Theory of doping graphene

H. Pinto, R. Jones

School of Physics, University of Exeter,
EX4 4QL, Exeter United Kingdom

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Graphene

Graphene is made by a single atomic layer of carbon atoms arranged in a honeycomb lattice.

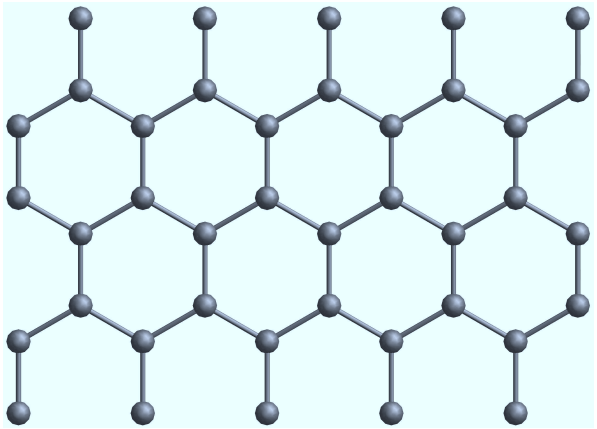

Figure 1: Structure of graphene.

Is a zero-gap semiconductor and has unique properties such as high carrier mobility and extreme sensitivity to molecular adsorbates.

The type and the concentration of carriers in graphene, electron or holes, can be controlled by the introduction of metals or molecules on the graphene surface.

Doping of graphene

n-type and p-type doping have been successfully demonstrated.

- n-type dopants
  K [1], Ti, Fe and Cr [2] atoms and NH_3 [3] molecules
- p-type dopants
  NO_2 [4].

[1] J. H. Chen, C. Jang, S. Adam, M. S. Fuhrer, E. D. Willams, *Nat. Mater.* **4** (2008) 377.

[2] K. Pi, K. McCreary, W. Bao, W. Han, Y. F. Chiang, Y. Li, S. Tsai, C. Lau, R. Kawakami, arXiv:0903.2837v2.

[3] X. Wang, X. Li, L. Zhang, Y. Yoon, P. Weber, H. Wang, J. Guo, H. Dai, Science **324** (2009) 768.

[4] S. Y. Zhou, D. A. Siegel, A. V. Fedorov, A. Lanzara, *Phys. Rev. Lett.* **101** (2008) 086402.

Schematic description of electronic doping

The relative position of the HOMO and LUMO of the adsorbate with respect to Dirac point in pure graphene determines the direction of charge transfer.

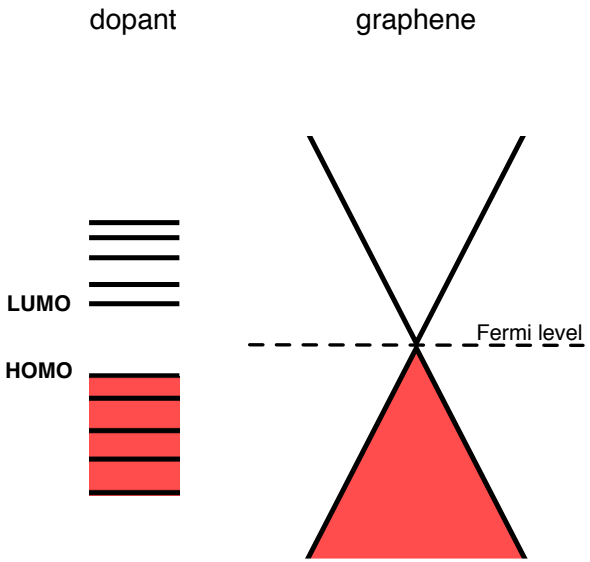

Figure 2: No charge transfer.

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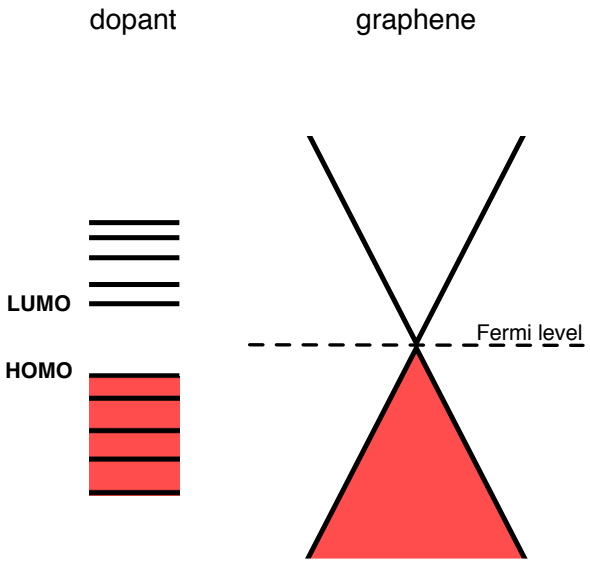

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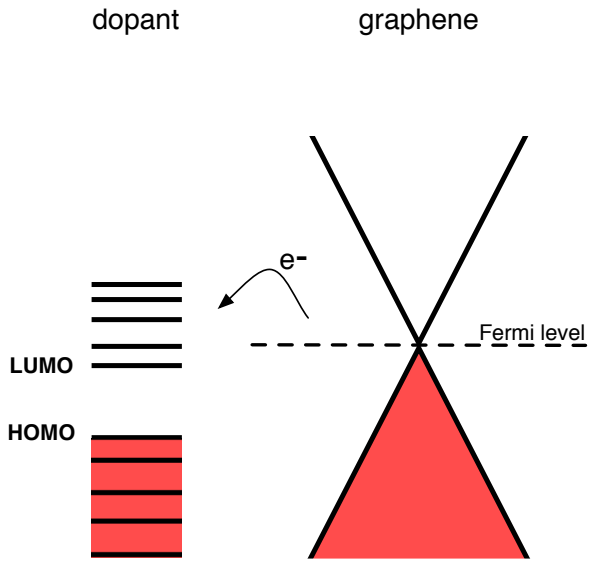

Figure 3: p-type doping.

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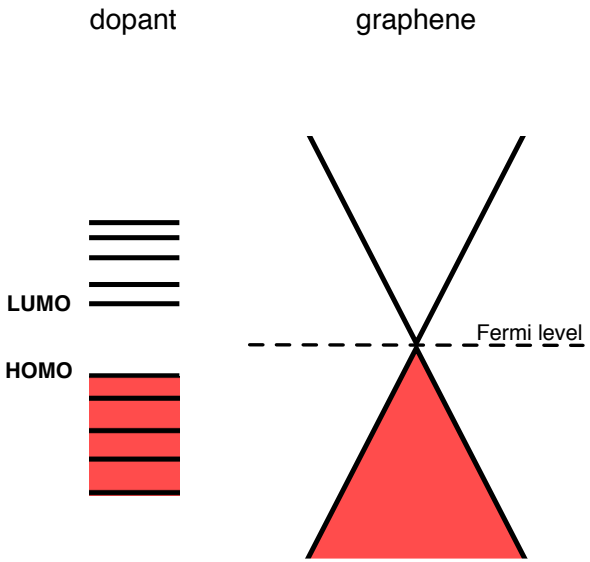

