Seminar LSI
27 March 2017

Modeling of graphene / CNT 'doping' by physisorption of organic molecules: understanding the role of Van der Waals (dispersion) forces and 'charge transfer'

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Introduction

- My PhD subject :

<u>Multi-scale</u> modelling of water quality nano-sensors based on carbon nanotubes and conjugated polymers

- Today : focusing only on polymer / carbon nanotube (CNT) **<u>non-covalent</u>** interaction.

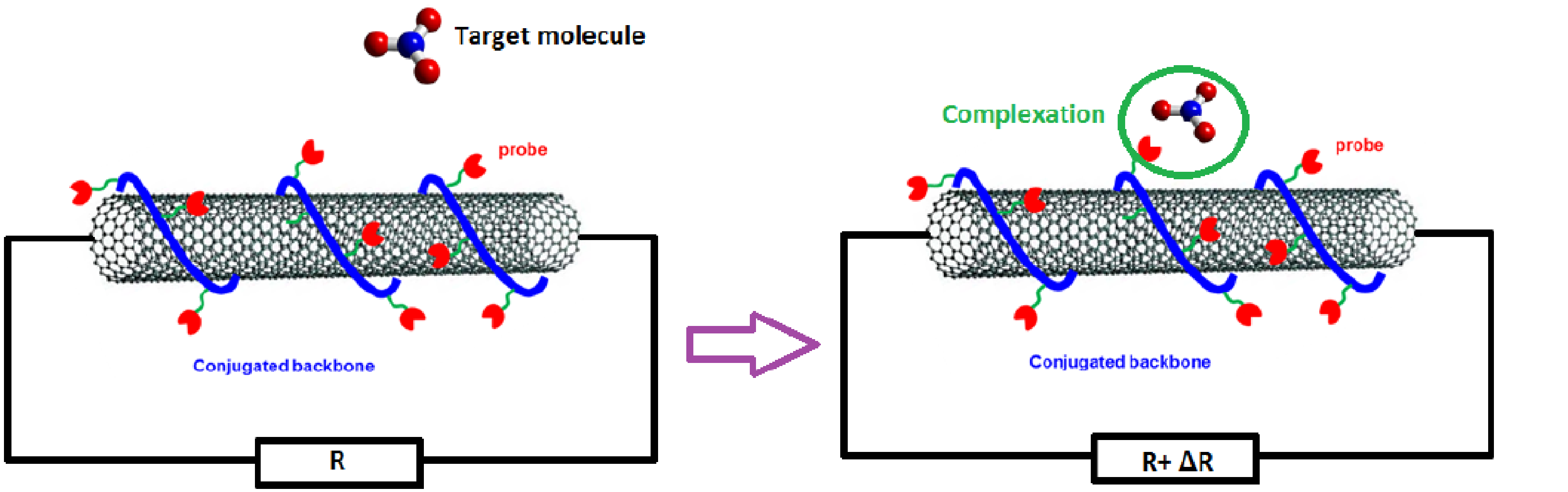
→ Which ingredients are needed in terms of electronic structure description ?

→ How to compute the charge transfer ?

Summary

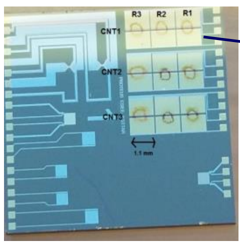
- I) Context : water-quality sensors based on CNTs and conjugated polymers
- II) Understanding π-π stacking interactions at play at the CNT/polymer interface : historical perspective on the different DFT 'ingredients'
- III) Benchmarking ReaxFF on higher theory levels for π-π stacked compounds
- IV) Possible definitions of the 'charge transfer'
- V) Molecular dynamics simulations (ReaxFF force field) to probe non-covalent functionalization of CNTs by conjugated polymers

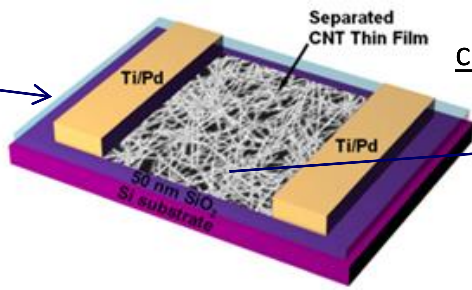
Part I :
Water-quality sensors based on CNTs and conjugated polymers



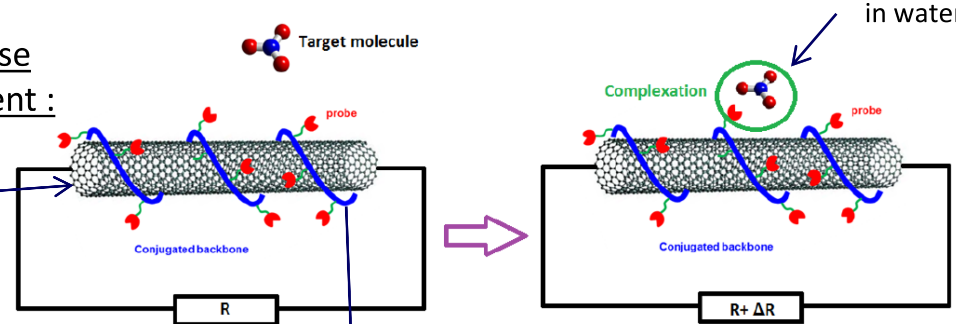
I) Water-quality sensors based on CNTs and conjugated polymers (1)

- Sensing element of the sensor : percolating networks of carbon nanotubes (CNTs) functionalized by conjugated polymers.

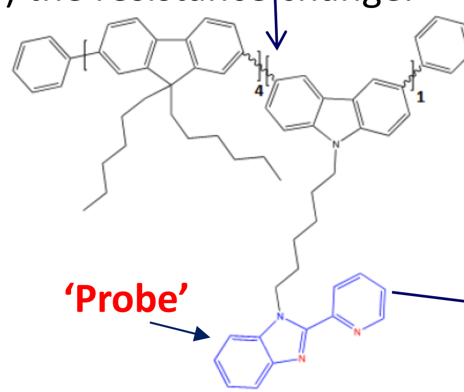




Unit base component :

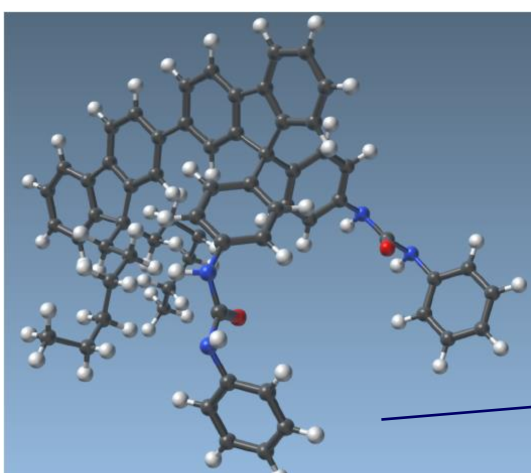


- **Modification of electronic properties** in water when increasing the concentration of a target ion
  => understanding / predicting (if possible) the resistance change.



Backbone

'Probe'

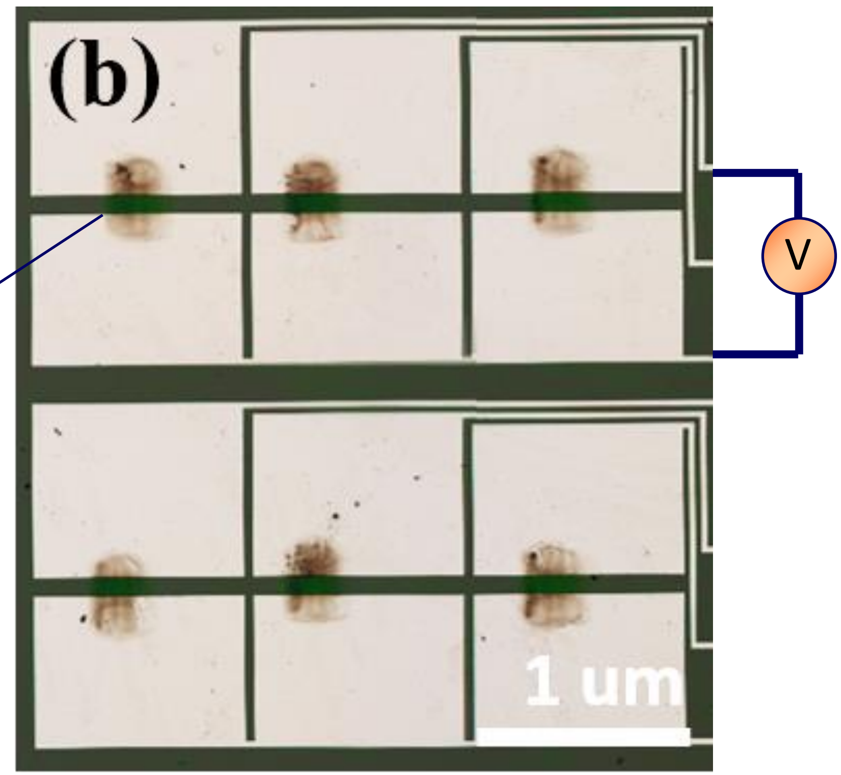


Polymers used :
polyfluorenes,
carbazole:fluorene copolymers
(ex : heavy metal detection (Cd^{2+}, Ni^{2+}, Cu^{2+}) or chloride Cl^-)

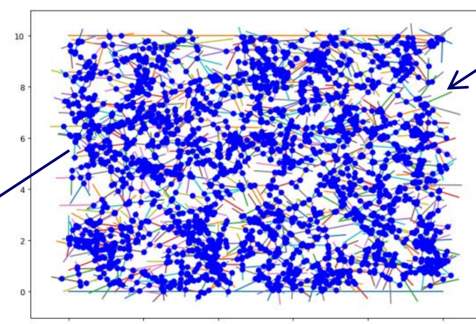
I) Water-quality sensors based on CNTs and conjugated polymers (2)

- « Ink » of CNTs printed in-between two metallic electrodes. Resistance measurement $\mathbf{R^{eq}}$.

- So far : sensors ***sensitive*** to variations of ion concentrations ($\mathbf{R^{eq}}$ changes) but not very ***selective*** (interfering ions, etc.) => More understanding needed.



6 sensors



Random percolating network of CNTs

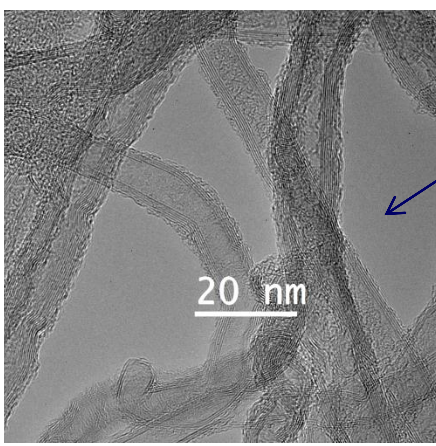


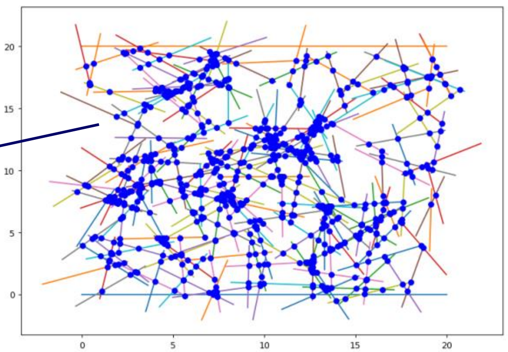
Image of a CNT network (Transmission Electron Microscope)

I) My contribution to the project (3)

Modeling at the different scales → ***bring them together.***

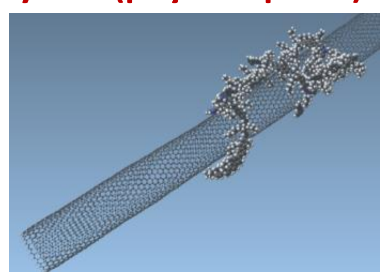
- Understanding of the origin of the resistance of random percolating networks of CNTs : linear vs. contact resistance ? (not discussed here)

Scheme of a CNT/CNT contact

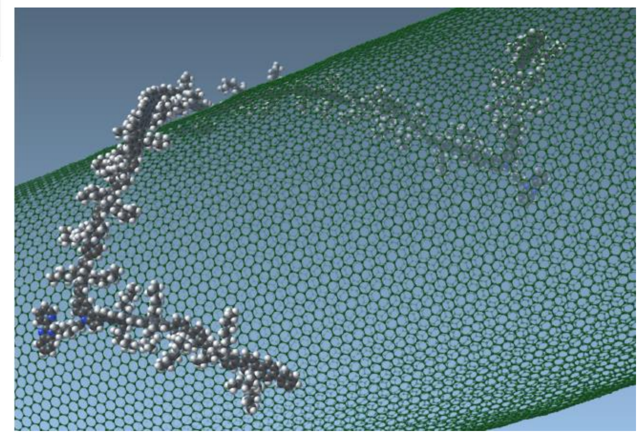


Paper in preparation

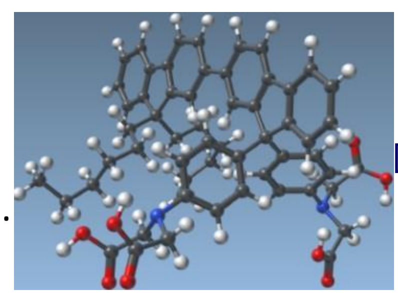
- **Interaction between CNT surface and polymer (physisorption). (discussed today)**
  - → Which type of interaction ?
  - → 'Ingredients' needed in DFT ?
  - → How to capture 'charge transfer' ?
  - → Molecular Dynamics (large systems).

