Bright and dark excitons in semiconductor carbon nanotubes: insights from electronic structure calculations

Svetlana Kilina, Ekaterina Badaeva, Andrei Piryatinski, Sergei Tretiak, Avadh Saxena and Alan R. Bishop

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We review electronic structure calculations of finite-length semiconducting carbon nanotubes using time-dependent density functional theory (TD-DFT) and the time dependent Hartree–Fock (TD-HF) approach coupled with semi-empirical AM1 and ZINDO Hamiltonians. We specifically focus on the energy splitting, relative ordering, and localization properties of optically active (bright) and optically forbidden (dark) states from the lowest excitonic band of the nanotubes. These excitonic states are very important in competing radiative and non-radiative processes in these systems. Our analysis of excitonic transition density matrices demonstrates that pure DFT functionals overdelocalize excitons making an electron–hole pair unbound; consequently, excitonic features are not presented in this method. In contrast, the pure HF and AM1 calculations overbind excitons, inaccurately predicting the lowest energy state as a bright exciton. Changing the AM1 with the ZINDO Hamiltonian in TD-HF calculations predicts the bright exciton as the second state after the dark one. However, in contrast to AM1 calculations, the diameter dependence of the excitation energies obtained by ZINDO does not follow the experimental trends. Finally, the TD-DFT approach incorporating hybrid functionals with a moderate portion of the long-range HF exchange, such as B3LYP, has the most generality and predictive capacity providing a sufficiently accurate description of excitonic structure in finite-size nanotubes. These methods characterize four important lower exciton bands: the lowest state is dark, the upper band is bright, and the two other dark and nearly degenerate excitons lie in between. Although the calculated energy splittings between the lowest dark and the bright excitons are relatively large (~0.1 eV), the dense excitonic manifold below the bright exciton allows for fast non-radiative relaxation leading to the rapid population of the lowest dark exciton. This rationalizes the low luminescence efficiency in nanotubes.

1. Introduction

Carbon nanotubes are one of the most auspicious examples of quasi-one-dimensional nanoscale materials which promise fascinating applications ranging from nanoelectronics and optoelectronics to medical technologies. However, in order to complete their proof-of-concept development stage, as well as to extensively integrate them into common experimental, medicinal and household usage, a detailed understanding and rational control of the electronic structure and the optical response of these materials is required. It is well recognized by now that the electron confinement along the circumference of the single-walled carbon nanotube (SWNT)
and its small dielectric constant lead to significant electron–hole binding energies and the formation of strongly bound excitons—strongly interacting electron–hole pairs—as the primary photoexcited species. Theoretical studies, transient spectroscopy and nonlinear absorption experiments have unambiguously proven that the lower energy optical excitations of SWNTs involve transitions to exciton states with large binding energies of 0.2–0.5 eV, depending on the tube diameter and chirality.

In addition, complex Coulombic interactions drive the existence of optically inactive (dark) excitons energetically closer to each of the optically allowed (bright) excitons. In a single particle representation, the states at the edges of conduction (CB) and valence (VB) bands in SWNTs are doubly degenerate because of the cylindrical symmetry of the tube. For free electron–hole pairs, this leads to four distinct but degenerate interband transitions with different angular momenta. However, the Coulombic interaction between a photoexcited electron and a hole lifts the degeneracy and introduces a complex structure of overlapping excitons, where only one is optically bright and the others are dark because of the difference in their parity. Interactions with the environment, edge effects, defects and impurities in the tube lattice further split and mix energies of excitonic bands. Mixing between different excitons, due to interactions and deviations from the ideal tube structure, makes some optically forbidden states weakly active (semi-dark), rather than being strictly dark.

Indeed, the energy position of the dark and semi-dark excitons with respect to the bright ones strongly affects the photophysical properties of SWNTs. Thus, recent theoretical studies explain the typical low photoluminescence quantum yield in SWNTs by the possible involvement of a dark excitonic state below the first optically allowed exciton (E_1), trapping much of the exciton population. The experimental evidence for the existence of the lowest energy
dark exciton has been obtained through magnetic brightening of SWNTs.\textsuperscript{30,35} Time-resolved spectroscopy reveals multi-exponential behavior of the radiative photoluminescence (PL) decay at room\textsuperscript{36} and low\textsuperscript{28,32} temperatures, demonstrating at least two different characteristic decay times.\textsuperscript{38} The first, fast, component can be associated with the rapid decay of the bright exciton to the lower-lying dark state. The long time dynamics are most readily accounted for by the trapping of a dark exciton that does not have a radiative recombination path.\textsuperscript{36}