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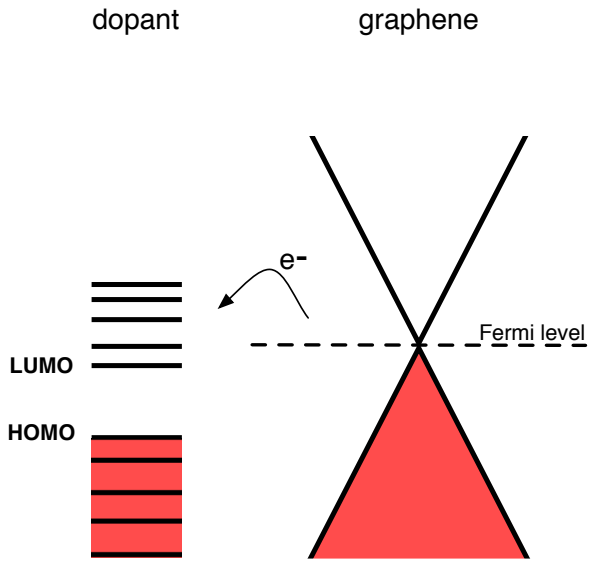

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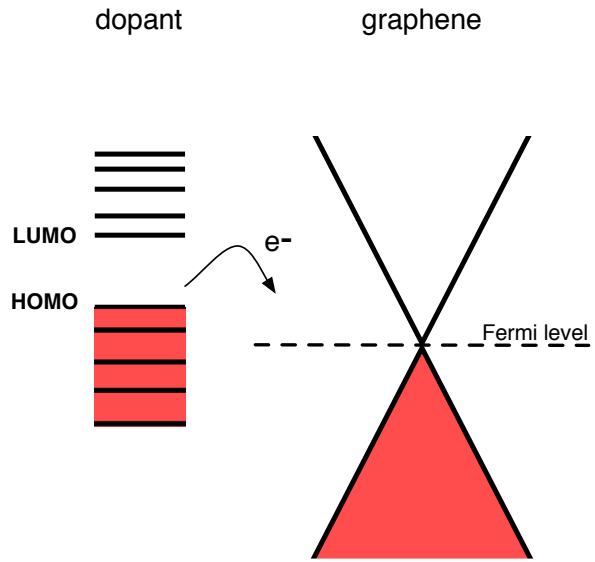
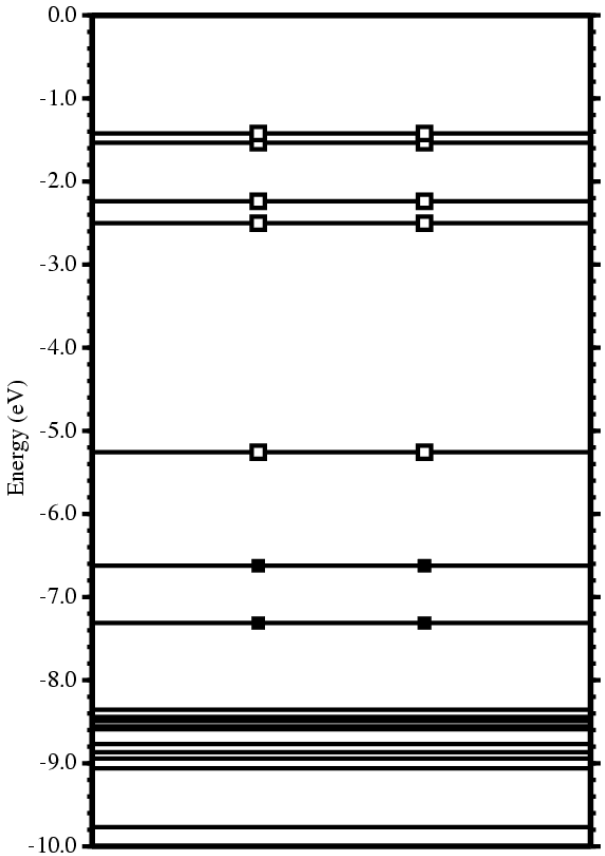


Figure 4: n-type doping.

F4-TCNQ molecular levels



F4-TCNQ (tetrafluoro tetracyanoquinodimethane) is an organic molecule with a strong electron affinity, 5.2 eV.

Figure 5: Kohn-Sham eigenvalues for F4-TCNQ.

F4-TCNQ molecule

- F4-TCNQ can be deposited easily for the fabrication of electronic devices.
- This molecule has been widely used in organic light-emitting diodes.
- It has been shown to be effective in p-doping diamond [5] as well as nanotubes [6].

[5] D. Dongchen, W. Chen, X. Gao, L. Wang, S. Chen, K. Loh, A. Wee, *Journal American Chemical Society* **129** (2007) 8084.

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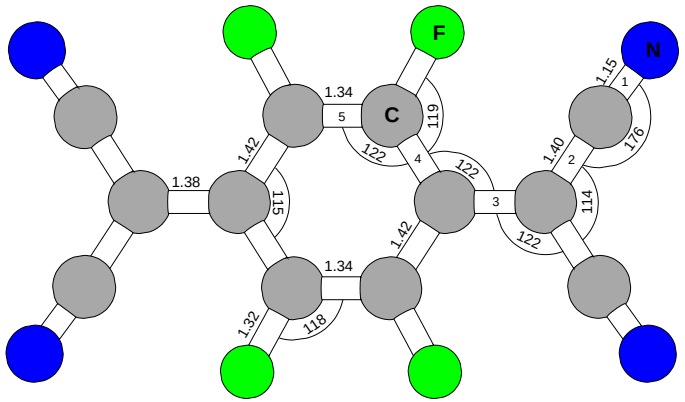

Figure 6: Molecular structure of F4-TCNQ. Bond lengths are in Å and angles in degrees.

[5] D. Dongchen, W. Chen, X. Gao, L. Wang, S. Chen, K. Loh, A. Wee, *Journal American Chemical Society* **129** (2007) 8084.

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F4-TCNQ on graphene

p-type doping of graphene with F4-TCNQ[7]

- Ultrathin epitaxial graphene (EG) prepared by chemical etching (n-type Si terminated 6H-SiC-(0001)).
- The thickness of the sample range from 1 monolayer to 3 monolayers of graphene.
- The F4-TCNQ were evaporated in situ from a low-temperature Knudsen cell onto EG at room temperature in the main UHV chamber.

[7] W. Chen, S. Chen, D. Qi, X. Gao, A. Wee, *Journal American Chemical Society* **129** (2007) 10418

Work function as function of F4-TCNQ deposition on graphene

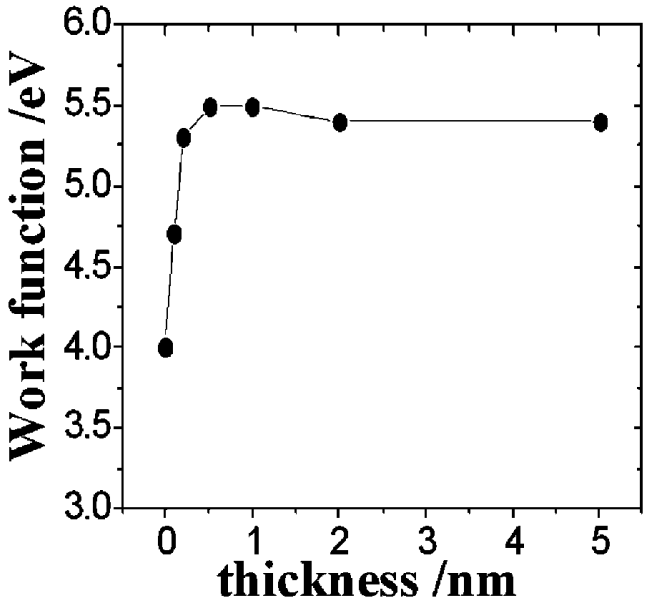


Figure 7: Plot of the sample work function as a function of the F4-TCNQ coverage.

