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Communication: Electronic band gaps of semiconducting zig-zag carbon nanotubes from many-body perturbation theory calculations

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Electronic band gaps for optically allowed transitions are calculated for a series of semiconducting single-walled zig-zag carbon nanotubes of increasing diameter within the many-body perturbation theory GW method. The dependence of the evaluated gaps with respect to tube diameters is then compared with those found from previous experimental data for optical gaps combined with theoretical estimations of exciton binding energies. We find that our GW gaps confirm the behavior inferred from experiment. The relationship between the electronic gap and the diameter extrapolated from the GW values is also in excellent agreement with a direct measurement recently performed through scanning tunneling spectroscopy. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4716178]

The design of electronic devices based on carbon nanotubes (CNTs), as a possible semiconductor material in the 2025 timeframe, has been the subject of significant effort during the last decade. The fundamental parameter which determines transport properties of any electronic device is the electronic band gap. Therefore, to control and engineer novel devices using these carbon nanostructures, it is essential to have a good understanding of the relation between the band gap and the corresponding geometrical structure of the nanotube. In particular, for semiconducting single-walled tubes, the knowledge of how the electronic gap depends on the chirality and the diameter should be addressed. However, the direct measurement of electronic band gaps in semiconducting CNTs is cumbersome due to the difficulties in performing combined direct/inverse photoelectron measurements and the large exciton energies in these one-dimensional systems when the optical gap is probed.[1] Indeed, when band gaps are optically probed the recorded energies account not only for the electronic band gaps but also for the exciton binding energies.[2] The electronic band gaps could in principle be obtained just by subtracting the exciton energies but these cannot be easily measured. Hence, for extracting the electronic gaps from the optical ones, it is necessary to rely on theoretical models for the exciton.[3,4]

Another path for accessing to electronic band gaps is theoretical modelling. However, the most common methods based on density functional theory (DFT) within local approximations for the exchange and correlation functional usually yield a significant underestimation of electronic gaps and cannot provide reliable estimations for CNTs. More accurate methods based on many-body perturbation theory proved to be successful in providing excitation properties in a large variety of materials.[5] In particular, the GW approximation in which the many-body self-energy operator is expressed as the product of the electronic Green's function (G) with the screened Coulomb interaction (W) (Ref. 6) usually reproduces band gaps and other electronic properties of sp-bonded materials with good accuracy.[7] It has been possible to apply with success the GW method to selected CNTs.[1,8–10] Unfortunately, not only is the computational cost of GW approaches significantly higher than that of simpler DFT schemes but also particular care is required for obtaining converged results.[11]

Recently, we have developed a method for performing accurate and well converged GW calculations in large simulation cells based on reduced basis sets for expressing the polarizability operators[12] and on Lanczos' chains for avoiding sums over unoccupied one-particle states.[13] Here, we adopt this scheme for investigating the dependence of electronic band gaps with respect to tube diameter for the case of semiconducting single-walled zig-zag carbon nanotubes. We have addressed tubes with diameters ranging from 0.56 nm to 1.27 nm. We have found that the GW results are in excellent agreement with previous estimates from optical measurements[3,4] combined with theoretical modelling for exciton energies.[4] Moreover, the extrapolated dependence of the gap with respect to the diameter is in good agreement with a direct measurement of an electronic gap which has been achieved recently.[14]

Electronic states in a weakly correlated system can be described as quasi-particle states and their energies can be probed through direct and inverse photoelectron spectroscopy. Many-body perturbation theory provides a formally exact approach for addressing quasi-particles though approximations are required for performing actual calculations. The so-called diagonal G_0W_0 or *one-shot* GW approximation[7] can be seen as the simplest of such approximations. The G_0W_0 scheme permits to apply many-body corrections to a starting DFT calculation and in many cases with great success. Within this

method the quasi-particle energy level E_i for the ith Kohn-Sham state is obtained from the solution of the following self-consistent one-variable equation:

$$E_i = \epsilon_i + \langle\psi_i|\Sigma_c(E_i)|\psi_i\rangle - \langle\psi_i|V_{xc}|\psi_i\rangle + \langle\psi_i|\Sigma_x|\psi_i\rangle, \quad (1)$$

where ψ_i is the ith Kohn-Sham eigen-state and ϵ_i its eigen-energy, V_{xc} is the exchange and correlation potential while Σ_c and Σ_x are the correlation and exchange part of the self-energy operator. According to the G_0W_0 approximation Σ_c is found from the convolution of the one-body Green's function G_0, obtained from the DFT calculation, with the correlation part of the screened Coulomb potential W_0^c, which is obtained through the random-phase approximation

$$\Sigma_c(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int d\omega' e^{i\eta\omega'} G_0(\mathbf{r},\mathbf{r}';\omega+\omega')W_0^c(\mathbf{r},\mathbf{r}';\omega'), \quad (2)$$

where η is a positive infinitesimal.

