Electronic properties of double-walled carbon nanotubes (DWNT) and the effect of functionalization

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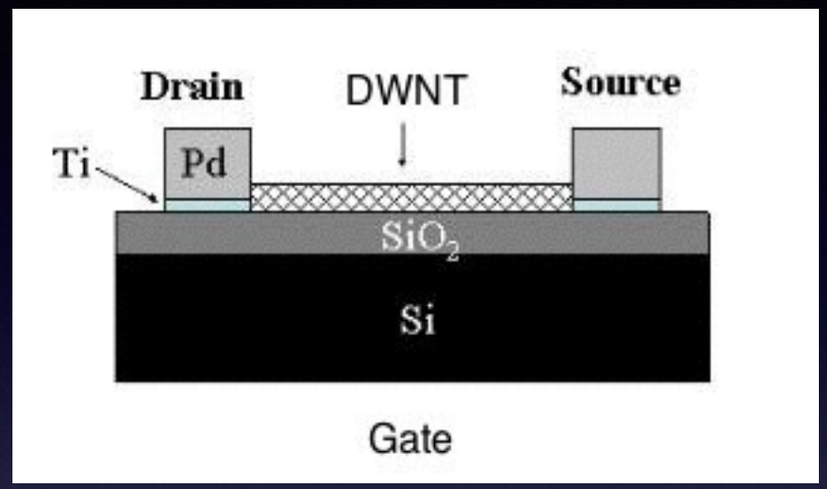
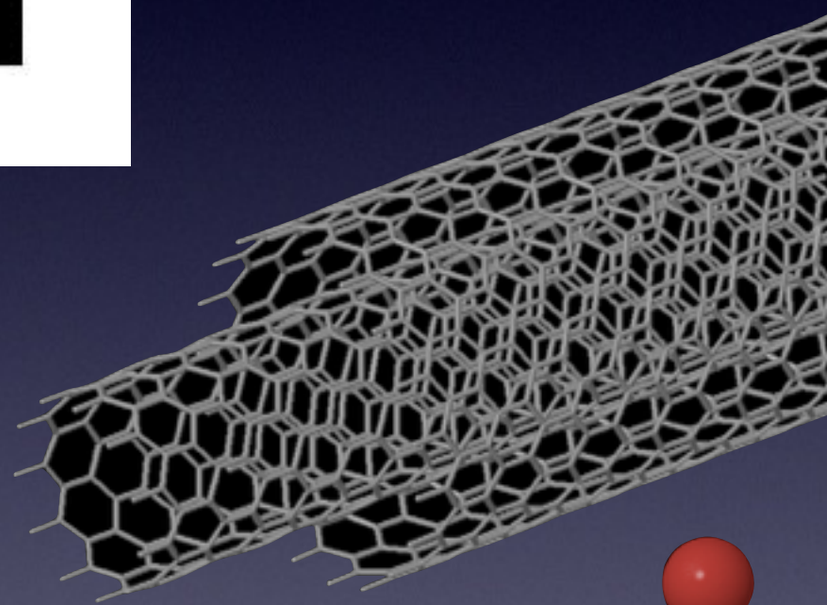
Peter Haynes
Imperial College, London, United Kingdom

Motivation

- DWNT : easier FETs

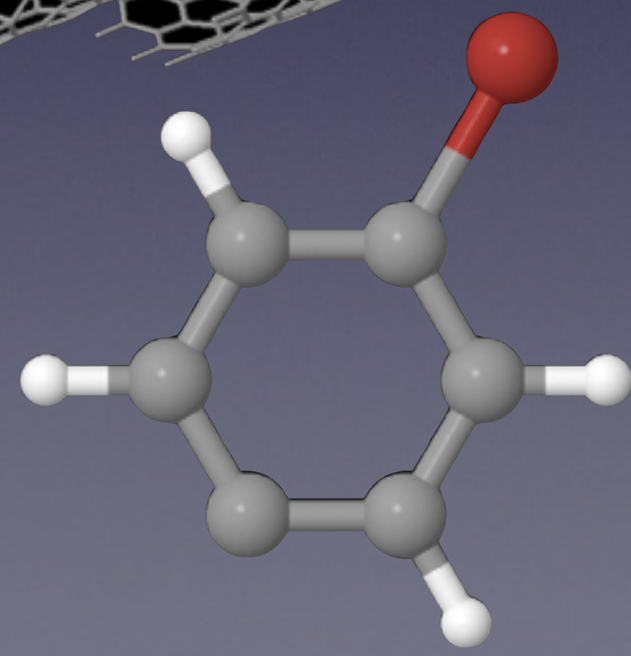


- S@S DWCNT



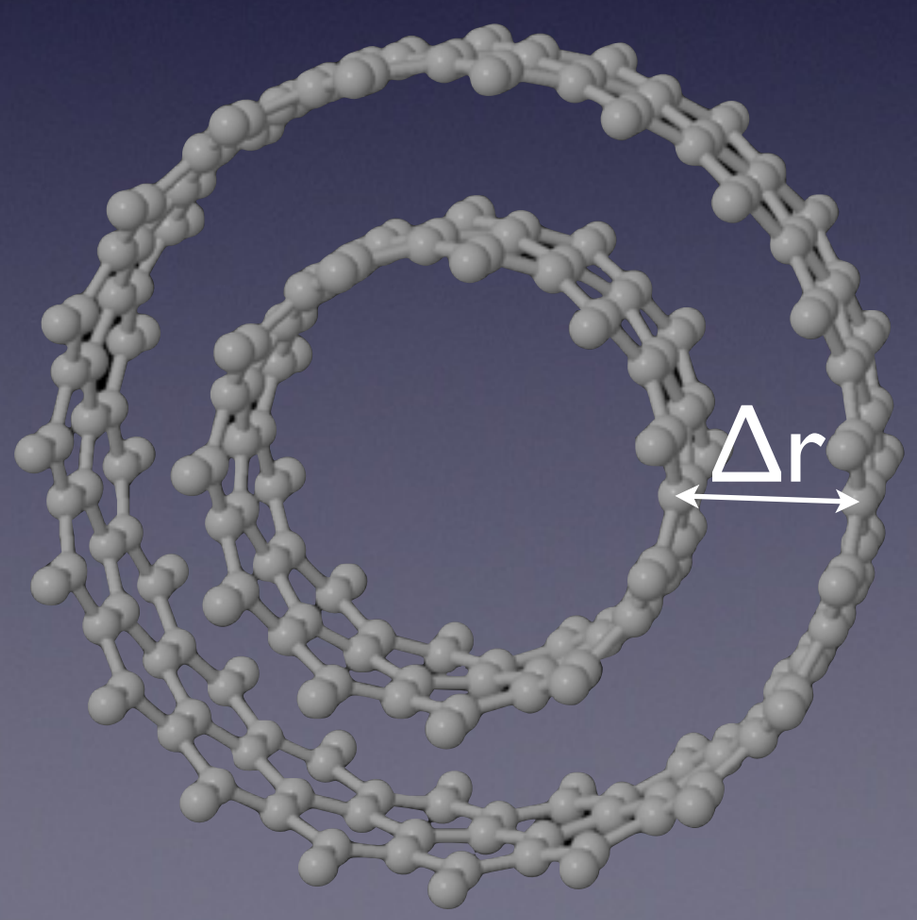
- Part 1 : wall interaction in DWNT?

- Part 2 : effect of functionalization? (bromo-phenyls)



Part I : interaction in DWNT

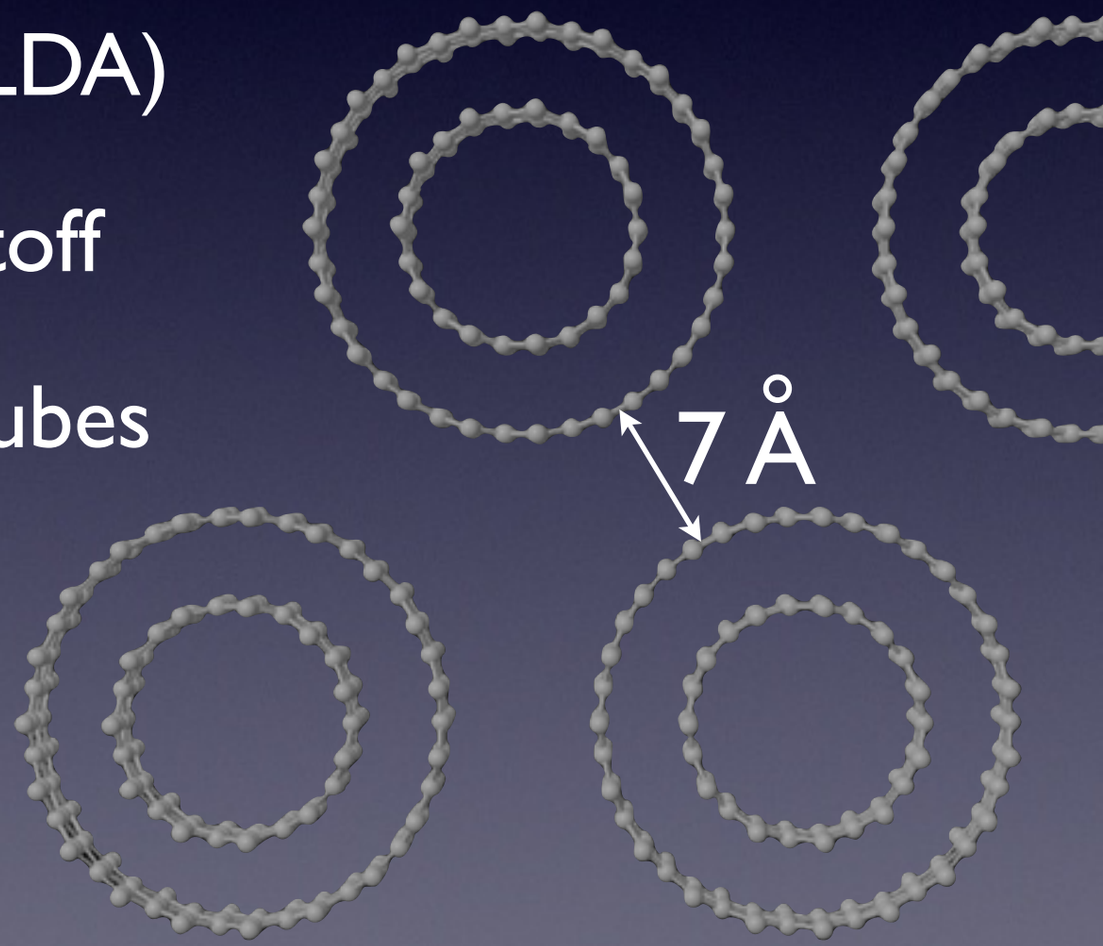
- Litterature :
  - S@S DWNT : semiconducting or metallic [1-3]
  - metallicity : comes from differences in work functions of NTs [4]
- Effect of interaction beyond mismatched work functions?
  - Structural deformation
  - Electronic interaction
- Importance of those effects with respect to interwall distance (Δr)



[1] : Okada and Oshiyama, PRL **91**, 216801 (2003)
[2] : Song et al., Chem. Phys. Lett. **414**, 429-433 (2005)
[3] : Pudlak and Pincak, Eur. Phys. J. B **67**, 565-576 (2009)
[4] : Shan and Cho, Phys. Rev. B **73**, 081401(R) (2006)

Method

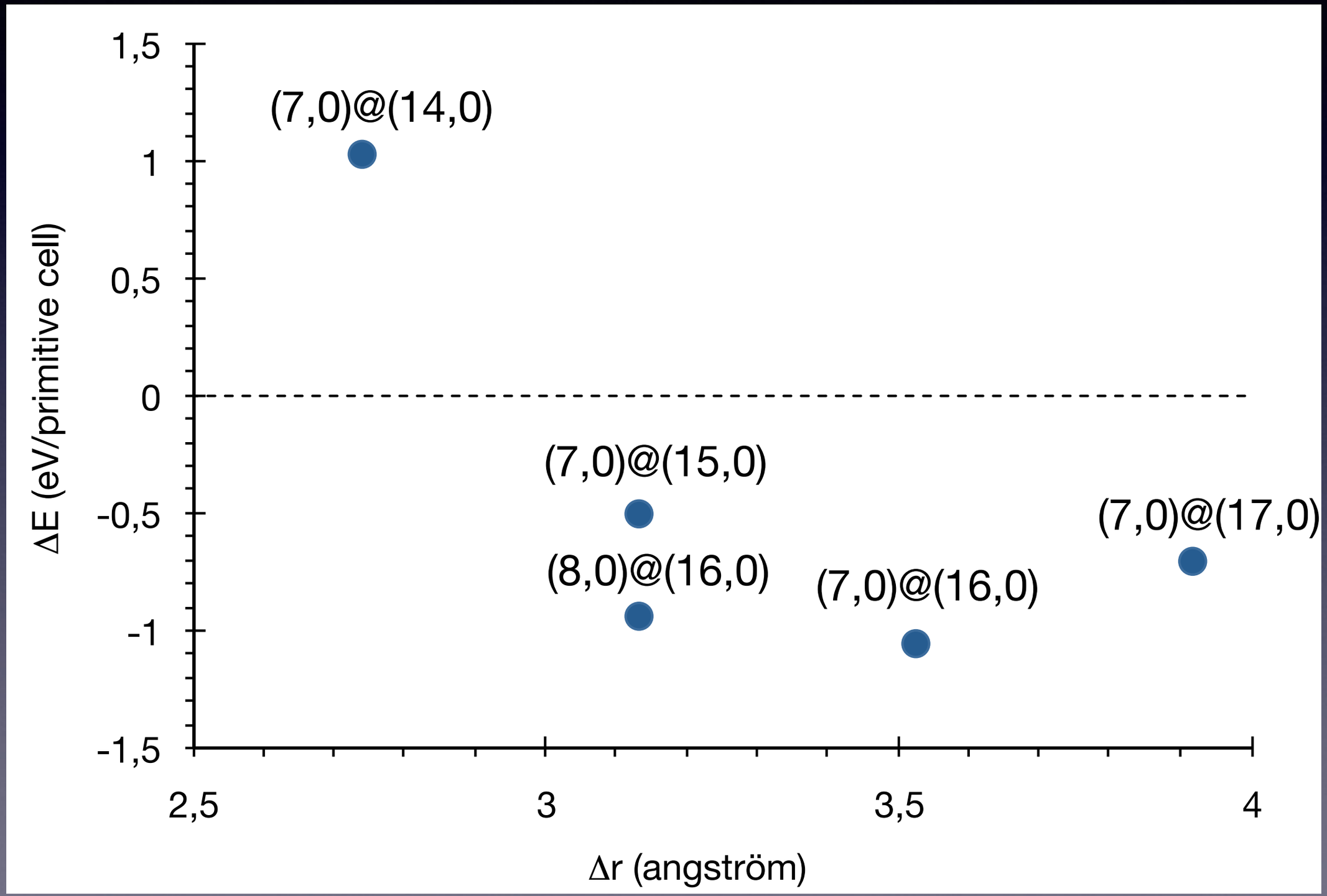
- Method : Density Functional Theory (DFT) as implemented in Abinit [5]
  - Local Density Approximation (LDA)
  - Plane wave basis set : 35 Ha cutoff
  - 7 angström distance between tubes
  - 1 1 6 k-points grid
  - Forces fully relaxed
  - (n,0)@(n,0) DWNT



[5] : Gonze et al. , Computer Phys. Commun. **180**, 2582-2615 (2009).

