

Subproject C4.11

Theory and simulation of molecular materials and functionality

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Introduction and Summary

Project C4.11 focuses on the theory and simulation of molecular materials and devices along two major strands of activity which are both closely intertwined with research, either experimental or theoretical, of other CFN groups. The first set of activities studies material properties of *graphene flakes*, the second set combines with STM experiments in the group of Wulf Wulfhchel and is devoted to *Molecular Electronics*. Some of these latter activities are closely related also to subproject C3.11 and have also received support from there.

Graphene: Since its fabrication in clean form has become technologically feasible [1], graphene has been in the focus of frontier research. [2,3] One of its most celebrated properties are its massless low energy excitations ("Dirac fermions"), which emanate from the symmetries of the honeycomb lattice. [3] The characteristic property of Dirac fermions is their dependency on wavenumber, $E(k) = (1/2)(v_F^2 k^2 + m^2)^{1/2}$, which becomes singular if the energy gap, m , between the valence band (π -band) and the conduction band (π^* -band) vanishes. The linear dispersion has a very distinct manifestation in the *quantum Hall effect*, which was very important for identifying the material quality in the first transport experiments: whereas for conventional probes the spacing between the quantum Hall steps is equidistant in energy, in graphene the spacing decreases when more and more electrons are removed from or added to the sample.

At present, an important topic for the production of graphene based electronics is how to increase the charge carrier mobility. Several possible candidates exist that could be the most important source for scattering centers limiting the mobility: surface corrugation (ripples), disorder in the substrate, adatoms or vacancies. In fact, the latter two are thought to be the most important ones at least in freely suspended samples. If the adatoms form chemical bonds, so a carbon atom is promoted from sp^2 to sp^3 -hybridization, their effect is very similar.

While epitaxial methods to grow graphene allow to achieve relatively large, clean and homogeneous films, chemistry technologies open up a way into mass production of smaller graphene *flakes*. Indeed, the electronic properties of such flakes can be quite different from bulk graphene, e.g., due to the finite size and the presence of edges. [4] In particular, recent theoretical studies on zigzag edged graphene flakes confirm a tendency towards edge magnetism. [5] An increased interest in the *elastic* properties of graphene has developed recently. This is, for instance, because experiments suggest that graphene samples exhibit a corrugated structure (*ripples*) even at relatively low temperatures. [6] Their origin is thought to be due to residual elastic strain produced by the experimental preparation technique. [7] Another interest in elasticity comes from exploring the feasibility of *strain* engineering the electronic band structure ("pseudomagnetic" fields). [8]

The first activity in C4.11 addresses the elastic properties of small graphene flakes by means of elaborate calculations based on the density functional theory as implemented in the TURBOMOLE package [9] and analytical considerations [C4.11.1]. We find that the edge can compress the chemical bonds internal to the flake so much, that the bond length decreases by $\sim 1\%$ for the smallest flakes that were investigated. This compression is accompanied by a decrease of elasticity: the flake becomes stiffer as indicated, e.g., by a change in the shear modulus by $\sim 50\%$. Most notably, even though this change is very large we can show, nevertheless, how to extrapolate from the smallest flake sizes into the bulk limit. We obtain all bulk parameters, (cohesive energy, lattice constant, compressibilities, ..) with the same accuracy reached only by the most recent electronic structure calculations.

Our second activity was performed in collaboration with A. D. Mirlin and M. Titov. It focuses on the effect of vacancies on the density of states and the mobility of charge carriers in graphene *films*. Indeed, when introducing a vacancy into a graphene flake something peculiar

happens. The unit cell of the honeycomb lattice comprises two atoms, so each unit cell feeds two states into the π / π^* -bands. Taking out one C-atom, the remaining C-atom can contribute only a single state. The energy of this state comes to lie in both bands, π / π^* , simultaneously since they are equivalent. Therefore a single vacancy introduces a state with energy at the boundary between π / π^* , i.e. between the HOMO/LUMO level. Such *zero modes* tend to be very important for the low energy response of graphene flakes. Our investigations demonstrate this for the special example of the conductivity. [C4.11:2] With increasing number of vacancies the conductivity first *increases* reaching a maximum value beyond which it starts decreasing again until it drops to zero in the percolation limit.

