Zero-field-splitting in triplet-state nanotubes

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Abstract

Zero-field-splitting parameters D and E are evaluated for various excited triplet carbon nanotubes. For cylindrical ($C_{n\mathrm{v}}$) tube geometries only parameter D is nonzero. Parameter E is nonvanishing either for chiral tubes which lack $C_{n\mathrm{v}}$ symmetry, or for those excited states of achiral tubes, which loose $C_{n\mathrm{v}}$ symmetry due to Jahn-Teller distortion. The splitting is found to decrease with increasing tube length and tube diameter. The decay is fast and tends to zero if the excitation affects surface type states, while D approaches a nonzero limit if the open shell orbitals are of bulk character.

1. Introduction

Zero field splitting (ZFS) is an energy separation of nonrelativistically degenerate spin states in the absence of external magnetic field. For triplets, it can be described by two parameters D and E. The splitting of the original $M_{\mathrm{S}} = \pm 1$ levels is defined as $2E$, while D is the difference of the average of the former two and the energy of the $M_{\mathrm{S}} = 0$ state. The source of the phenomenon is relativistic in nature, it may arise from spin-orbit (SO) and spin-spin (SS) coupling.

Curvature enhanced SO-coupling in carbon nanotubes has been studied both theoretically [1] and experimentally [2]. The SS-coupling, which was reported to be important in planar hydrocarbons as well as heteroatomic conjugated systems [3] has not yet been considered for nanotubes.

In this Letter we present computed values of parameters D and E, originating from SS coupling. The dependence of ZFS parameters on length, diameter and chirality of various carbon nanotubes is investigated. As some of the excited tubes

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are Jahn-Teller (JT) active [4], the influence of the geometry distortion is also considered.

2. Theory

2.1. ZFS parameters

The formula for ZFS parameters D and E originating in SS coupling can be given in the laboratory principal axis coordinate system as [5, 6]

$$\begin{aligned} D &= \frac{3g^2\beta^2}{4hca_0^3}\langle {}^3\Psi| \sum_{i<j} \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}^5} |\, {}^3\Psi\rangle \\ E &= \frac{3g^2\beta^2}{4hca_0^3}\langle {}^3\Psi| \sum_{i<j} \frac{y_{ij}^2 - x_{ij}^2}{r_{ij}^5} |\, {}^3\Psi\rangle. \end{aligned} \tag{1}$$

Here ${}^3\Psi$ is the triplet wavefunction, indices i and j run over electrons, β is the Bohr-magneton, a_0 is the Bohr-radius, g is the giromagnetic coefficient, h is Planck's constant, and c is the velocity of light.

Based on Eq.(1) it is possible to predict whether D and E may be nonzero by invoking group theoretical considerations. For example, $D \neq 0$ only if $x^2 + y^2 - 2z^2$ corresponds to the total symmetric representation of the point group. Since the latter condition holds for tubes oriented along axis z, in general $D \neq 0$ for nanotubes. To have a nonzero parameter E, $y^2 - x^2$ should be the totally symmetric. It follows that E is always zero for tubes belonging to $C_{n\mathrm{v}}$ $(n > 2)$ point groups, as they exhibit cylindrical symmetry. It may happen, that an excited state of a tube originally possessing $C_{n\mathrm{v}}$ symmetry undergoes JT distortion. This usually leads to the loss of cylindrical symmetry, as JT distortion takes to $C_{2\mathrm{v}}$ or C_{s} [4]. In such a case both D and E parameters may be nonzero.

2.2. Theoretical Model

To obtain the triplet wavefunction we applied the semiempirical xHUGE (extended HUbbard model with GEometry optimization) model [7]. This method was successfully used previously to predict the magnitude of the ZFS parameters in thiophene oligomers [3] and fullerenes [7]. The theory is based on the bond length optimization procedure of Longuet-Higgins and Salem [8]. The xHUGE Hamiltonian contains first-neighbour π-electron interactions, an empirical σ-potential

plus on-site and first-neighbour electron repulsion terms [9]:

$$\begin{aligned}\hat{H} &= \sum_{\mu\neq\nu}^{\text{neighbours}} \beta_{\mu\nu}(r) \sum_{\sigma} a^{+}_{\mu\sigma} a_{\nu\sigma} + \sum_{i}^{\text{bonds}} f_i(r) \\ &+ \frac{1}{2} \sum_{\mu}^{\text{atoms}} \gamma_\mu(\hat{n}^2_\mu - \hat{n}_\mu) + \sum_{i}^{\text{bonds}} \gamma(r_i)(\hat{n}_\mu - Z_\mu)(\hat{n}_\nu - Z_\nu). \end{aligned} \quad (2)$$