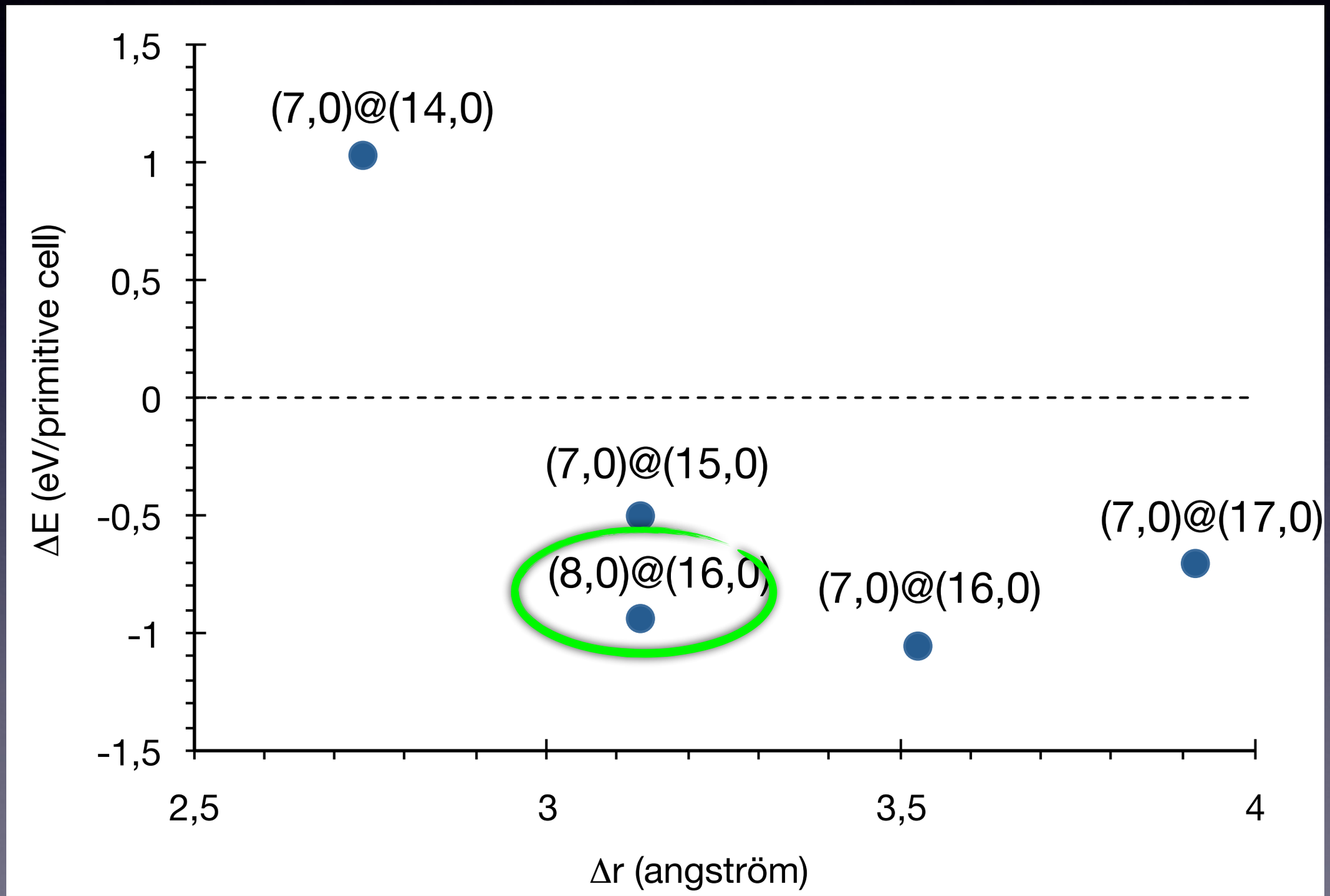
Bonding energy

dependance on Δr



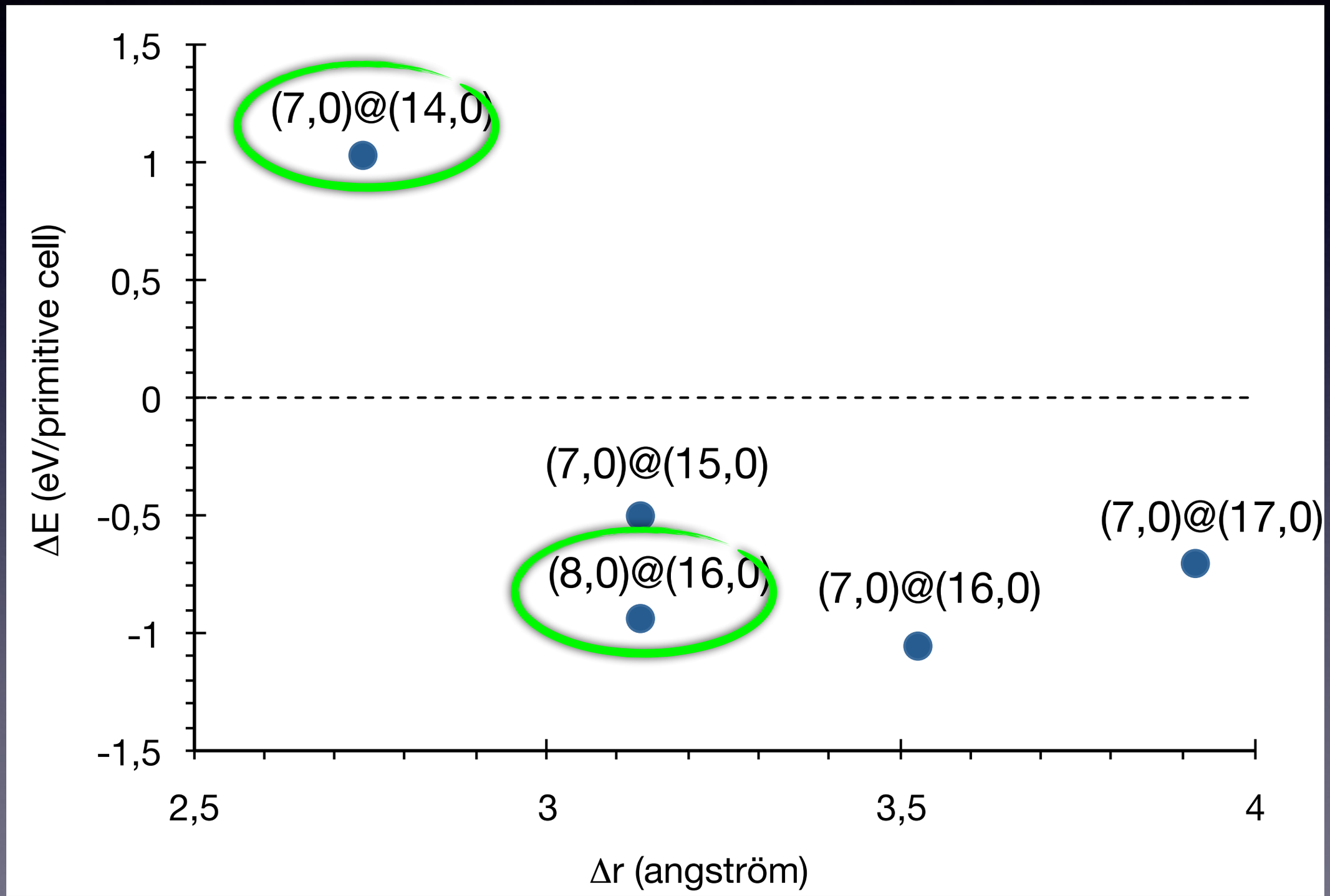
Bonding energy

dependance on Δr



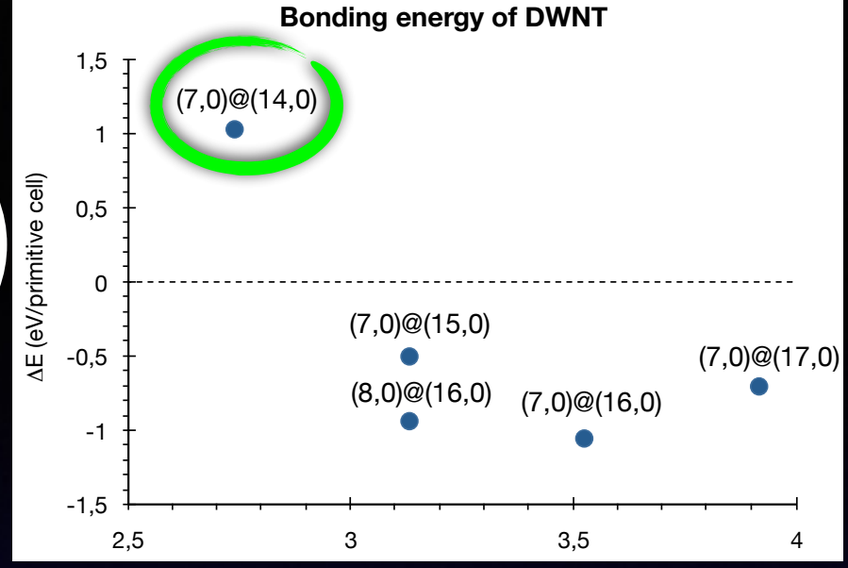
Bonding energy

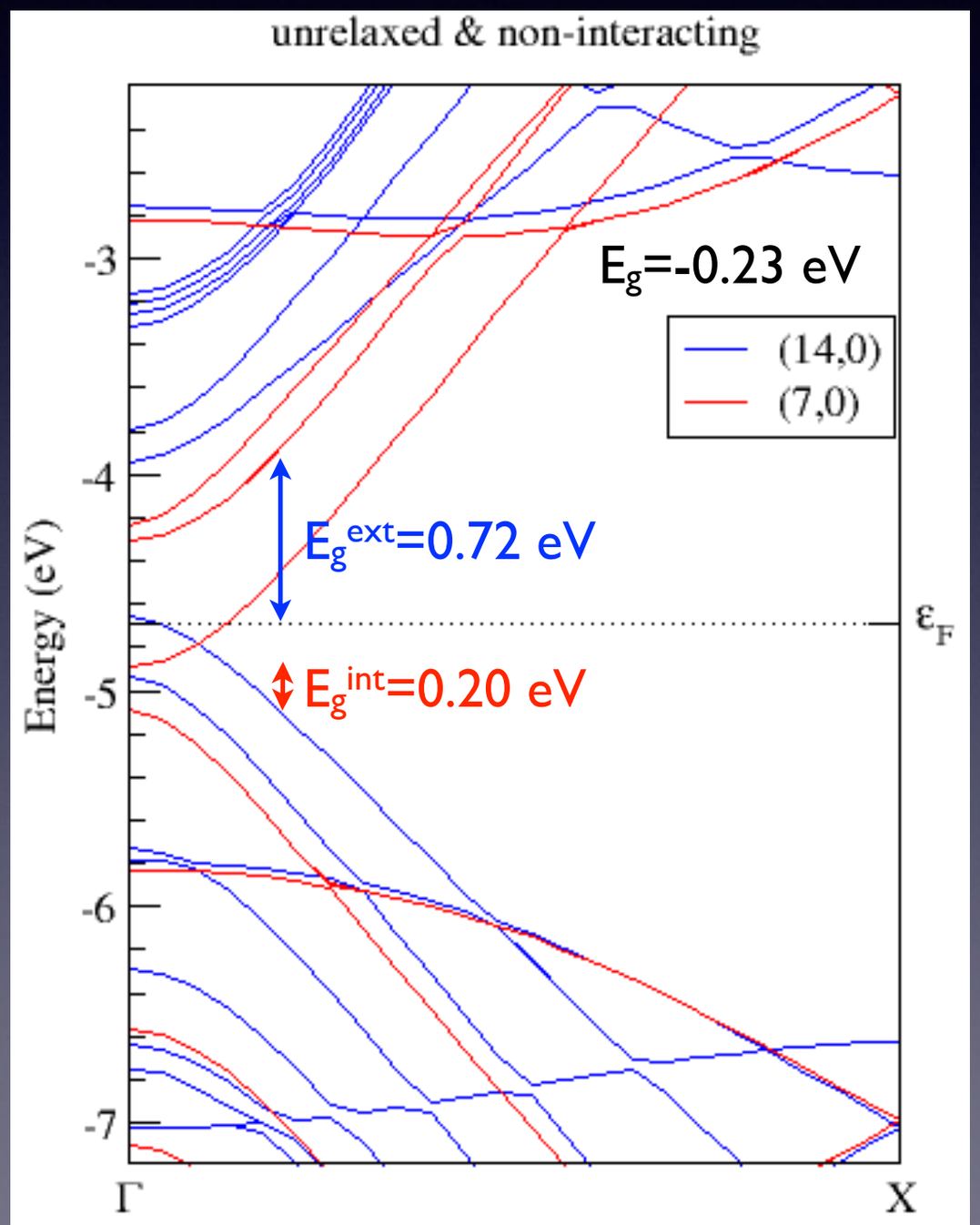
dependance on Δr

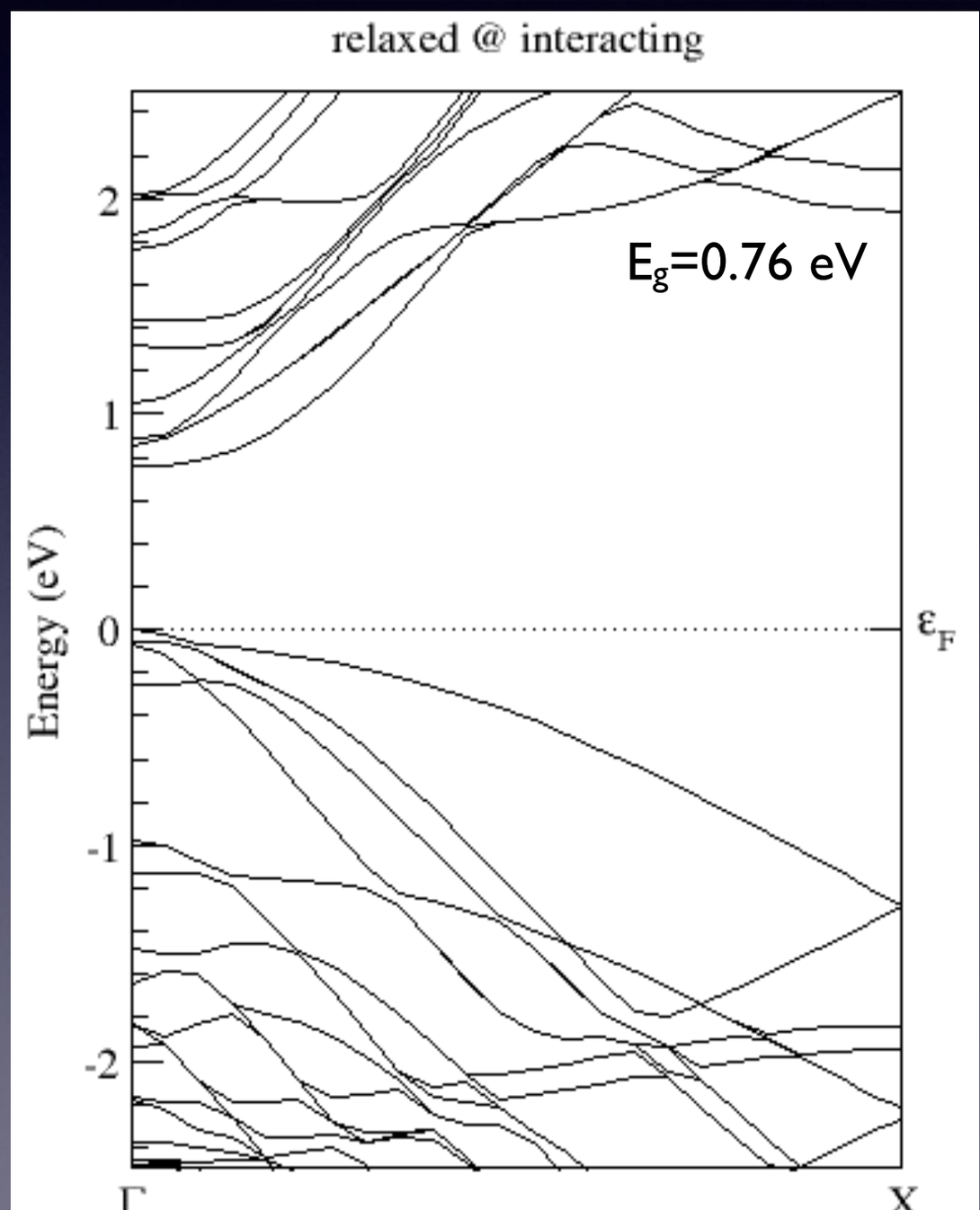


(7,0)@(14,0)

Δr = 2,7 Å

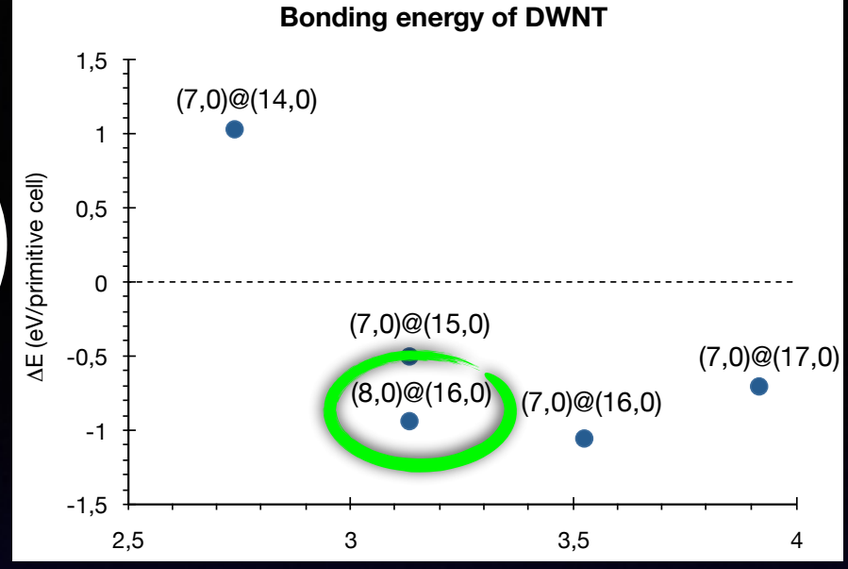

Bonding energy of DWNT
ΔE (eV/primitive cell)
1,5
1
0,5
0
-0,5
-1
-1,5
2,5
3
3,5
4
(7,0)@(14,0)
(7,0)@(15,0)
(8,0)@(16,0)
(7,0)@(16,0)
(7,0)@(17,0)

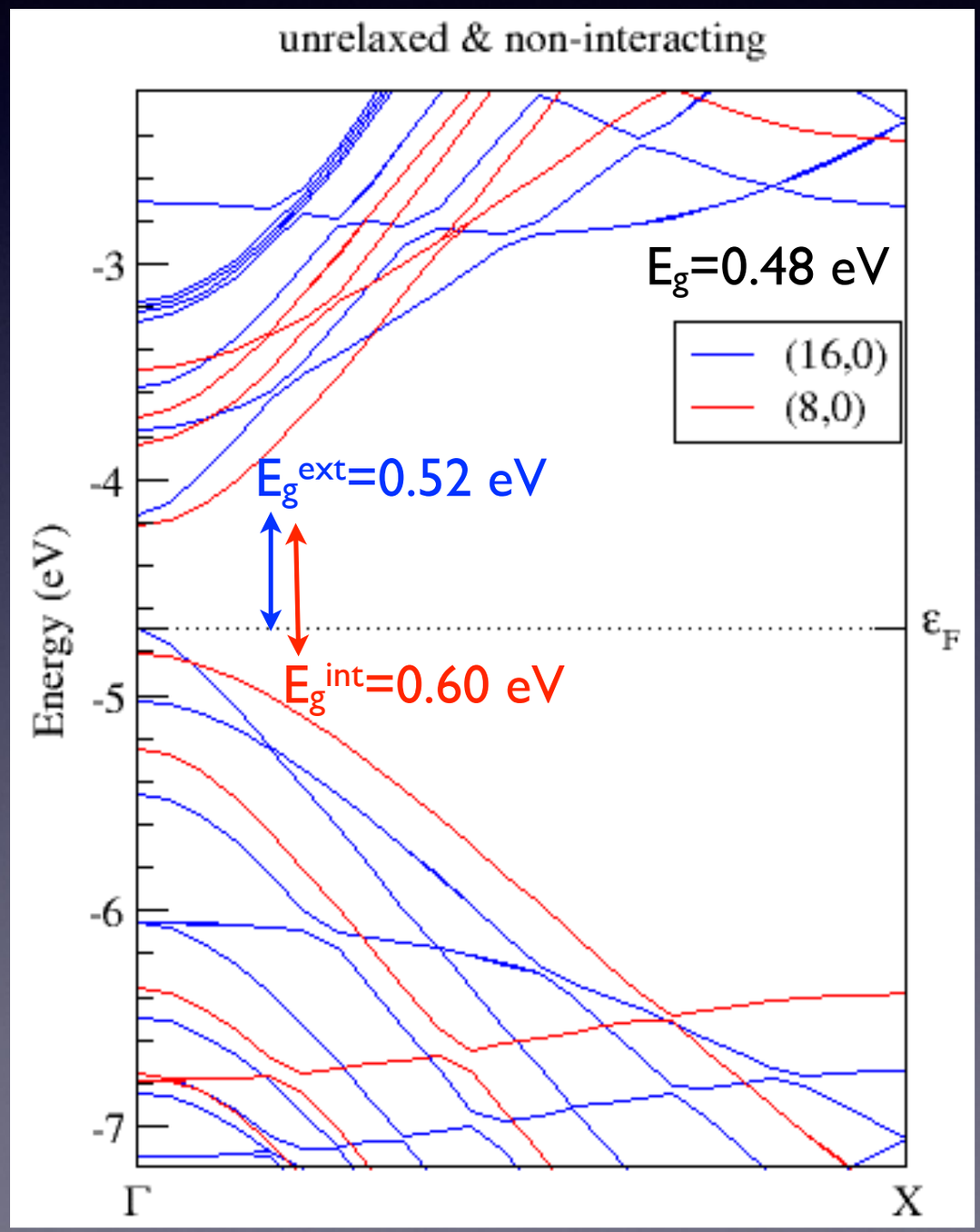

