fundamental science and in the interests of application to nanotechnology devices.1,2 Their physical and chemical properties change variously depending on geometries.1–3 In carbon nanotubes, diameters and chiral arrangements of hexagonal pattern on tubules decide whether they are metallic or not.1,2 The BN nanotubes are intrinsic semiconductors, which have been predicted theoretically.4 This property has been experimentally observed in single-wall BN nanotubes, quite recently.3

In this paper, we study optical absorption spectra of BN nanotubes. We use the single-excitation configuration interaction (single-Cl) technique in order to consider exciton effects.5 In the model, we have treated the difference between B and N by the site energies, $E_B > 0$ and $E_N < 0$. The same model should be valid for optical properties. We consider zigzag BN nanotubes with the chirality indices $(n, 0)$ for $n = 2, 3, 4, 5$. The calculations will be done for the real geometries, so thin nanotubes are treated only.

We will report the following properties: (1) the binding energy of excitons is about 0.5 eV at $(U, V) = (2t, 1t)$ with $t = 1.1$ eV for the $(5, 0)$ nanotube. Similar magnitudes have been obtained in the recent band calculations. (2) This binding energy is comparable with that of the carbon nanotube $\sim 0.4$ eV. (3) The constant optical gap and exciton binding energy with respect to the chirality index $(n, 0)$ are obtained. This property agrees with recent experiments.5

This paper is organized as follows. In §2, we explain the model and method. In §3, we report electronic density of states (DOS) and optical absorption spectra for the $(5, 0)$ nanotube. In §4, we discuss binding energy of the exciton. The paper is closed with a short summary in §5.

2. Model and Method

Figure 1(a) illustrates the geometry of the BN plane, where $N$ and $L$ are the width and length of the honeycomb structure, respectively. The filled and open circles are B and N atoms, respectively. After rolling up the plane in the $y$ direction, the plane becomes the nanotube as shown in Fig. 1(b). The electronic systems are imposed with periodic boundary condition in the $y$ direction. The $x$-axis is parallel to the nanotube cylinder.

We treat a half-filled $\pi$-electron system on the BN nanotube using the extended Hubbard Hamiltonian with the on-site $U$ and nearest-neighbor $V$ Coulomb interactions. The model is as follows:

$$H = E_B \sum_{i \in B, \sigma} c_{i,\sigma}^\dagger c_{i,\sigma} + E_N \sum_{i \in N, \sigma} c_{i,\sigma}^\dagger c_{i,\sigma}$$

$$- t \sum_{[i,j], \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}$$

$$+ U \sum_i c_{i, \uparrow}^\dagger c_{i, \uparrow} - \frac{n_d}{2} \left( c_{i, \downarrow}^\dagger c_{i, \downarrow} - \frac{n_d}{2} \right)$$

$$+ V \sum_{[i,j]} \left( \sum_{\sigma} c_{i,\sigma}^\dagger c_{j,\sigma} - n_d \right) \left( \sum_{\tau} c_{i,\tau}^\dagger c_{j,\tau} - n_d \right).$$

where $E_B$ and $E_N$ are the site energies at the B and N sites, respectively; the sum with $i \in B$ and $i \in N$ are taken over the B and N atoms, respectively; $c_{i,\sigma}$ annihilates a $\pi$-electron of spin $\sigma$ at the $i$th site; $t = 1.1$ eV is the hopping integral between the nearest neighbor $i$th and $j$th sites; the sum with $[i,j]$ is taken for all the pairs of the nearest neighbor sites; $n_d$ is the average electron density of the system. We adopt the Hartree–Fock approximation to this model.6

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**Exciton Effects in Optical Absorption Spectra of Boron–Nitride Nanotubes**

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Exciton effects are studied in single-wall boron–nitride (BN) nanotubes. The Coulomb interaction dependence of the band gap, the optical gap, and the binding energy of excitons are discussed. The optical gap of the $(5, 0)$ nanotube is about 6 eV at the onsite interaction $U = 2t$ with the hopping integral $t = 1.1$ eV. The binding energy of the exciton is 0.50 eV for these parameters. This energy agrees well with that of other theoretical investigations. We find that the energy gap and the binding energy are almost independent of the geometries of nanotubes. This novel property is in contrast with that of the carbon nanotubes which show metallic and semiconducting properties depending on the chiralities. © 2009 The Japan Society of Applied Physics

