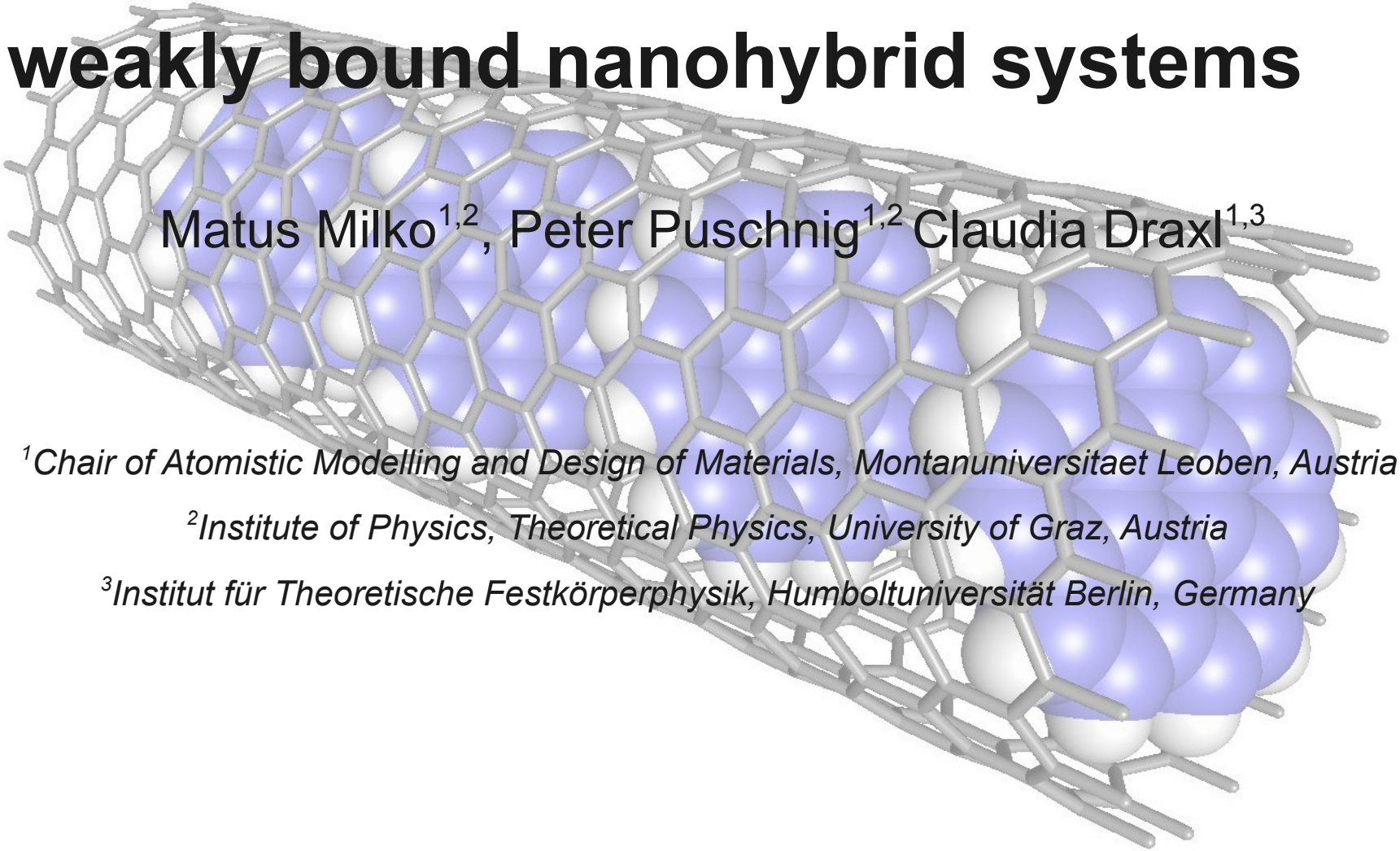
Understanding the electronic structure of weakly bound nanohybrid systems



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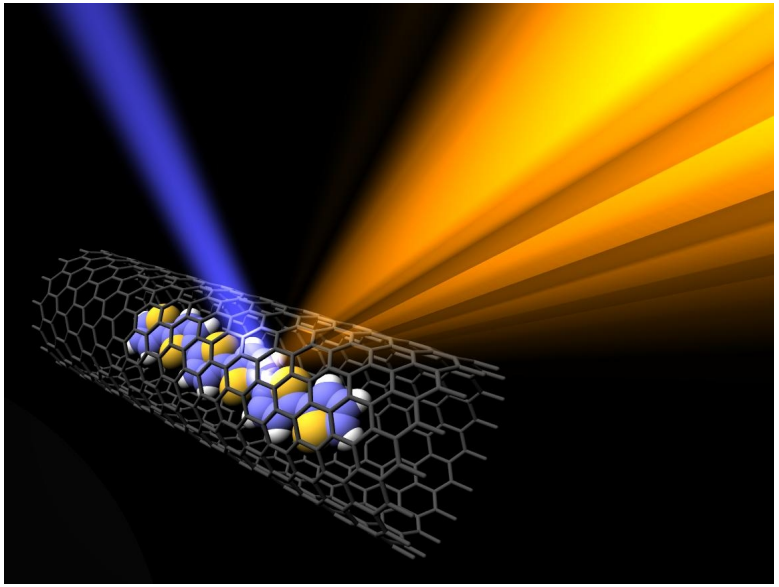
[3]*Institut für Theoretische Festkörperphysik, Humboltuniversität Berlin, Germany*

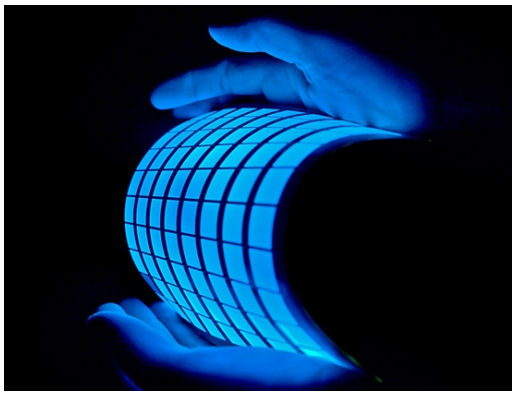
Motivation



understanding the system

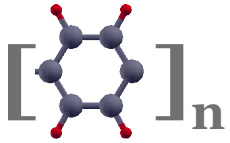
synthesis

materials with desired properties

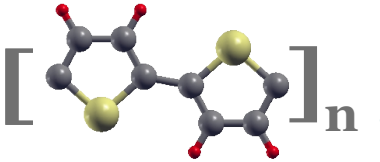


Systems

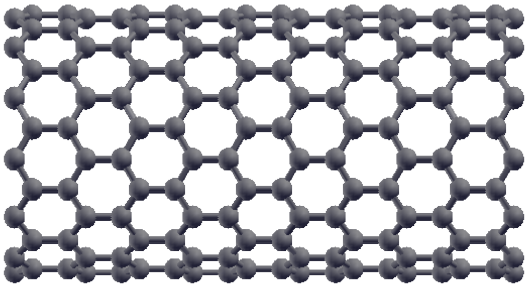
polyparaphenylene@(n,0)