unrelaxed & non-interacting
E_g=-0.23 eV
(14,0)
(7,0)
E_g^{ext}=0.72 eV
E_g^{int}=0.20 eV
Energy (eV)
-3
-4
-5
-6
-7
ε_F
Γ
X

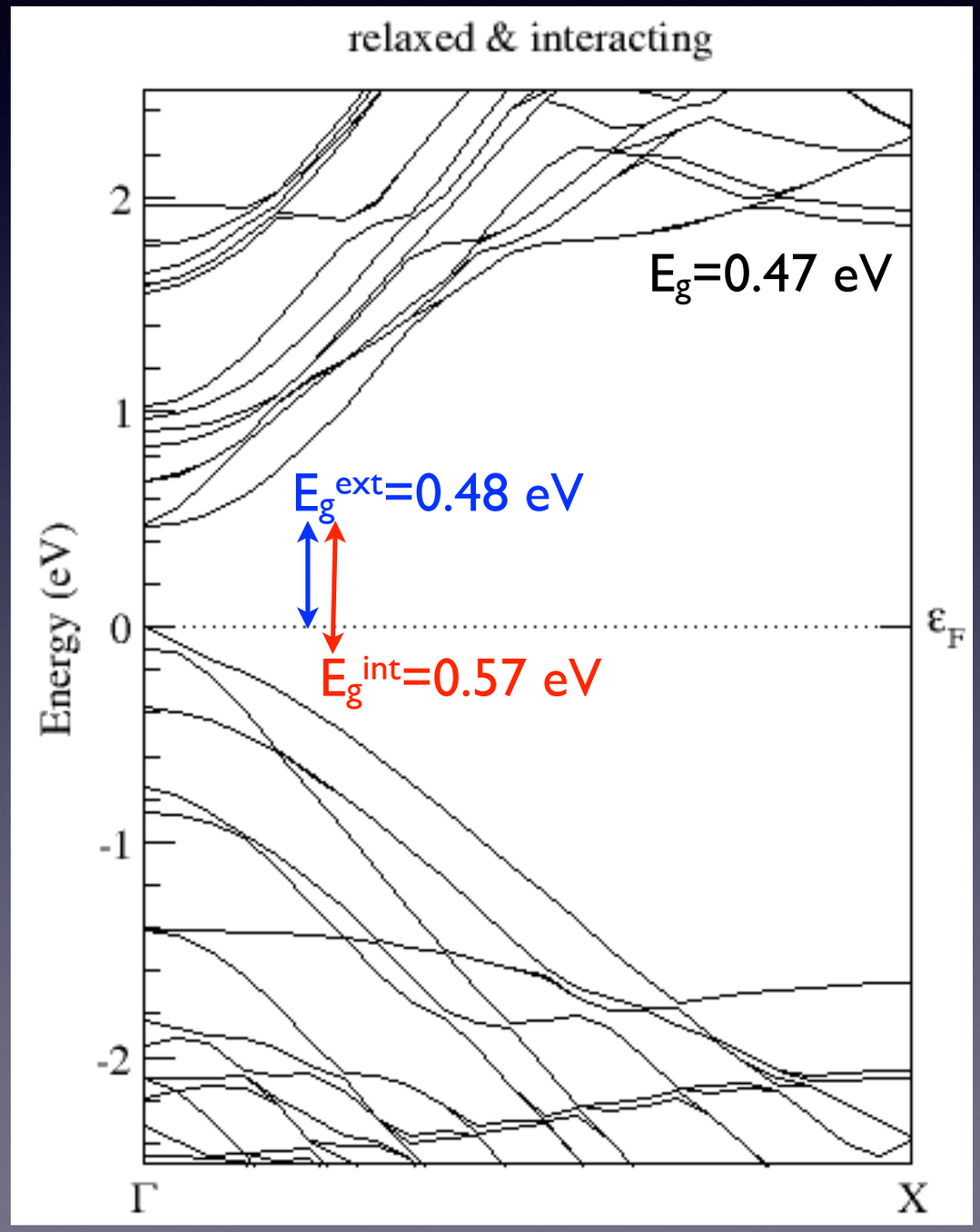

relaxed @ interacting
E_g=0.76 eV
Energy (eV)
2
1
0
-1
-2
ε_F
Γ
X

(8,0)@(16,0)

Δr = 3,1 Å


Bonding energy of DWNT
ΔE (eV/primitive cell)
1,5
1
0,5
0
-0,5
-1
-1,5
2,5
3
3,5
4
(7,0)@(14,0)
(7,0)@(15,0)
(8,0)@(16,0)
(7,0)@(16,0)
(7,0)@(17,0)

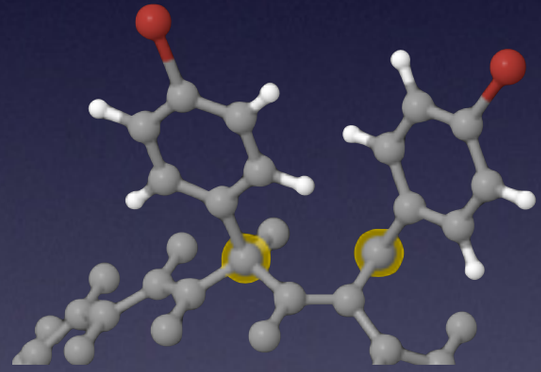

unrelaxed & non-interacting
Energy (eV)
-3
-4
-5
-6
-7
Γ
X
ε_F
(16,0)
(8,0)
E_g=0.48 eV
E_g^ext=0.52 eV
E_g^int=0.60 eV

