Many-body effects on the electronic and optical properties of strained semiconducting carbon nanotubes

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We present many-body \textit{ab initio} calculations of the electronic and optical properties of semiconducting zigzag carbon nanotubes under uniaxial strain. The GW approach is utilized to obtain the quasi-particle bandgaps and is combined with the Bethe-Salpeter equation to obtain the optical absorption spectrum. We find that the dependence of the electronic bandgaps on strain is more complex than previously predicted based on tight-binding models or density-functional theory. In addition, we show that the exciton energy and exciton binding energy depend significantly on strain, with variations of tens of meVs per percent strain, but that despite these strong changes the absorbance is found to be nearly independent of strain. Our results provide new guidance for the understanding and design of optomechanical systems based on carbon nanotubes.

I. INTRODUCTION

The electronic and optical properties of nanomaterials such as carbon nanotubes (CNTs), graphene, and nanowires show unique behavior due to their reduced dimensions. For example, the electronic properties of CNTs depend strongly on their diameter\cite{1}, and many-body effects are known to significantly increase CNT bandgaps compared to density functional theory (DFT)\cite{2}. In addition, CNT optical properties are dominated by excitons\cite{2,7} due to a combination between weak electrostatic screening\cite{1} and enhanced Coulomb effects in quasi-one-dimensional systems\cite{2,3}.

While the electronic and optical properties of isolated CNTs are well understood, external factors such as the dielectric environment\cite{5,8}, electrostatic doping\cite{9,10}, and nanotube-nanotube interactions\cite{11}, have recently been shown to modify CNT electronic and optical properties. Another important external factor that impacts CNT properties is strain. Indeed, it was recognized early on\cite{12,13} that strain can significantly modify CNT electronic properties, and this has been exploited to realize new types of nanoelectromechanical devices\cite{14}. However, to date theoretical studies of the impact of strain on CNT electronic properties have been mostly limited to tight-binding models and DFT; given the importance of many-body effects in unstrained CNTs, a question to address is the role of many-body effects in strained CNTs.

The role of many-body effects on the optical properties of strained CNTs has received even less attention. Experimental reports of strain modulation of CNT optical properties have recently emerged\cite{15,17}, and indicate that optical transition energies can shift by tens of meVs per percent strain. However, interpretation of these results has relied on non-interacting models developed for electronic transitions, which do not capture excitonic effects that dominate the optical response in CNTs. Progress in developing exciton-based models for the optical properties of strained CNTs has focused on approaches relying on the tight-binding or the $k \cdot p$ methods\cite{18,21}. However, a full many-body \textit{ab initio} calculation of CNT optical properties under strain is still missing.

In this paper, we present such calculations by combining the GW approach with the Bethe-Salpeter (BSE) equation to study the electronic and optical properties of strained semiconducting CNTs. We find that the dependence of the electronic bandgaps on strain is more complex than previously predicted based on tight-binding models or density-functional theory. In addition, we show that the exciton energy and exciton binding energy depend significantly on strain, with variations of tens of meVs per percent strain. Furthermore, the absorbance is found to be nearly independent of strain as a consequence of the increase in transition dipole matrix elements with increasing strain.

This paper is organized as follows. After this Introduction, section II describes the methodology and results for the electronic properties of strained CNTs. Section III discusses the methodology and results for the optical spectra, exciton energies, and exciton binding energies. A summary is presented in Section IV.

II. IMPACT OF MANY-BODY EFFECTS ON ELECTRONIC PROPERTIES

We perform our \textit{ab initio} calculations on the semiconducting (11,0) and (17,0) CNTs for uniaxial strains from 0% to 5%. We start by investigating the ground-state properties (e.g. relaxed atomic structure, electron density) within DFT. The DFT calculations are performed using the Quantum Espresso package\cite{22} within the Local Density Approximation (LDA), using \textit{ab initio} pseudopotentials in combination with a plane-wave basis set with a kinetic energy cutoff of 60 Ryd, in a supercell geometry with tube separation (center to center) of more than double the nanotube diameter. The atomic structure is relaxed until forces are smaller than 5 meV/Å for both the strained and unstrained cases. In the unstrained case the (11,0) and (17,0) CNTs have diameters of 8.6 and 13.2 Å respectively. The strain is applied by stretching (w.r.t. to the unstrained case) the nanotube unit cell lattice vector along the tube axis followed by...
atomic relaxation. This leads to a decrease in nanotube diameter and a Poisson ratio $\nu \approx 0.15$.