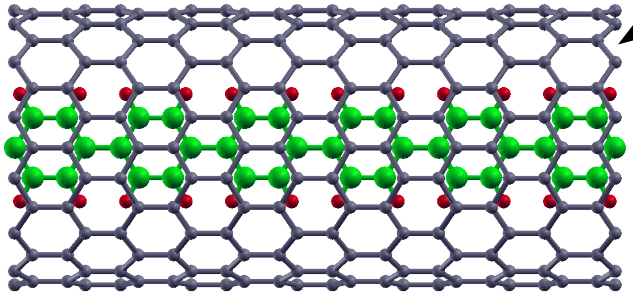
PPP 

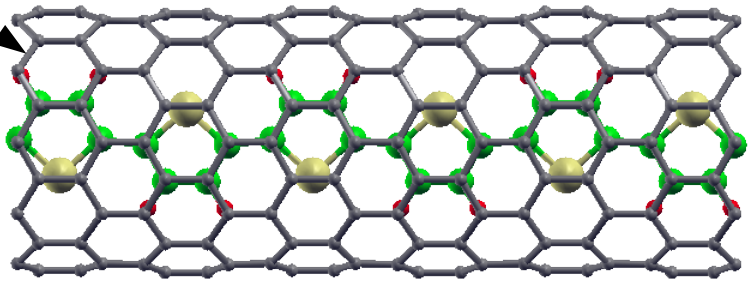
polythiphene@(n,0)