The last topic that we discuss here is a sideline of our research. It is motivated by the observation that the effect of many defects in graphene sheets ("disorder") cannot be understood by considering a single defect, e.g., a single vacancy alone. This is because in the presence of many defects electronic states form a complicated interference pattern which is accompanied by very large fluctuations of the wavefunction amplitude. These fluctuations become especially interesting in the presence of a strong magnetic field, i.e. in the quantum Hall effect. Graphene has the very special property, that even without fine tuning such wavefunction fluctuations not only become strong but even critical in sufficiently strong B-fields. It means that the moments of the wavefunctions $\langle |\Psi(r)|^{2q} \rangle$ scale with the flake size, N , in a power law manner, $\langle |\Psi(r)|^{2q} \rangle \sim N^{\tau_q}$, where each moment scales with its own exponent τ_q . The influence of such scaling behavior on the effective Coulomb interaction between the electrons can be very significant and was investigated in detail in collaboration with A. D. Mirlin and I. Burmistrov in [C4.11:3].

Molecular Electronics: Exploring the potential of single molecules for the building of functional devices always was a central topic of the CFN from early on. Our focus is on *Molecular Electronics* where molecules are investigated with respect to their properties concerning electronic functionality as, e.g., transistors or memory elements. In recent years we have been collaborating with several experimental groups in order to understand how the molecular design influences the current voltage characteristics.

Together with the groups of Th. Wandlowski and F. Pauly we have investigated how the current flow through a biphenyl-molecule depends on the tilting angle φ between the two 6-rings. [C4.11:4] As expected, we confirm an earlier result by the Columbia group [9]: the conductance follows a $\cos^2 \varphi$ -trend reflecting the change in wavefunction overlap between the two consecutive rings. Extensive transport calculations based on the density functional theory and the TURBOMOLE package have been performed to not only understand the general trend but also try to address pronounced deviations from it. [C4.11:5]

Wulf Wulfhekel and Stefan Schmaus have been able to measure the magnetoconductance of a single Phtalocyanine (Pc) molecule, see subproject C4.10. In the case of the H₂Pc molecule a value for the giant magnetoconductance (GMR) of 60% was reported. This value is extremely large, especially in view of the fact that H₂Pc does not contain any magnetic atoms. Motivated by this observation Alexei Bagrets has performed transport calculations which reveal that it is the spin selective broadening of the ligand based LUMO levels of H₂Pc which induces such a big GMR value. Theoretical and experimental results are to be published in a combined paper. [C4.11:6]

Material properties of graphene

1. Elasticity and edge effects in small flakes

The calculation of total energies for a given molecular structure, of deformation potentials, phonon spectra etc. are standard problems in quantum chemistry. With respect to such observables one can address systems comprising of a few hundred atoms if density functional theory is used and no additional major approximations other than the one for the functional are employed.

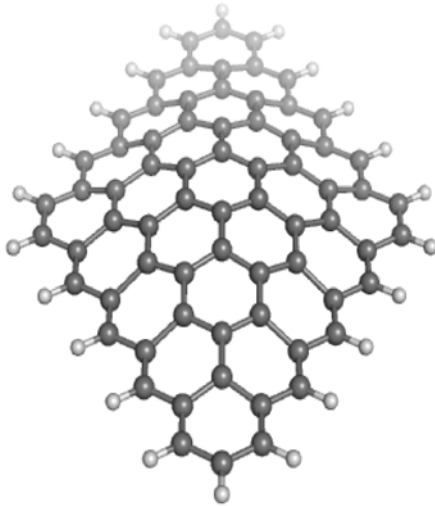


Figure 1: Graphene flake with hydrogen termination near the edges, size $N=5$. The flake buckles due to the application of isotropic pressure.

