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Quasiparticle and excitonic gaps of one-dimensional carbon chains[1]

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[1] E. Mostaani *et al.*, Preprint: arXiv:1601.04324

Linear carbon chains

Discovery

Discovered in interstellar molecular clouds formed with the explosions of carbon stars, novae and supernovae (1968).

Properties and applications

- High specific stiffness $\approx 10^9$ N.m/kg. More than carbon nanotubes and graphene (4.5×10^8 N.m/kg); and diamond (3.5×10^8 N .m/kg).
- Tunable energy gap.
- Promissing applications in molecular wire sensors and nano-sized molecular & mechanical devices.
- Precursors of soot formation and the intermediates for the synthesis of C_{60} and carbon nanotubes.

Linear carbon chains

Types

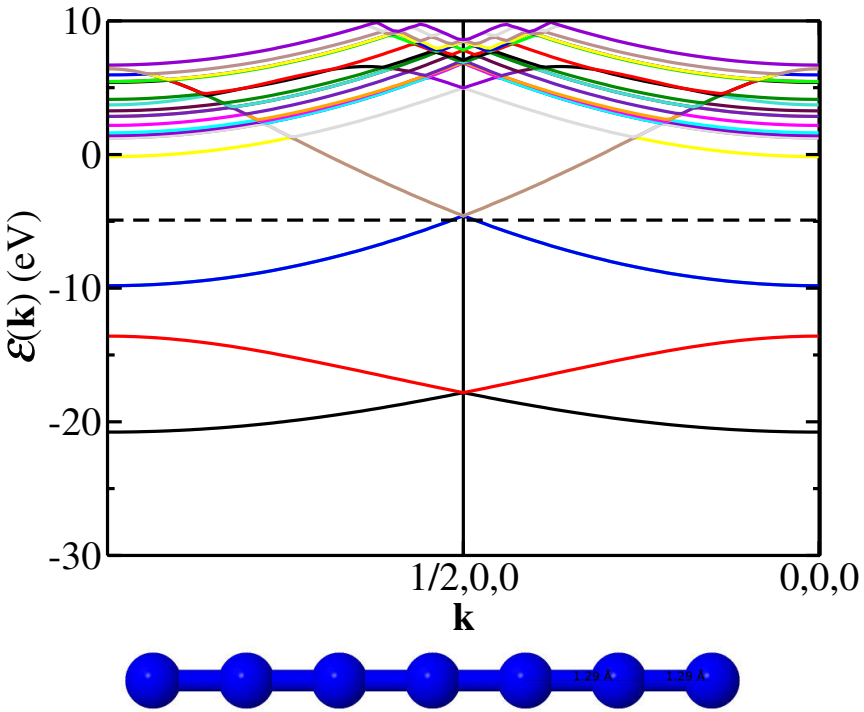
Polycumulene: Double bonds $(C = C =)_n$.
Polyyne: Alternating single and triple bonds $(C \equiv C-)_n$.
Oligoynes: stabilization of the polyyne chains by terminal groups (R-$(C \equiv C-)_n$R).

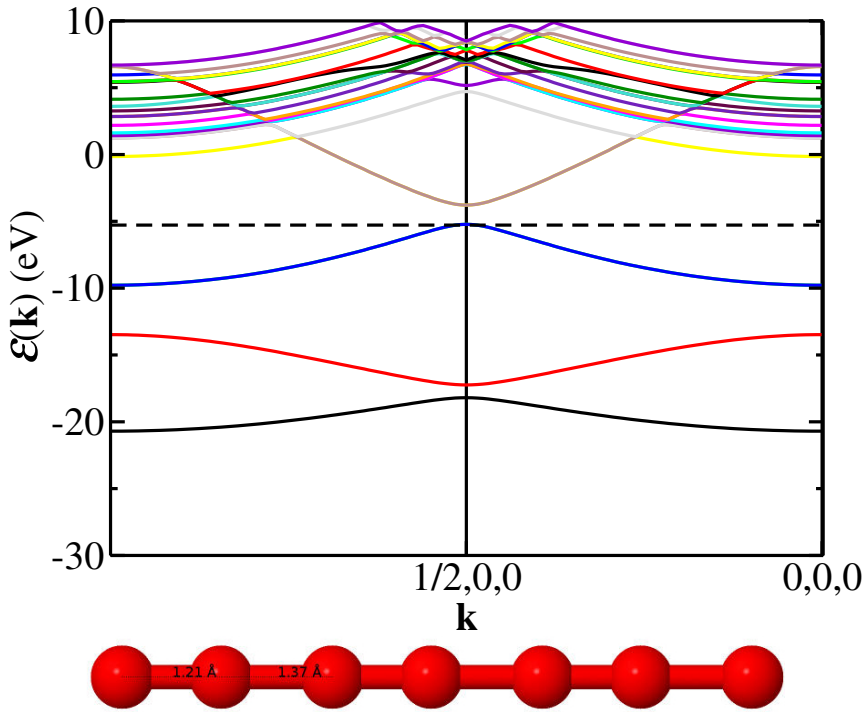
Current challenges

- Polyyne $(-C \equiv C-)_n$ and polycumulene $(C = C)_n$ are very fragile and reactive.
- Exposure to oxygen and water completely destroys these specious.
- Wide range of reported bond length alternation (BLA) and energy gap due to Peierls distortion.

