Universal nature of collective plasmonic excitations in finite 1D carbon-based nanostructures

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Abstract
We provide evidence of the plasmon resonances in a number of representative 1D finite carbon-based nanostructures using first-principle computational electronic spectroscopy studies. Our special purpose real-space/real-time all-electron time-dependent density-functional theory simulator can perform excited-states calculations to obtain correct frequencies for known optical transitions, and capture various nanoscopic effects including collective plasmon excitations. The presence of 1D plasmons is universally predicted by the various numerical experiments, which also demonstrate a phenomenon of resonance splitting. For the metallic carbon nanotubes under study, the plasmons are expected to be related to the Tomonaga–Luttinger plasmons of infinitely long 1D structures. In-depth quantitative understanding of such resonances which have not been clearly identified in experiments so far, would be invaluable for future generations of nano-photonic and nano-electronic devices that employ 1D conductors.

Keywords: nanoplasmonics, real-time TDDFT, 1D conductors, T–L plasmon, computational spectroscopy, plasmon velocity

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanoplasmonics is a field that has grown rapidly in the last few years [1, 2]. Covering a range from terahertz through infrared to visible light frequencies, this field already offers numerous applications to electronics and photonics. In the visible and near IR range, nano-antennas [3] and nanoparticles have provided drastically enhanced coupling to electromagnetic waves [4]. All of this research work has taken advantage of plasmonic surface modes—either on nanoparticles, or on metallic sheets—and has led to some initial practical applications. However, there are still significant fundamental limitations that must be overcome for further progress to be possible in this field [5]. While there is an extensive literature on 1D plasmons, these have not been emphasized for applications due to the difficulty of preparing devices and performing experiments. Yet, 1D conductors are of interest since they can potentially exhibit lower losses than the 2D ones. The chief signature of 1D plasmons is a high-frequency excitation (i.e. energy resonance) that depends inversely on the length of the conductor. Examples of nano-structures that can support 1D plasmons are graphene nanoribbons (GNRs), single wall carbon nanotubes (SWCNTs) and linear carbon chains. Due to the very strong coulomb interactions in such 1D systems, the low-energy excitations of interacting electrons cannot be adequately described by Landau’s Fermi liquid theory [6], which has to be replaced by Tomonaga–Luttinger (T–L) liquid theory [7–10]. Specifically, it was shown that metallic carbon nanotubes can be well described with the T–L theory [11, 12]. A bosonized representation of the Hamiltonian led to the following conclusions: (i) the density of single particle states is a power function of the energy and vanishes at the Fermi energy; (ii) consistent with (i) the conductance of electrons tunneling into the CNT has a universal power law dependence on voltage and temperature; (iii) the electron states are separated

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into charge states and spin states [13]. In the simulations that follow spin/charge separation effects are neglected; (iv) collective boson states form charge density waves in the CNT (‘T–L plasmons’) which propagate with a velocity \( v_p = v_F/g \) where \( v_F \) is the Fermi velocity \( \approx 1 \times 10^6 \text{ m s}^{-1} \), [14] and \( g \) is a parameter that depends on the strength of the Coulomb interaction and on screening by the electrostatic environment (the latter being a weak effect) [12]. The predictions (i) and (ii) have been well verified by transport [15, 16] and optical [17] measurements. The parameter \( g \) is \( <1 \) for T–L liquids and \( =1 \) for Fermi liquids, \( v_F \) is thus higher than \( v_p \). An average plasmon velocity of the predicted magnitude was recently deduced from absorption measurements on enriched SWCNTs films [18]. Ultra-fast time-dependent measurements evidenced ballistic electron oscillations in isolated SWCNTs, but the propagation velocity was equal to the Fermi velocity, consistent with single particle excitations, not plasmons [19]. Detailed experimental confirmation of the predicted plasmon resonance frequencies in isolated SWCNTs is thus still an unsolved problem. Estimates of \( g \) for CNTs yield values in the range 0.26 – 0.33 [12] resulting in \( v_p \) being in the range 3–4 \( \times 10^6 \text{ m s}^{-1} \). Electromagnetic simulations have yielded \( v_F \) up to 6.2 \( \times 10^6 \text{ m s}^{-1} \) [20]. Recently, T–L liquid behavior with \( g = 0.53 \) was verified in atomic gold chains by tunneling and optical measurements [21].