It should be noted that the G_0W_0 approximation is an approximation to the fully self-consistent GW method and in principle different results could be found.[15–18] However, the latter is still in its phase of development and an approach for performing self-consistent GW calculations avoiding explicit sums over empty states has still to be conceived.

Despite the apparent simplicity of this approach, its application requires a considerably larger effort than the starting DFT calculation. Not only does it involve the evaluation of operators at several frequencies but also the evaluations of G_0 and W_0^c contain sums over a large, in principle infinite, number of unoccupied Kohn-Sham states. These are the origins of the difficulties in obtaining well converged GW calculations.[11] Recently, we could present a GW scheme which permits to avoid these two difficulties: we express the bare and screened polarizability operators through reduced (optimal) basis sets,[12] retaining good accuracy, and we eliminate any explicit sum over empty unoccupied states through an approach[13] based on Lanczos' chains. In this approach all the operators are first evaluated on imaginary frequencies and then the expectation values of the self-energy operator are obtained upon analytic continuation,[19] avoiding the use of the so-called plasmon-pole approximation.

We have considered here the single-walled zig-zag CNTs with chirality indices:[20] (7,0), (8,0), (10,0), (11,0), (13,0) (14,0), (16,0) which are semiconducting. We adopted periodic simulation cells setting a distance of 10 Å between the next periodic replica of the tubes. We considered simulation cells comprising from 2 to 4 replica of the primitive cell along the tube direction. This choice led to a number of atoms in the simulation cells varying from 96 to 128. Details of the dimensions of the adopted simulation cells are reported on Table I.

The starting DFT calculations were performed using the local density approximation (LDA) for the exchange and correlation functional as described in Ref. 21. We used the *pw.x* code of the QUANTUM-ESPRESSO suite of DFT packages.[22] Within this package, wave-functions and charge-densities are expressed through plane-waves basis sets and the interaction between valence and core electrons is modeled through pseudo-potentials. We applied a normconserving pseudopotential for the carbon atoms[23] and an energy cutoff of 40 Ry. The G_0W_0 calculations have been performed with the GWL code[24] which has been implemented as a package in QUANTUM-ESPRESSO. This code uses a k-point mesh for sampling the Brillouin zone only for the long-range terms of the symmetric dielectric matrix. For this reason we used supercells containing up to four primitive cells. The DFT charge densities and the long-range terms of the symmetric dielectric matrix have been calculated using meshes from 4 to 9 k-points along the reciprocal direction of the tube (see Table I). For the GW calculation we built a basis for the polarizability operators as described in Ref. 13, using a cutoff $E^* = 3$ Ry and a threshold q^* varying from 1.8 Bohr^{-3} to 8.6 Bohr^{-3} yielding basis consisting of 4000 vectors in each case. The calculations were first carried out in imaginary frequency[19] using a grid consisting of 256 steps on the positive imaginary axis up to 20 Ry. Then the expectation values of the self-energy operator were obtained on real frequency through analytic continuation using three-poles expansion. We estimate a final global accuracy of 0.1 eV for the calculated quasi-particle energy levels.

In Table II we display the calculated band gaps relative to optically allowed electronic transitions for the tubes we have considered. In the tubes (7,0) and (8,0) the fundamental electronic band gap refers to transitions which are not optically allowed. We note that while the fundamental gap

TABLE I. Parameters for the simulation cells adopted in the GW calculations: chirality indices (m,n), number of primitive cells defining the cell (No. of cells), number of atoms in the cell (No. of atoms), number of k-points (No. of k-points) used for sampling the Brillouin's zone, and dimensions of the cell.

(m,n)	No. of cells	No. of atoms	No. of k-points	dimensions (Bohr)
(7,0)	4	112	4	30.0 × 32.0 × 30.0
(8,0)	3	96	4	30.0 × 24.3× 30.0
(10,0)	3	120	6	34.0× 24.0 × 34.0
(11,0)	3	132	6	36.0 × 24.0 ×36.0
(13,0)	2	104	9	39.0 × 16.0 × 39.0
(14,0)	2	112	9	40.0 × 16.0 × 40.0
(16,0)	2	128	9	40.0 × 16.0 × 40.0

TABLE II. Electronic band gaps from LDA, GW, and reference literature values, for selected semiconducting zig-zag CNTs of chirality indices (m,n). The gaps are relative to optically allowed transitions. When the electronic band gap for optically allowed transitions differs from the fundamental electronic band gap, we have reported also the latter in parenthesis both in the GW and in the reference column. Literature data are from: (a) Ref. 9, (b) Ref. 27, (c) Ref. 1, and (d) Ref. 8.

