

## Electronic and optical properties of finite zigzag carbon nanotubes with and without Coulomb interaction

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The effects of electron-electron interaction on properties of zigzag carbon nanotubes with caps at both ends are theoretically investigated by employing an extended Peierls-Hubbard model. The electron-electron interaction is treated within the frame of Hartree-Fock approximation. Then the electronic structures and optical properties of zigzag nanotubes with and without the electron-electron interaction are investigated. Furthermore, we also study the dependence of its electronic and optical properties on its length. [S0163-1829(98)06615-6]

### I. INTRODUCTION

A great deal of interest has been generated by  $C_{60}$  molecules, by their unique symmetry and by their special properties.<sup>1,2</sup> Closely related to the  $C_{60}$  molecules are higher-order fullerenes such as  $C_{70}$ ,  $C_{76}$ , and  $C_{84}$  which also have been studied.<sup>3</sup> A graphitic carbon nanotube has recently been obtained by wrapping a single graphite sheet onto a long tubule.<sup>4,5</sup> Carbon nanotubes are regarded as low-dimension carbon systems that have been widely used in applications as lightweight, strong, and conductive materials.<sup>6</sup> Considering the large optical nonlinearity of carbon fullerenes,<sup>7</sup> the carbon nanotubes may also be possible candidates for application in optical devices. So it is not only important but also interesting and useful to investigate properties of the carbon nanotubes both from experimental and theoretical viewpoints.

There are several classifications of the graphene nanotubes with caps, depending on whether they are related to a fivefold or threefold symmetry.<sup>8</sup> The graphene nanotubes consist of a graphene sheet rolled up in one dimension to form a cylinder with top and bottom edges that fit perfectly on a cap at either end. The caps can be formed by cutting the  $C_{60}$  molecule in half. So the carbon nanotubes can be generated as the members of a series of fullerenes as  $C_{60+10j}$  and  $C_{60+18j}$ , where  $j$  is a positive integer, and they can be considered as high-order fullerenes.

The electronic properties of carbon nanotubes have been investigated in some papers.<sup>9-11</sup> In a discussion of the metallicity and Peierls distortion, from the model including electron-phonon interaction, it is concluded that a carrier density of some kinds of fullerene nanotubes is similar to that of metals, and their band gaps are zero at room temperature.<sup>9</sup> Also, a simple tight-binding model shows that some tubes are metallic and stable against perturbation of the one-dimensional energy bands, but their conclusion is based on assuming all the bonds in a graphene carbon tube are identical.<sup>10</sup> In Ref. 11, Peierls distortion is considered to study the electronic properties of the carbon nanotubes, and more reasonable results are obtained, but there, only the nanotubes without caps are studied, in other words, the effects of the caps are omitted.

Further investigating in this direction, we will acquire de-

tailed knowledge about the properties of carbon nanotubes. It is well known that the electron-electron interaction plays an important role in the electronic properties of fullerenes. The electron-electron interaction should also be taken into account to investigate the optical properties of fullerenes.<sup>12</sup> In Ref. 12, to reasonably describe the optical absorption spectrum of fullerenes observed in experiment, Hubbard Coulomb terms are included in the model, and the obtained results are in good agreement with the experimental data, which implies that the electron-electron interaction affects the properties of the fullerene system. Now, detailed investigation for carbon nanotubes has been absent so far. Taking into account that the electronic interaction cannot be omitted, in this paper, taking the zigzag nanotube as an example, we study how electronic structures of carbon nanotubes are influenced as results of the mutual interaction. Since the investigation on optical properties of carbon nanotubes is also absent, based on the sum-over-states (SOS) approach,<sup>13</sup> we have studied the optical absorption spectrum for zigzag nanotubes. The dependencies of the electronic and optical properties of the nanotube on its length are also studied in this paper. The structure of the zigzag nanotube is depicted in Fig. 1. From Fig. 1(a), one can find that the cap of a zigzag nanotube is formed by truncating the  $C_{60}$  molecule, and it contains 39 carbon atoms. The cylindrical tube is formed by rows of nine zigzag hexagons, and its zigzag row is displayed by the dot-dash vector [see Fig. 1(b)]. Rolling up the sheet in Fig. 1(b), covering point  $B$  by point  $A$ , one can get a cylindrical tube which fits the cap well.

