Deformation effects: energy gap in lda and gw approximation

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Theoretical calculations and experimental measurements indicating the importance of many-body effects in reduced dimensional systems. We performed ab initio calculations based on density functional theory and many-body perturbation theory in the GW approximation. To illustrate our results, we consider a (8; 0) single wall carbon nanotube and by solving the Bethe-Salpeter equation calculate the macroscopic dielectric function Ïµ for both the undeformed and deformed nanotubes.

The radial deformation is obtained by squeezing the nanotube in the y direction and elongating in the x direction. Results show a decrease in band gap and a red shift in exciton transition energies for nanotubes of elliptical cross-section. The deformation can be proposed as ideas for the achieve to less excitonic energy. We implement the method in the ABINIT code for ground and excited states calculations.

Single wall carbon nanotubes (SWCNTs) are cylindrical structures that formed by rolling up a graphene sheet. SWNCTs geometric structures describe by chiral vector or positive integer pairs (n, m). Nanotubes with (n, 0) chirality is said to be of zigzag carbon nanotubes, with (n, n) are armchair nanotubes and tubes with (n, m) are chiral nanotubes.

In the zone folding approximation if the difference between these two integers (n, m) is an integer multiple of 3, tubes are metal, otherwise, the tubes show semiconducting properties1.

The observation and synthesis of single-walled carbon nanotubes in recent years, making possible the experimental study of the optical properties of individual SWCNTs. Because of the nature of quasione-dimensional carbon

nanotubes many-body effects have an important in uence on their optical properties and failure of single-particle theories not unexpected.

The rst optical data for carbon nanotubes was obtained in 1999 by Kataura2, which reports the transitions energies (Eii) as a function of the tube diameter for nanotube with different chirality (n, m).

A few years later with the precise spectroscopy3 showed some deviations from the analysis of Kataura.

In particular, the ratio (E22= E11), predicted to be equal to 2 in the approximation where bands are linear close to Fermi energy4 was found to be smaller3, and this problem was not justi ed by single-particle theories, this problem so-called ratio problem in SWCNTs5.

Recent predictions based on rst principles calculations and semi-empirical approaches show the existence of exciton with high binding energy in the carbon nanotubes, so that the unknown effects observed in the optical spectra of nanotubes can be attributed to excitons and by considering the excitonic effects the ratio probem would be solved.

An evidence for the excitons in carbon nanotubes is obtained in the theory6 and experiment3. A theoretical approach is the rst principles calculations of optical spectra of carbon nanotubes, using the Bethe-Salpeter equation. These calculations show exciton with large binding energy in semiconductor nanotubes and even excitonic effects in metallic nanotubes6.

In the present work, we obtain optical spectra with ab initio calculations for Bethe-Salpeter equation for nanotubes of elliptical cross-section.

To illustrate our results, we consider a (8, 0) single wall carbon nanotube, then in our model squeezing the nanotube in the y direction and elongating in the x direction, we study quasiparticle band structures and excitation energies for nanotubes with elliptical cross-section. With this model, the deformation effects on the exciton energies is investigated.

However, so far the excitation energies are calculated for nanotubes with elliptical cross-section, but this calculation is done with single-particle approach that regardless of the excitonic effects.

Shan and Bao7 investigated the deformation effects on the optical properties of carbon nanotubes based on the tight-binding model and describe the deformation of SWCNT under stretching, compression, torsion, and bending, they were shown the shifting, merging, and splitting of Van Hove Singularities in the DOS, and optical absorption properties variation with strains.

We present a framework to predict the optical absorption of deformed SWNTs using the Bethe-Salpeter equation with many-body approach, so far this work has not been done. The results can be employed to understand and guide experimental studies of electronic and optoelectronic devices based on the CNTs.

With density functional theory can be calculated ground state energy and charge density for a many-body interacting system. We obtain the DFT wave functions and eigenvalues of (8, 0) SWCNT by solving the Kohn-Sham equations8 within the local density approximation, with Teter Pade parametrization9 for the exchange correlation functional implemented in the

ABINIT computational package10. The code uses a plan-wave basis set and a periodic supercell method. For all studied systems, we have used the ab initio normconserving Troullier-Martins pseudopotentials11 and (1140) Monkhorst-Pack k-grid sampling of the Brillouin zone was taken, for the self-consistent calculations with an energy cutoff 60 Ry.

In the end of LDA calculations, we compare our LDA calculations with results obtained using the QUANTUM ESPRESSO12 package with the Perdew-Burke-Ernzerhof approximation and Ultrasoft pseudopotentials in a planewave basis. There is no difference between the two calculations for bandgap (8, 0) carbon nanonotube13.