Although both experimental and theoretical results conclude that the lowest energy exciton in SWNTs is the dark one, the relative ordering of other optically inactive excitonic states with respect to the bright one and their role in photophysical processes in SWNTs is still unclear. For example, \textit{ab initio} calculations of a few narrow tubes within the Bethe–Salpeter scheme\textsuperscript{25} show that the two remaining dark states from the four-fold first band are degenerate and lie slightly above the bright exciton. Tight binding modeling, including electron–hole interactions via the Bethe-Salpeter equation,\textsuperscript{23} also provides a similar energy band structure for the four lowest excitons. However, for long but finite-size tubes, calculations based on the semi-empirical Pariser–Parr–Pople (PPP) Hamiltonian\textsuperscript{24,33} predict two degenerate dark states and one weakly allowed state in between the bright exciton and the lowest dark one. In addition, the splitting between the lowest dark and the bright excitons predicted by this semi-empirical model is significantly larger than those derived from the \textit{ab initio} calculations.\textsuperscript{25,34} Other semi-empirical calculations based on the time-dependent Hartree–Fock (TD-HF) approach combined with an Austin model 1 (AM1) Hamiltonian predict the bright exciton as the lowest energy state,\textsuperscript{39} while the same method coupled with Zener’s intermediate neglect of differential overlap (ZINDO) Hamiltonian gives the bright exciton as the second state after the dark one and the two remaining states as semi-dark excitons lying above the bright state.\textsuperscript{40} Finally, our previous first-principle calculations based on the time-dependent density functional theory (TD-DFT), predict three nominally dark exciton bands below the bright exciton.\textsuperscript{28}

It is quite remarkable that each of the suggested electronic structures for the first four-fold excitonic band (\textit{i.e.} two dark or semi-dark states lying above or below the bright exciton) could be used as a reasonable model to describe the experimentally detected PL rates in SWNTs. For example, a two level model—the dark state followed by a bright one—was used to explain the transient absorption kinetics in (11,0) nanotubes.\textsuperscript{31,44} However, the calculated relative positions of the three lowest energy dark bands with respect to the bright exciton are in good agreement with fluorescence spectra as a function of temperature, and successfully explain the dual emission features observed in (7,5) and (7,6) tube samples.\textsuperscript{28} Thus, while qualitatively consistent, the precise ordering of bright and dark excitons, their energy splitting values and the dependence on the tube geometry are highly method-dependent and still under debate.

In the present work, we further explore low-energy dark and bright excitons, their ordering, sensitive energetics, optical activity and the dependence of the splitting between these states on the tube chirality and diameter by applying a TD-DFT methodology. It is important to note that TD-DFT is currently a mainstream approach and a method of choice for quantitative modeling of optical response in large molecular systems. However, this method was not broadly applied to SWNTs. Previously, we used TD-DFT to study electronic properties and energetics of singlet and triplet states in (7,5) and (7,6) tubes. Here we extend our studies to ten finite-size SWNTs with diameters ranging from 0.5–1.5 nm. We specifically explore the effect of different DFT functionals on the splitting between dark and bright singlet states and compare these results with TD-HF calculations based on semi-empirical Hamiltonians.

The outline of the paper is as follows. In section 2 we briefly define the methods that we use and sketch computational details. In section 3 we first compare the absorption spectra of SWNTs calculated with different DFT functionals. Then we report the localization properties of lower energy excitons based on the analysis of transition density matrices and identify four main excitonic bands, including optically dark and bright states. Also, the effect of the nanotube length and the changes in exciton energies and localization properties imposed by a different portion of the HF exchange in the functional are discussed in detail. Next, the dependence of the energy splitting between the lowest dark excitons and the bright excitons on the tube diameter is obtained and analyzed. The TD-DFT results are also compared with semi-empirical methods in subsection 3.2. Finally, concluding remarks are given in section 4.

2. Methods and computational details

2.1 Description of SWNTs studied

Each of the ten SWNTs we investigate here has a length of 8–12 nm and comprises several repeat units (see Table 1). Such a length is significantly larger than the tube diameter and characteristic exciton sizes,\textsuperscript{39,43} and, therefore, is expected to reproduce the basic properties of longer SWNTs and to be at least qualitatively consistent with the infinite-size limit. Calculations of conjugated oligomers provide a standard example of such an approach.\textsuperscript{44,46} On the other hand, the finite length of SWNTs introduces some extrinsic factors to the simulated systems. In contrast to the ideal nanotube systems typically considered in theory, actual SWNT samples can have inhomogeneity in the length (\textit{i.e.}, some species have much smaller length compared to the averaged tube length), inhomogeneity of the local dielectric environment, defects, and intertube interactions. Indeed, all these extrinsic features affect electronic structure, exciton localization properties and the overall optical response of the system.

