Possible electric-field-induced one-dimensional excitonic insulators in pairs of carbon nanotubes

Jay D. Sau* and Marvin L. Cohen
Department of Physics, University of California–Berkeley, Berkeley, California 94720, USA
and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
(Received 25 July 2008; revised manuscript received 25 August 2008; published 29 September 2008)

Recent experimental and theoretical works have shown that the Stark effect induced by the electric field from a scanning tunneling microscope (STM) can be used to reduce the gap of a boron nitride nanotube. In this paper, using density-functional theory calculations, we study the effect of an electric field on a pair of semiconducting carbon nanotubes and find that the application of an electric-field strength of 0.05 eV/Å can close the Kohn-Sham gap of the system. Using a tight-binding formulation of the GW and Bethe-Salpeter methods we determine the quasiparticle and optical excitation spectrum of the system in an electric field and show that an electric-field strength of 0.06 eV/Å fails to close the quasiparticle gap but closes the excitonic gap. This can cause a phase transition of the system into an excitonic phase where the ground state is populated with a quasi-one-dimensional repulsive gas of excitons. We discuss some of the properties of the resulting excitonic phase and the transition and also discuss how similar properties may be observed in experiments on nanotube bundles.

DOI: 10.1103/PhysRevB.78.115436 PACS number(s): 73.22.Lp, 71.35.−y

I. INTRODUCTION

Coherent states of excitons such as excitonic insulators are correlated electronic states that have been discussed in the literature since the 1960s.[1] Since bound excitons which are bound states of electron-hole pairs are bosons, they are expected to display coherence properties such as those seen in Bose-Einstein condensation and other interesting phenomena such as ferromagnetism, solitons, and superluminescense which are associated with coherence of this kind.[2] Excitonic insulator phases have been conjectured to exist at the boundary of small gap semiconductor to semimetal transitions[2,3] where the energy gap of the semiconductor approaches zero. At some point in the transition, before the quasiparticle gap closes completely, one expects the exciton binding energy of an electron-hole pair to exceed the energy gap of the semiconductor. It has been argued[3] that for such systems it becomes energetically favorable to create electron-hole pairs and bind them into excitons. The original semiconductor ground state then becomes unstable with respect to a distorted state where there is a population of electrons and holes in the ground state of the semiconductor. The resulting state, however, is still insulating. Such a state can be described by a wave function similar to the Bardeen Cooper Schrieffer (BCS) wave function used to describe the superconducting state in metals.[1] Despite the number of systems studied and proposed in the past four decades, confirmatory evidence for a material in an excitonic insulator phase remains elusive.

Recently an alternative approach to obtaining coherent states of excitons was adopted[4] where a bilayer semiconductor heterostructure was subjected to an optical pump pulse to create a population of excitons. An electric field was applied to the bilayer such that the bands in one layer were energetically lowered compared to the bands in the other layer. The optical pump pulse generates a population of excitons in each layer which then quickly relaxes into a population of spatially indirect excitons with the electrons and holes in different layers. These excitons now have a relatively long lifetime. At high exciton densities, the photoluminescence images are seen to display interesting patterns, which were interpreted as a signature of possible coherence.[4] More recently theoretical work on graphene bilayers in electric fields[5,6] seems to suggest the possibility of condensation of similar spatially indirect excitons occurring in these systems.

