BINDING ENERGY OF BILAYER GRAPHENE AND ELECTRONIC PROPERTIES OF OLIGOYNES

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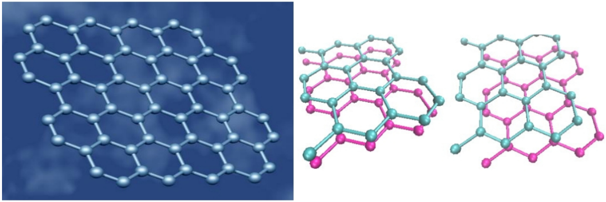
VAN DER WAALS INTERACTION

- Important contributions to the description of binding energy.
- caused by nonlocal electron correlation effects.
- Not described accurately by the current methods such as density functional theory (DFT) with various XC functionals and semi-empirical methods.

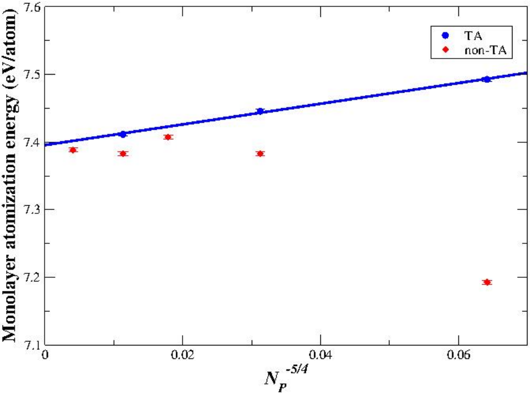
COMPUTATIONAL DETAIL



- VMC and DMC.
- Dirack-Fock pseudopotential.
- Finite-population errors and time step bias are controlled.
- Ground state energies for simulation cells including 3×3, 4×4 and 6×6 unit cells.
- Twist averaging by fitting $E(N_P, k_s) = \bar{E}(N_P) + b[E_{LDA}(N_P, k_s) - E_{LDA}(\infty))]$.
- Extrapolation to infinite system size by $\bar{E}(N_P) = E(\infty) + cN_P^{-5/4}$.

MONOLAYER ATOMISATION ENERGY

Difference between the energy of an isolated, spin-polarized C atom and the energy per atom of monolayer graphene.



Method	E_{atom} (eV/atom)
DFT-LDA[1]	8.96
DFT-LDA[2]	8.873
DFT-LDA (pres. wk.)	8.883
DFT-PBE[3]	7.847
DFT-PBE[1]	7.93
DFT-PBE (pres. wk.)	7.873
DMC[4]	7.464(10)
DMC (pres. wk.)	7.395(3)

[1] G. Graziano *et al.*, J. Phys.: Condens. Matter **24**, 424216 (2012).

[2] M. Hasegawa and K. Nishidate, Phys. Rev. B **70**, 205431 (2004).

[3] A. Hansson *et al.*, Phys. Rev. B **86**, 195416 (2012).

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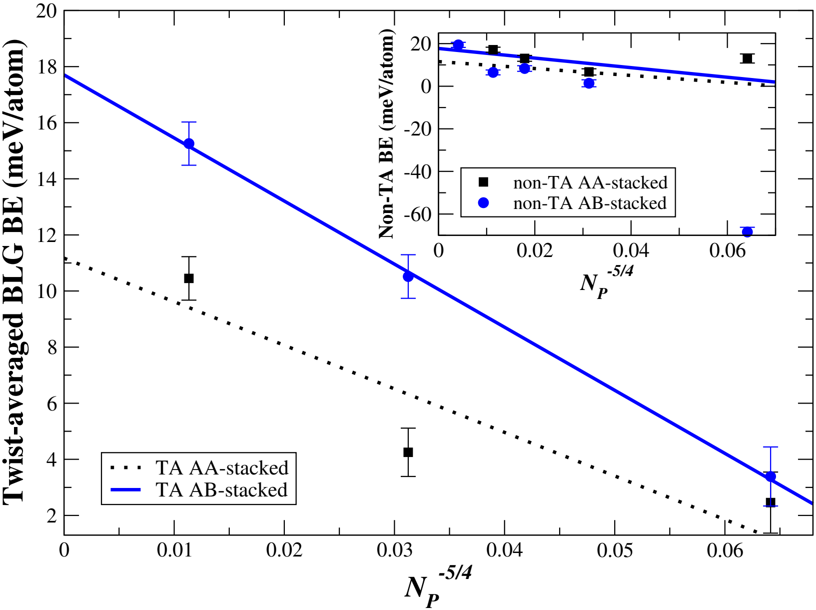
BINDING ENERGY OF BILAYER GRAPHENE



MONOLAYER ATOMISATION ENERGY

BE of BLG (both AA- and AB-stacked) obtained in recent theoretical studies. The layer separation *d* used in the calculations is given in each case.

Stacking	Method	*d* (Å)	BE (meV/atom)
AB	DFT-LCAO-OO[1]	3.1–3.2	70(5)
AB	SAPT(DFT)[2]	3.43	42.5
AB	vdW-DF[3]	3.6	45.5
AB	vdW-DF[4]	3.35	29.3
AB	DFT-D[5]	3.32	22
AB	DFT-D[3]	3.25	50.6
AB	DMC (pres. wk.)	3.384	17.7(9)
AA	vdW-DF[3]	3.35	10.4
AA	DFT-D[3]	3.25	31.1
AA	DMC (pres. wk.)	3.495	11.5(9)

LCAO-OO: Linear combination of atomic orbitals-orbital occupancy.