![DFT (LDA) bandstructure of the (17,0) and (11,0) CNTs at 0% and 2% strain. The electronic bandgaps and optical transitions studied in this paper are indicated with arrows. b$_3$ is the length of the Brillouin zone.](image)

**FIG. 1:** DFT (LDA) bandstructure of the (17,0) and (11,0) CNTs at 0% and 2% strain. The electronic bandgaps and optical transitions studied in this paper are indicated with arrows. $b_3$ is the length of the Brillouin zone.

Reasonable agreement with the LDA values can be obtained if one uses $\gamma = 3.3$ eV and $\nu = 0.15$, giving $\Delta E_g / \sigma = \pm 114$ meV/%.

While LDA and TB calculations agree to a large extent, an open question is whether many-body effects can change the above picture. To address this question, we performed quasiparticle calculations using the many-body GW approach $^{27}$. The electron self-energy $\Sigma = iGW$ is obtained within the $G_0W_0$ approximation, i.e. using the LDA eigenvalues and wavefunctions to construct the 1-particle Green’s function $G$. The screened Coulomb interaction $W$ is evaluated within the Random Phase Approximation and extended at non-zero frequencies using the Plasmon-Pole approximation $^{27}$. We consider empty states up to an energy cutoff of $\sim 60$ eV, and use the ‘static-remainder’ technique $^{28}$ to ensure convergence with respect to the number of empty states.

The electronic bandgaps and optical transitions studied in this paper are indicated with arrows. $b_3$ is the length of the Brillouin zone.

Figure 1 shows the DFT bandstructures at 0% and 2% strain, with the electronic bandgaps and optical transitions studied in this paper labelled in the figure. We note that for the unstrained (17,0) CNT the $E_{33}$ transition has higher energy than the $E_{44}$ transition due to trigonal warping $^{23}$. Within LDA (Table 1), the (17,0) fundamental bandgap is found to decrease with strain, with the GW calculations giving $\Delta E_g = 33$ meV/%, where $\gamma = 3$ eV and $\nu = 0.15$, giving $\Delta E_g / \sigma = \pm 114$ meV/%. These values can be compared with those obtained from the simple tight-binding (TB) expression for small strains $^{26}$ applied to zigzag CNTs

$$\Delta E_g^{kk} = (-1)^k 3 \gamma (1 + \nu) \sigma,$$

where $\gamma$ is the tight-binding overlap integral and $\sigma$ is the strain. Reasonable agreement with the LDA values can be obtained if one uses $\gamma = 3.3$ eV and $\nu = 0.15$, giving $\Delta E_g / \sigma = \pm 114$ meV/%.

Convergence with respect to k-point sampling is achieved with 128 k-points in the one-dimensional Brillouin zone. Also, the Coulomb potential is truncated $^{29, 30}$ in order to prevent tube-tube interactions or periodic image effects due to the use of a periodic supercell.

![DFT dependence of the DFT, GW, and BSE gaps for the (17,0) CNT.](image)

**FIG. 2:** Strain dependence of the DFT, GW, and BSE gaps for the (17,0) CNT.

Table 1 shows the calculated GW gaps as a function of strain for the (17,0) CNT. The qualitative dependence on strain is similar to that obtained within LDA, with the gaps increasing or decreasing with strain depending on the band index. However, we find that strain effects are much more complex within GW: for example $E_{11}$ and $E_{33}$ decrease by 213 meV/% and 231 meV/%, respectively, whereas $E_{22}$ and $E_{44}$ increase by 86 meV/% and 46 meV/%, much weaker than LDA predicts.

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**TABLE I:** Calculated transition energies for the (17,0) CNT using LDA, GW, and BSE. The exciton binding energy $E_b$ is calculated as the difference between the transition energies from GW and BSE.

| Strain (%) | $E_{11}$ (eV) | $E_{22}$ (eV) | $E_{33}$ (eV) | $E_{44}$ (eV) |
|-----------|-------------|-------------|-------------|-------------|
| LDA       | 0.606      | 0.968      | 2.495      | 2.153      |
| 2         | 0.356      | 1.184      | 2.223      | 2.329      |
| GW        | 1.291      | 1.761      | 3.741      | 3.385      |
| 2         | 0.864      | 1.934      | 3.278      | 3.478      |
| BSE       | 0.717      | 1.180      | 2.985      | 2.755      |
| 2         | 0.427      | 1.435      | 2.670      | 2.905      |
| $E_b$     | 0.574      | 0.581      | 0.756      | 0.630      |
| 2         | 0.437      | 0.499      | 0.608      | 0.573      |
TABLE II: Energies (in eV) for the $E_{11}$ transition in the (11,0) CNT calculated using LDA, GW, and BSE. The exciton binding energy $E_b$ is calculated as the difference between the GW and BSE energies.