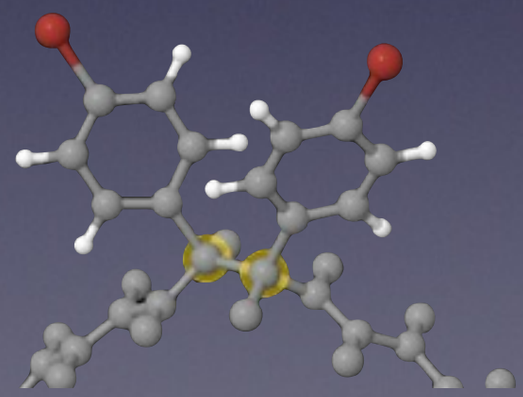

relaxed & interacting
Energy (eV)
2
1
0
-1
-2
Γ
X
ε_F
E_g=0.47 eV
E_g^ext=0.48 eV
E_g^int=0.57 eV

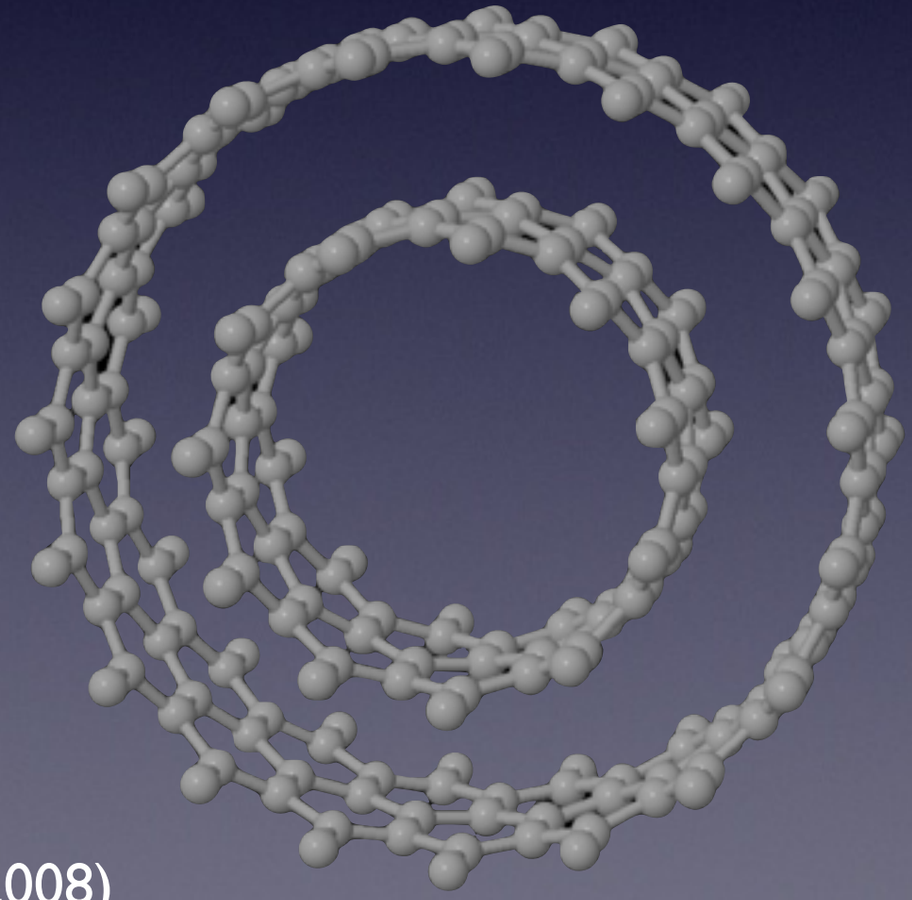
Part 2 : effect of functionalization

- functionalization with bromo-phenyls
- 2 most stables configurations on (5,5) SWNT [6] and graphene [7] (11,0)@(19,0)

- para :
  -1.51eV/pair
  (graphene)
- ortho :
  -1.25eV/pair
  (graphene)





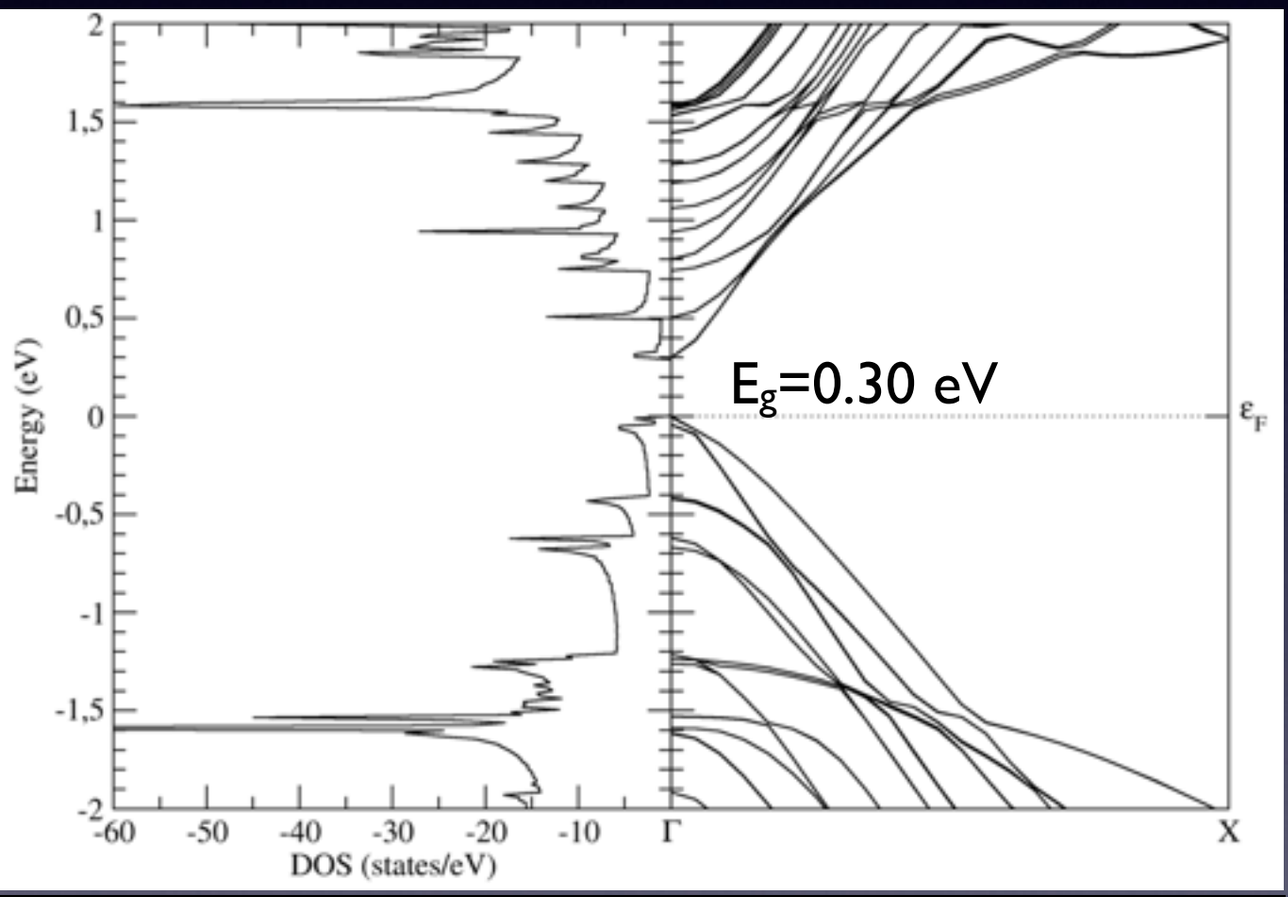


[6] : Lee, Nardelli and Marzari, PRL **95**, 076804 (2005)
[7] : Margine, Bocquet, Blase, Nano Letters **8**, 3315-3319 (2008)

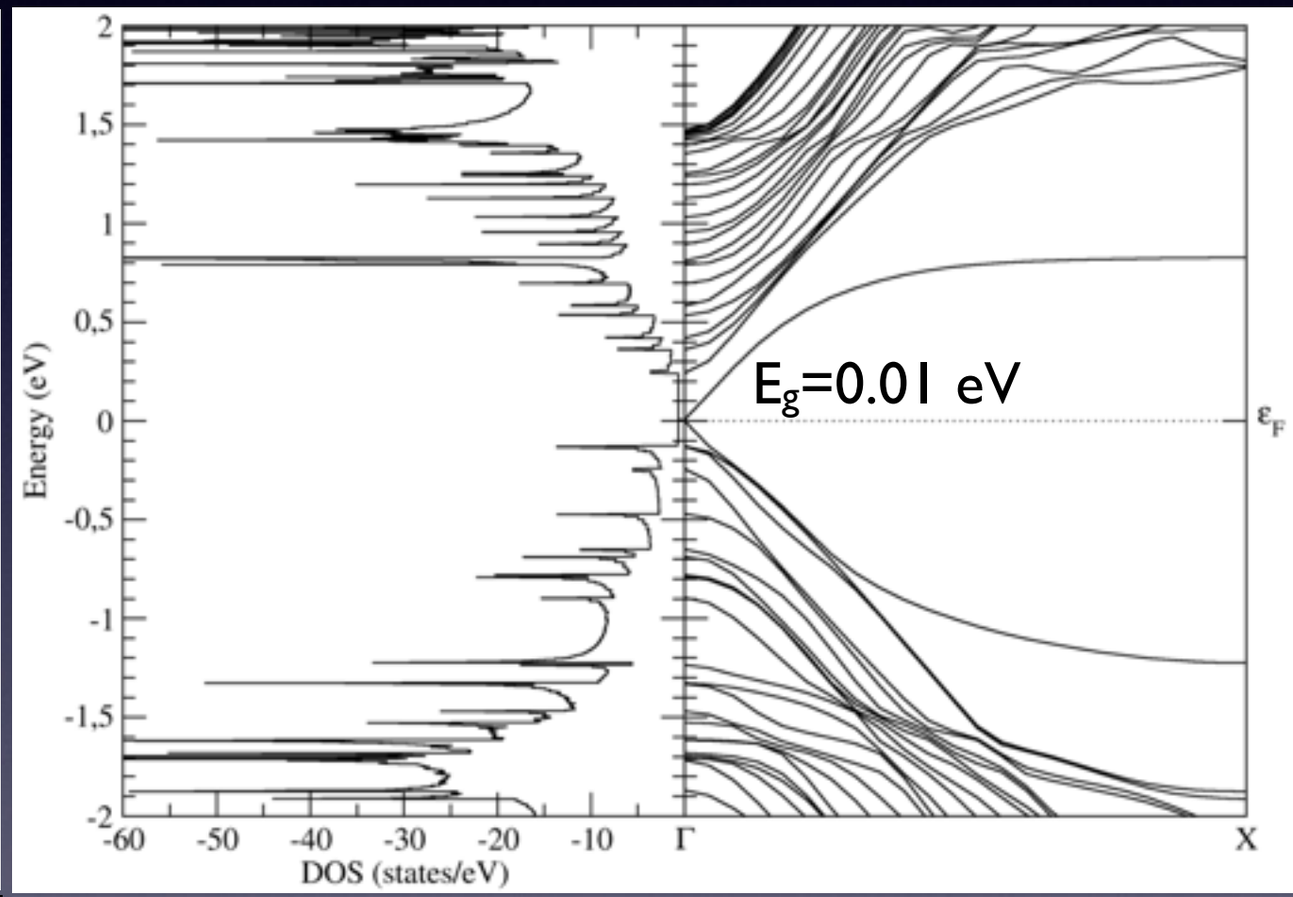
(11,0)@(19,0)

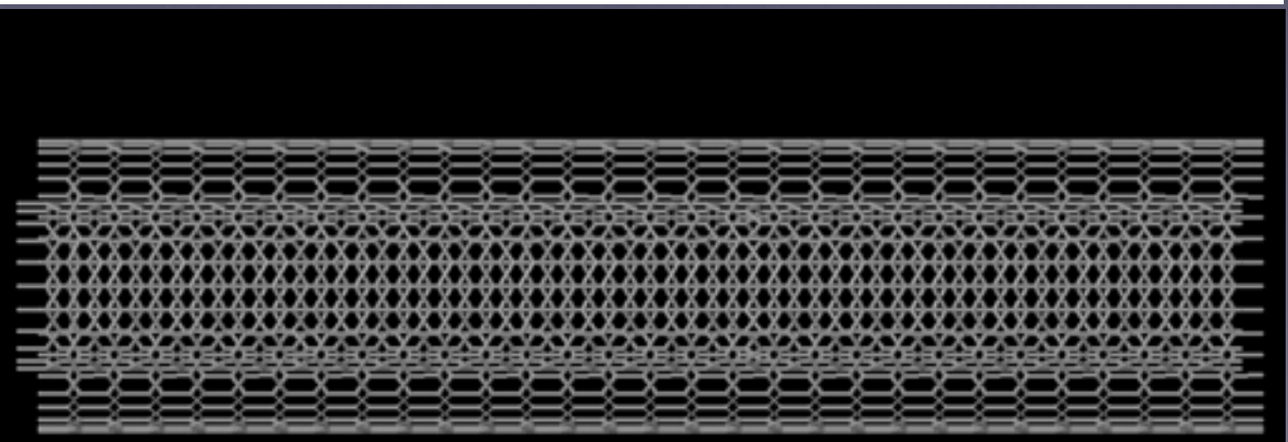
functionalized with bromo-phenyls

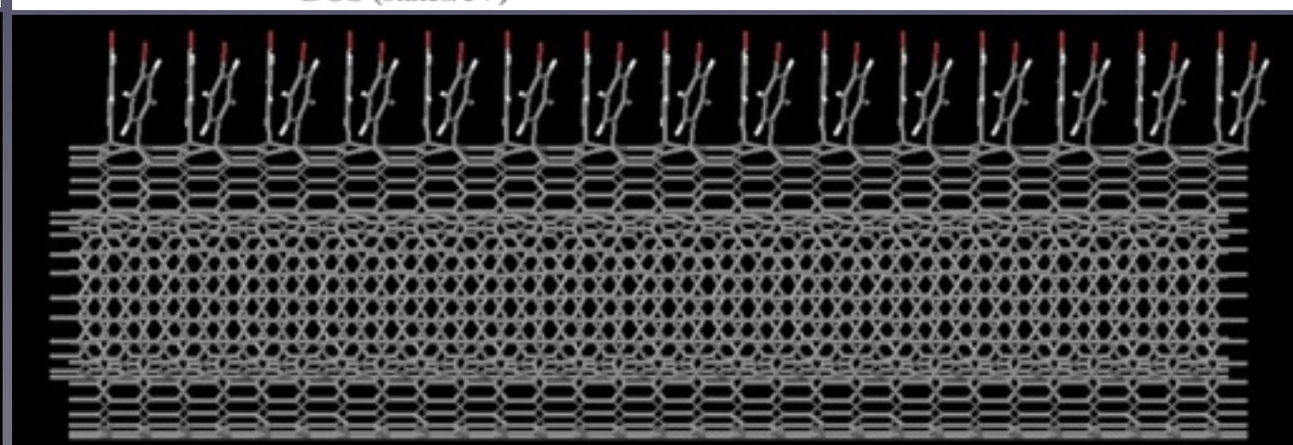
pristine



functinalized (para)



