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TDDFT-Based Spin-Orbit Couplings of 0D, 1D, and 2D Carbon Nanostructures: Static and Dynamical Effects

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Abstract

Carbon nanostructures (CNS) constitute an important class of materials derived from graphene that share remarkable photophysical and photochemical properties of potential interest for a number of technological applications, ranging from electron transport and spintronics to heat conduction and solar energy conversion. In this work, we use linear-response time-dependent density functional theory (LR-TDDFT) for the calculation of spin-orbit couplings (SOC) and intersystem crossing transitions in a number of CNS including: 0D quantum dots (C₆₀ and graphene nanoflakes), 1D carbon nanotubes, and 2D graphene. The method developed in [J. Chem. Phys. **140**, 144103 (2014)] and [J. Chem. Phys. **143**, 224105 (2015)] is able to capture

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the dependence of the SOC values on subtle electronic structure differences characterizing the different 0D, 1D and 2D CNS and on geometrical properties such as curvature and topological indices of carbon nanotubes. Compared to tight-binding calculations, our first-principles approach is able to reproduce very accurate results without the need of any *ad-hoc* parameterization. When combined with nonadiabatic dynamics, SOC can be used to compute intersystem crossing transitions between states of different spin multiplicities opening new avenues in the study of the complex dynamics of photoexcited CNS. In particular, we analyze the dependence of the intersystem crossing rates on thermal structural fluctuations in a carbon nanoflake.

1 Introduction

In the last decade graphene has emerged as one of the most promising two-dimensional (2D) materials with outstanding mechanical and physico-chemical properties¹⁻⁴. Among the most interesting properties are ballistic electron transport, heat conduction, anomalous quantum Hall effect, and the ability to sustain very high current densities. Of particular interest is the possibility to tune the electronic properties of graphene by means of chemical functionalizations and doping with other elements, formation of defects⁵ and generation of zero-dimensional (0D) and one-dimensional (1D) derivatives such as carbon dots (fullerenes), graphene nanoflakes, and carbon nanotubes. While the absence of an electronic band gap limits the efficiency of graphene-based electronic devices^{6,7}, 0D and 1D carbon nanostructures are very promising semiconductors thanks to lateral electron confinement. In addition to their unique properties, graphene-based carbon nanostructures also share other important characteristics including low production costs, low toxicity, chemical stability and biocompatibility, among others⁴.

0D carbon-based quantum dots (CQD) are grouped in two main classes: graphene quantum dots (GQDs) and carbon quantum dots (C-dots). GQDs consist of single- and multiple-layered graphene flakes of a size between 10 and 40 nm. Thanks to their unique electronic and magnetic properties such as photoluminescence, quantum confinement and edge effects, GQDs have already found many promising applications in optoelectronics, spintronics, and photoenergy conversion

as absorbing dyes in dye-sensitized solar cell devices. On the other hand, C-dots mainly refer to discrete quasi-spherical nanoparticles with a radius smaller than 5 nm. They are usually surface passivated by organic ligands and display light absorption and emission in the visible region, therefore becoming interesting materials for photovoltaics and optoelectronics in general.

Just as the 0D carbon dots, 1D carbon nanostructures can be grouped into two main classes: 1D graphene nanostructures (also known as graphene nanoribbons, GNRs) and carbon nanotubes (CNTs). GNRs have attracted much interest due to their semiconducting behavior and the possibility of tuning their properties by engineering their size (width) and the topology of their edges^{8–10}. Among the CNTs, single-walled CNTs (SWCNTs) are composed of a single graphene sheet rolled into a seamless cylinder. Depending on the way the wrapping is achieved, the SWCNT can display very different properties. In particular, the band gap can vary from 0 to about 2 eV resulting in a metallic or semiconducting behavior. Thanks to their peculiar physical and electronic properties, SWCNTs are very promising candidates for miniaturized electronics; this was demonstrated for the first time in 2001 with the realization of the first intermolecular logic gate based on SWCNTs field-effect transistors¹¹. Despite the relatively small size of these systems and their simple chemical compositions, their electronic properties show important variations depending on the nature of the edges and on their chemical functionalization, thermal distortions (conformational changes), and on the overall molecular topology. In the case of CNTs, the band-gap shows a nontrivial dependence on the diameter¹², which strongly reflects the relation between electronic structure properties and the wrapping topology. Thanks to their electronic properties, these carbon nanostructures are ideal materials for opto-electrical devices. Current applications range from ultrafast photo-resistors^{13,14} to photodetectors^{8,9} and light harvesting^{10,15}. In particular, the optical properties of carbon nanostructures can be easily tuned by controlling their size. In this way it is possible to engineer nanostructures with band-gaps in the visible range for applications in organic, single-junction, solar cell devices.

Of particular importance for these applications is a thorough understanding of the photophysical processes that govern the excited state dynamics of 0D and 1D carbon nanostructures. The

absorption of a photon induces an electronic transition from the molecular ground state into a resonant excited singlet state. At this point the system can either decay into the lowest singlet state through internal conversion (IC) and emit a photon (fluorescence), or it can relax into a triplet state through inter-system crossing (ISC), which is usually a long-lived state that decays over slower time scales (phosphorescence). In molecular systems like polycyclic aromatic hydrocarbons (0D and 1D carbon nanostructures), this second deactivation channel is usually less populated than the first one for two main reasons. First, the energy spacing between singlet and triplet states is typically of the order of 1 eV and therefore crossings are rare in the case of rigid structures. In addition, due to the absence of heavy elements, the spin-orbit coupling (SOC) matrix elements that govern the ISC are also relatively small ($\sim 1 \text{ cm}^{-1}$ or even smaller). However, in extended polycyclic aromatic hydrocarbons such as graphene the energy levels spacing reduces substantially through the delocalization of the photoexcited electron over a large surface, opening the possibility for new photophysical effects. In addition, molecular distortions induced by thermal fluctuations can also contribute to the enhancement of the ISC rates between singlet and triplet states through an increase of the SOC. This is particularly true in the case of relatively large carbon nanostructures, which show a large degree of flexibility. Recent experimental studies have confirmed the occurrence of ISC transitions in carbon nanostructures^{1,2} and more specifically, in graphene nanoflakes (0D graphene fragments). These phenomena have a significant relevance for many technological applications of carbon nanostructures in photovoltaics and nanotechnologies in general, since triplet states have longer diffusion lengths and longer lifetimes than singlets, thus favouring long-range charge separation and hampering charge carrier recombination.

While ISC events in CQDs are hard to investigate experimentally because of the ‘forbidden’ nature of these transitions, numerical simulations based on Tight-Binding (TB) and Density Functional Theory (DFT) can provide an accurate description of these phenomena. In particular, both methods can successfully reproduce the characteristic electronic structure properties of graphene and CNTs, namely the electron-hole symmetry and the linear dispersion relation at the K and K’ points in reciprocal space. Despite the success of TB, a quantitative description of the elec-

tronic properties of graphene and carbon nanostructures that also accounts for geometrical aspects like, conformational changes, asymmetrical distortions, curvature effects, and chirality in CNTs, requires the use of first-principles calculations. Among the most successful first-principles approaches, DFT and its time-dependent extension (LR-TDDFT) for the calculation of excited states dynamics^{16–20} and properties^{21–24} offer a well balanced compromise between accuracy and efficiency.