 pT

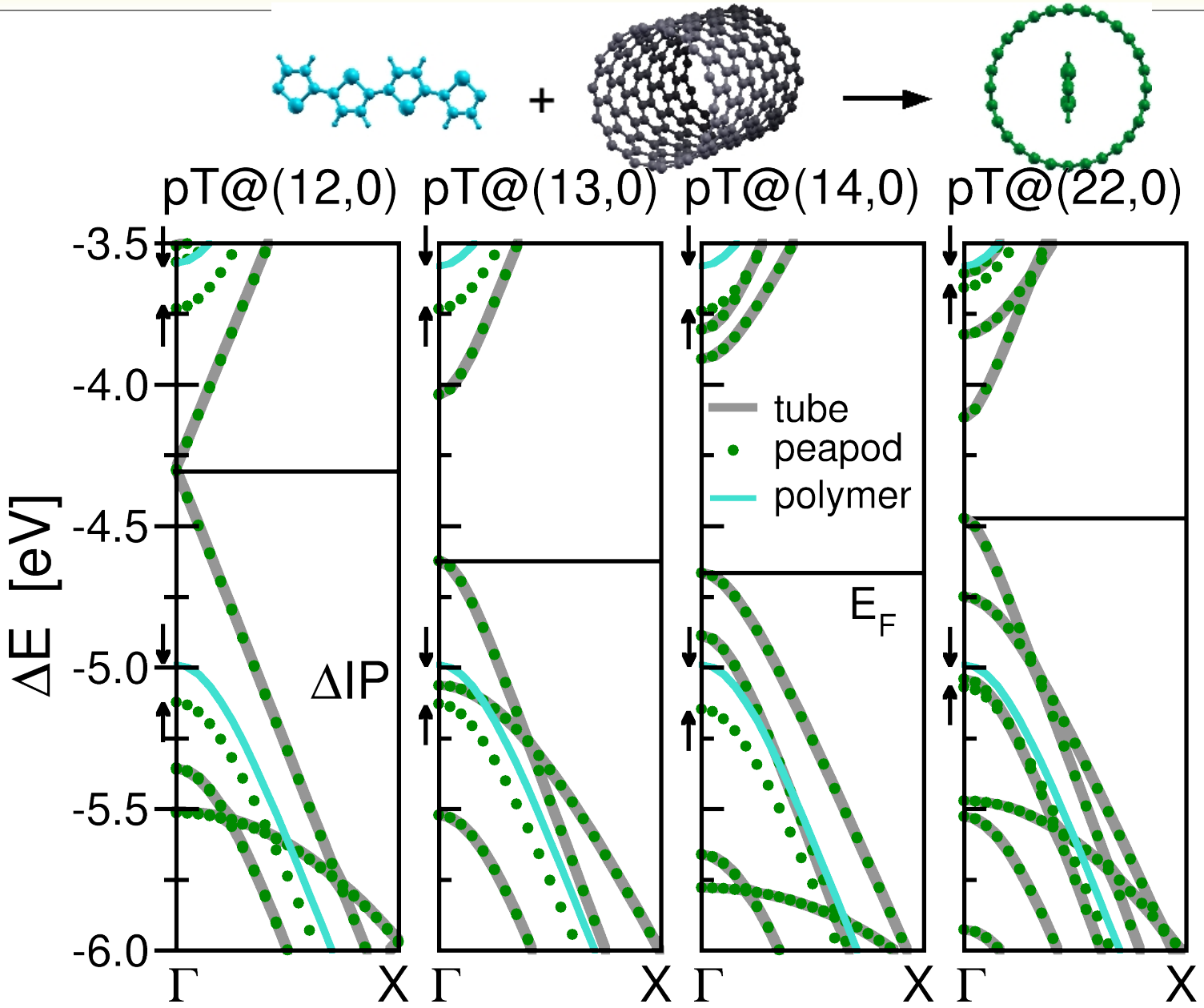
(n,0); n= 10 ,..., ∞



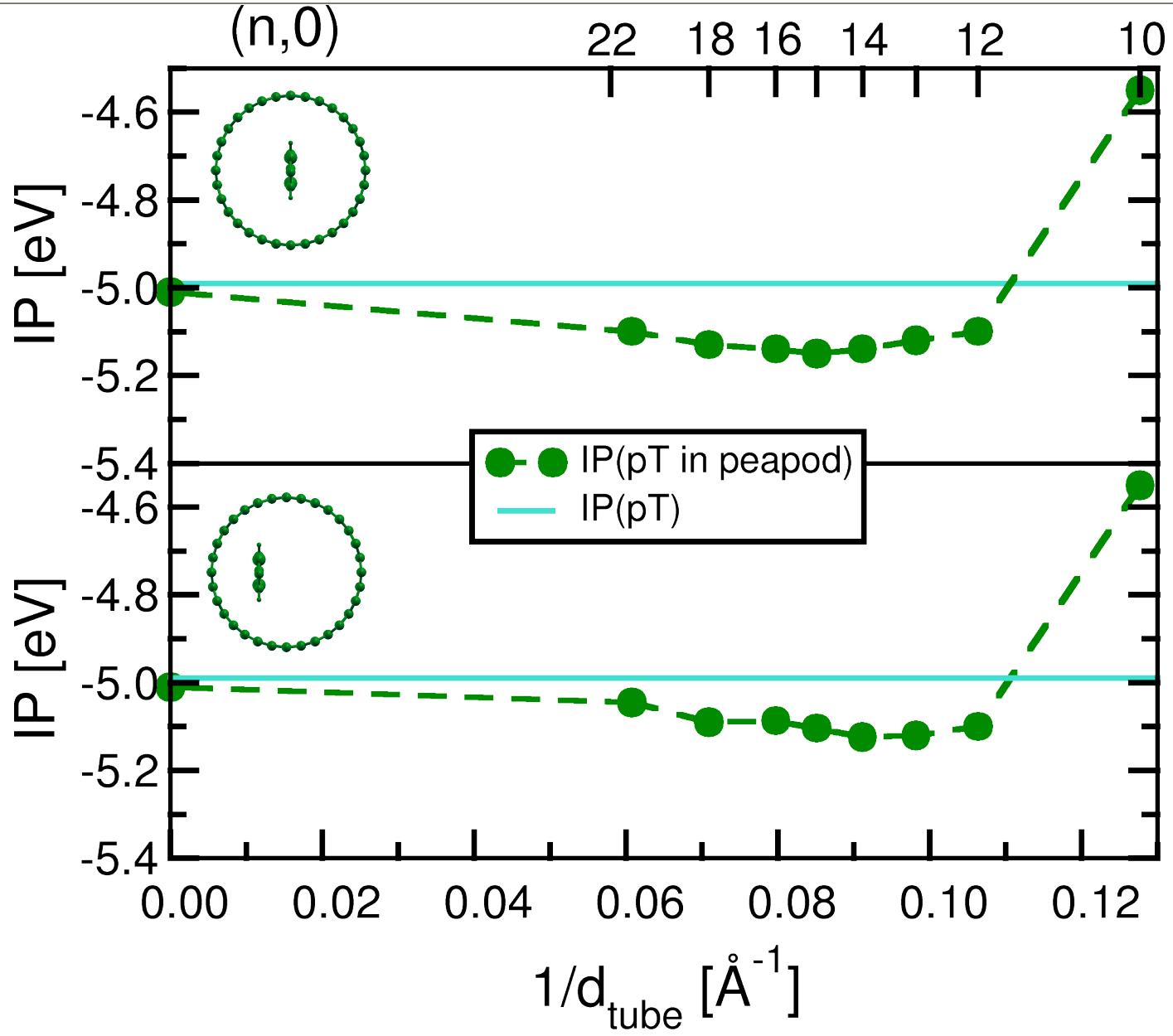




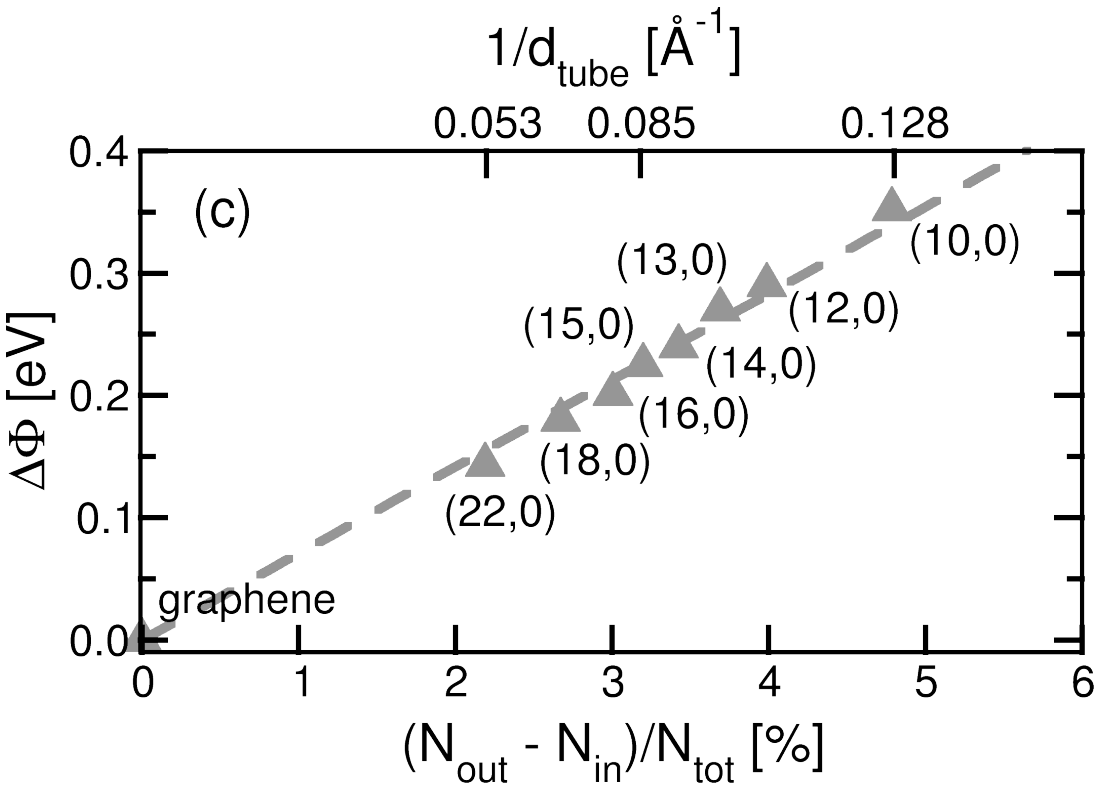
Electronic structure DFT

