Electron transition energies of single-walled carbon nanotubes: DFT and Hartree – Fock’s CNDOL approaches for describing excitations and related properties

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Abstract

Electronic properties of two kinds of zig-zag (13,0) and (9,0) single walled carbon nanotubes (SWCNT) are studied using both Density Functional Theory (DFT) and an approximate Hartree-Fock (HF) named as Complete Neglect of Differential Overlap considering the L azimuthal quantum numbers of basis orbitals (CNDOL) molecular-orbital method. The CNDOL procedure models the electron energy transitions and excited state charge distributions through a configuration interaction of singly excited determinants (CIS) allowing the direct understanding of properties related with the total electronic wave function of the system. Band structures and densities of states (DOS) of both SWCNT’s are initially calculated using DFT, showing insulating character for (13,0) and almost metallic character with a very small conduction gap for (9,0) SWCNTs. Similar behaviours of either insulating or metallic SWCNT's were interpreted in the framework of the CNDOL scheme by increasing the lengths of the tubes above 3 nm. The evolution of excited states for each SWCNT is different when the nanotube grows in length. It is discussed by taking into account electron – electron interactions as considered in the framework of the HF - CIS procedure. The predicted insulator (13,0) SWCNT does not show a decrease in the lowest energy excited states when the length increases, in contrast to the (9,0) SWCNT, which show more favoured conditions for photo-excitations. Analyzing the size-scaling behaviour of the excitation energies with the nanotube length, the (13,0) SWCNT presents a forbidden transition at the lowest energy followed by a strong dipole-allowed transition between 0.8 and 0.9 eV. They show no significant changes in longer systems, whereas the (9,0) SWCNT spectrum shows the lowest-allowed energy transition at less than 0.3 eV when nanotube length tend to infinite. Excitons appear more bounded in the insulating than in the conducting nanotube, as expected.
Introduction

The need to explain and predict the relationships between structural and electronic properties in nanoscale systems has brought together aspects of synthesis, measurements of physico-chemical properties and in particular, to select and adapt the most suitable methods for proper theoretical modelling. Relatively large polyatomic systems such as carbon nanotubes (CNT), in which the regular arrangements of atoms require the study of irreducible models, are presented as challenging for computational modelling even for the most approximate algorithms. In this field, many and different quantum theoretical methods have been explored to find a suitable way for representing and predicting the physical nature of the observed phenomena.1

Many efforts have also been made in order to verify and understand the inherent conduction characteristics of these materials in order to enhance their applications. In this sense, single-walled carbon nanotubes (SWCNT) are considered an ideal models because they behave as a one dimensional molecular system. Nowadays, Density Functional Theory (DFT) is the standard method to optimize the geometry and obtain the electronic properties of extended systems since it can incorporate periodic conditions to achieve infinite models of these systems with a relatively low computational cost. DFT is also the most used algorithm to corroborate experimental results, such as conducting/insulating character of materials, vibrational, thermal, and mechanical properties2-5. However, standard DFT methods fail to predict energy gaps in insulating and semiconducting materials, underestimating them by about 50% with respect to the experimental values.

Recent experimental results provide optical absorption6, 7 and fluorescence spectra 8-11 of isolated (non interacting) SWCNT’s, meaning that those electronic properties did not depend on perturbing molecular neighbours.

Electron excitations in these nanostructures can be easily interpreted in terms of exciton quasi – particles. Consequently, some research has been directed to explain their collective absorption capacity and redistribution of energy upon excitations by photons12. In the same way, there are many works devoted to the theoretical calculations of excitons in SWCNT’s13-15 where the electron-electron (e-e) interactions have been considered essential to achieve reliability for the calculated results16.

It is very important to notice that the inclusion of electron repulsion terms goes farther than a simple one-electron description of a Hückel type Hamiltonian17. Moreover, the application of configuration
interaction (CI) as a post HF procedure, where e-e terms involved in excitations are also considered and optimised, allows a correct description of electronic states and their energies. Zhao et al\textsuperscript{18,19} have used this methodology within the simple and elegant HF framework of the $\pi$ electron approximation named as the Pariser–Parr–Pople (PPP) parameterized Hamiltonian\textsuperscript{20-23} achieving a qualitative description of the excitons in conjugated polymers and SWCNT’s.