As for realistic tube lengths, SWNTs used in experiments typically have lengths of hundreds of micrometers. However, sample preparation such as sonication might lead to multiple nanotube breakages\textsuperscript{47} and significant reduction of the average nanotube length down to 10–15 nm.\textsuperscript{48} Thus, in experimental samples, tubes with small length, such as we consider here, can also be present. Since our tubes have a finite length, we cap unsaturated chemical bonds at the open tube ends with
geometries. Our previous calculations of a (7,6) tube show that the structure is expected to be weakly dependent on the optimized molecules. In SWNTs, due to their rigid geometry, the electronic properties are expected to be determined by the electronic states of the pristine tubes.

2.2 Geometry optimization

Optimal geometries of all tubes are obtained using the semi-empirical AM1 Hamiltonian, as implemented in the MOPAC-2002 code. This method works very well for geometry optimizations in a broad variety of π-conjugated molecules. In SWNTs, due to their rigid geometry, the electronic structure is expected to be weakly dependent on the optimized geometries. Our previous calculations of a (7,6) tube show that optimizations conducted with other methods lead to small changes in the electronic states of the tubes. We note that AM1 reproduces the curvature mediated electronic structure, compared to AM1 geometries. We note that AM1 reproduces the curvature mediated electronic structure, compared to AM1 geometries. We note that AM1 reproduces the curvature mediated electronic structure, compared to AM1 geometries. We note that AM1 reproduces the curvature mediated electronic structure, compared to AM1 geometries.

Taking into account the reduced computational cost in addition to all other benefits of this method, the AM1 approach is chosen for geometry optimizations of the SWNTs studied here.

2.3 TD-DFT excited state calculations

The AM1-optimized geometries provide input structures for further excited-state calculations performed by TD-DFT using the GAUSSIAN03 package. The STO-3G basis set is sufficient to accurately account for excited state electronic correlations and reproduce the excitonic structure in SWNTs. It is well known that the hybrid TD-DFT technique can account for excitonic phenomena due to the presence of a fraction of the long-range HF exchange. The excitonic size and its localization properties show strong dependence on the amount of the HF exchange. For example, in conjugated polymers, at 0% of HF exchange (LDA and GGA limits), there are no excitonic effects at all. In contrast, 100% of exchange typically produces the most accurate results for most organic molecules and, therefore, is expected to simulate an accurate excitonic structure in SWNTs. The performance of TD-PBE and TD-BLYP (GGA functionals), TD-B3LYP, TD-BHandHLYP (50% of HF exchange) and TD-HF functionals for the first band singlet manifold in SWNTs is well known. It is well known that the hybrid TD-DFT technique can account for excitonic phenomena due to the presence of a fraction of the long-range HF exchange. The excitonic size and its localization properties show strong dependence on the amount of the HF exchange. For example, in conjugated polymers, at 0% of HF exchange (LDA and GGA limits), there are no excitonic effects at all. In contrast, 100% of exchange (HF limit) would overbind the excitons. The right amount of orbital exchange is thus essential to capture excitonic effects and obtain correct electronic structure in π-systems, including SWNTs. 20% (B3LYP) of orbital exchange typically produces the most accurate results for most organic molecules and, therefore, is expected to simulate an accurate excitonic structure in SWNTs.

To investigate localization/delocalization properties of excitons, we further use a two-dimensional real-space analysis of transition density matrices, representing the electronic transitions between the ground state and an optically excited state. Photoexcitation creates an electron–hole pair or an exciton by transforming an electron from an occupied valence band to an empty conduction band.
unoccupied conduction band. Each element of the transition density matrix reflects the dynamics of this exciton projected on a pair of atomic orbitals (AO) given by its indices. Contour plots of these matrices thus show accompanying motions of optically induced charges and electronic coherences. Two characteristic lengths are relevant in these plots: the diagonal direction of the non-zero matrix elements reflects the degree of localization of the optical excitation, i.e., the position of the center of mass of the exciton. The largest off-diagonal extent of the non-zero matrix area — coherence length, $L_C$ — measures the maximal distance between the electron and hole (the exciton size). The larger the exciton size, $L_C$, the less binding between an electron–hole pair is expected. Both cross-sections of transition density matrices are shown below in Fig. 2.

