This was a presentation at the first day, so I will change the title.

ICCMSE – September 28, 2009

Exciton Effects in Optical Absorption of Boron-Nitride Nanotubes

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Theoretical Investigation on Electronic Properties of Topological Materials: Moebius Nanographite and Conjugated Polymers

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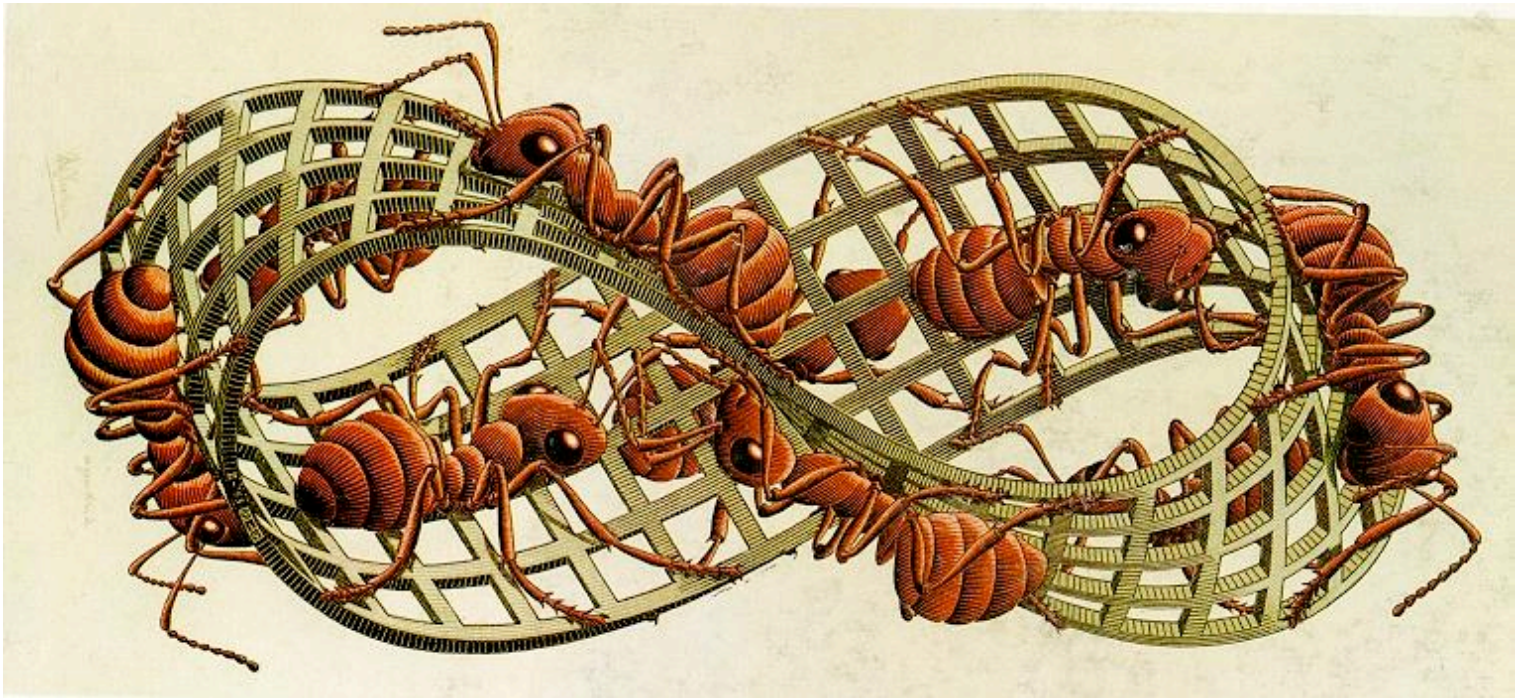
Outline

1. Electronic structure changes in Moebius boundary nanographite and conjugated polymers
2. Magnetic and optical properties: How the boundary conditions, periodic and Moebius, are effective?

Moebius strip

A Moebius strip is a twisted loop. This is the first one-sided surface discovered by A. F. Moebius (1790-1868).

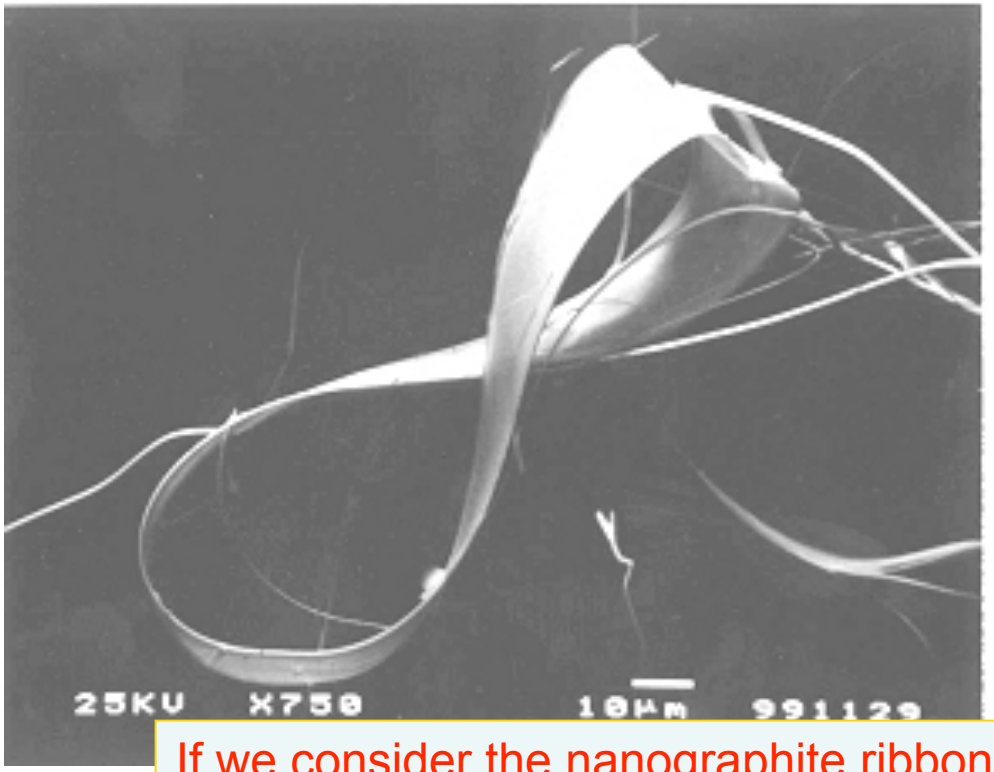


In this M.C.Escher's figure, all nine red ants crawl on same surface.

Material with Moebius Strip form now exists!

Recently the $NbSe_3$ Moebius strip has been synthesized by S. Tanda's Group.
S. Tanda et. al., Nature **417**, 397 (2002).

This intriguing topological material has initiated some theoretical researches in the mesoscopic physics.



(1) K. Yakubo, Y. Avishai, and D. Cohen, Phys. Rev. B **67**, 125319 (2003).

(2) M. Hayashi and H. Ebisawa, J. Phys. Soc. Jpn. **70**, 3495 (2002).

In these theoretical works, the square lattice geometry is used.

If we consider the nanographite ribbons with Moebius boundary condition, what will happen in their electronic and magnetic structures?

Moebius aromatic hydrocarbons have been synthesized!!

letters to nature

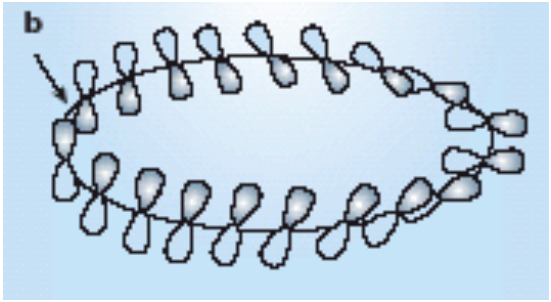
Synthesis of a Möbius aromatic hydrocarbon

D. Ajami[1], O. Oeckler[2], A. Simon[2] & R. Herges[1]

[1] *Institut für Organische Chemie, Universität Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany*
[2] *Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany*

Nature 426, 819 (2003)

Twisted π-electrons



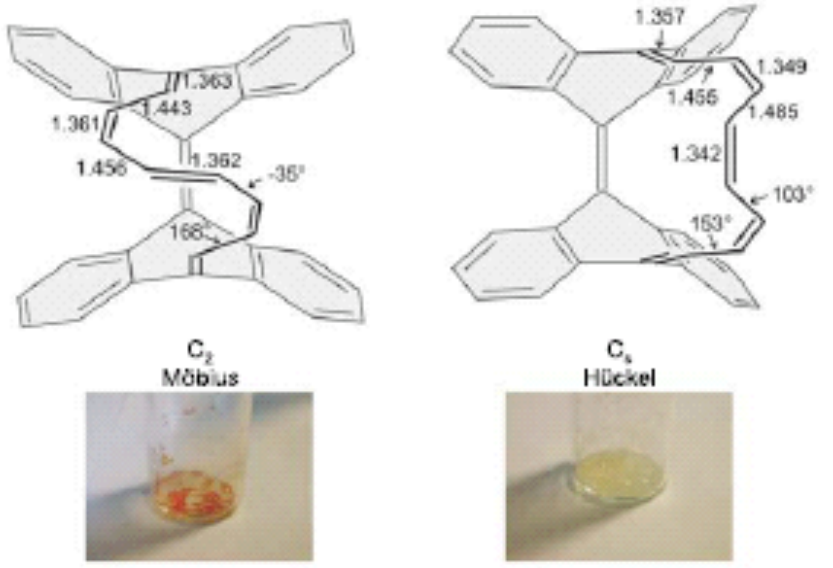
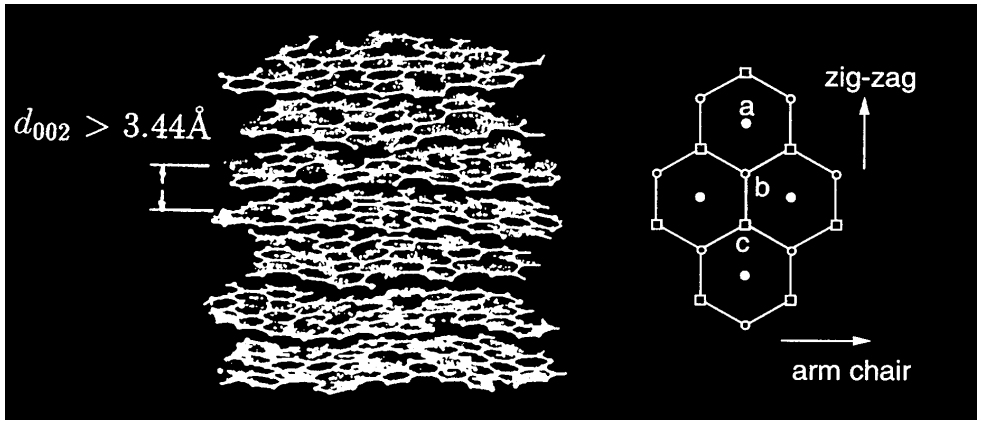


Figure 3 X-ray structures and photographs of the crystals of the C_2 Möbius and the C_s Hückel isomer. The structure plots are idealized for clarity (thermal ellipsoids are removed, and the bond orders are indicated by single and double lines). Structural parameters for the Hückel isomer are not reliable because of disorder (see text). Therefore the bond lengths (Å) and C=C–C=C dihedral angles for the polyene bridge shown in the figure are determined by DFT calculations (B3LYP/6-31G*). For the complete set of X-ray data and calculations, see Supplementary Information.