The essential advantage of using a molecular orbital approach consists in the final availability of a complete wave function of the system, even being approximate. CNDOL Hamiltonians\textsuperscript{24,25}, based on the neglect of differential overlap (NDO) of atomic orbital basis sets and considering their $l$ azimuthal quantum number is essentially an approximate Hartree-Fock (HF) SCF-MO methodology without "a posteriori" parameter adjustments that has demonstrated reliability. It allows modelling the change of electronic states (electron excitations) of systems with a very large number of atoms using the configuration interaction of single excited determinants (CIS) procedure for optimising the excited state energies, due to the relative simplicity of the basic calculations. The algorithm also admits increasing the active space (or number of CIS determinants) to be large enough for granting the best variational optimisation of excited states. This method has provided and adequate description of phenomena related with intermolecular charge transfers in Rhodopsin protein associated with human vision\textsuperscript{24} and the interaction between the chromophore and aluminosilicates to explain the stability of the ancestral Maya Blue color\textsuperscript{26}. Our aim now is to explore how CNDOL could describe the electronic properties of semiconducting materials, by means of the calculation of vertical electron transition energies and the corresponding charge distributions in the excited state of SWCNT’s. On the other hand, CIS of polyatomic systems that behave as molecules can be considered as a method to get optimised transition energies, electron – hole interactions and charge redistributions due to excitons originated upon light absorption.\textsuperscript{1}

Two zig-zag SWCNT’s with chiral numbers $(n,m)$, where $n = 13, 9$ and $m = 0$, were chosen as our model systems. The (13,0) and (9,0) SWCNT have diameters of 10.2 Å and 7.1 Å, respectively. According to the literature\textsuperscript{27}, the SWCNT electronic properties can be approximately predicted by the energy-band-folding theory of grapheme. That is, a zig-zag nanotube is a metal when $n-m$ is multiple of three or a semiconductor with a moderate band-gap for other values of $n$. Thus, the (13,0) SWCNT is expected to present a band gap, whereas the (9,0) SWCNT is expected to have no gap. Thus, the former can be considered as insulator and the later metallic.
In the present work, we are modelling the electronic properties of these SWCNT’s by two different approaches: DFT and CNDOL. DFT, as an established methodology, is used as a reference, whereas CNDOL allows us to analyze the electronic excitations. Our approach opens up a promising methodology to describe the electronic excitations of nanostructures.

In order to calculate properties of extended nanomaterials it is necessary to use models large enough to yield the best estimation of its macroscopic behaviour. Most of the research on nanoscale systems emphasizes the importance of combining advanced experimental information with theoretical models that can distinguish different atomic configurations. However, the size of the typical nanostructures frequently exceeds the capabilities of most of the computing frameworks. The recent developments are focused directly on the search of reliable models that include periodicity.

Theoretical and Computational details

DFT calculations on periodic SWCNT’s were performed using a plane-wave pseudopotential scheme as implemented in Quantum-ESPRESSO. The exchange and correlation parts of the electronic energy were calculated in the generalized gradient approximation (GGA) with the functional of Perdew, Burke and Ernzerhof (PBE). The effects of core electrons and nuclei are included in using Rabe–Rappe–Kaxiras–Joannopoulos ultrasoft pseudopotentials. We used the pseudopotential C.pbe-rrkjus.UPF from the Quantum-ESPRESSO distribution. A plane-wave basis set has been used, with kinetic energy cutoffs of 30 Ry and 200 Ry for the expansion of the wavefunctions and the charge density, respectively. The one-dimensional Brillouin zone of the (9,0) and (13,0) SWCNT was sampled using uniform grids of 14 and 6 k-points, respectively. To avoid convergence problems in the 'metallic' (9,0) SWCNT, the method of cold smearing was used, with a broadening parameter of 0.01 Ry. The selected cutoffs, k-point grid, and smearing scheme, allow to obtain energies, forces, and stresses converged within 0.002 eV/atom, 0.05 eV/angstrom and 0.5 kbar, respectively. The initial structures were relaxed using damped Beeman dynamics for the atoms and the simulation cell. The cell dynamics was restricted to the periodic direction of the SWCNT, and was determined by the Wentzcovitch extended Lagrangian with mass parameter of 0.0001 AMU/au². The supercell is 25 Å wide in the non periodic directions, whereas in the periodic direction it was optimized at 4.26356 Å for the (9,0) and 4.26450 Å for the (13,0) SWCNT. The stress tensor components of the relaxed structures were smaller than 0.5 kbar, the interatomic forces were smaller than 1 mRy/bohr, and the total energies were converged within $10^{-5}$ Ry.
The CNDOL/21 Hamiltonian\textsuperscript{24} has been used as described elsewhere. The NDOL2008 program version 6.0\textsuperscript{40} was used and it is available\textsuperscript{a} for calculations of systems of up to 2000 atoms and 4500 basis orbitals and can also provide calculated electron densities of CIS excited states. The calculated CIS transition energies always refer to vertical excitations with respect to fixed and previously optimised geometries of the ground state. The oscillator strength is the output quantity that is proportional to the transition dipole between the excited and the ground state and indicates the intensity of photon absorptions. Calculations can be performed in a reasonable computer time allowing applications to very big systems. The largest polyatomic system calculated in the present work at our HF level for the (13,0) SWCNT’s has 1066 atoms (1040 carbon atoms plus the hydrogen edges).