(m,n)	LDA (eV)	GW(eV)	Ref. GW(eV)
(7,0)	0.16	1.98 (1.47)	(0.60[a]−1.12[b])
(8,0)	0.5	2.24 (1.80)	2.54[c] (2.12−1.75[c]-1.51[d])
(10,0)	0.80	1.72	
(11,0)	0.95	1.66	
(13,0)	0.65	1.52	
(14,0)	0.74	1.36	
(16,0)	0.56	1.21	

for the (8,0) tube, 1.80 eV, is in good agreement with the previous GW results of 1.75 eV from Ref. 1 and of 1.51 eV from Ref. 8, our result for the (7,0) tube, 1.47 eV, is higher than the value 0.60 eV reported in a previous GW investigation.[9] However, for the latter case, in the literature different values are reported already at the LDA level possibly depending on subtleties in the structural optimization.[25,26] The calculated gap for the (8,0) tube relative to optically allowed transitions (2.24) is in agreement with the value of 2.54 eV from Ref. 1. The calculated gaps for the (7,0) and (8,0) CNTs are also in agreement with the results in Ref. 27, where we used a preliminary version of our method still requiring sums over empty states.

As our calculated electronic gaps have been obtained using periodic boundary conditions, we have estimated the maximal changes in the electronic gaps when the intertube distance goes towards infinity. We considered a (8,0) tube with a simulation cell comprising 32 atoms and varied the intertube distance. By extrapolating the gap/distance behavior we estimate a maximal increase in the electronic gaps in the isolate tube limit varying from 0.2 eV for the (8,0) tube to 0.1 eV for the (16,0) tube. We note that such extrapolations could be avoided using a more complex approach involving the cylindrical truncation of the Coulomb interaction.[1,28]

The electronic band gap of semiconducting nanotubes corresponds to the energy difference, usually indicated as E^{11}, relative to the van-Hove singularities appearing in the density of electronic states closest to the Fermi level. The energy difference relative to the second closest singularities is referred as E^{22}. When the band gap are investigated experimentally through optical spectroscopies, fluorescence lines do not match the electronic band gap E^{11} as electrons and holes in CNTs show strong correlated motion and their binding energy produces significant band gap renormalisation. In practice, experiments measure the energies of the lowest (E_{1A2}) and of the second lowest (E_{2A1}) optically active exciton states and their difference.

In principle, scanning tunneling spectroscopy (STS) could give a direct measure of electronic band gaps. However, in such a case a model is required for the estimation of the screening effects arising from the metal substrate on which the nanotube is dispersed and the final error bars are quite large.[14] Therefore, accessing electronic band gaps usually relies both on optical measurement and theoretical modeling. The edges for fluorescence emission have been measured for several tubes and then their dependence with respect to the diameter has been fitted with model functions.[2,3] In Ref. 3, the authors report the following behavior for the optical first emission gap $E_{\rm op}^{11}$

$$E_{\rm op}^{11} = \frac{1.11\ \text{eV}}{d_t + 0.11}, \tag{3}$$

where the diameter d_t is expressed in nanometers. Slightly different values for $E_{\rm op}^{11}$ are reported in Ref. 2, where the dependence of the optical gap with respect to the tube chirality is also considered. Indeed, the gap versus diameter function changes whether $mod(n - m, 3)$ equals 1 or 2 (m1 or m2 species, respectively):

$$E_{\rm op}^{11}(\text{m1}) = \frac{1.241 \times 10^3 \text{eV}}{157.5 + 1066.9 d_t} - \frac{0.0957[\cos(3\alpha)]^{1.374}}{d_t^{2.272}}\text{eV},$$
$$E_{\rm op}^{11}(\text{m2}) = \frac{1.241 \times 10^3 \text{eV}}{157.5 + 1066.9 d_t} + \frac{0.0431[\cos(3\alpha)]^{0.886}}{d_t^{2.129}}\text{eV}, \tag{4}$$

where α is the chiral angle.[20] For zig-zag CNTs we have $\alpha = 0$. Among the tubes we have examined, (7,0), (10,0), (13,0), and (16,0) are of m1 kind, while (8,0), (11,0), (14,0) are of m2 kind. In Ref. 2, fits for the second fluorescence gap $E_{\rm op}^{22}$ are also reported

$$E_{\rm op}^{22}(\text{m1}) = \frac{1.241 \times 10^3 \text{eV}}{145.6 + 575.7 d_t} + \frac{0.1651[\cos(3\alpha)]^{0.828}}{d_t^{1.809}}\text{eV},$$
$$E_{\rm op}^{22}(\text{m2}) = \frac{1.241 \times 10^3}{145.6 + 575.0 d_t} - \frac{0.1764[\cos(3\alpha)]^{1.110}}{d_t^{2.497}}\text{eV}. \tag{5}$$