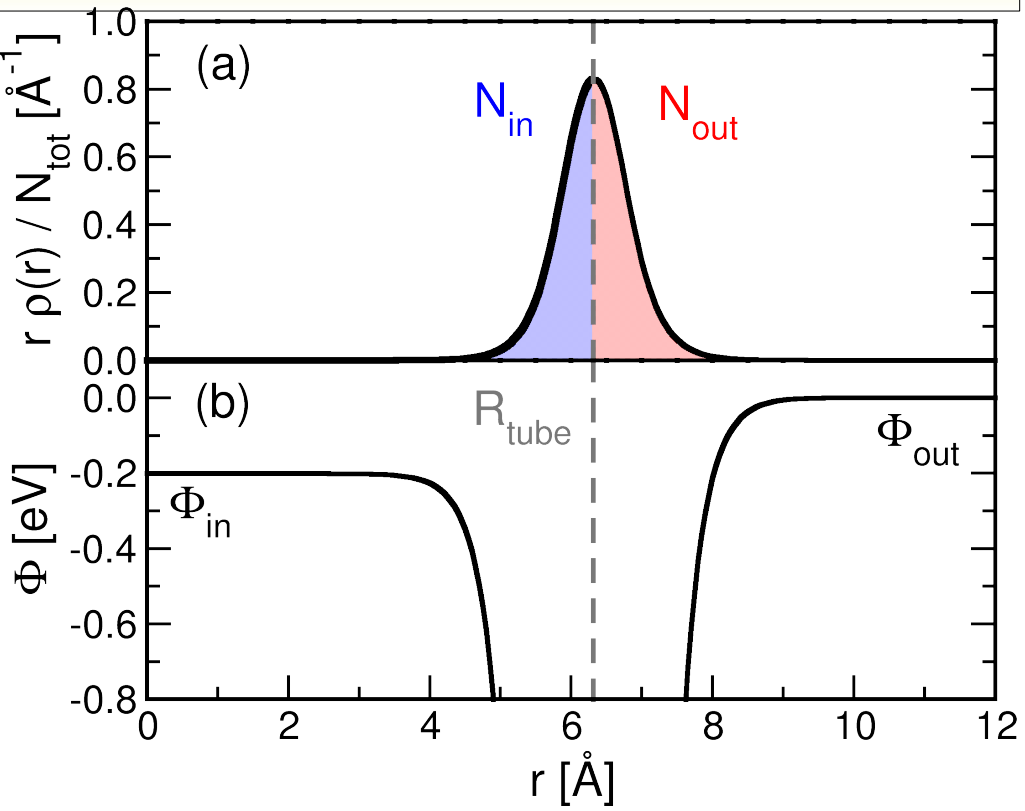


Errors in IP


(n,0)
22
18
16
14
12
10
-4.6
-4.8
-5.0
-5.2
-5.4
IP [eV]
IP(pT in peapod)
IP(pT)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
1/d_tube [Å^-1]