Density functional theory is used to study the ground state of the system and this theory cannot be used in the prediction of excited states. In the investigation of the excited states, the amount of band gap is greater than that is observed with the LDA calculations. So beyond the DFT should use a theory that describes excitations correctly. Our approach is the many-body perturbation theory14 based on the concept of quasi-particles and Green's function. In this theory, the quasi-particle energies obtain by solving the following equation that so-colled Dyson equation:

Where T is the kinetic energy, Vext is the external potential, and VHartree is the average Hartree potential.

is the self energy of the electrons and the indices refer to Bloch states n, k, thus problem of nding quasi-particle energies decreases to the problem of nding self-energy.

A good approach that has been used extensively for nding of self-energy is the GW approximation of Hedin15. In the GW approximation, using the following equation, self-energy (r; r′; E) can be calculated:

Here G is the Green's function of the electrons and W = ".. 1v is the screened Coulomb interaction determined by the inverse dielectric matrix ".. 1(r; r'; E) and + is a positive in nitesimal time.

Green's function is obtained with the Kohn-Sham wave functions and eigenvalues:

Since the wave functions are obtained with the LDA are appropriate, a rst order approximation is sufficient to correct the LDA energies, for this reason quasi-particle energies derived from the rst-order perturbation theory by the following equation:

Where V LDA

xc is the exchange-correlation potential and Zn; k is the renormalization factor of the orbital de ned as Zn; k = (1 ô€€ @=@E)ô€€1j

E= ELDA

n; k

.

In the equation (2), sigma is a convolution of G and W, this part of the calculation is very complex, because the matrix "

ô€€€1

GG′ (q; !) (in reciprocal space) must calculate for all frequencies !, in direction of the real and imaginary axis. Since only the value of the integral is important, with a simple and acceptable model can calculate the integrals. In this model the frequency dependence the matrix "

ô€€€1

GG′ (q; !) calculate with a plasmon pole model16:

In this equation, Ω2

GG′ (q) and ~!(q) are the parameters of model, the nal values for the parameters in this model is found in Ref. 16. Dielectric function in this model is approximated as a single-peak structure, this peak placed in the plasmon frequency ! p. Plasmon pole model not only reduces computation, but also makes an analytic calculation of the relation (2).

With the GW calculations, correction to the energy gap of the carbon nanotube is obtained. The ABINIT package has been used for the Hybertsen-Louie plasmon pole model calculations. For all the GW calculations, the energy cutoff is 36 Ry for the evaluation of the bare Coulomb exchange contribution x, and 24 Ry for the correlation part c.

With the many-body perturbation theory, can be calculate the excitation energies with obtaining self-energy using the GW approximation. In fact, an optical absorption will build a pair of bound electron-hole or exciton.

For the calculation of excitation energies, a good agreement between experiment and theory to be achieved when the interaction between the electron and hole are also considered. BSE17 takes into account coupling between electron and hole and absorption spectra that obtained by solving this equation, is more consistent with the experimental results. Bethe-Salpeter equation written for a bound two-body system, in condensed matter this equation has the form of as follows:

Where the quasiparticle energies Ec; Ev enter on the diagonal, and the indices v, c refers to the occupied valence and empty conduction band states, Wand V are screened and bare Coulomb potentials, respectively.

By solving the Bethe-Salpeter equation, exciton energies are calculated. In order to have an observation for the excitonic energies, the macroscopic dielectric function is calculated using the following equation18:

Where the Avc

s is exciton amplitude and Es is exciton energy. The relation between the imaginary part of ÏµM to the frequency ! gives the absorption spectrum.

In ABINIT, we use the option to evaluate the response function recursively with Haydock algoritm19 and TammDancoff approximation14. Calculations of optical properties via BSE are more expensive computationally. For both undeformed and deformed SWNTs, the BSE kernel, in which the energy cutoff is 16 Ry for V and W.

Fig. 3 shows the band structure for undeformed (8, 0) SWNT. According to the band structure, this SWNT is a semiconductor and amount of band gap is

0: 57 eV. We repeat the same calculation for elliptical tubes, with the previous parameters (the same cutoff energy, number of kpoint, : : :) and only the geometry of the tube will change.

Fig. 4 shows the band structure for deformed (8, 0) SWNTs with different values of . In this calculation, the band gap decreases from Egap = 0: 57 eV at = 1: 0 to the closing point, Egap = 0: 0 eV at = 0: 7. the energy gap is 0: 49 eV , 0: 26 eV for A, B elliptic nanotubes, respectively. For D, E and F, elliptic nanotubes no band gap is found.

In this calculation, A, B elliptic nanotubes remained semiconductor and the C elliptic nanotube represents the boundary of the metal. In this approximation D, E and F, elliptic nanotubes are metal.

By this calculation we show that when the deformation is highly intense, the band gap decreases and one insulator-metal transition occurs.