Peierls distortion

Polyyne has a half-filled band structure with the degenerate π orbitals; therefore a small distortion reduces the translational symmetry of the chain at or near the Fermi energy.





Theoretical methods

- Using DFT-PBE and DFT-HSE06 to compare the relaxed geometries of oligoynes.
- Using diffusion quantum Monte Carlo (DMC) to find the BLA of polyyne.
- Using DMC to find the energy gaps of oligoynes and polyyne.
- Considering the MD wave functions containing all the orbital occupancies that are degenerate.

Quasiparticle gap

$$E_{\mathrm{qp}} = E_{\mathrm{EA}} - E_{\mathrm{IE}}$$

Excitonic gap

$$E_{\mathrm{exc}} = E_{\mathrm{pr}} - E_{\mathrm{gs}}$$

DMC accuracy test for benzene

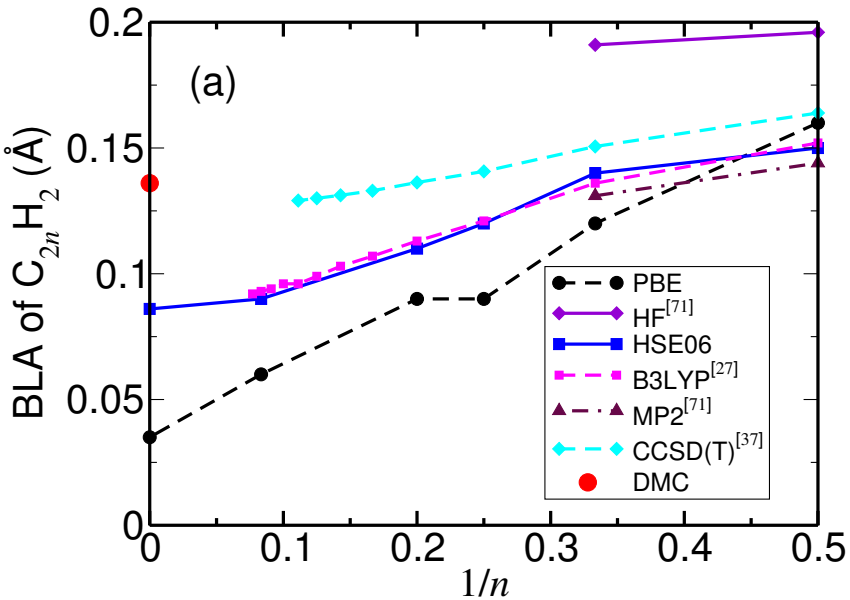
Static-nucleus energies

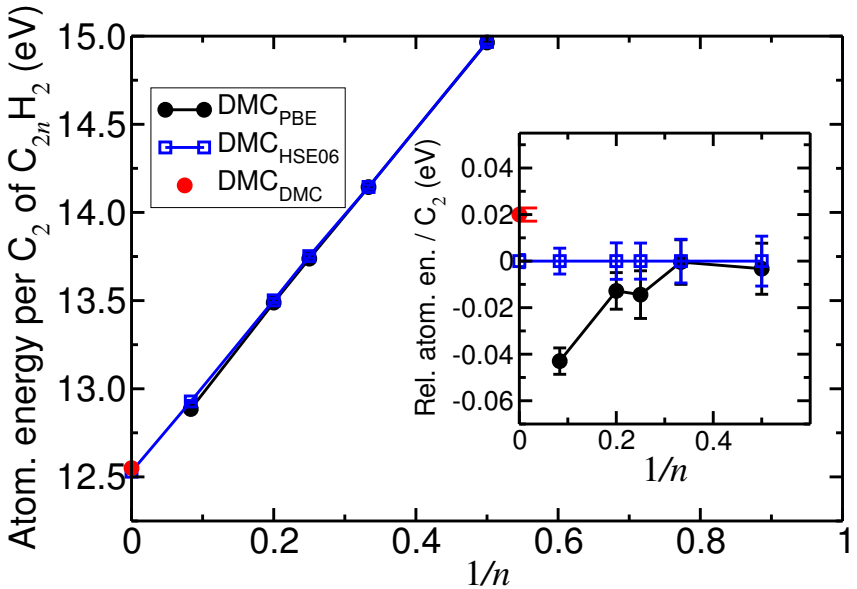
Parameter	DMC (eV)	Exp. (eV)
Ionisation energy	9.24(2)	9.24384(6)
Singlet E_{exc}	5.63(4)	4.9
Triplet E_{exc}	4.56(4)	3.9

