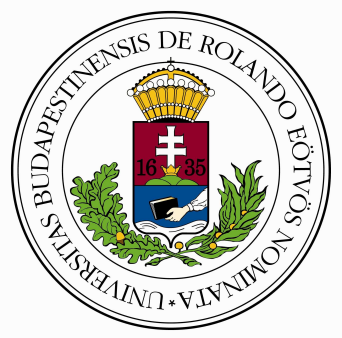
Splitting of degeneracies in carbon nanotubes

Thesis of Ph.D. dissertation

Péter Szakács

Supervisor: Prof. Péter Surján



Chemistry Doctoral School
Head of the School: Prof. György Inzelt
Theoretical and Physical Chemistry, Structural Chemistry Program
Head of the Program: Prof. Péter Surján

Eötvös Loránd University, Budapest
Institute of Chemistry,
Laboratory of Theoretical Chemistry
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Introduction

The dissertation is a summary of investigations of possible Jahn-Teller distortion in ionized and excited carbon nanotubes, as well as zero field splitting in triplet state tubes. Semiempirical quantum chemical models were used for this study.

In zigzag, armchair and some chiral tubes the tube axis is an axis of rotation, and there are mirror planes perpedicular to this axis, hence they correspond to the $C_{n\mathrm{v}}$ pointgroup (n being the chiralty index of the tube, in the case of chiral tubes the largest common division of the two tube indices). Having these pointgroups ($n > 2$) two dimensional irreducible representation, tubes hold two times degenerate molecular orbitals. When these levels are only partially occupied, the degeneracy splits, and the molecule distorts according to the Jahn-Teller theorem. The magnitude of distortion and its dependence on the properties of tubes was studied. The size of the distortion was characterized with the distortion energy and the bond-length-distortion parameter. The former is the difference of the energy of the distorted and the symmetrical ion, the latter is the rms-deviation of the distorted bond lengths from the symmetrical ones. For the calculations the semiempirical model of Longuett-Higgins and Salem was used, which is able to optimize bond lengths. I wrote all the necessary programs in FORTRAN language.

Zero field splitting (ZFS) originates from relativistic effects (spin-spin, and spin-orbit coupling). In such systems, where $S \geq \frac{1}{2}$ (S being the spin quantum number) the spin degeneracy maybe resolved even in the absence of external magnetic field. This phenomenon is known as zero field splitting. In the second part of the dissertation I present the values of the two parameters (D, E) describing the magnitude of ZFS, and their dependence on tube properties.

Jahn-Teller distortion in carbon nanotubes

1. Using only the group theory, one can answer three questions.

   (a) First I show in the example of the (8,0) tube one can decide to which of the subgroups of $C_{8\mathrm{v}}$ point group may the distorted ion belong to. In case when the tube distorts to the $C_{4\mathrm{v}}$ subgroup, rotation symmetry of $2\pi/8$, or $3 \cdot 2\pi/8$ radian and 4 pieces of mirror symmetry remain. The $C_{4\mathrm{v}}$ group possesses two dimensional irreducible representation, hence further distortion is possible. Distorting to $C_{2\mathrm{v}}$ group, the tube loses its fourfold rotational axis as well as two mirror planes. When the distorted ion corresponds to

the C_{S} point group, all the rotational symmetries vanish, only one mirror plane remains. However, when distortion happens to C_2 point group, only the rotation of 2π survives.

(b) Distorting the (8,0) nanotube to the $C_{4\mathrm{v}}$ subgroup, the degenerate molecular orbitals transforming according to E_1 or E_3 irreducible representation remain degenerate belongig to the E representation of the subgroup. The E_2 MOs split according to the $E_2 = B_1 \oplus B_2$ direct sum. In the $C_{2\mathrm{v}}$ subgroup all the degeneracies disappear in conformity with the $E_1 = E_3 = B_1 \oplus B_2$ and $E_2 = A_1 \oplus A_2$ equations. In C_2 pontgroup $E_1 = E_3 = 2B$ and $E_2 = 2A$; while in C_{S} the $E_1 = E_2 = E_3 = A' \oplus A''$ reductions show to which irreduclible represenations will the split MO belong.

(c) When an E_1 or an E_3 type MO pair of a (8,0) tube remains partially occupied, the distortion comes to pass along the normal mode transforming according to the E_2 irreducible representation. If the concerned MO pair corresponds to E_2 representation, the distortion may occur along both the B_1 or a B_2 vibrational mode.

2. I have deducted a method to calculate the energy and the bond lengths of the symmetrical ion locating the conical intersection on the LHS energy hypersurface. This method based on the process of Newton and Raphson applied to the LHS model. I have proved that the so-called "method of equally occupied degenerate MOs" is equivalent to the method based on the Newton-Raphon process, hence the former is exact – in LHS case – as well.

3. Due to the electron-hole symmetry of nanotubes, the distorted bond lengths and the total energy will be the same in cations and in ions having the same charges in absolute values.

4. The electronic structure of nanotubes correspond to the $C_{v\mathrm{v}}$ group near the Fermi level can be as follows:

   (a) The highest occupied molecular orbital (HOMO) and the next occupied MO are degenerate in zigzag tubes with odd n. Among these tubes instead of the ions of $4p$ charge (p is a natural number) – there is no partialy occupied degenerate MO – each ion is Jahn-Teller active.