### 2.4 Semi-empirical calculations of excited states

In addition to TD-DFT calculations, we also calculate vertical transition frequencies from the ground state to the singlet excited states, their oscillator strengths and transition density matrices using the semi-empirical approach based on the collective electronic oscillator (CEO) procedure. The CEO approach, described in detail elsewhere, involves the TD-HF formalism combined with semiempirical Hamiltonians. Here, we use both AM1 and ZINDO Hamiltonians. The TD-HF approximation coupled with semi-empirical Hamiltonians directly addresses essential electronic correlations and excitonic effects, while permitting calculations of hundreds of molecular excited states in very large systems (here, up to 1300 atoms in size) with only moderate numerical expense. This methodology has been successfully applied to simulations of optical responses in a variety of conjugated molecular materials. Recently, we used this technique to investigate a number of excited-state phenomena in SWNTs, including anharmonic coherent phonon dynamics, quantification of exciton-phonon coupling constants, effects of Peierls distortion and exciton self-trapping, characterization of high-energy excitonic transitions ($E_{11}$ and $E_{44}$) and analysis of parallel ($E_{11}$) and cross-polarized ($E_{12}$ and $E_{21}$) excitons. We carefully examine the dependence of the excitonic energies, specifically the bright–dark exciton splitting, on the parameters characterizing the softness of the π- and σ-bonds by changing the values of these parameters in the ZINDO Hamiltonian. These results are compared to AM1 and TD-DFT calculations, and to available experimental data (Table 1).

### 3. Results and discussion

#### 3.1 Variation of excitonic structure and optical spectra with density functional

Fig. 1 compares the spectra of all possible transitions, including dark and optically active transitions (absorption spectra) calculated with different DFT functionals for the (6,5) tube. As expected, pure GGA functionals, BLYP and PBE, result in red shifted excitation energies of both optically forbidden and allowed transitions. In contrast, increase in the portion of the HF exchange leads to a significant blue shift. For the considered energy range of about 0.6 eV, all functionals provide one state that collects most of the oscillator strength from its parent band. Thus, this state contributes most to the first distinct peak in the SWNT’s linear absorption spectra, which is commonly associated with the $E_{11}$ transition. The second small peak is roughly 0.2–0.4 eV away from the first one. This peak is formed from the states from the first excitonic band with a higher kinetic energy. The small oscillator strength of such states arises from the exciton scattering on the tube ends leading to the mixing of these states with the bright exciton. Increasing the portion of the HF exchange in the functional causes this second small peak to be consistently blue shifted and its relative intensity decreases with respect to the large first peak. Consequently, the presence of the long-range orbital exchange in the functional, which results in more localized excitons, leads to a significant reduction of the second peak intensity in the HF-limit.

![Fig. 1](image-url)
BHandHLYP (50% of HF exchange), compared to B3LYP (20% of HF exchange). The excitons become more localized, demonstrating a smaller coherence size of an exciton. For the PBE functional, the excitons are completely delocalized, so that there is no excitonic effect at all. With increase of the HF portion in the functional, the excitons will become more localized, demonstrating a smaller coherence size of an exciton. For the BHandHLYP (50% of HF exchange), compared to B3LYP (20% of HF exchange).

For all considered DFT functionals, the presence of several dark states below the bright exciton is clearly seen in Fig. 1. Thus, the bright exciton is the fifth state from the lowest state predicted by TD-BLYP, TD-PBE, and BHandHLYP calculations of the (6,5) tube, while it is the seventh state in TD-B3LYP approach. In contrast, HF provides the lowest energy state as the bright one. As expected, based on the results obtained for conjugated polymers, the TD-HF not only significantly overestimates the excitation energies, but also overbinds excitons and unrealistically lowers the energy of the bright exciton with respect to other dark states. A similar trend in the bright–dark state ordering and its dependence on the functional is observed for all other tubes, as presented in Table 1. The main conclusion drawn from Fig. 1 and Table 1 is that calculations involving the pure and hybrid DFT functionals result in several optically forbidden (or nearly forbidden) exciton states positioned slightly below (~0.1 eV) the bright state in all the considered SWNTs. While the splitting between the bright and the lowest dark state stays nearly the same for hybrid functionals, the relative numbering of the bright exciton, with respect to the lowest dark one, varies.

To explain the observed difference in the ordering of the bright exciton and its dependence on the functional, we recall that each exciton forms a band owing to the periodicity of the wave function along the tube axis. Stated differently, in quasi-one-dimensional structures, delocalized excited states can be considered as standing waves. Then, the number of nodes in their transition charge density is related to the exciton momenta, \( k \). Consequently, the zero-node state is associated with the \( k = 0 \) momentum exciton in the infinite-size limit. States having one or more nodes in their transition densities belong to the same band as the respective zero-node exciton but will have higher momenta \( (k \geq 1) \) in the infinite-size limit. Note that, owing to their finite-length, quantum confinement is introduced in the SWNTs considered and, thus, their electronic structure has a ladder of levels for each exciton band rather than a continuous band. The density of states in each exciton band will increase as the SWNT length approaches infinity under ideal conditions.