In Ref. 4, Deslippe and co-workers proposed a model for the electron-hole exciton Hamiltonian which yields exciton binding energies in agreement with accurate GW-Bethe-Salpeter[29] first-principles calculations. Moreover, they found for semiconducting CNTs that the binding energy $E_{1A2}^{\rm bind}$ for the lowest 1A2 exciton could be expressed as

$$E_{1A2}^{\rm bind} \approx 2.3\left(E_{\rm op}^{22} - E_{\rm op}^{11}\right). \tag{6}$$

Equation (6) combined with the data of Ref. 3 leads to the following expression for $E_{1A2}^{\rm bind}$:

$$E_{1A2}^{\rm bind} \approx \frac{0.55\text{eV}}{d_t}. \tag{7}$$

The electronic band gap E^{11} corresponding to optically allowed transition can now be found from the Eqs. (1)–(4) through

$$E^{11} = E_{\rm op}^{11} + E_{1A2}^{\rm bind}. \tag{8}$$

In Figure 1, we compare our GW results with combined theoretical-experimental estimates using Eq. (6) combined with either the experimental values from Refs. 3 or 2. The latter are reported for the case of zig-zag semiconducting CNTs ($\alpha = 0$) for both m1 and m2 cases. We note a very good agreement of the calculated GW electronic gaps with the previous estimates for the entire diameter range. It should be noted that LDA results, not shown in the figure, would be very far from the theoretical/experimental lines as can be seen from Table II. The GW results for the largest tubes we have considered here are also in excellent agreement with the direct measurement of an electronic gap[14] which in turn is in nice agreement with the experimental/theoretical lines.

As, usually, the nanotubes which are used in devices have diameters which are larger than those studied here, it is interesting to fit our GW results for extrapolating the electronic gap-diameter function. For the purpose of extrapolating our data for larger tubes we fitted the GW results for tubes larger than 1.0 nm with the simple relation $E^{11} = a/d_t$ which goes towards a closed gap in the large diameter limit

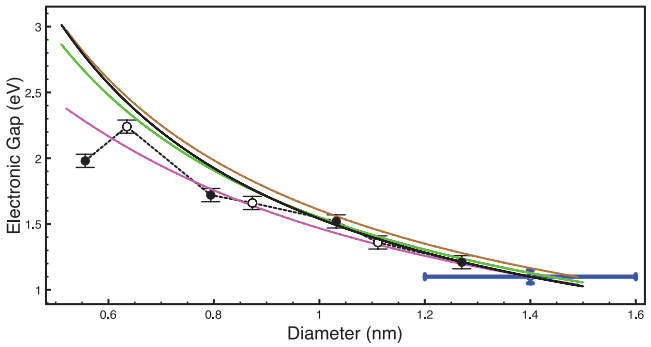

FIG. 1. Electronic band gaps for semiconducting carbon nanotubes of diameter d_t, corresponding to optical transitions. Black discs: first-principles GW results for m1 zig-zag CNTs. White circles: first-principles GW results for m2 zig-zag CNTs (see text). The error bars refer to the final estimated accuracy of the GW energy levels. The dashed black line is a guide for the eye. Bold black line: fit of GW results for large tubes (see text). Theoretical estimates for semiconducting nanotubes are obtained from: Eqs. (3) and (7) (green line) for generic tubes, Eqs. (5) and (6) for m1 (purple line) and m2 (brown line) zig-zag tubes. The experimental STS measurement of Ref. 14 is reported together with error bars (blue).

as expected from the observed closed gap in graphene. We find a value a of 1.54 ± 0.14 eV×nm. From Fig. 1, we see that our fitted behavior agrees well with the previous mixed theoretical/experimental estimates. At smaller diameters evidence of hybridization further reduces the band gap from this relationship.[25,30]

In conclusion, we have studied the electronic band gap of zig-zag semiconducting carbon nanotubes using the GW approach and have found agreement with estimations from optical measurements coupled with theoretical modelling for the exciton binding energies. We could extrapolate the gap/diameter behavior for larger diameters with a $1/x$ function. As for larger semiconducting CNTs the dependence of the gap on the tube chirality becomes smaller,[2] our relation $E_{\text{gap}} = 1.54$ eV×nm can be used for providing estimates for electronic gaps of generic semiconducting tubes.

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