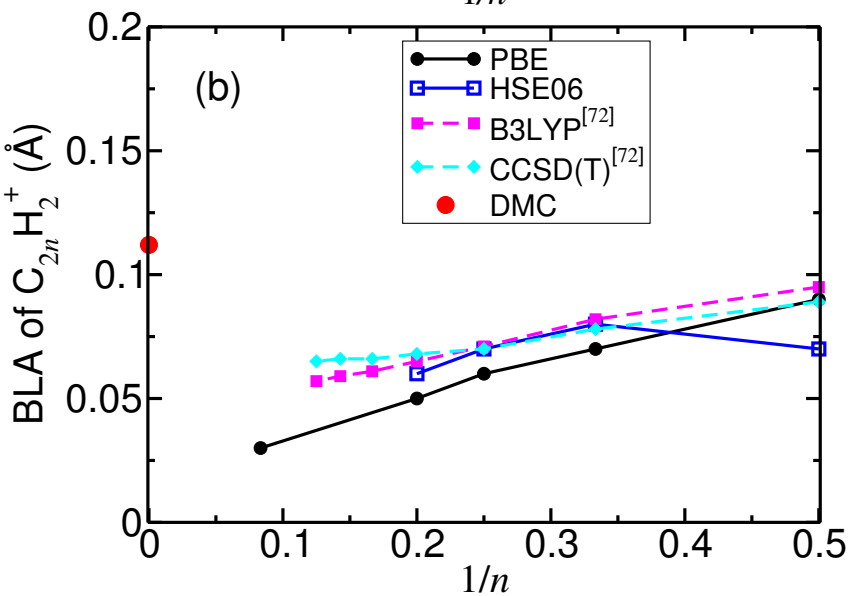
Atomic structure of oligoynes

H–· · ·–C≡C–C≡C–· · ·–H

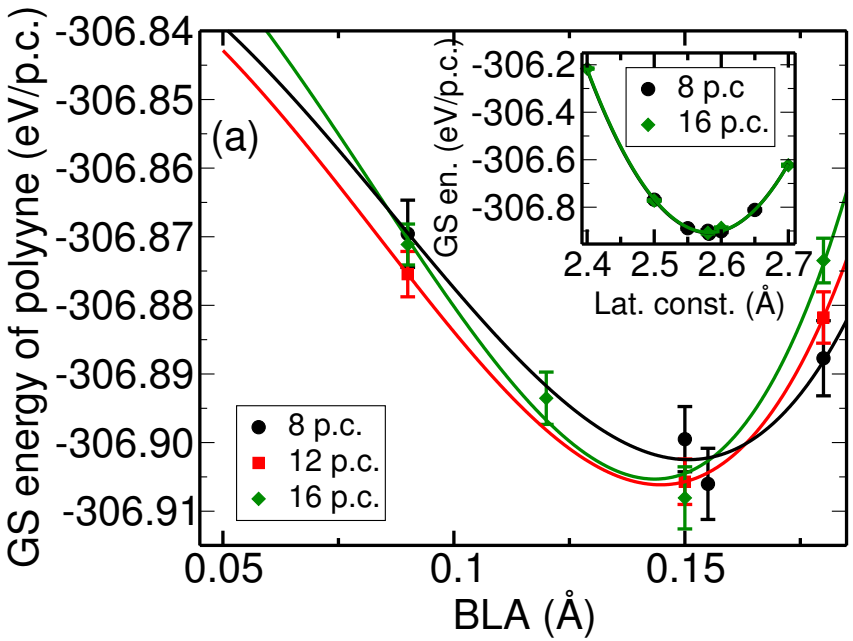
BLA=r_{single}–r_{triple}