1st topic: Magnetism in Moebius nanographite ribbons

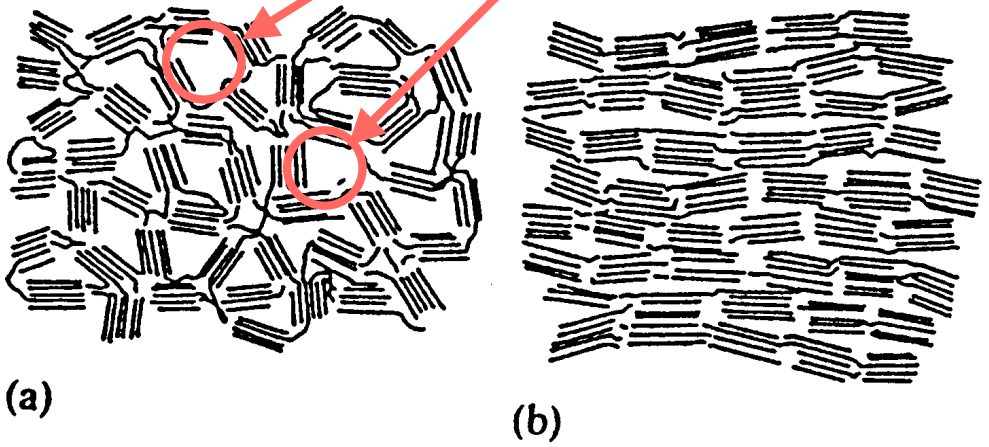
1. Discussion on topological materials: Moebius strips
2. Magnetic domain wall states
   vs.
   helical spin orders

Stacking of graphene planes

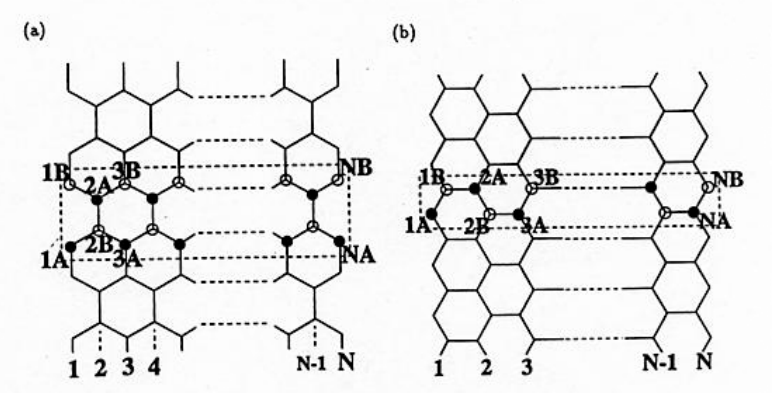


Activated carbon fibers (ACF)

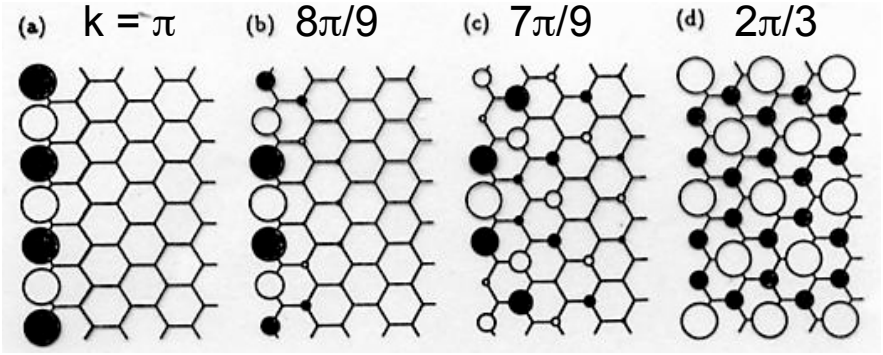
(a) high surface area with nanopore
(structural unites randomly arranged)
(b) a fiber after heat treatment



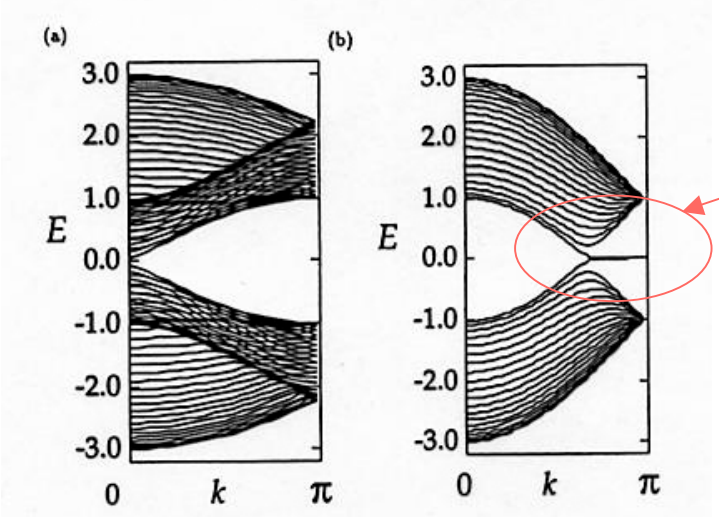
Localized states along zigzag edges



Armchair v.s. zigzag edges



Wave function amplitudes



Band structures of π-electrons

Edge states along zigzag edges

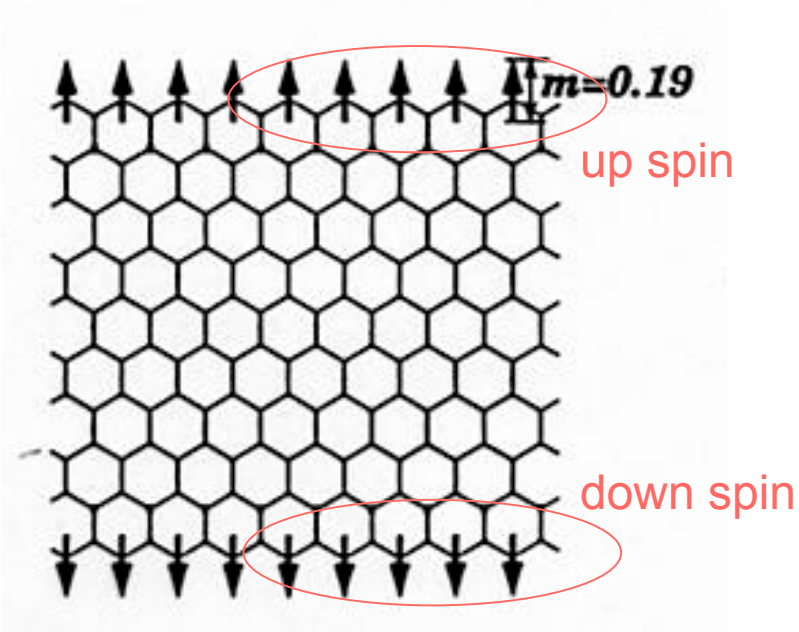
M. Fujita et al, J. Phys. Soc. Jpn. 65 1920 (1996); 66 1864 (1997).

K. Nakada et al, Phys. Rev. B 54 17954 (1996).

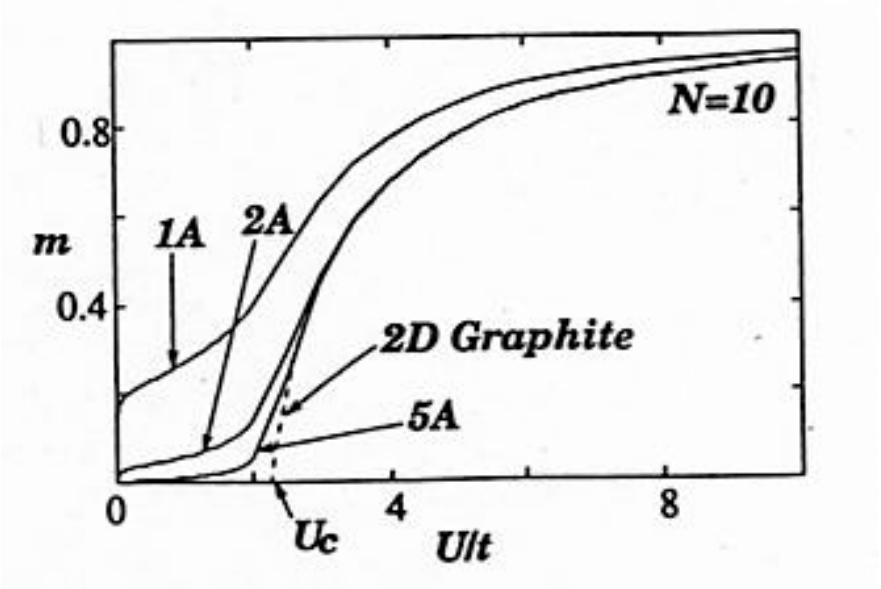
Magnetic moment along the zigzag edge by the Hubbard model

One dimensional Hubbard model for a graphene ribbon

the nearest neighbor hopping t, onsite repulsion U



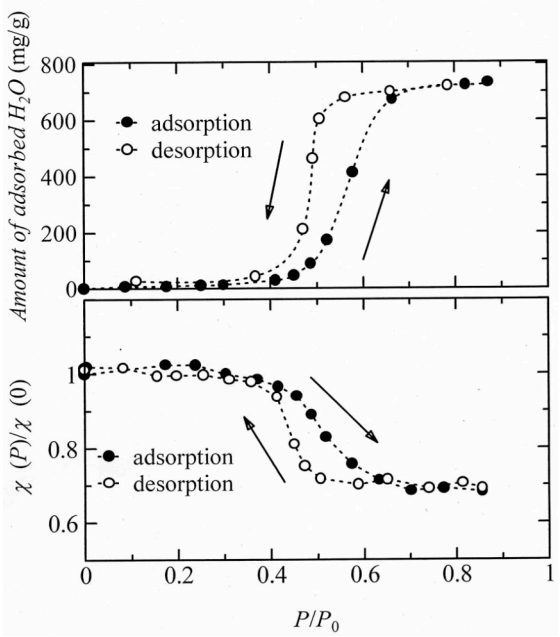
Spin alignment along the zigzag edges



Spin becomes larger as U increases

Adsorption of molecules and magnetic properties

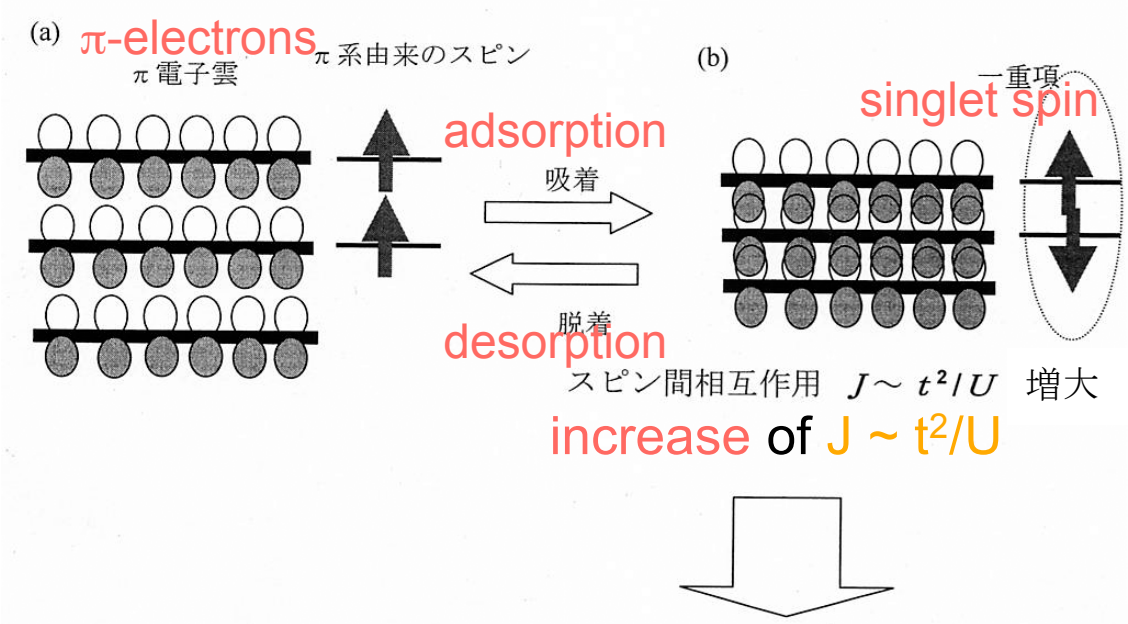
Experiments



Adsorption of H_2O molecules

→ decrease of χ

Interpretations



decrease of χ

N. Kawatsu, Master Thesis (2001); H. Sato et al, Solid State Commun. 125, 641 (2003).

Analysis by the cluster type model

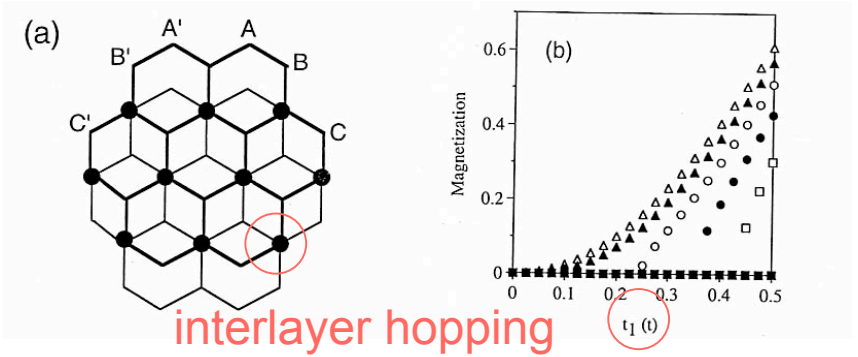
★ Closed shell electron case:

Increase of interactions → Increase of total magnetic moment

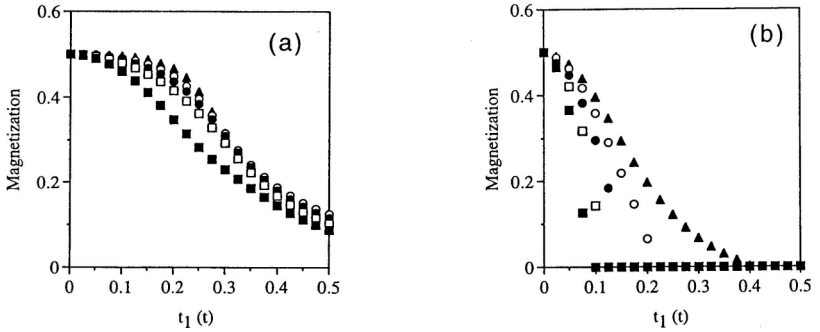
★ Open shell electron case:

Increase of interactions → Decrease of total magnetic moment

→ In agreement with experiments



interlayer hopping



K. Harigaya, J. Phys.: Condens. Matter 13, 1295 (2001);
K. Harigaya, Chem. Phys. Lett. 340, 123 (2001);
K. Harigaya and T. Enoki, Chem. Phys. Lett. 351, 128 (2002).