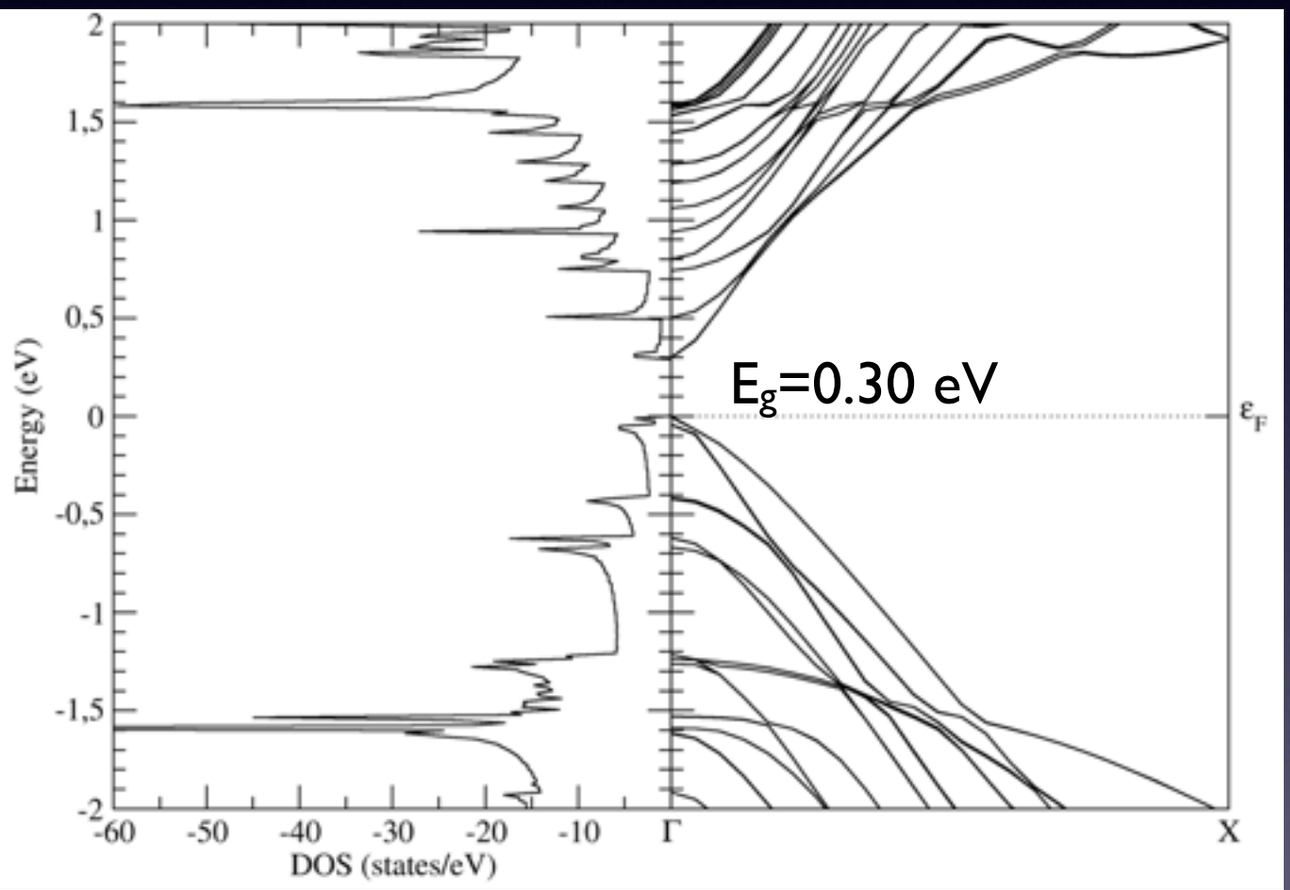




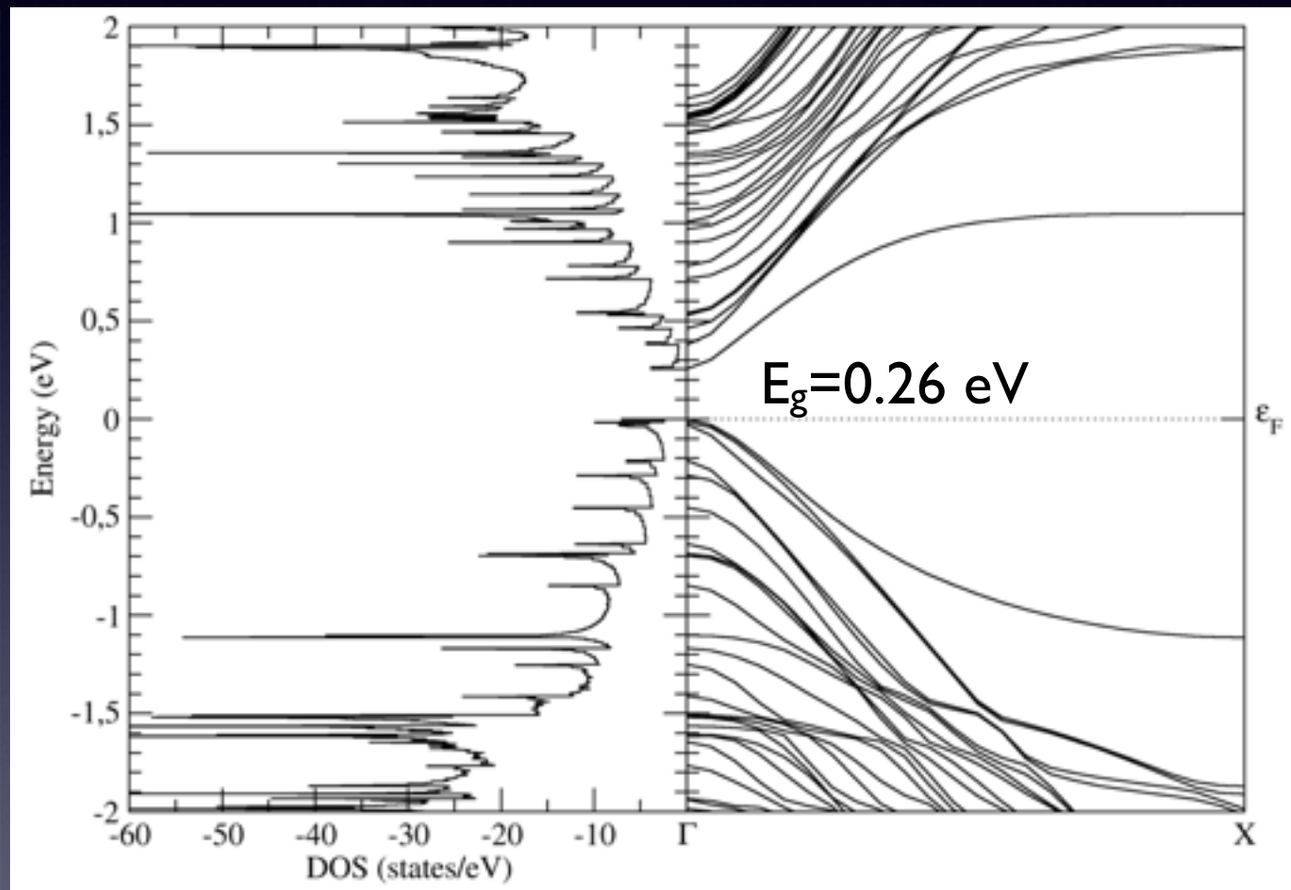
(11,0)@(19,0)

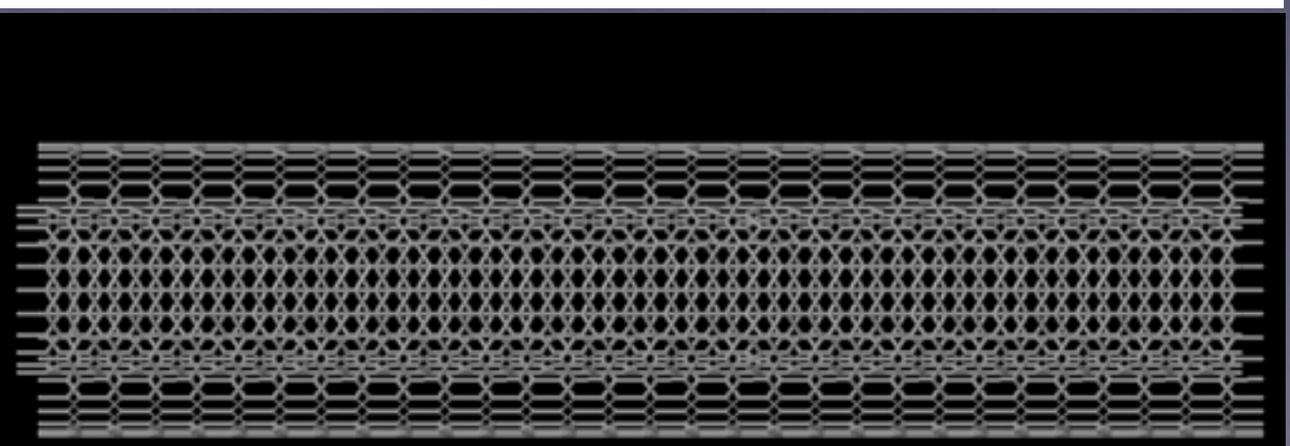
functionalized with bromo-phenyls

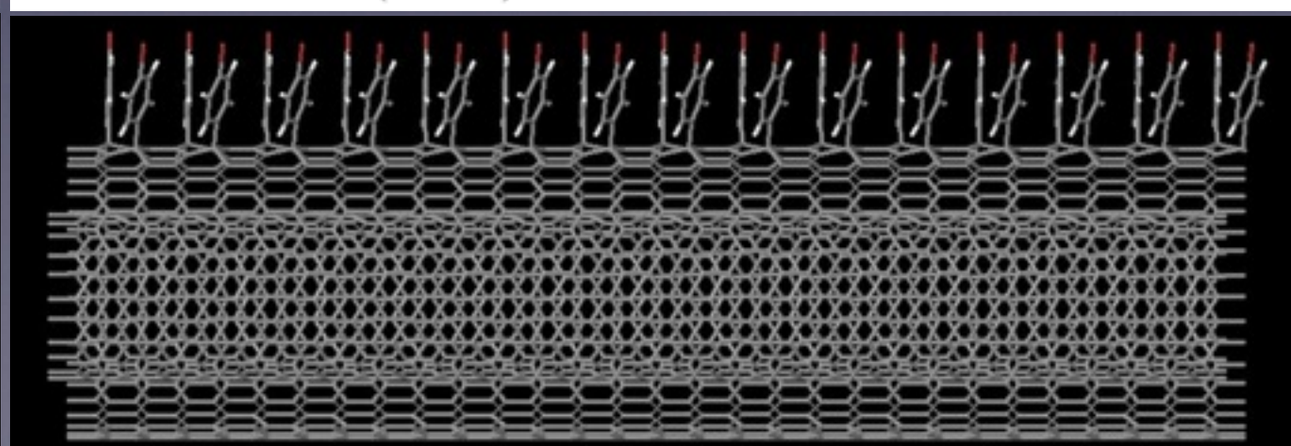
pristine



functionalized (ortho)