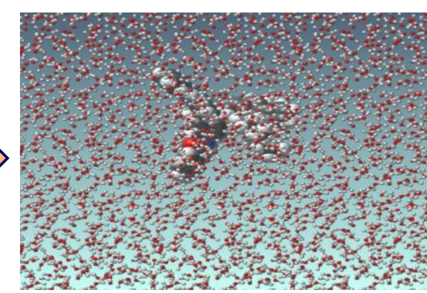


Physisorption of fluorene/carbazole copolymers on SWNT and MWNT outer shells

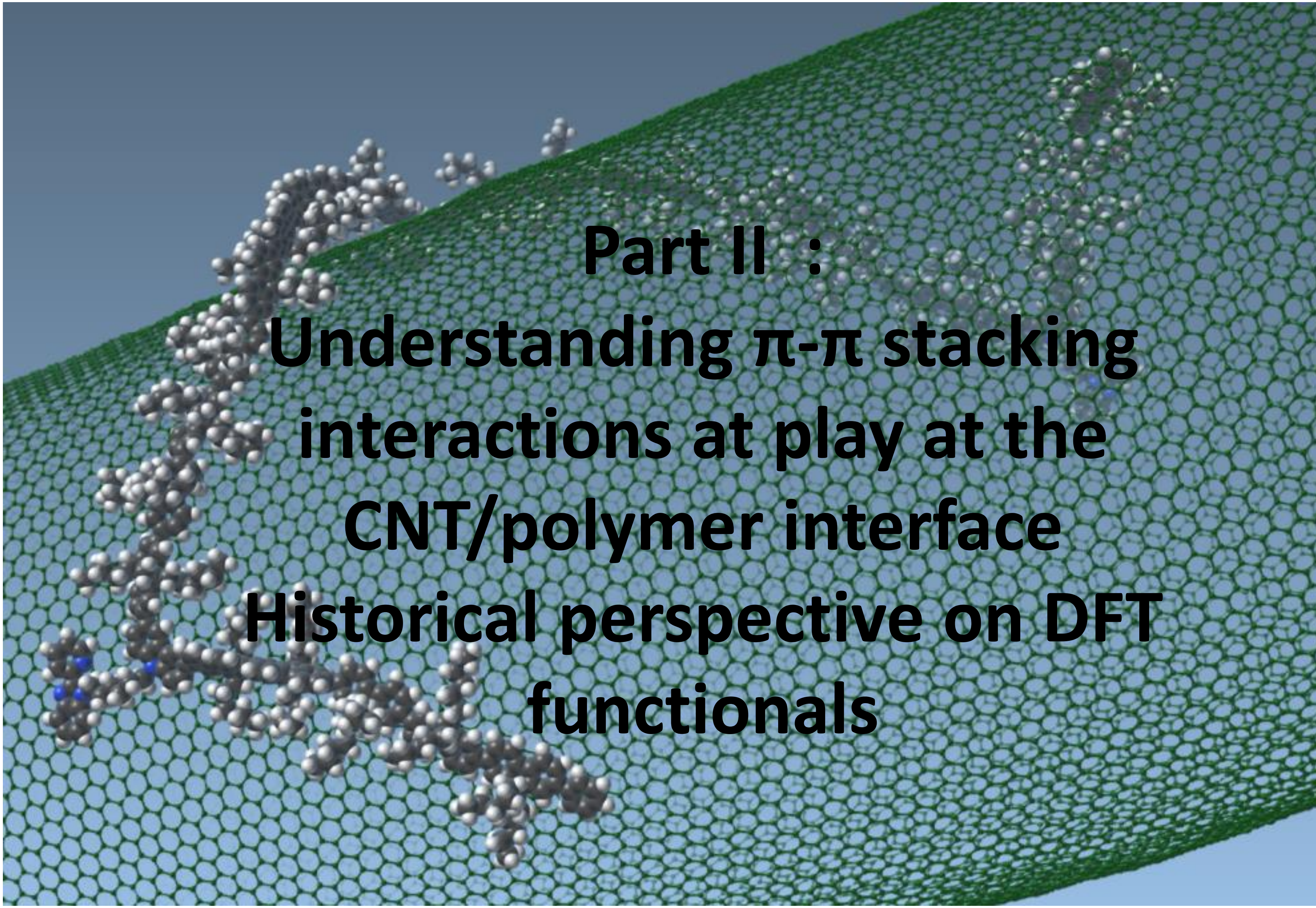


- Ion and polymer interaction in solvent (understanding selectivity)
  - → Parametrization for a given Force Field.
  - → Molecular dynamics (free energy calculations).





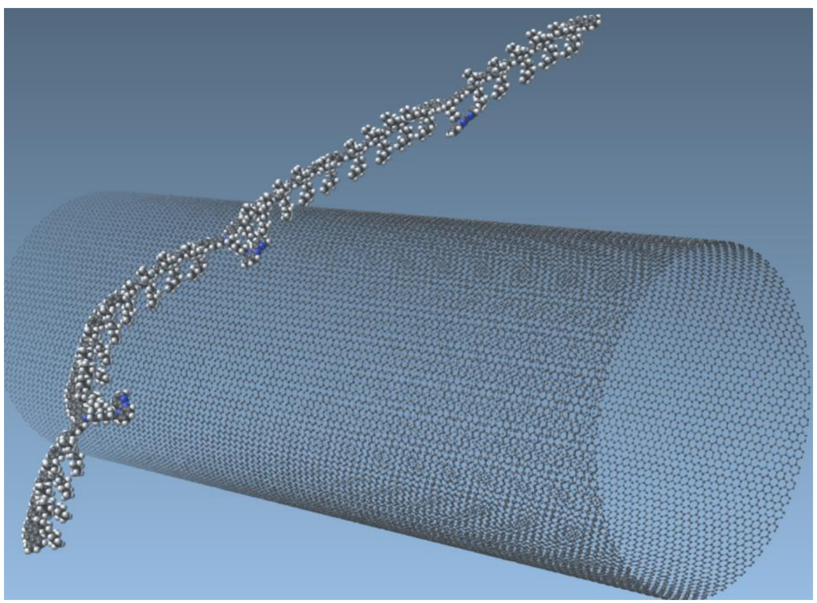
Solvatation with GROMACS program



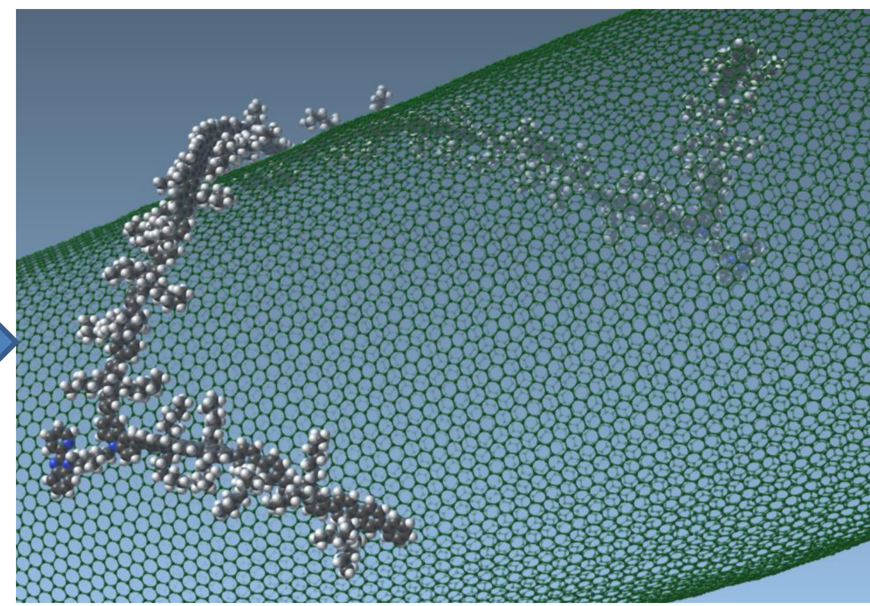
Part II :
Understanding π-π stacking interactions at play at the CNT/polymer interface Historical perspective on DFT functionals

II) Non-covalent functionalization of CNTs by conjugated polymers (1)

- Carbazole:fluorene copolymer (for heavy metal ions sensing) next to a 9 nm diameter CNT.
- Molecular Dynamics simulations (LAMMPS code, ReaxFF force field).
- Competition between torsional energy and **π-π stacking** (mix of **Van der Waals** and electrostatic interactions).



*Initial geometry, 'XW P2' polymer next to a **8.5 nm** diameter, 20 nm long CNT*



'Final' adsorption geometry after 300 000 steps of 0.3 fs

II) Non-covalent functionalization of CNTs by conjugated polymers (2)

- Non-covalent functionalization of CNTs by conjugated polymers is driven by **π-π stacking** interaction.
- What is exactly **π-π stacking** interaction ? How can it be captured ?

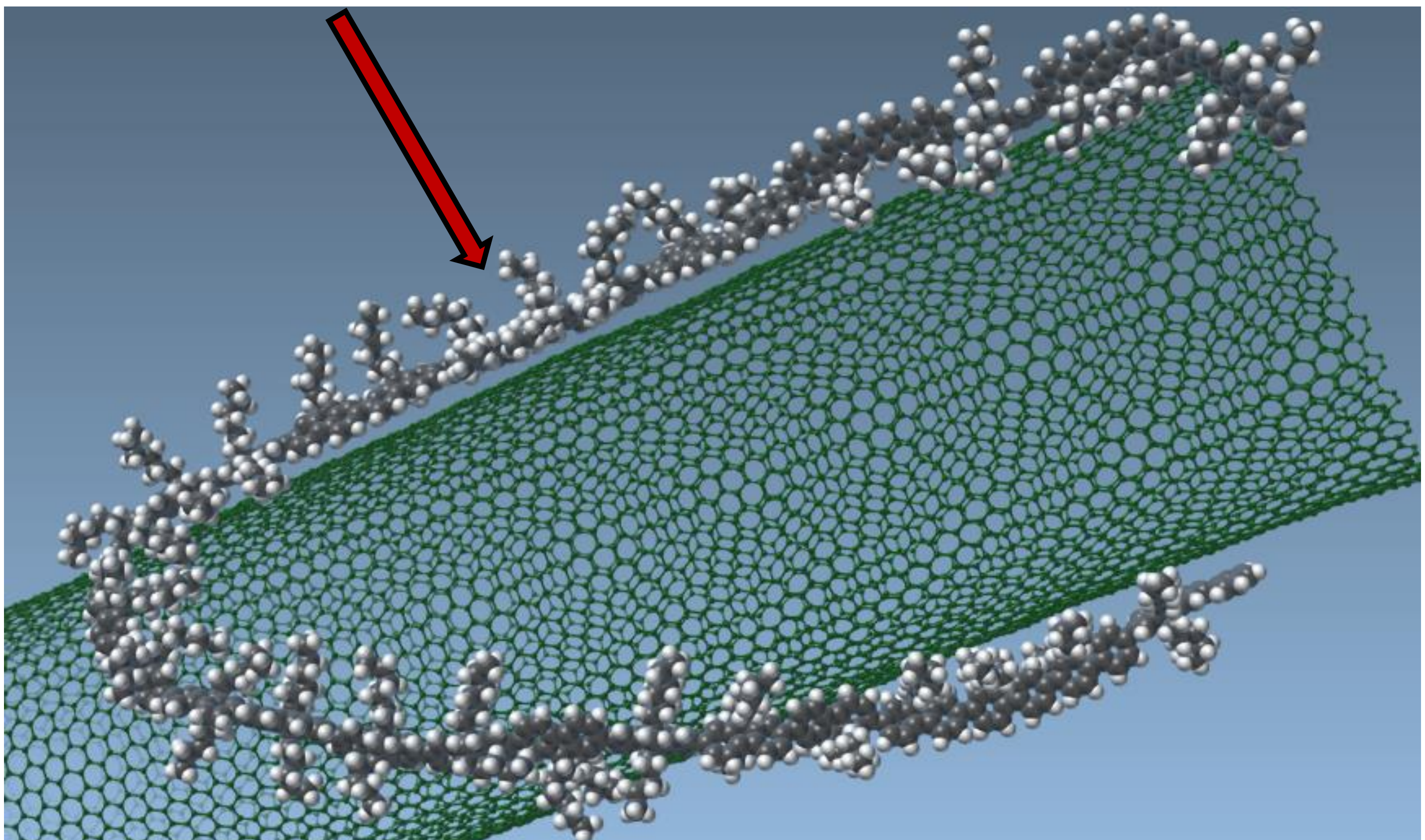


Image : SAMSON software

*Adsorption of a poly(9,9-di**hexyl**fluorène), 30 monomers long.*

II) Van der Waals interactions : a quick reminder

- <u>Permanent dipole – permanent dipole</u> interaction : **Keesom** effect.
  Vanishes at sufficiently high temperature.
  Similar for permanent dipole-permanent quadrupole interactions, permanent quadrupole-permanent quadrupole interactions, etc.

$$E_{Keesom} \propto -\frac{1}{k_B T}\frac{\mu_1^2\mu_2^2}{r^6}$$

- <u>Permanent dipole-induced dipole</u> interaction (**Debye** induction).
  Independent of temperature. <u>Not additive.</u>
  Similar for **permanent quadrupole / dipole induced** interactions.

$$E_{Debye} \propto -\frac{\alpha_1\mu_2^2 + \alpha_2\mu_1^2}{r^6}$$

$$\tilde{E}_{Debye} \propto -\frac{\alpha_1 Q_2^2 + \alpha_2 Q_1^2}{r^8}$$

- Instantaneous dipole-instantaneous dipole interaction (**London** dispersion).
  Independent of temperature. <u>ADDITIVE</u>.
  Purely quantum effect (fluctuations due to zero-point energy).
  Higher order terms : $-\frac{1}{r^8}$; $-\frac{1}{r^{10}}$ (<u>perturbative developement</u> in $\frac{\alpha}{r^3}$).

$$E_{disp} = -\frac{3}{4}\frac{h\nu_0\alpha^2}{r^6}$$

- All these interactions are **attractive** at long range.

- Keesom and Debye energies should be well captured within DFT (with rung 2 functionals).

- How about <u>**London dispersion effect**</u> ?

II) Main questions of this part

- Where is Van der Waals (London dispersion only) 'hidden' in DFT (in the exchange-**correlation** term) ?

- Which part of the dispersion energy **is already captured** by DFT 'usual' functionals only (before adding semi-empirical corrections) ?

  ⇒ 'short-range' part only ?

- How to capture dispersion energy otherwise (not with DFT) ?

- Van der Waals dispersion interactions are **'long-range'** *(i.e.* non local) **electron-electron (two-point) correlations**.

⇒ Reminder of the history of the different *exchange-correlation functionals*.

II) The (exact) exchange-correlation energy

- **Exact** definition of the exchange-correlation energy in the most general case (many-body viewpoint) using the exchange-correlation 'hole' $\mathbf{h_{xc}}(\vec{\boldsymbol{r}},\vec{\boldsymbol{r}}')$:

$$E_{xc}[n] = (T[n] - T_s[n]) + (U_{Coul}^{exact} - E_H[n]) = \frac{1}{2}\int\int \frac{n(\vec{r})h_{xc}(\vec{r},\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r}d\vec{r'}$$

- Includes both potential **and** kinetic energy.