### II. MODEL AND THE NUMERICAL METHOD

It is known that the electron-phonon interaction in the one-dimensional system gives rise to instabilities and dimerization. Regarding the carbon nanotubes as one-dimensional systems, we employ the extended Peierls-Hubbard model,<sup>14,15</sup> where the on-site and nearest-neighbor Coulomb interactions are taken into account in the Su-Schrieffer-Heeger (SSH) model. As we know that the electron-phonon interaction is included in the SSH model, which will cause the Peierls distortion, in our present investigation, the dimerization in carbon nanotubes due to the Peierls instabilities is included, or, in other words, the change in the bonds is considered. Because in systems like carbon nanotubes the inter-

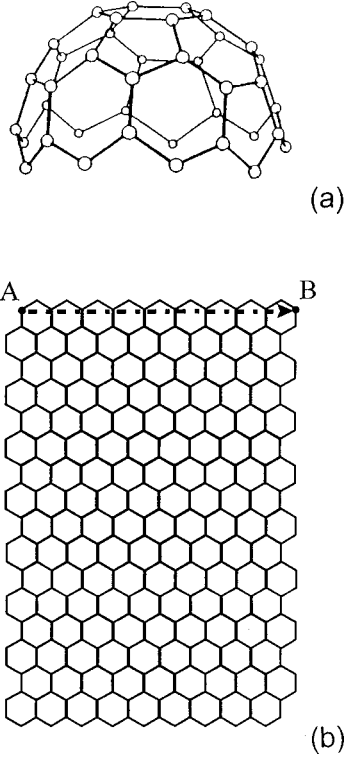


FIG. 1. The structure of the zigzag carbon nanotube. (a) The cap formed by truncating a  $C_{60}$  molecule. (b) The cylindrical tube formed by rolling up this sheet and joining points A and B which are two ends of the dot-dash vector indicating the zigzag row.

action is not strong, the Hartree-Fock approximation is appropriate. In the meantime, it can be assumed that Coulomb interaction strength decreases exponentially as the electrons separate distantly. So the interactions are naturally limited to the electrons only on one site and on nearest-neighbor sites.

To examine the property of carbon nanotubes, we take the zigzag nanotubes as examples. According to the topological structure of the zigzag carbon nanotubes in Fig. 1, one can construct its Hamiltonian matrix.

In order to describe the zigzag nanotubes, we utilize the extended Peierls-Hubbard Hamiltonian,<sup>14</sup>

$$H = \sum_{\langle ij \rangle, s} (-t_0 - \alpha_0 y_{ij}) (c_{is}^\dagger c_{js} + \text{H.c.}) + \frac{K_0}{2} \sum_{\langle ij \rangle} y_{ij}^2 + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} + V \sum_{\langle ij \rangle} \left( \sum_s c_{is}^\dagger c_{is} \right) \left( \sum_{s'} c_{js'}^\dagger c_{js'} \right), \quad (1)$$

where  $c_{is}^\dagger$  and  $c_{is}$  are the usual creation and annihilation operators of a  $\pi$  electron at the  $i$ th carbon atom with spin  $s$ , respectively;  $t_0$  is the hopping integral of the undimerized system,  $\alpha_0$  is the coupling constant between electron and phonon, and  $y_{ij}$  is the change of the bond length between  $i$ th and  $j$ th atoms. The sum over  $\langle ij \rangle$  is taken over nearest-neighbor pair sites  $\langle ij \rangle$ . The second term is the elastic energy of the phonon system with the  $K_0$  as the spring constant.  $U$  is the on-site Coulomb repulsion strength, and  $V$  is the Coulomb strength between the nearest-neighbor sites.

Assuming the electron-electron interaction is not strong, the above-mentioned Hamiltonian can be treated by Hartree-Fock approximation. We utilize the same method as used in Refs. 15 and 16. From mean-field theory, we can use

$$U[\langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle c_{i\downarrow}^\dagger c_{i\downarrow} + c_{i\uparrow}^\dagger c_{i\uparrow} \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle - \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle] \quad (2)$$

and

$$V \sum_{s, s'} [(\langle c_{is}^\dagger c_{is} \rangle c_{js'}^\dagger c_{js'} + c_{is}^\dagger c_{is} \langle c_{js'}^\dagger c_{js'} \rangle - \langle c_{is}^\dagger c_{is} \rangle \langle c_{js'}^\dagger c_{js'} \rangle) - (\langle c_{is}^\dagger c_{js'} \rangle c_{js'}^\dagger c_{is} + c_{is}^\dagger c_{js'} \langle c_{js'}^\dagger c_{is} \rangle) - (\langle c_{is}^\dagger c_{js'} \rangle \langle c_{js'}^\dagger c_{is} \rangle)] \quad (3)$$

to replace the third and fourth terms of Eq. (1), respectively. Then Eq. (1) would be

$$H_{\text{HF}} = \sum_{\langle ij \rangle, s} (-t_0 - \alpha_0 y_{ij}) (c_{is}^\dagger c_{js} + \text{H.c.}) + \frac{K_0}{2} \sum_{\langle ij \rangle} y_{ij}^2 + U \sum_i \left( \sum_s \rho_{i, -s} c_{is}^\dagger c_{is} - \rho_{i\uparrow} \rho_{i\downarrow} \right) + V \sum_{\langle ij \rangle, s, s'} \rho_{js'} c_{is}^\dagger c_{is} - V \sum_{\langle ij \rangle, s, s'} \rho_{is} \rho_{js'} - V \sum_{\langle ij \rangle, s} [\tau_{ij, s} (c_{is}^\dagger c_{js} + \text{H.c.}) - \tau_{ij, s}^2]. \quad (4)$$