In this work, LR-TDDFT is used for the calculation of the photophysical properties of several 0D, 1D and 2D carbon nanostructures, with particular attention to the structural and dynamical effects that influence the ISC rates. We show that, despite the absence of heavy atoms, SOC in these compounds can become sizeable, leading to the possibility of population transfer from the singlet to the triplet state manifolds and vice versa. In particular, we emphasize the dependence of the magnitude of the SOC on the curvature of the nanostructures, together with other effects related to the topological indices in CNTs.

The paper is organized as follows. Section 2 describes the methods used for the calculation of the SOC using TB and DFT/LR-TDDFT with a short summary of the basic theory of nonadiabatic dynamics with ISCs. In Section 3 we will briefly summarize the computational details, while in Section 4 we will report all results for 0D (C_{60} and nanoflakes) and 1D (nanotubes) carbon nanostructures, and for graphene. In particular, in subsections 4.2 and 4.4 we will describe the effects of room-temperature dynamics and structural distortions on the size of the SOC values and corresponding ISC rates for a carbon nanotube and a prototypical carbon nanoflake. Section 5 summarizes and concludes.

2 Theory and Methods

2.1 Electronic structure and SOC of carbon nanostructures: tight-binding model

Carbon atoms arranged in a hexagonal lattice have a unique electronic structure that arises from the formation of a very neat and regular arrangement of π bonds. In particular, these structures show a very symmetric electron-hole (valence-conduction bands) linear dispersion behavior at the K and K' points in the reciprocal lattice^{25,26}. Due to the lack of nuclear spins (for pure ^{12}C compositions) the spin-orbit interactions occur exclusively between the electron spin and angular momentum, which are often suppressed because of symmetries. The principal aim of this work is to investigate topological properties (e.g. chirality in nanotubes), finite size effects (like 0D confinement in nanoflakes), and distortions induced by thermal fluctuations and captured by means of ground state and excited state molecular dynamics.

Atomic carbon with electronic configuration ($1s^2, 2s^2, 2p^2$) has an estimated atomic spin-orbit splitting of about 6-10 meV ($\sim 48 - 81 \text{ cm}^{-1}$)^{27,28}. However, as mentioned above, several factors can influence the magnitude of this interaction.

Before addressing these issues, we give a very brief introduction about the electronic properties of the two representative carbon structures for which a simple TB model already gives a good qualitative description: graphene and nanotubes.

2.1.1 Graphene

Within TB, graphene can be fully described by the p_z -orbitals coupled through nearest neighbor interactions. Considering the fundamental basis units made of two inequivalent carbon atoms (A and B defining two inequivalent sub-lattices), the electronic structure of graphene can be described by the basis set $B = \{p_z^A(\uparrow), p_z^A(\downarrow), p_z^B(\uparrow), p_z^B(\downarrow)\}$. A detailed account of the band-structure of graphene within TB in absence of SOC can already be found in the literature (see for instance Ref.²⁹) and therefore we will not develop further on this issue.

When SOC is included, the picture becomes slightly more complex. In fact, SOC induce interactions between all p -orbitals at each carbon atom, therefore allowing for the physical coupling between next-nearest-neighbours atoms. This process can be enhanced by doping and/or distortion from planarity, which induce a $\sigma - \pi$ rehybridization at the carbon sites with consequent increase of the SOC. To account for this effect, the TB basis needs to be further extended to include the p_x -orbitals and p_y -orbitals at each carbon site and the σ -orbitals in the graphene plane.

SOCs have two effects on the electronic structure of graphene^{30–33}. First they allow ISC between states of different spin multiplicity, which is the main topic of this investigation. However, SOC also have a direct effect on the graphene band structure introducing a k -dependent shift of the electronic bands through a second order mechanism, which can be summarized as follows: the $p_z^A(\uparrow)$ electron of atom A can hop onto a $p_x^A(\downarrow)$ electron through the effect of the SOC; then the interaction is ‘transported’ through σ -couplings from this A-center to a second one in its neighborhood passing through a B-center and, finally, interact with the $p_z^A(\uparrow)$ electron of the second A-carbon through a second SOC. This effect was investigated by Min et al³³ using TB. They arrived at the following interesting second order correction for the band energies

$$\Delta E_{SOC}^{(2)} = \frac{|s|}{18(sp\sigma)^2} \Delta_{SOC}^2, \quad (1)$$

where $|s| = 8.87$ eV is the energy splitting between carbon s and p orbitals, and $sp\sigma$ is the band parameter used in Min’s model³³. Using an average value of $\Delta_{SOC} = 10$ meV for the atomic SOC one gets an average effect of about $1.6 \mu\text{eV}$.

Another interesting effect on the magnitude of the SOC in graphene is induced by the curvature. By bending the carbon sheet uniformly one produces a lowering of the symmetry of the orbitals with a consequent increase of the overlap between atomic orbitals sitting on different carbon atoms. In particular, through bending one can achieve overlap between p_z and p_x -orbitals of neighbor atoms on different A and B sub-lattices therefore contributing to an increase of the overall SOC (whose main contribution is intra-atomic). Huertas-Hernando and co-workers³⁴ estimated this

contribution to be

$$\Delta_{SOC}^{curv} = \frac{V_{pp\sigma} - V_{pp\pi}}{V_1} \left(\frac{a}{R_1} + \frac{a}{R_2} \right) \frac{V_1^2}{V_2^2} \Delta_{SOC} \quad (2)$$

where $a = 1.42 \text{ \AA}$ is the carbon-carbon bond length, R_i are the curvature radii in x and y directions, and $V_1 = 2.47 \text{ eV}$, $V_2 = 6.33 \text{ eV}$, $V_{pp\sigma} = 5.38 \text{ eV}$, $V_{pp\pi} = -2.24 \text{ eV}$ and $V_1 = 2.47 \text{ eV}$ are the band parameters of the model Hamiltonian³⁴. Using a standard value for the intra-atomic SOC energy of about 12 meV one gets $\Delta_{SOC}^{(curv)} \sim 0.25 \text{ meV}$ (1.97 cm^{-1}) for an average curvature radius $R = 50 \text{ \AA}$, which grows to 1.23 meV (9.9 cm^{-1}) for $R = 10 \text{ \AA}$.

2.1.2 Carbon nanotubes

Carbon nanotubes have different topologies, each one characterized by a couple of numbers (n, m) , with $n \geq m$ which indicate how a graphene sheet is rolled up. When picturing an unrolled carbon nanotube on a graphene sheet with primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, the circumferential vector

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2, \quad (3)$$

connects equivalent atoms of the nanotube (1) and defines its diameter $d = \frac{\|\mathbf{C}_h\|}{\pi}$ and curvature

$$\kappa = \frac{2\pi}{a\sqrt{n^2 + nm + m^2}} \quad (4)$$

where $a = \|\mathbf{a}_1\|$. Figure 1 is a schematic depiction of how to build the $(4, 2)$ nanotube; the grey area represents the surface of the unrolled nanotube superposed on a graphene lattice. For completeness, we also mention that nanotubes can also be classified according to their chirality, which is also a function of the pair of indices (n, m) and defined by the chiral angle θ with

$$\cos \theta = \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{\|\mathbf{C}_h\| \|\mathbf{a}_1\|} = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}}. \quad (5)$$

Achiral nanotubes are those with $(n, 0)$ (called *zig-zag*) and those with $n = m$ (called *armchair*); all others are chiral nanotubes. More important for us is to investigate the relation between the

topology of the nanotubes and their electronic structure properties.