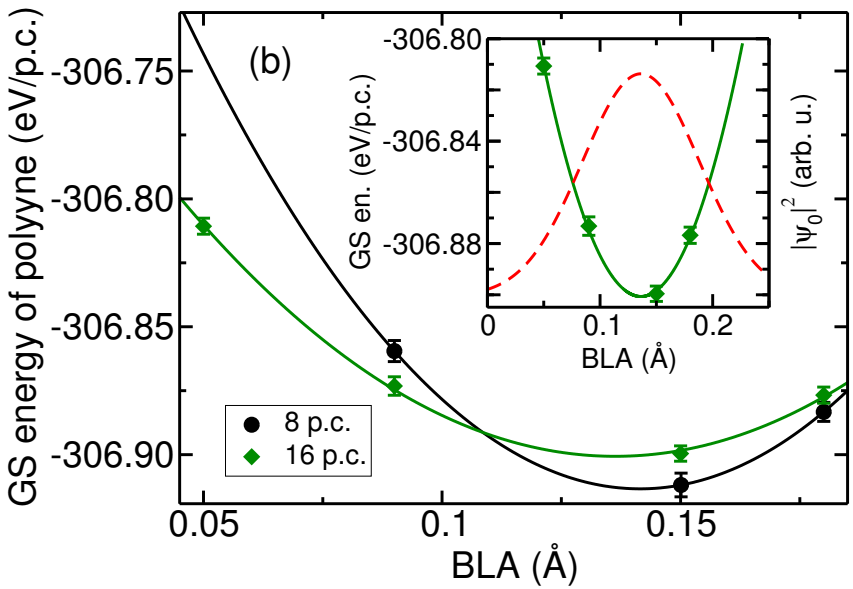


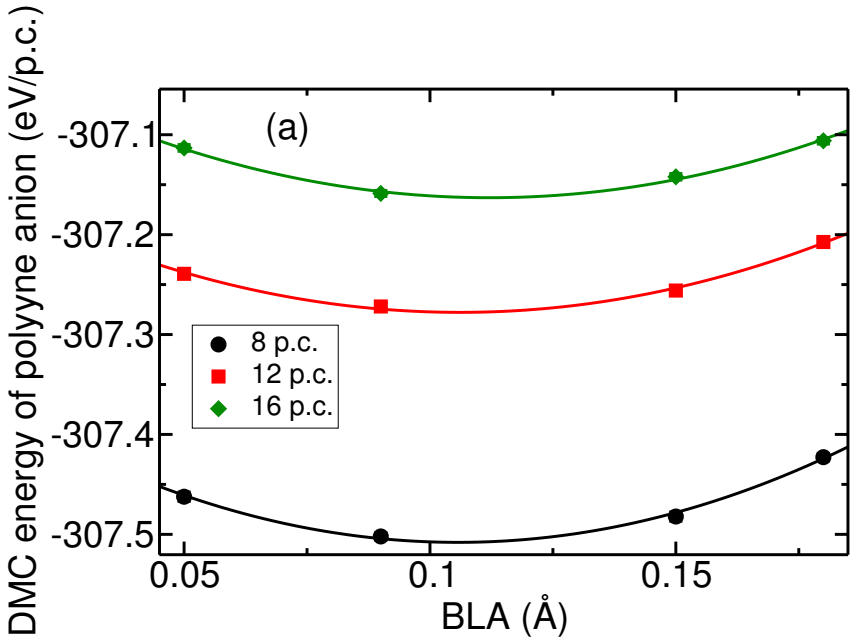


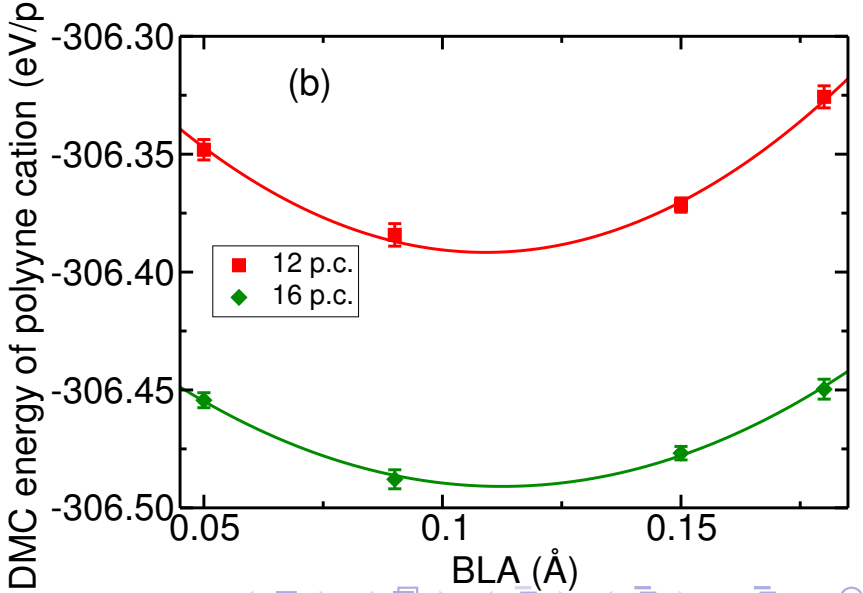


Atomic structure of polyyne $(C{\equiv}C{-})_n$