Then the eigenvalue  $\epsilon_{ks}$  and eigenfunction  $\psi_{ks}$  are determined by

$$\epsilon_{ks} \psi_{ks}(i) = \sum_{\langle ij \rangle} (-t_0 - \alpha_0 y_{ij} - V \tau_{ij, s}) \psi_{ks}(j) + V \sum_{\langle ij \rangle, s'} \rho_{js'} \psi_{ks}(i) + U \rho_{i, -s} \psi_{ks}(i), \quad (5)$$

where the  $\rho_{is}$  is the electron density,

$$\rho_{is} = \langle c_{is}^\dagger c_{is} \rangle = \sum_k' \psi_{ks}^2(i), \quad (6)$$

and

$$\tau_{ij, s} = \langle c_{is}^\dagger c_{js} \rangle = \langle c_{js}^\dagger c_{is} \rangle = \sum_k' \psi_{ks}(i) \psi_{ks}(j), \quad (7)$$

where the prime indicates the sum over occupied states. Using the constraint condition  $\sum_{\langle ij \rangle} y_{ij} = 0$ , we can obtain the self-consistency equation for  $y_{ij}$ ,

$$y_{ij} = \frac{2\alpha_0}{K_0} \sum_{k, s}' \psi_{ks}(i) \psi_{ks}(j) - \Delta y, \quad (8)$$

where

$$\Delta y = \frac{1}{N} \sum_{\langle ij \rangle} \frac{2\alpha_0}{K_0} \sum_{k, s}' \psi_{ks}(i) \psi_{ks}(j), \quad (9)$$

where  $N$  is the number of  $\pi$  bonds. The coupled equations (5)–(9) can be solved iteratively and the ground state within

the frame of Hartree-Fock approximation is obtained. Then the total energy  $E$  is raised as follows:

$$E = \sum'_{k,s} \epsilon_{ks} + \frac{K_0}{2} \sum_{\langle ij \rangle} y_{ij}^2 - U \sum_i \rho_{i\uparrow} \rho_{i\downarrow} - V \sum_{\langle ij \rangle} \left( \sum_s \rho_{is} \right) \times \left( \sum_{s'} \rho_{js'} \right) + V \sum_{\langle ij \rangle, s} \tau_{ij,s}^2. \quad (10)$$

### III. ELECTRONIC PROPERTIES OF ZIGZAG CARBON NANOTUBES

The above-mentioned Hartree-Fock approximation is valid as the electron-electron interaction is not strong, and it is applied successfully within  $2.0t_0 \geq U \geq 0$  and  $1.0t_0 \geq V \geq 0$ .<sup>15</sup> In the numerical calculation, parameters are taken to be same as those used for other carbon fullerenes in Refs. 7 and 17:  $t_0 = 2.5$  eV,  $\alpha_0 = 6.31$  eV/Å, and  $K_0 = 49.7$  eV/Å<sup>2</sup>. According to the topological structure of zigzag tubules, we construct the iterative equations and compute them.

It is known that the zigzag nanotubes with caps possess threefold symmetry, which causes the symmetries among the elements of the initial matrix of the Hamiltonian. However, the symmetries among the initial elements of the Hamiltonian matrix are destroyed gradually by the iteration, which is reflected in the topological structure by  $y_{ij}$ . The undimerized zigzag nanotubes possess threefold symmetry, however, if the dimerization presents, or, in other words, the atom leaves its initial site, the threefold symmetry is destroyed. This phenomenon is described by  $y_{ij}$ , which shows the change in bonds. So it is necessary to develop an investigation of  $y_{ij}$ . Furthermore, from the sum-over-states approach,<sup>7</sup> one can know that the change of topological structures of the system will affect its optical properties. Therefore it is important to analyze  $y_{ij}$  for various lengths of zigzag nanotubes and various strengths of electron-electron interaction.