**Results and discussion**

In order to obtain the best structural model to allow comparisons, a unit cell of each SWCNT was optimized using infinite arrays in one axis (CNT axis). The other axis was kept fixed checking that such cell size was large enough in order to avoid spurious interactions between the array periodic replicas. The procedure began minimizing the size of the electronic basis (cut-off and k points) and the simulation cells, as detailed above. Then, the nanotubes were obtained as the minimum energy structures.

Figure 1 shows the band structures and density of states (DOS) of the two SWCNT’s, with the unit cell employed in the optimized geometries. Based on the same level of the DFT approximation used for geometry relaxations, we have obtained good agreement with previous published results\textsuperscript{41}. The (13,0) SWCNT is predicted as insulator with a band gap of 0.62 eV. Comparatively, the (9,0) SWCNT shows different conductivity properties in spite of the zig-zag geometry character of both structures. The (9.0) SWCNT energy gap predicted by this method could be as low as 0.11 eV.

Figure 1

A HF-based approach as CNDOL can address the electronic structure on the ground of a molecular like construction thus allowing the possibility to include non periodic structural features of real systems. The availability of a wave function of the whole system allows a consistent picture of charge

displacements (charge transfer) and state energies, considering the explicit inclusion of electron interactions in the Hamiltonian.

For each chirality, we have studied ten finite H-terminated SWCNT’s. Each one was constructed replicating the unit cell (see Fig. 2) in even numbers between 2 and 20. The SWCNT’s range lengths between 0.71 and 8.39 nm. The finite SWCNT’s were labelled as \((n,m,L)\), following the notation of Ref. 42, where \(n\), and \(m\) are the chiral numbers, and \(L\) is the number of units in each segment.

Figure 2

CNDOL initially provides a set of eigenvalues and eigenfunctions or molecular orbitals (MO), expressed as a linear combination of atomic orbitals (AO) for each studied system. Up to this point, this approximation gives ground-state wave function considering that all electrons remain strictly at the lowest energy states. However, an uncertain description of the virtual or empty states arise during the wave function optimization by a variational procedure due to the null density matrix elements of these orbitals. It occurs in all one electron like (tight binding, Hückel Molecular Orbital (HMO), Kohn – Sham’s DFT, etc.) as well as HF calculations. Therefore, considering the conduction process as a charge displacement and promotion in molecular materials, one electron MO’s could not describe accurately the excitation phenomenon up to this point of the calculation. Recently, Scholes and Rumbles14 published a review on excitons in nanoscales materials. An exciton approach is appropriate for understanding processes following light absorption in carbon nanotubes. The author’s report that attractive interactions arise between electron – hole states (excitons described by their corresponding wave functions) spreading over an expanse of atoms. Therefore, exciton states can be described by optimised single electron wave functions where the Coulomb and exchange terms are considered and also optimised. In this sense, performing the large scale CIS - CNDOL calculations allows modelling the electronic nature of those chosen SWCNT’s excitons.

Initially, the relationship between energy profiles of the lowest singly excited states and the length of each model of SWCNT’s was assessed in order to evaluate the influence of our finite model lengths on their electronic properties. Figure 3 shows the graphs with the first three CIS state energies calculated for each nanotube. Notice that both SWCNT’s reveal irregular values of excitation energies when the nanotube lengths are smaller than about 3 nm. It could be explained by taking into account the very molecule–like behaviour of short length structures for representing the periodic character of those
materials in our MO scheme. The effect of the artificial edges breaking the C-C conjugate bonds could be too strong. Thus, these short length models will not be considered for the following analysis.