- The exchange-correlation 'hole' has an exact many-body expression as can be guessed from :

$$U_{Coul}^{exact} = \langle\Psi|\frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r_i}-\vec{r_j}|}|\Psi\rangle = \frac{1}{2}\int\int\frac{P_2(\vec{r},\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r}d\vec{r'}$$

where :

$$P_2(\vec{r},\vec{r'}) = \frac{N(N-1)}{2}\int..\int d\vec{r_3}..d\vec{r_N}|\Psi(\vec{r},\vec{r'},\vec{r_3},..,\vec{r_N})|^2$$

$$U_{Coul}^{exact} = E_H[n] + \frac{1}{2}\int\int\frac{n(\vec{r})h_1(\vec{r},\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r}d\vec{r'}$$

$$h_1(\vec{r},\vec{r'}) = \frac{P_2(\vec{r},\vec{r'})}{n(\vec{r})} - n(\vec{r'})$$

$$E_H[n] = U_{class} = \frac{1}{2}\int\int\frac{n(\vec{r})n(\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r}d\vec{r'}$$

*(Part of) the exchange-correlation hole expressed thanks to the **2-point** correlation function $\boldsymbol{P_2}(\vec{\boldsymbol{r}},\vec{\boldsymbol{r}}')$*
which should capture entirely VdW London dispersion
(Coulomb : ***two-body*** operator)

Ref. : A. D. Becke. Correlation energy of an inhomogeneous electron gas: A coordinate-space model. The Journal of Chemical Physics, 88(2):1053–1062, jan 1988.

II) Exchange-correlation (approximate) functionals in DFT : historical perspective (1)

- Approximations (of increasing complexity) of the exact exchange-correlation hole !
- '**Pure**' DFT methods : LDA (**local**), GGA, meta-GGA (**semi-local**)

  => no exact (Hartree-Fock) exchange included.

$$\Rightarrow E_{xc}^{LDA}[n] = \int n(\vec{r}) e_{xc}^{HEG}(n(\vec{r}))\, d\vec{r} \quad \Rightarrow E_{xc}^{GGA}[n] = E_{xc}^{LDA}[n] + \int e_{xc}^{GGA}(n(\vec{r}), \nabla n(\vec{r}))\, d\vec{r}$$

$$\Rightarrow E_{xc}^{meta-GGA}[n] = \int n(\vec{r}) e_{xc}^{meta-GGA}(n(\vec{r}), \nabla n(\vec{r}), \tau(\vec{r}))\, d\vec{r}$$

- $\tau(\vec{r})$ in meta-GGA is related to the <u>local kinetic energy density</u> (of the Kohn-Sham system of non-interacting electrons) .

$$\tau(\vec{r}) = \frac{1}{2}\sum_i |\nabla\psi_i(\vec{r})|^2 = \frac{1}{4}\left[\Delta n(\vec{r}) - \sum_{i/occ.} \left(\psi_i^*(\vec{r})\nabla^2\psi_i(\vec{r}) + \psi_i(\vec{r})\nabla^2\psi_i^*(\vec{r})\right)\right]$$

- Local or semi-local functionals => **no 'long-range' correlation captured**.

- '**Pure**' methods as opposed to '**hybrid**' functionals (including exact exchange).

II) Exchange-correlation functionals in DFT : historical perspective (2)

- '**Hybrid**' functionals : some **exact exchange** is added to the DFT energy (*) [great improvement on the computed properties of a wide range of systems]. Description with **occupied** Kohn-Sham orbitals only (as opposed to '**double-hybrid**' functionals).

$$E_x^{HF} = -\int\int \frac{|\gamma(\vec{r},\vec{r'})|^2}{|\vec{r}-\vec{r'}|} d\vec{r} d\vec{r'} = -\sum_{i/occ}\sum_{j/occ.} \delta_{\sigma_i,\sigma_j} \int\int \frac{\psi_j^*(\vec{r'})\psi_i^*(\vec{r})\psi_j(\vec{r})\psi_i(\vec{r'})}{|\vec{r}-\vec{r'}|} d\vec{r} d\vec{r'} < 0$$

$$\gamma(\vec{r},\vec{r'}) = \sum_{i/occ.} \psi_i^*(\vec{r'})\psi_i(\vec{r})$$: one-particle density matrix.

- Exchange accounts for purely quantum effects (lowered Coulomb electron-electron repulsion (electron of same spins) due to **Pauli principle**) and **correction of self-interaction error**.

- Exchange is also a type of correlation (same-spin correlation) ?

- Correlations : between electrons of same spins **and** between electrons of opposite spins.

- Example : **B3LYP** (*) : GGA functional + 20 % HF exchange (same % on the whole range [both short and long range])

  => hence the asymptotic behavior (**at long-range**) of the exchange potential in $\frac{0.2}{r}$ in B3LYP (instead of the correct dependence in $\frac{1}{r}$).

- In practice : Hartree-Fock 'exact' exchange computed with Kohn-Sham orbitals.

(*) Axel D. Becke. Density-functional thermochemistry. III. the role of exact exchange. The Journal of Chemical Physics, 98(7):5648–5652, apr 1993.

II) Exchange-correlation functionals in DFT : historical perspective (3)

- '**Long-range corrected** methods'
- Example : CAM-B3LYP : Coulomb attenuated methods (*), or **ω**B97X, etc.
- Idea : correcting the wrong long-range behavior of the exchange potential in $\frac{\mathbf{0.2}}{\boldsymbol{r}}$ (in B3LYP) **adding more 'exact' exchange at long-range** to get the correct dependence in $\frac{1}{r}$.
- Example : in CAM-B3LYP (*) :
  - At short range : 19% HF exchange, 81% Becke88 exchange [*i.e.* from the exchange-correlation functional]
  - At long range : **65% HF exchange**, 35% Becke88 exchange **at long range**.

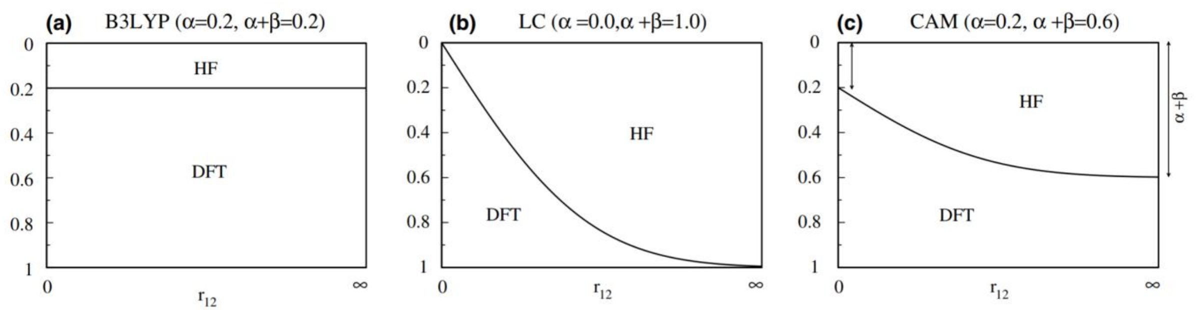


Fig. 2. Schematic plots of the contributions to exchange from r_{12}^{-1}, apportioned into DFT and HF, for: (a) B3LYP, (b) LC, and (c) CAM

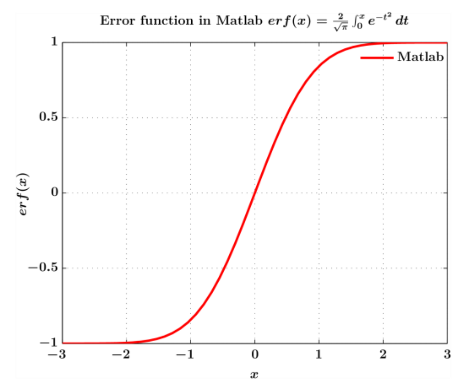
(*) Takeshi Yanai, David P Tew, and Nicholas C Handy. A new hybrid exchange–correlation functional using the coulomb-attenuating method (CAM-B3LYP). Chemical Physics Letters, 393(1-3):51–57, jul 2004

II) Exchange-correlation functionals in DFT : historical perspective (4)

- Coulomb attenuating method is kind of a « screened » Hartree-Fock, with an ad-hoc parameter **μ** which controls when the exact exchange 'replaces' (smoothly) the **local** exchange of the XC functional (not valid / active at long-range) :

$$E_x^{HF} = -\int\int \frac{erf(\mu|\vec{r}-\vec{r'}|)}{|\vec{r}-\vec{r'}|}|\gamma(\vec{r},\vec{r'})|^2 d\vec{r}d\vec{r'}$$

where : $$erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt$$



- **μ** controls the **balance** between DFT exchange and HF exact exchange **at intermediate values** of the separation $|\vec{r}-\overrightarrow{r'}|$.

- Adding more HF exact exchange at long-range proved to be very important for excited states (to capture charge transfer excitations, *e.g.* situations with charges + and – very well separated in a molecule).

II) DFT corrections to take into account dispersion (long-range, non local) interactions (1)

- Several possible rationales to ‘correct’ DFT energy including VdW **dispersion** terms :
  - **Semi-empirical** corrections (DFT-D)

$$E_{disp}^{DFT-D} = -\sum_{A,B}\left(\sum_{n=6,8,10,..} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{damp}(R_{AB})\right)$$

  - vdW-DFT methods (non empirical, based on the density only)

(*) Stefan Grimme. Density functional theory with London dispersion corrections. Wiley Interdisciplinary Reviews : Computational Molecular Science, 1(2):211–228, mar 2011.

II) DFT corrections to take into account dispersion interactions (2)

- The ‘medium-range’ problem :

*“The electron correlations in this problematic region are difficult to classify but they often have the typical **WF signatures of dispersion-type interactions** and are nowadays usually termed ‘medium-range’ correlation” (*)*

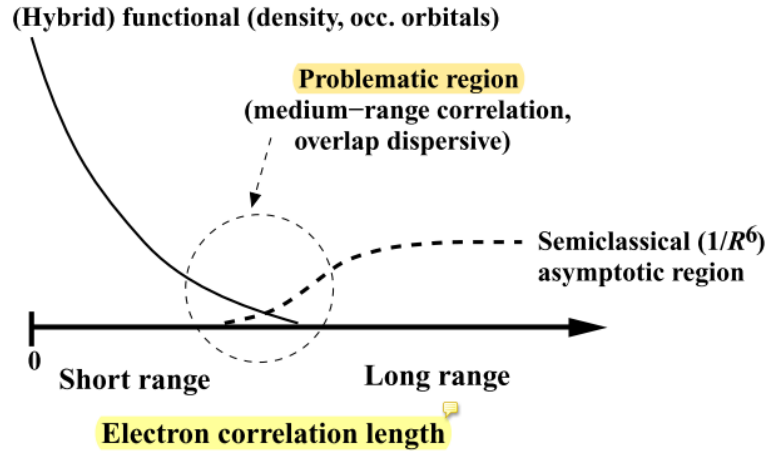


FIGURE 3 | Schematic classification of the correlation and dispersion problems on different electron correlation length scales.

- Double-counting effect (problematic ‘branching’ region) :

  - ‘short-range’ dispersion interactions already accounted for by the usual (local, or semi-local) correlation functional ?

  - possible **overlap** at intermediate separations (medium-range) with the semi-empirical corrections for dispersion (depending more or less on the damping function).

(*) Stefan Grimme. *Density functional theory with London dispersion corrections*. Wiley Interdisciplinary Reviews : Computational Molecular Science, 1(2):211–228, mar 2011.

II) DFT corrections to take into account dispersion interactions (3)

- The exact exchange-correlation functional is not known => difficult to find a functional of the density capturing London dispersion effects.

➡ <u>Question</u> : Need of describing **excitations / excited states** to capture correctly dispersion effects ? Need of a wave-function view-point ?

II) Dispersion interactions within a wave-function based level of theory : MP2 (1)

- Van der Waals dispersion interactions within Moller-Plesset second order perturbation theory (MP2) are much better described.

- Indeed : quantum fluctuations (due to zero-point energy, creating the instantaneous dipoles) imply a distortion of the electronic cloud => towards empty (but **eligible**) states.

- Wave-function based theory (FCI, CCSD, MP2) => possible to represent excited states ('virtual', empty but eligible) molecular orbitals (labeled ***a, b***) with an underlying basis containing excited Slater determinants (*).

$$E_0^{MP2} = E_0^{HF} - \frac{1}{4} \sum_{i,j} \sum_{a,b} \frac{|\langle ij||ab\rangle|^2}{\epsilon_a + \epsilon_b - (\epsilon_i + \epsilon_j)}$$

Part of the MP2 energy correction to HF *is* dispersion energy.

- MP2 correction to Hartree-Fock can be expressed as a function of (antisymetrized) **two-electron repulsion integrals** involving occupied orbitals (labeled ***i,j***) and empty ('virtual') orbitals (labeled ***a, b***).

$$\langle ij||ab\rangle = \int \int \frac{\psi_a(\vec{r})\psi_b(\vec{r'}) \left(\psi_i^*(\vec{r})\psi_j^*(\vec{r'}) - \psi_i^*(\vec{r'})\psi_j^*(\vec{r})\right)}{|\vec{r} - \vec{r'}|} d\vec{r}d\vec{r'}$$

(*) Michael F. Herbst, phD thesis, *Development of a modular quantum-chemistry framework for the investigation of novel basis functions with an application to Coulomb-sturmians* (2018).