Figure 1: Graphene sheet with lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. The grey area represents the surface area of an unrolled $(4,2)$ nanotube. The vector $\mathbf{C}_h = 4\mathbf{a}_1 + 2\mathbf{a}_2$ becomes circumference of the nanotube, while the τ runs along its axis.

According to the TB model in the zone-folding approximation, the electronic properties of the nanotubes can also be easily classified in terms of the topology indices (n, m) . Due to the constraint induced by the periodicity of the CNT along its circumference and differently from the graphene case, CNT molecular wavefunctions are described by a discrete set of electronic momenta ($\mathbf{k}$) that satisfy the relation

$$\mathbf{k} \cdot \mathbf{C}_h = 2\pi l, \quad (6)$$

for integer l , which is equivalent to confine the $\mathbf{k}$ in discrete planes in the Brillouin zone that intersect the 2D graphene band-structure into a set of discrete subbands.

When one of the subbands includes the K-point at the Dirac cone, the CNT is metallic^{25,35–38}. This condition is achieved when $\mathbf{K} \cdot \mathbf{C}_h = 2\pi l$, which can be translated into the simple relation $n - m = 3l$. According to this model, all armchair (n, n) CNTs, the zig-zag CNTs with the topology $(3n, 0)$, and a good subset of chiral CNTs with indices or $(3l - m, m)$ are metallic. In case the subbands do not include the K-point, for $n - m = 3l \pm 1$, the CNT will present an energy gap and

therefore becomes a semiconductor. According to TB, the gap opening amounts to

$$E_g = \frac{2\pi a t_0}{\sqrt{3}||\mathbf{C}_h||} \quad (7)$$

and is therefore inversely proportional to the CNT diameter (and proportional to the curvature κ). In Eq. (7), t_0 corresponds to the TB *transfer integral* between nearest neighbor carbon atoms.

Concerning the estimation of the SOC, Huertas-Hernando et al., developed a model based on and extended tight-binding two-component spinor Hamiltonian³⁴. However, the effect of the spin-orbit interaction enters merely as a consequence of the curvature of the CNT and is therefore insensitive to the specific electronic properties of the CNTs that depend on the topological indices (n, m) . Using the result for graphene (Eq. (2)) and considering a single curvature along the circumference of the CNT, one gets

$$\Delta_{SOC}^{CNT} = a \frac{V_{pp\sigma} - V_{pp\pi}}{V_1} \frac{V_1^2}{V_2^2} \frac{\Delta_{SOC}}{d} \quad (8)$$

where d is the diameter of the CNT. While this formula is very useful for a rationalization of the dependence of the SOC as a function of the CNT dimensions, its quantitative predictions are in many cases unsatisfactory. This is mainly due to the limits of the assumptions in the TB model for CNTs, which, as mentioned above, does not fully account for the dependence of the electronic structure on the topological properties of the CNT. In particular, the map: $(n, m) \rightarrow d$, is non-injective and therefore Eq. (8) cannot unambiguously describe the SOC of the different CNT topologies.

2.2 Electronic structure and SOC of carbon nanostructures

2.2.1 Electronic structure of graphene and CNT with DFT

While successful in many aspects, the TB model also shows some important deficiencies. In particular, the assumptions used to evaluate electronic structure properties (such as SOC) introduce notable discrepancies that mask the complex dependence on the topological structure of interest.

As a consequence, CNTs with similar curvature may have strikingly different electronic structure properties, which cannot be captured by these models.

In order to shed new light on this issue, we plan to investigate the electronic structure of CNTs using DFT and LR-TDDFT, focusing our attention on the magnitude of the SOC and their dependence on the topology indices (n, m) and the curvature κ (Eq.(4)).

The main advantage of the DFT/LR-TDDFT approach compared to tight binding can be summarized in the following four points: *(i)* DFT is a first-principles approach that can be considered parameter-free. This is particularly true in case of the use of the PBE³⁹ functional that, for the purpose of this study, offers a very favorable compromise between accuracy and computational costs. In particular, DFT/PBE does not require any system specific parametrization for the study of carbon nanostructures. *(ii)* DFT can naturally account for effects like σ - π -rehybridization⁴⁰, which are difficult to capture using TB based approaches. In fact, TB assumes no interaction between the p_z -orbitals and the σ bands (or subbands in CNTs). While this is the case in perfectly flat graphene, curvature will induce coupling between the σ and the π/π^* manifolds, especially for CNTs with relatively short diameters (< 1 nm). *(iii)* Contrary to TB, DFT/LR-TDDFT calculations can account for the asymmetry between the valence and conducting π/π^* that arise from overlaps between p_z orbital not included in the model Hamiltonians. *(iv)* DFT/LR-TDDFT can describe without further modeling the complex dependence of the electronic structure of CNTs from the topological indices (n, m) .

2.3 SOC and nonadiabatic dynamics within the LR-TDDFT framework

In this section we review the method for the calculation of SOC within the TDDFT framework in the linear-response regime (LR-TDDFT) and present the basic scheme used to model nonadiabatic dynamics with intersystem crossings.

SOC calculations in LR-TDDFT. The computation of SOC within LR-TDDFT involves the use of the many-electron auxiliary wavefunction (AMEWF) introduced in^{19,41,42},

$$|\tilde{\Psi}_I\rangle = \sum_i^N \sum_{\xi=\{\alpha,\beta\}} \hat{r}_{i\xi}^{\dagger I} \hat{a}_{i\xi} |\tilde{\Psi}_0\rangle, \quad (9)$$

where $|\tilde{\Psi}_0\rangle$ is the Slater determinant of all the occupied KS orbitals, N is the number of electrons, $\hat{a}_{i\xi}$ is the annihilator operator for the occupied KS orbital $\phi_i(r)$ with spin ξ and $\hat{r}_{i\xi}^{\dagger I}$ is the creator operator for the corresponding linear-response (LR) orbital $\phi_i^I(r)$ associated to the excited state I within the Sternheimer formulation of LR-TDDFT^{43,44}. The LR KS-orbitals satisfy the Sternheimer equations

$$[\epsilon_k - \omega_I - H^{KS}] \phi_k^I(\mathbf{r}) = \mathcal{Q}[\delta V(\mathbf{r}) + \delta V^{SCF}(\omega)] \phi_k(\mathbf{r}), \quad (10)$$

where H^{KS} is the KS Hamiltonina, ϵ_k is the KS orbital energy associated to $\phi_k(r)$, ω_I is the excited state energy of state I , and $\mathcal{Q} = 1 - \sum_{i=1}^N |\phi_i\rangle\langle\phi_i|$ is the projector onto the subspace of virtual KS orbitals.