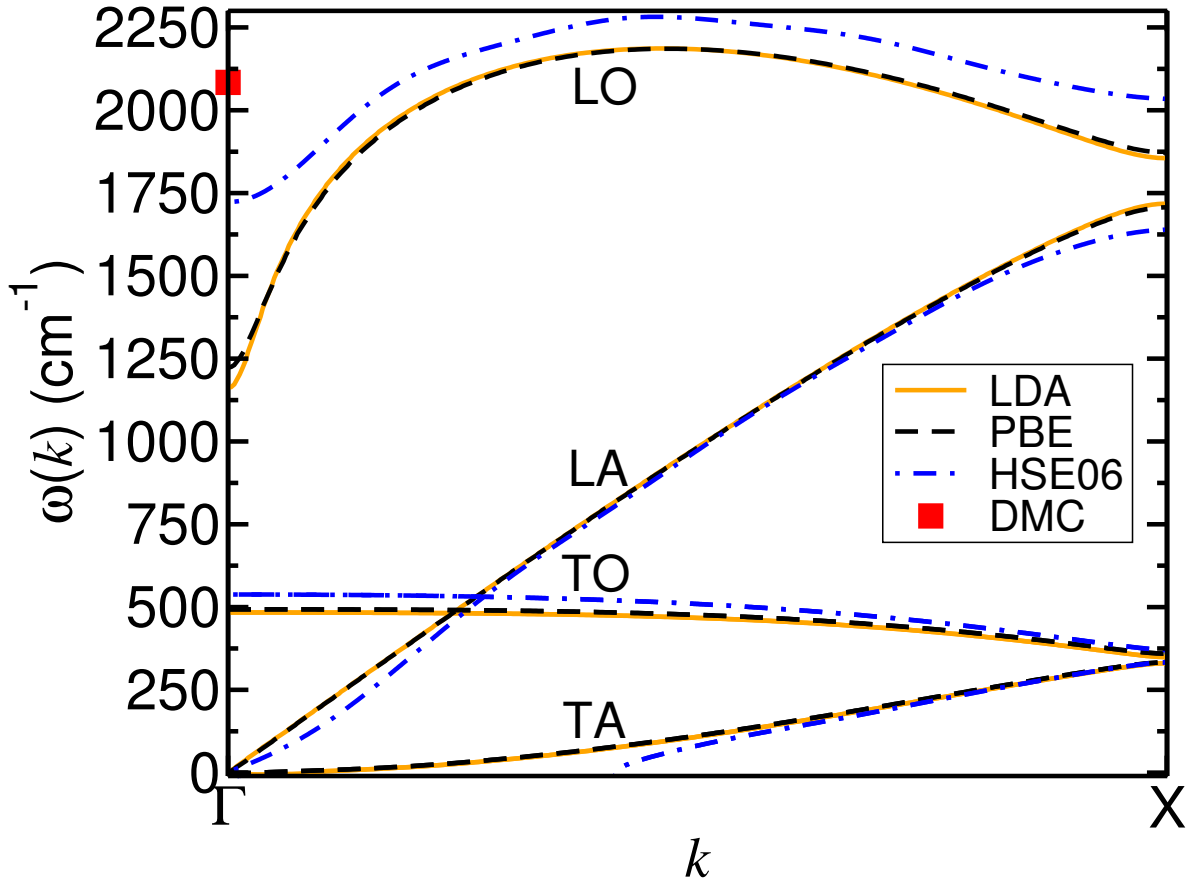








Vibrational properties of polyyne



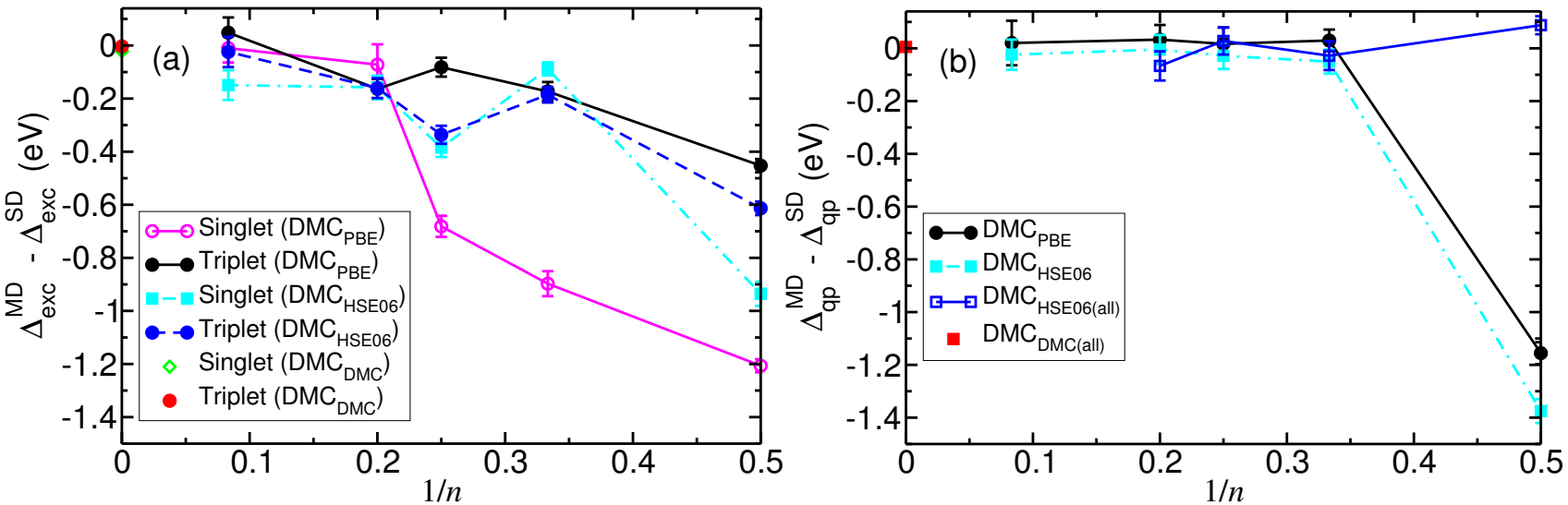
LO Raman spectroscopy: 1900–2300 cm^{-1}