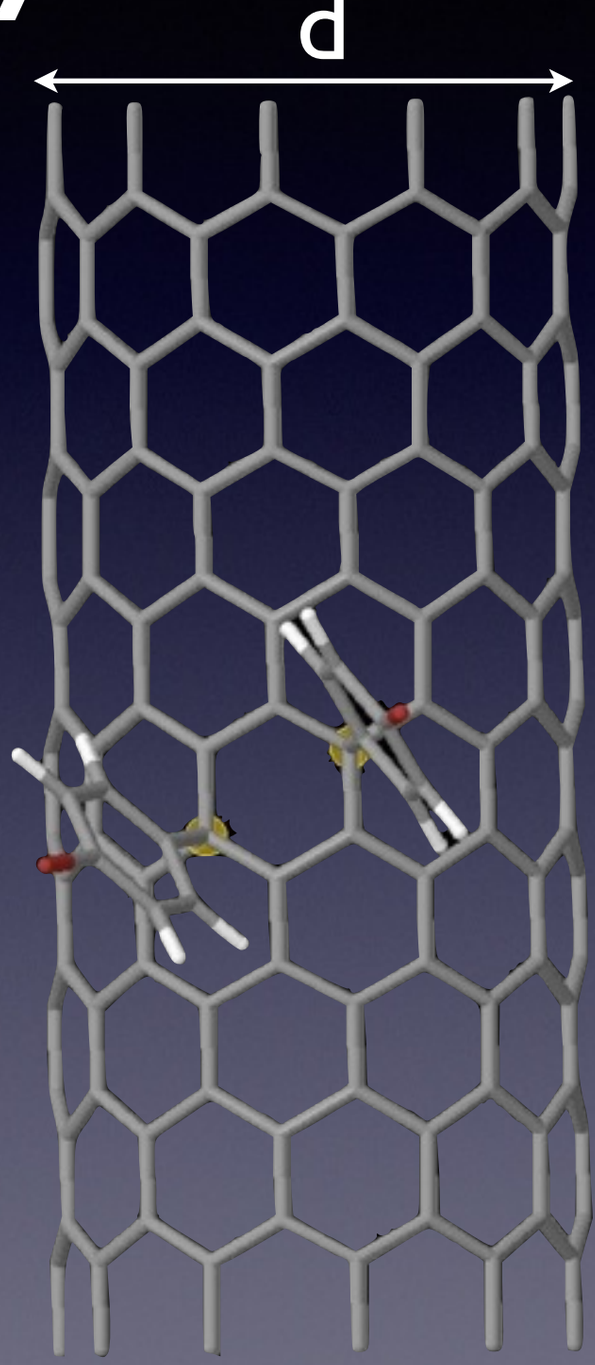






Bonding energy

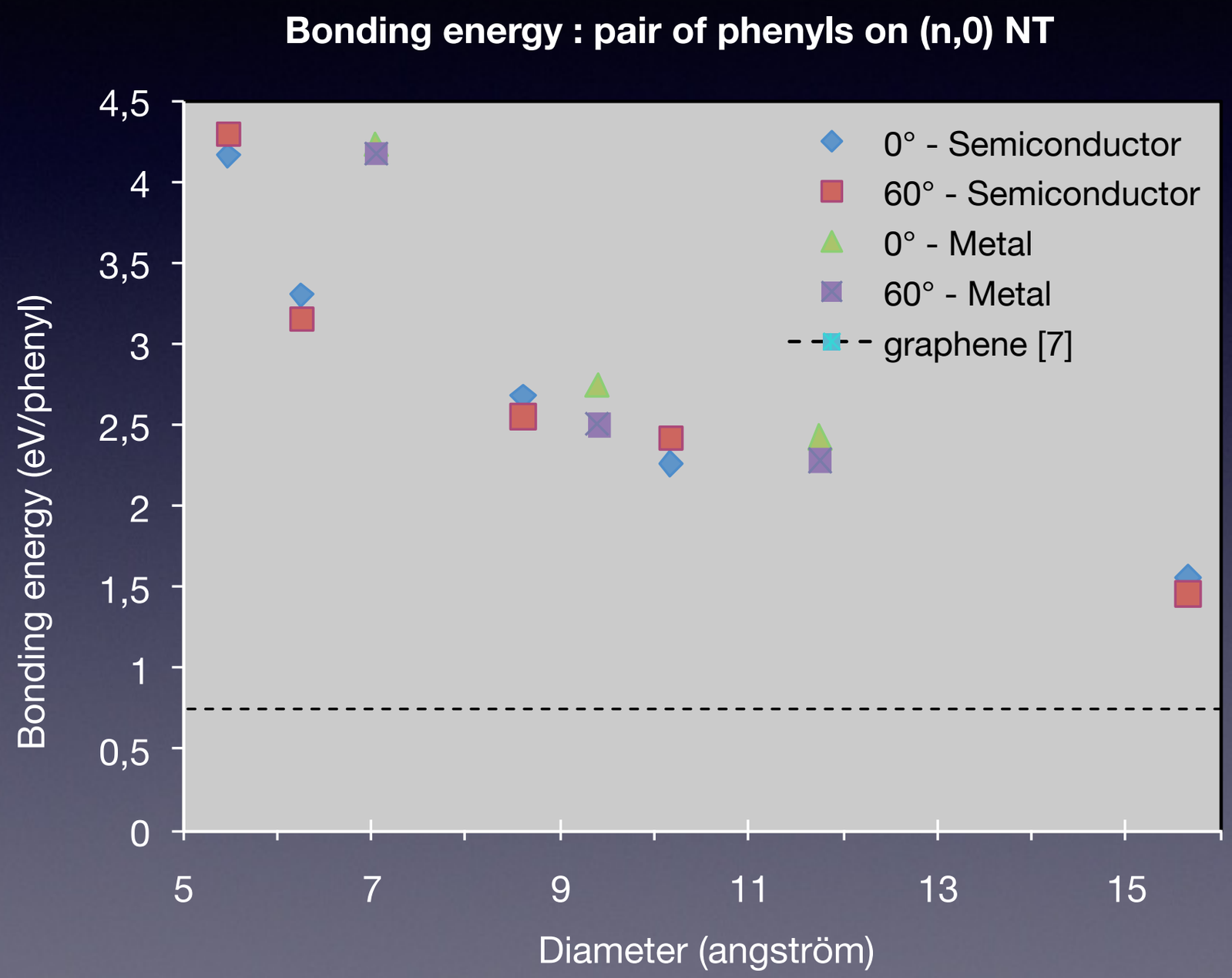
- Which tubes are functionalized?
  - Isolated pairs
  - on zigzag SWNT
  - Para configuration
- Bonding energy (ΔE) with respect to
  - tube diameter (d)
  - metallicity or semiconductivity
  - angle w/r to tube axis (0° or 60°)
- Calculations done using ONETEP [8]



[8] Skylaris, Haynes, Mostofi and Payne, J. Chem. Phys. **122**, 084119 (2005)

Bonding energy

- Trend :
  - E_b ↘ if d ↗ tend to graphene's
  - E_b for M > E_b for S
  - no clear trend for angle



[7] : Margine, Bocquet, Blase, Nano Letters **8**, 3315-3319 (2008)

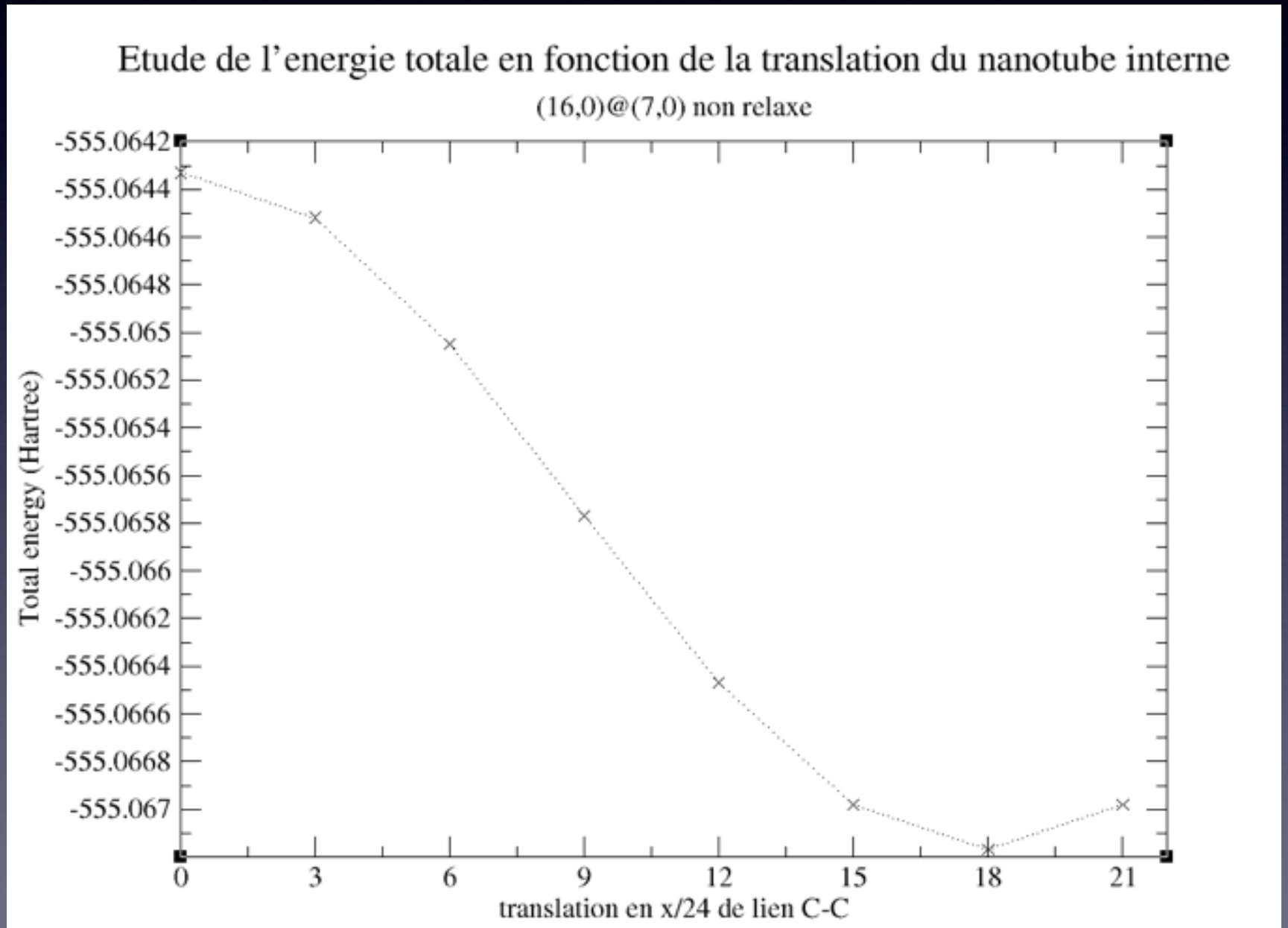
Conclusion

- Band structure of DWNT :
  ~ superposition of SWNT for bonded DWNT
- Effect of functionalisation (bromo-phenyl) :
  electronic states in the gap
- Pairs of phenyls : more sable for
  - small diameters
  - metallic tubes

Acknowledgments

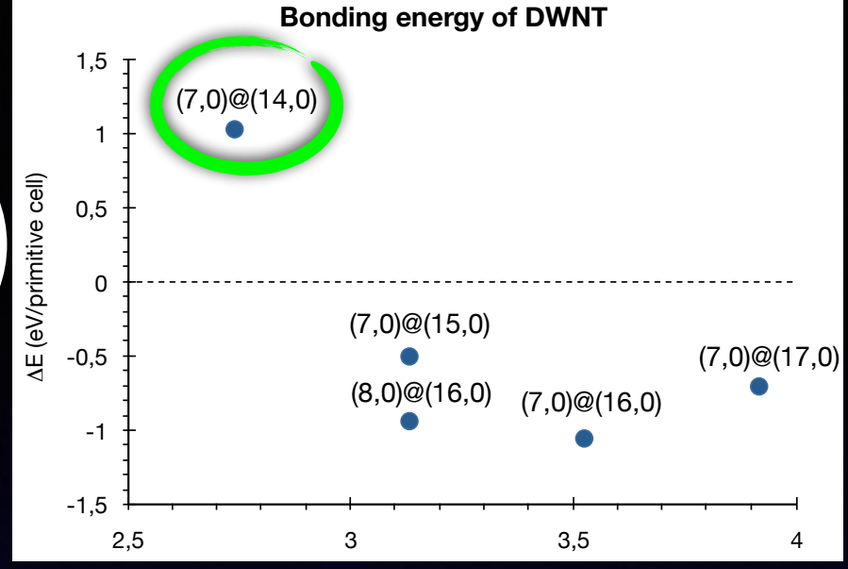
- Delphine Bouilly, Janie Cabana and Richard Martel for the expermiental data on DWNT FETs

Supplements :
DWNT coaxial translation



(7,0)@(14,0)