The transition density matrices for each state, plotted in a real-space representation in Fig. 2, demonstrate a characteristic standing wave structure of low energy excitons and enable us to assign each band. For example, for TD-B3LYP calculations, four bands are seen, with their lowest states (zero-node excitons) being numbered 1, 3, 4, and 8 in Fig. 2, first column. The standing waves for the next states in each band have one node, for example, numbers 2, 5, and 6, second column in Fig. 2. We label each exciton band I, II, III, and IV, as indicated in Fig. 2, and the sub-band states with one or more nodes are marked as I′, I′′, II′, III′, and so on. Independent of the functional used, excitons II and III (zero-node states) are always dark or semi-dark and nearly degenerate. These states have energy lower than that of the bright exciton IV, but higher than the energy of the dark exciton I for all the tubes considered.

In contrast, the relative energy position of the sub-band states having node structure is very sensitive to the portion of the HF-exchange changes in the functional. Thus, for BHandHLYP calculations, only the sub-band state I′ (with one node) has energy smaller than the bright exciton IV, so that the bright exciton is the fifth state from the ground state for all tubes (see Table 1). However, in the case of the B3LYP functional, not only sub-band state I′ but also sub-band II′, III′, and even I″ (with two nodes) have lower energies than the bright exciton IV. Therefore, B3LYP calculations provide the bright exciton as the eighth state from the ground state in the (9,1) tube. For most tubes, however, the I″ state is slightly higher in energy than the IV exciton. Therefore, the bright exciton is the seventh state in B3LYP calculations for most nanotubes (Table 1). For the (8,0) and the (9,4) tubes, even more sub-band excitons with higher kinetic energies are introduced in between the I and IV zero-node excitons. For...
BHandHLYP functionals, shows a much smaller
Comparison of exciton sizes calculated using B3LYP and
ficant degrees of spatial localization, Fig. 2 (top panels).
hybrid functionals recover bound excitonic states with signi-
calculations of excitonic properties of SWNTs. In contrast, all
conclude that pure DFT functionals cannot be applied for
either sub-band exciton III
nodes can easily mix with the other excitons, including the
tube chirality, in the case of the functionals with a small or
zero portion of the HF exchange can be explained by an
increase in the delocalized character of excitons with a
decrease in the long-range exchange portion in the functional.
For the B3LYP functional, in fact, this delocalization leads to
a smaller energy splitting (~0.03 eV) between states inside
the band compared to those calculated by BHandHLYP
(~0.04 eV). Therefore, TD-B3LYP calculations predict a
larger number of sub-band states in between the lowest dark
exciton I and the bright exciton IV than the TD-BHandHLYP
approach.

The exciton delocalization trend in the limit of pure DFT
functionals is clearly reflected in the transition density dis-
tribution presented in Fig. 2 (lowest row). All transition
densities obtained by the PBE model represent completely
delocalized excitons. For this calculation, the coherence size of
excitons ($L_c$) — the off-diagonal cross-section of the transition
density matrix — is undefined approaching infinity. Con-
sequently, the PBE functional does not provide excitonic
features at all, leading to over-delocalized and non-bound
electron–hole states in SWNTs. Analogous results have also
been obtained for excitons in conjugated polymers. Thus, we
conclude that pure DFT functionals cannot be applied for
calculations of excitonic properties of SWNTs. In contrast, all
hybrid functionals recover bound excitonic states with signi-
ificant degrees of spatial localization, Fig. 2 (top panels).
Comparison of exciton sizes calculated using B3LYP and
BHandHLYP functionals, shows a much smaller $L_c$ predicted
by the BHandHLYP model. Thus, exciton localization
increases with an increase of the HF-exchange. Indeed,
excitons with a nodal structure (i.e., with higher kinetic
energy) have a more delocalized character compared to the
zero-node excitons, specifically near the tube edges. Therefore,
such states interact more strongly with tube ends. As a result
of this interaction, the tube geometry, including chirality,
capping and length, should more significantly affect sub-band
states than zero-node excitons.