- Synchroton-based photoemission spectroscopy (PES) measurements show that the deposition of F4-TCNQ increases the work function from 4.0 eV (pristine graphene) to 5.3 eV.
- For greater thicknesses of F4-TCNQ the work function remained almost constant.

Method

All the calculations were performed using the AIMPRO density functional code.

- The local density approximation (LDA) was used to represent the exchange correlation potential.
- The system was modelled using periodic boundary conditions, as in the supercell method.
- The Brillouin zone was sampled with a grid of $8\times8\times1$ **k**-points within the Monkhorst-Pack scheme.
- To study the charge transfer, one molecule of F4-TCNQ was placed onto a graphene $6\times6\times1$ supercell containing 72 carbon atoms.

F4-TCNQ on top of graphene

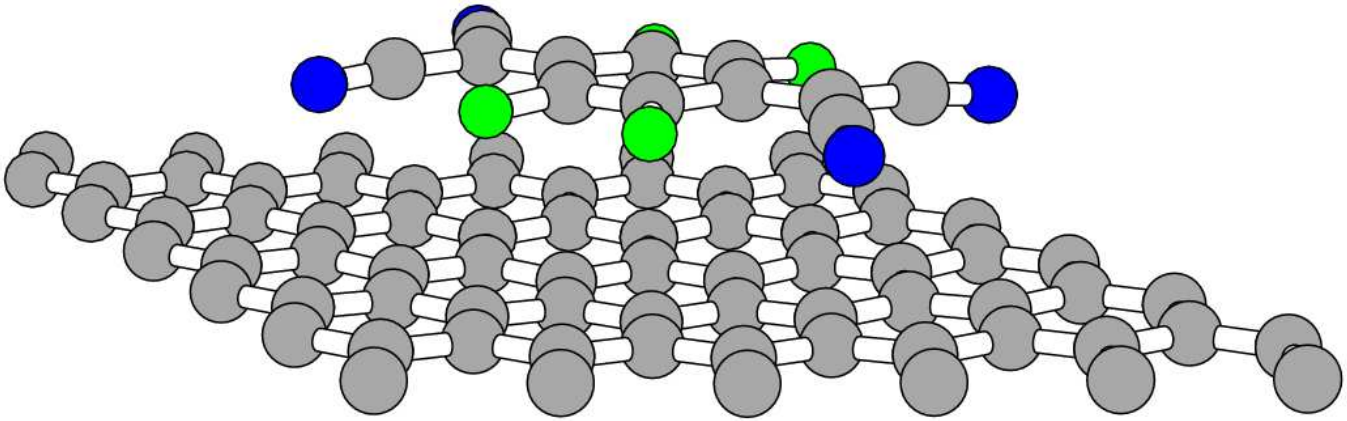


Figure 8: Molecule of F4-TCNQ on top of graphene.

- During the relaxation all the atoms were allowed to move to their equilibrium positions..
- The molecule adopts an approximately planar geometry 3.1 Å above the graphene sheet.
- The calculated binding energy of the molecule to graphene is 1.26 eV.

Electronic band structure

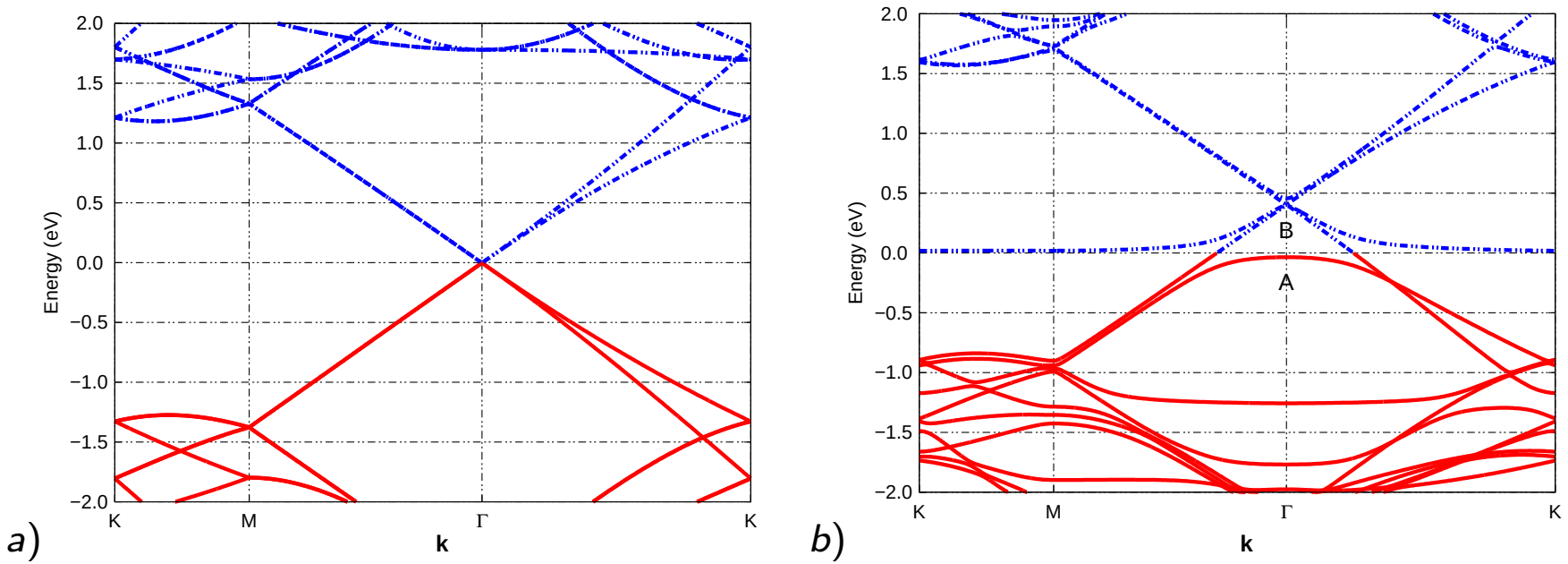


Figure 9: Band structure (eV) of a) pristine graphene and b) F4-TCNQ on top of graphene plotted in the vicinity of the Fermi energy along the high symmetry branches of the graphene Brillouin-zone. Full lines denote occupied states while dashed lines show empty levels. The Fermi level is set to zero.