Δr = 2,7 Å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1,5
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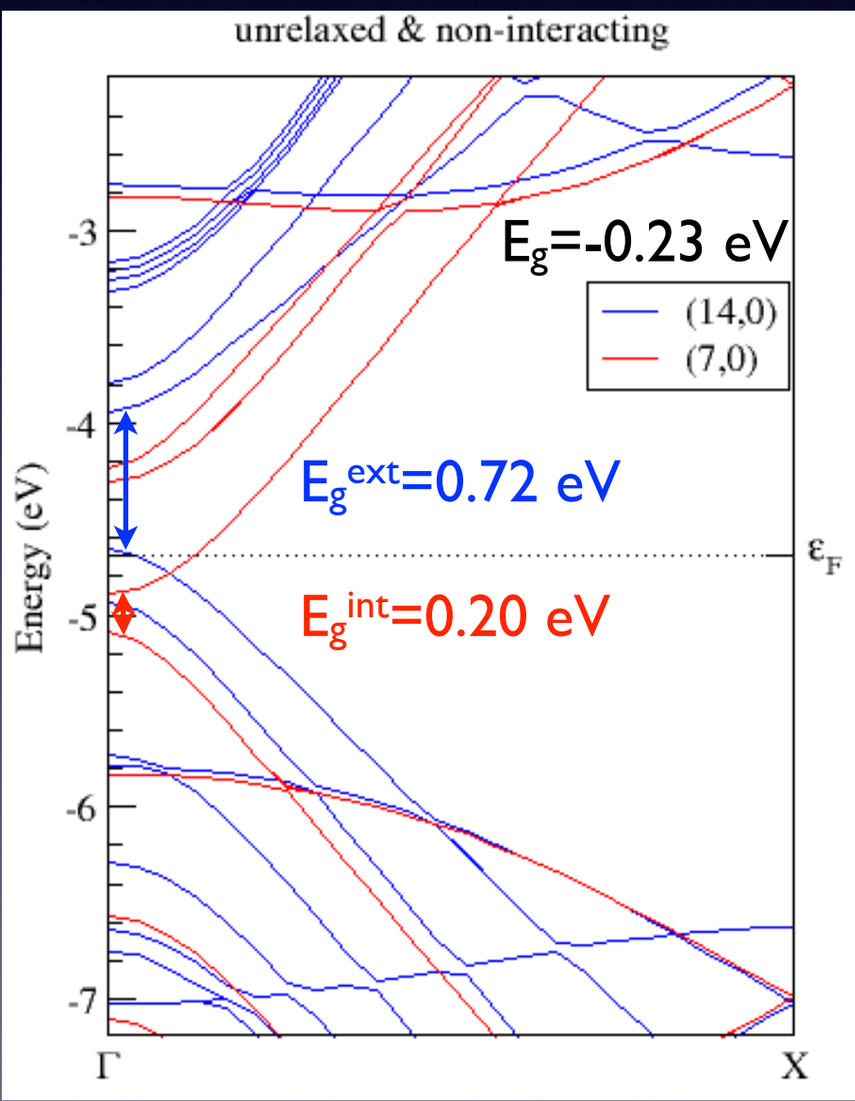
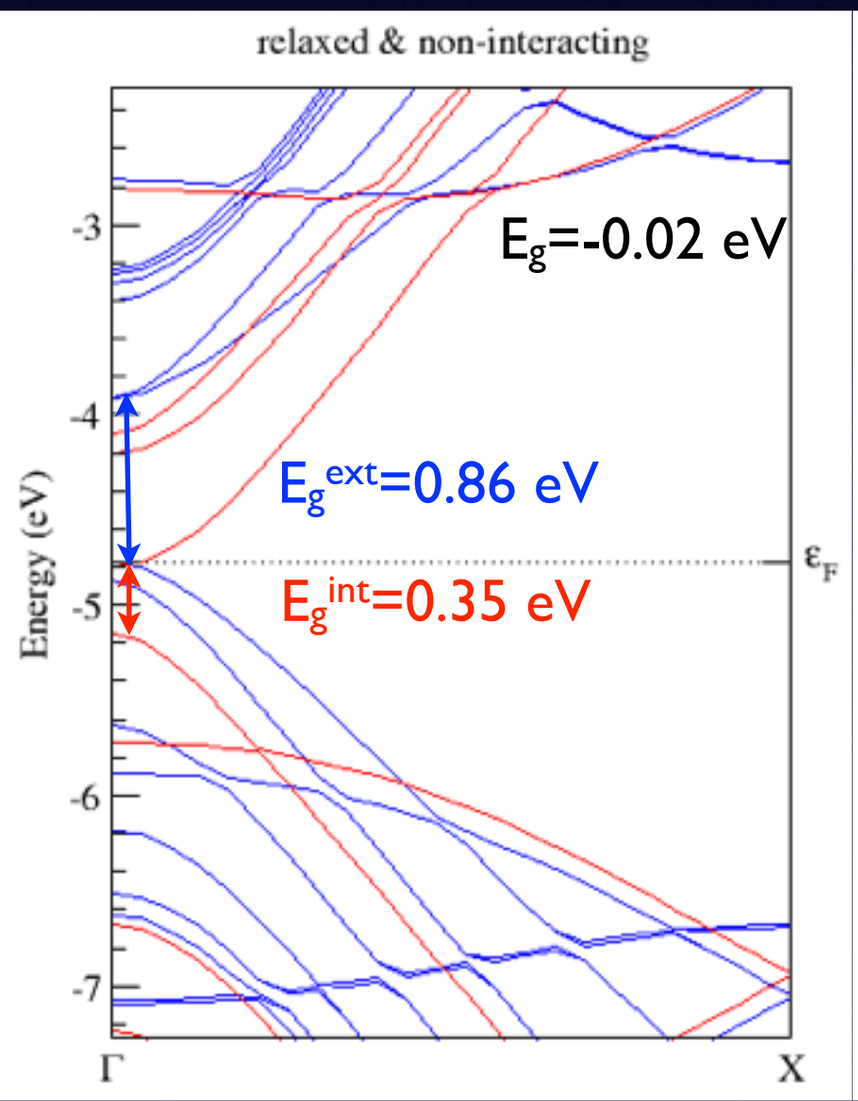
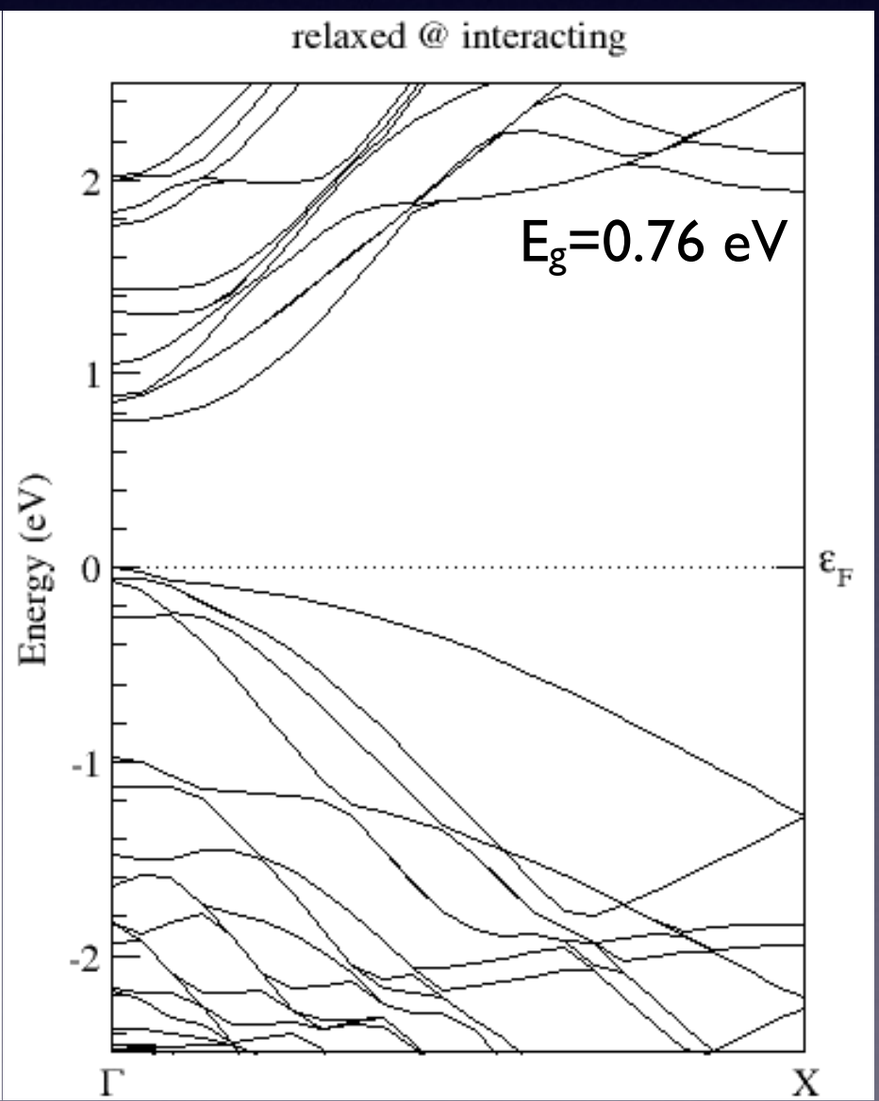
0,5
0
-0,5
-1
-1,5
2,5
3
3,5
4
(7,0)@(14,0)
(7,0)@(15,0)
(8,0)@(16,0)
(7,0)@(16,0)
(7,0)@(17,0)

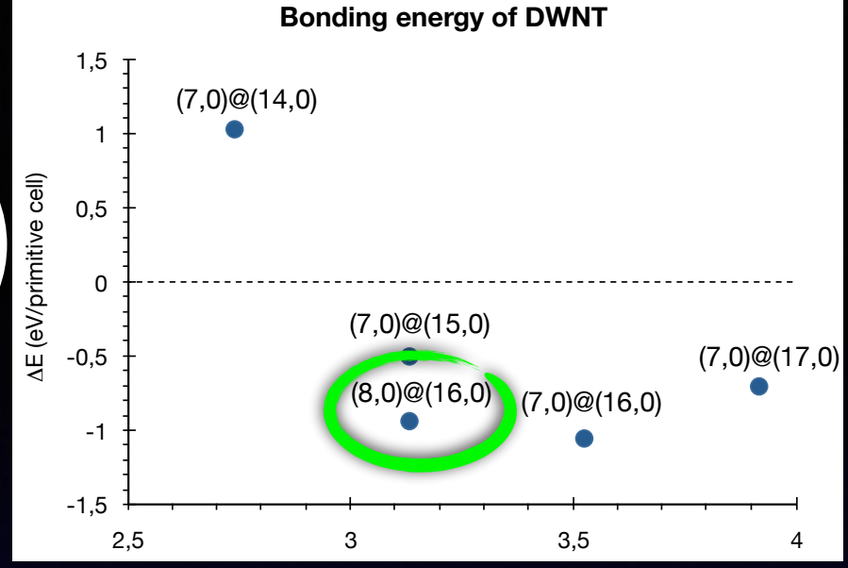

unrelaxed & non-interacting
Energy (eV)
-3
-4
-5
-6
-7
Γ
X
ε_F
E_g=-0.23 eV
(14,0)
(7,0)
E_g^{ext}=0.72 eV
E_g^{int}=0.20 eV


relaxed & non-interacting
Energy (eV)
-3
-4
-5
-6
-7
Γ
X
ε_F
E_g=-0.02 eV
E_g^{ext}=0.86 eV
E_g^{int}=0.35 eV


relaxed @ interacting
Energy (eV)
2
1
0
-1
-2
Γ
X
ε_F
E_g=0.76 eV

(8,0)@(16,0)

Δr = 3,1 Å


Bonding energy of DWNT
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1,5
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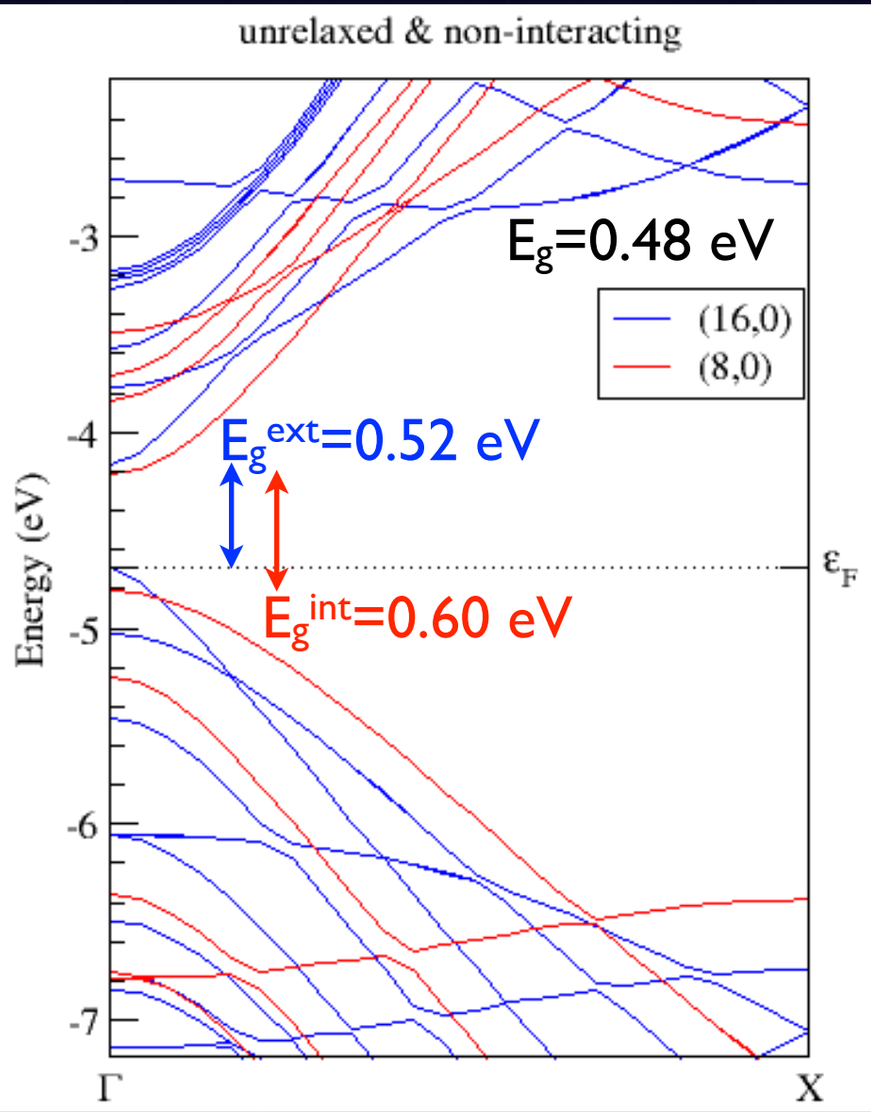
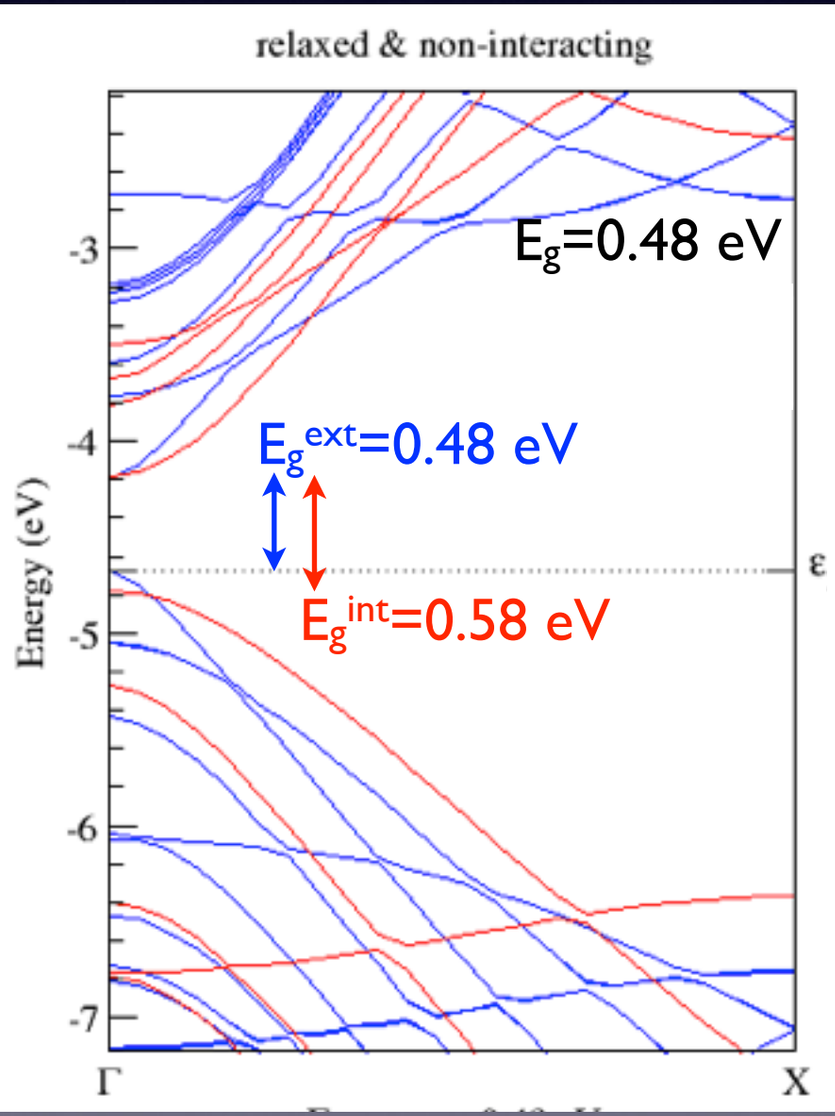
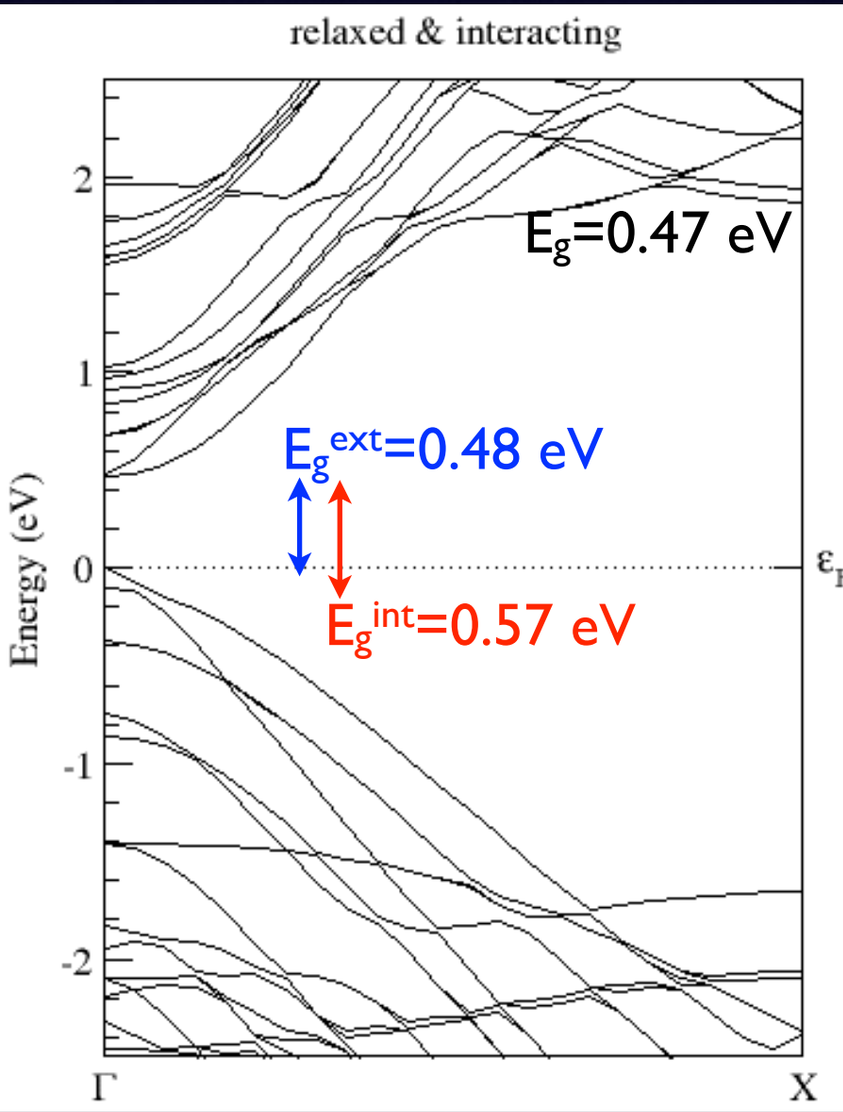
(7,0)@(15,0)
(8,0)@(16,0)
(7,0)@(16,0)
(7,0)@(17,0)