Citation by “Nature”

Magnetic carbon

Tatiana L. Makarova*†‡, Bertil Sundqvist†, Roland Höhne§, Pablo Esquinazi§, Yakov Kopelevich‖, Peter Scharff‡, Valerii A. Davydov¶, Ludmila S. Kashevarova¶ & Aleksandra V. Rakhmanina¶

The discovery of nanostructured forms of molecular carbon has led to renewed interest in the varied properties of this element. Both graphite and C_{60} can be electron-doped by alkali metals[1] to become superconducting; transition temperatures of up to 52 K have been attained by field-induced hole-doping of C_{60} (ref. 2). Recent experiments[3,4] and theoretical studies[5,6] have suggested that electronic instabilities in pure graphite may give rise to superconducting and ferromagnetic properties, even at room temperature. Here we report the serendipitous discovery of

6. Harigaya, K. The mechanism of magnetism in stacked nanographite: theoretical study. *J. Phys. Condens. Matter* **13**, 1295–1302 (2001).

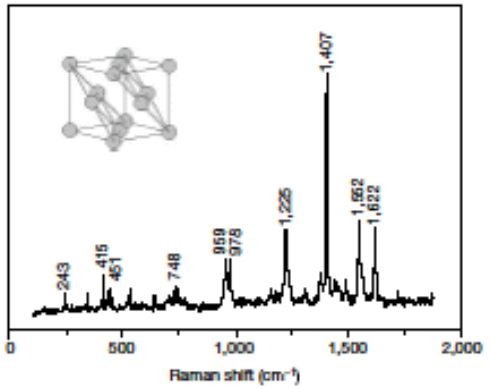


Figure 1 Raman spectrum of magnetically ordered rhombohedral C_{60} polymer (Rh-C_{60}). Inset, illustration of the relation between the structures of the pressure-induced polymer and the original cubic lattice of the pristine C_{60}.

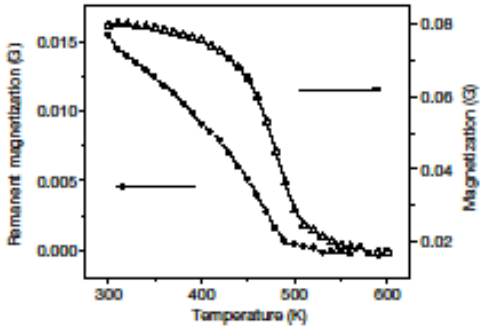
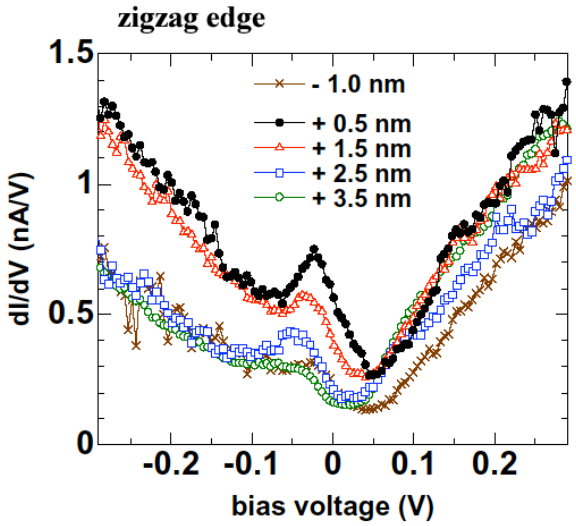


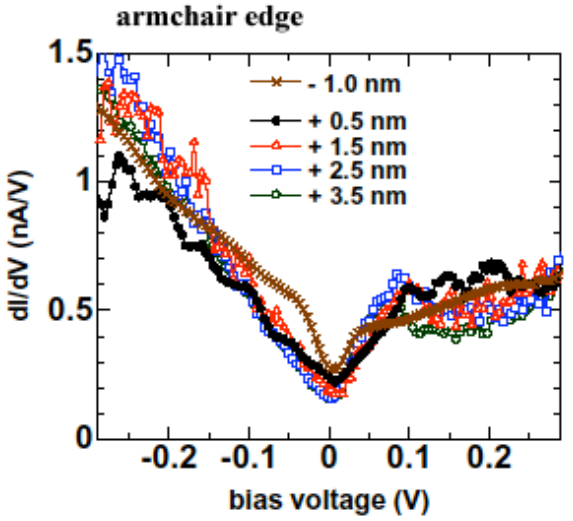
Figure 4 Magnetization of Rh-C_{60} in a fixed applied field of 0.2 T (upper curve, triangles) and the remanent magnetization obtained at $H = 0$ T (lower curve, circles) as a function of temperature. The Curie temperature is about 500 K.

Observation of edge states

- Recently, edge states have been observed by STS for zigzag edges by Prof. T. Enoki's group (Tokyo Inst. of Tech.) and by Prof. Fukuyama's group (Univ. Tokyo), almost simultaneously.
- There are not edge states for the armchair edges.
- Therefore, the nanographite model has become more realistic.

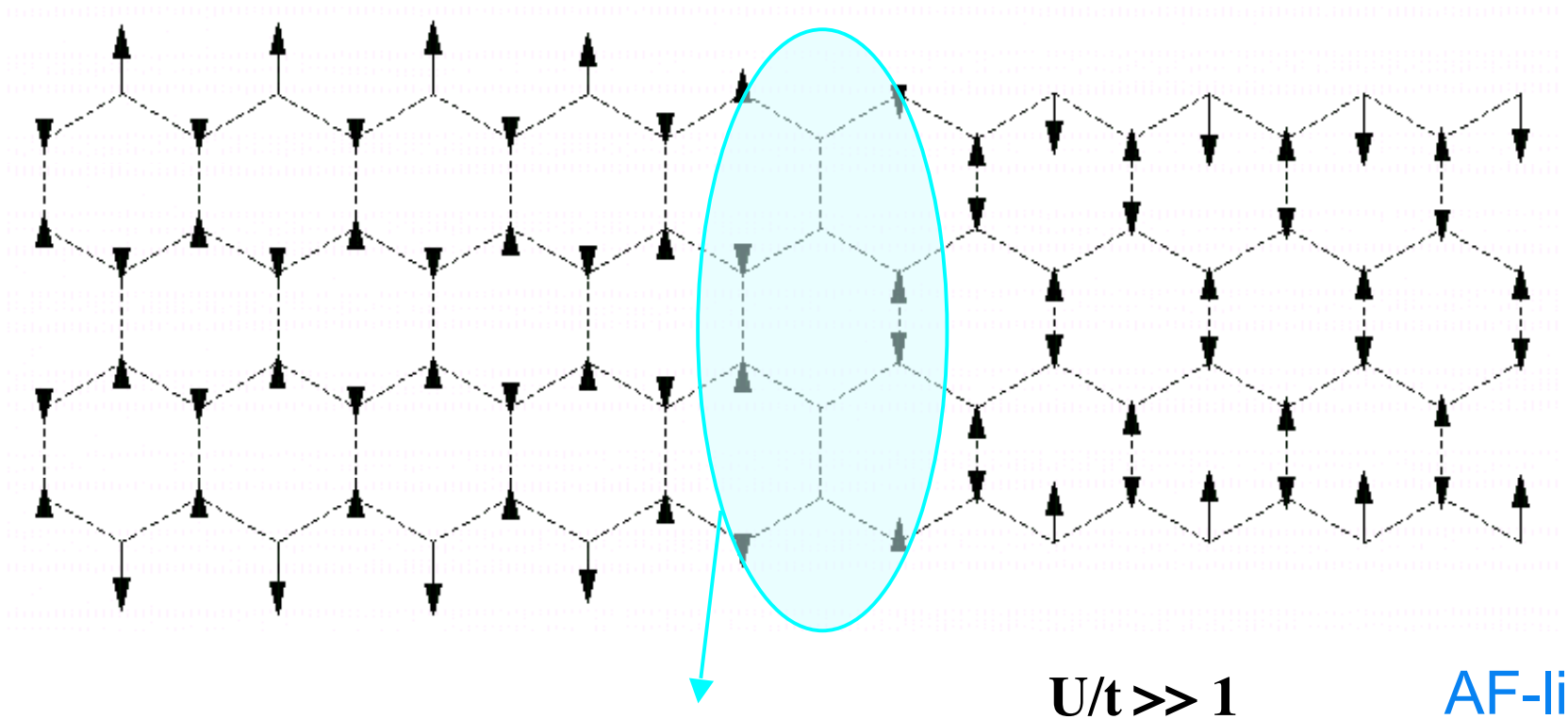
  Y. Niimi et al, Appl. Surface Sci. 241, 42 (2005).





Spin density distribution of magnetic solutions

Moebius ribbon: U=t, V=0; 4x20 carbon atoms

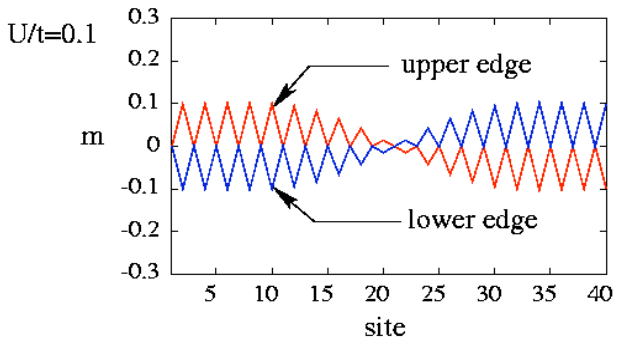


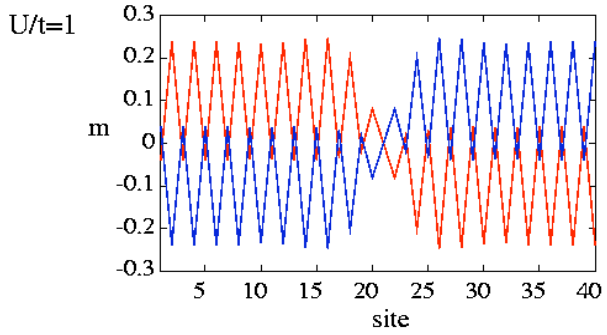
Magnetic domain wall → (U/t >> 1) AF-like domain wall

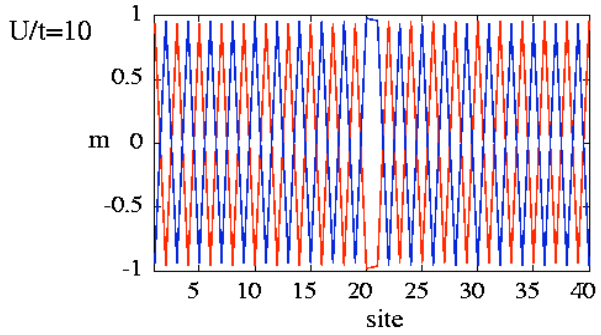
Mid-gap state in electronic structures

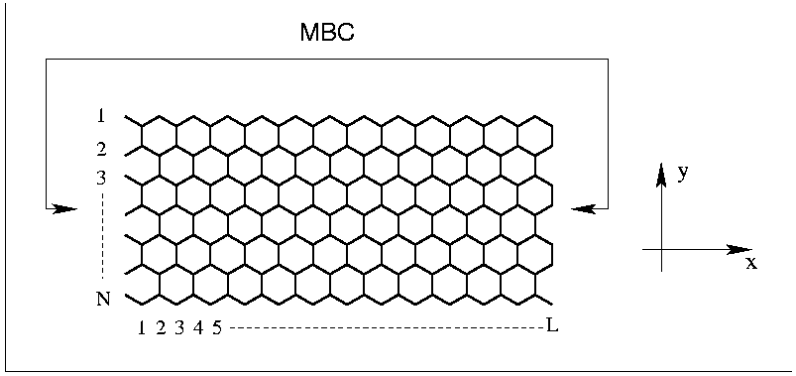
The magnetic domain wall

N=4, L=40





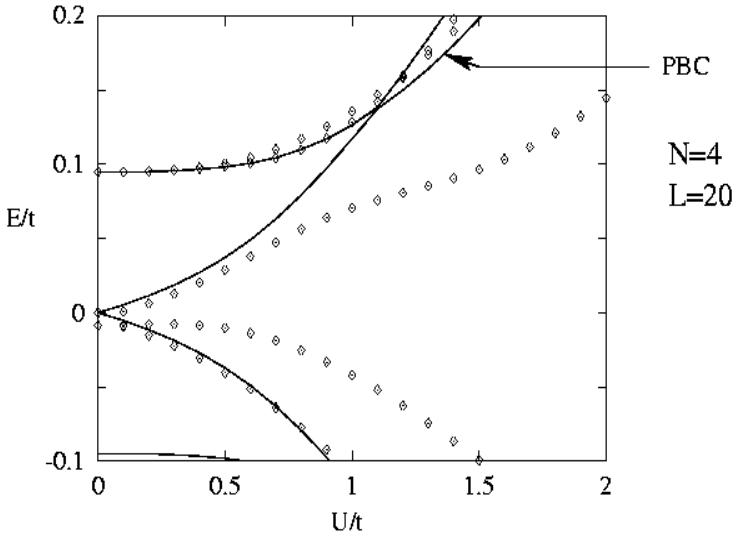




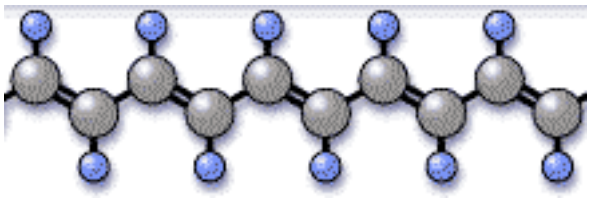
The width of the magnetic domain wall decreases with increasing the Coulomb interaction U/t.