It is important to mention that the concept of AMEWF also applies to the Casida's formulation of LR-TDDFT^{41,42,45,46}. However, the Sternheimer approach has the advantage of describing each individual excitation in the subspace of N linear independent LR KS orbitals, therefore making the calculation of a large number of virtual KS orbitals unnecessary. The AMEWF of Eq. (9) is a linear combination of singly-excited Slater determinants and is specific for each electronic excited state I . Note that these wavefunctions have no direct physical meaning (they are not eigenstates of the electronic Hamiltonian), but when used in the calculation of matrix elements of one-body operators $\langle\tilde{\Psi}_0|\mathcal{O}|\tilde{\Psi}_I\rangle$, they provide the exact linear response quantity⁴¹ (within the approximations used in the LR-TDDFT calculations). Recently, we also proved that the same procedure can be used to approximate second-order response quantities of the form $\langle\tilde{\Psi}_I|\mathcal{O}|\tilde{\Psi}_J\rangle$ between pairs of excited states wavefunctions $|\tilde{\Psi}_I\rangle$ and $|\tilde{\Psi}_J\rangle$ ⁴⁷.

Of particular relevance for this study is the calculation of the SOC matrix elements between

a pair of singlet and triplet excited state wavefunctions. To this end, we use the Breit-Pauli one-electron description of the SOC operator

$$\hat{H}_{1el}^{SO} = \frac{\alpha^2}{2} \left[\sum_{\gamma=1}^{N_\gamma} \sum_{i=1}^N \frac{Z_\gamma}{r_{i\gamma}^3} (\mathbf{l}_{i\gamma} \cdot \mathbf{s}_i) \right], \quad (11)$$

evaluated for 2-component KS-spinors and LR KS-spinors with α and β components⁴⁸

$$\boldsymbol{\varphi}_i(\mathbf{r}) = \begin{pmatrix} \varphi_{i,\alpha}(\mathbf{r}) \\ \varphi_{i,\beta}(\mathbf{r}) \end{pmatrix} \quad \text{and} \quad \boldsymbol{\phi}_i^I(\mathbf{r}) = \begin{pmatrix} \phi_{i,\alpha}^I(\mathbf{r}) \\ \phi_{i,\beta}^I(\mathbf{r}) \end{pmatrix}. \quad (12)$$

In Eq. 11, α is the fine structure constant, Z_γ are the nuclear charges, γ is the index for the nuclei, i the one for the electrons, and $r_{i\gamma}$ measures their relative distance. $\mathbf{l}_{i\gamma}$ and $\mathbf{s}_i$ are the angular momentum and spin angular momentum operators, respectively⁴⁸. For a detailed description of the calculations of the SOC matrix elements $\langle \tilde{\Psi}_I | \hat{H}_{1el}^{SO} | \tilde{\Psi}_J \rangle$, including spin-flip transitions between states with different spin quantum numbers M_s , see reference⁴⁸, where both Casida's and Sternheimer's formulations of LR-TDDFT are presented.

Mixed quantum-classical dynamics with ISC. Excited state dynamics is performed using a mixed quantum-classical approach based on LR-TDDFT for the solution of the electronic structure problem at each nuclear configuration⁴². For this study, we use a recent extension of the algorithm⁴⁹, which can compute *on-the-fly* nonadiabatic transitions between states with the same spin multiplicity (internal conversions) as well as between singlet and triplet states (intersystem crossings). The method, named TSH $\otimes$ LZ algorithm⁴⁹, evaluates nonadiabatic transition probabilities using the Tully's surface hopping algorithm⁵⁰ in the spin-free part of the electronic Hilbert space, while ISC probabilities in spin space are computed using the Landau-Zener formalism^{51,52}.

Nuclear trajectories are therefore propagated *on-the-fly* using Newton's equations of motion with forces derived at LR-TDDFT level of theory. In parallel, a set of amplitude coefficients C_K

(one for each electronic state K) associated to each nuclear trajectory are propagated according to

$$\dot{C}_K(t) = -iC_K(t)\omega_K - \sum_I C_I(t)\sigma_{IK}(t), \quad (13)$$

where $\sigma_{IK}(t)$ are the nonadiabatic coupling coefficients obtained from the scalar product between the nuclear velocities and the nonadiabatic coupling vectors for the adiabatic states I and K ^{42,47}.

The probability for a nuclear trajectory to hop from state I to state K in the time interval $[t, t + \delta]$ is given by

$$p_{KI} = -2 \int_t^{t+\delta} \frac{\text{Re}[C_K(\tau)C_I^*(\tau)\sigma_{KI}(\tau)]}{C_I(\tau)C_I^*(\tau)} d\tau. \quad (14)$$

meaning that it occurs when the inequalities

$$\sum_{L \leq K-1} p_{LI} < \zeta < \sum_{L \leq K} p_{LI}, \quad (15)$$

hold for a random number ζ generated in the interval $[0, 1]$.

In the spin space, ISC probabilities between two states I and J of different spin multiplicity are computed *on-the-fly* using the Landau-Zener expression

$$p_{IJ}^{LZ} = 1 - e^{-2\pi\Gamma_{IJ}}, \quad (16)$$

where the Landau-Zener parameter is approximated with^{53,54}

$$\Gamma_{IJ} = \frac{|\langle \Psi_I | H_{1el}^{SO} | \Psi_J \rangle|^2}{d\omega_{IJ}/dt}. \quad (17)$$

In Eq. (17) the energy difference $\omega_{IJ} = |\omega_I - \omega_J|$ is the absolute value of the energy gap between the two states evaluated in the spin-diabatic representation^{48,49}. If the state J is a triplet, then it has three sublevels (J^{-1} , J^0 and J^{+1}), which are degenerate in LR-TDDFT. We chose to treat J as single state, and its total SOC with a singlet state I is given by

$$\langle \Psi_I | H_{1el}^{SO} | \Psi_J \rangle = \sqrt{\sum_{M_s=-1}^{+1} |\langle \Psi_I | H_{1el}^{SO} | \Psi_J^{M_s} \rangle|^2}. \quad (18)$$

According to this formulation, an ISC event occurs stochastically at the crossing point between states I and J , when the probabilities p_{IJ}^{LZ} is larger than a random number generated in the interval $[0, 1]$.

3 Computational details

All calculations were performed with the plane-wave-pseudopotential code CPMD⁵⁵, which uses the Sternheimer's formulation of LR-TDDFT^{43,44} within the Tamm-Dancoff approximation (TDA)^{44,56}. The PBE approximation³⁹ to the exchange-correlation functional was used in all calculations together with the adiabatic approximation^{57,58} for the LR-TDDFT kernel. The Trouiller-Martins norm-conserving pseudopotentials⁵⁹ were used for both carbon and hydrogen atoms, and the chosen plane-wave cutoff value was 40 Ry.

For the molecular dynamics simulation on the single-layer graphene dot a time-step of 5 a.u. (0.121 fs) was used. The molecule, composed of 38 carbon atoms and capped by 16 hydrogen atoms, was placed in a box of size $18\text{\AA} \times 10\text{\AA} \times 18\text{\AA}$ and periodic images were screened using the Martyna-Tuckerman algorithm⁶⁰. The system was equilibrated using Born-Oppenheimer dynamics MD in the ground state at room temperature (300 K). A random frame was selected as a starting point for the excited state nonadiabatic dynamics beginning in the first singlet excited state S_1 . Spin-orbit couplings were calculated every 10 time-steps of dynamics (approximately 1.2 fs) and the inter-system crossing transition probabilities were evaluated using the approach described in Ref⁴⁹. All static calculations on nanotubes were performed using periodic boundary conditions in the three dimensions with box sizes that were adapted to the particular structure considered.