II) Dispersion interactions within a wave-function based level of theory : MP2 (2)

- Part of MP2 energy correction to Hartree-Fock approximated energy captures exactly dispersion energy :

$$E_{disp}^{(2)} = -\sum_{i \longrightarrow a} \sum_{j \longrightarrow b} \frac{(\psi_i \psi_a|\psi_j \psi_b)\left[(\psi_i \psi_a|\psi_j \psi_b) - (\psi_i \psi_b|\psi_j \psi_a)\right]}{\epsilon_a + \epsilon_b - (\epsilon_i + \epsilon_j)}$$

Dispersion energy with its explicit dependence on wave-functions given in Ref. (*)

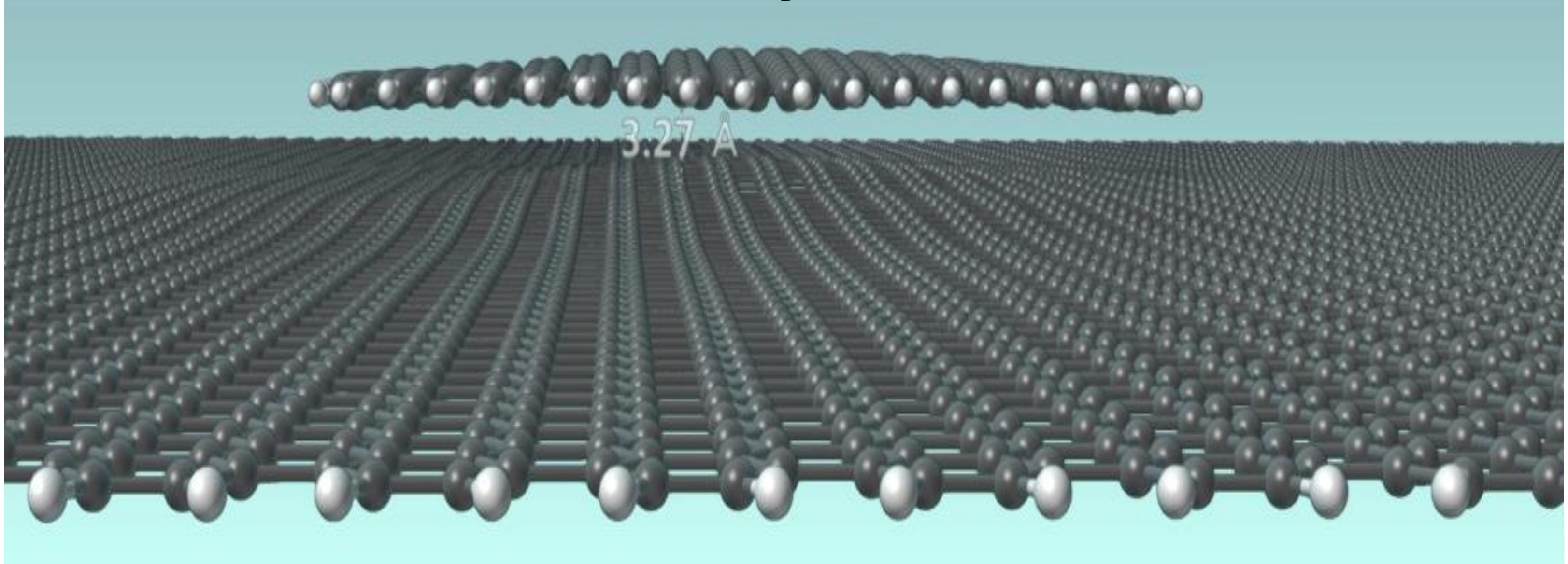
- Corresponds to **Coulomb** [electrostatic] (1st term) and **exchange interactions** (2nd term) **between (single-electron) transition (pseudo-) densities** (*).

- Is this explicit description of excited, ‘eligible’ states mandatory to capture correctly dispersion effects ?

- Conventional (hybrid) functionals don’t use virtual orbitals or transition densities (ground state density only) => don’t represent these forces (at least at long-range). What about ‘short’ / ‘medium’ range ?

(*) Stefan Grimme. Density functional theory with London dispersion corrections. Wiley Interdisciplinary Reviews : Computational Molecular Science, 1(2):211–228, mar 2011.

Part III :
Benchmarking ReaxFF for π-π stacking interactions on higher theory levels

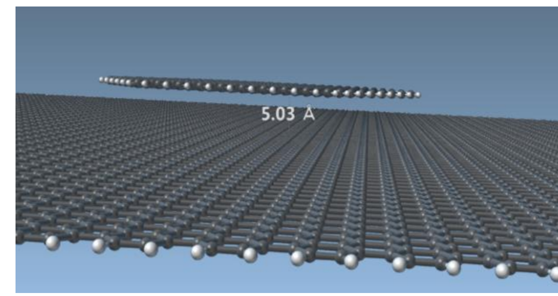


III) Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (1)

- Benchmark of adsorption energies and **geometries** with "VdW-corrected" DFT calculations on much simpler situations (than the real CNT/polymer hybrid).

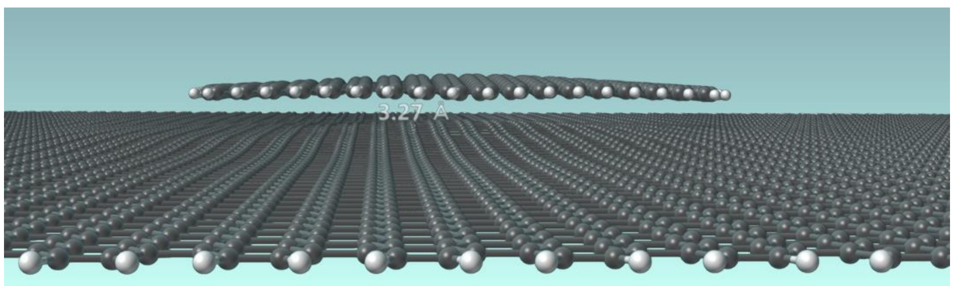
- Aromatic molecules (benzene, perylene, coronene) on a 'model' graphene sheet (hydrogenated large polyaromatic hydrocarbon).

- Structural optimizations (with ReaxFF) from initial geometries :

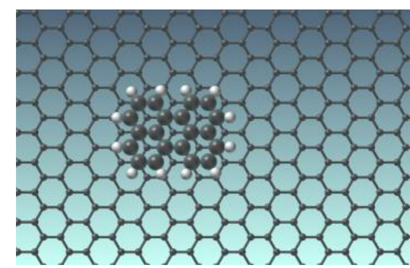


Initial geometry

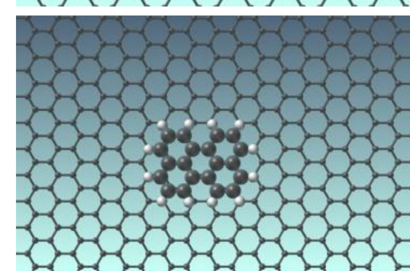
Optimized geometry



'Coronene' molecule ($C_{378}H_{48}$) on a graphene model sheet



AB



AA

- Magnitude of the interaction energy.
- Energy difference between AB '**stacked**' and AA '**sandwich**' geometries.

- *Charge transfer aromatic molecule / graphene (or CNT).*

III) Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (2)

- Example : study of the **binding energy separation** of different adsorption sites for benzene on graphene.

- Comparison of **ReaxFF** with a **DFT-D** method.

Adsorption mode	Adsorption energy (ReaxFF)	Adsorption energy ([4])	Adsorption distance (ReaxFF)	Adsorption distance ([4])
Stacked	-67.99	-78.7	3.22	3.22
Sandwich	-67.32	-74.0	3.23	3.26
'pd1'	-67.90	-77.9	3.2	3.22
'pd2'	-67.66	-76.8	3.23	3.18
'rst'	-67.70	-78.2	3.22	3.22
'rsw'	-67.78	-74.4	3.22	3.23

TABLE I: Comparison of adsorption energies of benzene (C_6H_6 *i.e.* 6 carbon atoms) on a graphene sheet computed with ReaxFF and with DFT+D (GGA exchange-correlation function and semi-empirical corrections to account for VdW interactions) [4]. Energies are expressed in kJ/mol and distances in Å.

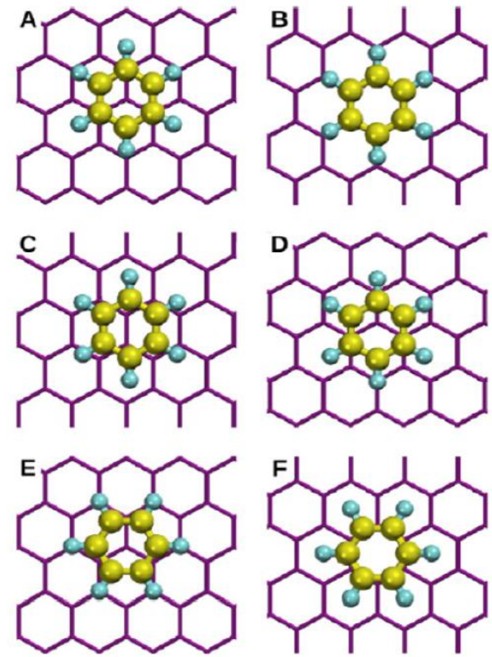


Fig. 2 – Adsorption geometries of benzene on graphene: (A) stacked, (B) sandwich, (C) parallel displaced 1 (pd 1), (D) parallel displaced 2 (pd 2), (E) rotated stacked (rst), and (F) rotated sandwich (rsw). Yellow and cyan spheres correspond to C and H atoms, respectively; The graphene backbone is displayed in purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Some possible adsorption sites for benzene on graphene Ref. (*)

The magnitude of the binding energy is consistent with DFT but the energy separation of different sites is underestimated with ReaxFF (by almost one order of magnitude).

(*) Sergey M. Kozlov, Francesc Vines, and Andreas Görling. On the interaction of polycyclic aromatic compounds with graphene. Carbon, 50(7):2482–2492, jun 2012

III) Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (3)

- **ωB97X-D** (hybrid, Coulomb attenuated functional, semi-empirical VdW correction) 6-31G* basis-set (*), polycyclic aromatic molecules on graphene 'models' :

  - -78.3 meV/C atom adsorption energy found for benzene on a graphene model ($C_{116}H_{28}$), -72 meV/C atom for coronene ($C_{24}H_{12}$)

  - $\Delta E_{AB/AA}$ = -11 meV/ C atom

  - $\frac{\Delta E_{AB/AA}(\omega B97X-\boldsymbol{D})}{\Delta E_{AB/AA}(\omega B97X)}$ ranges from 1.00 up to 1.04 for C_6H_6, $C_{10}H_8$, $C_{24}H_{12}$, $C_{32}H_{14}$ molecules *i.e.* **including dispersion term does not affect** (less than 4%) **the value of the energy barrier** obtained.

(*) Olga V. Ershova, Timothy C. Lillestolen, and Elena Bichoutskaia. Study of polycyclic aromatic hydrocarbons adsorbed on graphene using density functional theory with empirical dispersion correction. Physical Chemistry Chemical Physics, 12(24):6483, 2010

III) Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (4)

- DFT-D (**PBE** functional), semi-empirical VdW correction (*), **bilayer graphene** :
  - -50.6 meV/atom interlayer binding energy (-45.7 meV/atom with a Lennard-Jonnes potential only)
  - $\Delta E_{AB/AA}$ = -19.5 meV/atom (-0.9 meV/atom with a Lennard-Jonnes potential only)

- *« Though the dispersion term strongly affects the **overall interlayer binding energy**, the contributions of the dispersion term to the **barrier** for relative motion of graphene layers[...] were found to be 1.4% and 0.6%, respectively »*

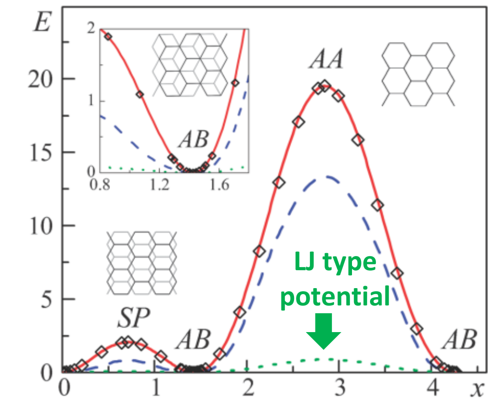


Fig. 1 Calculated interlayer interaction energy E (in meV per atom) of bilayer graphene at the equilibrium interlayer spacing as a function of the relative displacement x (in Å) of the layers along the armchair direction for different potentials: Lennard-Jones potential (dotted line), Kolmogorov–Crespi potential (dashed line) and potential developed in the present work (solid line). The data obtained from the DFT-D calculations are shown with rhombs. The energy is

(*) Irina V. Lebedeva, Andrey A. Knizhnik, Andrey M. Popov, Yurii E. Lozovik, and Boris V. Potapkin. Interlayer interaction and relative vibrations of bilayer graphene. Physical Chemistry Chemical Physics, 13(13):5687, 2011.

III) Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (5)

- <u>Conclusion of the benchmark</u> : ReaxFF captures the good order of magnitude of **binding energy** (cf comparison with **ωB97X-D** functional) but not **energy separation** between different adsorption sites.

- **Although VdW (dispersion) energy is the main contributor to the pi-pi stacking energy (75 to 90 % reported), it accounts very few for AB ('stacked') / AA ('sandwich') energy separation (see Ref (*), (**)).**

- The magnitude of the AB/AA barrier is largely underestimated with VdW only (case of force fields).

- In DFT-D : $E_{tot}[n] = E_{DFT}[n] + E_{VdW}$

$E_{DFT}[n]$ ⇩ *'Small' but allows to capture more subtle electronic effects (correlation, etc.) in π-π stacking (difference AB/AA) ?*

E_{VdW} ⇩ *Main contribution, but almost independent of the particular adsorption geometry*

(*) Irina V. Lebedeva, Andrey A. Knizhnik, Andrey M. Popov, Yurii E. Lozovik, and Boris V. Potapkin. Interlayer interaction and relative vibrations of bilayer graphene. Physical Chemistry Chemical Physics, 13(13):5687, 2011.
(**) Olga V. Ershova, Timothy C. Lillestolen, and Elena Bichoutskaia. Study of polycyclic aromatic hydrocarbons adsorbed on graphene using density functional theory with empirical dispersion correction. Physical Chemistry Chemical Physics, 12(24):6483, 2010

III) Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (6)

- **ωB97X-D** : (one of) the best performing functional on the standard S22 Benchmark set for intermolecular, weak interactions, see Review Grimme 2011, Table 2 (*).

- **ωB97X-D** functional seems to capture correctly the **binding energy** and energy **barrier** with ingredients :
  - **Dispersion correction** (mandatory, non-covalent interactions).
  - Some exact (Hartree-Fock) exchange at short range (**hybrid** functional), GGA type.
  - Long range correction, **Coulomb attenuation** (exact exchange included also at long range).

➡ Which ingredients necessary to capture correctly the '**charge transfer**' (important for the CNT conductivity) ?

- Still more literature date needed to conclude on charge transfer. See Annex.