Figure 3

The respective patterns of the results of both largest SWCNT’s help us to explain the differences of their electronic properties. In the case of (13,0) SWCNT’s, no significant changes appeared in the energies of the lowest three excited states with an increase in the nanotube model length. The independence of electron excitation energies with length has also been shown by this nanotube model when we explore all the calculated excited states below 1.5 eV. This curious behaviour can be considered as a distinctive feature of this type of SWCNT. That is, the electronic properties of these materials appear independent from the length of models when they are large enough. In the case of (9,0) SWCNT’s, the energy of the first excited state (E₁) remains constant as in the (13,0) SWCNT. However, an inverse dependence with the size is observed for the higher energy states E₂ and E₃. For this type of nanotubes the energies of CIS states appear dependent on the size of the model. An inverse proportionality has been found for energy gap calculations in other SWCNT’s where the \[ n-m=3M \] rule is verified. This can be related with the small gap semiconducting character of these materials. It is important to point out that the second excited state branches into two CIS states for SWCNT’s length longer than 4 nm, although both (E₂ and E₃) follow the same tendency, i.e. an inverse dependence on length.

The lowest excited state (E₁) of (13,0) SWCNT is optically forbidden as shown in Fig. 3 (a). E₂ and E₃ upper excited states appear as strong transitions due to their oscillator strengths. This behaviour has also been found for other zig-zag insulating SWCNT’s as obtained by HF-PPP method with a CIS scheme. Reference 16 highlights the coincidence of the features of the spectra with those obtained in conjugated polymers. Then, they discuss the possibility that these systems could be deactivated quickly from their optically excited states to their low-energy dipole-forbidden state, instead of their decay to the ground state by photon emission. Our CNDOL results of the second and third transition energies are similar and also agree with the experimental optical transition energy (0.9 eV) of this (13,0) SWCNT in surfactant solution to isolate nanotube molecules.

We have not found experimental data on absorption spectra to compare the results for the (9,0) SWCNT. An estimation of the behaviour of CIS state energy could have an uncertain character due to the shape of the Fig. 3(b), at least for nanotube’s lengths below 5 nm approximately. Above this length,
all states show a clear tendency to decrease energy. Nevertheless, it is possible to perform a comparison with the spectrum of the (13,0) SWCNT. Some interesting features merit to be commented. In the (9,0) SWCNT, the lowest CIS states obtained are dipole-allowed, appearing the E₁ and E₂ as weak transitions and E₃ as a strong one. Therefore, we could expect that this SWCNT, has favourable conditions for direct excitation by photons at very low energies.

Different authors emphasize the interesting finite-size quantum effects of the energy gap of the carbon nanotubes, because these materials are obtained experimentally as finite with an average length of several hundred nanometers. To extrapolate our results to infinite nanotubes, we performed a linear regression of CIS energies as functions the inverse of nanotube lengths (1/L) (Fig. 4). We prefer a qualitative assignment by only differencing the strongest allowed, the forbidden and the weak transitions. In the case of (13,0) SWCNT the slopes obtained from regression are close to zero, showing almost no dependence of the CIS energies with the length of the model (Fig. 4 (a)). The values of the linear regression data in each case are summarized in Table 1. All regressions present a high linear correlation. Similar behaviour is observed for the E₁ state in the (9,0) SWCNT, in contrast with E₂ and E₃ in the same nanotube (Fig. 4 (b)). This figure clearly shows a different behaviour of E₂ and E₃ for SWCNT lengths larger than 5 nm, indicating the minimum length needed to simulate these nanotubes with our molecular approach.

Figure 4

<table>
<thead>
<tr>
<th></th>
<th>ordinate</th>
<th>Intercept (a)</th>
<th>Slope (b)</th>
<th>Regression coeff. (r)</th>
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</thead>
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<tr>
<td><strong>CNT (13,0)</strong></td>
<td>E₁ (f)</td>
<td>0.57</td>
<td>-0.11</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>E₂ (s)</td>
<td>0.79</td>
<td>-0.13</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>E₃ (s)</td>
<td>0.87</td>
<td>-0.17</td>
<td>0.984</td>
</tr>
<tr>
<td><strong>CNT (9,0)</strong></td>
<td>E₁ (w)</td>
<td>0.54</td>
<td>-0.13</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>E₂ (w)</td>
<td>0.28</td>
<td>3.62</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>E₃ (s)</td>
<td>0.45</td>
<td>3.49</td>
<td>0.994</td>
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</table>
The limit of these functions for large nanotube lengths (L) corresponds in each case with the value of the intercept. An inspection of these extrapolated values allow us to consider that the very long (13,0) SWCNT’s could show its first excitations at energies in the range of 0.8-0.9 eV, whereas long (9,0) SWCNT’s needs only about 0.28 eV to be photoexcited. Other excited states at 0.45 and 0.54 eV could also be found in these materials. A picture of these differences is shown in figure 5 for the sake of a better understanding.