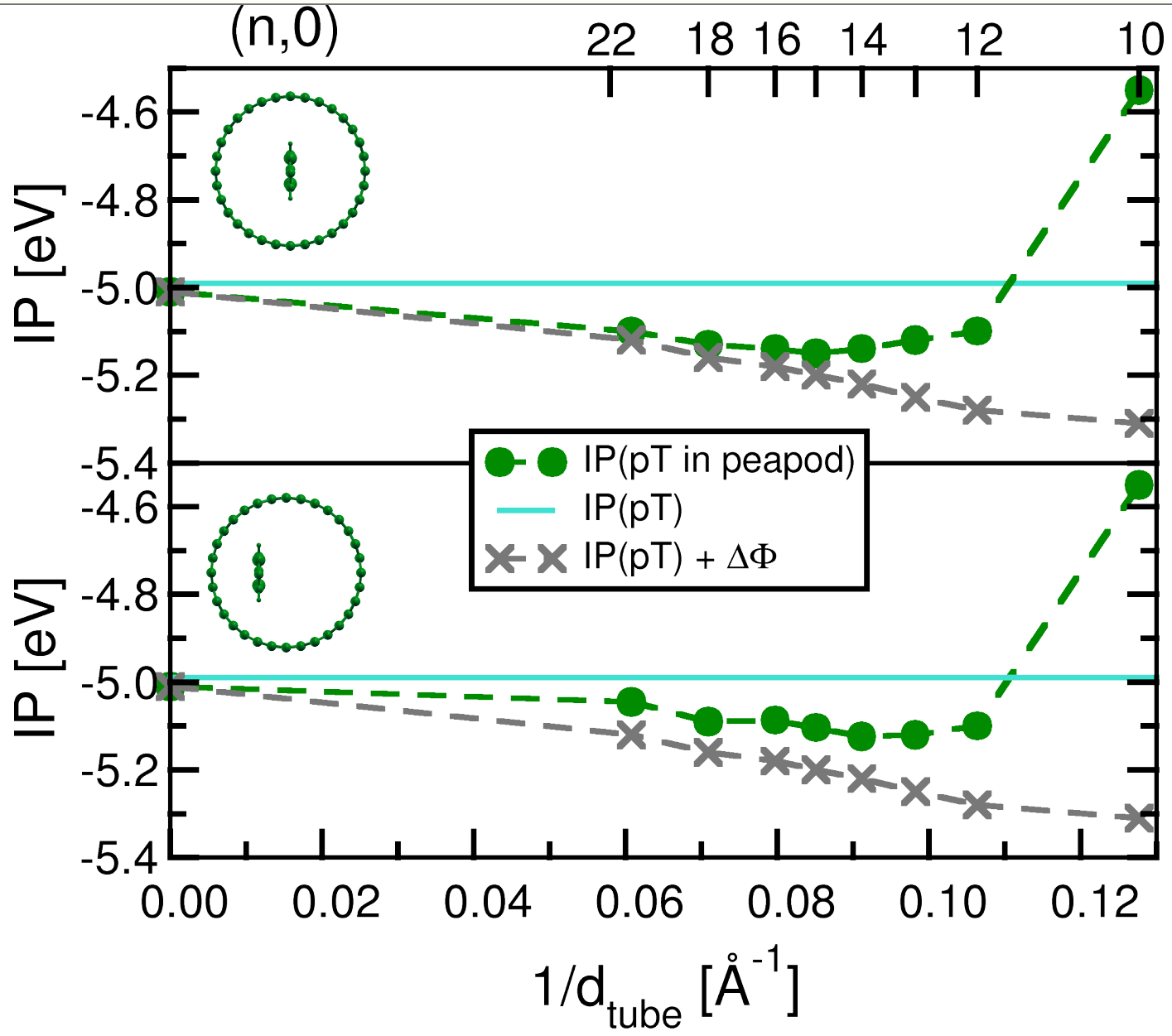
Effect of the curvature





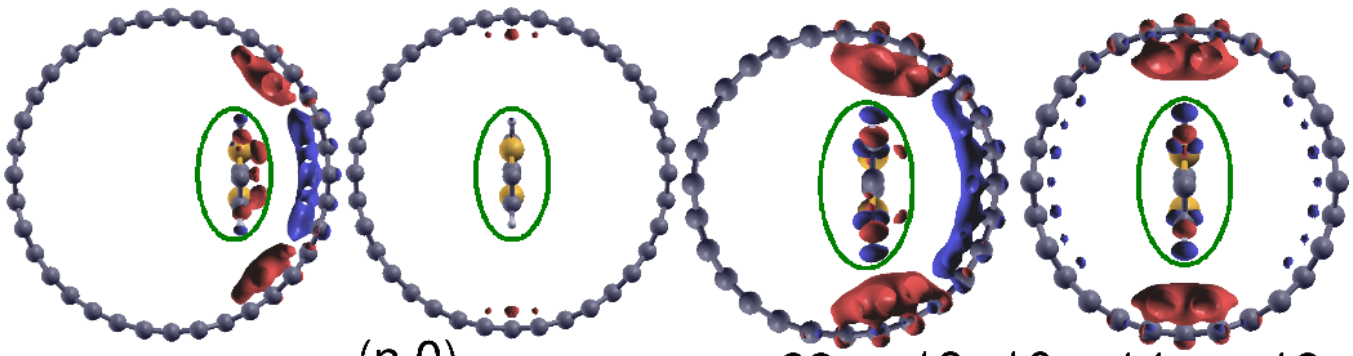
Example : (16,0)

Errors in IP


(n,0)
22
18
16
14
12
10
IP [eV]
-4.6
-4.8
-5.0
-5.2
-5.4
IP(pT in peapod)
IP(pT)
IP(pT) + ΔΦ
0.00
0.02
0.04
0.06
0.08
0.10
0.12
1/d_tube [Å^-1]

Charge transfer & bond dipole

pT@(22,0) pT@(14,0)

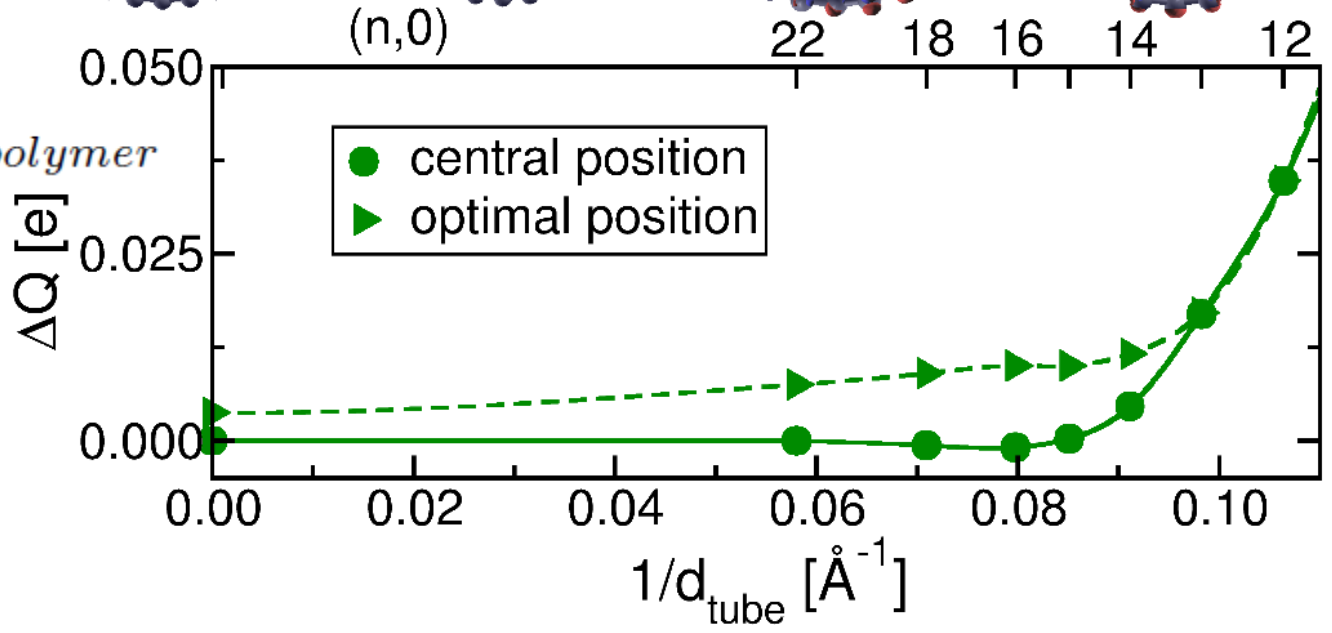


Diff. charge density:

$$\Delta\rho = \rho_{peapod} - \rho_{tube} - \rho_{polymer}$$

Bond dipole

$$\nabla^2 \Phi_{corr} = \Delta\rho$$



Errors in IP

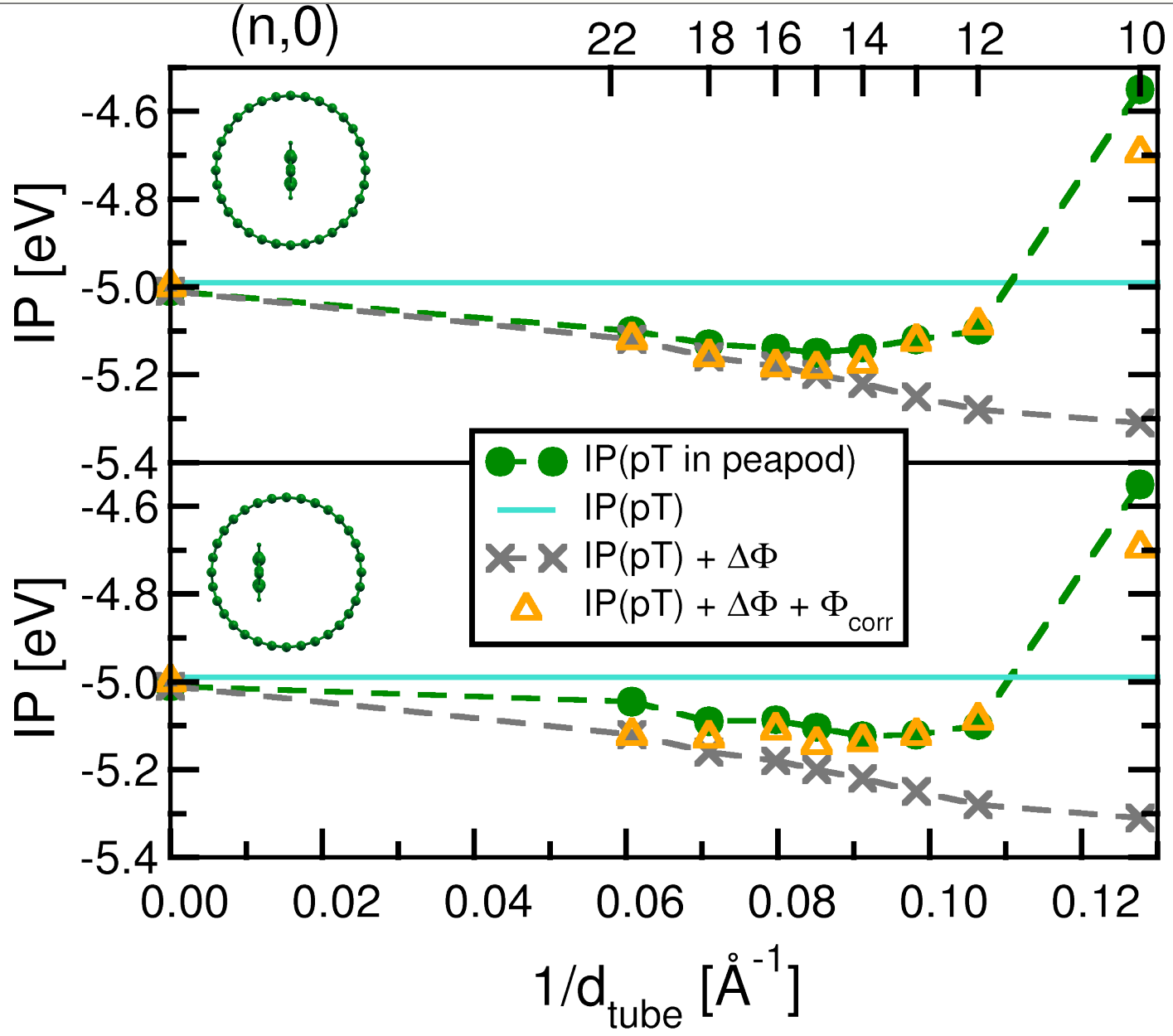
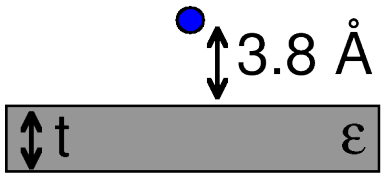
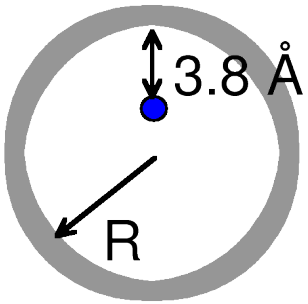

(n,0)
22
18
16
14
12
10
IP [eV]
-4.6
-4.8
-5.0
-5.2
-5.4
IP(pT in peapod)
IP(pT)
IP(pT) + ΔΦ
IP(pT) + ΔΦ + Φcorr
0.00
0.02
0.04
0.06
0.08
0.10
0.12
1/dtube [Å-1]