- No consensus in the literature on :
  - The magnitude of the charge transfer ?
  - The difference of charge transfer for AA/AB stacked geometries ?
  - The ingredients needed to capture 'charge transfer' between organic molecules and graphene ?
  - The ***definition of the charge transfer*** itself ?

(*) Stefan Grimme. *Density functional theory with London dispersion corrections*. Wiley Interdisciplinary Reviews : Computational Molecular Science, 1(2):211–228, mar 2011.

Part IV : Possible definitions of the 'charge transfer'

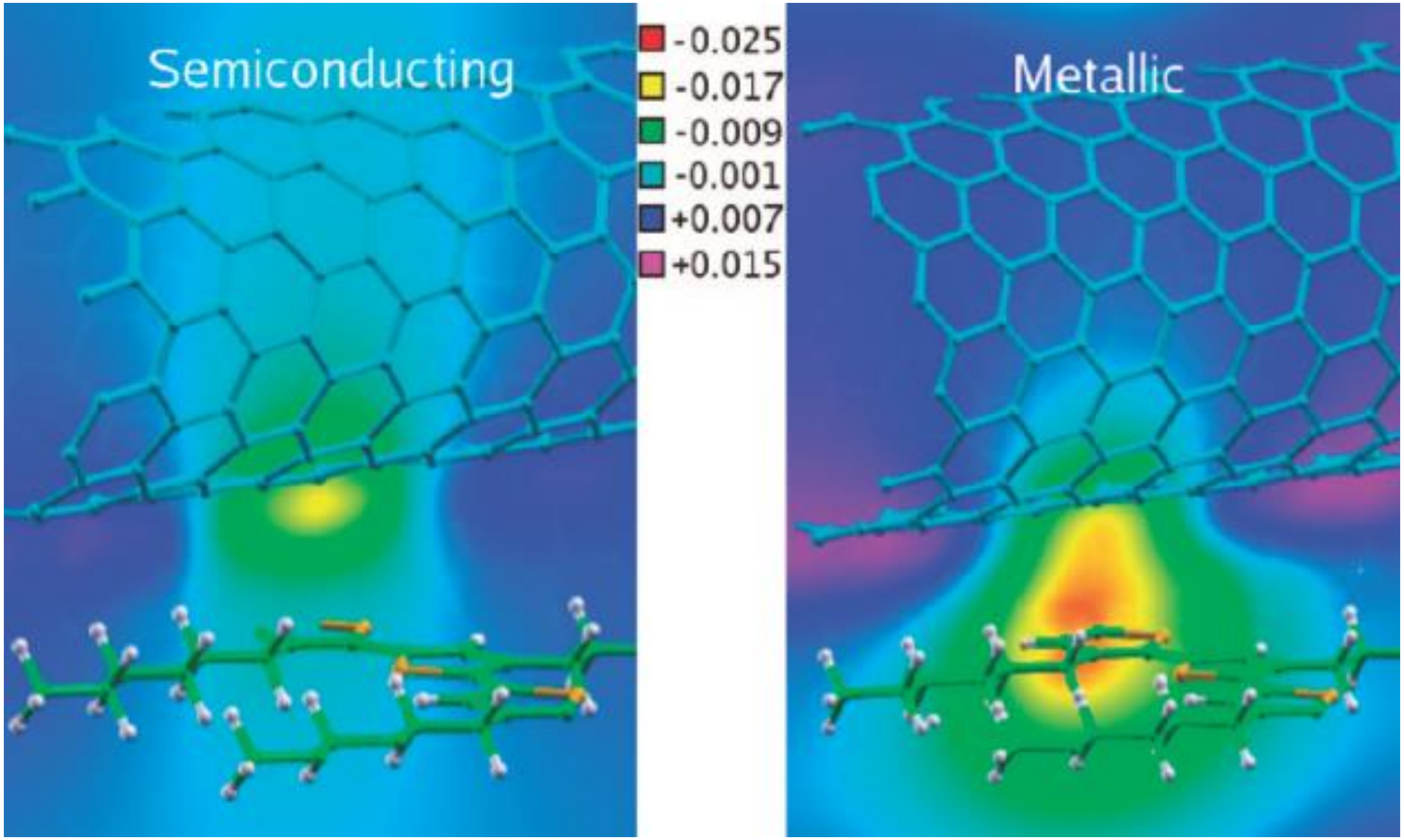


Image : Yosuke Kanai and Jeffrey C. Grossman, Role of Semiconducting and Metallic Tubes in P3HT/Carbon-Nanotube Photovoltaic Heterojunctions: Density Functional Theory Calculations, Nano Letters 2008, Vol. 8, No. 3, 908-912

IV) Possible definitions of 'charge transfer' (1)

- If atomic 'partial' charges point of view (ex : ReaxFF, classical force fields, 'chemist language' [donor / acceptor interactions, etc.]) :

→ summing 'partial' charges over graphene, over each molecule/fragment separately.

- If electronic density $\boldsymbol{n}(\vec{\boldsymbol{r}})$ available :

  - Either : $\Delta n(\mathbf{r}) = n_{A+B}(\mathbf{r}) - n_A(\mathbf{r}) - n_B(\mathbf{r})$.
  - Or : reduction of the electronic density $n_{A+B}(\mathbf{r})$ to partial charges ('monopoles') or dipoles, quadrupoles, etc.

- Then : summing over partial charges on the two fragments ('donor'/acceptor') to estimate the 'doping'.

- Some atomic charge calculation schemes (from the density or orbitals) :
  - **Electrostatic Potential fitting methods** (grid of points necessary).
  - **Atomic population analysis schemes** (Mulliken, Bader, DDEC6, etc.).

IV) Possible definitions of ‘charge transfer’ (2)

- The density difference $\Delta\rho(r) = \rho_{A+B}(r) - \rho_A(r) - \rho_B(r)$:

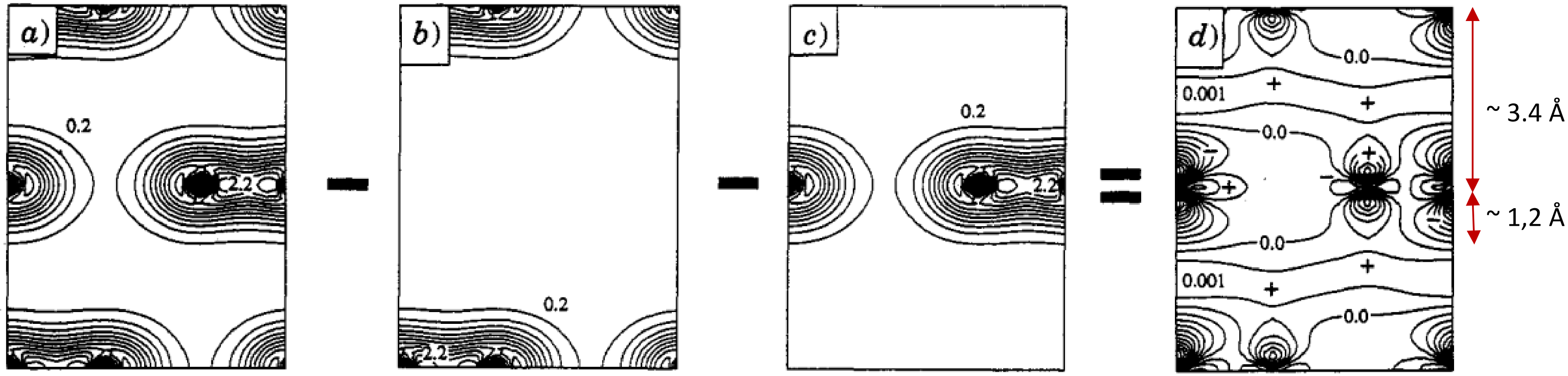


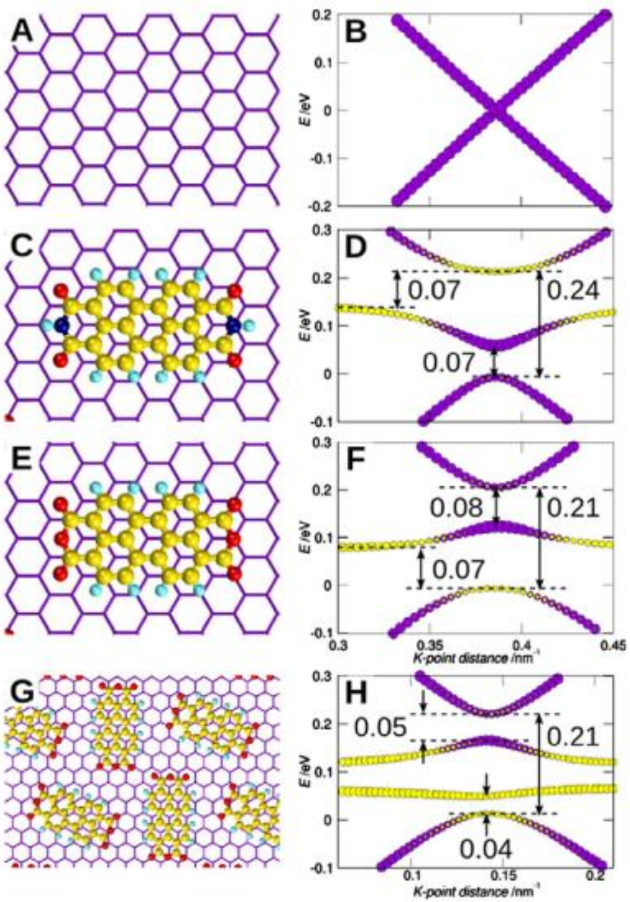
Fig. 3. – *Ab initio* valence electron pseudocharge density of *a*) graphite in a plane perpendicular to the graphene sheet and containing α and β atoms, *b*) A-type isolated graphite layer along the *c*-axis as in *a*), *c*) B-type isolated graphite layer along the *c*-axis as in *a*). Contours are drawn every $0.2\ e^-/Å^3$. *d*) Contour plot of the transfer of charge due to the stacking of graphene layers obtained by the processus described in this figure: density of graphite (*a*)) minus that of reference graphite layers: A-plane (*b*)) and B-plane (*c*)). Positive and negative zones of electronic density are labelled by + and −, respectively, between the lines of $0.0\ e^-/Å^3$. Contours are drawn every $0.1 \cdot 10^{-3}\ e^-/Å^3$. The maximum in the interplane region is found at $1.7 \cdot 10^{-3}\ e^-/Å^3$. Atomic locations are denoted by solid squares.

Example : electronic cloud delocalisation in-between the sheets in graphite.

J.-C Charlier, X Gonze, and J.-P Michenaud. Graphite interplanar bonding: Electronic delocalization and van der waals interaction. Europhysics Letters (EPL), 28(6):403–408, nov 1994.

IV) Possible definitions of ‘charge transfer’ : the band structure ‘picture’ (3)

- If energy levels (HOMO/LUMO) of the adsorbed molecule is very close to the Dirac point : **band gap opening, p (or n) can be guessed.**



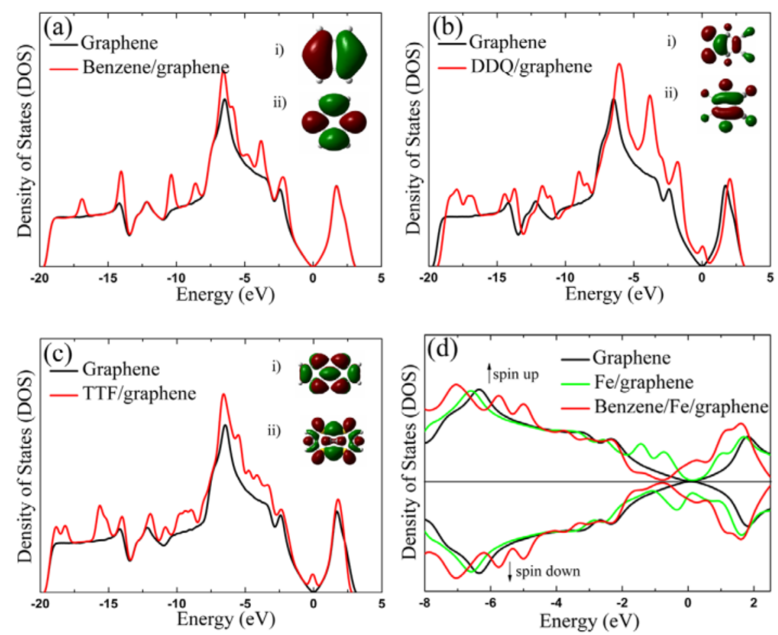


Figure 2. Total electronic DOSs ((a)–(c)) for pristine graphene (black) and the molecule/graphene systems (red) calculated for the corresponding configurations shown in figure 1 (a3, b2 and c1). The HOMO (i) and LUMO (ii) of the corresponding molecules are shown as the insets. (d) Plots of the spin up and spin down channels of the pristine graphene, Fe/graphene, and benzene/Fe/graphene. The Fermi level is set to zero.

Yong-Hui Zhang, Kai-Ge Zhou, Ke-Feng Xie, Jing Zeng, Hao-Li Zhang, and Yong Peng. Tuning the electronic structure and transport properties of graphene by noncovalent functionalization: effects of organic donor, acceptor and metal atoms. Nanotechnology, 21(6):065201, jan 2010

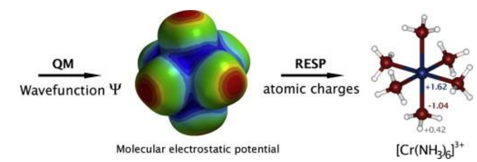
Sergey M. Kozlov, Francesc Vines, and Andreas Görling. On the interaction of polycyclic aromatic compounds with graphene. Carbon, 50(7):2482–2492, jun 2012.

IV) Possible definitions of ‘charge transfer’ : atomic population analysis (4)

- <u>**Electrostatic Potential fitting methods :**</u>

- <u>Ex :</u> Kollman-Singh scheme (*). Idea : fitting the electrostatic field generated by the electronic density $\boldsymbol{n(\vec{r})}$ (derived by DFT) to the field induced by partial charges $\mathbf{q_i}$, only :

$$\vec{r} \longrightarrow \mathcal{E}_{q_1,..,q_N}(\vec{r}) = \sum_{i=1}^{N} \frac{q_i}{4\pi\epsilon||\vec{r} - \vec{r_i^0}||}$$



- Minimization under constraint of global neutrality :

$$(q_1,..,q_N) = \arg \min_{q'_1,..,q'_N} \left[||\mathcal{E}_{q_1,..,q_N}(\hat{\vec{r_1}}) - E^{elec}_{QM}(\hat{\vec{r_1}})||^2 + ... + ||\mathcal{E}_{q_1,..,q_N}(\hat{\vec{r_K}}) - E^{elec}_{QM}(\hat{\vec{r_K}})||^2 \right]$$

- ChelpG anaysis (Charges from Electrostatic Potentials Using a Grid-based Method)
- RESP (Restrained electrostatic Potential) method

⇨ Numerous grid points $\mathbf{r_1}$, .., $\mathbf{r_K}$ (many selection methods, problems for **large molecules** and ‘buried’ atoms [far from the surface/grid]) .
Sensitivity of the estimated charges to the grid points ? Overfitting ?