Another system where interesting exciton physics has been observed is one composed of carbon nanotubes. Excitonic transitions are seen to dominate the low energy optical behavior of these systems, and the observed exciton binding energies are found to be an order of magnitude higher than in bulk semiconductor or semiconductor heterostructure systems. Furthermore, recent experimental and theoretical studies[7,8] have shown that it is possible to tune the gaps of semiconducting boron nitride nanotubes[9] through a Stark shift obtained by the application of an electric field. This creates the possibility of an electric field driven semiconductor to semimetal transition in analogy with that envisioned for bulk excitonic insulators as discussed earlier. Since the electron and hole states closest to the gap on the boron nitride nanotube are found to be localized on opposite sides of the tube, this implies the existence of indirect excitons in this system similar to those observed in the semiconductor heterostructure systems.[4]

Despite the possibility of being able to tune the gap of boron nitride nanotubes through the Stark shift, one needs a very large electric field to close the gap of such a nanotube because of the large initial gap of the boron nitride nanotube. Furthermore the conduction-band states of the boron nitride nanotubes are only 0.2 eV below the vacuum level making any possible excitonic state unstable in the presence of large electric fields. Semiconducting carbon nanotubes have a smaller gap and hence would be expected to require smaller fields to close the gap, however, the large screening effect from the small gap causes the Stark effect to be very weak for carbon nanotubes. As will be discussed later, the screening of the electric field in carbon nanotube bundles is much weaker than in carbon nanotubes leading to a significant Stark effect. This leads to the possibility that applying an

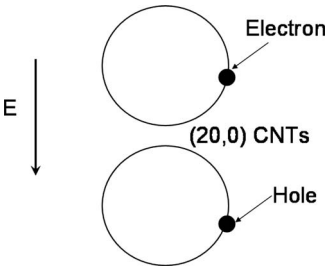

FIG. 1. Schematic cross section of a pair of semiconducting carbon nanotubes in an electric field.

electric field of strength around 0.05 eV/Å closes the gap in multiple carbon nanotube systems such as the one shown in Fig. 1 and creates a one-dimensional excitonic state with interesting optical, magnetic, and transport properties. Such electric-field strengths are easily achievable through the use of scanning tunneling microscope (STM) tips.[7]

In this paper, using a tight-binding Bethe-Salpeter method in conjunction with *ab initio* density-functional theory calculations we study the parameter regimes of the existence of such excitonic states in a pair of carbon nanotubes, which constitutes the smallest bundle. We also discuss some basic experimental signatures of such systems.

II. STARK EFFECT IN CARBON NANOTUBE BUNDLES

The separation between carbon nanotubes in a carbon nanotube bundle is comparable to that of graphene sheets in graphite. Thus the electronic states on individual nanotubes in a carbon nanotube bundle hybridize weakly with electronic states on other nanotubes in the bundle because of the weak overlap of the wave functions. Based on Stark effect studies in boron nitride nanotubes, the localized nature of the states in such bundles leads to the possibility of a larger Stark effect in nanotube bundles compared to single nanotubes. In order to study this possibility we performed an *ab initio* calculation of the electronic structure of a pair of (20,0) carbon nanotubes in an electric field with the electric field pointing along the line joining the axes of the tube as shown in Fig. 1. The calculations were performed using density-functional theory (DFT) within the local-density approximation (LDA) using a localized atomic-orbital basis and the SIESTA code.[10] We find the lattice constant and diameter of the nanotube to be 4.24 and 15.6 Å, respectively. The distance between the pair of nanotubes is chosen such that at the closest point they are 3.3 Å apart, which is the graphite intersheet distance within DFT-LDA.

Within LDA, the band gap of the pair of nanotubes is similar to that of a single nanotube and is calculated to be $E_{g,\mathrm{LDA}}=0.4$ eV. The band structure of the nanotube system is shown in Fig. 2 relative to the vacuum which is at 0 eV. The work function of the pair of tubes is found to be $W_f=4.7$ eV.