LUMO level marked as B

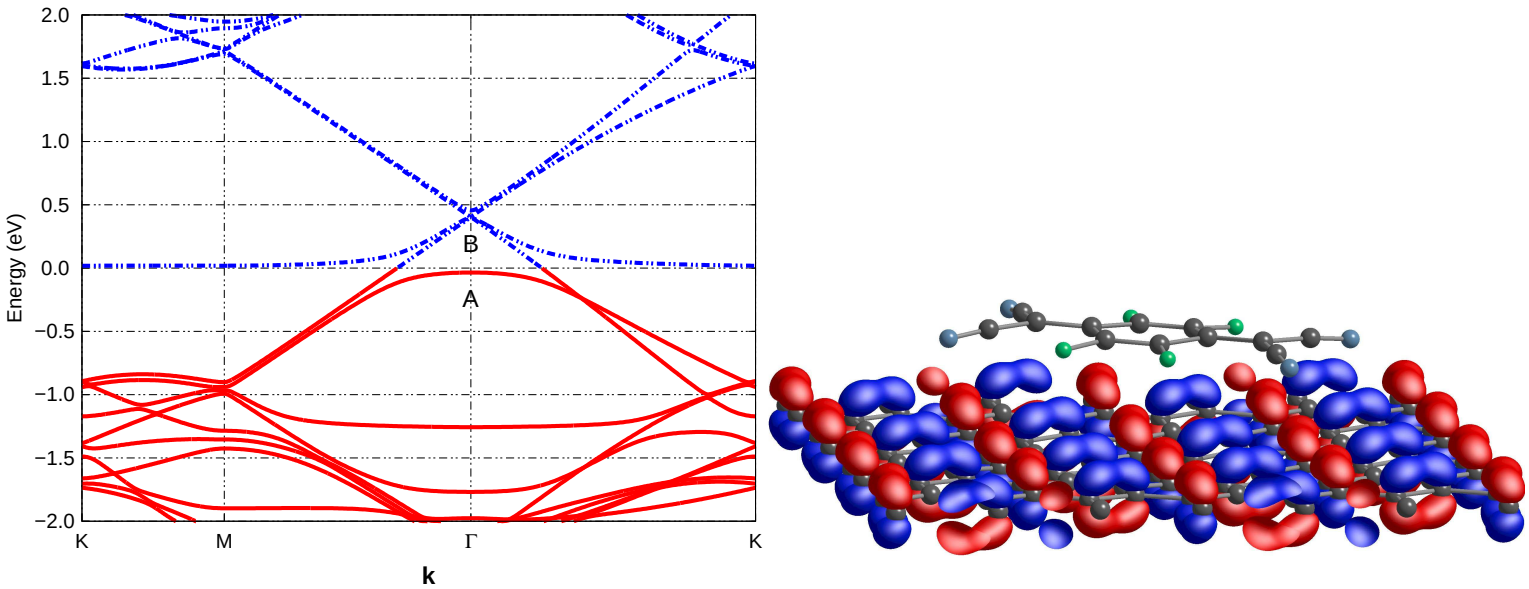


Figure 10: a) Wave function shows strong delocalisation of a pi-bonding orbital over graphene but avoids F4-TCNQ. b) Band structure of F4-TCNQ on graphene.

HOMO level marked as A

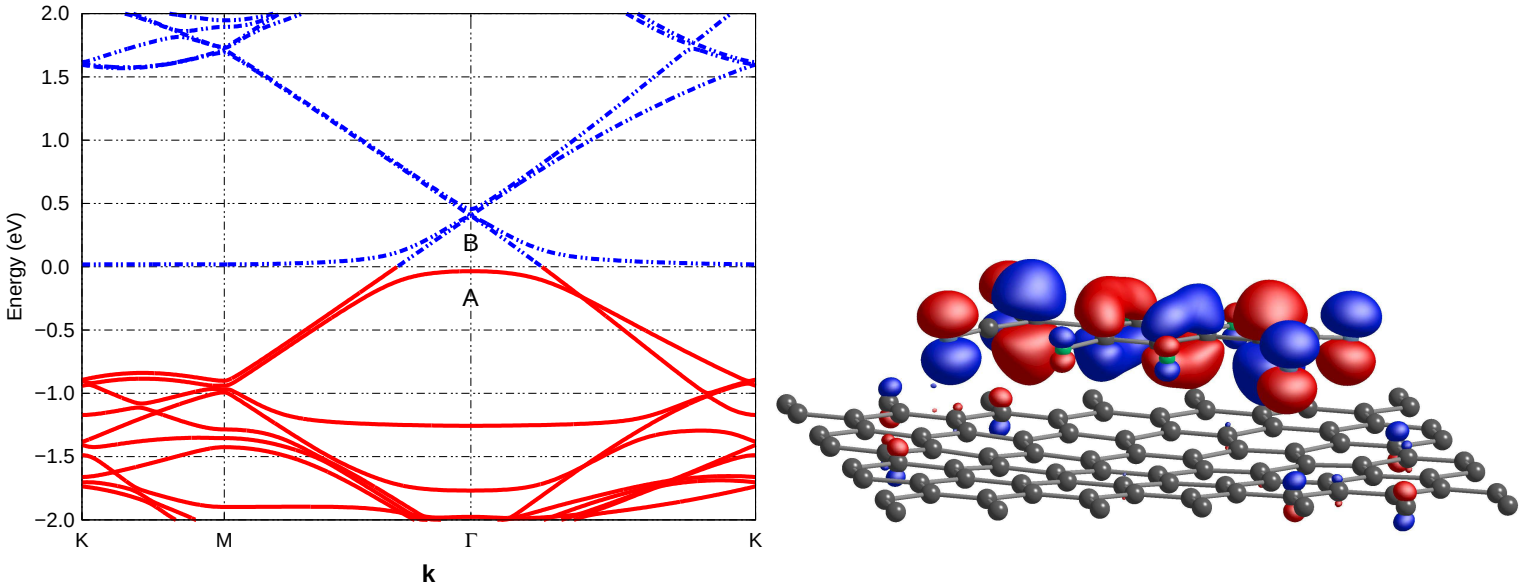
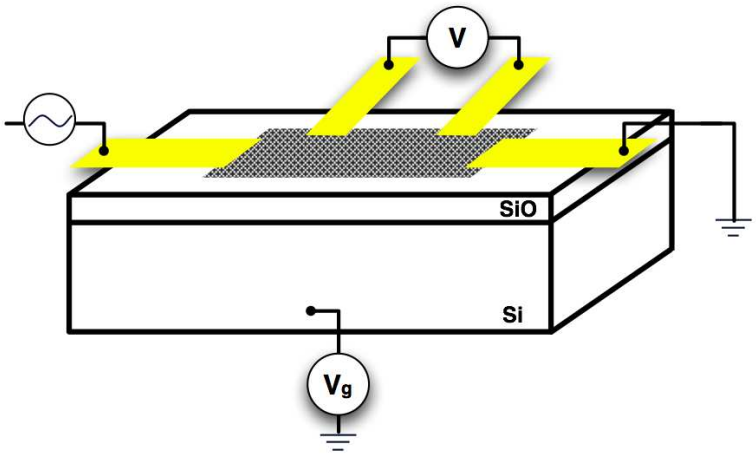


Figure 11: a) Wave function shows strong localisation on F4-TCNQ. b) Band structure of F4-TCNQ on graphene.

Summary

- We have shown that the F4-TCNQ molecule is a p-type dopant for graphene.
- These results are in agreement with synchrotron-based high-resolution photoemission spectroscopy measurements which show an increase of the work function with the increase of the thickness of F4-TCNQ on top of graphene.
- We estimate a charge transfer of 0.3 electrons from graphene to a molecule of F4-TCNQ.
- This work was published *J. Phys.: Condens. Matter* **21** (2009) 402001

Toluene on graphene



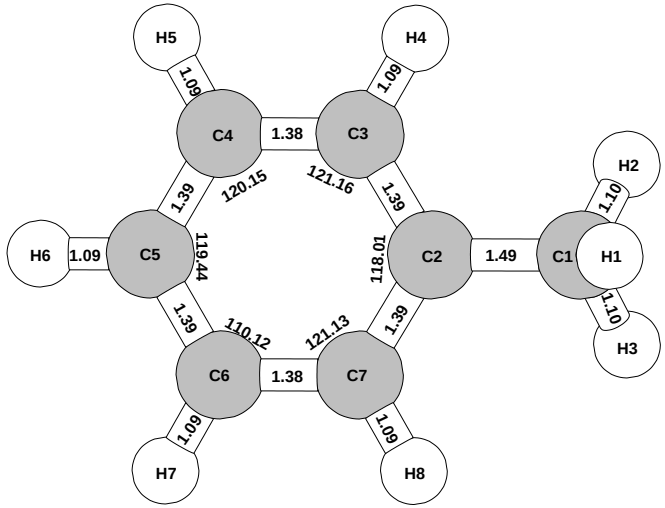


Figure 12: Toluene molecule.