Image charge effect

The presence of a charge induces its image in the substrate NOT captured by DFT

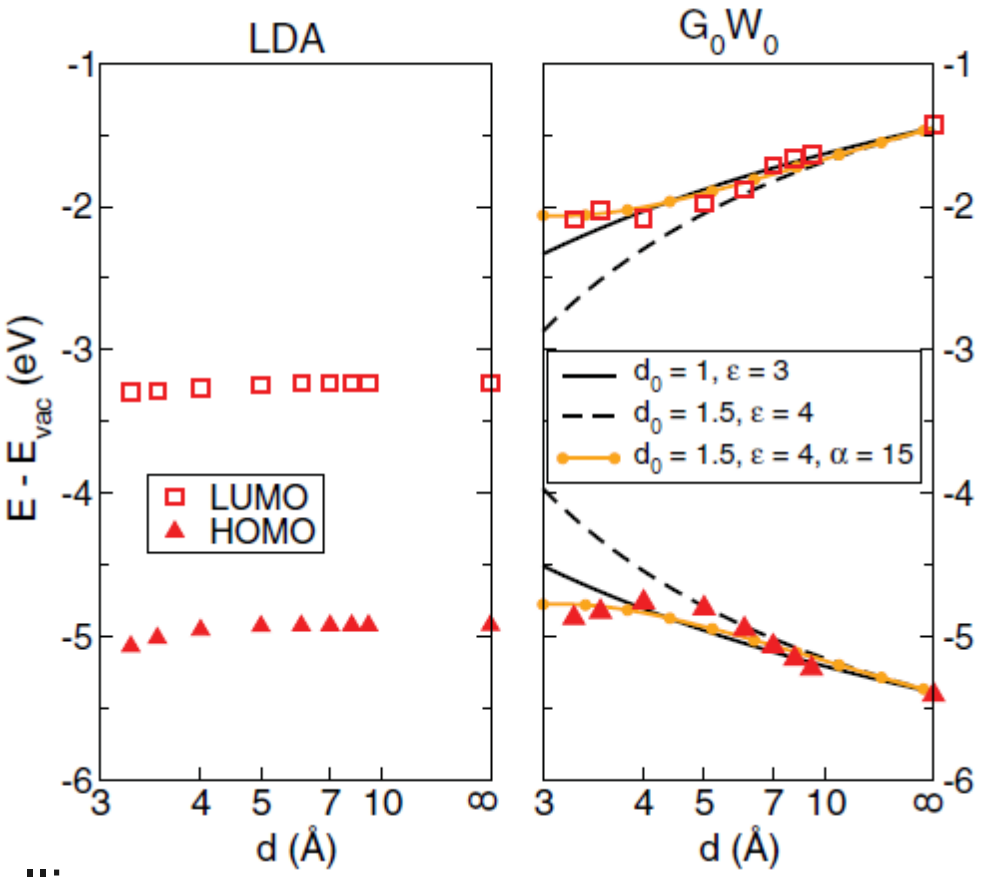
Two electrostatic models





Charge in vicinity of a dielectric slab

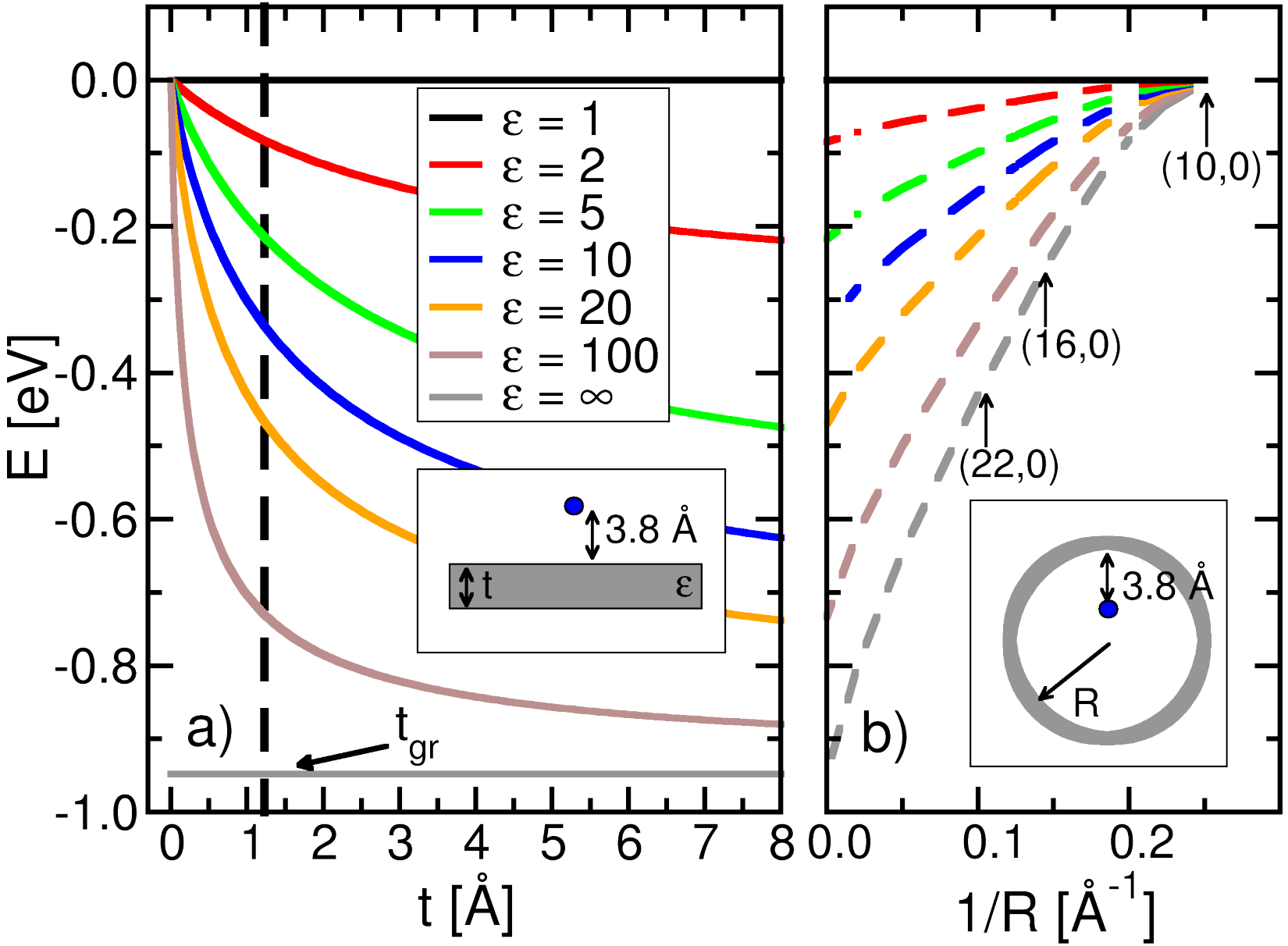
Charge in a metallic infinite cylinder



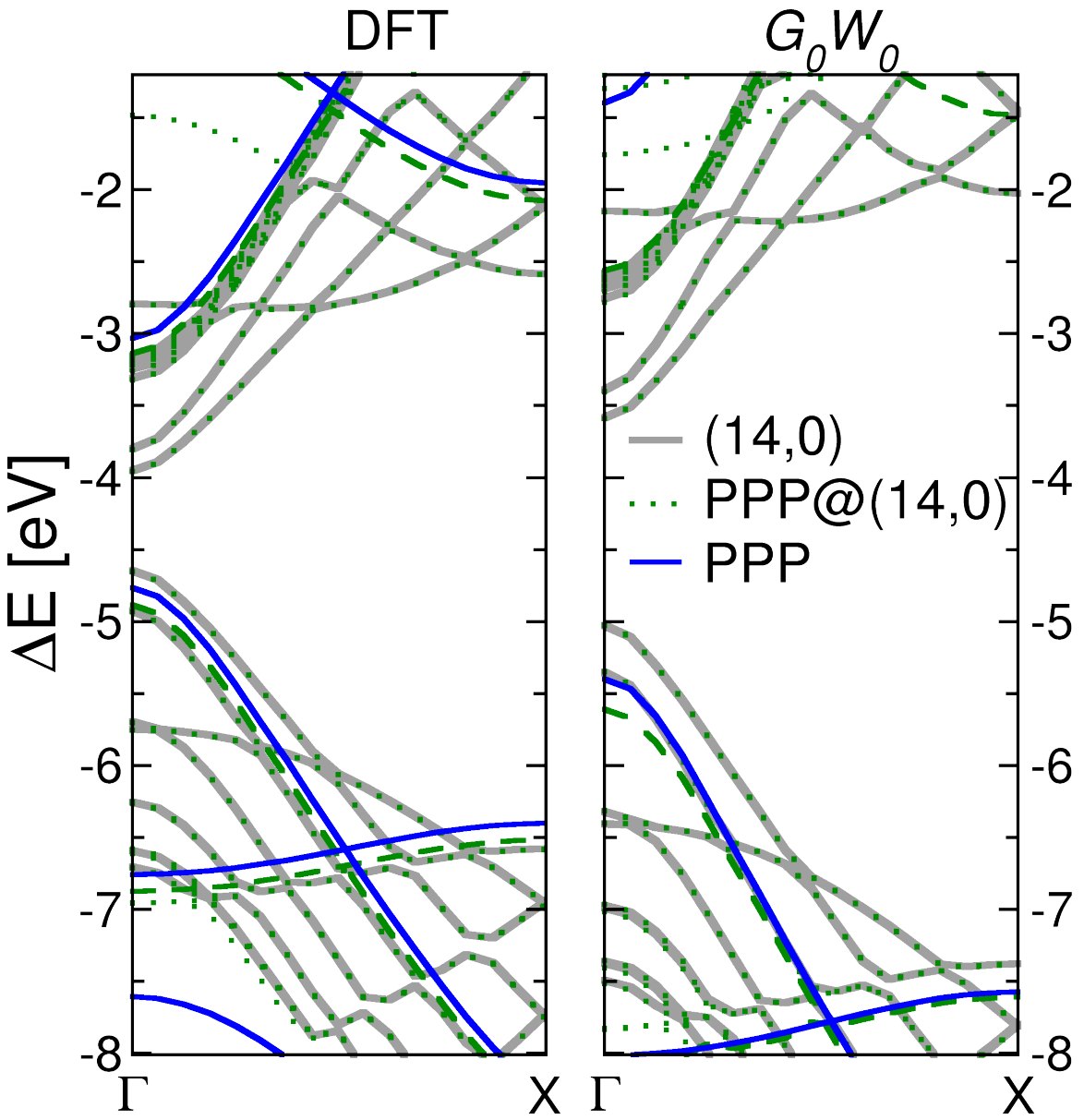
Barrera, Balaguer Am.J.Phys. 46,1172 (1978)
Hernandes, Assis, J. Electrostat. 63, 1115, (2005)