In the above $\hat{n}_\mu = \sum_\sigma a^{+}_{\mu\sigma} a_{\mu\sigma}$ is the particle number operator, Z_μ is the core charge of atom μ (1 for carbon atoms), and σ refers to the spin. The on-site Hubbard type repulsion integral is denoted by γ_μ. There are three bond-length dependent parameters in the theory. In the first, Hückel-type term the resonance integrals $\beta(r)$ are expressed as $\beta_{\mu\nu}(r) = Ae^{-r/\zeta}$ [10]. In the fourth, first neighbour repulsion term $\gamma(r) = 1/\varepsilon r$, with an effective dielectric constant ε. Finally, the effect of the σ-core is described by $f(r)$. This is defined by requiring that Coulson's bond-order-bond-length relation $r_i = r_0 - \kappa P_i$ [11] is satisfied by an optimized set of bond lenghts r_i and bond orders $P_i = P_{\mu\nu} = \langle {}^3\Psi | \sum_\sigma a^{+}_{\mu\sigma} a_{\nu\sigma} | \, {}^3\Psi \rangle$, at the $\partial E/\partial r_i = 0$ minima of the potential energy surface (bond i being formed by atoms μ and ν). This defines the σ potential $f_i(r)$ [7] as

$$f_i(r) = \gamma(r)(P_i^2/2 - q_\mu q_\nu) + 2\beta(r)(\zeta/\kappa - P_i) + \frac{r_0 \log(r_i) - r_i}{\varepsilon\kappa^2},$$

where q is the atomic charge. Self-consistent solution of the xHUGE model consists of determining bond orders P_i and the corresponding bond lengths r_i by an iterative procedure. Having obtained the bond lengths, cartesian coordinates are calculated by simple molecular mechanics leading to the desired bond lengths, with bond and dihedral angles least-distorted from their standard values.

The parameters of the model are [7] $A = -179.7003$ eV, $\zeta = 0.326288$ Å, $r_0 = 1.54$ Å, $\kappa = 0.21$ Å, $\gamma_\mu = 3.536$ eV and $\varepsilon = 2.24$ (eVÅ)$^{-1}$.

The triplet wavefunction (for $M_S = 0$) is generated by considering all single excitations from the Hartree-Fock ground state $|0\rangle$:

$${}^3\Psi = \sum_{i}^{\text{occ}} \sum_{p}^{\text{virt}} C_{ap} \left(a^{+}_{p\alpha} a_{a\alpha} - a^{+}_{p\beta} a_{a\beta} \right) \, |0\rangle$$

(configuration interaction singles, CIS), with C_{ap} being the weight of the $a \rightarrow p$ excitation in the excited CIS wavefunction. To determine the CIS coefficients variationally, Davidson's direct CI [12] algorithm was used.

2.3. Spin density and spin localization

Spin density distribution on atoms can be used to assist the interpretation of ZFS parameters. The spin density on atom μ (ρ^S_μ) is defined as $\rho^S_\mu = P^\alpha_{\mu\mu} - P^\beta_{\mu\mu}$. For the $S_z = 1$ triplet state the atomic spin density takes the form:

$$\rho^S_\mu = \sum_{ab}^{occ} \sum_{p}^{virt} C_{ap} C_{bp} c_{a\mu} c_{b\mu} + \sum_{a}^{occ} \sum_{pq}^{virt} C_{ap} C_{aq} c_{p\mu} c_{q\mu}.$$

Here $c_{a\mu}$ is the μth coefficient of MO a.

The sum of atomic spin densities satisfy

$$\sum_\mu \rho^S_\mu = 2$$

for the $S_z = 1$ state, with $0 \leq \rho^S_\mu \leq 2$ for all μ. As a qualitative measure of spin localization, we define the quantity

$$\rho^{LOC} = \sum_\mu \left(\rho^S_\mu\right)^2. \tag{3}$$

The value of ρ^{LOC} is between 0 and 4. The fewer sites μ contribute to ρ^{LOC} the closer it gets to 4. Hence its deviation from the value 4 is a good measure of spin density localization. The value of ρ^{LOC} measures merely the extent of localization, and does not carry any information on which part of the tube the spin density is localized. In our studies, however, we have never observed localization except on tube ends (surface states).