BLA of polyyne

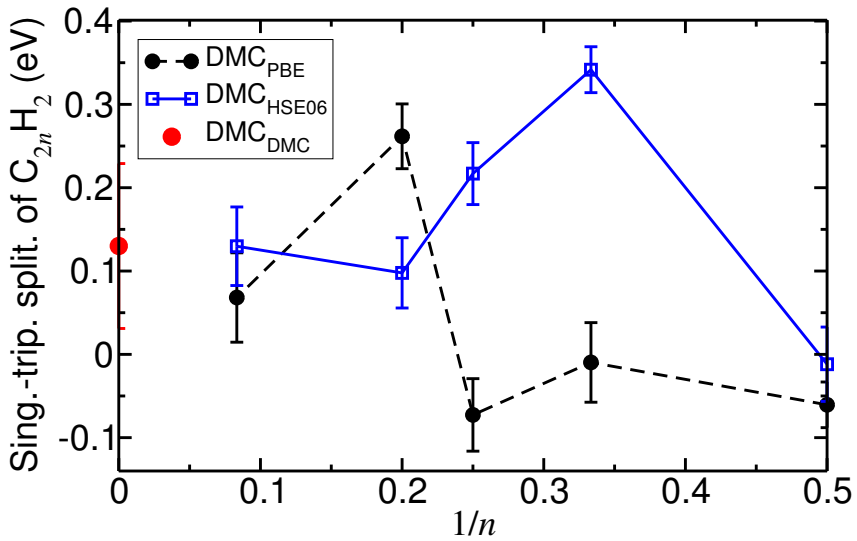
Table : BLA and lattice constant a of polyyne as calculated or measured by different methods.

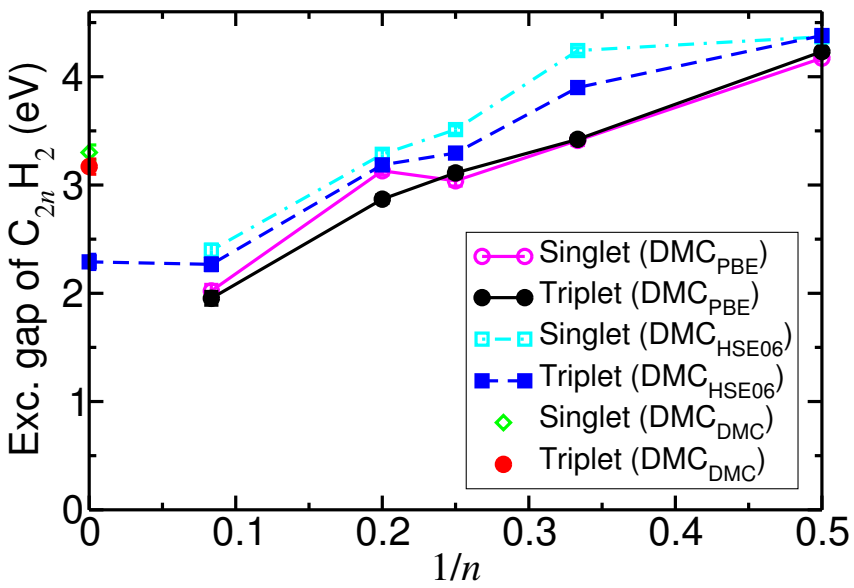
Method	n	a (Å)	r_1 (Å)	r_2 (Å)	BLA (Å)
DFT-PBE (PWK)	PBC	2.565	1.300	1.265	0.035
DFT-HSE06 (PWK)	PBC	2.56	1.323	1.237	0.086
DFT-KMLYP	36				0.135
DFT-BHHLYP	36				0.134
DFT-B3LYP	36				0.088
HF	36				0.183
MP2	20				0.060
MP2		2.554	1.337	1.217	0.120
CCSD		2.559	1.362	1.197	0.165
CCSD(T)		2.565	1.358	1.207	0.151
CCSD(T)	9	2.586	1.357	1.229	0.128
DMC (PWK)	PBC	2.5817(9)	1.359(2)	1.223(2)	0.136(2)
Exp. in DWCNT	~ 200	2.558	1.329	1.229	0.100