For instance, using the TURBOMOLE package we were able to treat graphene flakes of the geometry given in the Figure 1 with sizes up to $N=9$ benzene rings per side.

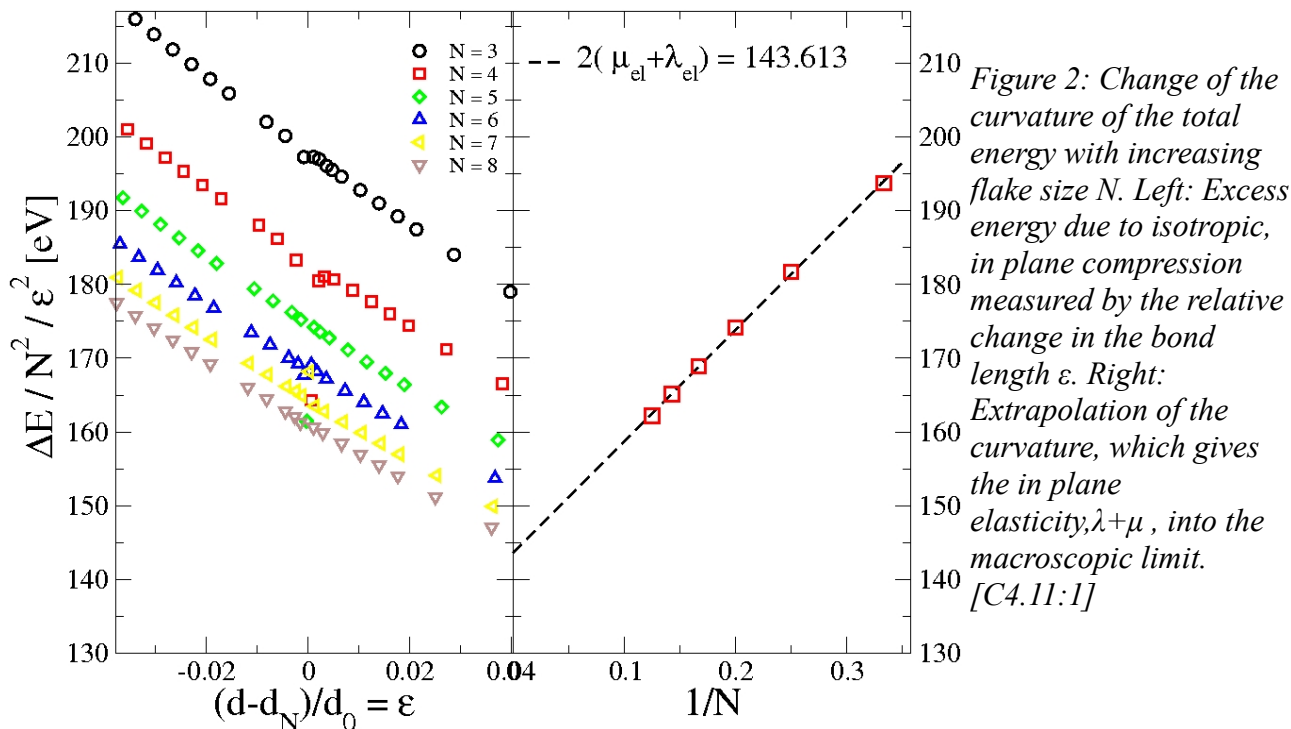
With an eye on applications to experimentally relevant flake sizes one would like to go to bigger flakes, however. In typical measurements flake sizes are typically of sizes of $N=1000$. Therefore, it is important to investigate how to extrapolate in a reliable way from very small systems into the experimentally relevant regime. Apart from the fundamental interest already outlined in the introduction, this question was a second motivation for our research. [C4.11:1]

The basic observable that we study is the energy E_{tot} of flakes such as depicted left. We are interested in how E_{tot} depends on the flake geometry – buckling, compression, shear – and how it changes with the flake size, N . For the latter we find that a parametrization works well, in which we account separately for the energy contributed by a number of hydrogen atoms, N_H , and the carbon atoms in the bulk, N_C^b , near the edge, N_C^e , and corner, N_C^c . With this notation the following parametrization works well:

$$E_{tot} = N_C^b E_C^b + N_C^e E_C^e + N_C^c E_C^c + N_H E_H + \frac{\phi^e}{N_C^e} + \frac{\phi^b}{N_C^b}$$

Equation (1).