K. Wakabayashi and K. Harigaya, J. Phys. Soc. Jpn. 72, 998 (2003).

U/t dependence of the energy spectrum (MBC)



trans-polyacetylene



Prof. Shirakawa

The soliton levels appear inside the Hubbard gap like in conjugated polymers e.g. polyacetylene.

Model and Method

Extended Hubbard model

$$H = \sum_{i,j,\sigma}^{n.n.} t_{i,j}\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma} + \sum_{i} U(\hat{n}^{\uparrow}_{i} - \frac{1}{2})(\hat{n}^{\downarrow}_{i} - \frac{1}{2}) + \sum_{i,j}^{n.n.} V(\hat{n}_{i} - 1)(\hat{n}_{j} - 1).$$

Mean Field Approx. with Spin Rotation

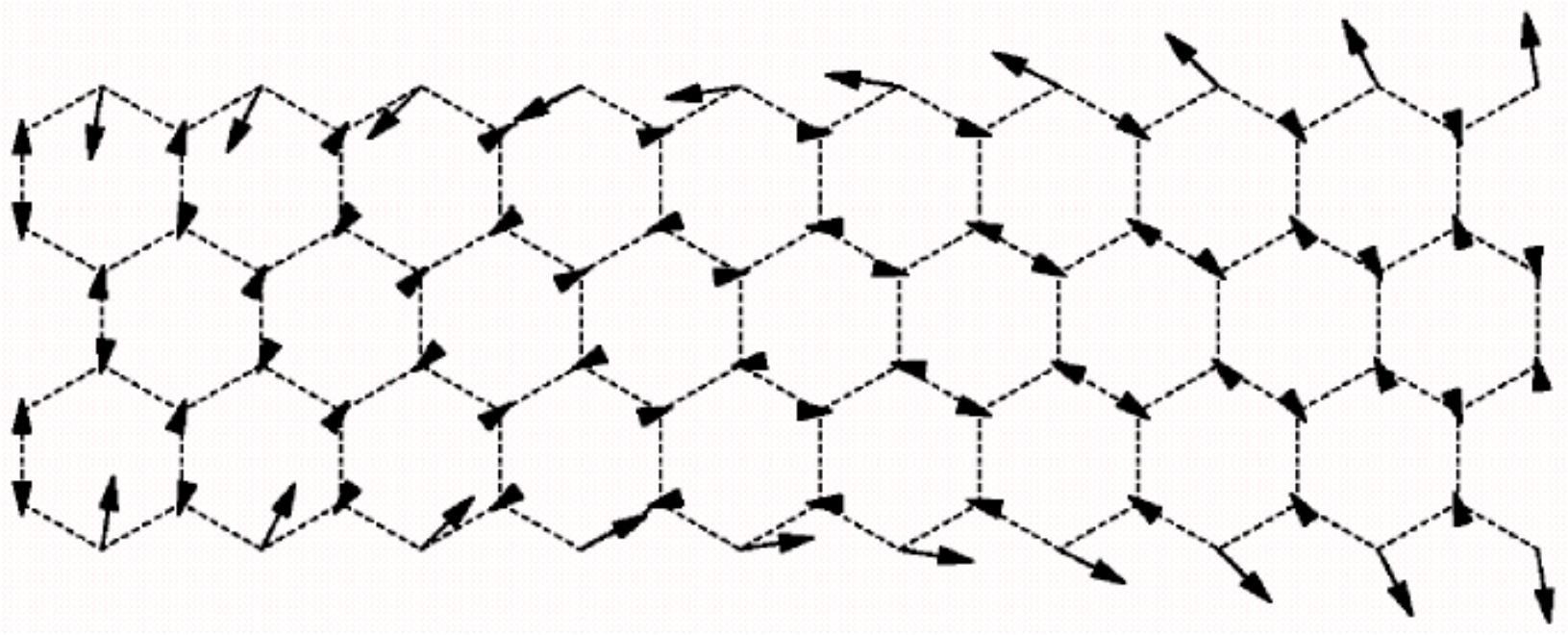
$$\hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\uparrow}\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\downarrow}$$

$$\rightarrow \langle\hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\uparrow}\rangle\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\downarrow} + \hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\uparrow}\langle\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\downarrow}\rangle - \langle\hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\uparrow}\rangle\langle\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\downarrow}\rangle$$

$$- (\langle\hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\downarrow}\rangle\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\uparrow} + \hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\downarrow}\langle\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\uparrow}\rangle - \langle\hat{c}^{\dagger}_{i,\uparrow}\hat{c}_{i,\downarrow}\rangle\langle\hat{c}^{\dagger}_{i,\downarrow}\hat{c}_{i,\uparrow}\rangle)$$

Spin density distribution of helical magnetic order

Moebius ribbon: U=t, V=0; 4x20 carbon atoms

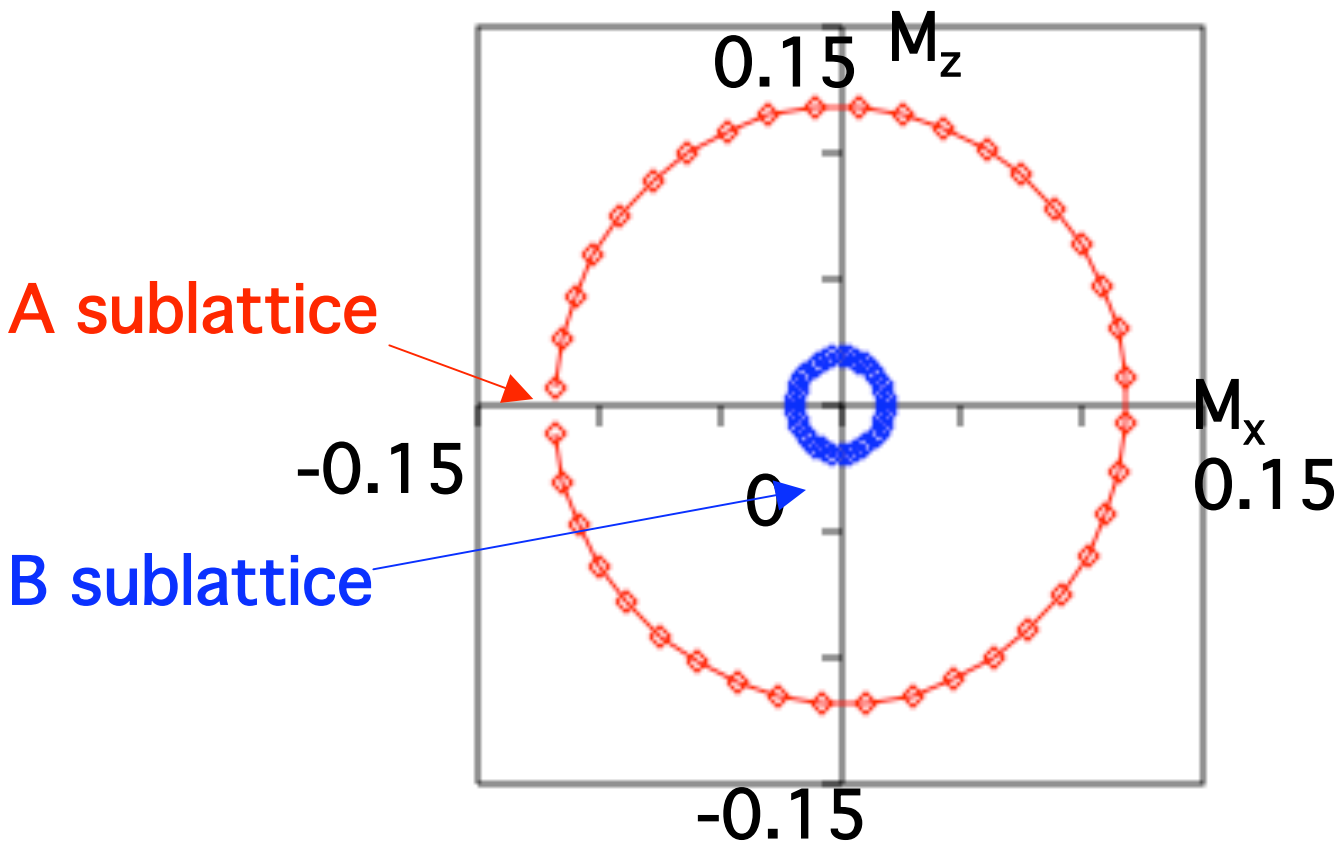


Ferrimagnetic ordering $\xrightarrow{U/t >> 1}$ **AF-like ferrimagnetic state**

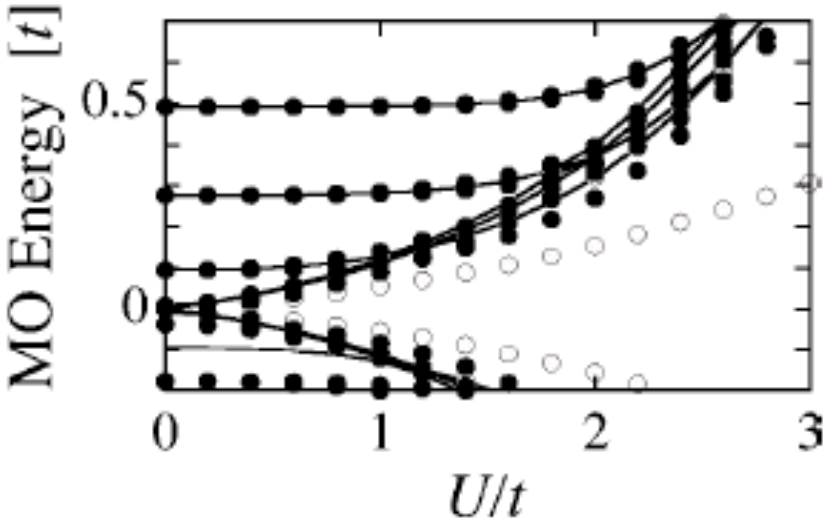
Localized state is not present in the energy gap.

Magnetic moment (M_x,M_z) at the edges

Moebius strip, 4x40 atoms, U/t=1, V/t=0



Energy spectra vs. *U/t*



Localized magnetic state

—

Magnetic domain wall state

○

Helical magnetic state

●

U opens the energy gap between the HOMOs and LUMOs in the localized magnetic and helical magnetic state,

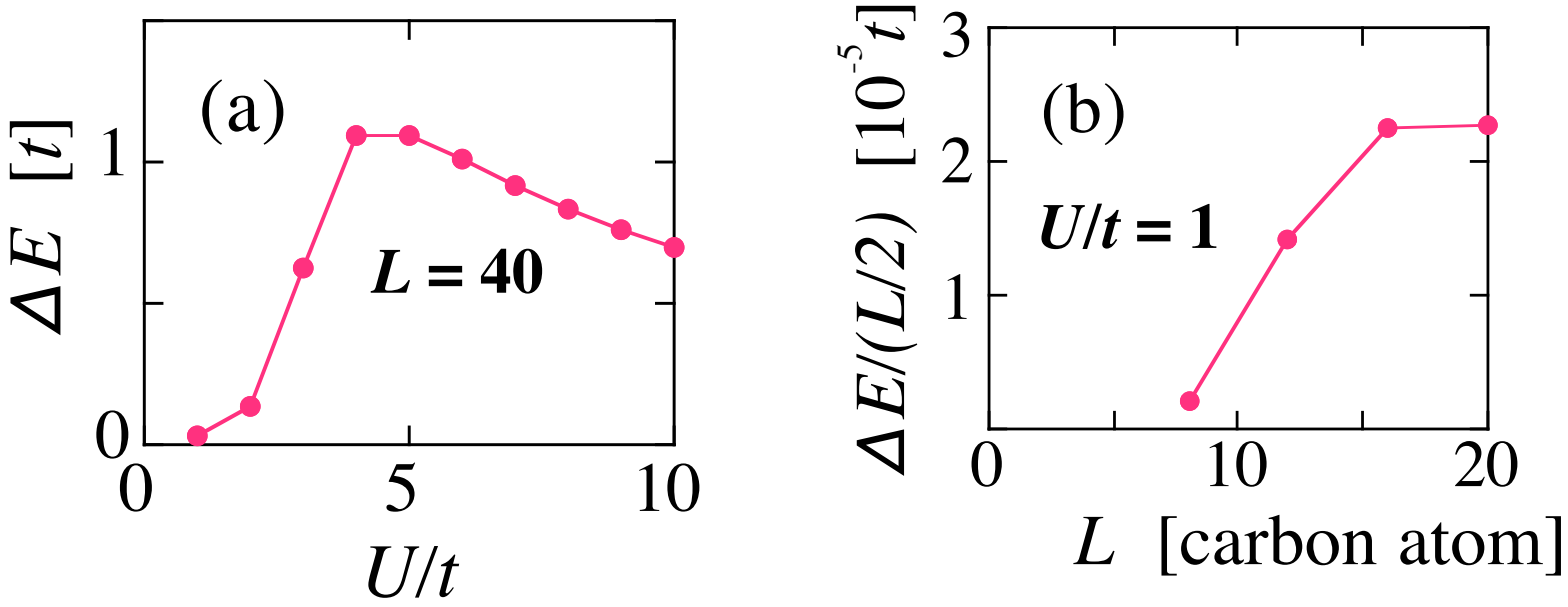
while mid-gap levels appear in the magnetic domain wall state.