For comparison, we also performed LR-TDDFT SOC calculations with the ZORA Hamiltonian^{61,62} as implemented in the ADF software package⁶³ using the PBE functional and a TZP basis set.

4 Results and Discussion

4.1 0D carbon nanostructures

4.1.1 C₆₀ Buckminsterfullerene

The best known fullerene-type carbon nanostructure is the C₆₀ molecule. The molecule is composed of 60 carbon atoms arranged in 20 hexagons and 12 pentagons. It is worth mentioning that C₆₀ is not an aromatic molecule, despite the large number of carbon-carbon π -bonds. C₆₀ can exist either as a molecular compound or as a van der Waals fcc solid (fullerite). In this work we have performed SOC calculations on a single C₆₀ molecule for which TB spin-orbit coupling results are available in literature. The DFT/PBE optimized structure shows C-C bond lengths of 1.45 Å (hexagon/hexagon edge) and 1.40 Å (hexagon/pentagon edge) and a diameter of 7.12 Å, in good agreement with experimental measurements. The LR-TDDFT/PBE SOC values obtained for C₆₀ range between 0.03 and 4.95 cm⁻¹ and are all reported in table 1.

Table 1: LR-TDDFT/PBE SOC values for the lowest 8 singlet and triplet states of C₆₀.

	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8
S_0	0.09	0.12	0.21	0.49	0.03	0.14	0.74	4.39
S_1	3.49	1.35	0.51	0.45	2.80	2.57	0.30	1.42
S_2	0.33	3.46	1.61	1.42	2.68	1.75	2.60	1.54
S_3	1.67	0.56	0.82	1.72	0.06	1.89	3.68	2.13
S_4	2.37	1.65	3.33	1.45	3.86	1.85	0.59	1.93
S_5	1.10	0.54	0.30	2.65	2.57	3.19	3.26	3.72
S_6	1.07	1.25	1.02	1.14	2.35	2.98	2.29	3.02
S_7	1.35	1.99	0.88	4.59	2.01	2.73	2.19	2.75
S_8	2.06	1.05	0.81	1.16	2.01	2.97	2.82	0.96

These values fall within the range of SOC values that we obtained for bent graphene flakes (1-3 cm⁻¹) and CNTs with rather small curvature (see section 4.2 below). Comparing the curvature of the C₆₀ molecule (~ 0.28 Å⁻¹) with that of CNTs of similar transverse curvature, we could have expected a larger SOC value. However, this does not come as a surprise. First, the chemical composition of C₆₀ and CNT is different (pentagons and hexagons in the C₆₀ *versus* hexagons

in CNTs) and, second, in CNTs there is no curvature along the main longitudinal axis. It is also interesting to note that LR-TDDFT/PBE allows access to higher excited states compared to TB. Huertas *et. al.* reported TB values for the SOC-induced splitting of triplet states in C_{60} of the order of only 10^{-2} cm^{-1} , which are in good agreement with the values we obtained for the coupling between low lying excited states. At higher energy, we observe an enhancement of the SOC between singlet and triplet states that may play an important role in determining the photophysical properties of C_{60} , especially in optoelectronics. Furthermore, SOC calculations performed using the ZORA Hamiltonian implemented in ADF yield results in good agreement with the values reported in Table 1, confirming the validity of our approach.

The magnitude of the SOC in 0D carbon nanostructures (in particular fullerenes) also decreases with the increase of the molecular diameter. However, this behavior is only observed for structures up to 94 carbon atoms (C_{94})⁶⁴. In fact, larger fullerenes deviate substantially from the spherical symmetry (of the buckyballs) and the local curvature is no longer a simple function of the global molecular diameter.

Figure 2: Kohn-Sham orbitals of the C_{60} molecule. From left-to-right, top-to-bottom: HOMO-1, HOMO, LUMO, LUMO+1.

4.1.2 Nanoflake

As a second example of CQD (0D structure) we consider a graphene nanoflake composed of 38 carbon atoms saturated at the edges with hydrogen atoms. This structure can also be seen as a

constituent unit (a ‘tile’) of a larger 1D molecule (like CNTs) and of graphene. While flat in its optimized ground-state structure, this system undergoes important conformational changes during ground state as well as excited state dynamics at room temperature. In this section, we will start by investigating the electronic properties of the nanoflake in its perfectly flat geometry; the excited state dynamics of the same system, including transitions mediated by ISCs, will be addressed in section 4.4.1.

Table 2 reports the excited state energies, oscillator strengths and corresponding assignments of the first three excited singlet and triplet states of the nanoflake, evaluated at the ground state optimized geometry. The oscillator strength of the S_1 is much larger than those of all other excited singlet states (S_2 and S_3 , as well as S_4 and S_5 not shown in the table), and it is therefore the state most likely populated upon photoexcitation. Concerning the triplet states, T_1 is significantly lower in energy than S_1 (of about 1 eV) and we do not expect it to play any important role in the photophysics of the system. On the other hand, T_2 and T_3 are energetically very close to S_1 (around 0.1 and 0.2 eV, respectively) and therefore, for sufficiently large values of the SOCs, there is a sizable probability of an ISC between S_1 and one of these triplets.

Concerning the character of these transitions, we observe that both S_1 and T_1 are well described by ‘pure’ HOMO to LUMO transitions, while the other two states (S_2 , S_3 , and the corresponding triplets) involve transitions from the three highest occupied orbitals (HOMO-2, HOMO-1, and HOMO) to three lowest unoccupied orbitals (LUMO, LUMO+1, and LUMO+2). Six of these orbitals are shown in Figure 3 and display, as expected, a clear π character for the occupied frontier orbitals and a mixture of π and π^* character for the unoccupied ones. As confirmed by our LR-TDDFT/PBE calculations (see table 2), the SOC between these states is around 1/10 of the atomic carbon SOC between p -orbitals, which is therefore much lower than what expected for organic molecules with hetero-atoms (nitrogen, oxygens or other heavier atoms) in which El-Sayed (n, π^*)/(π, π^*)-type of transitions induce large SOCs. The situation changes when thermal effects are included. Dynamics induces conformational distortions that affect the curvature of the nanoflake with a consequent increase of the SOCs (thanks to a larger overlap between p -type or-

bitals), as discussed in Section 2.3. A detailed analysis of the ISC dynamics in this compound will be given Section 4.4.1.

Figure 3: Kohn-Sham orbitals of the nanoflake. From left-to-right, top-to-bottom: *HOMO-2*, *HOMO-1*, *HOMO*, *LUMO*, *LUMO+1*, *LUMO+2*.

Table 2: Characterization of the lowest electronic excited states of the nanoflake at LR-TDDFT/PBE level of theory.