As can be seen from Fig. 3, the gap of the pair of nanotubes is significantly reduced on the application of an electric field of 0.04 eV/Å. We find the gap to depend linearly on the electric field with a derivative given by $\frac{dE_g}{dE}=9$ Å until the

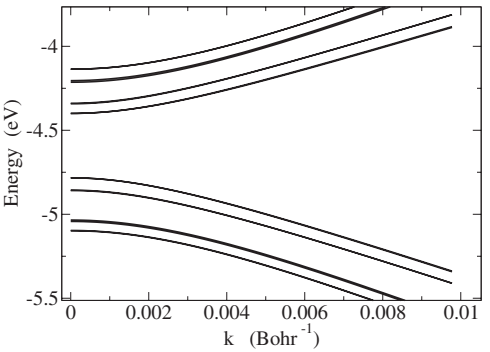

FIG. 2. Band structure for a pair of (20,0) semiconducting nanotubes.

closure of the gap, which within LDA is at a field strength of around 0.05 eV/Å.

The large Stark shift seen in the case of a pair of carbon nanotubes as compared to the single nanotube case can be understood physically as arising from the states on each nanotube being localized. The states on the two carbon nanotubes hybridize only weakly because of the small overlap in their wave functions. An applied electric field can reduce the band gap of the pair of nanotubes by shifting the valence state of one nanotube up and the conduction state on the other tube down.

III. QUASIPARTICLE AND OPTICAL SPECTRA WITHIN THE TIGHT-BINDING METHOD

The quasiparticle and optical properties of small diameter carbon nanotubes have been calculated from first principles with remarkable success.[11,12] The quasiparticle band structure of these tubes is obtained by applying the self-energy corrections calculated within the GW approximations to the LDA band structure.[13] Optical properties are influenced by bound and unbound excitons. Excitonic wave functions can be obtained using the Bethe-Salpeter equation.[14] The exciton wave functions are then used to calculate the optical properties of nanotubes. In the current work we are interested in calculating the electronic properties of (20,0) carbon nanotubes, which are semiconducting carbon nanotubes of diameters significantly larger than those that have been calculated

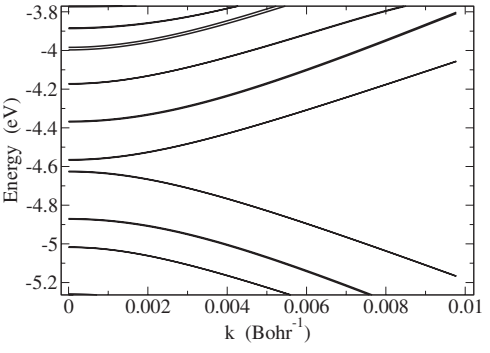

FIG. 3. Band structure for a pair of (20,0) semiconducting nanotubes in an electric field of strength 0.04 eV/Å.

from first principles. Fortunately it has been shown that for larger diameter tubes, because of the weakness of curvature effects, tight-binding Hamiltonian based formulations of the GW and Bethe-Salpeter methods can be successfully used to predict the quasiparticle and optical properties of these large nanotubes.[15] We use an approach that closely resembles the simple tight-binding formulation presented in a previous study[15] where only the p_z orbitals on the carbon atoms are used to represent the electronic states. Within the tight-binding approximation, we ignore the overlap between orbitals on different nanotubes. Thus within our approximation electrons cannot hop between nanotubes. However, electrons and holes on the different nanotubes still interact via the screened Coulomb interaction that has been calculated within the tight-binding approximation for the pair of nanotubes. Since we have ignored intertube hopping in these calculations, the screening of the Coulomb interaction is a result of the polarizability of individual nanotubes.

Self-energy corrections within the GW approximation are found to correct the band gap of semiconductors to a value in better agreement with experiment.[13] The reduced dimensionality of quasi-one-dimensional nanotubes enhances such self-energy corrections and is found to increase the band gap of nanotubes in first-principles calculations for (8,0) nanotubes by 1.15 eV.[11] This large increase in the band gap has been argued to be generally true of semiconducting nanotubes.[16] Similar to previous work we select a noninteracting overlap integral of γ=2.7 eV,[15] and calculate the self-energy shift as discussed in previous similar calculations[15] to determine the quasiparticle spectrum of a pair of (20,0) carbon nanotubes.