Toluene on graphene

Effect of toluene on graphene (experimental measurements).

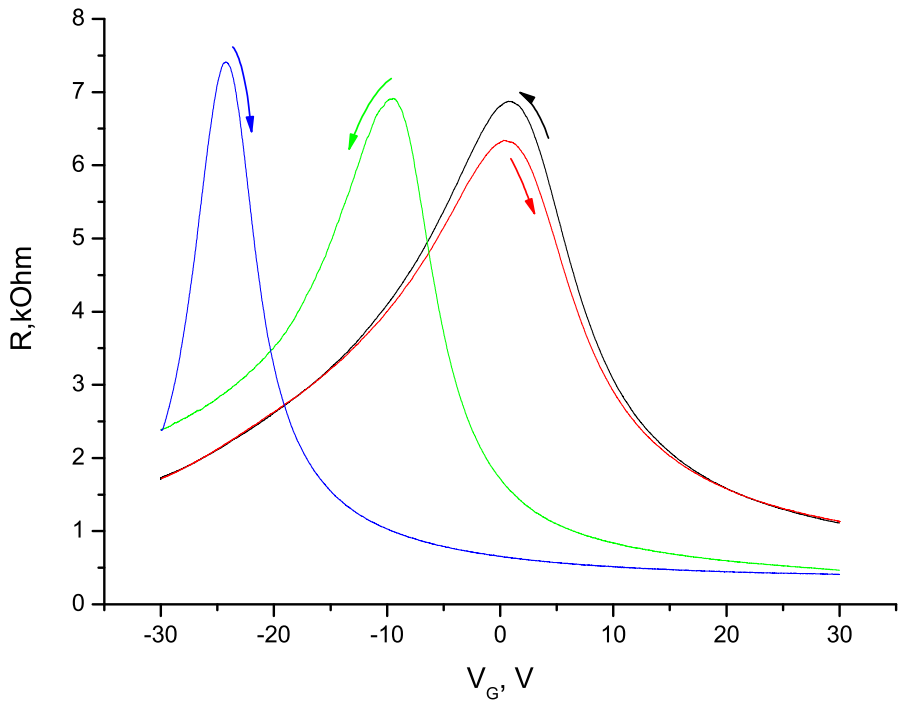


Figure 13: The black and red lines are measured after He-annealing. The green and blue lines are for measurements after the sample has then be exposed to toluene for 2.5 hrs . The direction the gate voltage is swept is indicated by the arrows

Band structure of toluene on graphene

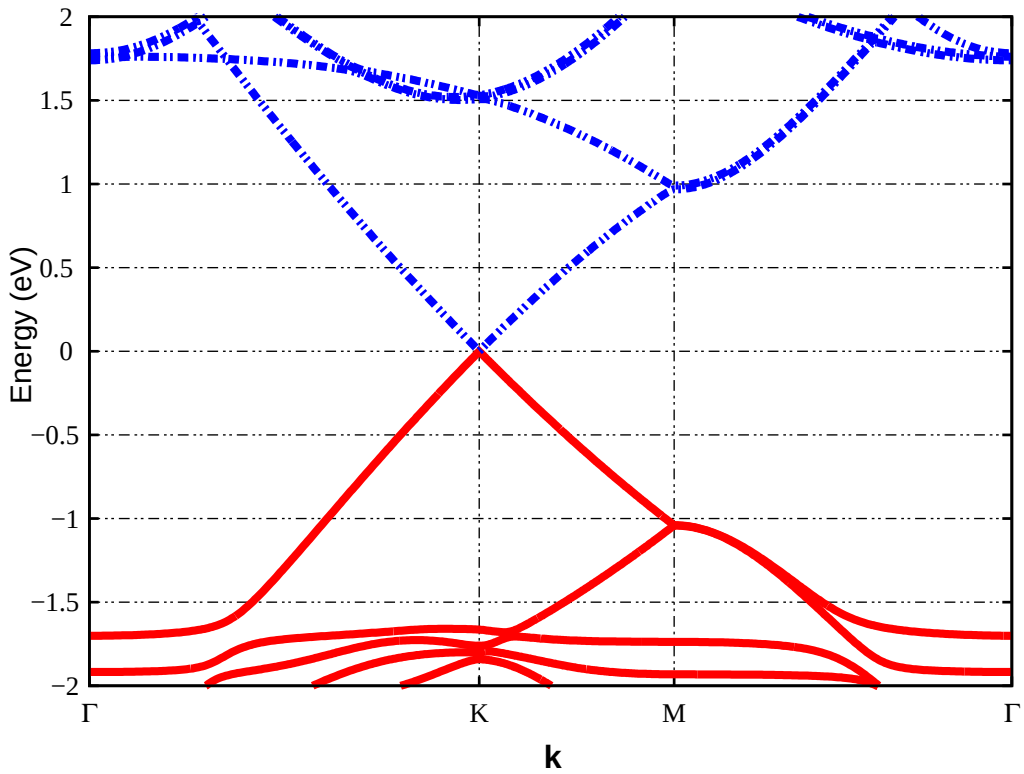


Figure 14: Band structure (eV) of toluene on top of graphene plotted in the vicinity of the Fermi energy along the high symmetry branches of the graphene Brillouin-zone. Full lines denote occupied states while dashed lines show empty levels. The Fermi level is placed at zero.

Metals on graphene

Since the contacts are made with metals, we studied the effect of a single Ti, Cr and Au atom on top of graphene.

- Spin-polarised calculations were performed using the AIMPRO density functional code.
- The system was modelled using 4×4×1 supercell of graphene, enclosing a total of 32 carbon atoms.
- The Brillouin zone was sampled with a grid of 8×8×1 **k**-points within the Monkhorst-Pack scheme.

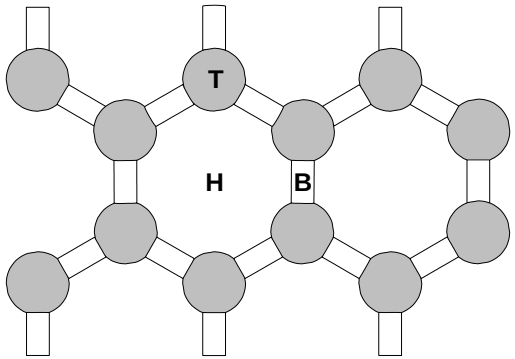


Figure 15: Adsorption sites studied, T directly on top of a carbon atom, H above the center of the hexagon and B above the C-C bond.

Ti and Cr on graphene

We found that Ti and Cr are n-type dopants.