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We write the singlet electron–hole excitations as
\[
|\mu, \lambda\rangle = \frac{1}{\sqrt{2}} (c_{\mu, i}^\dagger c_{\lambda, i} + c_{\lambda, i}^\dagger c_{\mu, i}) |g\rangle,
\]
where \( \mu \) and \( \lambda \) mean unoccupied and occupied states, respectively, and \( |g\rangle \) is the Hartree–Fock ground state. The general expression of the \( k \)th optical excitation is:
\[
|k\rangle = \sum_{(\mu, \lambda)} D_{k, (\mu, \lambda)} |\mu, \lambda\rangle.
\]
After inserting the relation with the site representation \( e_{\mu, \sigma} = \sum_i a_{\mu, i} c_{i, \sigma} \), we obtain
\[
|k\rangle = \frac{1}{\sqrt{2}} \sum_{(i, j)} B_{k, (i, j)} (c_{i, j}^\dagger c_{j, i} + c_{j, i}^\dagger c_{i, j}) |g\rangle,
\]
where
\[
B_{k, (i, j)} = \sum_{(\mu, \lambda)} D_{k, (\mu, \lambda)} e_{\mu, i}^* e_{\lambda, j}.
\]
Optical absorption spectra are calculated with the above formalism.

3. Density of States and Optical Spectra

The density of states (DOS) and optical spectra of the (5, 0) tube are shown in Fig. 2 as the representative case. The unit of the energy is scaled with \( t \). Figures 2(a) and 2(b) show the DOS for the parameters \( (U, V) = (0, 0) \) and \( (2t, 1t) \). The site energies \( E_0 = +t \) and \( E_N = -t \) are assumed. The same parameters have been used in ref. 8. When there is not the Coulomb interactions, intrinsic band gap exists owing to the large site energies. The one-dimensional van-Hove singularities are seen clearly in Fig. 2(a). When the Coulomb interactions are switched on, the band gap becomes larger due to the one-site correlation after the Hartree–Fock treatment. This property can be seen in Fig. 2(b).

The optical spectrum for \( (U, V) = (0, 0) \) is shown in Fig. 2(c). There is the on-set of the optical absorption at the energy about \( 2t \). Some structures from the van-Hove singularities are present also. When the Coulomb interactions are included, the optical spectrum becomes narrow as shown in Fig. 2(d) for \( (U, V) = (2t, 1t) \). The main feature shifts to higher energies due the wider band gap. The narrowness of the feature is due to the one-dimensional exciton effects, which have been reported for conjugated polymers \(^9\) and carbon nanotubes. \(^{10}\)

4. Binding Energy of Exciton

The binding energy of the exciton is calculated as the difference between the on-set energy of the optical absorption (optical gap) and the energy gap of the Hartree–Fock ground state. This definition is explained in the literature, for example. \(^9\) The binding energy will be reported as the function of the chirality index \((n, 0)\) and the Coulomb interaction \( U \). We fix \( V = U/2 \), because of our finding of this empirical relation in the optical properties of \( C_60 \) \(^6\) and conjugated polymers. \(^9\)

Figures 3(a)–3(d) show the Hartree–Fock band gap (circles), the optical gap (triangles), and the binding energy (squares), for the chirality indices \((n, 0)\) with \( n = 2–5 \), respectively. We find almost negligible dependence on the chirality index. This is due to the large on-site energy, and the intrinsic gap magnitude \( 2\Delta \equiv E_0 - E_N \). The effect of the chirality index dependence is the correction of the order
The energy is in the unit of functions. They become $2/C_1$ (optical gap, triangles), and exciton binding energy (squares) vs $\frac{1}{2} \sqrt{\Delta^2 + \gamma^2 (k_y^2 + k_z^2)}$. These three quantities depend on the difference of the atom species. Between the two systems seems interesting in view of the difference in the ideas between the Bethe–Salpeter approach and the Hartree–Fock plus CI method.

5. Summary

In summary, the binding energy of excitons of the BN nanotubes is considered by the single-CI method. We have found that the magnitude is about 0.5 eV at the parameters $(U, V) = (2t, 1t)$ with $t = 1.1$ eV for the $(5,0)$ nanotube. We have noted that the similar values have been obtained in the recent band calculations. This binding energy is comparable with that of the carbon nanotube $\sim 0.4$ eV, too. The constant optical gap and exciton binding energy with respect to the chirality index $(n,0)$ have been obtained in agreement with recent experiments.

Appendix

In the continuum model of the BN nanotubes, the dispersion relation of the electrons is,

$$E = \pm \sqrt{\Delta^2 + \gamma^2 (k_y^2 + k_z^2)},$$  

(A-1)

where the wavenumber $k_y$ is parallel to the nanotube axis. As $k_y$ is of the order of $2\pi/L$, $E$ is expanded as follows at the bottom or top of the energy bands $k_y = 0$:

$$E \sim \Delta (1 + \gamma^2 k_y^2 / 2\Delta^2).$$  

(A-2)

Using the relation $\gamma = \sqrt{3}\alpha t / 2$, we have obtained that the second term is of the order of $[(t/\Delta) \times (a/L)]^2$.

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