   (b) Zigzag tubes with even index n possess nondegenerate HOMO. However, the MOs below the HOMO are degenerate. Hence, ionizing one or two electrons does not give rise to distortion. Three

or more times ionized species (instead of $2 + 4p$, p is a natural number) undergo distortion. The same spectra was found in the case of the chiral (12,4) nanotube.

(c) Of armchair type tubes the first degenerate occupied MO pair sinks when increasing the tube length. Therefore the criteria for charge causing Jahn-Teller distortion depends on the length of the tube.

5. The values of the parameters characterizing the distortion tends to zero increasing the tube length.

6. Ions where one of the degenerate MO is empty and the other is fully occupied are more stable than the ions contain unpaired electron, therefore the distortion is larger.

7. Ionization from a surface type degenerate MO causes faster decrease of distortion with tube length than an ionization from a delocalized (bulk) MO.

8. Of tubes having larger diameter (in case of same charge) undergo smaller distortion.

9. Application of symmetry adaptation results differing distorted bond lengths with similar energy (using LHS method).

10. Tubes having nondegenerate HOMO distort under the influance of HOMO $\longrightarrow$ LUMO + 1 excitation. Using LHS method the value of the distortion parameters is equal to the one times ionized tube ($l > 2$ UC). Tubes having degenerate HOMO undergo distortion under the influence of a HOMO $\longrightarrow$ LUMO excitation. The effect is larger than in the previous case, because here two partially occupied degenerate MO pairs exist.

11. Only 1 UC long neutral nanotubes have distorted geometry (alternating bond lengths), while longer neutral tubes remain undistorted.

Zero field splitting in triplet state carbon nanotubes

12. Appling π-electron models the spin-orbit contribution to ZFS is zero.

13. In tripet tubes corresponding to $C_{n\mathrm{v}}$ pointgroup ($n > 2$) the three fold spin degeneracy splits only to two parts, therefore one of the two parameters describing the energy differences of the split levels remain

zero. However, if these tubes undergo Jahn-Teller distortion, all three spin states become nondegenerate.

14. In zigzag tubes with even index n, the HOMO and the LUMO are extremely localized MOs having nonzero coefficients only at the two opposite ends of the tube. The longer the tube, the deeper these surface-type states lying, therefore the HOMO and LUMO became delocalized. In cases when the excitation happens from and to an extremely localized state, the ZFS tends to zero in longer tubes. When the excitation happens from and to a delocalized state, the ZFS is not zero even in longer tubes.

15. In Jahn-Teller distorted tubes the decreasing tendency of the distortion with tube length determines the magnitude of ZFS, too. The value of parameter D of distorted tubes tends to the value of undistorted ones in long tubes. Parameter E tends to zero as the distortion became less important.

16. ZFS parameters of zigzag tubes fall off with increasing diameter, if the Jahn-Teller active and inactive species are considered separately. The values of the parameter D tends to the value of the derived graphene ribbon increasing the tube diameter. The value of parameter D of armchair type tubes is smaller in tubes having larger diameter.

17. The values of the ZFS parameters do not change tendentiously against the chiral angle.

Publications supporting the thesis

1. Péter Szakács, Dorina Kocsis, Péter R. Surján: *Jahn-Teller distortion of ionized and excited carbon nanotubes*, J. Chem. Phys. **132**, 034309 (2010)

   was selected to:

   Virtual Journal of Nanoscale Science & Technology Vol **21**, Issue 5.

2. Péter Szakács, Péter R. Surján:
   Zero-field-splitting in triplet-state nanotubes, Chem. Phys. Lett. *(in press)*

List of further publications

1. Péter Szakács and Péter R. Surján: *Iterative solution of Bloch-type equations: Stability conditions, and Chaotic behavior*, J. Math. Chem. **43**, 314, (2008).

2. Péter Szakács and Péter R. Surján: *Stability condition for the Coupled Cluster Equations* Int. J. Quantum Chem. **108**, 2043, (2008).

3. Péter Szakács, Debashis Mukherjee, Sanghamitra Das and Péter R. Surján:
   Effective π-electron Hamiltonian for small-radii nanotubes: novel interpretation of curvature-induced conductivity, Phys. Rev. B **77**, 193407 (2008).

   was selected to:

   Virtual Journal of Nanoscale Science & Technology Vol **17**, Issue 22.

Posters

1. P. Szakács, S. Das, D. Mukherjee, P. R. Surján:
   Exact π-electron Hamiltonians for curved systems
   Central European Symposium on Theoretical Chemistry,
   Litschau, 2007.09.23-26.

2. P. Szakács, D. Kocsis, P. R. Surján:
   Jahn-Teller distorsion of ionized and excited carbon nanotubes
   Central European Symposium on Theoretical Chemistry,
   Hejnice, 2008.09.28 - 10.01.
   (*Díjazott poszter*)

3. P. Szakács, P. R. Surján:
   Zero-field splitting of excited carbon nanotubes
   Central European Symposium on Theoretical Chemistry,
   Dobogókő, 2009.09.25-28.

Talk

1. Péter Szakács; Péter R. Surján:
   Jahn-Teller distortion and zero field splitting in carbon nanotubes
   Central European Symposium on Theoretical Chemistry,
   Nový Smokovec, 2010.09.12-15.