The focus of this paper is the dynamic behavior of the collective medium in 1D conductors and its resonances. A physical picture of the resonances can be gained by realizing the equivalence of the finite length 1D conductor to a transmission line [22, 23]. Both single quasi-particles and plasmon waves resonate as they are reflected at the ends of the conductor, and their respective fundamental resonance frequencies are calculated as \( f = v_F/(2L) \) (the single quasiparticle case) and \( f = v_p/(2L) \) (the plasmon case) where \( L \) is the length of the conductor. For the basic T–L model the waves are non-dispersive (i.e. the phase velocity is equal to the group velocity) and the plasmon resonance frequency is then expected to vary in inverse proportion to the length of the 1D nanostructure conductors. Although this is no longer true for the short structures simulated here, we still find a monotonic decrease of the resonant frequencies as \( L \) increases for all resonances which we can identify as collective, and the above definition for the velocity allows us to show the trend of plasmon velocity versus length. As the length of the structure increases, the dispersion relation will asymptotically become linear and the group velocity will become equal to the phase velocity and approach a constant value.

The paper analyzes excitations in four different types of carbon nanostructures: (1) carbynes (carbon chains); (2) narrow (2-ZGNR) GNRs with zigzag edges (acenes), (3) narrow (3-AGNR) GNRs with armchair edges (PPP); and (4) metallic single wall carbon nanotubes (SWCNTs). We identify collective excitations in all four different types of carbon nanostructures. Despite their different detailed structure, the main results of this work summarized in figure 1 indicate that the plasmon velocity variation with length follows a general trend i.e. the velocity shows a monotonic increase with the length of the structure and it is expected that it will asymptotically become independent of length. Using our numerical simulations we identify and discuss in detail the plasmon resonances, as well others such as single quasi-particles, band-to-band, \( \pi \) and \( \sigma + \pi \) plasmons.

### 2. Methodology

First-principle calculations are becoming critical to provide evidence of plasmon resonances in 1D carbon-based nanostructures. Such quantitative simulations are known to be challenging, since they should be both capable to provide reliable information on the many-body excited states (beyond ground state theory), and to address large-scale computational needs of finite dimensional systems (beyond the solid-state unit-cell). The time dependent density functional theory (TDDFT) [24] alongside with the simple adiabatic local density approximation (ALDA) for the many-body exchange-correlation term, has been very successful for providing accurate absorption spectra of a large number of complex molecular systems [25]. The real-time TDDFT approach introduced by Yabana and Bertsch [26, 27], in particular, combines both potential for parallel computing scalability, and an intuitive treatment of the real-time spectroscopy that can deal with any form of excitations. Our in-house simulator, named NESSIE, is performing both all-electron real-space DFT ground state and real-time TDDFT excited states calculations. NESSIE benefits from the high-performance capabilities of the FEAST eigensolver [28, 29], which has also allowed to efficiently redesign various stages of the electronic structure numerical modeling process [30–32]. Detailed information on our numerical real-space and real-time modeling framework is provided within the supporting document of this article.

Two types of real-time TDDFT simulations are considered in our experiments. First, the spectroscopic information is obtained from linear response calculations after a short and weak polarized impulse is applied along the longitudinal or perpendicular direction of the 1D nanostructure. Then, once resonances of interest are identified in the absorption spectrum, new time-dependent calculations are performed in response to a realistic stimulus, such as a laser tuned to each resonance frequency (e.g. sinusoidal excitation along the longitudinal direction). Such simulations aim at providing more detail on the 3D electron dynamics of the particular resonances with relevant information about their nature. From atom and benzene-like chain structures to short carbon nanotubes, our numerical experiments discussed below progressively account for an increase in the physical and computational complexities of the 1D atomic structure.