3. Results

3.1. Surface states

Emergence of surface states – i.e. MOs localized at tube ends – is a peculiarity of finite size tubes, studied with open-end boundary conditions. In the present work, such states were observed e.g. for the (n,0) type tubes.

At the Hückel-level surface states of (n,0) tubes occur in degenerate pairs. When including electron-repulsion, the degeneracies split. The gap between the pair of surface states lying nearest to the Fermi level is 0.74 eV for the (6,0) tube, irrespective of the tube length. For short (n,0) tubes one electron transition between these two states gives rise to the lowest triplet state of the system. As

the tube is lenghtened, bulk states are increased in number their gap becoming gradually smaller and tending to zero in metallic tubes. As a consequence at some intermediate tube length, a crossing occurs between surface and bulk MOs both in the virtual and in the occupied spectrum. The crossing of MOs induces a crossing of triplet states, hence the lowest wavefunction of $S = 1$ quantum number is characterized by a transition between bulk MOs for long tubes. In case of the (6,0) tube the MO crossing occurs at 12 unit cells (UC), for the (10,0) tube it takes place at 4 UC.

If the tube possesses a σ_h mirror plane, surface states are necessary symmetry breaking at the Hubbard level, as they are nondegenerate and localized at opposite ends of the tube. There is no symmetry violation however if considering the triplet state characterized by a single particle transition between these MOs, since the wave function

$$^3\Psi = a^+_{2\uparrow}\, a^+_{1\uparrow}\, |\text{core}\rangle$$

is invariant (up to a phase) under the action of σ_h if $\sigma_h a^+_1 = a^+_2$ and $\sigma_h a^+_2 = a^+_1$.

Surface states may vary in the extent of localization, the extreme being represented by the pairs lying closest to the Fermi level for short (6,0) and (10,0) tubes. These are literally localized on the end atoms with MO coefficients $1/\sqrt{12}$ for the (6,0) tube and $1/\sqrt{20}$ for the (10,0) tube.

Elimination of surface states would be possible by using periodic boundary conditions. Putting caps on tube ends may also be a solution.

3.2. Symmetry considerations

When generating triplet wavefunctions from the Hartree-Fock determinant, electron excitation may affect degenerate levels. In such a case the tube undergoes a JT distortion and the original symmetry is lowered. Tubes of (n,0) type with n odd are JT active if we perform a HOMO-LUMO excitation, the stable structure belonging to point group $C_{\rm s}$ [4]. When determining distorted structures, degenerate levels were reduced to subgroup symmetries $A^{'}$ or $A^{''}$ by standard group theoretical techniques. The numerical effect of JT distortion on ZFS parameters is studied in detail in Section 3.4. In some cases JT distortion of excited states was ignored, in order to get a comparison with tubes unaffected by the JT effect. Geometries of such structures were optimized with constraints.

3.3. Dependence on tube length

Values of parameter D for (6,0), (10,0) and (6,6) tubes of different lengths are listed in Table 1. The calculations were done for geometries with cylindrical

symmetry thus $E = 0$ in each case. In zigzag (armchair) nanotubes 1 UC is a single zigzag (armchair) ring of carbon atoms.

When the lowest triplet state emerges by a transition between the HOMO and the LUMO localized on the terminal rings of the tube, the localization index becomes $\rho^{LOC} = \sum_{i=1}^{12}((1/\sqrt{12})^2 \cdot 2)^2 = 1/3$ for the (6,0) tube and $\rho^{LOC} = \sum_{i=1}^{20}((1/\sqrt{20})^2 \cdot 2)^2 = 1/5$ for (10,0) tube. Wherever these numbers show up in Table 1, they indicate that open shells are localized on terminal rings. For such a state – e.g. the lowest triplet state of the (6,0) tube – we observe a fast decay in parameter D with increasing tube length. This is the result of the weakening interaction between spins localized at tube ends.

Table 1: ZFS parameter D and localization indices ρ^{LOC} in triplet excited states of (6,0), (10,0) and (6,6) nanotubes. Tube lengths l are given in unit cells (UC). Parameters D are in $[cm^{-1}]$.