1 Y.J. Dappe *et al.*, J. Phys.: Condens. Matter **24**, 424208 (2012).
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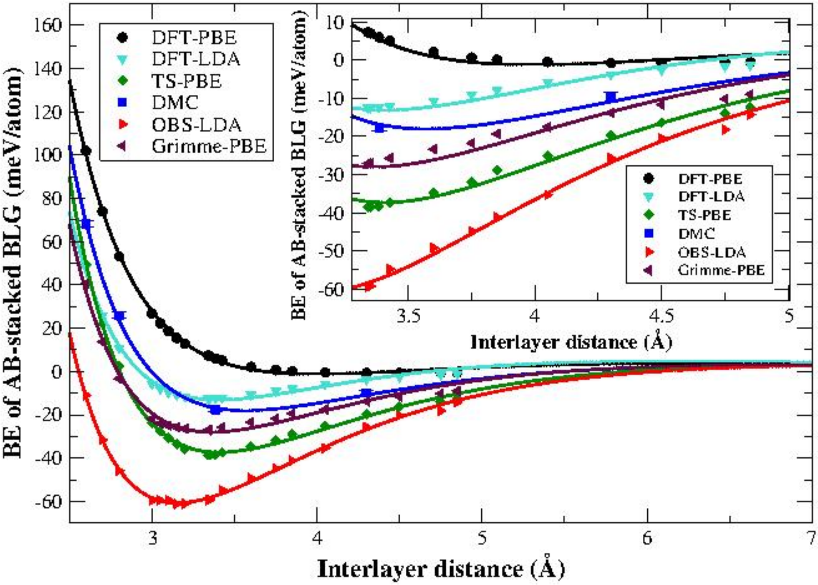
BINDING ENERGY CURVE



SUMMARY OF FIRST PART

1. Binding energy of AA- and AB-stacked BLG at their experimental equilibrium separations are 11.5(9) and 17.7(9) meV/atom, respectively.
2. Long-range charge fluctuations are more important in the AB-stacked geometry than the AA-stacked, results in larger finite size errors in AB-stacked.

Electronic properties of oligoynes
(Preliminary results)

CARBON ALLOTROPES

Binding in carbon

- sp^3**:** Diamond.
- sp^2**:** Graphite, graphene, fullerenes and nanotubes.
- sp**:** Carbon chain.

LINEAR CARBON CHAIN DISCOVERY

When? Linear carbon chain discovered in nature as late as in 1968 eventually lead to the discovery of C_{60}.
Where? Recognized in interstellar molecular clouds formed with the explosions of carbon stars, novae and supernovae.

TYPES OF LINEAR CARBON CHAIN

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

SYNTHESIS AND CHARACTERISATION

- The first and second type may be stable at high temperatures (3000 K) as naturally formed in such environments as shock-compressed graphite, interstellar dust, and meteorites.
- The third type is artificially produced by different chemical routes
- Information of carbon chains is mainly based on vibrational spectroscopy of stabilized linear carbon chains.
- The most convenient method of characterising is absorption spectroscopy.

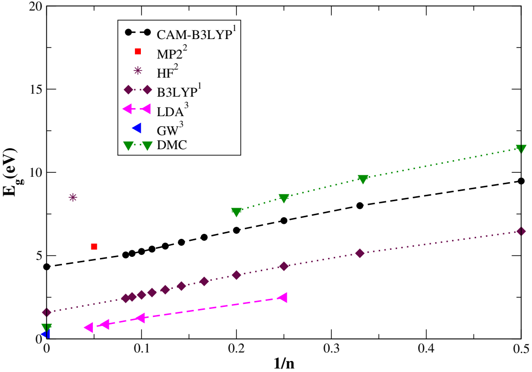
PROPERTIES OF CARBON CHAIN

- Specific stiffness $\approx 10^9$ N.m/kg. More than 2-fold improvement over known materials carbon nanotubes and graphene (4.5×10^8 N.m/kg); and almost 3-fold over diamond (3.5×10^8 N .m/kg).
- Particular applications, such as molecular wire sensors and nano-sized molecular devices, photophysics and photovoltaic devices.
- Precursors of soot formation and the intermediates for the synthesis of C_{60} and carbon nanotubes.

WHY OLIGOYNES?

- Polyyne $(-C \equiv C-)_n$ and polycumulene $(= C =)_n$ are very fragile and reactive.
- Exposure to oxygen and water completely destroys these specious.
- Currently, synthetic of polyyne and polycumulene are based on the high pressure and high temperature which makes it hard to be synthesised.
- Tendency to undergo chain-chain cross-linking reaction causing the evolution towards an sp^2 phase.
- Experimental information of carbon chains is mainly based on vibrational spectroscopy of stabilized linear carbon chains.

CONTROVERSY IN HOMO-LUMO GAP OF OLIGOYNES



n is the number of paired carbons $(-C \equiv C-)$ in unit cell

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[2] S. Yang and M. Kertesz, J. Phys. Chem. A. **110**, 9771 (2006).

[3] A. Al-Backri, *et. al*, submitted.

SUMMARY

- QMC can be used to find an accurate band gap of materials whose experimental value are not available.
- Accurate band gap is an important input for investigating the electronic properties of materials.
- Still continuing $\cdots$.

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Thank you