- <u>Rq 1</u> : Same idea applicable to fit to the electrostatic field induced by a family of dipoles, quadrupoles (multipole expansion).
- <u>Rq 2</u> : Same methods for parametrization of atomic partial charges in classical force fields (against QM density data at optimized geometry).

*(*) U. Chandra Singh and Peter A. Kollman, An Approach to Computing Electrostatic Charges for Molecules, Journal of Computational Chemistry, Vol. 5, No. 2, 129-145 (**1984**)*

<u>Image</u> *: taken from Ivana Djordjevic and al., Computational and Theoretical Chemistry 1001 (2012) 20–25.*

IV) Possible definitions of 'charge transfer' : atomic population analysis (5)

- **Other methods :**

  - Mulliken charges (from atomic and molecular orbitals) : very (atomic orbital) **basis-set** dependent.

  - Bader charges.

  - Lowdin charges. Example : Ref (*) : charge transfer estimation of 0.3e from P3HT to metallic CNTs and 0.02e to semiconducting CNT.

  - Natural Bond Orbital (NBO) analysis (more sophisticated) : charge transfer 'energy'

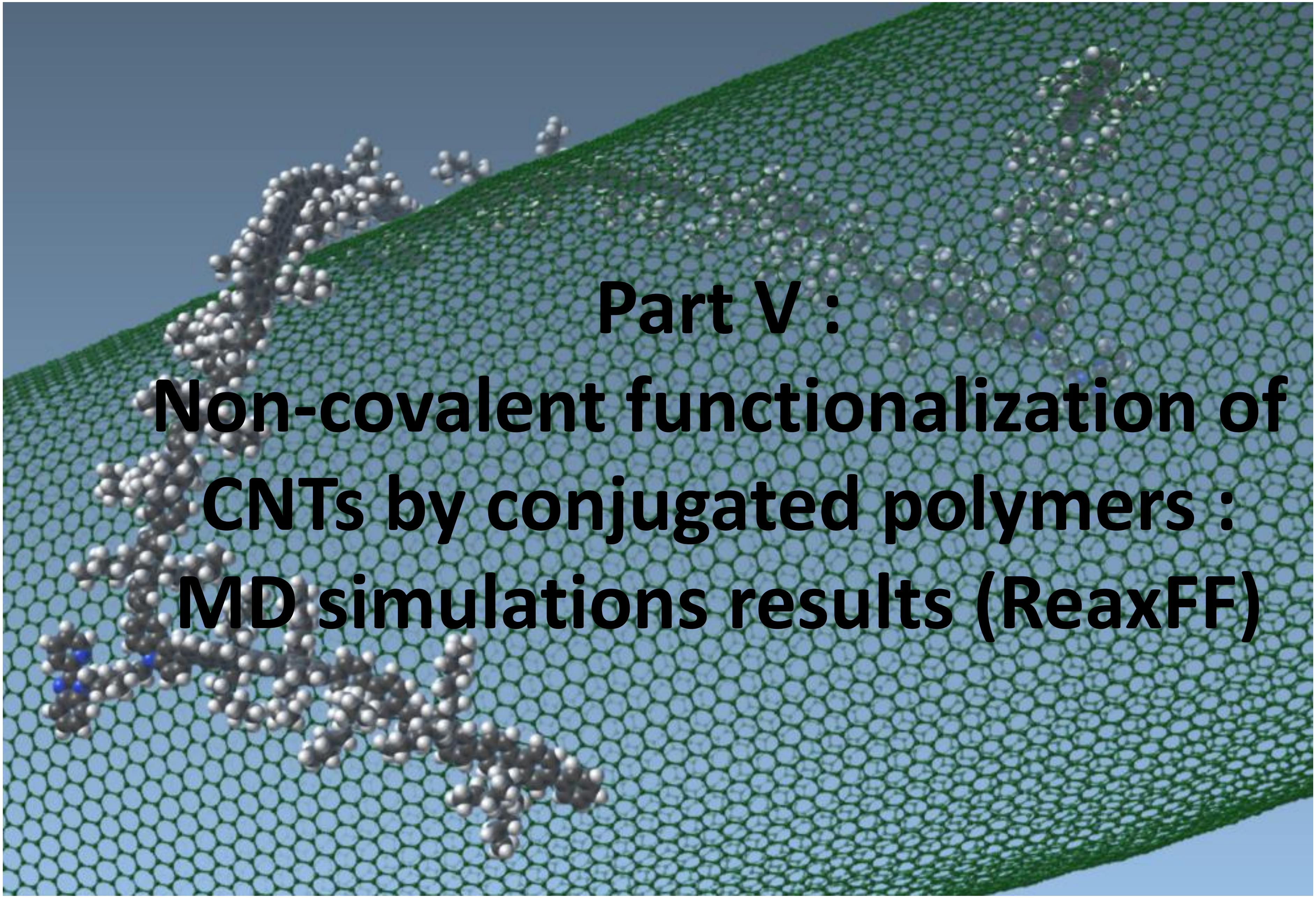
  - DDEC(6) method (Density Derived Electrostatic and Chemical Methods) => net atomic charges as functionals of the electron density => **basis set independent** (**).

  - Quantum Theory of Atoms in Molecules (QTAIM) analysis

(*) Yosuke Kanai and Jeffrey C. Grossman, Role of Semiconducting and Metallic Tubes in P3HT/Carbon Nanotube Photovoltaic Heterojunctions: Density Functional Theory Calculations, Nano Letters 2008, Vol. 8, No. 3, 908-912.
(**) Thomas A. Manz and Nidia Gabaldon Limas. Introducing DDEC6 atomic population analysis: part 1. charge partitioning theory and methodology. RSC Advances , 6(53):47771–47801, 2016.

Part V :

Non-covalent functionalization of CNTs by conjugated polymers : MD simulations results (ReaxFF)

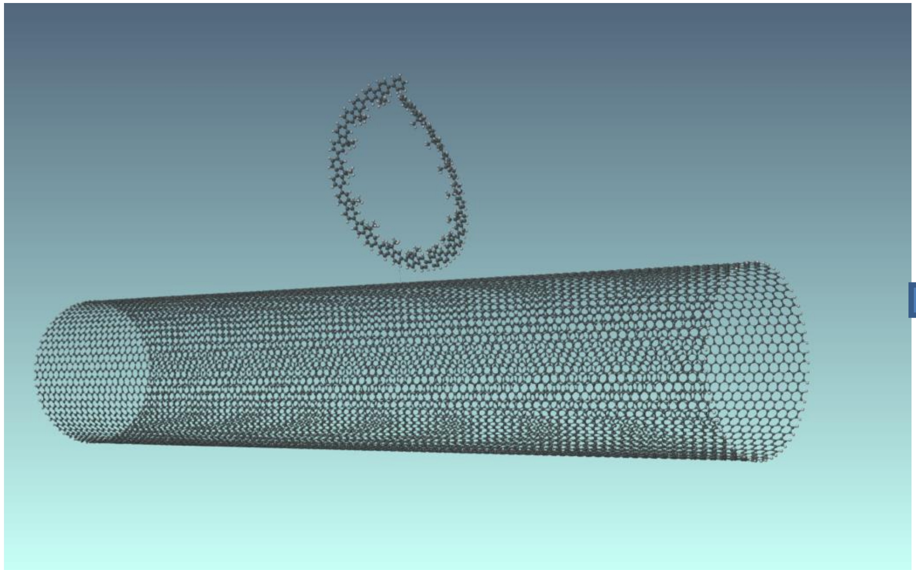


V) Non-covalent functionalization of CNTs by conjugated polymers (1)

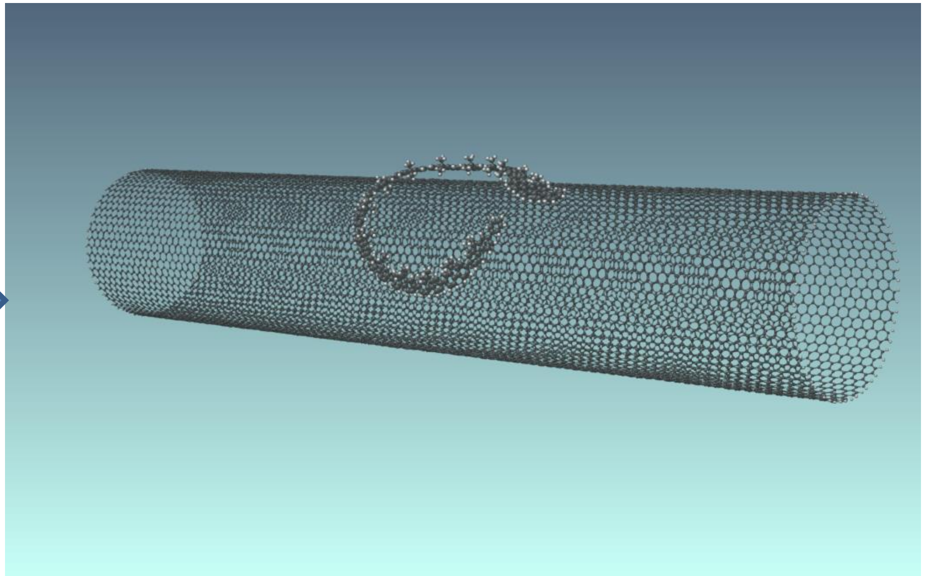
- Insight into the non-covalent functionalization (local adsorption geometries) thanks to MD :

- LAMMPS code, ReaxFF (*) : **variable charge** MD (very large systems, DFT not affordable).
- NVT thermostat (Nosé-Hoover), 300 K, 0.3 fs time-step (no Periodic Boundary Conditions).
- Velocity Verlet integration scheme.

<u>**Example**</u> **: simulation with a** 'benchmark' polymer :



*Initial geometry Poly(9,9-di**méthyl**fluorène), 15 monomers long. 4 nm diameter, 20 nm long CNT.*

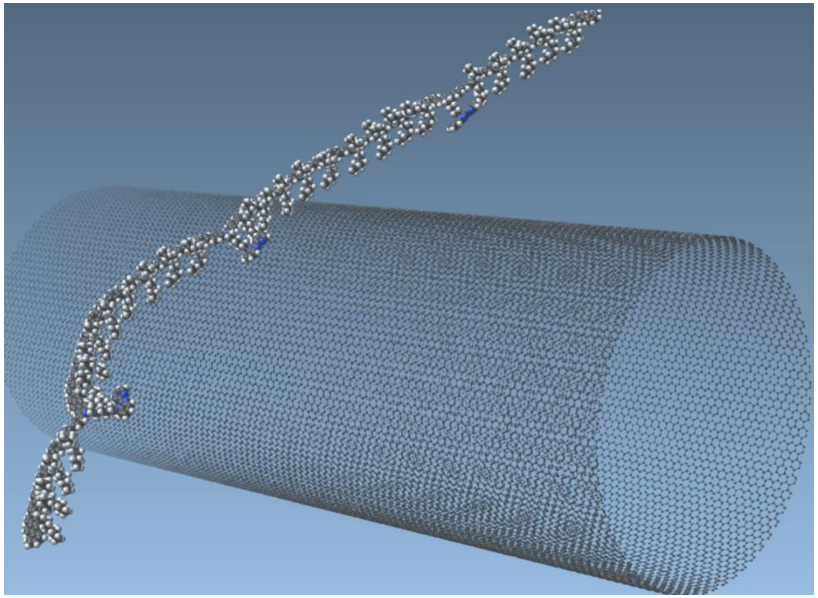


Final adsorption geometry after 60 000 steps

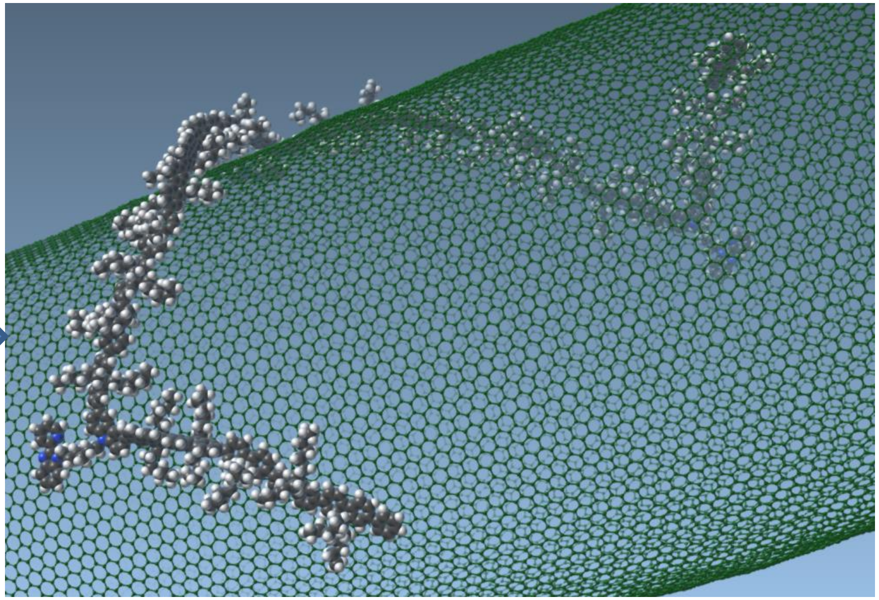
*(*) Adri C. T. van Duin, Siddharth Dasgupta, Francois Lorant, and William A. Goddard III, ReaxFF : a Reactive Force Field for Hydrocarbons, J. Phys. Chem. A, **2001**, 105 (41), pp 9396-9409*

V) Non-covalent functionalization of CNTs by conjugated polymers (2)

- Carbazole:fluorene copolymer (for heavy metal ions sensing) next to a 9 nm diameter CNT.
- Around **20 000 atoms** : very big systems, ***difficult to periodize***.
- Same simulation method.