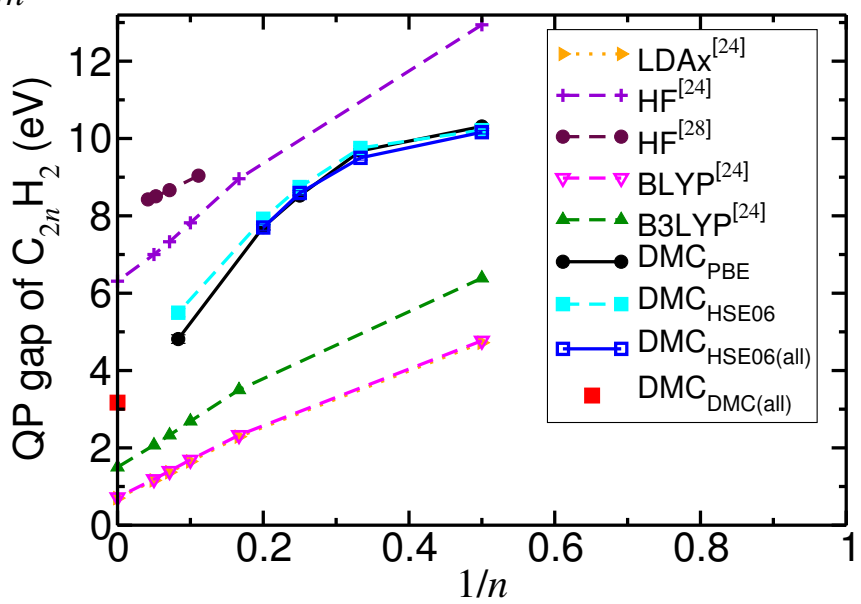
Effect of MD and SD on the gaps



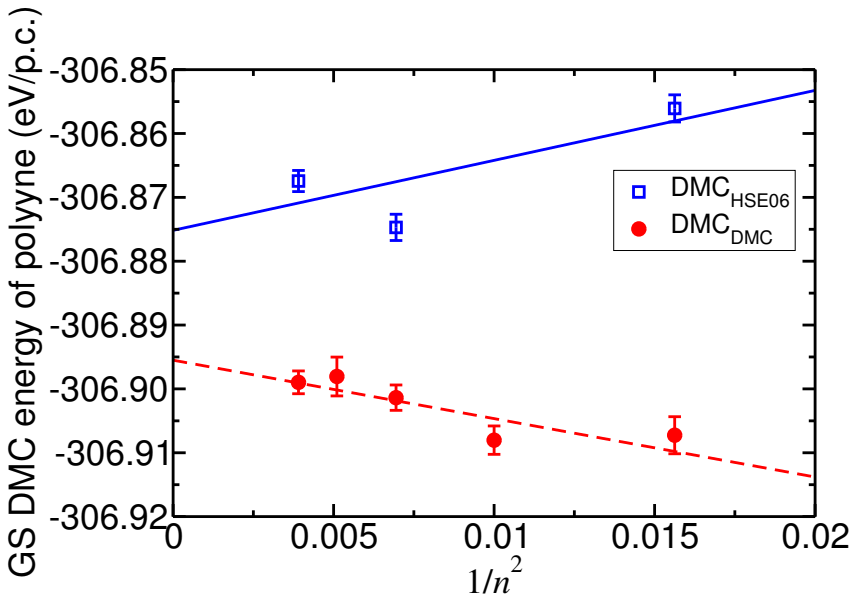
Gaps of oligoynes

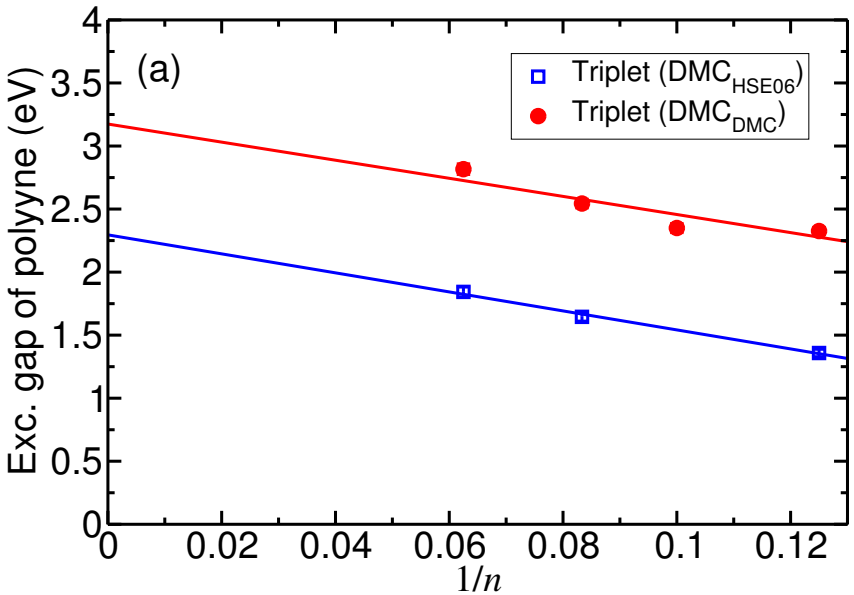


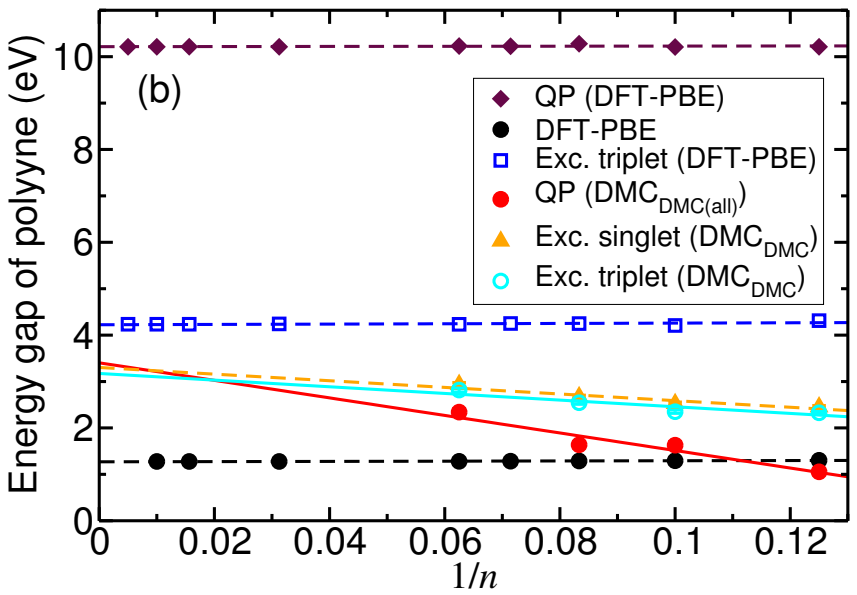




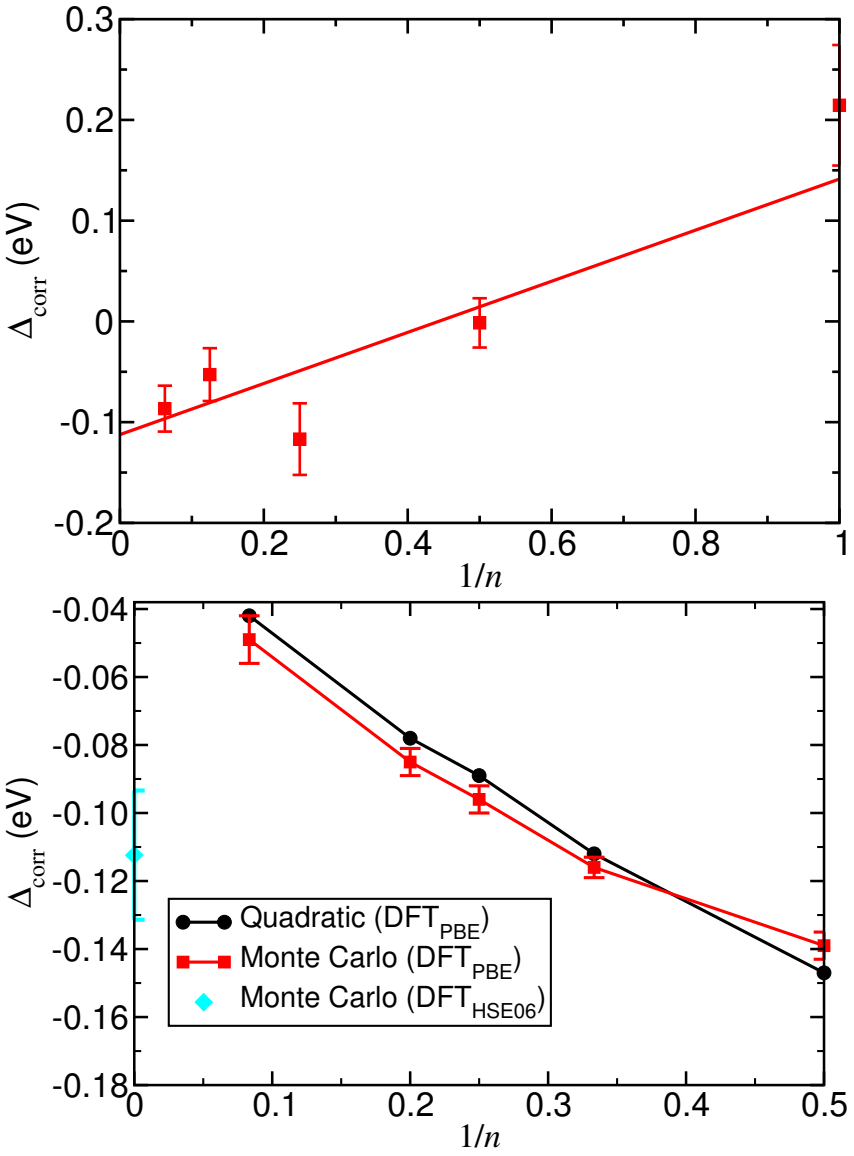
Gaps of polyyne







Vibrational effects



- The DFT vibrational renormalization of the excitonic gap of benzene ranges from -0.45 eV to -0.50 eV, depending on the choice of exchange–correlation functional.
- The vibrational correction to the gap is not as large as in benzene, and the zero-point correction linearly extrapolated to the thermodynamic limit is $-0.11(2)$ eV.

Theory and experiment gaps of polyyne

Table : Singlet excitonic gaps Δ_{exc} and quasiparticle gaps Δ_{qp}

Method	n	Δ_{exc} (eV)	Δ_{qp} (eV)
DFT-LDA	PBC		0.246
DFT-PBE (PWK)	PBC		1.277
DFT-HF	36		8.500
DFT-BLYP	PBC		0.320
DFT-BHHLYP	36		3.946
DFT-HSE06 (PWK)	PBC		1.301
GW	PBC		2.15
MP2	20		5.541
$\mathrm{DMC}_{\mathrm{DMC(all)}}$ (PWK)	PBC	3.30(7)	3.4(1)
Experiment	12	2.18–2.36	
Experiment	10	2.33	
Experiment	10	2.18	
Experiment	12	2.16	
Experiment	12	1.24–1.88	
Experiment	22	2.56	

Summary

- DMC can be used to find an accurate band gap of materials.
- Accurate gaps of polyyne and oligoynes depend considerably on an accurate geometry because of Peierls distortion.
- BLA of polyyne calculated by DMC is accurate and in agreement with quantum chemistry method.
- Vibrational renormalisation for carbon chain is not as important as that in other materials such as benzene.