State	Excitation energy [eV]	Oscillator strength	Assignment
S_1	1.973	0.23785	HOMO $\rightarrow$ LUMO (86.9%)
S_2	2.213	0.00029	HOMO $\rightarrow$ LUMO + 1 (50.7%) HOMO - 1 $\rightarrow$ LUMO (48.2%)
S_3	2.384	0.00111	HOMO $\rightarrow$ LUMO + 2 (47.3%) HOMO - 2 $\rightarrow$ LUMO (42.4%) HOMO $\rightarrow$ LUMO + 1 (5.0%) HOMO - 1 $\rightarrow$ LUMO (4.4%)
T_1	1.013	—	HOMO $\rightarrow$ LUMO (98.7%)
T_2	1.980	—	HOMO - 1 $\rightarrow$ LUMO (52.8%) HOMO $\rightarrow$ LUMO + 1 (42.4%)
T_3	2.185	—	HOMO $\rightarrow$ LUMO + 1 (52.5%) HOMO - 1 $\rightarrow$ LUMO (43.1%) HOMO $\rightarrow$ LUMO + 2 (2.4%) HOMO - 2 $\rightarrow$ LUMO (1.8%)

4.2 1D: Carbon Nanotubes

As described in Section 2.1, the physical properties of CNTs depend in a non trivial manner on the topological indices (n, m) , which determine both their size (diameter and curvature) and their electronic properties (metallic vs. semiconducting) including the magnitude of the SOC. As a validation of DFT calculations, in Figure 4 we report the CNT bandgaps for different topological indices; the closure of the gap is well reproduced in all metallic CNTs for which $n - m = 3l$.

Figure 4: LR-TDDFT/PBE bandgaps for a series of nanotubes. Left panel: zig-zag CNTs with indices $(n,0)$; right panel: CNTs within the family $(2m,m)$. Metallic CNTs are characterized by the relation $n - m = 3l$.

TB predicts a dependence of the SOC on the curvature of the CNT without however, providing a detailed picture of the phenomena in terms of electronic structure properties valid for all points of the Brillouin zone. In this study, we investigate the dependence of the SOC on the topological indices (n, m) using first-principles LR-TDDFT/SOC calculations on 13 different CNTs that sample a good portion of the (n, m) space for $4 \leq n \leq 14$ and $0 \leq m \leq 5$ (see table 3) including zig-zag and chiral structures.

We computed SOC between the first 9 singlet states (including the ground state) and first 8 triplet excited states, for a total of 72 values for each CNT. All calculations are performed at the Γ -point using a supercell periodically replicated in the three spatial dimensions. Along the CNT principal axis the supercell comprises a multiple of the primitive translation vector τ , namely $3\|\tau\| = 12.78 \text{ \AA}$ in the case of the zig-zag CNTs and $\|\tau\| = 11.27 \text{ \AA}$ for the chiral CNTs in order to guarantee a comparable length for all structures. The other two edges of the supercell (perpendicular to the principal axis) are fixed at $10 \text{ \AA}$ plus the diameter of the tube for all CNTs.

Figure 5: Maximum SOC values (over the first 8 excited states) for different CNTs plotted against their curvature, κ . Red dots represent the metallic nanotubes, while green and blue dots correspond to mod-2 and mod-1 semiconducting CNTs, respectively. The (4,2) CNT is excluded from the fit of the mod-2 structures due to its peculiar properties related to the extremely small diameter.

All the 72 values of SOC calculated for the (6,0) nanotube are given in Table 4. In order to visualize the dependence of the SOC on the nature and the topology of the different CNTs, we decided to report the value of the maximum SOC for each structure as a function of the curvature and of the topological indices (n, m) . In fact, due to the large variety of the structures considered it is not possible to select a characteristic pair of singlet and triplet states to analyze across the entire series of CNTs considered in this study. The maximum SOC values give a good description of the trends; however, the mean values over the 72 SOC values calculated for each CNT also reproduces the same scenario (see SI).

Optical spectra measurements on CNTs have revealed the existence of two sub-classes among the semiconducting CNTs, which are characterized by the remainder of the division of $(n - m)$ by 3, i.e., the value of $\text{mod}(n - m, 3)$ ^{65,66}. While the physical origin of this classification is still not well understood⁶⁵, we also found this subdivision to be very useful for the interpretation of our results. Figure 5 reports all the maximum SOC values considered in this study organized according to their electronic properties and topology indices. Metallic CNTs (red dots) occur for $\text{mod}(n - m, 3) = 0$ while the semiconducting CNTs are divided into the mod-2 (blue dots) and mod-1 (green dots) sub-classes according to the value of $\text{mod}(n - m, 3)$. As predicted from the TB model, we observe a linear increase of SOC values as a function of the curvature, which is particularly conspicuous for

metallic nanotubes. However, we also obtain a very good linear correlation for the semiconducting CNTs when we consider the two families, mod-1 and mod-2, separately. Note that CNT (4,2) is the only non-metallic CNT that falls outside the observed trend. This can be explained with the fact that (4,2) is the smallest synthesized free-standing CNT and, due to its reduced diameter, it has peculiar chemical and physical properties⁶⁷. In summary, our LR-TDDFT results confirm a correlation between the curvature of the CNTs and the intensity of the SOC. The picture that emerges from first-principles calculations confirms the existence of a non trivial dependence on the topological indices that characterize the CNTs, which goes beyond the simple classification as metallic ($\text{mod}(n - m) = 0$) and non-metallic structures. In particular, a linear fit of the SOC data for semiconducting CNTs is only possible if we distinguish between the mod-1 and mod-2 families, with the mod-2 class showing the largest dependence on the curvature.

Table 3: *Characteristic properties of the CNTs investigated in this study.*

<i>zig-zag</i>			
structure	diameter [Å]	curvature [$1/\text{\AA}$]	n. atoms
(6,0)	4.70	0.24	72
(7,0)	5.48	0.36	84
(8,0)	6.26	0.31	96
(9,0)	7.04	0.28	108
(10,0)	7.83	0.26	120
(11,0)	8.61	0.23	132
(12,0)	9.40	0.21	144
(13,0)	10.18	0.20	156
(14,0)	10.96	0.18	168
<i>chiral $n = 2m$</i>			
(4,2)	4.14	0.48	56
(6,3)	6.22	0.32	104
(8,4)	8.29	0.24	112
(10,5)	10.36	0.19	140

Table 4: LR-TDDFT/PBE SOC values for the lowest 8 singlet and triplet states of the (6,0) CNT.

	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8
S_0	0.01	3.77	1.72	1.72	0.00	0.00	0.00	0.00
S_1	21.21	0.01	0.02	0.02	1.27	0.00	0.00	0.00
S_2	0.24	3.70	1.47	1.49	0.02	0.00	0.00	0.03
S_3	1.27	21.49	0.00	0.00	20.50	0.00	0.00	0.00
S_4	0.09	1.52	12.91	31.54	0.00	0.02	0.00	0.06
S_5	0.00	1.53	17.41	27.60	0.00	0.01	0.00	0.05
S_6	0.00	0.00	0.00	0.00	0.00	0.01	3.73	0.00
S_7	0.00	0.00	0.14	0.09	0.00	20.50	0.01	2.18
S_8	0.00	0.00	0.02	0.13	0.00	1.98	0.00	20.18

Figure 6: LR-TDDFT/PBE SOC values (maximum over the first 8 singlet and triplet states) for 12 different geometries of the (6,0) CNT collected along the dynamics. The value corresponding to the optimized structures is shown with a dashed line.