The properties of the excitons are determined through the solution of the Bethe-Salpeter equations in a way similar to the approach described for the calculation of quasiparticle properties. This approach has proved successful in previous work.[15] As found in previous work,[14] the binding energy of the excitons calculated from the Bethe-Salpeter equations reduces the optical gap significantly from the quasiparticle gap.

IV. EXCITON CALCULATION RESULTS FOR A PAIR OF SEMICONDUCTING NANOTUBES

Using the methods described in Sec. III, it is possible to calculate the quasiparticle gap and optical spectra of a pair of carbon nanotubes. We calculate the quasiparticle gap of a pair of (20,0) single walled carbon nanotubes to be $E_{g,\mathrm{QP}}$ =0.83 eV, which is slightly lower than the quasiparticle gap of $E_{g,\mathrm{QP}}$=0.9 eV calculated for a single carbon nanotube. The lowest excitonic transition energy for the pair of nanotubes is found to be $E_{\mathrm{exc,gap}}$=0.26 eV, which is similar to the value for a single nanotube. However, in the case of a pair of nanotubes, in addition to the spatially direct excitons where the electrons and holes are on the same nanotube, there is an additional spatially indirect exciton which as depicted in Fig. 1 has an electron on one tube and a hole on the other tube. This exciton is similar in nature to the indirect excitons that appear in the experiments on exciton gases observed in two-dimensional electron-gas bilayers.[4] As expected from the fact that the electrons and holes of the indirect excitons are further separated compared to the direct excitons, the indirect excitons have a lower binding energy of $E_{\mathrm{exc,binding}}$=0.3 eV compared to the binding energy of direct excitons which is found to be around $E_{\mathrm{exc,binding}}$=0.57 eV. The indirect excitons in the carbon nanotubes are found to be large as shown in Fig. 4 with a spatial extent of 160 Å. In comparison we find that the direct excitons in the individual nanotubes are much smaller with a spread of 106 Å. Thus at low electric-field strengths the spatially direct exciton forms the lowest excitonic transition energy since the excitonic transition energy for the lowest spatially indirect exciton is found to be $E_{\mathrm{exc,gap}}$=0.53 eV.

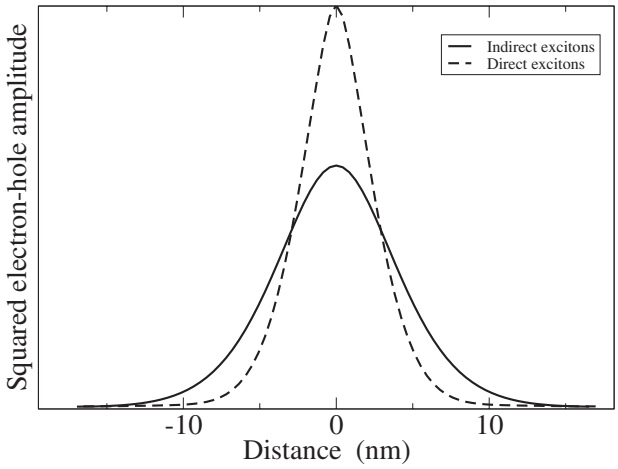

FIG. 4. Axial distribution of the exciton wave function.

However, the excitation energy for the spatially indirect excitons has a much stronger Stark shift than the direct excitons. This is because of the fact that the spatially indirect excitons have their electrons and holes on different nanotubes. Thus the transition energy of the spatially indirect excitons is lowered at almost the same rate as the LDA gap was calculated to reduce in Sec. II. The effect of the electric field on the direct excitonic transitions is much weaker since they are similar to excitons on the single carbon nanotubes, where the electric fields are strongly screened. Thus on the application of a sufficiently strong electric field, the transition energy of the indirect excitons is not only found to decrease below the transition energy of the direct excitons, but also to vanish at an electric-field strength of $E_{\mathrm{transition}}$=0.06 eV/Å.