Note that because of the stronger delocalization, specifically
for PBE and B3LYP calculations, excitons with one or more
nodes can easily mix with the other excitons, including the
bright one, gaining some oscillator strength. For example,
either sub-band exciton III’ or II’ is usually semi-dark for all
tubes calculated by TD-B3LYP. As can be seen in the absorp-
tion spectra of the tube (6,5), Fig. 1, in the case of the functionals with a zero (PBE and BLYP) and small
(B3LYP) portion of the HF exchange, the brightest state is
accompanied by nearly isoenergetic semi-dark sub-band
states, e.g., states 4 and 6 in PBE calculations and state 5 in
B3LYP calculations. The oscillator strength of these sub-band
states vanishes in the spectra calculated using functionals with
a higher percentage of the HF exchange (BHandHLYP and
HF limits). Similar to excitons in the tube (9,1) shown in
Fig. 2, the strongly delocalized character of the excitonic
transition densities of the tube (6,5) obtained with GGA
functionals leads to a substantial mixing between neighboring
sub-band states. This mixing rationalizes the appearance of
weakly optically allowed transitions close in energy to the
brightest exciton in the spectra obtained by TD-GGA simul-
ations, Fig. 1. Such trends in optical signatures as a function of
the tube length may be detected in future spectroscopic measure-
ments of finite size SWNTs or highly disordered samples.

Fig. 3 Effect of the tube length on optically dark and bright states.
The density of all possible transitions through the band gap (black
lines) and absorption spectra (red lines) of (6,5) (a) and (8,0) (b)
SWNTs of different lengths calculated with the TD-B3LYP model.
Dashed lines correspond to spectra of shorter tubes, while solid lines
show the spectra of longer tubes. The red vertical lines represent the
oscillator strengths of optical transitions. The increase in the tube
length leads to the red shift of transition energies. This shift is more
pronounced for the first optically allowed transitions compared to the
lowest-energy dark transitions. In the longer tubes, only one transition
dominates the first absorption peak, while several transitions signi-
ficantly contribute to the first absorption peak of shorter tubes,
resulting in larger broadening and a complicated structure of spectra
for short tube segments.
Increasing the tube length also leads to a weakening of the oscillator strength of such sub-band excitons. As can be seen in Fig. 3, for longer tubes calculated with the TD-B3LYP model, only one transition dominates the first absorption peak. For the shorter tubes, several other transitions significantly contribute to the first absorption peak, resulting in a larger broadening and more complicated structures of the absorption spectra of tubes with length <10 nm. When the length of the tube is much larger than the exciton size (0.3–0.5 nm),\textsuperscript{39} interactions and mixing between different excitons are hindered, since excitons are more localized and not notably affected by the tube ends. Therefore, the main contribution to the absorption peak comes from only one exciton, namely IV, that is strongly optically allowed. In addition, increasing the tube length leads to a red shift of transition energies. Interestingly, this shift is more pronounced for the first optically allowed transitions compared to the lowest dark transitions. Consequently, the splitting between dark and bright excitons is smaller in longer nanotubes. It should be noted that TD-DFT calculations are relatively expensive, even when combined with a small basis set such as STO-3G. Therefore, we are limited to explore the whole range of possible lengths of tubes with this method. Nonetheless, our results obtained for several tube lengths (8, 9, 10, 11 and 12 nm) allow us to conclude that the qualitative structure of the optical spectra changes insignificantly with the length if the tubes are longer than 10 nm.

The dependence of the energies of the lowest dark I and bright IV excitons on the tube diameter, presented in Fig. 4, demonstrates good qualitative agreement with experimental data\textsuperscript{57} for both TD-B3LYP and TD-HF-AM1 simulations. However, both functionals overestimate the exciton energies (by \textasciitilde 0.3 eV, B3LYP, and \textasciitilde 0.7 eV, BHHandHLYP) compared to the experimental $E_{11}$ transitions. This discrepancy can be explained by two reasons. The first one deals with the small basis set, STO-3G, used in our calculations. It was shown previously\textsuperscript{42} that increasing the basis set to 6-31G would decrease transition energies by about 0.15 eV. Secondly, the finite length of the tubes considered further contributes to the blue shift of excitonic energies compared to the infinite-length limit in real SWNTs samples. Taking these reasons into account, we conclude that the TD-B3LYP model is sufficient for a reasonable quantitative picture of electronic excitations and, in particular, the energy splitting between bright and dark excitons in SWNTs. As was mentioned above, the splitting between the lowest dark and bright excitons is almost independent of the portion of the HF exchange in the functional. This splitting also shows a weak dependence on the tube chirality, Table 1. Roughly, the averaged bright–dark exciton splitting is about 0.1 eV. This value is much larger than the calculated splitting of 0.03 eV in the infinite-length tubes,\textsuperscript{25,34} but very close to the results obtained for long finite tubes with the semi-empirical PPP model.\textsuperscript{24,33}