| Strain (%) | LDA | GW | BSE | $E_b$ |
|------------|-----|----|-----|-------|
| 0          | 0.950 | 1.922 | 1.062 | 0.860 |
| 2          | 0.694 | 1.540 | 0.775 | 0.764 |
| 5          | 0.319 | 0.837 | 0.348 | 0.488 |

The increased screening affects the screened Coulomb interaction $W = \varepsilon^{-1}v$ and hence the electron self-energy $\Sigma = iGW$ present in the many-body calculations. More exactly, the contribution $\Sigma_g$ of the electron self-energy to the quasiparticle bandgap $E_g^{GW} = E_g^{LDA} - V^{xc} + \Sigma_g$, decreases appreciably (same order of magnitude as the change in the LDA bandgap) upon strain: $\delta\Sigma_g = \Sigma_g(\sigma) - \Sigma_g(\sigma = 0) < 0$. This is a many-body effect not captured by the LDA exchange-correlation Kohn-Sham potential $V^{xc}$, and as expected we find $\delta V^{xc}/\delta \Sigma_g \ll 1$. Thus, the change in the fundamental quasiparticle bandgap upon strain as obtained within GW is more pronounced than the one obtained within a mean-field (LDA) theory, with appreciable contribution from self-energy corrections: $\delta E_g^{GW} \approx \delta E_g^{LDA} + \delta \Sigma_g$. For $E_{11}$ and $E_{33}$ this leads to a larger decrease in the bandgap compared to LDA since both $\delta E_g^{LDA}$ and $\delta \Sigma_g$ are negative; in contrast, $\delta E_g^{LDA}$ is positive for $E_{22}$ and $E_{44}$, and the still negative $\delta \Sigma_g$ leads to a smaller increase of the bandgap with strain.

![FIG. 3: Strain dependence of the $E_{11}$ transition for the (11,0) CNT.](image)

We next turn to the optical properties. To calculate these, we start from the GW results and couple them with the BSE. Both the BSE and GW calculations were performed using the BerkeleyGW package. We solve the BSE for excitons within the static approximation for the dielectric screening and within the Tamm-Dancoff approximation for excitons. Having obtained the excitonic properties one can then obtain the optical response of CNTs using the standard approach. The optical bandgap is equal to the quasiparticle bandgap minus the binding energy of the lowest bright exciton, a quantity which results from the overall attractive electron-hole interaction between the (quasi)electron and the (quasi)hole forming the exciton.

![FIG. 4: Strain dependence of the dielectric screening $\varepsilon^{-1}$ for the (11,0) CNT. $b_3$ is the length of the unit cell.](image)

**III. IMPACT OF MANY-BODY EFFECTS ON OPTICAL PROPERTIES**

FIG. 4: Strain dependence of the dielectric screening $\varepsilon^{-1}$ for the (11,0) CNT. $b_3$ is the length of the unit cell.

The differences between the GW and LDA results stem from the fact that with reduction (augmentation) of the fundamental bandgap there is an increase (decrease) in the dielectric screening $\varepsilon$ of the CNT. Consider the case where the fundamental bandgap decreases with strain: we plot in Fig. 4 the dielectric screening $\varepsilon^{-1}(q, \omega = 0)$ for the (11,0) CNT for strains of 0%, 2%, and 5%. The increased screening affects the screened Coulomb interaction $W = \varepsilon^{-1}v$ and hence the electron self-energy $\Sigma = iGW$ present in the many-body calculations. More exactly, the contribution $\Sigma_g$ of the electron self-energy to the quasiparticle bandgap $E_g^{GW} = E_g^{LDA} - V^{xc} + \Sigma_g$, decreases appreciably (same order of magnitude as the change in the LDA bandgap) upon strain: $\delta\Sigma_g = \Sigma_g(\sigma) - \Sigma_g(\sigma = 0) < 0$. This is a many-body effect not captured by the LDA exchange-correlation Kohn-Sham potential $V^{xc}$, and as expected we find $\delta V^{xc}/\delta \Sigma_g \ll 1$. Thus, the change in the fundamental quasiparticle bandgap upon strain as obtained within GW is more pronounced than the one obtained within a mean-field (LDA) theory, with appreciable contribution from self-energy corrections: $\delta E_g^{GW} \approx \delta E_g^{LDA} + \delta \Sigma_g$. For $E_{11}$ and $E_{33}$ this leads to a larger decrease in the bandgap compared to LDA since both $\delta E_g^{LDA}$ and $\delta \Sigma_g$ are negative; in contrast, $\delta E_g^{LDA}$ is positive for $E_{22}$ and $E_{44}$, and the still negative $\delta \Sigma_g$ leads to a smaller increase of the bandgap with strain.