	(6,0)				(10,0)		(6,6)	
l	D_{surf}	ρ^{LOC}_{surf}	D_{bulk}	ρ^{LOC}_{bulk}	D	ρ^{LOC}	D	ρ^{LOC}
1	0.0359	0.333	-0.0121	0.333	0.0224	0.2	0.0121	0.166
2	-0.0384	0.333	-0.0361	0.194	-0.0221	0.2	0.0040	0.132
3	-0.0159	0.333	-0.0314	0.137	-0.0090	0.2	-0.0007	0.095
4	-0.0079	0.333	-0.0253	0.107	-0.0143	0.096	-0.0009	0.084
5	-0.0044	0.333	-0.0185	0.129	-0.0088	0.089	-0.0023	0.073
6	-0.0026	0.333	-0.0169	0.073	-0.0055	0.085	-0.0030	0.062
7	-0.0017	0.333	-0.0142	0.064	-0.0035	0.083	-0.0026	0.056
8	-0.0011	0.333	-0.0121	0.084	-0.0023	0.082	-0.0036	0.051
10	-0.0006	0.333	-0.0093	0.046	-0.0011	0.082	-0.0038	0.042
12	-0.0003	0.333	-0.0094	0.058	-0.0005	0.112	-0.0037	0.036

For the (10,0) tube open shells are localized on terminal rings only till 3 UC. However, for 4 UC or longer tubes ρ^{LOC} does not fall below 0.08. This indicates that open shells are still somewhat localized since a transition between completely delocalized (bulk) MOs would generate a localization index decaying as $1/(5l)$. The fast decaying parameter D of the (10,0) tube also indicates, that open shells tend to be localized around tube ends.

Returning to the (6,0) tube, its second triplet state is characterized by a localization index decaying in an oscillatory manner. In parallel with this, D param-

eters of this state are significantly larger than for the surface-type triplet of the same length. Open shell MOs still show some localized character which induces a slow decay of ZFS splitting with increasing tube length.

Tube (6,6) represents an example where the effect of MOs localized around tube ends are not observable. The localization index decays monotonically while parameter D seems to tend to a limit $D \approx -0.004$ cm^{-1}, in agreement with the bulk nature of this transition.

3.4. Effect of JT distortion

The effect of JT distortion is studied on the example of the (5,0) tube shown in Table 2. Both the HOMO and the LUMO are doubly degenerate and localized around tube ends, consequently the D parameter of the undistorted tube shows a monotonic decay for $l \geq 2$. When performing an optimization of the triplet state geometry, the final symmetry of the state may belong either to the A' or A'' irreducible representation of the point group C_s. Loss of cylindrical symmetry leads

Table 2: ZFS parameters of the first triplet excited states of symmetrical and JT distorted (5,0) nanotubes.

	Undistorted	Distorted			
	C_{5v}	C_s, A'		C_s, A''	
l[UC]	D[cm^{-1}]	D[cm^{-1}]	E [10^{-3} cm^{-1}]	D[cm^{-1}]	E [10^{-3} cm^{-1}]
1	-0.0008	0.0251	22.110	0.0570	61.829
2	-0.0560	-0.0496	3.7205	-0.0262	19.361
3	-0.0412	-0.0367	1.2629	-0.0240	8.7281
4	-0.0274	-0.0260	0.3049	-0.0201	4.8260
5	-0.0170	-0.0176	0.0003	-0.0159	2.6305
6	-0.0107	-0.0099	0.4375	-0.0078	1.0309
7	-0.0064	-0.0061	0.2522	-0.0049	0.2834
8	-0.0038	-0.0038	0.1216	-0.0033	0.1233
9	-0.0024	-0.0024	0.0559	-0.0021	0.0550
10	-0.0015	-0.0015	0.0255	-0.0014	0.0238

to nonzero E parameters in both cases observable in Table 2. The value of parameter E falls off rapidly with increasing tube length in accordance with a previous finding [4], that the JT effect induces smaller distortion in longer tubes. Regarding

parameter D, upon JT distortion we observe a decrease of the splitting due to distortion, but the effect falls off in parallel with the disappearance of parameter E. For long tubes D values converge to the results computed for undistorted tubes.