The elastic parameters of the flakes, stiffness under out of plane deformations (“buckling”), κ , and the Lamé parameters, λ, μ , follow from the parabolic variation of E_{tot} with buckling (κ), isotropic pressure ($\lambda+\mu$) and shear (μ). With increasing flake size the energy coefficients E_C^b, E_C^e, E_C^c contribute in different ways to E_{tot} and its parabolic shape under deformation. Therefore the elastic parameters change with system size in a way predicted by the Eq. (1). Our result for homogenous in plane compression is depicted in Figure 2. The left hand side of Fig. 2 illustrates how the curvature of the total energy E_{tot} decreases with increasing flake size. The linear variation near zero compression results from anharmonic (cubic) terms. The right hand side of Fig.2 illustrates the extrapolation to large flake sizes $1/N \rightarrow 0$. We witness a change of the elastic modulus by 30% in this process. The decrease is understood as a consequence of the edge compressing the bulk. Since edge bonds have a tendency to be shorter than bulk ones, smaller flakes have a shorter C-C bond length also in the bulk due to edge compression. The shorter bonds go together with an increase of the inter-atomic forces which in turn make the material stiffer, so the elastic moduli grow. The effect is strongest for the shear modulus, μ , where it reaches 70%.



2. Signatures of criticality in systems of disordered Dirac particles

We investigate the effect of vacancies on the transport properties of large graphene flakes focusing on two different topics. First, we essentially neglect the Coulomb interaction between the charge carriers and only study how charge transport changes when punching holes (*vacancies*) into the graphene sheet. In a second study we take the Coulomb interactions into account. We investigate how the energy exchange between the electrons, that takes place at nonzero temperatures, leads to a loss of phase coherence of the individual particle (“dephasing”).

2.1 Effect of vacancies on transport in graphene

At first instance one might suspect that adding vacancies to a sheet of graphene would decrease its ability to carry a current since an additional “obstacle” has been added. By contrast, this is not what actually happens. As may be inferred from Fig. 3, adding a small number of holes *increases* the conductance up to a maximum value before it decreases again and returns to the value of the unperturbed sheet. [C4.11:2] Only at a very large concentration of vacancies, when the percolation limit is reached, the conductance eventually drops to zero.

The data shown in Fig. 3 have been calculated semi-analytically with a method devised by P. Ostrovsky, M. Titov and I. Gornyi within an effective model. Their results were confirmed in the limit of low concentrations by our methods which represent the graphene sheet as a tight binding (Hueckel-) method. Specifically, we have implemented the Kubo conductance and tested it against the same Landauer-type approach that also is employed for calculating the transport properties of single molecules, see below.

