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

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ABSTRACT

Optical properties of two kinds of zig-zag (13,0) and (9,0) single walled carbon nanotubes (SWCNT) are modeled by an approximate Hartree-Fock's (HF) Hamiltonian under the restrictions of the *Complete Neglect of Differential Overlap* considering the *L* azimuthal quantum numbers of basis orbitals (CNDOL). Here is shown that the procedure can bring models of electron energy transitions and exciton features through a configuration interaction of singly excited determinants (CIS). It allows the direct understanding of properties related with the total electronic wave function of the system. We show that 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. (13,0) SWCNT does not appear to decrease the lowest energy excited states when the length increases, in contrast with (9,0) SWCNT, which shows more favored conditions for photo-excitations when grows to infinite.

Keywords: CNDOL, single walled carbon nanotubes, electronic wave functions, excited states of nanoscopic systems

1 INTRODUCTION

The molecular orbital approach was developed for modeling relatively small systems, more related to the "picoscopic" scale [1]. However, further developments in theoretical methods and computing technology allow the treatment of increasingly large systems providing the advantage of interpreting nanoscopic phenomena with an appropriate theory [2,3]. 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 [4,5], are simplifying the Hartree – Fock's approach for molecules [6,7] to neglect of differential overlap (NDO) of atomic orbital basis sets although

considering their *l* azimuthal quantum number. It is essentially tested as an approximate SCF-MO methodology without "a posteriori" parameter adjustments. Nowadays it allows modeling 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 optimizing the excited state energies, due to the relative simplicity of the basic calculations. The algorithm also admits the increase of the active space (or number of CIS determinants) to be large enough for granting the best variational optimization of excited states. This method has provided and adequate description of phenomena related with intermolecular charge transfers in Rhodopsin protein associated with human vision [5] and the interaction between the chromophore and aluminosilicates to explain the stability of the ancestral Maya Blue color [8].

Relatively large polyatomic systems such as single walled carbon nanotubes (SWCNT) allow the use of periodic procedures for theoretical modeling of their properties at the nanoscopic level when "perfection" is presupposed because the regular arrangements of atoms. However, they require the use of irreducible models when real systems are to be understood. Therefore, they represent a real challenge for computational modeling even using the most approximate quantum mechanical algorithms. Our aim now is to explore how CNDOL could describe the behavior of systems as large and complex as SWCNT's, by calculating vertical electron transition energies and related properties.

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 photons [9]. In the same way, there are many works devoted to the theoretical calculations of excitons in SWCNT's [10,11] where the electron-electron interactions have been considered essential to achieve reliability for the calculated results [12].

CIS of SWCNT's that behave as molecules can be considered as a method to get optimized transition energies,

electron – hole interactions and charge redistributions due to excitons originated upon light absorption [13]. What we pursue is that our approach could open up a promising methodology to describe the electronic excitations of nanostructures.

2 METHODS

Two zig-zag SWCNT's with chiral numbers (n,m), where $n = 13, 9$ and $m = 0$, were chosen as our model systems. (13,0) and (9,0) SWCNT's have diameters of 10.2 Å and 7.1 Å, respectively.

In order to get reliable basis structures of those chosen SWCTN's DFT calculations were performed for obtaining the unit cell geometry by using a plane-wave pseudopotential scheme as implemented in Quantum-ESPRESSO [14]. 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) [15]. The effects of core electrons and nuclei are included in using Rabe–Rappe–Kaxiras–Joannopoulos ultrasoft pseudopotentials [16]. 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 initial structures were relaxed using damped Beeman dynamics [17] 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 [18] with mass parameter of 0.0001 AMU/au^2. 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 [5] has been used as described elsewhere. The NDOL2008 program version 6.0 [19] was used and it is available[1] for calculations of systems of up to around 2000 atoms and 4500 basis orbitals and can also provide calculated electron densities of CIS excited states. Calculated CIS transition energies always refer to vertical excitations with respect to fixed 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 for the (13,0) SWCNT's has 1066 atoms (1040 carbon atoms plus the hydrogen edges).