3.5. Dependence on tube diameter

Diameter dependence was monitored for (n,0)-type 5UC long tubes. The results are collected in Table 3. Tubes with odd n are JT active, those of even n are inactive species [4]. Considering these two types of tubes separately, one observes decreasing D values with increasing diameters in both cases, except for the (6,0) tube. The splittings described by D are significantly larger for n even, than for odd n's.

Table 3: Dependence of ZFS parameters on the diameter (d) of (n,0)-type 5UC long tubes. JT active tubes were reduced to the A' irreducible representation of the C_s subgroup. The Table also contains the ZFS parameters of the corresponding graphene ribbon, of width w.

	Tubes			Ribbons		
Tube index	d[Å]	D[cm^{-1}]	E[10^{-3} cm^{-1}]	w[Å]	D[cm^{-1}]	E[10^{-3} cm^{-1}]
(5,0)	3.9	-0.0176	0.0003	9.7	-0.0109	16.970
(6,0)	4.7	-0.0044	0.0	12.2	-0.0103	10.592
(7,0)	5.4	-0.0069	0.1514	14.7	-0.0068	3.6551
(8,0)	6.2	-0.0133	0.0	17.1	-0.0052	1.9242
(9,0)	7.0	-0.0041	0.0536	19.5	-0.0036	1.0091
(10,0)	7.8	-0.0090	0.0	21.9	-0.0084	7.4257
(11,0)	8.6	-0.0028	0.0676	24.4	-0.0068	5.0693
(12,0)	9.3	-0.0054	0.0	26.9	-0.0057	3.5552

In Table 3 ZFS parameters of the tubes are compared to the corresponding graphene ribbon. The latter was obtained by unwrapping the tube, producing rectangle shaped graphene sheet with height of 5 UC. The width of the ribbon is indicated in Table. Since tube curvature decreases with increasing diameter, ZFS parameters are expected to tend to the value of the corresponding ribbon. This phenomenon is indeed observed for parameter D. When comparing E values of tubes and ribbons we note that E is significantly larger for the ribbon since the planar geometry allows larger splitting than a JT distorted geometry. In the diameter range collected in Table 3 we do not observe any agreement between

E parameters of tubes and ribbons. This indicates that graphene-like behaviour builds up much slower for the splitting described by E than for those characterized by D.

3.6. Dependence on chirality

Chiral tubes lack C_n symmetry, thus their parameter E may be nonzero in principle. In Table 4 we show ZFS parameters of some chiral tubes. It is notable that E values of chiral tubes are smaller than those induced by JT distortion. Values for D fall into the same range for the tubes of same length collected in the table, while parameters E differ by orders of magnitude.

Table 4: Dependence of ZFS parameter on the chirality of the tubes. Here, $\tan\alpha = [(n-m)/\sqrt{3}(n+m)]$ is the tangent of the chirality angle. Tubes are 11 Å long.

Tube	d[Å]	$180\alpha/\pi$[deg]	D[cm^{-1}]	E [10^{-3}cm^{-1}]
(5,5)	6.7	0.0	-0.0052	0.0
(6,4)	6.8	6.6	-0.0092	1.0410
(7,3)	6.9	13.0	-0.0067	0.0530
(8,2)	7.1	19.1	-0.0057	0.0034
(9,1)	7.4	24.8	-0.0039	1.3924
(10,0)	7.8	30.0	-0.0090	0.0

4. Summary

Several short pieces of achiral and chiral carbon tubes was studied in their low-lying triplet states. Spin-spin coupling induced parameters D and E were calculated which characterize the splitting of the degenerate levels in the absence of an external magnetic field.

Parameter D is found to decrease with increasing tube length in all cases studied. There is a fast decay of D when lengthening the tube if surface states are partially filled in the triplet wavefunction. On the other hand, D tends to a nonzero limiting value if the open shell orbitals are of bulk character. Parameter E was calculated for tubes lacking cyclindrical symmetry, e.g. chiral tubes or Jahn-Teller distorted achiral tubes. There is a large difference between the magnitudes of E values for JT distorted tubes and chiral tubes, the former being larger. Diameter depence of the splitting is related to the splittings of the corresponding graphene

ribbon. Parameter D gets into close agreement with the value for the ribbon with increasing diameter, while parameter E follows a rather irregular pattern.

Acknowledgement

This work was supported by the Hungarian Research funds OTKA NI-67702, K-81588 and K-81590.

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