By computing coupled equations (5)–(9), from Eq. (8),  $y_{ij}$ , the change in bond length between the  $i$ th and  $j$ th atoms in an undimerized system can be obtained. The  $1/N$  dependence of the average of the absolute value of  $y_{ij}$ ,  $\overline{|y_{ij}|}$ , which indicates the strength of distortions, is shown in Fig. 2, where lines (1), (2), and (3) are for  $U=V=0$ ;  $U=1.0t_0$ ,  $V=0.5t_0$ ; and  $U=2.0t_0$ ,  $V=1.0t_0$ , respectively, and  $N$  is the number of carbon atoms. In Fig. 2,  $N$  are 132, 168, 204, ..., 384, respectively, and the unit for the y axis is Å. From Fig. 2, one can know that for a fixed  $N$ , the stronger electron-electron interaction, the larger  $\overline{|y_{ij}|}$ . This indicates that Coulomb interaction obviously raises the distortion of the topological structure of the system. One can also notice all three lines decrease linearly along with the decrease of  $1/N$ . From lines (1), (2), and (3), the extrapolated values  $\overline{|y_{ij}|}$  at  $N \rightarrow \infty$  for  $U=V=0$ ;  $U=1.0t_0$ ,  $V=0.5t_0$ ; and  $U=2.0t_0$ ,  $V=1.0t_0$  are figured out as 0.0022, 0.0027, and 0.0033 Å, respectively. Comparing these values with that of  $C_{60}$ , 0.022 Å, we can conclude that the infinitely long zigzag carbon nanotubes are almost exempted from distortion in spite of Coulomb interaction, and their threefold symmetries can be nearly preserved. The diameter of the experimentally

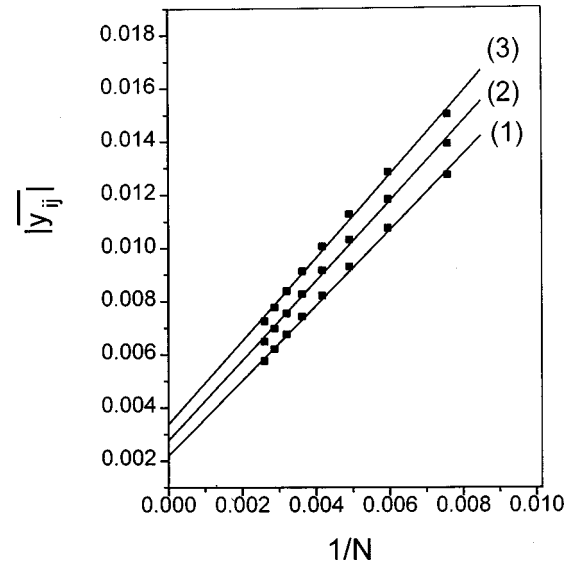


FIG. 2. Dependence of average absolute value of the bond change  $\overline{|y_{ij}|}$  on  $1/N$ . Lines (1), (2), and (3) are for  $U=V=0$ ;  $U=1.0t_0$ ,  $V=0.5t_0$ ; and  $U=2.0t_0$ ,  $V=1.0t_0$ , respectively. The unit of the y axis is Å.

generated nanotube is of the order of 1 nm and its length can reach 1  $\mu$ m, therefore, so it can be regarded as infinitely long, and its distortion should be much less.

Because the levels near the Fermi level play an important role in the properties of the material, we compute band gaps  $E_g$  with various numbers of carbon atoms of zigzag nanotubes for various  $U$  and  $V$ . We plot the dependence of  $E_g$  on  $1/N$  in Fig. 3, where  $N$  stands for the number of carbon atoms and is 96, 132, 168, ..., 384 respectively. As the  $1/N$  decreases, in Fig. 3, the values of lines (1), (2), and (3) for  $U=V=0$ ;  $U=1.0t_0$ ,  $V=0.5t_0$ ; and  $U=2.0t_0$ ,  $V=1.0t_0$ , respectively, decrease linearly. One can notice that at any  $1/N$  point, the  $E_g$  for  $U=0$ ,  $V=0$  is always lower than the one for  $U=1.0t_0$ ,  $V=0.5t_0$  which is always lower than the

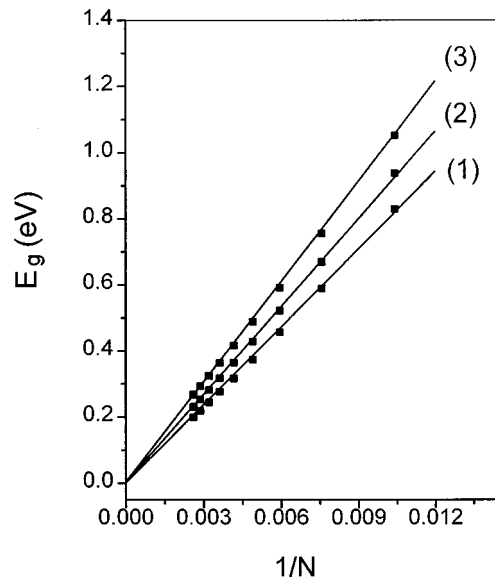


FIG. 3. Dependence of energy gap  $E_g$  on  $1/N$ . Lines (1), (2), and (3) are for  $U=V=0$ ;  $U=1.0t_0$ ,  $V=0.5t_0$ ; and  $U=2.0t_0$ ,  $V=1.0t_0$ , respectively.