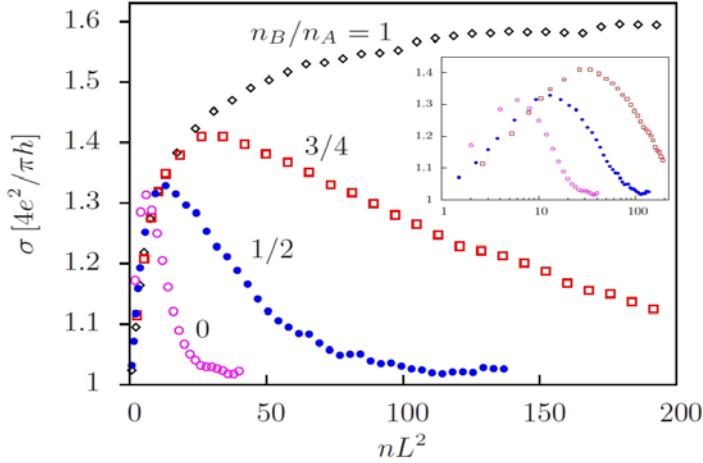


Figure 3: Conductance of a graphene sheet, size $L \times L$, over the number of vacancies. The black curve shows the result for vacancy concentrations in both sublattices (A, B , $n_A + n_B = n$) being the same, $n_B/n_A = 1$. For the other curves the relative concentration of impurities on one sublattice is reduced against the other one. Inset: Scaling property of the conductance curve on the logarithmic scale. [C4.11:2]

A first intuition for this surprising conductance increase at low vacancy concentrations may be gained by recalling the introduction: adding a vacancy to the graphene flake produces an electronic state in the flake with energy close to zero. Therefore, an additional state is added with an energy right at the value where it can contribute to the current flow. Since the conductance of the sheet in the absence of this state was already quite low to begin with, of the order of a single conductance quantum, adding one state can provide a large conductance increase.

A remarkable finding that should not go unnoticed is that it seems to make a big difference as to whether or not the vacancies share the same sublattice, see Fig. 3. Further research is required in order to provide a more intuitive explanation for this perhaps somewhat unexpected observation.

2.2 Sideline: Multifractality and interaction effects near the integer quantum Hall transition

If many vacancies are added to the graphene sheet then the zero modes associated with each one begin to hybridize and form an impurity band. The wavefunctions in such “disordered” environments are very far from the regular shapes familiar from crystals with an (approximate) translational invariance (*Bloch states*). Their most important characteristic is that the amplitudes of the wavefunctions, $|\Psi(r)|^2$, undergo very strong fluctuations when going from one site to another or from one state to the state neighboring in energy.

This behavior is generic for any sufficiently strongly disordered metal. The special aspect of graphene-type materials occurs in the presence of a magnetic field which is pointing perpendicular to the sheet. Namely, without selecting special values for the magnetic field wavefunction fluctuations not only become strong but even critical. It means that the average moments of the wavefunctions $\langle |\Psi(r)|^{2q} \rangle$ scale with the flake size in a power law manner, $\langle |\Psi(r)|^{2q} \rangle \sim L^{\tau_q}$ where each moment scales with its own exponents τ_q . This behavior is called *multifractality* and it has been predicted to exist near any integer quantum Hall transition. [10]

All matrix elements of such “multifractal” states exhibit unusual properties related to scaling in position and energy. This is true, in particular, also for the matrix elements of the Coulomb interaction. A particularly interesting situation has been studied in [C4.11:3]. It occurs when the magnetic field is strong enough so as to drive the electrons into full spin polarization. In this case, the exchange contribution in the interaction matrix elements cancels the Hartree term. What remains are the electronic correlation effects and they scale with their own set of (“subleading”) exponents. The scaling behavior of the corresponding correlation function, $K_2(\rho, R)$, for the quantum Hall transition is displayed in Fig. 4.