### 3. Carbyne

Carbyne is a chain of carbon atoms that comprises either double or alternating single and triple atomic bonds. With recent progress in synthesis [33], first-principle theoretical
Figure 1. Summary of plasmon velocities computed for all of the 1D carbon nanostructures considered in this work using different lengths (numerical values are provided in the supporting information document). Two main plasmon modes are represented (except for the carbyne and the 5-PPP cases). We note the universal monotonic increase of the plasmon velocities for longer structures, while the less regular behavior in the 15–20 Å range (in particular for the 5-PPP and the 7-unit cell (3,3) SWCNT) is likely due to coupling effects between the plasmons and the ‘band-to-band’ transitions that occur in the same energy range.

Figure 2. Computed absorption spectra of NC$_{2n}$N with lengths $n = 1, 2, 4, 8$ (using the single-triple bond alternation structure and the optimized geometries reported in [40]). The plot on the top for $n = 4$ is associated with the perpendicular response of a weak impulse applied along the same direction. All the other plots consider the response of an excitation applied along the longitudinal direction of the chain. The figure insets illustrate the variation of the induced dipole obtained from our real-time TDDFT calculations and that are used to derive the absorption spectra of the corresponding structures.
investigations have become increasingly more relevant to study the various attractive physical properties of this material [34]. In our numerical simulations of NC$_{2n}$N shown in figure 2, the strong longitudinal resonance shifts progressively towards the left of the spectrum with longer chains (i.e. red shift). Their oscillator strength increases with the length of the chain indicating that more electrons can participate in the plasmonic collective excitations. These results are in excellent agreement with previous studies of carbon chains using the TDDFT approach that have been reported in [35–37] which compare well with the experimental data reported in [38]. References [35, 37] also identify these excitations as collective plasmons. Furthermore, the associated velocity of the resonances is in the typical range of collective plasmons (as discussed in the introduction and further below). We note that the carbynes are not metallic and thus are not expected to conform with the T–L theory. Nevertheless, carbynes show strong 1D plasmon excitations. Moreover, our results show that these longitudinal resonances do not appear with a perpendicular excitation (see the NC$_{2n}$N plot at the top of figure 2). In contrast, one can identify other small resonances for instance, at 11.01 eV, and at 14.68 eV which do not depend on the length of the chain. These particular energy transitions are comparatively close to the ionization potentials of the local atoms C and N, respectively at 11.26 eV and 14.53 eV [39].

The longitudinal resonances can be observed in more detail in figure 3 (left plot) for the CH$_{16}$N, HC$_{18}$H, and HC$_{24}$H chains. We note that the spectra produced for the C$_{16}$ chain using the H or N termination are very similar. Our results are also quantitatively close to the ones obtained in [37] for the HC$_{2n}$H chain that makes use of the projector augmented-wave (PAW) pseudopotential and performs TDDFT linear response simulations in the frequency domain. The lowest energy plasmon resonances found in these results are also in agreement with earlier real-time TDDFT simulations performed in [36] using a smooth pseudopotential. In comparison with the latter however, both the PAW and our full-core potential treatments reveal additional plasmonic resonances at higher energies. These oscillations can be observed in the experimental data of the NC$_{2n}$N chains [41]. In our simulations, the splitting between these resonances becomes narrower for the HC$_{2n}$H and only two main peaks can be observed instead of three for HC$_{16}$H. The isosurface snapshot plots in figure 3 represent three additional real-time TDDFT simulation results that can help provide more insights on the time-dependent electron dynamics of the plasmonic resonances in HC$_{16}$H. The strongest resonance at the lowest energy transition gives rise to a distinguishable plasmon that can oscillate back and forth along the longitudinal direction. It has the signature of a plasmon with a calculated velocity of $v_p = 3.18 \times 10^6$ m s$^{-1}$ which increases to $v_p = 3.64 \times 10^6$ m s$^{-1}$ for HC$_{24}$H. The results for the other two snapshot plots confirm the presence of additional longitudinal resonance modes that were mentioned in [37], with cosine and sine like envelope features for the plasmonic excitations. These two excitations have a different character in that the charge density alternates from positive to negative for each atom pair, analogous to optical phonon modes. Finally, we note that no single particle excitation at the Fermi velocity is observed since the carbon chain family considered here is semiconducting.