Figure 5

A qualitative explanation of these CNDOL’s description is obtained by exploring the nature of each electron transition by means of the wave function probability (the squared coefficients of the originating basis set orbitals). Thus, we can infer the corresponding distributions of the excitons. Table 2 shows the energies of the excited states and their corresponding oscillator strengths for two of the largest models: (13,0,18) and (9,0,18) SWCNT’s. It is important to notice that only non-degenerate states (ΔE > 0.05 eV) are shown graphically for the sake of clarity. The topologies of the omitted states are equivalent to those represented in the table. Schematic representations of MO’s that have the largest contributions on each CIS transition are shown to the right of each numerical columns. Letter ‘A’ in green denotes in all cases the zone in the nanotube where the occupied MO’s responsible of the charge donation during the transition is localized. The zone of the empty MO that should accept the charge appears as ‘B’ in red. HOMO’s and LUMO’s have also been highlighted when they are involved.

The first forbidden CIS state in the (13,0,18) SWCNT is mostly described as a transition between occupied and virtual MO’s that are both localized in one side of the tube edge (without participation of ending H atoms). Thus, the charge transfer could be seen in a local section of the nanotube that is independent of the length. The following allowed transitions of this SWCNT are mainly described as charge transfers between MO’s also localized at the extremes, although being scattered on both sides of the nanotube. These results are consistent with those previously obtained for finite graphene ribbons, where hydrogen atoms have also been used to saturate the edges. Indeed, this edge effect appears only related to the π topology of zig-zag type structures, either in graphene ribbons or in semiconducting SWCNT. The authors of Ref. 43 claim that this interesting feature has a great significance in nanoscale materials, and it is expected that this “edge localized” states may play an important role in interfacing either between different carbon nanotubes or with another molecular systems.
Table 2. Qualitative representation of the MO’s for long models of both SWCNT’s

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>Int.</th>
<th>CIS model</th>
<th>Model</th>
</tr>
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<tbody>
<tr>
<td>0.56 (d)</td>
<td>f</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>0.78 (d)</td>
<td>s</td>
<td>I and II</td>
<td>II</td>
</tr>
<tr>
<td>0.84 (d)</td>
<td>s</td>
<td>I and II</td>
<td>III</td>
</tr>
<tr>
<td>1.02 (d)</td>
<td>s</td>
<td>I and II</td>
<td>IV</td>
</tr>
<tr>
<td>1.52 (d)</td>
<td>s</td>
<td>II</td>
<td>III</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>Int.</th>
<th>CIS model</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>W</td>
<td>II</td>
<td>II</td>
</tr>
<tr>
<td>0.76</td>
<td>w</td>
<td>III and IV</td>
<td>III</td>
</tr>
<tr>
<td>0.92</td>
<td>s</td>
<td>IV</td>
<td>IV</td>
</tr>
<tr>
<td>1.05</td>
<td>w</td>
<td>III</td>
<td>III</td>
</tr>
<tr>
<td>1.42 (d)</td>
<td>s</td>
<td>III</td>
<td>III</td>
</tr>
</tbody>
</table>

Letters f, s, and w mean forbidden, strong, and weak transitions, respectively. Each type of CIS transitions is represented by I, II, III and IV in the columns at right.

It is important to notice that the first weak electronic transition of the (9,0,18) SWCNT that we obtained for this nanotube size is the size-independent E₁, at values around 0.5 eV. However, this is not the predicted lowest energy state that the system can reach at infinite lengths, according to the above mentioned extrapolation for large models (Fig. 5). Those to be found at the lowest energies in long systems are the here weak E₂ and the strong E₃ states. Both are mostly originated by a charge transfer that involve delocalized orbitals over the nanotube as a major contribution, including frontier orbitals. They are very size-dependent and it predict that long (9,0) SWCNT’s absorb a low energy photon in the infrared (0.3 eV ~ 2400 cm⁻¹) and keeps alive the exciton due to the charge transfer process over the nanotube. According to the extrapolation, a length larger than approximately 40 nm is needed for E₂ becoming as the lowest excitation in (9,0,L) SWCNT.