Finally, we also investigated the effects of thermal fluctuations on the magnitude of SOC. To this end, we performed ground-state Born-Oppenheimer MD at room temperature (300 K) on a prototypical (6,0) CNT and analyzed the SOC between singlet and triplet states for different configurations sampled along the trajectory. Figure 6 shows the results for 12 MD frames separated from each other by ~ 230 fs. We observe that, compared to the optimized (minimum energy) geometry (frame 0), the SOC of the ‘thermalized’ structures are systematically lower by about 5-20 %, showing that temperature can have a considerable effect on SOC. This suggests that, while the perfect curvature of the optimized structure gives rise to an increase of the SOC (compared to

flat graphene), the asymmetric distortions induced by thermal vibrations cause a reduction of the orbital overlaps and the consequent decrease of the SOC.

4.3 2D: Graphene

For a perfectly flat graphene sheet, the TB model predicts very small SOC values in the order of the atomic spin-orbit splitting of isolated carbon atoms (~ 6 meV). However, the SOC in graphene differs for different positions (k -vectors) of the Brillouin zone and in particular it is greatly reduced at the degeneracy point of the Dirac cones (the K-points) for which TB predicts values below $1 \mu\text{eV}$.

In this study we applied a supercell description of graphene generated from the fundamental hexagonal unit cell characterized by a lattice parameter $a = 2.46 \text{ \AA}$. The calculation were done on two types of supercells, both with hexagonal symmetry. The first supercell corresponds to 3×3 graphene unit cells for a total of 18 C atoms. This is a peculiar choice characterized by the back-folding of the K-points onto the Γ -point in reciprocal space, therefore offering the possibility to compute the electronic properties at the Dirac cone using a supercell calculation at the Γ -point. Due to the degeneracy of the K-points we expected and obtained the first 4 LR-TDDFT transitions to be nearly zero, while the second tier of excitations (with finite energy gaps) corresponds to transitions between the π and σ^* KS states, which have notoriously large SOC contributions (see Figure 7). The second supercell corresponds to 7×7 graphene units for a total of 98 atoms. In this case, the surface of the corresponding Brillouin zone in reciprocal space shrinks further, meaning that more points of the electronic bands fold back at Γ , including points of the Π and Π^* bands with, however, the exception of the K-points, which are not sampled in this case. For this supercell, the π and π^* states (sampled in the vicinity of the Dirac cone) dominate the density of states at the gap in Γ , therefore making the calculations of $\pi\sigma^*$, $\sigma\pi^*$ and $\sigma\sigma^*$ SOC values computationally very expensive (due to the large number of LR-TDDFT solutions required).

For the 3×3 supercell, we obtained a maximum SOC value of 68.65 cm^{-1} (8.51 meV), which falls within the $6 - 12$ meV range evaluated with TB between σ and π bands at the Γ -point³². On

Figure 7: σ (left) and π (right) KS-orbitals computed for the 3×3 supercell of graphene.

the other hand, the SOC between π and π^* bands at the K-point (for vanishing energy gaps) is of the order of 0.001 cm^{-1} (0.00012 meV), which, again, is in good agreement with second-order TB. In fact, as discussed in Section 2.1 due to symmetry arguments³⁴ TB predicts a vanishing SOC, that becomes finite only if second-nearest neighbor couplings between equivalent carbon atoms (AA or BB) are considered. (It is important to stress that LR-TDDFT can reproduce this result using standard GGA functionals, while second-order TB requires an *ad hoc* parametrization). The results obtained for the 7×7 supercell are also in good agreement with the TB predictions. All SOC values fall in the range $0.000 - 0.001 \text{ cm}^{-1}$, meaning that the vanishing of the couplings extends to the entire π and π^* bands and is not limited to the K-points.

In summary, the calculations for flat graphene show a good agreement with the known experimental and TB results, therefore validating our LR-TDDFT/PBE implementation, which is able to capture quantitatively the different physical mechanisms at the origin of the SOC level splitting, without the need of any correction to the theory. A further topic of interest, is the characterization of the effect of the curvature on the SOC in corrugated graphene. However, due to the size of the supercell required for this type of investigation we will not address this issue directly. On the other hand, in the next Section we will explore the effect of the curvature on the value of SOC by investigating the gas phase dynamics of a GQD.

4.4 ISC dynamics of a graphene quantum dot

It is a well established result that ISCs in CQDs are in general less efficient than ICs due to large energy spacings between singlet and triplet states and weak SOC. However, as shown in section 4.1.2, topological features and structural modifications (in particular changes of the curvature) can influence the strength of the SOC and increase the ISC rates. In this section, we investigate the excited state nonadiabatic dynamics of the 0D nanoflake described in section 4.1.2 with the aim of shedding new light on the mechanism of ISC in a prototypical carbon nanostructure.

4.4.1 Description of the dynamics

After a ground state equilibration dynamics at 300 K, the system is excited into the first singlet excited state, S_1 and propagated according to the LR-TDDFT based TSH $\otimes$ LZ nonadiabatic MD scheme described in section 2.2.1. This choice is motivated by the magnitude of the corresponding oscillator strength and by the fact that, due to the relatively small SOC of CQDs, ISCs occur when the system is relaxed (through IC) in the lowest singlet state. Figure 8 shows the time evolution of the energies of the states involved in the dynamics, namely S_1 , S_2 , together with T_2 and T_3 . T_1 lies lower in energy and never interferes with the dynamics during the entire time span of our simulation. During the dynamics, the force state S_1 approaches the two triplet states T_2 and T_3 , however it actually only intersects T_2 at several points. The time evolution of SOC between S_1 and the triplet states T_2 and T_3 is reported in Figure 9. Both curves show a very similar behavior, which is not surprising considering that both triplets share a very similar electronic character (note that the energy profiles, even though separated by about 0.2 eV, run almost parallel to each other). Since T_3 never crosses S_1 during the first 1ps of dynamics, ISC between these two states cannot occur. On the other hand, in the same time interval S_1 and T_2 intersect about 50 times; at each crossing point the computed SOC are small, but clearly measurable (between 0.1 and 2.5 cm^{-1}) giving rise to non-vanishing ISC probabilities.

Of particular interest is the comparison of the time evolution of the S_1 - T_2 SOC with that of a structural parameter such as the overall curvature of the flake, which is estimated by means of

Figure 8: *Nanoflake dynamics. Time evolution of the singlet S_1 , S_2 (black), and triplet T_2 , T_3 (red) excited state energies evaluated during 1 ps of dynamics. The energy differences with respect to the ground state are (excitation energies) shown. The inset reports the state energies for S_0 (ground state), S_1 and T_1 . The purple circles indicate the force state (i.e. the state that drives the dynamics in the TSH algorithm).*

the distance between two extreme points of the molecule (Figure 10). This quantity is inversely proportional to the curvature, since this end-to-end distance decreases as the curvature increases. Notice that since the structure always bends along the same axes, only the selected distance gives a correct estimate of the curvature (with oscillations between 12.5 Å and 14.5 Å). The other, orthogonal, end-to-end distance varies less during the dynamics, oscillating fast around its mean value. As in the case of CNTs, we observe a clear correlation between the magnitude of the SOC and the curvature of the sheet during the dynamics. As a consequence, we expect an increase of the ISC probability every time the structure bends into a bowl shape. These results show that the effect of the curvature on magnitude of SOC is not only valid for extended carbon nanostructures such as graphene sheets and carbon nanotubes, but also holds for finite-sized, low-symmetry molecules. We believe that this mechanism can play an important role in enhancing the ISC rates in carbon nanostructures used in organic photovoltaics, where the transition to triplet states can hamper electron-hole recombination at heterojunctions^{1,3}.