Comparison of the total energy

Moebius strip, 4xL (L=40,20,16,12,8) carbon atoms
Hubbard model with $0 < U/t < 10$

Lower energy for helical magnetic orders

ΔE= (total energy of magnetic domain wall)
- (total energy of helical magnetic state)



L : Length of strip

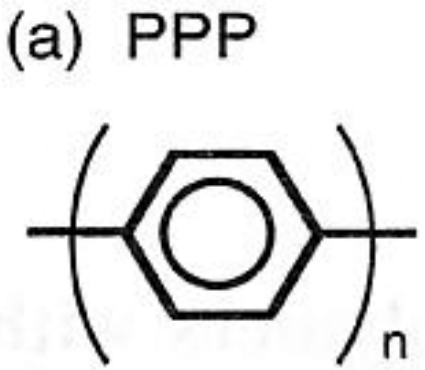
2nd topic: Optical excitations in Moebius conjugated polymers

1. How effects of the unique Moebius geometries are observed in optical experiments?
2. Two types of Moebius boundaries: uniform ring torsions vs. localized twists

Model for poly(*para*-phenylene)

PPP: poly(*para*-phenylene)

tight binding model with long range interaction



$$H = H_{\mathrm{pol}} + H_{\mathrm{int}}$$

$$H_{\mathrm{pol}} = \sum_{i,\sigma} E_i c_{i,\sigma}^{\dagger} c_{i,\sigma} - \sum_{\langle i,j\rangle,\sigma} (t_{i,j} - \alpha y_{i,j})(c_{i,\sigma}^{\dagger} c_{j,\sigma} + \mathrm{HC}) + \frac{K}{2} \sum_{\langle i,j\rangle} y_{i,j}^2$$

$$H_{\mathrm{int}} = U \sum_i \left(c_{i,\uparrow}^{\dagger} c_{i,\uparrow} - \frac{n_{\mathrm{el}}}{2}\right)\left(c_{i,\downarrow}^{\dagger} c_{i,\downarrow} - \frac{n_{\mathrm{el}}}{2}\right) + \sum_{i,j} W(r_{i,j})\left(\sum_{\sigma} c_{i,\sigma}^{\dagger} c_{i,\sigma} - n_{\mathrm{el}}\right)\left(\sum_{\tau} c_{j,\tau}^{\dagger} c_{j,\tau} - n_{\mathrm{el}}\right).$$

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/aV)^2}}$$

Ohno potential
U: onsite repulsion
V: long range int.

κ-th optical excitation
determined by the single-CI method

$$|\kappa\rangle = \sum_{(\mu,\lambda)} D_{\kappa,(\mu,\lambda)} |\mu, \lambda\rangle.$$

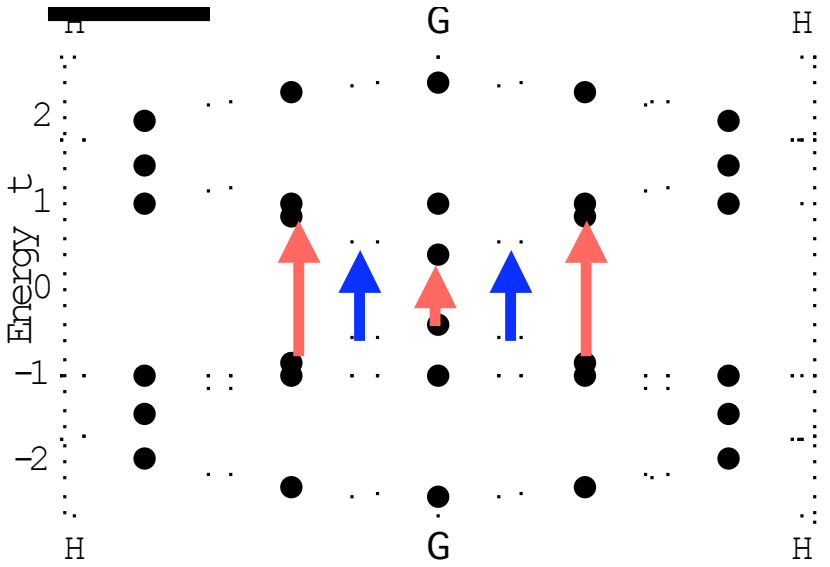
electron-hole excitation from
the Hartree-Fock ground state

$$|\mu, \lambda\rangle = \frac{1}{\sqrt{2}}(c_{\mu,\uparrow}^{\dagger} c_{\lambda,\uparrow} - c_{\mu,\downarrow}^{\dagger} c_{\lambda,\downarrow})|g\rangle$$

Electronic bands in oligomers

Electronic bands for the number of phenyls: N=5

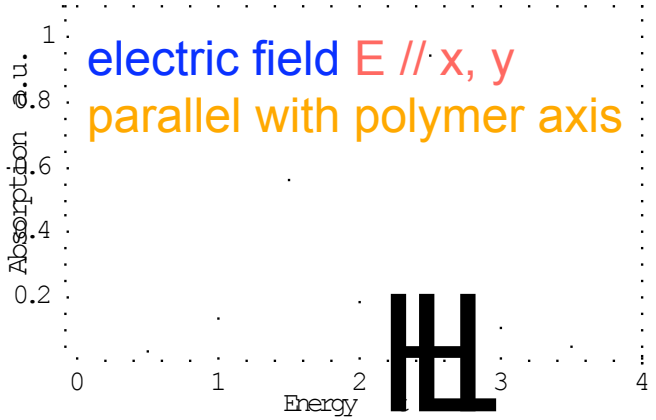
- ● Periodic boundary
- ○ Moebius boundary
- ↑↑ Optical excitations

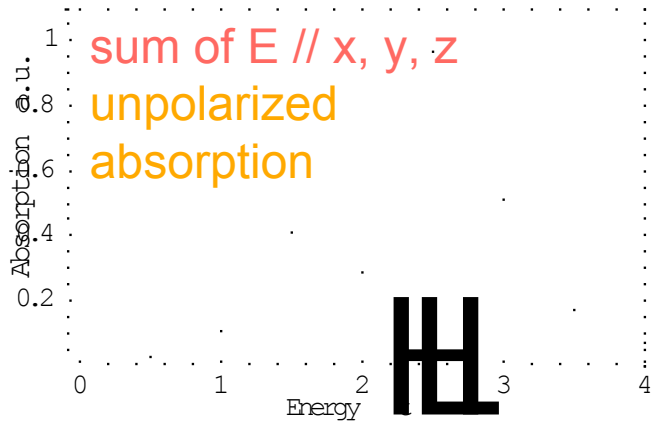


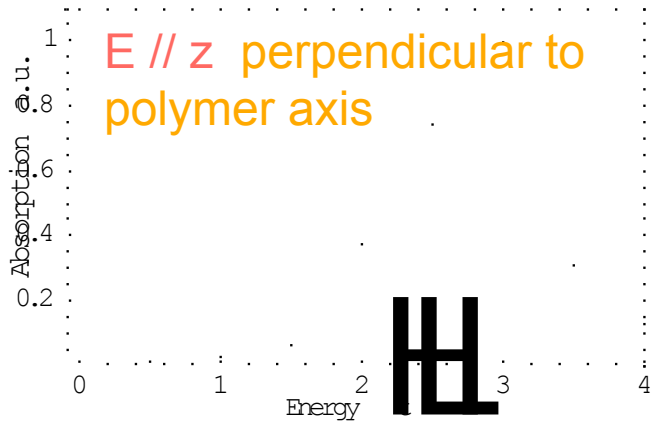
Energy difference of the optical excitations is found between two boundary conditions. This could be observed for oligomers due to the sparse population in the wavenumber space.

Optical absorption of poly(*para*-phenylene): periodic case

Ring torsion angle: Φ=0°
N=20: number of phenyl rings
U=2.5t, V=1.3t: Coulomb interactions reported in K. Harigaya, J. Phys.: Condens. Matter 10, 7679 (1998).

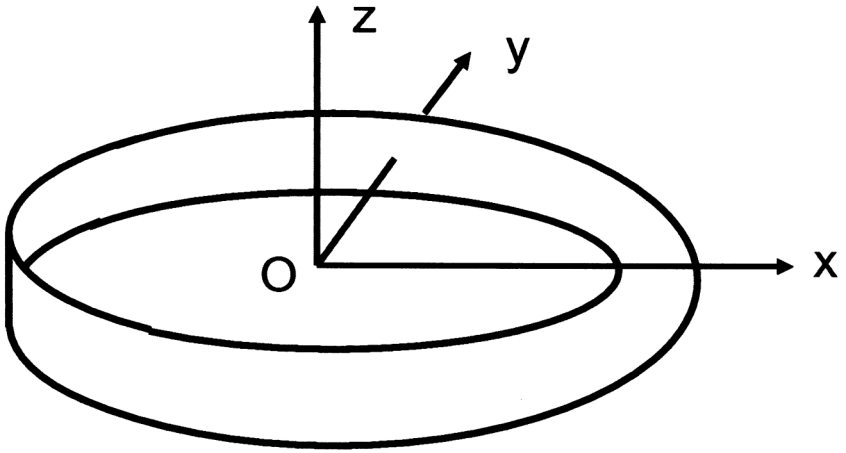


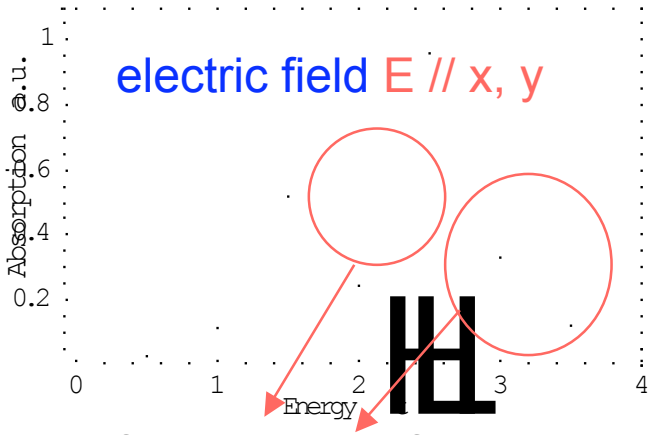




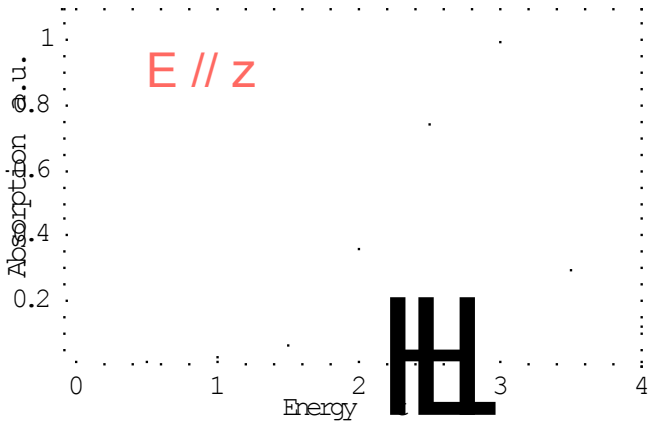
Optical absorption of poly(*para*-phenylene): Moebius case 1

Ring torsion angle: Φ=180°/N
uniform for all over the system
(N=20: number of phenyl rings)