one for  $U=2.0t_0$ ,  $V=1.0t_0$ . Therefore it can be concluded that the electron-electron interaction widens the band gaps. But we are more interested in the energy gaps with and without Coulomb interaction when  $N \rightarrow \infty$ . From Fig. 3, one can notice that at the  $N=384$  point, the energy gap for  $U=V=0$  is about 0.198 eV, and the one for  $U=2.0t_0$ ,  $V=1.0t_0$  is about 0.267 eV. The tendencies of three lines fit to three group data indicate that the energy gap should further decrease along with the increase of the length of the nanotube. So we can infer that as  $N$  is large enough,  $E_g$  can be, at least, less than 0.1 eV. On the other hand, from Fig. 3, one can notice that at the  $N=96$  point, the difference between the  $E_g$  for  $U=2.0t_0$ ,  $V=1.0t_0$  and the one for  $U=V=0$  is about 0.22 eV, but the difference at  $N=384$  is about 0.068 eV. It is obvious that the difference should further decrease along with the increase of  $N$ . Figure 3 indicates that the three lines fit to three groups of data almost reach the same value at  $N \rightarrow \infty$  which is a little over zero. The extrapolated values for three cases at  $N \rightarrow \infty$  are of order of  $10^{-3}$  eV. According to the extrapolated values from three lines, we may conclude that regardless of Coulomb interaction, the energy gap of a long enough zigzag nanotube with caps is still low enough to induce metallic behaviors.

We know that to fit to the edge of caps, every zigzag circle should contain 18 carbon atoms in this kind of zigzag nanotubes. It is already known there are some other kinds of zigzag carbon nanotubes without caps. Every kind corresponds to a particular number of carbon atoms contained in the zigzag circle. Furthermore, zigzag nanotube without caps can be metallic or semiconducting depending on the number, or speaking alternatively, depending on the diameter of the zigzag nanotube. However, we wonder whether Coulomb interaction changes the character of the semiconducting zigzag nanotube. It is known that in semiconducting cases, the energy gaps at  $N \rightarrow \infty$  reach a saturation value which is of the order of 1 eV.<sup>11</sup> From Fig. 3, it seems that the longer the tube, the weaker the effect of Coulomb interaction for energy gaps. So we can conclude that in the semiconducting case, the energy gap of a long enough tube for the Hamiltonian including Coulomb interaction may approximately preserve its value from the free electron model. In other words, a long enough semiconducting nanotube preserves its character in spite of mutual interaction.

From Ref. 11, one can know that in the metallic case, the per site energy is very insensitive to the change of the length of tubes, whose value is about  $-3.93$  eV. On the other hand, the electron-electron interaction inevitably affects the ground state of the system, and Fig. 3 can verify this viewpoint. Thus it is more interesting to investigate how the mutual interaction influences the per site energy. It is easy to compute the per site energy from the total energy given by Eq. (10). We plot our numerical results in Fig. 4. Figure 4(a) shows the dependence of per site energy on  $U$ , while the  $V$  is chosen as 0. Figure 4(b) shows the dependence of per site energy on  $V$ , while the  $U$  is chosen as  $2.0t_0$ . In Fig. 4, the number of carbon atoms  $N$  is chosen as 132. From Fig. 4(a), one can know that at the  $U=V=0$  point, the per site energy is a little less than  $-3.9$  eV. The per site energy increases along with the increase of the strength of electron-electron interaction. Figure 4(b) shows that the per site energy is a little over  $-2.2$  eV at the  $U=2.0t_0$ ,  $V=1.0t_0$  point. Consid-