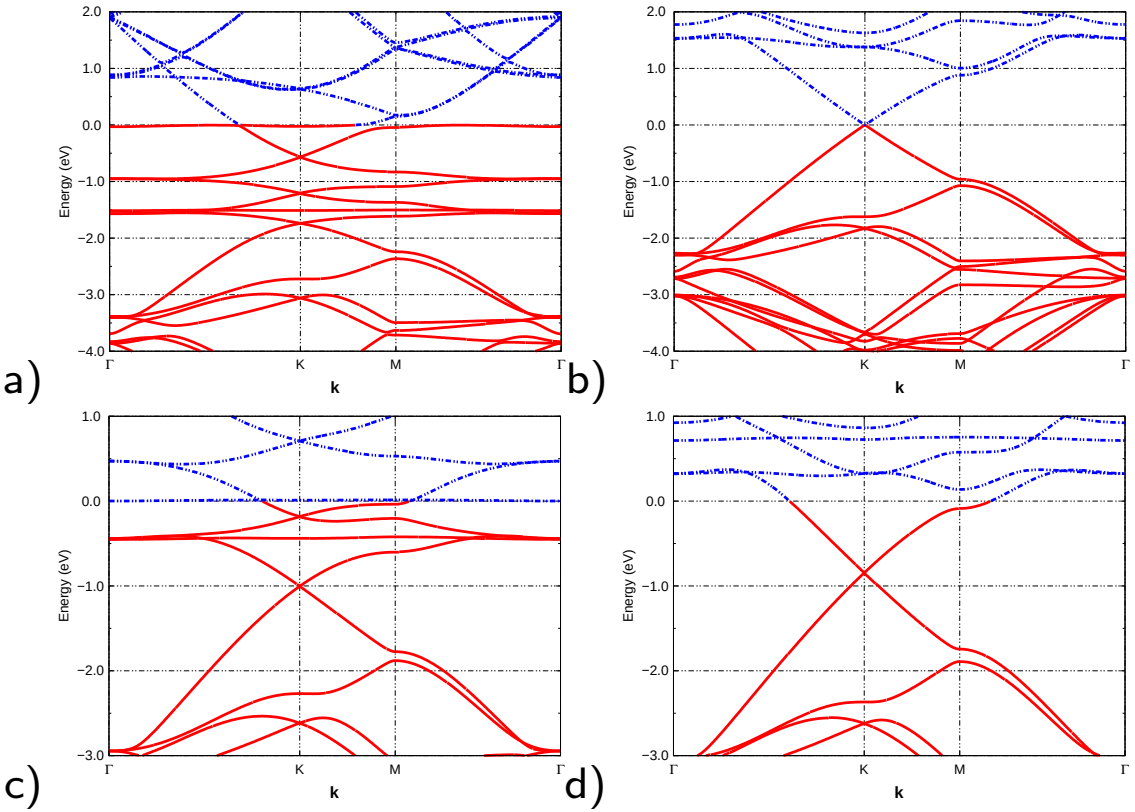


Figure 16: (Color online) Spin-polarized band structures (eV) of Cr, a), b), and Ti, c), d) in the vicinity of the Fermi energy. The majority spin band structures are on the left and and the minority spin band structures are on the right. The Fermi level is set to zero.

Au on graphene

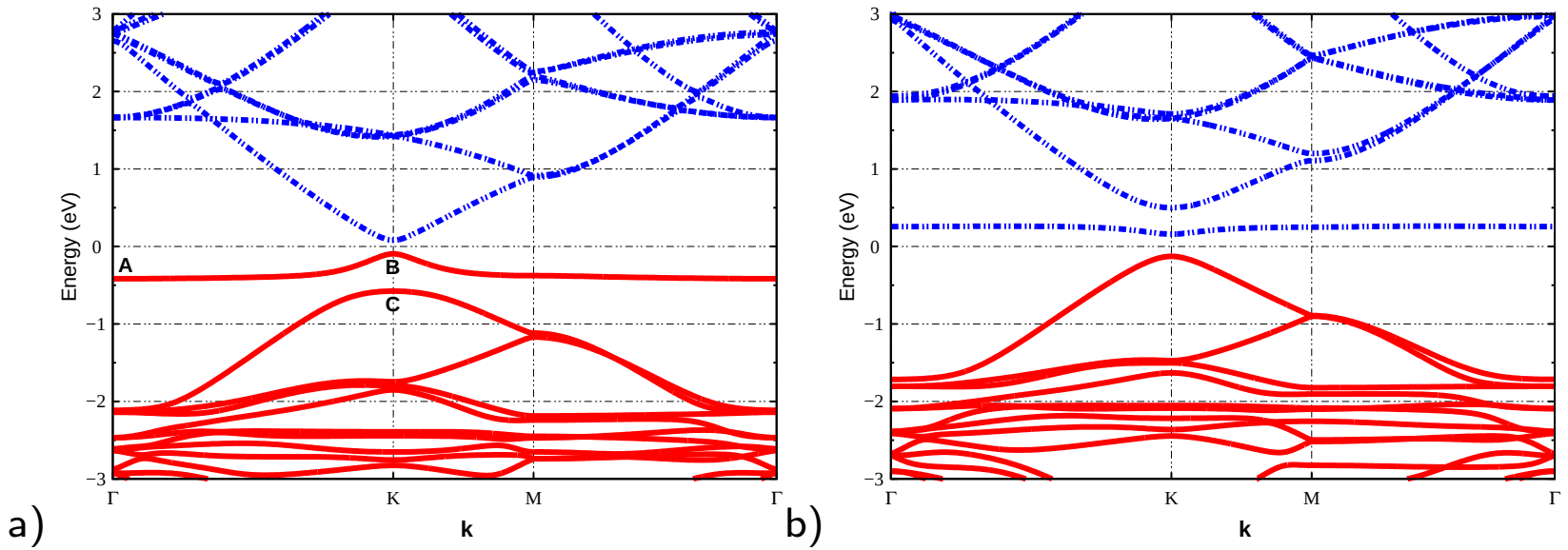


Figure 17: Band structure (eV) of Au single atom on top of graphene plotted in the vicinity of the Fermi energy along the high symmetry branches of the graphene Brillouin-zone. Full lines denote occupied states while dashed lines show empty levels. The Fermi level is placed at zero.

Metals intercalated between graphene and toluene

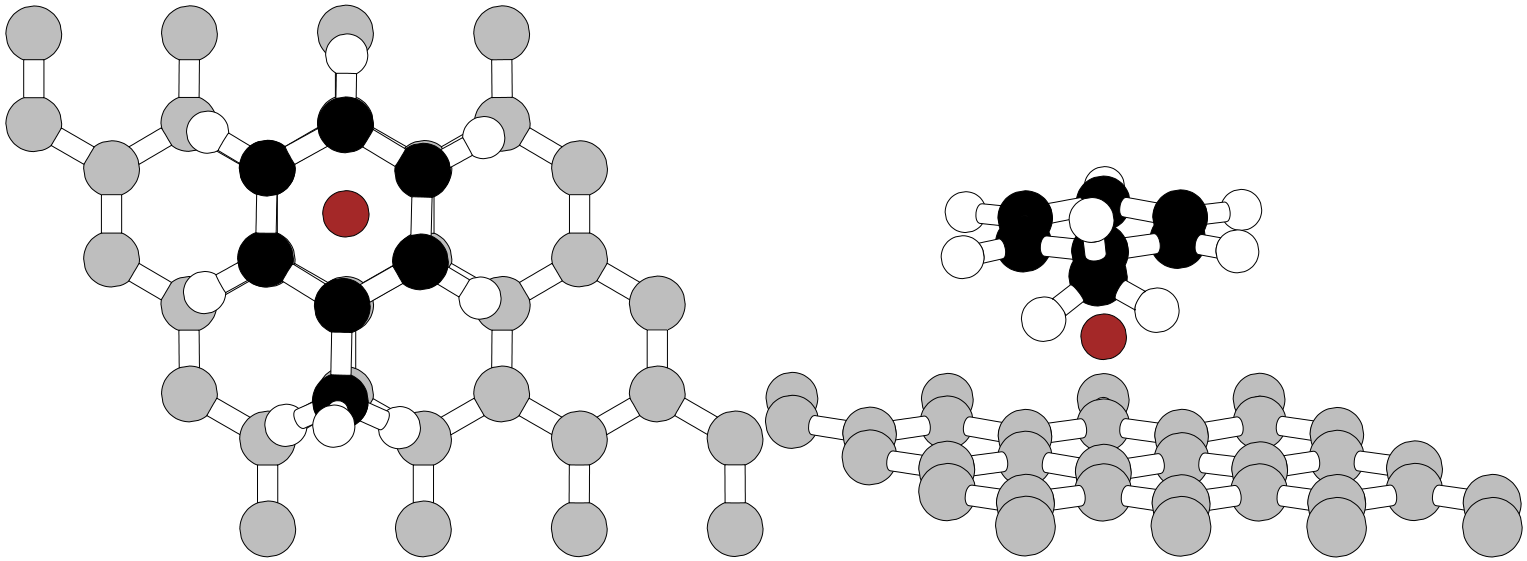


Figure 18: (Color online) Side a) and top b) view of the minimum energy configuration of Ti intercalated with an overlayer of toluene and the graphene surface.