4. Acenes and poly(p-phenylene) (PPP)

Acenes and PPP are polycyclic aromatic hydrocarbons consisting of linear benzene rings that are respectively fused or attached. They can also be thought of as the narrowest GNRs of finite lengths, associated with the zig-zag configuration for acenes (2-ZGNR) and the armchair one for PPP (3-AGNR). Understanding the properties of long acenes in particular, is the subject of active research [43].

Results for anthracene, tetracene and pentacene reported in figure 4 confirm that the strong longitudinal UV resonances along the z-direction are in very good agreement with the experimental data reported in [44]; the peaks appear respectively at 4.85 eV (exp: 4.89 eV), 4.30 eV (exp: 4.46 eV), and 3.88 eV (exp: 3.99 eV). While advanced exchange-correlation functionals for TDDFT are often suitable to describe the singlet low-lying excited states in acenes located at lower energies [45], the TDDFT/ALDA model then appears capable to accurately capture the bright components at higher energies which account for the main nanoscopic effects in finite systems. These resonances are plasmoniclike, since we note a progressive shift towards the left of the spectrum with longer chains accompanied by an increase in oscillator strength. They are also absent from the results of excitations along the x and y directions. For the latter, in turn, one can identify two other resonances that stay independent of the chain length, at 11.22 eV using an x-polarized impulse that equally excites all the carbon atoms in the y–z plane (energy relatively close to the ionization potential of C), and at 7.55 eV using a y-polarized impulse that equally excites all the individual fused benzene rings (energy relatively close to the $\pi \rightarrow \pi^*$ transition in benzene). For the case of pentacene, in addition to a strong plasmon resonance at 3.88 eV, we note a couple of weaker longitudinal resonances at 4.84 and 5.25 eV (see top right plot of figure 4). The latter comes close to the experimental HOMO-LUMO gap at 5.2 eV [46] (this gap is known to be severely underestimated by DFT at ~1eV). The results on heptacene and nonacene in figure 4, clearly show that as the length of the structure increases, a second strong resonance appears. The isosurface snapshots representing the electron dynamics for the two main resonances of heptacene confirm the presence of two plasmons. In contrast to the case of carbon chains, this second resonance does not result from an additional longitudinal confinement mode, and the results indicate the presence of another channel (i.e. two confinement modes are then present in the transverse x, y plane). We note that similar double plasmon resonances have also been recently observed using semi-empirical simulations applied to GNR structures with variable widths [47]. The calculated plasmon velocities associated with the first and second resonances of heptacene, $v_{pl1} = 2.77 \times 10^6$ and
\[ v_{pl_1} = 3.61 \times 10^6 \text{ m s}^{-1}, \quad \text{increase to} \quad v_{pl_2} = 3.18 \times 10^6 \text{ m s}^{-1} \text{ for nonacene.} \]