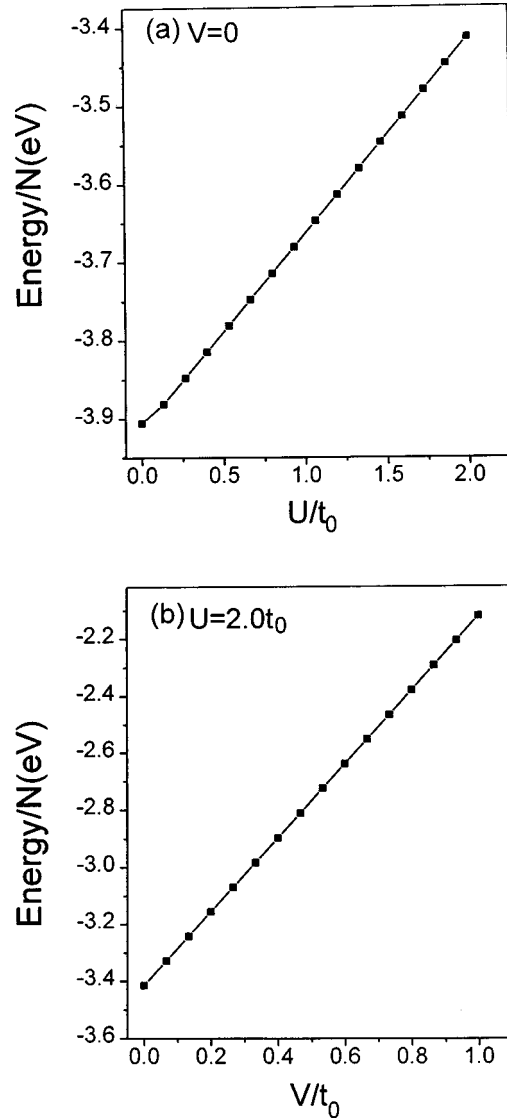


FIG. 4. Dependence of energy per site of tubes  $E/N$  on (a)  $U/t_0$  with  $V=0$ ; (b)  $V/t_0$  with  $U=2.0t_0$ .

ering that in the carbon fullerenes the electron-electron interaction is not strong, we can conclude that the energy per site of zigzag nanotubes should be in the range  $-2.0$ – $-4.0$  eV.

#### IV. OPTICAL PROPERTIES OF ZIGZAG CARBON NANOTUBES

Because the optical absorption spectrum reflects the electronic structure, we also investigate it for the zigzag nanotubes. Within the sum-over-states approach, the linear polarizability (optical absorption)  $\alpha(\omega)$  is<sup>7,13</sup>

$$\alpha(\omega) = \sum'_m \sum''_n \mu_{mn} \mu_{nm} \left( \frac{1}{E_{nm} - \omega - i\eta} + \frac{1}{E_{nm} + \omega + i\eta} \right), \quad (11)$$

where the prime indicates the sum over occupied states and double primes indicate sum over unoccupied states, and  $E_{nm} = \epsilon_n - \epsilon_m$ . The lifetime broadening factor  $\eta$  is included in the denominator of the above equation, which suppresses

the height of the resonant peaks, and is taken to be  $1.68 \times 10^{-2}$  eV. The dipole transition matrix is expressed as

$$\langle n | \mu_r | m \rangle = \sum_{j,s} \psi_{ns}^* (-er_j) \psi_{ms}(j). \quad (12)$$

Note that in the SOS approach, the contribution to the spectrum is given by every dipole transition between the occupied state  $|m\rangle$  and the unoccupied state  $|n\rangle$  in ground state. So the optical absorption spectrum is partially determined by the ground state of systems. Considering that the Hartree-Fock method is valid applicable to small values of  $U$  and  $V$  compared with the transfer energy, from this method, one can obtain the ground state for the cases with the electron-electron interaction. Based on the ground state gained within the frame of the Hartree-Fock method, we can investigate the optical absorption spectrum of the system with Coulomb interaction. Then the optical absorption can also reflect the changes of levels motivated by the mutual interaction.

From Eq. (11), one can know that the main contribution to static  $\alpha$  is given by the hopping from the level under the Fermi level to one higher than the Fermi level in the energy region around the Fermi level. Furthermore, the contribution is inverse to the energy difference between the two levels. So the low-energy gap may lead to strong static optical absorption. Figure 3 suggests that the value of the static optical absorption spectrum for small  $N$  may be less than the one for large  $N$  due to a large energy gap, and since Coulomb interaction widens the energy gap, it would lower the value of the static optical absorption.

According to the standard method, we study the spatially averaged optical absorption, and it is given by

$$\alpha(\omega) = [|\alpha_{xx}(\omega)| + |\alpha_{yy}(\omega)| + |\alpha_{zz}(\omega)|] / 3. \quad (13)$$

We plot the numerical results for the optical absorption spectrum for zigzag nanotubes in Fig. 5. Figures 5(a) and 5(b) are for  $U=V=0$  and 5(c) and 5(d) are for  $U=2.0t_0$ ,  $V=1.0t_0$ . In Fig. 5, the unit of the  $x$  coordinate is eV, and the unit of the  $y$  coordinate for  $\alpha(\omega)$  is  $10^4 e^2 a_0^2 E_h^{-1}$ , which is in atomic units. Here  $1E_h = 4.359 \times 10^{-18}$  J,  $1a_0 = 0.529 \times 10^{-10}$  m, and  $10^4 e^2 a_0^2 E_h^{-1} = 1.649 \times 10^{-37}$  C<sup>2</sup> m<sup>2</sup> J<sup>-1</sup>. We compute the spectra of a series of nanotubes with different lengths. The results for  $N=96$  are depicted by the thin lines in Figs. 5(a) and 5(c), and the thin lines in Figs. 5(b) and 5(d) are for  $N=204$ . The heavy lines in Figs. 5(a) and 5(c) are for  $N=312$ , and the heavy lines in Figs. 5(b) and 5(d) are for  $N=420$ . From Figs. 5(a) and 5(b) for  $U=V=0$ , comparing results for  $N=96$ , 204, 312, and 420, it is obvious that the long zigzag nanotube possesses strong optical properties. From Figs. 5(b) and 5(d) for  $U=2.0t_0$  and  $V=1.0t_0$ , the same conclusion can be drawn. We are also interested in the effects of Coulomb interaction on the optical absorption spectrum. From Fig. 5, one can know that the peaks of the spectrum of a zigzag tube are shifted backwards by mutual interactions, and meanwhile, their heights are suppressed. For an example, the main peaks of the line for  $N=96$  in Fig. 5(a) are located around 1.5 and 2.75 eV, and the highest peak is more than 3 units of the  $y$  axis. But main peaks for  $N=96$  with  $U=2.0t_0$ ,  $V=1.0t_0$  are located around 1.75 and