It is important to note that in both ab-initio\textsuperscript{25,34} and the effective-mass\textsuperscript{23} calculations within the Bethe–Salpeter scheme of infinite tubes, the lowest dark exciton is followed by the bright one and then two dark, degenerate states lie above the bright exciton. In contrast, the semi-empirical modeling of long finite tubes\textsuperscript{24,33} predicts doubly degenerate dark excitons to be in between the lowest dark exciton and the bright one, which is in agreement with our TD-DFT results. It was shown\textsuperscript{24,33} that increase of the tube length from 10 to 40 nm decreases the energy of the dark-bright splitting by nearly half, while the relative ordering of the four lowest excitons remains unchanged. The lowering of doubly degenerate dark excitonic states with respect to the bright one may be related to the specific computational methodologies applied to the infinite-size tubes and finite clusters. Since there are no direct experimental data on the relative ordering of these optically inactive excitonic states with respect to the bright ones, conclusions on the reliability of either of the methods discussed are currently hindered.

\subsection*{3.2 Energies of bright and dark excitons in semi-empirical calculations}

For comparison, the energy of the bright exciton calculated by TD-HF based on the semi-empirical AM1 Hamiltonian is also presented in Fig. 1, demonstrating a red shift of about 0.2 eV with respect to the experimental values of the first bright transition $E_{11}$. Similar to the TD-HF based on an ab initio Hamiltonian (see Fig. 1), AM1 calculations predict the lowest energy state as the bright exciton. Despite inaccurate ordering of the bright and dark excitons, the AM1 method gives a
sufficient qualitative dependence of the excitation energy on the tube diameter, slightly failing only for the tubes with diameters exceeding 1 nm. Substitution of the AM1 Hamiltonian with the semi-empirical ZINDO model leads to the appearance of the dark exciton below the bright one, see Table 1. However, in contrast to TD-DFT calculations, ZINDO yields the bright exciton as the second one after the lowest dark exciton for all tubes except the very narrow (6,2) and (8,0) chiralities. The splitting between these two excitons is notably smaller than those obtained with hybrid functionals. Particularly for long (6,5) and (8,6) tubes, dark and bright states are nearly degenerate. Compared to the other methods used here, the absolute values of excitation energies obtained using the ZINDO model are closer to the experimental ones (with a maximum deviation of ±0.1 eV for tubes with diameter exceeding 0.8 nm). Unfortunately, the dependence on the tube diameter is not satisfactory in the ZINDO case, even qualitatively.

The common concern with ZINDO is that it lacks a consistent parameterization. Particularly, it includes two fitting parameters that renormalize the Hamiltonian matrix elements and can be roughly related to the softness of π- and σ-bonds. These parameters are 1.267 and 0.585 in the ZINDO/S parameterization commonly used for spectroscopic property computations, respectively. To rationalize various results for the excitonic structure in SWNTs previously obtained with various theoretical methodologies and in this work, we artificially varied the ZINDO/S parameters and observed the following emerging trends.

Fig. 5 demonstrates the dependence of excitation energies of the lowest dark and bright excitons on ZINDO parameters in SWNTs. Keeping one of the bond parameters as it is defined in ZINDO, the parameter of the other bond was varied. The larger the parameter, the more rigid and localized the bond appears, which is also related to the increase of long-range Coulombic interaction. Thus, approaching the π-bond parameter value of 1, (i.e., making this bond more rigid), leads to a significant blue shift of excitation energies and simultaneously increases the bright–dark exciton splitting. In contrast, decreasing the π-bond parameter to 0.5 eV leads to red shifts and nearly degenerate bright and dark exciton states. Similar to the dependence on the π-bond parameter, increasing the softness of σ-bonds leads to a decrease of the bright–dark exciton splitting. Decrease of σ-bond to 1 results in the switching of the ordering between the bright and the dark excitons: the bright state becomes the lowest in energy, similar to the results obtained with the AM1 approach (insert in Fig. 5b). However, the excitation energies are shifted to the blue for small σ-bond parameter values, while increasing the σ-bond parameter leads to a red shift, compared to experimental values of the $E_{11}$ transition. The tube length insignificantly affects the dependence of the bright-dark exciton splitting on the π-bond parameter. Thus, increase of the length results in a slight red-shift of the excitation energies and a small decrease in the splitting (Fig. 5b). Importantly, the dependence of the dark–bright exciton splitting on the π- and σ-bond parameters varies slightly with the tube chirality (Fig. 5a). This indicates that the same parameter might not work equally well for different tubes and explains the failure of ZINDO to accurately reproduce the diameter dependence of the excitation energies.