Puschnig et al. PRB 86, 085107,(2012)

Image charge effect



GW-calculations PPP@(14,0)



overall band gap correction

the band gap of PPP reduces by ~1.0 eV upon encapsulation

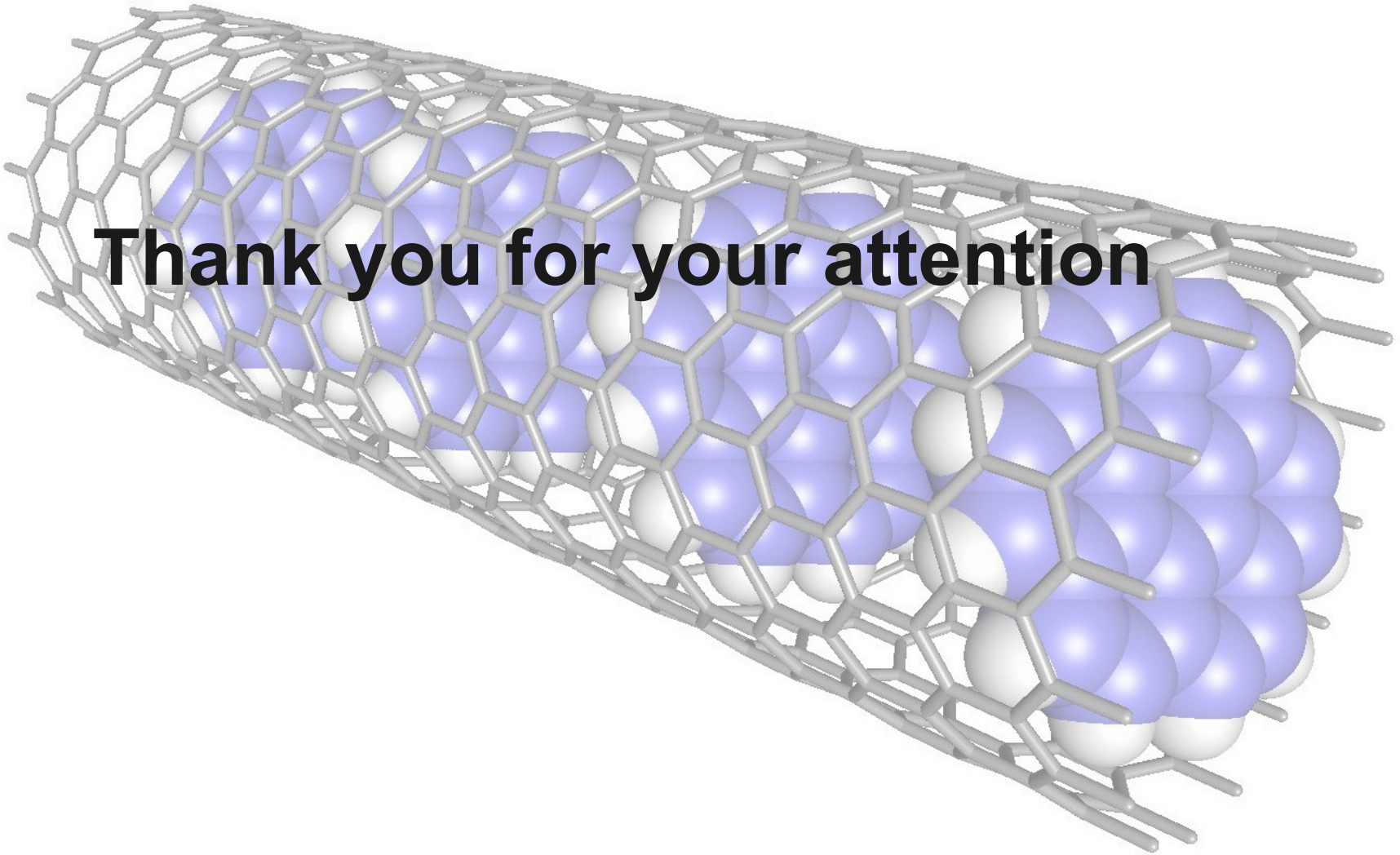
Estimation:

$$LL^{PPP} = -IP^{free} + \Delta\Phi + \Phi_{corr} + IC \sim -5.5 \text{ eV}$$

- point charge only
- no image charge induced in polymer

Conclusions

- The band structure appears as a mere superposition of the band structures of the constituents
- The curvature gives rise to a radial charge asymmetry leading to a jump in the electrostatic potential
- An additional correction comes from bond dipole
- The image charge effect might play an important role
- For weakly interacting hybrids like here, one can predict the electronic properties purely from the knowledge of its subunits by just simple electrostatic models within ~ 0.1 eV



Thank you for your attention