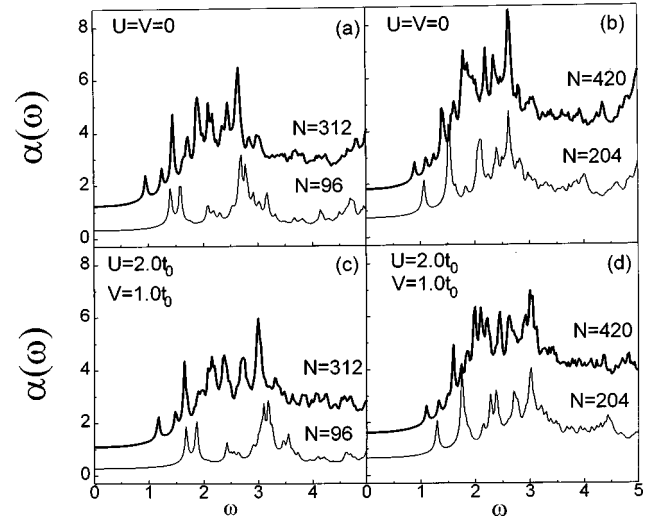


FIG. 5. The optical absorption spectrum for zigzag nanotubes: (a) and (b) are for  $U=V=0$ , and (c) and (d) are for  $U=2.0t_0$ ,  $V=1.0t_0$ . The thin lines in (a) and (c) are for  $N=96$  and the thin lines in (b) and (d) are for  $N=204$ . The heavy lines in (a) and (c) are for  $N=312$  and the heavy lines in (b) and (d) are for  $N=420$ . The unit of the  $x$  coordinate is eV and the unit of the  $y$  axis is  $10^4 e^2 a_0^2 E_h^{-1}$ .

3.1 eV, and the highest peak is less than 3 units of the  $y$  axis. One can also find that mutual interactions with  $U=2.0t_0$ ,  $V=1.0t_0$  shift backwards the highest peak for  $N=204$  with  $U=V=0$  from 2.6 to 3 eV, and lessen its value from 4.8 units to 4 units. The same conclusion can be drawn from two lines for  $N=312$ . For an example, the highest peak of  $N=312$  in Fig. 5(a) is suppressed from more than 6 units to less than 6 units, and its location is shifted backwards from 2.6 to 3.0 eV [see Fig. 5(c)]. Careful comparison indicates that the whole line for  $N=420$  in Fig. 5(b) is lower than the one for  $N=420$  in Fig. 5(d), moreover, its peaks are shifted backwards obviously by Coulomb interaction. Our conclusion for Coulomb interaction on optical properties of zigzag nanotubes agrees well with that for  $C_{60}$ .<sup>12</sup> Further comparing Figs. 5(a), 5(b), 5(c), and 5(d) carefully, one can easily find that the longer the zigzag tube, the larger the value of its static  $\alpha$ . Moreover, it is obvious that the value of static  $\alpha$  without Coulomb interaction is higher than the one with Coulomb interaction. For an example, the line for  $N=420$  in Fig. 5(b) indicates the value of static  $\alpha$  is about 1.8 units of the  $y$  axis, but its value in Fig. 5(d) is about 1.6 units. So our above inference deduced from Fig. 3 in the preceding paragraph is justified. We know the static optical absorption is important in experiment. To get the detailed information, we investigate the static optical absorption  $\alpha(0)$ . The numerical results for static  $\alpha$  are plotted in Fig. 6, where lines (1) and (2) are for  $U=2.0t_0$ ,  $V=1.0t_0$  and  $U=V=0$ , respectively. In Fig. 6,  $N$  stands for the number of carbon atoms in the tube, and is 96, 132, 178, ..., 420, respectively. The unit of the  $y$  coordinate is the same as used in Fig. 5. Two lines in Fig. 6 indicate that the increase of static  $\alpha$  almost yields linearity along with the increase of  $N$ . The difference between the value of  $\alpha(0)$  for  $U=V=0$  and the one for  $U=2.0t_0$ ,  $V=1.0t_0$  increases along with the increase of the  $N$ . One can also find that at any  $N$  point, the static  $\alpha$  for  $U$