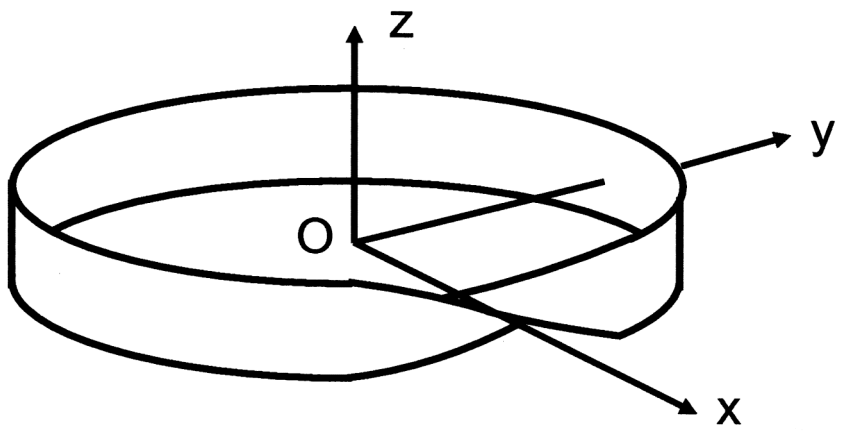


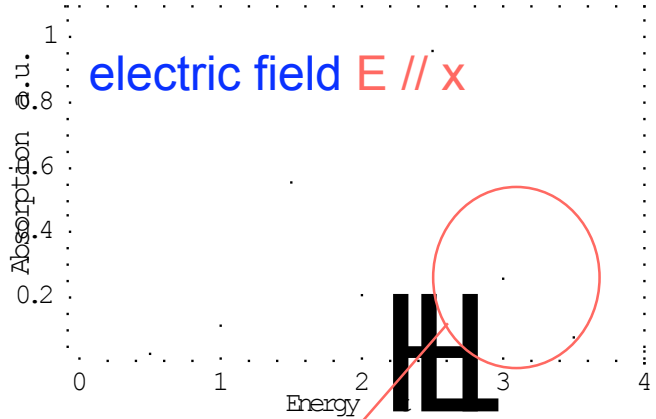
Mixing of absorption of E//z component of the periodic boundary case



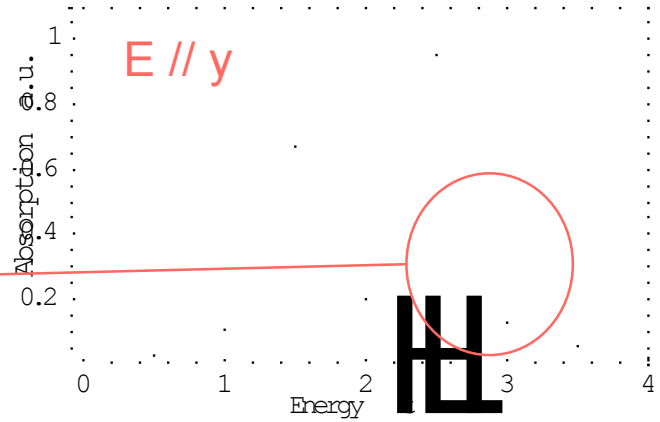
Optical absorption of poly(*para*-phenylene): Moebius case 2

Ring torsion angle: Φ=30°
localized for five phenyl rings
(N=20: total number of phenyls)



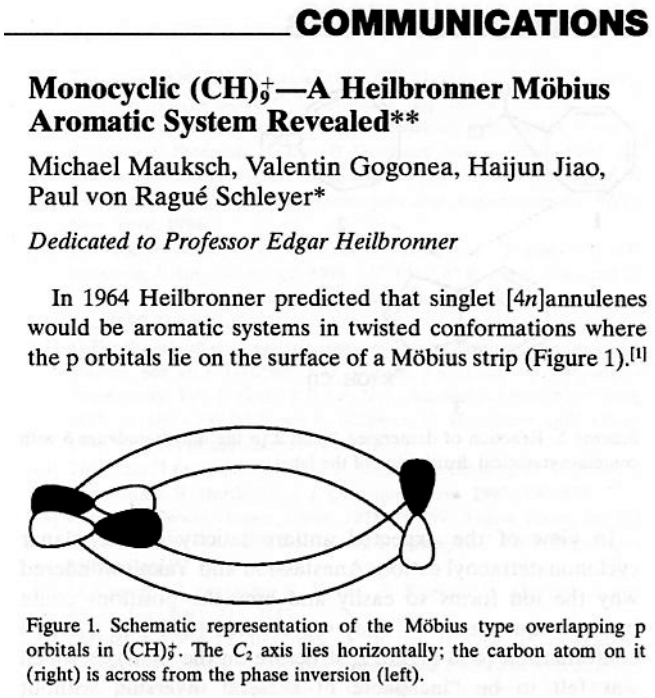


Mixing of absorption of E//z component of the periodic boundary case



Smaller mixing of E//z component because of the localized torsions

Moebius molecules and oligomers



COMMUNICATIONS

Monocyclic $(CH)_9^+$—A Heilbronner Möbius Aromatic System Revealed**

Michael Mauksch, Valentin Gogonea, Haijun Jiao, Paul von Ragué Schleyer*

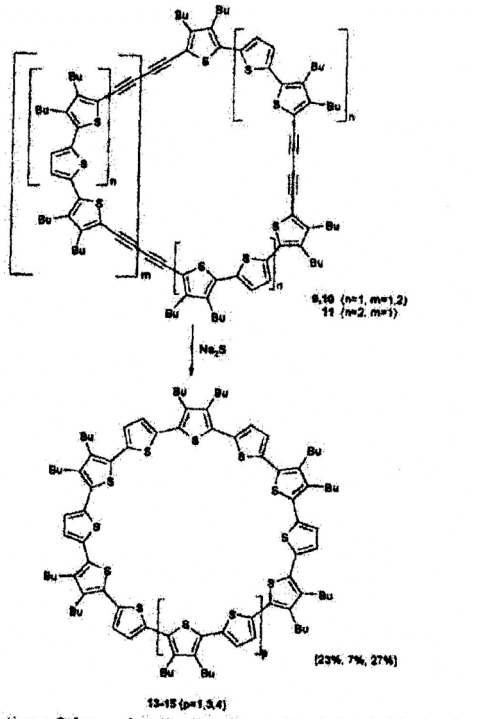
Dedicated to Professor Edgar Heilbronner

In 1964 Heilbronner predicted that singlet [4*n*]annulenes would be aromatic systems in twisted conformations where the p orbitals lie on the surface of a Möbius strip (Figure 1).[1]

Figure 1. Schematic representation of the Möbius type overlapping p orbitals in $(CH)_9^+$. The C_2 axis lies horizontally; the carbon atom on it (right) is across from the phase inversion (left).

Moebius annulene

M. Mauksch et al, Angew. Chem. Int. Ed. 37, 2395 (1998).

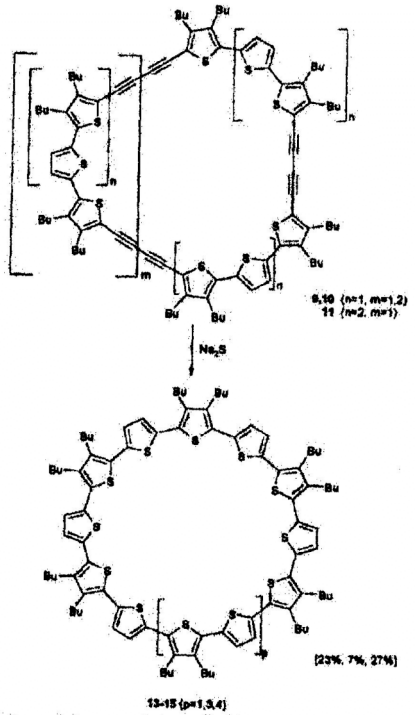


Scheme 3: Reaction of the cyclo(oligothiophene-diacetylene) **9-11** to the fully α-conjugated cyclo[n]thiophenes **13-15**.

Polythiophene oligomers: Synthesis with Moebius boundary?

G. Fuhrmann et al, Synth. Met. 119, 125 (2001).

Moebius conjugated polymers?



Scheme 3: Reaction of the cyclo(oligothiophene-diacetylene) 9-11 to the fully α-conjugated cyclo[n]thiophenes 13-15.

Possibly, by manipulating monomers by STM, Moebius polymers could be synthesized.

Ring torsions could be fixed by bridging nearby aromatic rings.

Polythiophene oligomers:
G. Fuhrmann et al, Synth. Met. 119, 125 (2001).

2nd topic: NLO in Moebius polymers

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Cited in “Nature Asia Materials”

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featured highlight

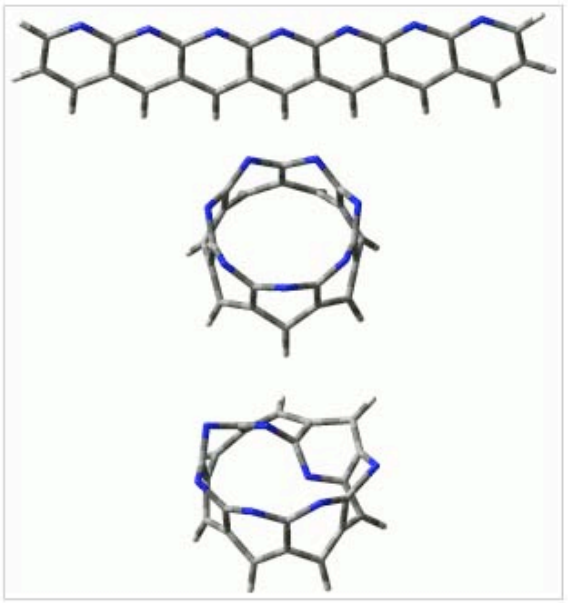
Twisted molecules lock down electrons

Published online 30 April 2008

Researchers from China and Japan have studied how the twist in a molecule can affect the way its electrons are positioned; a fundamental factor in understanding how molecules interact with light.

Zhi-Ru Li and colleagues from Jilin University in China, along with Kikuo Harigaya of AIST, Tsukuba and Feng Long Gu of Kyushu University, Fukuoka, Japan created a computer simulation of a molecule shaped like a Möbius strip—a loop with a twist that has only one, continuous face. Chemists have already created various molecular analogues to this mathematical figure that have unusual electronic and optical properties[1].

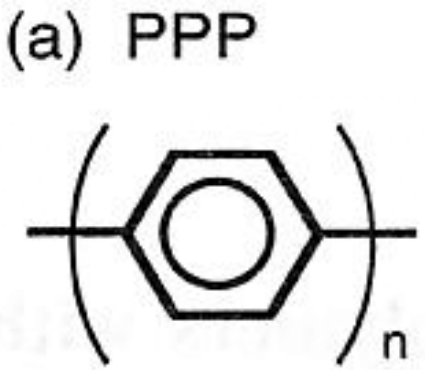
The scientists calculated how clouds of electrons are spread around these twisted molecules, known as cyclacenes, and compared their results with simple



Model for poly(*para*-phenylene)

PPP: poly(*para*-phenylene)

tight binding model with long range interaction



$$H = H_{\mathrm{pol}} + H_{\mathrm{int}}$$

$$H_{\mathrm{pol}} = \sum_{i,\sigma} E_i c_{i,\sigma}^{\dagger} c_{i,\sigma} - \sum_{\langle i,j\rangle,\sigma} (t_{i,j} - \alpha y_{i,j})(c_{i,\sigma}^{\dagger} c_{j,\sigma} + \mathrm{HC}) + \frac{K}{2} \sum_{\langle i,j\rangle} y_{i,j}^2$$

$$H_{\mathrm{int}} = U \sum_i \left(c_{i,\uparrow}^{\dagger} c_{i,\uparrow} - \frac{n_{\mathrm{el}}}{2}\right)\left(c_{i,\downarrow}^{\dagger} c_{i,\downarrow} - \frac{n_{\mathrm{el}}}{2}\right) + \sum_{i,j} W(r_{i,j})\left(\sum_{\sigma} c_{i,\sigma}^{\dagger} c_{i,\sigma} - n_{\mathrm{el}}\right)\left(\sum_{\tau} c_{j,\tau}^{\dagger} c_{j,\tau} - n_{\mathrm{el}}\right).$$

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/aV)^2}}$$

Ohno potential
U: onsite repulsion
V: long range int.