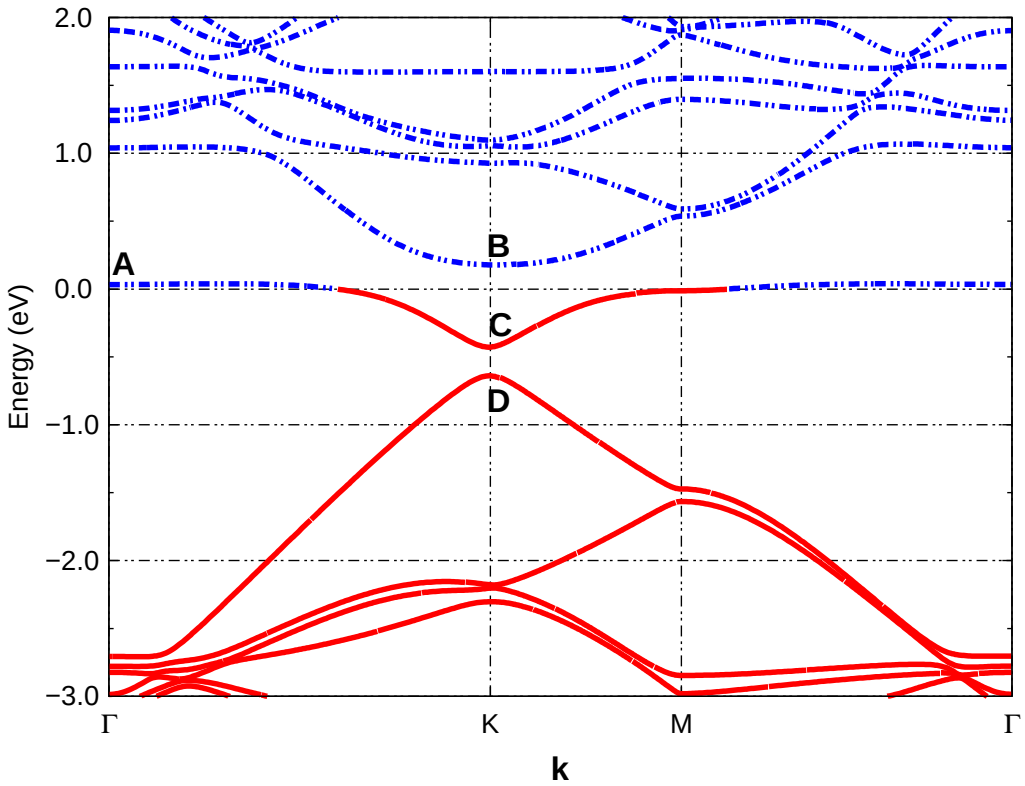


Figure 19: Band structure (eV) of Au intercalated between an overlayer of toluene and the graphene surface in the vicinity of the Fermi energy along the high symmetry branches of the graphene Brillouin-zone. Full lines denote occupied states while dashed lines show empty levels. The Fermi level is placed at zero.

Bilayer graphene with Au

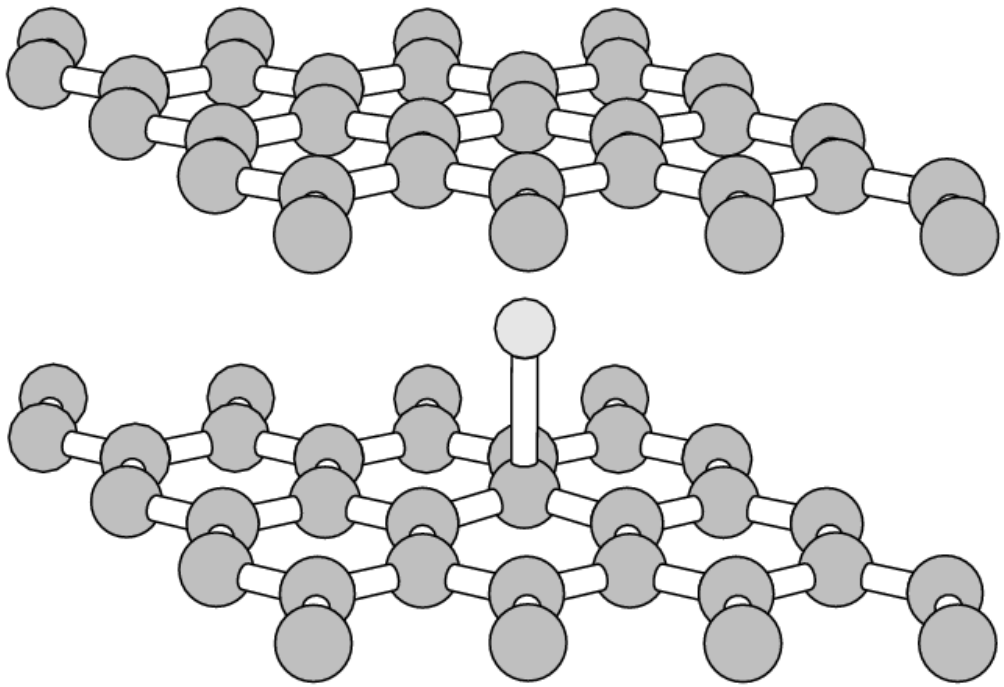


Figure 20: Equilibrium structure of a Au atom inserted between a graphene bilayer.