The case of finite PPP is shown in Figure 5 using lengths of 5 and 10 unit cells. Excitations along the perpendicular directions (including the x-direction not shown here) provides results comparable to the ones obtained for acenes in Figure 4. However, we note one additional resonance at around 6.55 eV for an excitation along the y perpendicular direction (curve denoted ‘ST’) which is also present (and amplified) with an excitation along the longitudinal z direction for both 5 and 10-PPP. All the other longitudinal resonances at lower energies are absent from the ‘ST’ curve. The isosurface snapshots of the charge oscillations, provide some useful information on the nature of the three main selected longitudinal resonances for 5-PPP. The strong first peak can be associated with a plasmon, while the second and third peaks reveal different characteristics related to ‘band-to-band’ transitions. In particular, the second peak shifts from 3.86 to 3.3 eV for the long 10-PPP which is in very good agreement with the strong experimental absorption peak (related to the bandgap) found at 3.4 eV for PPP [49]. The position of the third peak, in turn, is not sensitive to variation in length. A closer look at the isosurface plots show that the charge oscillations at 6.55 eV are somehow localized within each attached benzene ring. We note that a broader ‘band-to-band’ transition region appears at around 5 eV for both 5 and 10-PPP. Finally, the main plasmon resonance at 2.67 eV i.e. \( v_{pl} = 2.44 \times 10^6 \text{ m s}^{-1} \) shifts towards the left of the spectrum of the 10-PPP and, similarly to the case of long acene, splits into two peaks. The calculated plasmon velocities associated with the two resonances are \( v_{pl_1} = 3.97 \times 10^6 \text{ m s}^{-1} \) and \( v_{pl_2} = 4.83 \times 10^6 \text{ m s}^{-1} \).

5. Single-wall carbon nanotube

Figure 6 shows our results for simulations of a finite (3,3) armchair SWCNT. To stabilize the structure one additional carbon ring, and hydrogen atoms were added at the ends. The H atoms are expected to have only minor effects on the resonances observed. Armchair SWCNTs are known to exhibit metallic conduction [14] and, as mentioned in the introduction, they can be described by the T–L theory (i.e. the Landau–Lifshitz (L) theory) [11, 12]. We simulated tubes of three different lengths, 3, 5, and 7 ‘unit cells’, respectively. The simulations were performed for an E-field parallel to the z-axis of the tubes (the long axis), marked ‘3’, ‘5’ and ‘7’, as well as perpendicular to that axis (for the 5 unit cell case, marked ‘5 T’). We first distinguish resonances that do not

![Figure 3](image-url)
change with the length \((L)\) of the tube. The peak at about 4.44 eV can be identified as being due to the \(\pi\)-plasmon \((E_\pi)\) in the figure which agrees with the experimental value 4.5 eV in [50, 51]. Note the characteristic distribution of the oscillating charges, following the bonds, in the snapshot displayed below the spectra. A broad band with a peak at \(\sim 15\) eV due to the \(\pi + \sigma\) plasmon can also be observed in the spectra (observations are included in the supporting information document). Since the above plasmons are basically of the bulk (3D) type, they can also be excited by a field in the direction perpendicular to the tube. Both of these resonances are well known for SWCNTs and have been detected experimentally by electron energy loss spectroscopy [52] as well as by optical spectroscopy (the \(\pi\)-plasmon) [50, 51]. We note that the \(\pi\)-plasmon resonance for perpendicular excitation is shifted to a higher energy, 5.8 eV, in qualitative agreement with the experimental data (exp: 5.25 eV) [51].

The \(\pi\)-plasmon resonance for the 3 unit cell case is not so easy to identify, see further discussion below. There is also a resonance for all values of \(L\) at about 3.25 eV \((E_{bb}\) in figure 6). This resonance energy agrees with experimental optical data (exp: 3.1 eV) [50, 53, 54] and it can be identified as a ‘band-to-band’ resonance for infinitely long tubes and for higher energy bands. The simulations show that this peak does not vary with \(L\), and also that it can not be excited perpendicular to the axis, as expected for a band-to-band transition. The charge distribution under sinusoidal excitation shown in figure 6 clearly lacks the collective character evident in the plasmon resonances.

One type of resonance that does vary with \(L\) occurs in the lowest energy range, from about 1.4 to 2.2 eV \((E_{e}\) in the figure). Calculating a velocity for this resonance we find a value \(0.98 \times 10^6\) and \(1.18 \times 10^6\) m s\(^{-1}\) respectively for the 5 and 7 unit cell cases, which is close to the Fermi velocity. We
note that this resonance can only be excited by a field parallel to the tube axis, as expected if it is due to electrons resonating from one end of the tube to the other. This is the type of single particle excitation resonance that was measured in [19]. Further evidence for this interpretation is obtained by inspecting the top 4D isosurface snapshots to the right of the spectra (‘single excitation—$E_{e^-} = 1.63 \text{ eV}$’), which show the periodic oscillation of the charge density.