As already discussed, at the point the excitonic gap closes, the conventional ground state becomes unstable to the formation of bound electron-hole pairs. Thus for electric-field strengths beyond which the spatially indirect excitonic transition goes to zero we expect the carbon nanotube pair to become populated with bound spatially indirect electron-hole pairs.

The electron-hole pairs so formed are stable as they are part of the ground state of the system. Moreover they modify the response of the nanotube to photons with a polarization along the nanotube, which should excite the indirect excitons from their ground state to the first excited state. Experimentally this should be observable as an absorption peak at an energy of $E_{\mathrm{exc,transition}}$=0.1 eV. Since the lowest excitonic transition of the single nanotube is at $E_{\mathrm{exc,gap}}$=0.26 eV and this is almost unaffected by the electric field or the presence

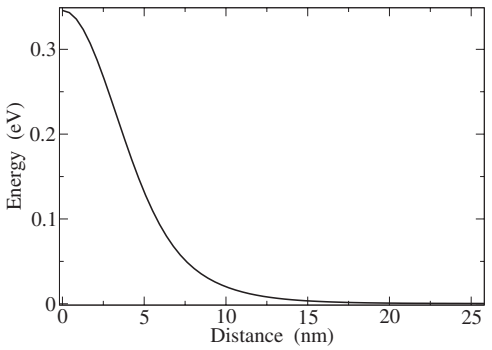

FIG. 5. Exciton-exciton repulsion as a function of distance.

of a neighboring nanotube, one does not expect any other optical features to be present in the optical-absorption spectrum in the neighborhood of the new absorption peak.

V. COLLECTIVE PROPERTIES OF EXCITONS FOR A PAIR OF SEMICONDUCTING NANOTUBES

In Sec. IV we discussed how the application of an electric field to a pair of (20,0) nanotubes causes a transition of the system to an excitonic state where the nanotubes became populated with bound spatially indirect excitons with the electrons of the exciton residing on one tube and the holes on the other tube. However, several interesting properties of the exciton system such as the possibility of coherence and other transport properties depend on properties other than the excitonic gap of the system such as the kinetic and interaction properties of the excitons.

As can be seen from Fig. 5, the exciton-exciton interaction is always repulsive for the spatially indirect excitons which is similar to what was observed in the experiments on the two-dimensional electron gas.[4] This can be attributed to the fact that each indirect exciton carries a dipole moment. The exciton-exciton interaction was calculated directly by integrating the exciton density and accounts for only the Coulomb interaction between the exciton and ignores exchange interactions. The repulsive interaction between the excitons stabilizes the excitons against collapsing into an electron-hole droplet, which would be possible if the exciton-exciton interaction was attractive. The repulsive exciton-exciton interaction causes the interaction to remain uniformly spread out through the condensate and the exciton density depends on the electric field applied. This provides another interesting experimental signature where the strength of the absorption peak corresponding to the transition is linearly proportional to the excess electric field applied beyond the transition. The proportionality constant is related to the integrated exciton-exciton interaction $\mathcal{E}_{\text{exc,total}} = \int V_{\text{exc-exc}}(x)dx = 8.48$ eV Å. The average exciton density is then given by $(E - E_{\text{transition}}) \times 9.0/8.48/\text{Å}$. For an excess electric-field strength of 0.01 eV/Å we find an exciton density of one exciton per 80 Å. The optical-absorption strength is expected to be proportional to the average exciton density.

The kinetic properties of the excitonic system can be related to the effective mass of the exciton which is found to be $m^*_{\text{exciton}} = 0.41 m_e$ which is determined from calculating the excitation energy of the excitons as a function of center-of-mass momentum of the excitons. Hence the excitons in the nanotubes form a one-dimensional repulsive gas. The low-energy excitations of this system consist of collective motions of the excitons in the form of soundlike modes. Using the effective mass and the exciton-exciton interaction shown in Fig. 5 we obtain a sound velocity for these phonons in the exciton gas of $v_s = 0.96$ eV Å at the density corresponding to an excess electric-field strength of 0.01 eV/Å. Since the excitons form a one-dimensional gas of bosons, the coherence properties of such an exciton gas can be somewhat complex. To get a sense of the parameters associated with these properties we estimate the Bose condensation temperature of a noninteracting gas at the typical density mentioned to be $T_{\text{BEC}} = 25$ meV. The interplay of the motional coherence properties of the condensate and the optical transitions of the excitons may be expected to result in properties such as superradiance.