4. Conclusions

We have reported computational results for excitonic structure in ten finite-size SWNTs obtained using TD-DFT and semiempirical TD-HF methods. We found that pure DFT functionals strongly delocalize electronic excitations, giving almost unbound electron–hole states; consequently, these functionals cannot be used for studies of excitonic effects in SWNTs. Correlated methods such as GWA and BSE built on top of the pure DFT overcome this problem. Unfortunately, it is not currently feasible to apply this computationally intensive approach to a wide range of nanotube sizes. On the other hand, our calculations show that the pure TD-HF, while having only a moderate numerical expense, overbinds excitons because it does not account for dielectric screening effects related to the higher order electronic correlations. In particular, this method incorrectly predicts the lowest energy state to be the bright exciton.

In between these two limiting cases—0% (pure DFT functionals) and 100% (HF) of the long-range HF-exchange
contribution—there is a family of hybrid density functionals with varying portion of the HF-exchange fraction parametrically accounting for the dielectric screening effects. For example, the B3LYP (20%) model accurately describes electronic spectra in a variety of molecular systems. We found that this model provides the most accurate description of excitons and their energy splitting in SWNTs. Similar to conjugated polymers, increase of the HF-exchange in the functional (BHandHLYP, 50%) leads to substantial blue shifts of excitonic energies and a strong exciton localization, i.e., a smaller particle-hole separation. Yet, the relative ordering and the energy splitting between the lowest dark and bright excitons, and the qualitative behavior of the excitation energy dependence on the tube diameter, are almost independent of the hybrid functional.

Thus, our TD-DFT calculations based on hybrid functionals unambiguously indicate that there are four important exciton bands (I–IV) related to the $E_{11}$ transition, which is consistent with previous reports on finite-length SWNTs. The lowest state is dark, the upper transition is bright (the first peak in the linear absorption spectra) and two semi-dark and nearly degenerate excitons lie in between. Because of the tube chirality and finite length of the considered tubes, sub-band states with the nodal structure in their transition density matrices appear weak in the spectra, which is consistent with experimental data. The energy and oscillator strength of states are found to be very sensitive to the functional used and on the tube length and chirality. In particular, decreasing the portion of the HF-exchange in the functional lowers energies of the sub-band states with respect to the bright exciton, while the splitting between the fundamental dark and bright excitons remains unchanged. The more delocalized character of the sub-band excitons allows mixing between neighboring excitons, including the bright one, making some of the sub-band states weakly optically active rather than strictly dark.

As expected, an increase of the tube length leads to a small red shift of excitation energies and a decrease of the bright-dark exciton splitting, as can be explained by simple confinement effects introduced by the finite-length of the tubes we considered. For the short tubes with length smaller than 10 nm, semi-dark sub-band states noticeably contribute to the first absorption peak resulting in a larger broadening of absorption spectra. Importantly, the qualitative picture, including the relative position of dark I, semi-dark II–III, and bright IV excitons, and the overall structure of absorption spectra, are not changed for tubes with length exceeding 10 nm, i.e., when the length of the tube is much larger than the exciton size. The calculated splitting between energies of the bright IV and dark I excitons in tubes longer than 10 nm is about 0.1 eV, showing weak dependence on the tube chirality. Although the splitting obtained is much larger than those calculated for infinite-length tubes, this splitting could be further reduced with increase of the tube length.

Finally, we compared results of the first principles TD-DFT calculations with semi-empirical TD-HF methods. Similar to the ab initio TD-HF approach, the TD-HF method coupled with the AM1 Hamiltonian places the bright exciton below the dark one, which does not correlate with the results of recent time-resolved experiments and TD-DFT results. However, the dependence of the excitation energies on the tube diameter agrees well with experimental data, showing a consistent small red shift. The TD-HF method and the ZINDO Hamiltonian lead to changes in the exciton ordering, so that the lowest energy exciton is the dark one, followed by the bright exciton with a very small energy splitting (~0.3 eV for most tubes). However, the ZINDO model does not provide an accurate dependence of excitation energies on the tube diameter, even qualitatively. This discrepancy is likely to originate from the lack of a consistent parameterization in this Hamiltonian. Our analysis of trends in excitation energies appearing when varying ZINDO parameters allows us to link subtle interplays of the energetics of dark and bright excitons with the softness of chemical bonds and electronic delocalizations, which are accounted for differently in various theoretical methodologies used for modeling the electronic structure of SWNTs.

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