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Figure 5 shows the optical absorbance for the (17,0) CNT calculated within GW (no excitonic effects) and calculated within BSE (i.e. including excitonic effects) for the two lowest optical transitions. Here the absorbance is obtained from $A(\omega) \sim \omega e_2(\omega)$ where $e_2(\omega)$ is the imaginary part of $\varepsilon$. The peaks in the figure for the BSE results indicate the lowest energy bright exciton for light polarization parallel to the nanotube axis. At zero strain (Fig. 5a), the $E_{11}$ and $E_{22}$ transitions show strong many-body effects, with exciton binding energies of 574 meV.
and 581 meV. Similar results are obtained for the $E_{43}$ and $E_{44}$ transitions (Table 1) with $E_{43}^{33} = 756$ meV and $E_{44}^{33} = 630$ meV.

Upon application of strain (Fig. 5b) one can see that the $E_{11}$ exciton energy $\Omega_{11}$ decreases by 145 meV/% while $\Omega_{22}$ increases by 128 meV/%. Results for $\Omega_{33}$ and $\Omega_{34}$ (Table 1) give values of $-157$ meV/% and $+75$ meV/%, respectively. Thus, the qualitative trends observed from the GW calculations are maintained with the optical properties; however, because the quasiparticle bandgap and the exciton energy have a different dependence on strain, $dE_g^{\mathrm{GW}}/d\sigma \neq d\Omega/d\sigma$, one can deduce that the exciton binding energy $E_b = E_g^{\mathrm{GW}} - \Omega$ depends on strain. This can be seen in Fig. 5 and in Table 1 where all of the exciton binding energies are decreased under strain by amounts ranging from 28 meV/% for the $E_{44}$ transition to 74 meV/% for the $E_{43}$ transition. Much like the changes in the quasiparticle gap, the decrease in binding energy also stems from the change in dielectric screening upon applied strain. Indeed, the attractive interaction between the electron and hole forming the exciton is mediated by the screened Coulomb interaction $W = \varepsilon^{-1}W$, and because $\varepsilon$ is always determined by the lowest energy electronic bandgap, all of the optical transitions will be affected in the same way leading to the common decrease in binding energy.

It should also be noted that the exciton oscillator strength shows very small variation with strain. Since the oscillator strength is $\sim \Omega \mu_0^2/\alpha$, with $\mu_0^2/\alpha$ the squared exciton transition dipole matrix element per unit tube length $[34]$, the implication is that $\mu_0^2/\alpha$ strongly increases with increasing strain. Indeed, for the (17,0) CNT, we find that $\mu_0^2/\alpha$ increases from $\sim 3.9$ a.u. at zero strain to $\sim 6.8$ a.u. at 2% strain.

The optical results for the (17,0) CNT can be generalized to the (11,0) CNT as well, at least for the lowest optical transition (Fig. 3 and Table 2). Indeed we find $d\Omega^{11}/d\sigma = -142$ meV/% and a reduction of the exciton binding energy by several tens of meV/%. (At 2% the reduction in $E_b$ is about 3.5 times as large as that obtained using a tight-binding approach for excitons[19] for the (11,0) CNT.) Furthermore, the exciton energy is found to depend linearly on strain, and turns out to be relatively close to the DFT result. As we discussed above, with decreasing bandgap the dielectric screening gets enhanced, and thus the binding between electron and hole decreases. This effect also explains why the change in optical gap $\Omega$ upon applied strain is similar to that obtained at the LDA level: it is due to cancellation effects between quasiparticle self-energy corrections and excitonic effects.

IV. SUMMARY

In summary, we performed many-body ab initio calculations of the electronic and optical properties of semiconducting zigzag CNTs under uniaxial strain. We find that the fundamental electronic bandgap depends more strongly on strain than previously predicted by non-interacting models. In addition, we find that self-energy corrections generally decrease the bandgaps, which enhances or reduces the impact of strain compared to DFT depending on which transition is considered. Furthermore, the optical transitions are also found to be affected by many-body effects. In particular, the exciton binding energy decreases with increasing strain regardless of the transition, with variations of several tens of meVs per percent strain. More generally, our results indicate that quasiparticle and excitonic effects are strongly tied, and that the interpretation of optomechanical experiments in CNTs requires a more in-depth consideration of many-body effects. This is further supported by other many-body calculations on strained bulk[32, 36] and two-dimensional materials[37, 38] where material-specific and dimensionality phenomena have been observed.

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FIG. 5: Optical absorption spectrum of the (17,0) CNT calculated without the electron-hole interaction (GW) and with the electron-hole interaction (BSE). Panel (a) is for the unstrained case and panel (b) is for 2% strain.
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