Finally, we find two strong peaks at energies of 3.69 − 3.89 eV (a split peak for the longest tube) and 3.89 eV (marked $E_{pl}$ in the figure) that vary with L as expected for T–L plasmon type resonances. These resonances can only be excited with a parallel field as was confirmed by a simulation of the 5 unit cell tube with perpendicular excitation (marked ‘5 T’). One of the series of 4D snapshots (collective oscillation—$E_{pl} = 3.89 \text{ eV}$) shows how the charge density waves travel back and forth on the tube under sinusoidal excitation at the resonance frequency. There is a related plasmon resonance at a higher energy ($E_{pl}$ at 4.76 eV) for the 5-unit cell case. Thus we find split plasmon resonances for both cases—the 5 unit and 7 unit cell ones—with a much smaller split for the longer tube. The calculated velocities for the two T–L plasmons for the 5 unit cell case are $2.35 \times 10^6$ and $2.87 \times 10^6 \text{ m s}^{-1}$, and they increase to $3.12 \times 10^6$ and $3.29 \times 10^6 \text{ m s}^{-1}$ for the 7 unit cell. The side view snapshots of the charge distribution in figure 6 can now be used to discuss further the different characters of the resonances $E_{e^-}$, $E_{pl}$ and $E_{pl}$. The charge density for the single (quasi-particle) excitation ($E_{e^-}$) is spread across the cross-section. In contrast, the plasmon excitations concentrate the charges around the periphery and at the ends of the tube as expected for a boson-type mode [7, 8, 10]. The split between the two plasmon frequencies can be interpreted as related to two different modes quantized around the periphery. Given our interpretation of the peaks from 3.69 to 3.89 eV as T–L plasmon resonances, we would expect a similar T–L plasmon resonance for the 3 unit cell case at a somewhat higher energy, where we see two peaks. As indicated earlier, this brings us to the expected energy of the $\pi$-plasmon, however, and a possible interpretation of the two
peaks at 4.32 eV and 4.81 eV for the 3 unit cell tube is that the T–L plasmon and the π-plasmon are coupled.

6. Conclusions

This paper has simulated molecular absorption spectra employing accurate all-electron real-time TDDFT simulations. The range in size has been extended from small molecules such as C₂H₂ or benzene to carbon nano-structures that are equivalent to 1D conductors with finite lengths. Very good agreement with experimental spectra is obtained when such data is available. We find universal features for all structures investigated which include carbon chains, narrow armchair and zigzag GNRs (i.e. acenes and PPP), as well as short carbon nanotubes. All structures show collective plasmon oscillations characterized by resonant frequencies that vary roughly inversely with the length of the structure. For the metallic structures (in our case only the SWCNTs) the plasmons are expected to be related to the T–L plasmons of infinitely long 1D structures. Another notable characteristic is that the main plasmon resonance is split into two components due to transverse quantum confinement effects (except for the case of carbyne that presents two to three longitudinal resonance modes). The simulations allow vivid 4D visualizations of the electron charge distributions for different types of resonant modes, which then provide more insights on their nature. As summarized in figure 1, the velocity of plasmon propagation shows a monotonic increase with the length of the structure and it is expected that the plasmon velocity will asymptotically become independent of length. Further optimization of our present high performance computing techniques should allow the extension of the simulations to longer structures (up to tens of unit cells for SWCNT), and lead to accurate predicted data that will guide future photonic and electronic applications of nanostructures over a wide frequency range, from visible to terahertz.
Supplementary information

The supplementary document to this article includes detailed information about the theoretical models and numerical methods used in this study, additional information data about the $\pi$ and $\pi + \sigma$ resonances in SWCNT, and a table of numerical values for the plasmon velocities.

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