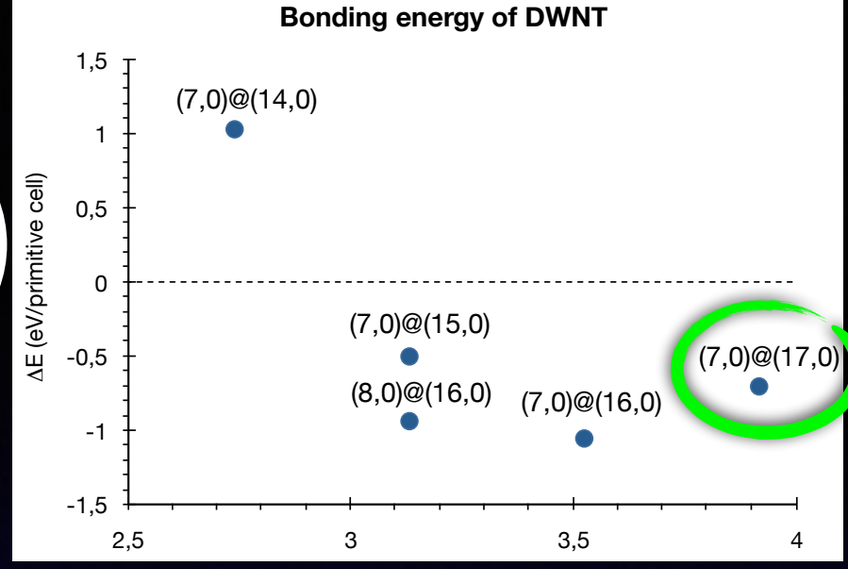

unrelaxed & non-interacting
Eg=0.48 eV
(16,0)
(8,0)
Eg ext=0.52 eV
Eg int=0.60 eV
Energy (eV)
εF
Γ
X


relaxed & non-interacting
Eg=0.48 eV
Eg ext=0.48 eV
Eg int=0.58 eV
Energy (eV)
Γ
X


relaxed & interacting
Eg=0.47 eV
Eg ext=0.48 eV
Eg int=0.57 eV
Energy (eV)
εF
Γ
X

(7,0)@(17,0)

Δr = 3,9 Å


Bonding energy of DWNT
ΔE (eV/primitive cell)
1,5
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0,5
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-0,5
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2,5
3
3,5
4
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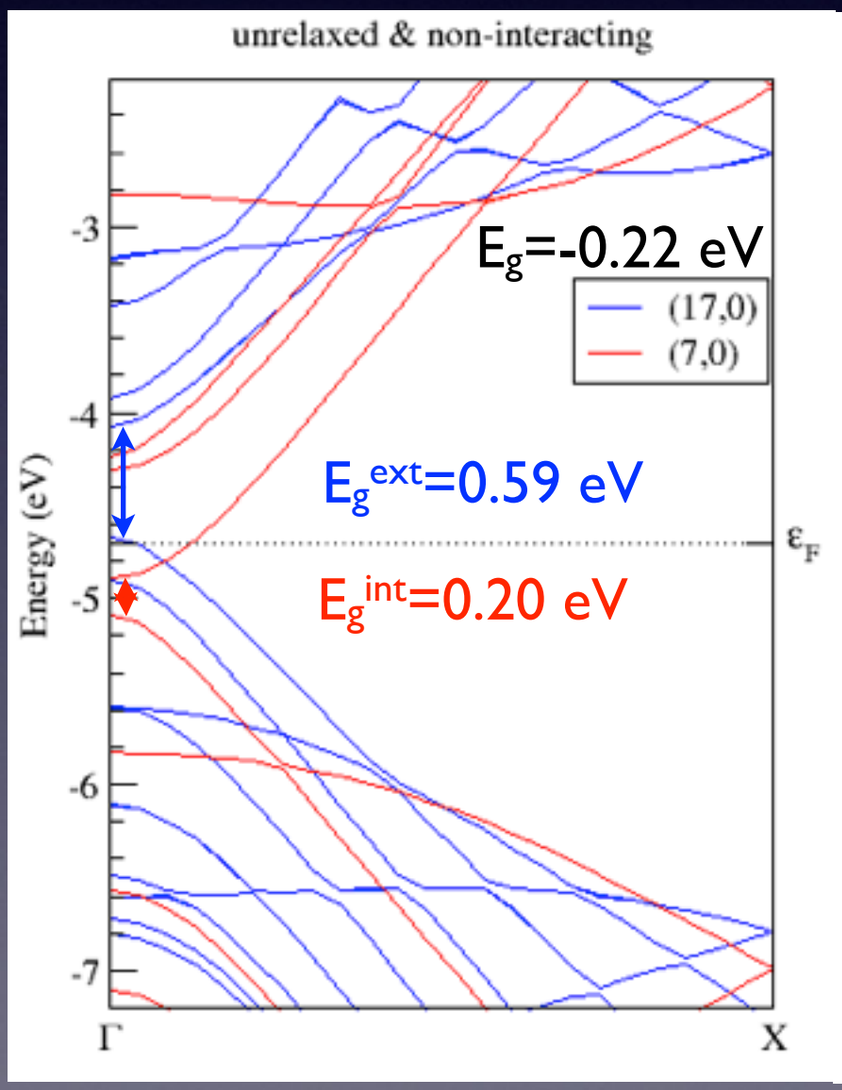
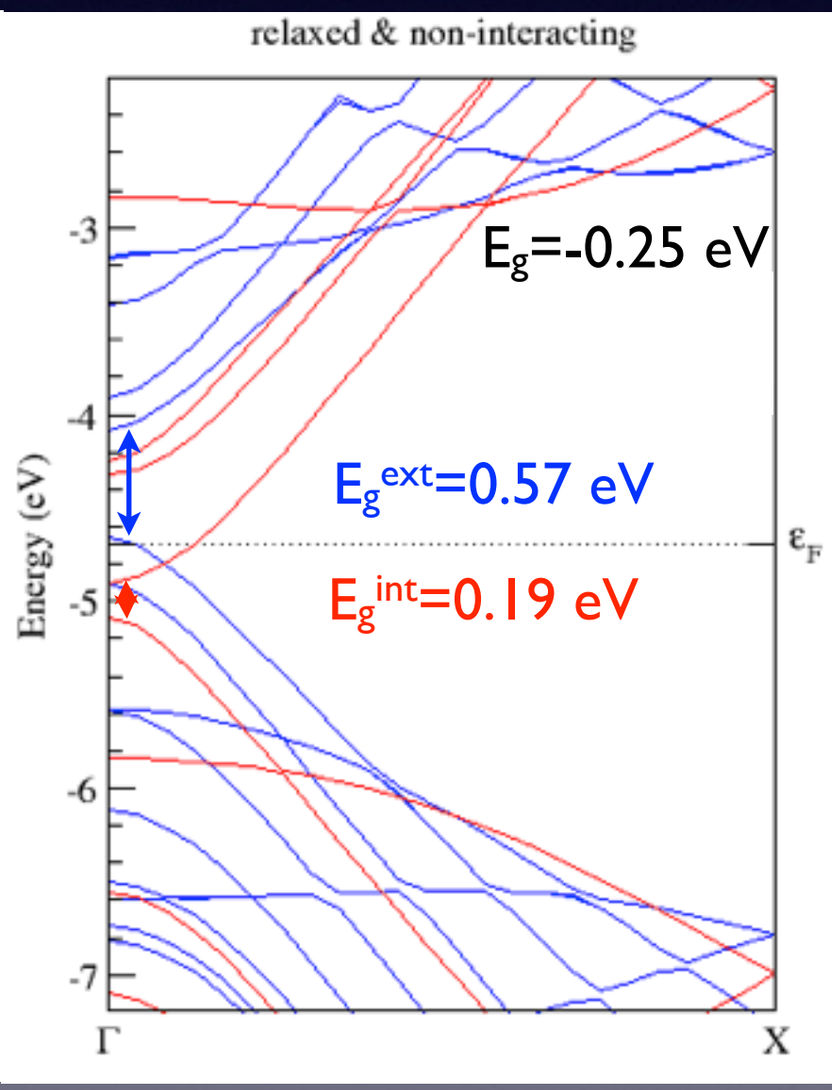
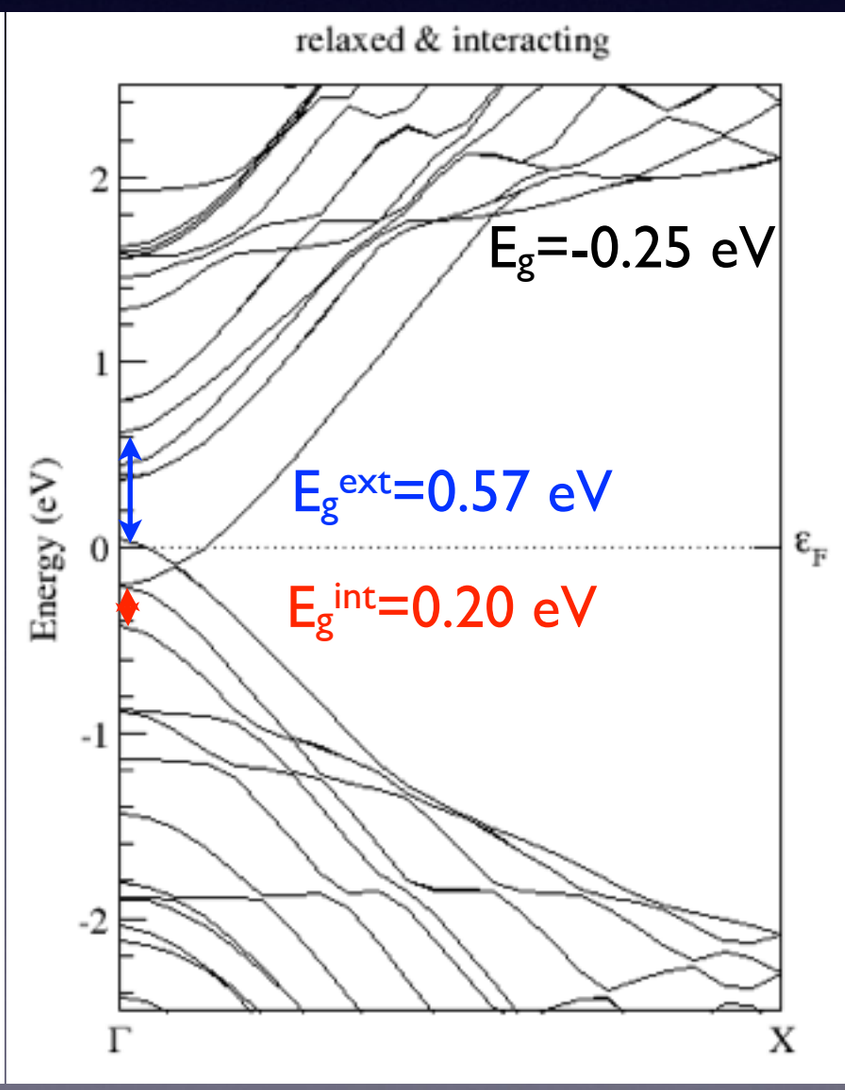
(7,0)@(15,0)
(8,0)@(16,0)
(7,0)@(16,0)
(7,0)@(17,0)


unrelaxed & non-interacting
E_g=-0.22 eV
(17,0)
(7,0)
E_g^{ext}=0.59 eV
E_g^{int}=0.20 eV
Energy (eV)
ε_F
Γ
X


relaxed & non-interacting
E_g=-0.25 eV
E_g^{ext}=0.57 eV
E_g^{int}=0.19 eV
Energy (eV)
ε_F
Γ
X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X