κ-th optical excitation
determined by the single-CI method

$$|\kappa\rangle = \sum_{(\mu,\lambda)} D_{\kappa,(\mu,\lambda)} |\mu, \lambda\rangle.$$

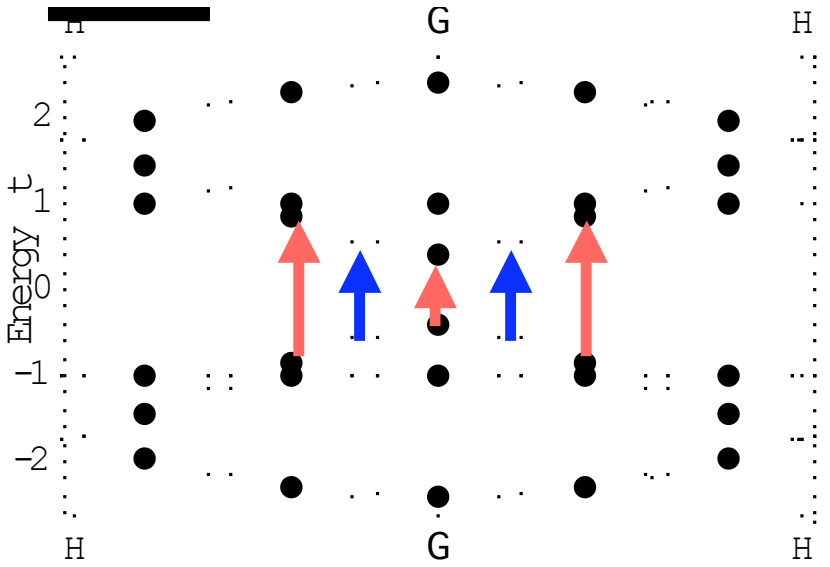
electron-hole excitation from
the Hartree-Fock ground state

$$|\mu, \lambda\rangle = \frac{1}{\sqrt{2}}(c_{\mu,\uparrow}^{\dagger} c_{\lambda,\uparrow} - c_{\mu,\downarrow}^{\dagger} c_{\lambda,\downarrow})|g\rangle$$

Electronic bands in oligomers

Electronic bands for the number of phenyls: N=5

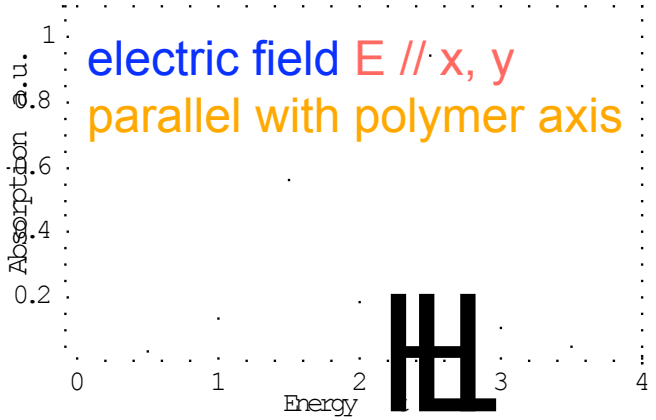
- ● Periodic boundary
- ○ Moebius boundary
- ↑↑ Optical excitations

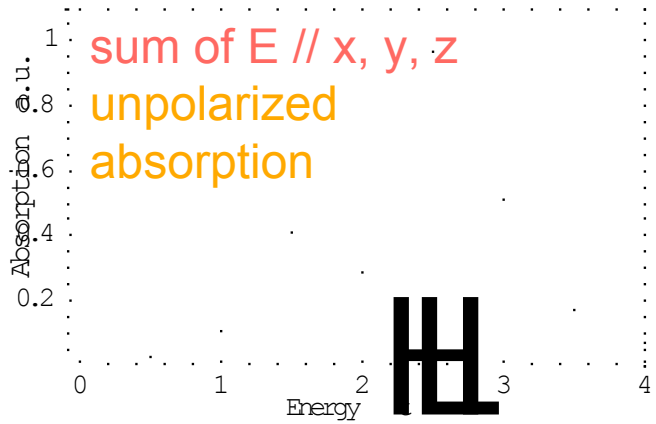


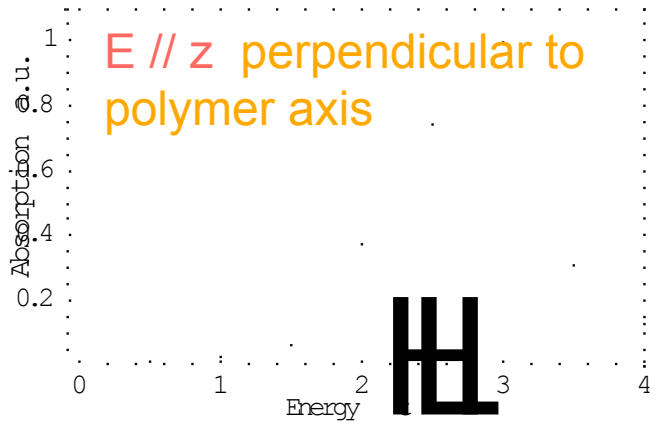
Energy difference of the optical excitations is found between two boundary conditions. This could be observed for oligomers due to the sparse population in the wavenumber space.

Optical absorption of poly(*para*-phenylene): periodic case

Ring torsion angle: Φ=0°
N=20: number of phenyl rings
U=2.5t, V=1.3t: Coulomb interactions reported in K. Harigaya, J. Phys.: Condens. Matter 10, 7679 (1998).

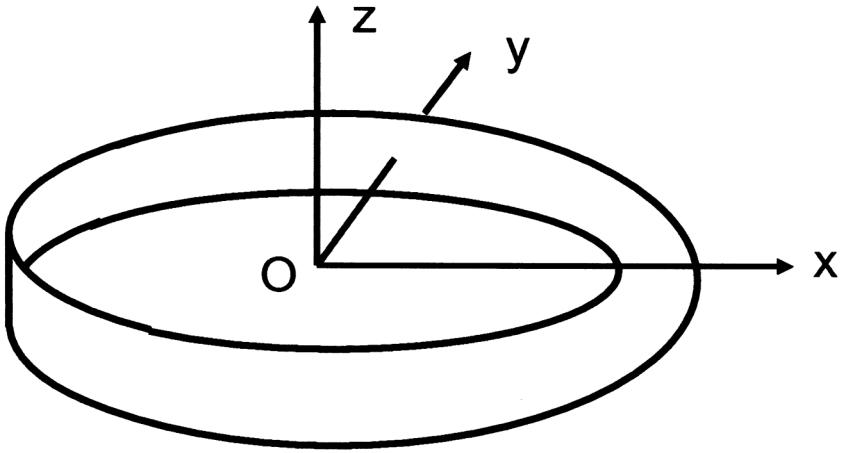


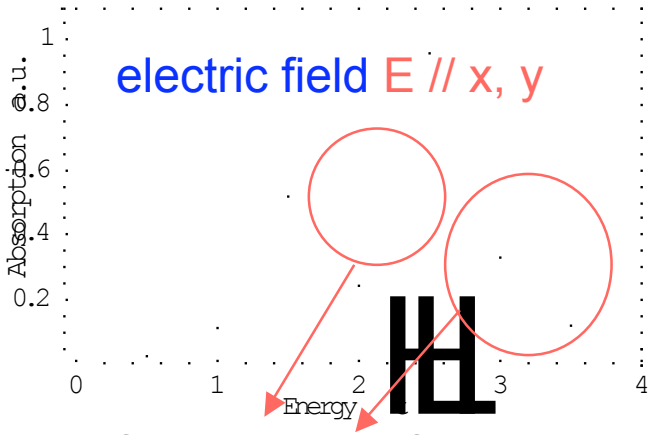




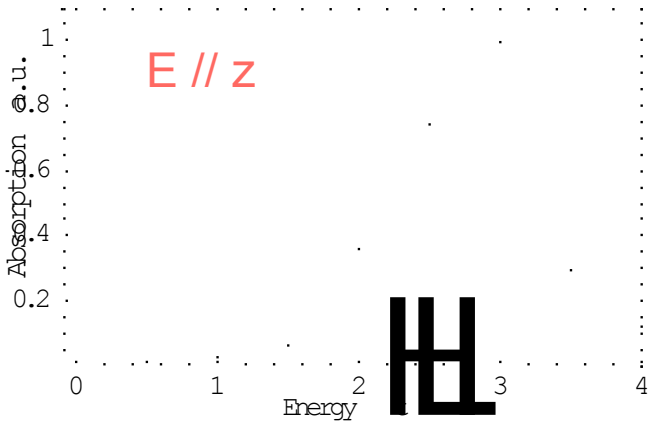
Optical absorption of poly(*para*-phenylene): Moebius case 1

Ring torsion angle: Φ=180°/N
uniform for all over the system
(N=20: number of phenyl rings)



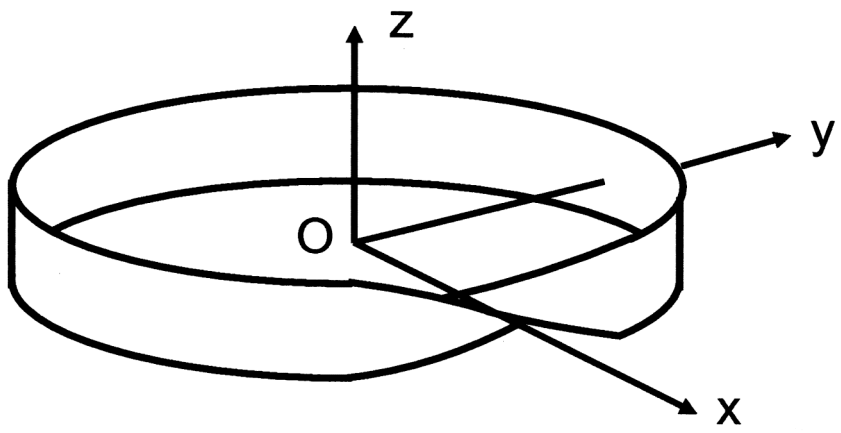


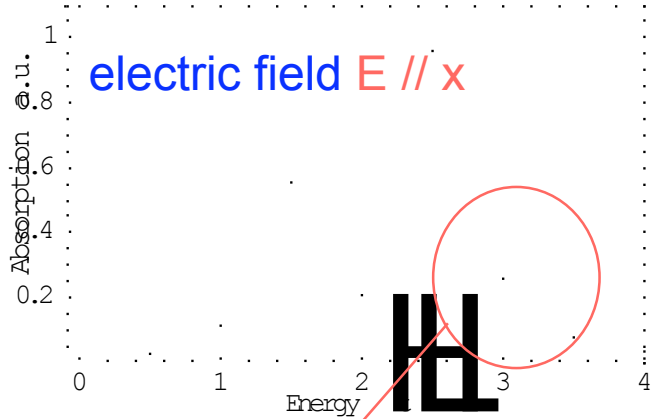
Mixing of absorption of E//z component of the periodic boundary case



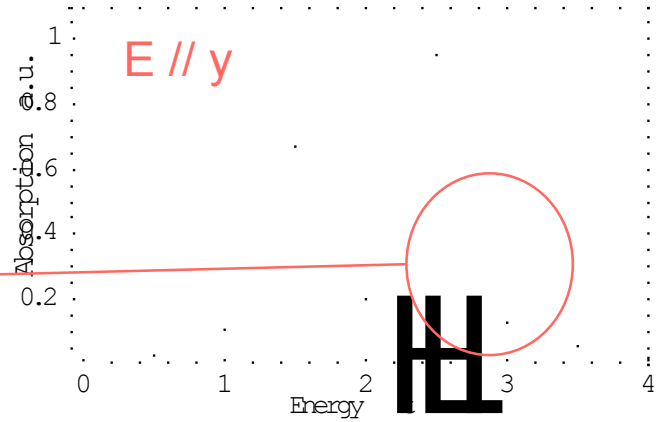
Optical absorption of poly(*para*-phenylene): Moebius case 2

Ring torsion angle: Φ=30°
localized for five phenyl rings
(N=20: total number of phenyls)