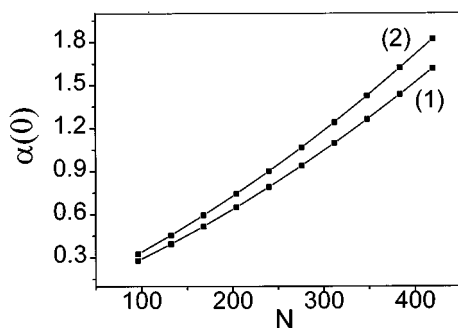


FIG. 6. Dependence of the static optical absorption spectrum on the number of carbon atoms of zigzag tubes. Lines (1) and (2) are for  $U=2.0t_0$ ,  $V=1.0t_0$  and  $U=V=0$ , respectively. The unit of the y coordinate is the same as that used in Fig. 5.

$=V=0$  is always larger than the one for  $U=2.0t_0$ ,  $V=1.0t_0$ , which agrees with Fig. 5. We know that the zigzag nanotubes can be divided into several kinds. One kind of infinitely long zigzag tubes preserves zero energy gap, and the semiconducting kind preserves about 1 eV gap. It is obvious that our inference in the preceding paragraph is justified completely by Figs. 5 and 6, so we can further conclude that the value of static  $\alpha$  of an infinitely long zigzag tube with caps should be higher than that of the infinitely long semiconducting one. We think the above results and conclusions can be verified by future experiments.

## V. SUMMARY

In this paper, taking the zigzag carbon nanotubes with caps at both ends as examples, we study the electronic and optical properties of zigzag carbon nanotubes. It is shown that Coulomb interaction raises the distortion in the zigzag nanotubes with caps, but it seems that the long enough tubes possess very slight distortion. Although Coulomb interaction heightens the energy gaps, we find that the longer the zigzag nanotubes, the lower the energy gaps, which indicates that a long enough zigzag carbon nanotube still induces its metallic behavior. Moreover, based on assuming that the electron-electron interaction is not strong, it is concluded that the energy per site of tubes is in the range  $-2.0$ – $-4.0$  eV.

On the other hand, Coulomb interaction shifts the peaks of the optical absorption spectrum to a relatively high-energy region, and suppresses the height of the peaks of the optical absorption spectrum. However, from the comparison among the optical absorption spectra for  $N=96$ , 204, 312, and 420, it can be concluded that the long zigzag nanotubes would possess strong optical properties. From the static  $\alpha$  spectrum for various lengths of zigzag nanotubes, the same viewpoint could be drawn. Although the value of parameters  $U$ ,  $V$  in the model should be determined by experiments, because the parameters used in this paper reveal how Coulomb interaction influences the electronic and optical properties, our conclusion remains valid for different strengths of electron-electron interaction.

<sup>1</sup>W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990).

<sup>2</sup>G. Meijer and D. S. Bethune, *J. Chem. Phys.* **93**, 7800 (1990).

<sup>3</sup>F. Diederich, R. Ertle, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani, and A. Koch, *Science* **252**, 548 (1991).

<sup>4</sup>S. Iijima, *Nature (London)* **354**, 56 (1991).

<sup>5</sup>S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993).

<sup>6</sup>M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain, and H. A. Goldberg, in *Graphite Fibers and Filaments*, edited by M. Cardona, Springer Series in Materials Science Vol. 5 (Springer-Verlag, Berlin, 1988).

<sup>7</sup>J. Dong, J. Jiang, J. Yu, Z. D. Wang, and D. Y. Xing, *Phys. Rev. B* **52**, 9066 (1995).

<sup>8</sup>M. S. Dresselhaus, G. Dresselhaus, and R. Saito, *Phys. Rev. B* **45**,

6234 (1992).

<sup>9</sup>J. W. Mintmire, B. I. Dunlap, and C. T. White, *Phys. Rev. Lett.* **68**, 631 (1992).

<sup>10</sup>R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **46**, 1804 (1992).

<sup>11</sup>K. Harigaya and M. Fujita, *Phys. Rev. B* **47**, 16 563 (1993).

<sup>12</sup>K. Harigaya and S. Abe, *Phys. Rev. B* **49**, 16 746 (1994).

<sup>13</sup>Z. Shuai and J. L. Bredas, *Phys. Rev. B* **46**, 16 135 (1992).

<sup>14</sup>A. J. Heeger, B. Kivelson, J. R. Schrieffer, and S. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).

<sup>15</sup>K. Harigaya, *J. Phys.: Condens. Matter* **3**, 8855 (1991).

<sup>16</sup>K. Harigaya, A. Terai, Y. Wada, and K. Fesser, *Phys. Rev. B* **43**, 4141 (1991).

<sup>17</sup>J. Dong, J. Jiang, Z. D. Wang, and D. Y. Xing, *Phys. Rev. B* **51**, 1977 (1995).