3 RESULTS AND DISCUSSION

Ten finite H-terminated SWCNT's for each chirality were studied. They were constructed by replicating the unit cell in even numbers between 2 and 20. SWCNT's ranged lengths between 0.71 and 8.39 nm. The finite SWCNT's were labelled as (n,m,L), following the notation of Ref. [20], where n, and m are the chiral numbers, and L is the number of units in each segment. See Fig. 1.

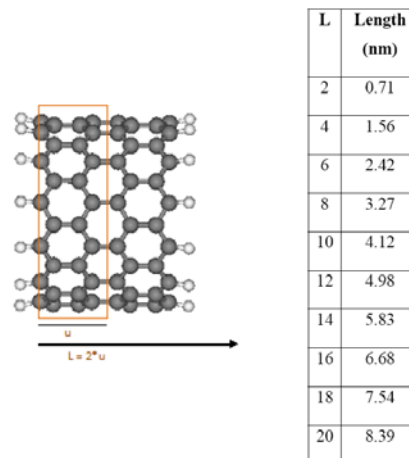| L	Length (nm)
2	0.71
4	1.56
6	2.42
8	3.27
10	4.12
12	4.98
14	5.83
16	6.68
18	7.54
20	8.39

Figure 1: Nanotube geometries and lengths

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. Therefore, an uncertain description of the virtual or empty states arises during the wave function optimization by a variational procedure due to the null density matrix elements of these orbitals, as occurs in all one electron like (tight binding, HMO, Kohn – Sham's DFT, etc.) as well as in other kinds of HF calculations. If we consider electron state changes in molecular materials as a charge displacement and promotion, one electron MO's could not describe accurately the excitation phenomenon up to this point of the calculation. As it was mentioned above, exciton states can be described by optimized wave functions where the Coulomb and exchange terms are considered and also variationally optimized [13]. Therefore, performing large scale CIS after the CNDOL calculations allows to model 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 2 shows the graphs with the first three CIS state energies calculated for each nanotube. Notice that both

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[1] It can be downloaded in a both MS-Windows and GNU/Linux version as http://karin.fq.uh.cu/~lmc/ndol2009-6.6.zip.

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 behavior 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 also be too strong. Thus, these short length models will not be considered for the following analysis.
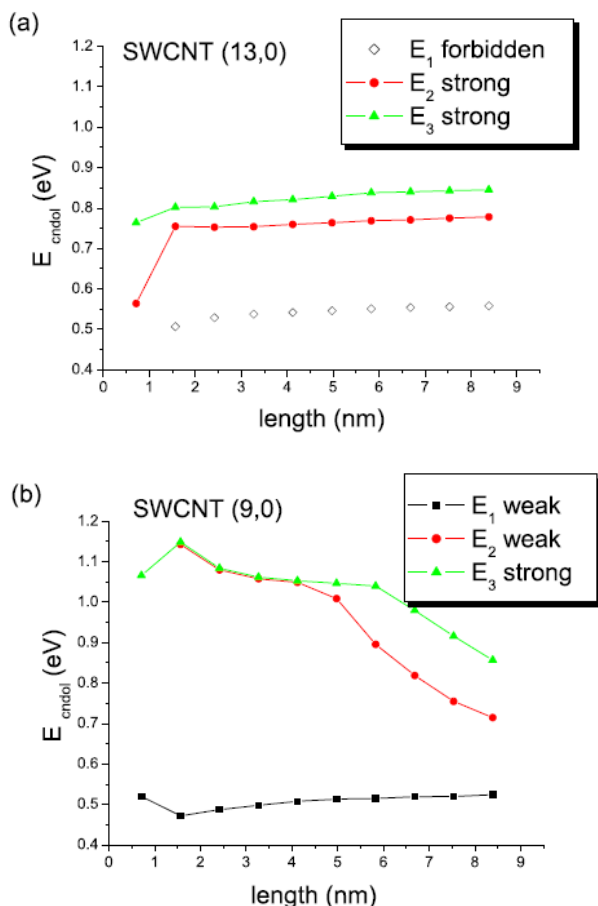

Figure 2. Dependence of CIS lowest excited states vs. SWCNT length. a) (13,0); b) (9,0)

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 behavior 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 (E_1) remains constant as in the (13,0) SWCNT. However, an inverse de-

pendence with the size is observed for the higher energy states E_2 and E_3. For this type of nanotubes the energies of CIS states appear dependent on the size of the model. 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 (E_2 and E_3) follow the same trend, i.e. an inverse dependence on length.