VI. CONCLUSION

In conclusion, using first-principles DFT-LDA calculations in conjunction with GW and Bethe-Salpeter calculations within a tight-binding formalism, shown to provide reliable optical spectra for large nanotubes, we have analyzed the ground state and optical properties of a pair of (20,0) semiconducting nanotubes in an electric field. We find that for an electric field of 0.06 eV/Å, easily accessible through a STM, the excitonic gap of the system closes and the system undergoes a transition to a state where the ground state is populated with spatially indirect excitons whose density increases linearly with electric-field strength beyond the transition. The transition to the excitonic phase should be visible via the optical response of the system as a function of electric field where accompanying the phase transition we expect the appearance of a peak in the absorption at an energy of 100 meV whose intensity increases linearly with increasing electric fields. This should be visible in experiment since the lower energy threshold for absorption before the transition is above 200 meV.

Further we estimate certain collective properties such as a sound velocity for the exciton gas. The effective Bose condensation temperature is $T_{\text{BEC}} = 25$ meV at a field strength of 0.07 eV/Å, however, given the repulsive interaction between the excitons and the one-dimensional nature of the gas, we do not expect Bose condensation in this system. However, T_{BEC} can still be expected to govern partially coherence properties and manifest itself as superradiance.

Finally it should be noted that the physics discussed in this paper depends on relatively general arguments and should apply to other quasi-one-dimensional systems with transversely localized electrons such as nanotube bundles. These might constitute systems that are more easily accessible in experiment, however, some of the experimental signatures might not be as clear and the theoretical analysis might be more difficult than the case considered here.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. DMR07-05941 and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U.S. DOE under Contract No. DE-AC02-05CH11231. Computational resources have been provided by the NSF through TeraGrid resources at SDSC, DOE at the NERSC, TACC, Indiana University.

*jaydeep@socrates.berkeley.edu

[1] B. I. Halperin and T. M. Rice, Solid State Phys. **21**, 115 (1968).
[2] L. Balents and C. M. Varma, Phys. Rev. Lett. **84**, 1264 (2000).
[3] R. S. Knox, Solid State Phys. **5**, 100 (1963).
[4] L. V. Butov, A. C. Gossard, and D. S. Chemla, Nature (London) **418**, 751 (2002).
[5] H. Min, R. Bistritzer, J. Su, and A. H. Macdonald, Phys. Rev. B **78**, 121401 (2008).
[6] C. H. Zhang and Y. N. Joglekar, Phys. Rev. B **77**, 233405 (2008).
[7] M. Ishigami, J. D. Sau, S. Aloni, M. L. Cohen, and A. Zettl, Phys. Rev. Lett. **94**, 056804 (2005).
[8] M. Ishigami, J. D. Sau, S. Aloni, M. L. Cohen, and A. Zettl, Phys. Rev. Lett. **97**, 176804 (2006).
[9] A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B **49**, 5081 (1994).
[10] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[11] C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).
[12] T. Miyake and S. Saito, Phys. Rev. B **72**, 073404 (2005).
[13] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
[14] M. Rohlfing and S. G. Louie, Phys. Rev. B **62**, 4927 (2000).
[15] J. Jiang, R. Saito, G. G. Samsonidze, A. Jorio, S. G. Chou, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **75**, 035407 (2007).
[16] T. Ando, J. Phys. Soc. Jpn. **94**, 056804 (2005).