*Initial geometry, 'XW P2' polymer next to a **8.5 nm** diameter, 20 nm long CNT*

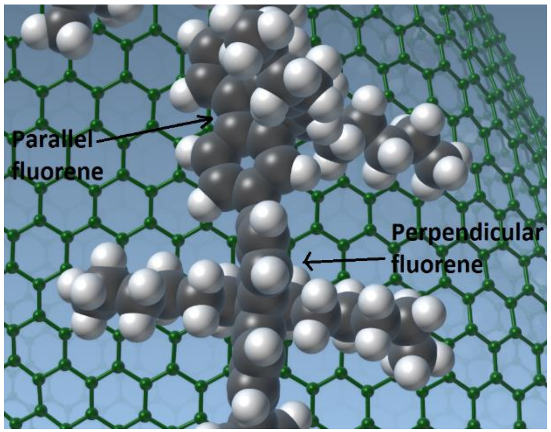


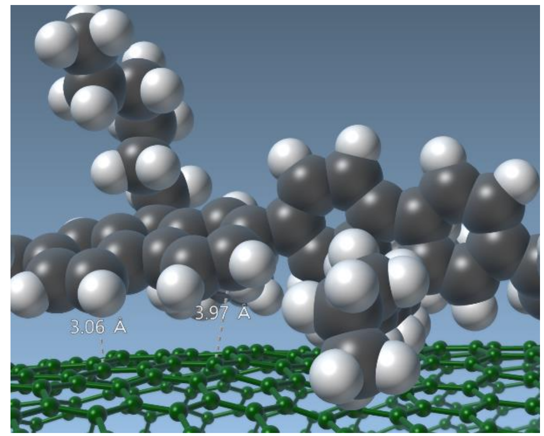
'Final' adsorption geometry after 300 000 steps of 0.3 fs

- Competition between torsional energy and **π-π stacking** (mix of VdW and electrostatic).

V) Non-covalent functionalization of CNTs by conjugated polymers (3)

- Locally perpendicular or parallel adsorption geometries :

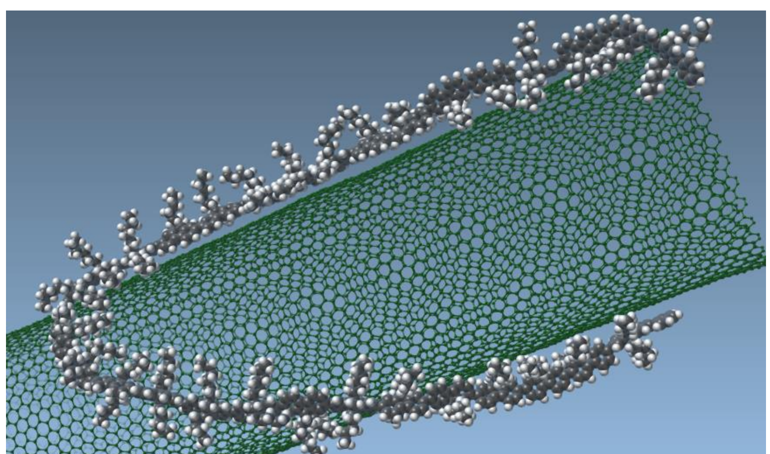




→ Steric hindrance due to **hexyl** chains.

- Non-covalent functionalization : average distance of 3.4 Å .

Adsorption of a poly(9,9-di**hexyl**fluorène), 30 monomers long.



Images : SAMSON software

V) Non-covalent functionalization of CNTs by conjugated polymers (4)

- Classical force fields :

'Bonded' terms

$$U_{\mathbf{p}}(\vec{r_1}, .., \vec{r_N}) = \sum_{bonds} k_b (b - b_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} k_\phi (1 + \cos(n\phi - \delta)) + \sum_{impropers} k_\chi (\chi - \chi_0)^2$$

$$+ \sum_{i<j|d(i,j)\geq 3} C \frac{q_i q_j}{4\pi\epsilon r_{ij}} + \sum_{i<j|d(i,j)\geq 3} \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right]$$

'Non-bonded' terms (electrostatics +VdW)

➡ Use fixed 'partial' (atom-centered) charges (optimized initially, **at a given geometry**, to fit QM or experimental data).

- ReaxFF : slighlty more complicated expression of interatomic potentials (same spirit).

- Main difference : ReaxFF is combined to a 'charge equilibrium scheme' (Qeq) **(*)** recomputing partial charges at each step (minimizing the total electrostatic energy).

__(*)__ A. K. Rappe and al., Charge equilibration for Molecular Dynamics simulations, The Journal of Physical Chemistry, 95 (8), 3358-3363, __1991__.

V) The charge equilibration scheme (5)

- What the charge equilibration 'Qeq' scheme simply does :
- Minimizing, at each geometry, the function :

$$F\left(\{q_i\}_i\right) = \sum_i \left[E_i^{(0)} + (q_i - q_0^i)\chi_i + \frac{(q_i - q_0^i)^2}{2}\eta_i + C \sum_{j>i} \frac{q_i q_j}{\left(r_{ij}^3 + \gamma_{ij}^3\right)^{\frac{1}{3}}} \right]$$

Atomic energy

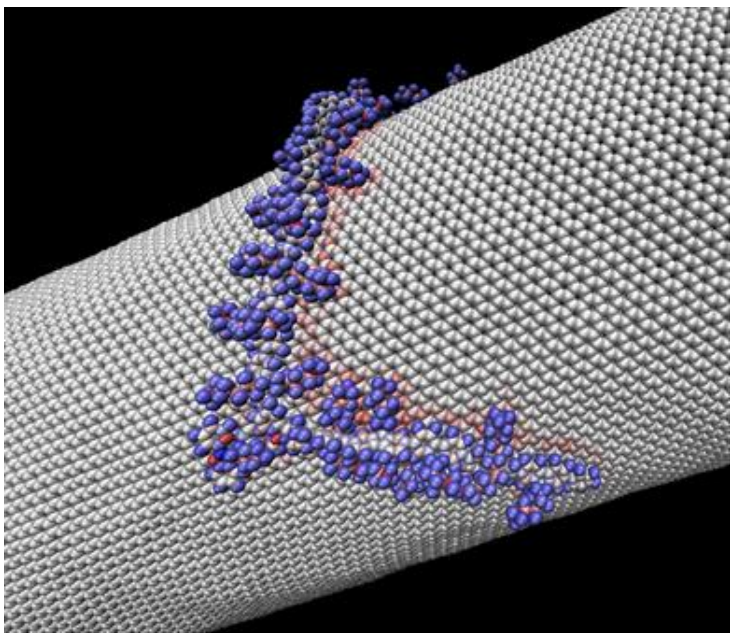
Electrostatic energy

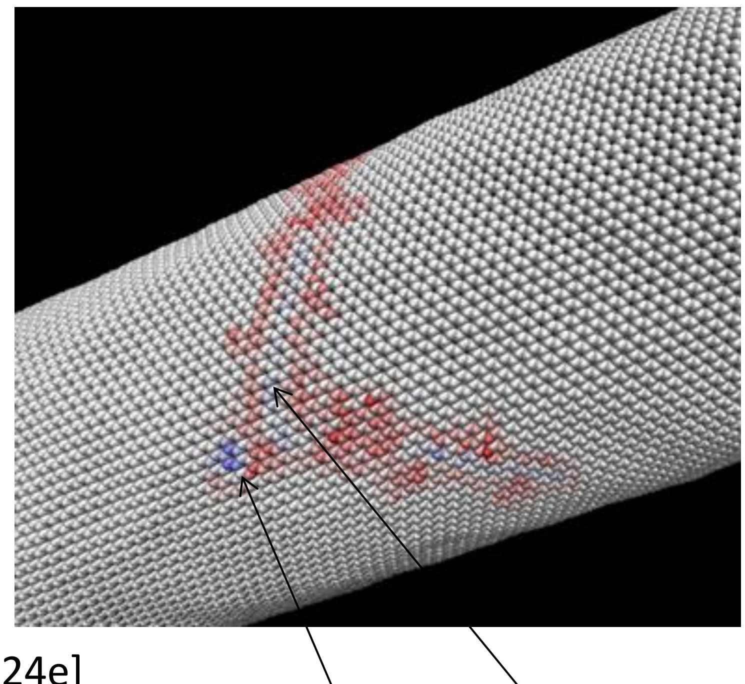
- Under the constraint of global charge neutrality.
- Yields a **set** of (correlated) partial charges (q_1 ,..., q_N).
- Equivalent to impose that all atoms (in the molecule / system) have the same 'generalized electronegativity' (modified by the environment) **μ** *(Electronegativity Equalization Method).*
- Better approximation for single molecules than for hybrid systems (as a CNT/polymer compound) ?

V) Non-covalent functionalization of CNTs by conjugated polymers (6)

From the MD trajectory, possible to have an estimation of the ‘charge transfer’ (in terms of partial charges) upon adsorption of the polymer.

- CNT atoms become negatively charged when the polymer (known as a ‘donor’) adsorbs
- Small charge transfer (<= 0.025 electron per atom for some CNT atoms)





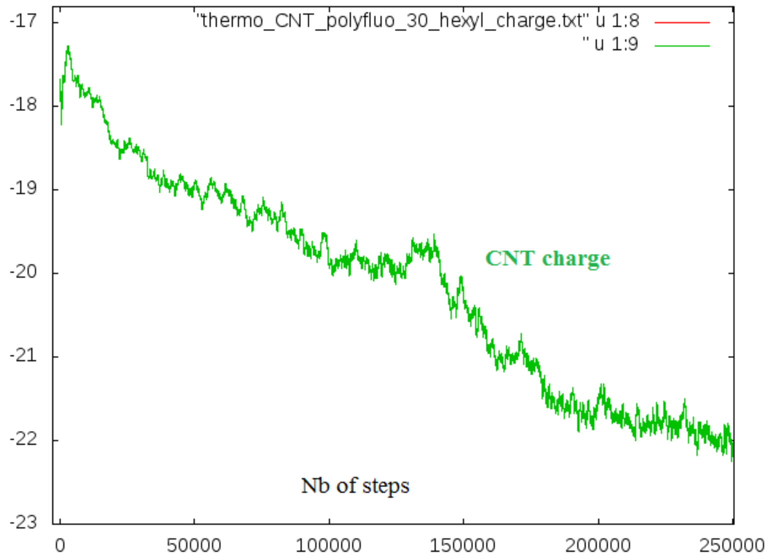
- Color scale for CNT partial charges : [-0.026e,+0.024e]
- Color scale for polymer partial charges : [-0.34e,+0.23e]

(**red**) (**blue**)

Images : VMD software

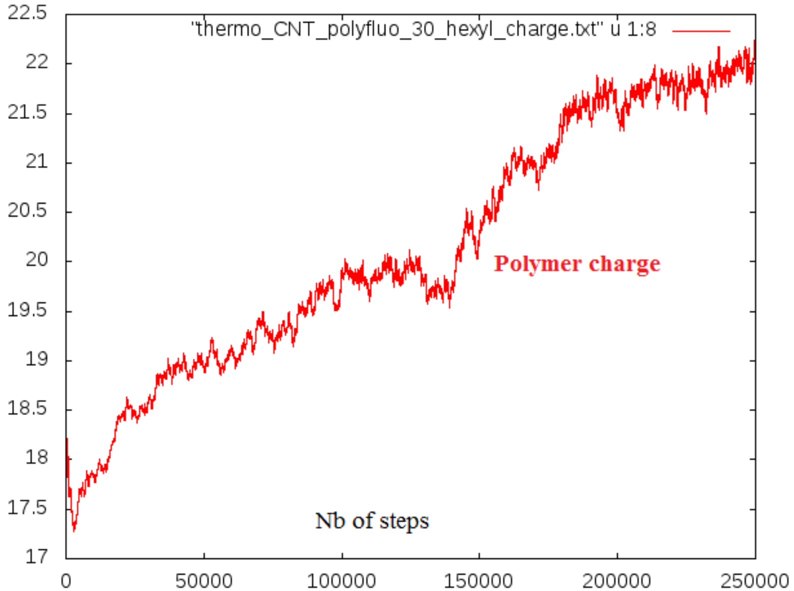
V) Non-covalent functionalization of CNTs by conjugated polymers (7)

- Estimated transfer of ~ **4e** from the polymer to the CNT for 30 monomers.



Evolution of the total charge of the **CNT** during adsorption ('Qeq' scheme)

Adsorption completed



Evolution of the total charge of the **polymer** during adsorption ('Qeq' scheme)

Adsorption completed

- Is this charge transfer mostly due to parallel or perpendicularly 'stacked' fluorene groups ? To hexyl chains ?

Still work in progress.

V) Non-covalent functionalization of CNTs by conjugated polymers (8)

- Is this estimated ‘charge transfer’ reliable ? How does it compare to the literature ?
  Other definitions of ‘charge transfer’ ?
  => Cf. Part III) and IV)

- Atomic ‘partial charges ’ : order 0 of the description of the charge distribution (‘monopoles’).

- More precise description of anisotropy of the charge distribution needed ?

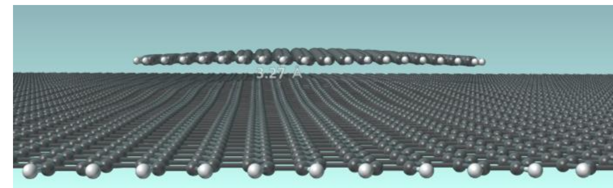
<u>Example</u> : dipole and quadrupole moments associated to each atom (fixed), **induced dipoles** (recomputed at each step) in the spirit of AMOEBA (polarizable force field).

- Benchmark on higher level methods based on electronic density (or wave-functions) : DFT (Van der Waals corrected), MP2 / CCSD(T) ?

- Which level of theory / which ingredients needed to capture correctly the energetics / **geometry**, and **charge distribution** features of non-covalently interacting systems ?
  => Cf. Part II)

Conclusions

- Dispersion interactions happen to be Coulomb interactions between (local) transition densities centered on each fragment (benzene / graphene) of the system (separated enough).



- Functional **ω**B97X-D used for the benchmark :
  - dispersion corrected (semi-empirical Grimme corrections)
  - hybrid functional (exact exchange included)
  - long-range corrected (100 % exact echange for long-range electron-electron interactions, 16% at short range)
  - B97 exchange funtional at short-range, B97 **correlation functional at both short and long-range**.