Au on graphene bilayer

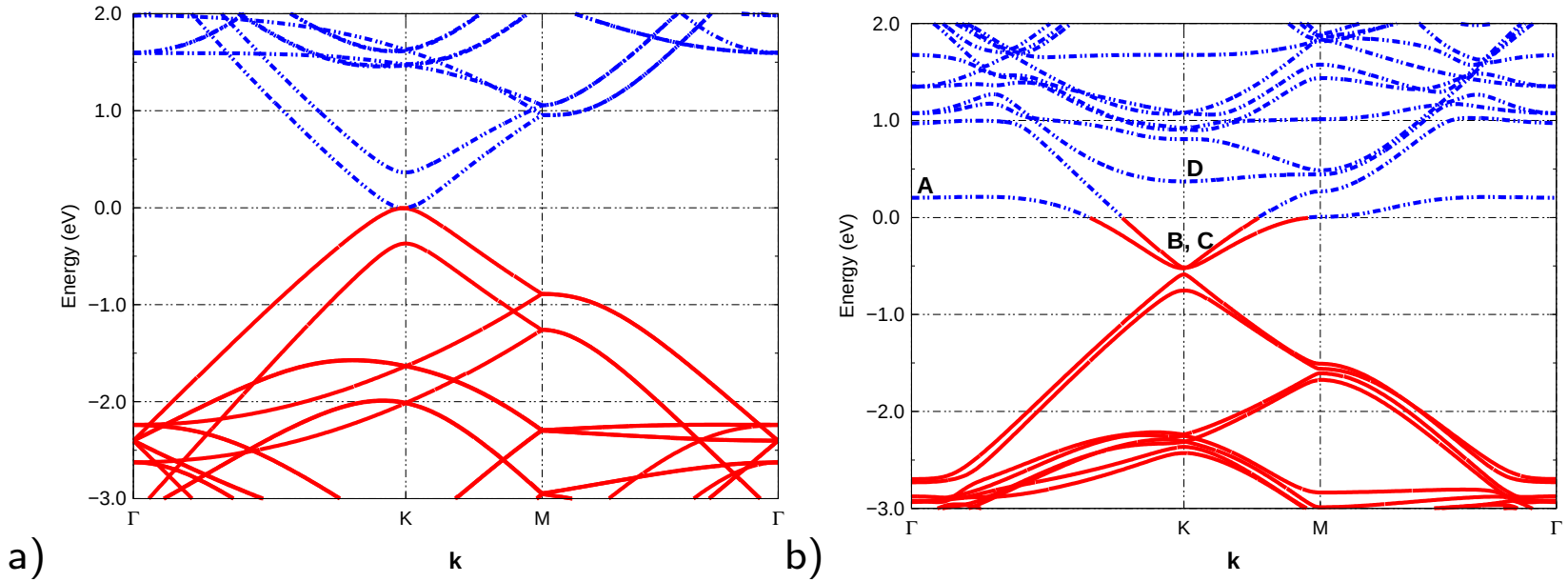


Figure 21: Band structure (eV) of a) bilayer of graphene and b) Au atom between bilayer of graphene in the vicinity of the Fermi energy along the high symmetry branches of the graphene Brillouin-zone. Full lines denote occupied states while dashed lines show empty levels. The Fermi level is placed at zero.

Summary

- Ti and Cr atoms were found to act as n-type dopants in agreement with experiment.
- Au seemed to be a marginal case with only limited or zero doping.
- A toluene molecule leaves the electronic structure of graphene unaffected.
- However, Au intercalated between a graphene sheet and and a toluene layer, leads to n-doping of graphene.
- The same effect is found when a Au atom is placed between a graphene bilayer.
- We suppose the effect comes from a compression of the 6*s* Au wavefunction with an upward shift of the 6*s*-level.

Electrochemical doping

Electrochemical doping involves redox reactions of graphene with water and adsorbates, involving changes in the charge state of the participants.

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- We need to assume that there is water in contact with graphene.
- Water molecules can be in the interface between graphene and SiO_2.
- X-ray spectroscopy showed 4 or 5 layer of water on top of SiO_2.
- Vibrations of water molecules on the surface of SiO_2 were observed by FTIR.
- Is also believed that water can exist in voids in SiO_2

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Whether such reaction to occur require the change in the total free energy to be less than zero (spontaneous reaction).

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The total Gibbs free energy is then ΔG-W, where ΔG is free energy change of reaction and W is the workfunction of graphene.

Electrochemical doping

One possibility is that toluene is oxidised to benzyl alcohol.

[8] D. R. Loveley, D. J. Lonergan, *Applied Environmental Microbiology* **56** (1990) 1858

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- Thus the electrochemical oxidation of toluene to benzyl alcohol is spontaneous as the work functions exceeds 3.95 eV and the liberated electron will be trapped by graphene achieving n-type doping.

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- Thus the electrochemical oxidation of toluene to benzyl alcohol is spontaneous as the work functions exceeds 3.95 eV and the liberated electron will be trapped by graphene achieving n-type doping.
- For negative bias condition, OH^- will drift through the SiO_2 substrate towards graphene, removing a source of scattering centres and leading to an increase in mobility

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We conclude that there are three mechanisms of doping graphene.

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- The two mechanisms described above are expected to decrease the mobility of the carriers on graphene since extra Coulomb scatters are introduced by the former ions but without any hysteresis effects.

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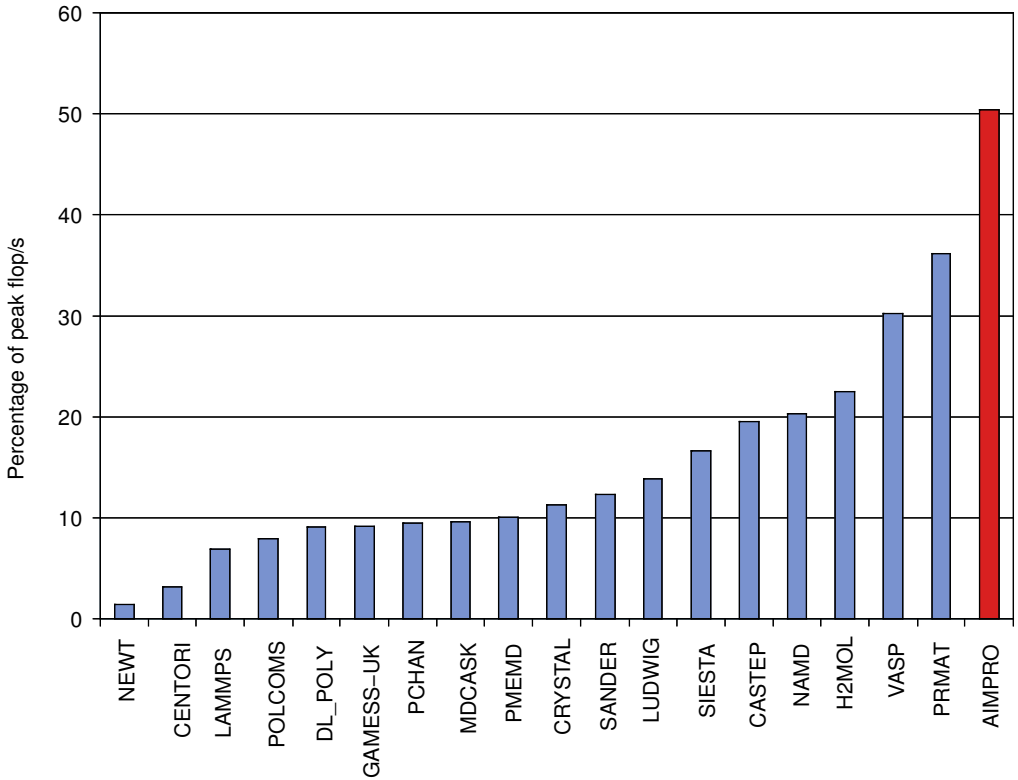
- The two mechanisms described above are expected to decrease the mobility of the carriers on graphene since extra Coulomb scatters are introduced by the former ions but without any hysteresis effects.
- A third electrochemical mechanism for doping graphene can be expected when redox reactions occur at the surface.
- This can lead to an increase in carrier mobility but requires appreciable time to occur.
- This leads to hysterisis effects. The assumption that one or both of the charged products OH^- or H^+ is mobile and responds to the field due to the gate voltage could explain increases in carrier mobility.

Acknowledgements

I am thankful to Derek Palmer for the helpful discussions.

Method


Percentage of peak flop/s
60
50
40
30
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10
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NEWT
CENTORI
LAMMPS
POLCOMS
DL_POLY
GAMESS-UK
PCHAN
MDCASK
PMEMD
CRYSTAL
SANDER
LUDWIG
SIESTA
CASTEP
NAMD
H2MOL
VASP
PRMAT
AIMPRO