In the second stage, we calculate correction band gap energy and quasi-particle band structure with GW approximation. Fig. 5 shows the quasiparticle band structure for undeformed (8, 0) SWNT, in the GW approximation band gap is 1: 76 eV that is greater than the amount predicted in the LDA.

Result for undeformed nanotube agrees well with ab initio calculations presented in Ref. 6, that the calculated value of the quasiparticle energy gap is given:

1: 75 eV for undeformed (8, 0) SWCNT. We perform one-shot" GW or G0W0 model where the convergence studies have been carried out with respect to various parameters (naumber of bands, cutoff energy, . . .).

In the previous stages, A, B elliptic nanotubes remained semiconductor and the C elliptic nanotube represents the boundary of the metal. We performed GW calculations only for semiconducting nanotubes.

Fig. 6 shows the quasiparticle band structure and the calculated value of the quasiparticle energy gaps that they are 1: 65 eV , 1: 34 eV for A, B elliptic nanotubes, respectively, and for the C elliptic nanotube no band gap is found. For deformed nanotubes only the ground state energy is calculated by many-body approach in Ref. 20, so far no GW calculations have been done for deformed nanotubes to compare our results with them.

With the GW calculations, we conclude that when the deformation is highly intense the band gap decreases, too. We show the evolution of the energy band gap (Egap) as a function of radial deformation in the Fig. 7, where the band gap in LDA and GW calculations represents for nanotubes with different values of the deformation.

The values of the contributions of LDA exchangecorrelation potential Vxc, the exchange x and the correlation c part of the self energy are displayed in Table I-Table IV. Results are for plasmon pole models, in the Hybertsen-Louie approach presented in Ref.

16. We calculate the screened interaction W(! = 0) be expressed in terms of the inverse dielectric matrix ".. 1(r; r''; E), which describes screening in a

solid when local elds due to density inhomogeneities and manybody effects are taken into account, to obtain self energy by (2).

However, we found gap correction for undeformed and deformed nanotubes, but electron-hole interaction decreased the excitation energy in these structures. The calculations include the electron-hole interaction (excitonic effects) are closer and better values to experiment.

In the third stage the macroscopic dielectric function ÏμM(!) has been calculated by (7) including local eld effects with solving the Bethe-Salpeter equation.

In Fig. 8 A1 and B1 are peak for undeformed SWNT, A2, B2 and A3, B3 are for A, B deformed SWNT, respectively.

The gure shows that with apply more deformation A, B peaks shift to lower energy, and red shift occurs in the optical spectra of carbon nanotubes. Therefor the low energy exciton can be occurred by deformation on the nanotubes. Table V shows the values of lowest two optical transition energies for the undeformed SWCNT in the present work and, ab initio calculations and experiment. The value of ratio E11= E22 = 1: 18 for the (8, 0) tube is in agreement with the experiment findings of Bachilo et al3. Bachilo and coworks in their work with Spectrouorimetric measurements obtained rst and second transition energies for more than 30 semiconductor CNTs with different (n, m). their results shows ratio equal to 1. 17 for the (8, 0) nanotube and 1. 85 for nanotube with a diameter larger, while a single-particle model, such as a tight bonding model is expected 2 value for this ratio. In considering excitonic effects the ratio problem will be resolved and

these calculations give us better results. We rst obtains values of the rst and second excitation energy for the undeformed SWNT and were compared with computational and exprimental values, then we repeated calculations for deformed nanotubes to get results. Table VI shows lowest two optical transition energies for the undeformed and deformed SWNTs. The value of E11 and E22 decreases with deformation.

In conclusion, we study the optical absorption spectra of deformed and undeformed semiconducting small-diameter SWCNT and survey the agreement with available experimental data. We show by applying deformation on the nanotubes one insulator-metal transition occurs, and peaks shift to lower energy, and red shift occurs in the optical spectra of carbon nanotubes. The deformation can be proposed as ideas for achieving to less excitonic energy. The results can be employed to understand and guide experimental studies of electronic and optoelectronic devices based on the carbon nanotubes. So far GW calculations and absorption spectra with excitonic effects for deformed tubes has not been obtained.

We investigate deformation effects on the energy gap in LDA and GW approximation and optical spectra including excitonic effects. These calculations shows that with apply deformation on the SWNT structure, energy gap decrease, and lowest two optical transition energies for the deformed SWNTs shift to lower energy. The deformation can be proposed as ideas for the achieve to less excitonic energy. The results can be employed to understand and guide experimental studies of electronic and optoelectronic devices based on the carbon nanotubes.

We compare our results with experimental data and ab initio calculations for undeformed nanotube, then repeat calculations for deformed nanotubes and investigate deformation effects on the energy gap in LDA and GW approximation and optical spectra. Investigation of excitonic effects so far has not been done with many-body approach for Bethe-salpeter equation for deformed nanotubes. Results are agreed with sing-particle calculations that presented in Ref. 7.