- Is this level of theory enough to capture VdW **London dispersion** correctly (and be used as a benchmark <u>for the energy</u>) ?
  => Supposedly yes.

- Is this level of theory enough to capture '**charge transfer**' (and its possible variations between AA and AB geometries) correctly ? Are higher levels of theory (MP2 / CCSD(T), etc.) needed for this charge transfer benchmark ?
  => Still an open problem … !

THANK YOU FOR YOUR ATTENTION !

Annex : Benchmarking ReaxFF for π-π stacking interactions on higher theory levels

Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (3)

- Binding energies derived from structural minimizations (ReaxFF force field) :

Aromatic molecule	Benzene (C_6H_6)	Perylene ($C_{20}H_{12}$)	Coronene ($C_{378}H_{48}$)
Number of C atoms	6	20	378
Adsorption energy (AB stacked geometry)	-68 kJ/mol (-707 meV)	-187 kJ/mol (-1.94 eV)	-2826 kJ/mol (-29.4 eV)
Per atom binding energy	-5.7 kJ/mol (-59 meV)	-5.8 kJ/mol (-61 meV)	-6.6 kJ/mol (-69.0 meV)
Per carbon atom binding energy	11 kJ/mol (114 meV)	9 kJ/mol (97 meV)	7.4 kJ/mol (78 meV)
Molecule-graphene distance	3.22 $\mathring{A}$	3.27 $\mathring{A}$	3.26 $\mathring{A}$

Comparison of adsorption energies and per-atom binding energies on graphene for the different aromatic molecules studied.

The most stable stacked AB configurations (on a much larger graphene sheet underneath) are chosen.

1 kJ/mol = 10,4 meV

Experimental range for the adsorption energy : **35 (+/-15) to 52 (+/-5) meV/atom** (averages over a few Polycyclic Aromatic Hydrocarbons(Δ))

(Δ) Renju Zacharia, Hendrik Ulbricht, and Tobias Hertel. Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons. Physical Review B, 69(15), apr 2004.

Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (4)

System	Interlayer (or binding) energy	Equilibrium distance	Method used	Number of atoms	Energy difference between AB and AA configurations $\Delta E_{AB/AA}$	Reference
Benzene on a graphene model (C_{574} to C_{1006})	-96 to -75 meV/C atom (-55.2 to -43.9 kJ/mol)	Not precised	Dispersion corrected semi-empirical method (MO theory) PM6-DH2, compared to DFT (B3LYP-D, M06-2X and ω−B97X-D functionals), several basis sets tested	6 C atoms (benzene) and graphene model (medium-size finite sheet). Solvent (H_2O) also considered.	$\Delta E_{AB/AA}$ not studied	[7]
Benzene stacked on a $C_{150}H_{30}$ coronene (graphene model)	-87 meV/C atom (-50.2 kJ/mol in total)	Not precised	Symmetry adapted perturbation theory (SAPT)	6 C atoms (benzene) on a $C_{150}H_{30}$ coronene molecule mimicking graphene	Not studied	[8]
Benzene stacked stacked on $C_{110}H_{26}$ ('coronene 43') graphene model	-92.1 meV/C atom (-53.1 kJ/mol in total)	'AB' (3.35 Å) and 'PD' (3.34 Å) optimized adsorption geometries ('PD' slightly more stable)	ωB97X-D (DFT level, semi-empirical VdW correction), TZVPP basis sets	6 C atoms (benzene) on a $C_{110}H_{26}$ coronene molecule	$\Delta E_{AB/AA} \approx$ -6.3 meV/C atom, $\Delta E_{PD/AB} \approx$ -0.9 meV (**in total**)	[9] (same authors as Ref. [8])
Benzene stacked stacked on $C_{110}H_{26}$ ('coronene 43') graphene model	-92.2 meV/C atom (-57.2 kJ/mol in total)	'AB' (3.35 Å) and 'PD' (3.34 Å) optimized adsorption geometries	(Spin Component Scaled) SAPT0, aug-cc-pVDZ basis set	6 C atoms (benzene) on a $C_{110}H_{26}$ coronene molecule	$\Delta E_{PD/AB} \approx$ -1.3 meV (**in total**)	[9] (same authors as Ref. [8])

Benchmark of (absolute) adsorption energies and adsorption energies separations (1)

References for the benchmark (1)

- **[7]** Mark A. Vincent and Ian H. Hillier. Accurate prediction of adsorption energies on graphene, using a dispersion-corrected semiempirical method including solvation. Journal of Chemical Information and Modeling, 54(8):2255–2260, aug 2014.

- **[8]** Weizhou Wang, Tao Sun, Yu Zhang, and Yi-Bo Wang. Substituent effects in the $\pi - \pi$ interaction between graphene and benzene: An indication for the noncovalent functionalization of graphene. Computational and Theoretical Chemistry, 1046:64–69, oct 2014.

- **[9]** Weizhou Wang, Yu Zhang, and Yi-Bo Wang. Noncovalent $\pi - \pi$ interaction between graphene and aromatic molecule: Structure, energy, and nature. The Journal of Chemical Physics, 140(9):094302, mar 2014.

Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (5)

System	Interlayer (or binding) energy	Equilibrium distance	Method used	Number of atoms	Energy difference between *AB* and *AA* configurations $\Delta E_{AB/AA}$	Reference
Coronene ($C_{24}H_{12}$) on graphene	-72 meV/C atom (-1.73 eV total binding energy)	3.38 Å	ωB97X-D (DFT level, semi-empirical VdW correction) 6-31G* basis-set	24 C atoms (coronene), 116 C-atoms hydrogenated graphene sheet ($C_{116}H_{28}$)	-11 meV/ C atom	[1]
Benzene on graphene	-78.3 meV/C atom (-470 meV total binding energy)	3.35 Å	ωB97X-D (DFT level, semi-empirical VdW correction) 6-31G* basis-set	6 C atoms (benzene), 116 C-atoms hydrogenated graphene sheet ($C_{116}H_{28}$)	-9.4 meV/C atom	[1]
Benzene on graphene	-136 meV/C atom	3.22 Å (*AB* stacking), 3.26 Å (*AA* stacking)	DFT-D (GGA exchange-correlation functional, semi-empirical VdW correction)	6 C atoms (benzene), p(4×4) supercell of the graphene sheet (PBC)	-8.1 meV/ C atom (-49 meV in total), about -5.8 meV/C atom due to $\Delta E^{VdW}_{AB/AA}$ and -2.3 meV/ C atom due to $\Delta E^{DFT}_{AB/AA}$	[3]
Benzene on graphene	-114 meV/C atom	3.22 Å	**ReaxFF**	6 C atoms (benzene), hydrogenated graphene sheet ($C_{873}H_{83}$)	-1.2 meV/C atom	This work
Perylene on graphene	-97 meV/C atom	3.27 Å	**ReaxFF**	20 C atoms (perylene), hydrogenated graphene sheet ($C_{873}H_{83}$)	-1.8 meV/C atom	This work
Coronene on graphene	-78 meV/C atom	3.22 Å	**ReaxFF**	378 C atoms (coronene), 13772 atoms (20 nm × 20 nm) hygrogenated graphene sheet	-0.85 meV/C atom	This work

Benchmark of (absolute) adsorption energies and adsorption energies separations (2)

References for the benchmark (2)

- **[1]** Olga V. Ershova, Timothy C. Lillestolen, and Elena Bichoutskaia. Study of polycyclic aromatic hydrocarbons adsorbed on graphene using density functional theory with empirical dispersion correction. Physical Chemistry Chemical Physics, 12(24):6483, 2010.

- **[3]** Sergey M. Kozlov, Francesc Vines, and Andreas Görling. On the interaction of polycyclic aromatic compounds with graphene. Carbon, 50(7):2482–2492, jun 2012.

Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (9)

System	Interlayer (or binding) energy	Equilibrium distance	Method used	Number of atoms	Energy difference between AB and AA configurations $\Delta E_{AB/AA}$	Reference
Two-circular shaped graphene sheets (diameter 16 nm)	-44 meV/atom	3.34 Å	Kolmogorov-Crespi registry-dependent interlayer interaction potential (modified LJ)	15 355 atoms (two sheets)	-3 meV/atom	[4]
Two flat graphene sheets (one fixed, one movable)	-17.72 meV/atom (AB stacking) vs. -17.36 meV/atom (AA stacking)	3.35 Å (AB stacking) and 3.38 Å (AA stacking)	Lennard-Jones potential $4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$ ($\epsilon = 2.168meV$ and $\sigma = 3.36Å$)	1560 atoms (sheet underneath) and 366 atoms (movable sheet)	From -0.59 to -0.36 meV/atom	[12]
Graphene bilayer	−17.7 meV/atom (AB stacking) vs. −11.5 meV/atom (AA stacking)	3.43 Å	Diffusion quantum Monte-Carlo calculations	3 × 3 supercell, PBC	-6.2 meV/atom	[8]
$ABAB$ graphite and $AAAA$ stacking of sheets	-20 meV/atom in graphite (-11.6 meV/atom due to E_{xc}) *i.e.* -10 meV/atom for two sheets only	3.30 Å (AB stacking) and 3.66 Å (AA stacking)	DFT (**VdW assumed included in the exchange-correlation term** E_{xc})	Unit cell (4 atoms for $ABAB$ stacking), PBC$^{(*)}$	-9.7 meV/atom for graphite *i.e.* -4.9 meV/atom for two sheets	[2]
Graphene bilayer	-50.6 meV/atom (DFT-D), -29.3 meV/atom (vdW-DFT)	3.25 Å	DFT-D (PBE XC functional and correction for dispersion terms), and vdW-DFT	4.271 Å× 2.466 Å× 20 Å cell, PBC	-19.5 meV/atom (DFT-D), -18.9 meV/atom (vdW-DFT)	[7]
Graphene bilayer ('AB' stacking geometry)	-48 meV/atom (-51 meV/atom for a graphene trilayer	3.45 Å	vdW-DFT (correction to VdW included as a (non-local) functional of the density. Double zeta polarized basis sets of pseudo atomic orbitals	Unit cell : 18.7 Å × 20.7 Å in the x, y directions, 20 Å in the vertical direction	Not studied	[1]

TABLE VI: Interlayer binding energies found in the literature for **graphene bilayers** systems. Energies are expressed in meV per carbon atom, distances in Å . (∗) Periodic Boundary Conditions.

Benchmark of interlayer binding energies of graphite graphene bilayers

References for the benchmark

- [4] Yufeng Guo and Wanlin Guo. Interlayer energy-optimum stacking registry for two curved graphene sheets of nanometre dimensions. Molecular Simulation, 34(8):813–819, jul 2008.

- [12] Yasushi Shibuta and James A. Elliott. Interaction between two graphene sheets with a turbostratic orientational relationship. Chemical Physics Letters, 512(4-6):146–150, aug 2011.

- [8] E. Mostaani, N. D. Drummond, and V. I. Fal'ko. Quantum monte carlo calculation of the binding energy of bilayer graphene. Physical Review Letters, 115(11), sep 2015.

- [2] J.-C Charlier, X Gonze, and J.-P Michenaud. Graphite interplanar bonding: Electronic delocalization and van der waals interaction. Europhysics Letters (EPL), 28(6):403–408, nov 1994.

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- [1] Steven Bailey, David Visontai, Colin J. Lambert, Martin R. Bryce, Harry Frampton, and David Chappell. A study of planar anchor groups for graphene-based single-molecule electronics. The Journal of Chemical Physics, 140(5):054708, feb 2014.

Benchmarking ReaxFF for π-π stacking interactions on higher theory levels (7)

Adsorbed molecule	Distance from the surface	Charge transfer to graphene (per adsorbed molecule)	Method for charge transfer estimation	Force field for structural minimization	Reference
Benzene stacked	4 Å initially, 3.22 Å in the end	0.026e	Partial charges, Qeq [9]	ReaxFF	This work
Benzene stacked	5.5 Å initially, 3.22 Å in the end	0.045e	Partial charges, Qeq [9]	ReaxFF	This work
Benzene stacked	3.17 Å (equilibrium)	0.03e	Mulliken population analysis [8]	DFT (LDA), **no VdW correction** (not reliable)	[19]
Benzene sandwich	3.40 Å (equilibrium)	0.02e	Mulliken population analysis [8]	DFT (LDA), **no VdW correction** (not reliable)	[19]
Benzene stacked	3.22 Å (equilibrium)	0.01e	Bader analysis on the density (accuracy of order ± 0.01e)	DFT-D (GGA), semi-empirical VdW correction	[3]
Benzene stacked on a $C_{150}H_{30}$ coronene	Not precised	-0.004e (transfer of electrons **from graphene to benzene**)	Mulliken population analysis [8] from the density $n(\vec{r})$	Symmetry adapted perturbation theory (SAPT)	[8]
Benzene stacked stacked on $C_{110}H_{26}$ ('coronene 43') graphene model	3.35 Å	0.02e	Mulliken net charges from the density $n(\vec{r})$	ωB97X-D (DFT level, semi-empirical VdW correction), TZVPP basis sets	[9]
Perylene stacked	3.21 Å (equilibrium)	0.01e	Bader analysis on the density (accuracy of order ± 0.01e)	DFT-D (GGA), semi-empirical VdW correction	[3]
Perylene stacked	4 Å initially, 3.27 Å in the end	0.04e	Partial charges, Qeq [9]	ReaxFF	**This work**
Perylene stacked	5.5 Å initially, 3.27 Å in the end	0.08e	Partial charges, Qeq [9]	ReaxFF	**This work**
Perylene sandwich	4.5 Å initially, 3.28 Å in the end	0.06e	Partial charges, Qeq [9]	ReaxFF	**This work**
Perylene sandwich	5.5 Å initially, 3.28 Å in the end	0.08e	Partial charges, Qeq [9]	ReaxFF	**This work**
Coronene	5 Å initially, 3.26 Å in the end	0.28e	Partial charges, Qeq [9]	ReaxFF	**This work**

Benchmark of charge transfer : can ReaxFF (Qeq scheme) capture the correct charge transfer ?

References for the benchmark (3)

- **[19]** Yong-Hui Zhang, Kai-Ge Zhou, Ke-Feng Xie, Jing Zeng, Hao-Li Zhang, and Yong Peng. Tuning the electronic structure and transport properties of graphene by noncovalent functionalization: effects of organic donor, acceptor and metal atoms. Nanotechnology, 21(6):065201, jan 2010.