Most of the current quantum mechanical calculations in this field consider the simple MO’s scheme as essential to study the ground state characteristic in the absence of external perturbations⁴². This kind of
description could help us to understand the origin of the different behaviours corresponding to both types of SWCNT’s thanks to the obtained profile of CNDOL excited states. However, the reliability of the information regarding virtual orbitals that can be obtained is lesser due to the above mentioned limitations of the HF procedure. Figure 6 shows the density of states at the single particle level (i.e., the MO’s), of both SWCNT’s. Here the eigenvalues of both a short (L=6) and a large (L=20) SWCNT are shown. We can observe that the DOS near the band edges increases for the longest SWCNT’s. Sharp peaks are characteristic of shorter nanotubes. On the other hand, the wide peaks corresponding to long SWCNT remain at the same energy values in the case of semiconducting (13,0) SWCNT’s, whereas the small gap (9,0) SWCNT’s shows a clear reduction of HOMO-LUMO gap ($\Delta E_{HL}$) when the length increases.

Figure 6

Electron density distributions corresponding to each peak of the longest (L=20) SWCNT’s is shown at an offset to DOS graphs in Fig. 6 as squared values of atomic orbital coefficients. This illustration is useful to explain how DOS and the delocalization of MO’s wave functions along the (9,0) SWCNT axis increases as the $\Delta E_{HL}$ value decreases. As described before, one of the lowest CIS excited states ($E_3$) in the longest nanotube is fundamentally explained as a charge transfer between HOMO and LUMO. Thus, we could consider that both, $\Delta E_{HL}$ and $E_3$ are correlated, and their difference could be considered as related to the exciton binding energy. Likewise, $E_2$ is essentially a very delocalized state that could be also considered under the same approach. An estimation of the Coulomb and exchange terms between the occupied and virtual MO’s to give the possible singlet transition has been taken into account to construct the CIS matrix, according well known formulas. Then, it becomes clear that during the CIS matrix diagonalization, the energy of an excited state decreases if the electronic transition is stabilized by a favourable e-e interaction.

The same feature is observed in the (13,0) SWCNT. The first allowed singlet transition ($E_2$) originates from transitions between MO’s corresponding to the frontier peaks of the DOS scheme. However, in this case such peaks reflect the previously described edge effect. Therefore, from the point of view of our approximation, neither the $\Delta E_{HL}$ nor $E_2$ show size dependence in the (13,0) SWCNT. In the same way, the favourable e-e interaction between these frontier MO’s makes possible to find the first CIS electronic excited state at a lower energy.

Figure 7
Figure 7 shows the $\Delta E_{\text{HL}}$ and the lowest excited state dependence on the model length for both SWCNT. As expected, the $\Delta E_{\text{HL}}$ for each SWCNT behaves in a similar way to that obtained for lowest excited states. In the graph, the empty symbols represent the $\Delta E_{\text{HL}}$ in each case, and they obviously appear at higher energies. The energies related to exciton binding (vertical dashed lines) show the relevance of the e-e interaction in the CIS states for each of the long SWCNT’s. Clearly, this energy is higher in the large gap (13,0) than in the small gap (9,0) SWCNT.

Conclusions

Two kinds of SWCNT’s with different expected behaviours regarding electronic conduction have been simulated by both DFT and HF’s CNDOL methods. The DOS and band structures obtained for infinite SWCNT’s by DFT method are in agreement with the expected results: the (13,0) SWCNT is insulating, and the (9,0) is a kind of semiconductor. CNDOL calculations of the molecular electronic wave function were performed over a set of increasingly long, although finite, SWCNT’s and then projecting the results to infinite lengths. The results show that it is important to consider finite models of SWCNT’s with length larger than 3 nm in order to simulate realistic properties corresponding to experimental systems. The excited states of both SWCNT’s also show the expected different behaviours. The (13,0) SWCNT shows the lowest excited state energies which are nearly independent of the SWCNT length. The lowest state appears around 0.5 - 0.6 ev and must be forbidden for population by interaction with light. Upper states appear around 0.8 – 0.9 ev and are strong allowed transitions. In contrast, the allowed excited state in (9,0) SWCNT tends to reduce the energy for longer nanotubes, suggesting favourable conditions for excitations in real long systems. The importance of the e-e interaction (that is related with the exciton binding energy), as given by the CIS calculation, was discussed for each SWCNT. Our results suggest that the exciton is more bounded in the larger gap SWCNT’s.

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