4.4.2 Estimation of the ISC rate

From the dynamics described in the previous section it is possible to derive a quantitative estimate of the ISC rate. As described in section 2.3, the probability for a singlet-to-triplet transition at

Figure 9: *Nanoflake dynamics. Time evolution of the SOC values between S_1 and T_2 (black curve) and S_1 and T_3 (red curve) evaluated during 1 ps of dynamics.*

a crossing point is given by the Landau-Zener formula in Eq. (16). In the most general case, the effective ISC rate calculation would require the average over an ensemble of trajectories. However, due to the relatively small values of SOC, we do not expect any appreciable transition within the affordable time scale (1 ps) and therefore a single trajectory can become representative of the dynamics of the ensemble, which will behave as an homogeneous trajectory bundle. The total probability P_{ISC} of an ISC to occur (at least once) in a given time interval T is given by

$$P_{\text{ISC}}(T) = 1 - \prod_0^T (1 - p_{\text{LZ}}(t)) , \quad (19)$$

where $p_{\text{LZ}}(t)$ is the Landau-Zener probability of a singlet-to-triplet ISC event at time t . Figure 11 (black curve) reports the time evolution of $P_{\text{ISC}}(T)$ in the time interval the $[0, 1 \text{ ps}]$. Notice that $P_{\text{ISC}}(T)$ undergoes two main “steps” at around 400 and 900 fs. These coincide with points along the trajectory where crossing occurs at relatively large values of the SOC matrix elements, i.e. for large values of the nanoflake curvature (Figure 10). Considering the $S_1 \rightarrow T_2$ transition as a first-order process, we fitted the curve $P_{\text{ISC}}(T)$ with an exponential function of the form $1 - e^{-k_{\text{ISC}}T}$, where k_{ISC} corresponds to the ISC rate constant, i.e. the inverse of the ISC lifetime τ_{ISC} . The fit (red line in Figure 11) performed using the least squares routine of SciPy library⁶⁸ gives an estimation for k_{ISC} of about $2.1 \times 10^{-6} \text{ fs}^{-1}$ with a standard deviation of $8.5 \times 10^{-8} \text{ fs}^{-1}$.

Figure 10: Nanoflake dynamics. Time evolution of the SOC values for states S_1 and T_2 (black curve) and of the distance between two hydrogen atoms at opposite extremes of the nanoflake (blue curve) as an estimate of the flake curvature. The insets show the structures of the nanoflake that correspond to the maxima and minima of the distance profile, with the dashed red lines representing this distance between the relevant hydrogen atoms.

A direct comparison with experiments is not possible. However, the study of a similar but larger graphene nanoflake by Mueller *et al.*¹ revealed that, even though the SOC values are in average small ($< 1 \text{ cm}^{-1}$), the measured phosphorescence rates are relatively fast with a rate constant in the order of the $1 \mu \text{ s}$. Interestingly enough, the authors explained this effect with an increase of the SOC values between singlet and triplet states induced by thermal structural distortions, which also favor singlet-triplet curve crossings. Our results confirm these predictions, highlighting the importance of the curvature of the nanoflake.

Another interesting compound that shares some similarities with our system is anthracene. This is a well studied carbon molecule composed of 3 benzene rings for which – as is the case of many smaller aromatic hydrocarbons – k_{ISC} is available from experiments. Unlike other aromatic hydrocarbons, which display mostly $S_1 \rightarrow T_1$ ISC, anthracene has $S_1 \rightarrow T_2$ ISC, just as in the case of the molecule of this study. This is an important factor that determines the relatively high ISC rate of anthracene; in fact, the small energy gap between S_1 and T_2 ⁶⁹ induces many surface crossings that enhance the rate. The k_{ISC} for anthracene is of $5.0 \times 10^8 \text{ s}^{-1}$, not far from what we estimated for the nanoflake ($2.1 \times 10^9 \text{ s}^{-1}$). The discrepancy can be attributed to the size difference of the two systems.

Figure 11: *Nanoflake dynamics. Time evolution of the total probability for ISC, $P_{\text{ISC}}(T)$, calculated according to the Eq. (19) (black curve) together with the mono-exponential fit (red curve).*

5 Conclusions

In this work, we applied the recently developed LR-TDDFT scheme for the calculation of SOC⁴⁸ to a series of carbon 0D (C_{60} and graphene nanoflakes), 1D (CNTs with different topologies), and 2D (graphene sheet) nanostructures. The results obtained for all investigated electronic properties including energy gaps, oscillator strengths, KS-orbital characters, and SOC are in very good agreement with available experimental data and TB calculations. In the case of CNTs, LR-TDDFT is able to reproduce the gap closure in metallic systems as well as the dependence on the topological indices (n, m) . Concerning the magnitude of the SOC, we observe vanishing small values at the K-points and a clear dependence on the CNT curvature, κ . However, differently from the TB predictions, the overall increase of the SOC values as a function of κ is strongly dependent on the topological nature of the CNT; in particular, we identified different linear coefficients (slopes) for metallic CNTs and two different classes of semiconducting CNTs characterized by values of $\text{mod}(n - m, 3)$ equal to 1 and 2, respectively. Finally, we observed that thermal distortions in CNTs produce a systematic decrease of the magnitude of the SOC by perturbing the optimal orbital overlap between σ and π electronic bands.

This finding also applies to other carbon nanostructures. In particular we investigated the dependence of the SOC values on the curvature for a prototypical 0D graphene nanoflake. Excited

state dynamics at room temperature reveals a clear correlation between the magnitude of the SOC and the flake curvature measured along one of the main molecular axis. This has a significant impact on the ISC rate; when a singlet state crosses a triplet state at a maximally curved geometry the Landau-Zener transition probability becomes large, contributing significantly to the overall transition rate. As a consequence, while the SOC in a flat graphene nanoflake is in general very small ($\sim 0.25 \text{ cm}^{-1}$), during the dynamics the ISC rate becomes appreciable ($\sim 2 \times 10^9 \text{ s}^{-1}$). This has important implications for applications in nanotechnology, as for instance in the realization of graphene based organic photovoltaic devices. In fact, large ISC rates allow for an efficient transfer of the photoexcited population into a triplet state, protecting the system from electron-hole back recombination and therefore favoring charge separation at the interface between the donor (the carbon nanoflake) and the acceptor (a polymer).

The proposed LR-TDDFT-based nonadiabatic dynamics scheme⁴⁹ has the necessary accuracy and computationally efficiency to become one of the most promising tools for the simulation of IC and ISC processes in medium to large carbon nanostructures, as well as other organic and inorganic chromophores in gas phase and in solution^{21–24,70,71}.

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