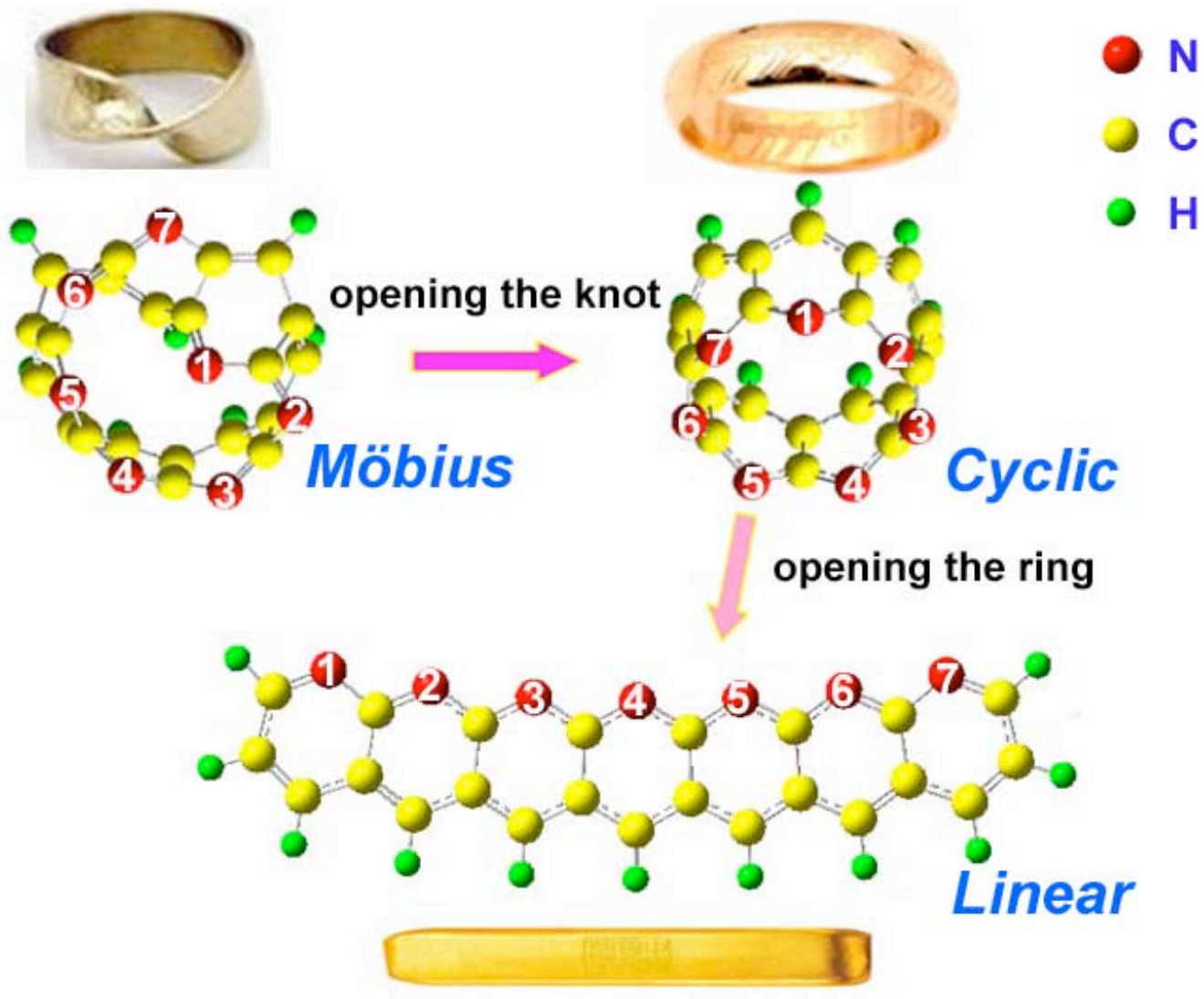


Mixing of absorption of E//z component of the periodic boundary case



Smaller mixing of E//z component because of the localized torsions

Mobius strip cyclacene, cyclic cyclacene, and linear strip



Optimized Geometries

Method: MP2/6-31+G(d) in Gaussian 03 package

C-N	Möbius		cyclic	linear	
1	1.290 1.445	**distorted region**	1.349	1.304 1.383	**end part**
2	1.305 1.403		1.349	1.322 1.359	
3	1.297 1.384	**nondistorted region**	1.349	1.334 1.348	**Non-end part**
4	1.336 1.346		1.349	1.342 1.341	
5	1.375 1.311		1.349	1.349 1.334	
6	1.460 1.221	**distorted region**	1.349	1.360 1.322	**end part**
7	1.263 1.431		1.349	1.383 1.304	
N-N					
1-2	2.399		2.268	2.294	
2-3	2.384		2.268	2.287	
3-4	2.250		2.268	2.286	
4-5	2.287		2.268	2.286	
5-6	2.327		2.268	2.287	
6-7	2.484		2.268	2.294	
7-1	3.280		2.268	13.658	

Calculated μ, α, β, etc

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \qquad \alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad \beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}), i, j, k = x, y, z$$

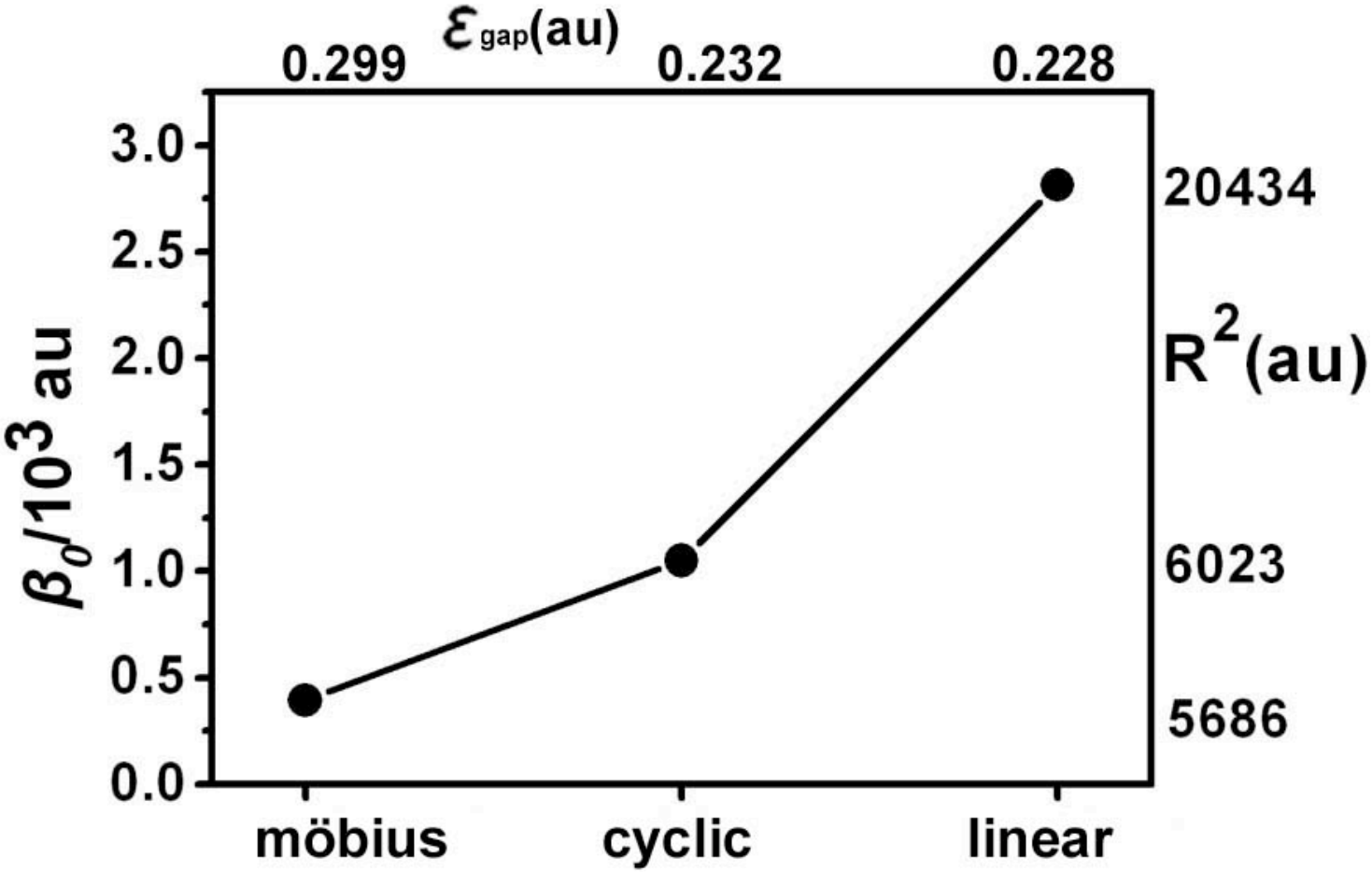
	μ_0	α_0(au)	β_x(au)	β_y(au)	β_z(au)	β_0(au)	R^2(au)	$\Delta\mu$(au)	f_0	ΔE(eV)	$f_0 \cdot \Delta\mu$
Möbius	3.46	268.12	-383	61	67	393	5686	0.484	0.395	6.144	0.191
Cyclic	5.33	323.38	0	1	1049	1049	6023	1.039	0.624	5.222	0.648
Linear	5.34	476.33	100	-2812	-1	2814	20434	0.437	2.031	5.634	0.867

Atomic Unit

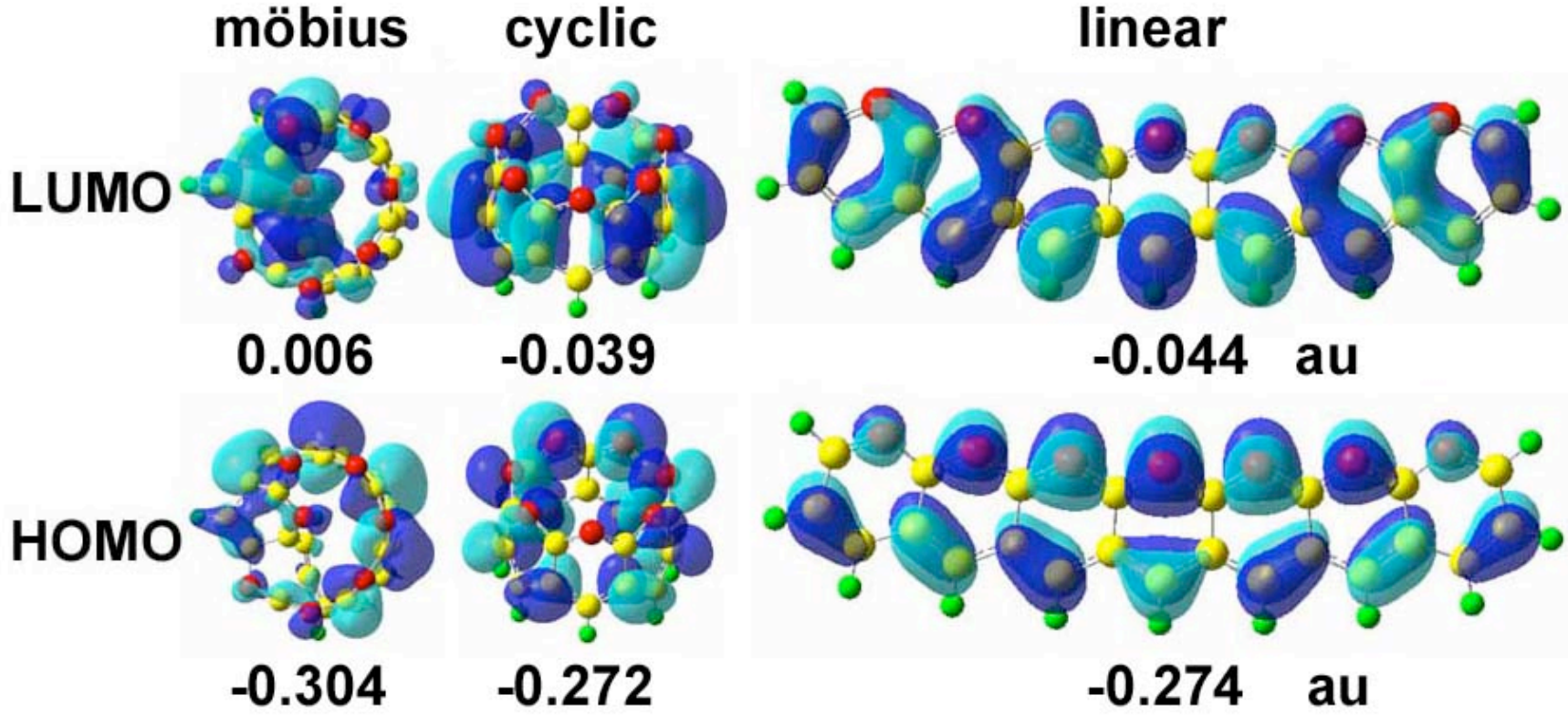
Fundamental Atomic Units

Quantity	Name	Symbol	SI value	Planck unit scale
mass	electron rest mass	m_e	9.109 3826(16)×10^{-31} kg	10^{-8} kg
length	Bohr radius	$a_0 = \hbar/(m_e c\alpha)$	5.291 772 108(18)×10^{-11} m	10^{-35} m
charge	elementary charge	e	1.602 176 53(14)×10^{-19} C	10^{-18} C
angular momentum	Reduced Planck's constant	$\hbar = h/(2\pi)$	1.054 571 68(18)×10^{-34} J s	(same)
energy	Hartree energy	$E_h = m_e c^2 \alpha^2$	4.359 744 17(75)×10^{-18} J	10^{9} J
electrostatic force constant	Coulomb's constant	$1 / (4\pi\varepsilon_0)$	8.9875516×10^{9} C^{-2} N m^2	(same)

β_0 values versus to the electronic spatial extent $<R^2>$ and ε_{gap}(LUMO-HOMO)



LUMO and HOMO orbitals



Summary

1. Topological materials: Moebius nanographite and conjugated polymers
2. Magnetic domain wall states [1] vs. helical magmetic order in nanographite [2]

[1] K. Wakabayashi and K. Harigaya, J. Phys. Soc. Jpn. 72, 998 (2003).

[2] A. Yamashiro, Y. Shimoi, K. Harigaya, and K. Wakabayashi, Physica E 22, 688 (2004).

Summary

3. Optical response in Moebius poly(*para*-phenylene): Certain components of the optical absorption for the electric field perpendicular to the polymer axis mix with the absorption spectra for the electric filed parallel with the polymer axis as a signature of the Moebius polymers.

   →Promotion of materials synthesis

[3] K. Harigaya, J. Phys. Soc. Jpn. 74, 523 (2005).

Summary

3. Static polarizability α and the first hyperpolarizability β are studied, comparing three models: Mobius strip cyclacene, ring cyclacene, and linear strip.
4. Opening the knot of the Mobius to form the ring leads to the increase of α from 268 to 323 a.u. and β increases about three times from 393 to 1049 a.u.
5. Opening the ring to form the linear strip, α increases from 323 to 476 a.u. β as well increases about three times from 1049 to 2814 a.u.

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Experimental:

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K. Takai (Tokyo Inst. of Technology)

T. Enoki (Tokyo Inst. of Technology)

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K. Wakabayashi (NIMS)

Y. Shimoi (AIST), F. L. Gu (Kyushu University)

Z. R. Li (Jiling University, China)