The lowest excited state (E_1) of (13,0) SWCNT is optically forbidden as shown in Fig. 2 (a). E_2 and E_3 upper excited states appear as strong transitions due to their oscillator strengths. This behavior has also been found for other zig-zag SWCNT's [12] as obtained by HF-PPP method with a CIS scheme. H. Zhao and S. Mazumdar [12] 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 decaying to the ground state by photon emission. Our CNDOL results of the second and third transition energies are similar and also agree with the first allowed electron transitions for (13,0) SWCNT that is predicted at 0.9 eV by a regression analysis of spectrofluorimetic data [21].

To extrapolate our results to infinite nanotubes, we performed a linear regression of CIS energies as functions the inverse of nanotube lengths (1/L) (Table 1).

Table 1. Linear regression data of $E_i = a + b$ (1/L), where E_i is in eV and L in nm

	CIS state	Intercept (a)	Slope (b)	Regression coeff. (r)
CNT (13,0)	E_1 (f)	0.57	-0.11	0.985
	E_2 (s)	0.79	-0.13	0.987
	E_3 (s)	0.87	-0.17	0.984
CNT (9,0)	E_1 (w)	0.54	-0.13	0.993
	E_2 (w)	0.28	3.62	0.999
	E_3 (s)	0.45	3.49	0.994

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.

Finally, we can infer and compare the corresponding distribution of the excitons by taking into account the origin of electron transitions. In the case of (9,0) SWCNT's the frontier MO's are delocalized wave functions along the tube axis. Moreover, E_2 and E_3 CIS excitations of these nanotubes are described by those frontier orbitals. We could consider that the HOMO-LUMO gap (ΔE_{HL}) and these lowest CIS's transitions are related. The difference between

both energy values can be considered as the binding energy of the exciton associated to the HOMO-LUMO transition, which is stabilized by the e-e interaction. The same situation occurs for the E_2 transition of (13,0) SWCNT. In figure 3 is shown the ΔE_{HL} and the lowest CIS excited state dependence on the model length for both SWCNT's. As expected, the ΔE_{HL} for each SWCNT behaves in a similar way to that obtained for lowest excited states. In the graph, empty symbols represent the ΔE_{HL} in each case, and they obviously appear at higher energies. Those related to exciton binding (vertical dashed lines) show the relevance of the e-e interaction on the CIS states for each of the long SWCNT's. Clearly, this energy is higher in the (13,0) than in the (9,0) SWCNT, meaning a less bounded charge displacement of the last one.
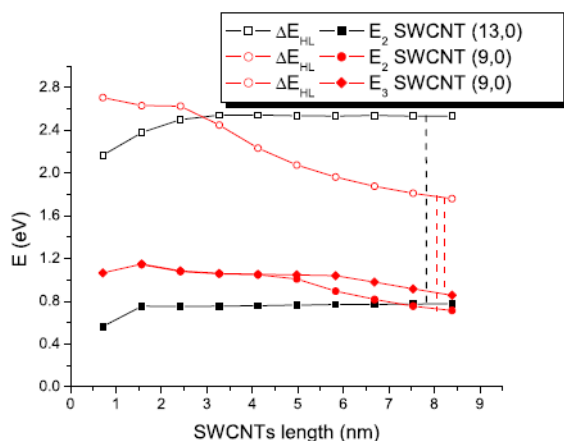

Figure 3. CIS states vs. HOMO – LUMO gap.

4   CONCLUSIONS

Two kinds of SWCNT's have been simulated by the CNDOL method. 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. Results show that it is important to consider finite models of SWCNT's with length longer than 3 nm in order to simulate realistic properties corresponding to experimental systems. The excited states of both SWCNT's also show different behaviors. 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 to be populated 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 favorable conditions for excitations in real long systems. The importance of e-e interaction (that is related with the exciton binding energy), as given by the CIS calculation. Our results suggest that the exciton is more bounded in the (13,0) SWCNT's.

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