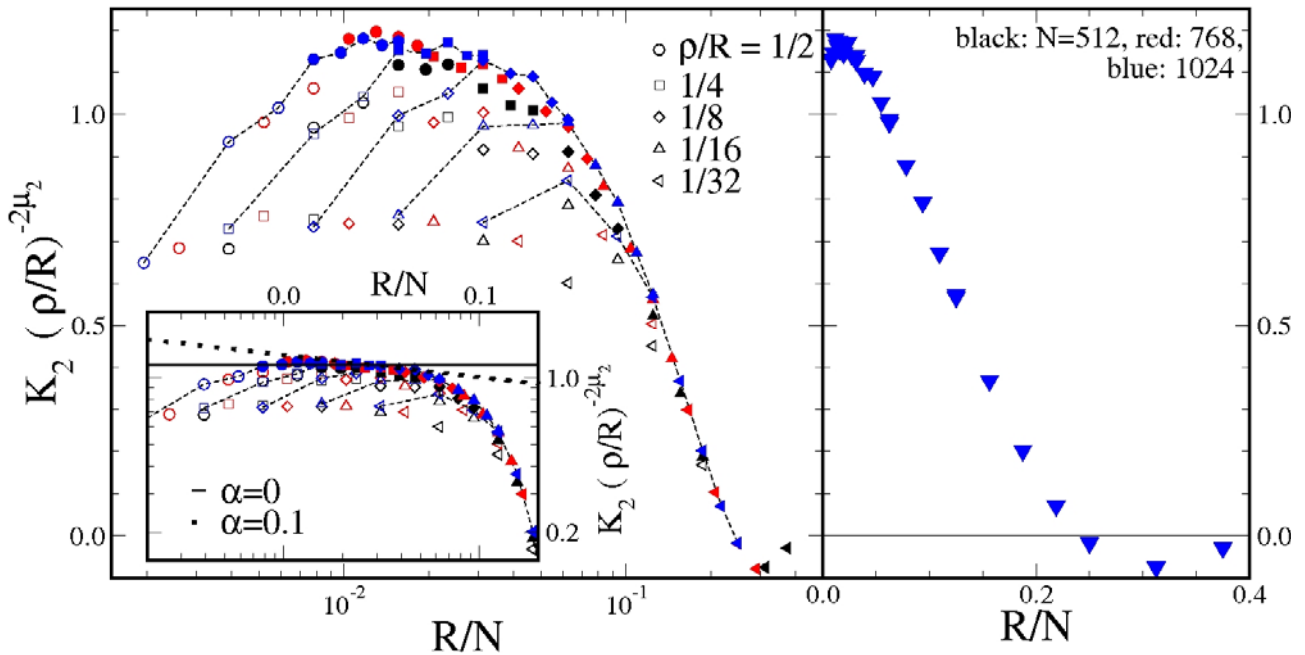


Figure 4: Scaling function associated with the correlation function, $K_2(\rho,R)$, of two particle-hole pairs, where ρ is the separation of particle and hole and R is the distance of the pairs. Different colors refer to different sample sizes with linear dimension N . The inset emphasizes the asymptotic behavior of K_2 in the limit of large sample sizes, when $R/N \rightarrow 0$; the numerical data are consistent with a flat curve (exponent $\alpha=0$ in the double logarithmic plot) indicating that K_2 does not introduce another power law singularity. [C4.11:3]

The outcome of our study [C4.11:3] is important. If the scaling function $K_2(\rho,R)$ would have displayed a more singular behavior at small distances, $\alpha \gg 0$, then interaction effects could have seriously invalidated our understanding of the quantum Hall effect in graphene which is essentially based on a picture of effectively non-interacting particles. Our result confirms that the energy redistribution amongst the electrons in the disordered sheet is slow enough, so that dephasing does not destroy the step formation in the quantum Hall transitions.

3. Spectral signatures of symmetry in transport through single molecules

3. Dependency of the conductance of Biphenyl-Dithiole on the tilting angle

A systematic understanding of transport experiments on single molecule requires a careful study of model systems. In experiments performed by the Columbia group it has been investigated, how the conductance of a biphenyl-dithiole molecule, Fig. 5, changes upon tilting the phenyl units against each other [2]. A similar study has been repeated recently by Mayor, Wandlowski, Bagrets, Pauly et al. who have corroborated the most important finding, namely that the transmission through the molecule is roughly proportionate to the $\cos^2\varphi$ of the tilting angle, φ . [C3.11:3]

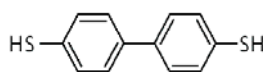


Figure 5: Biphenyl-dithiole molecule. Steric hindering by H-atoms (not shown) induces tilting between the rings $\varphi \sim 30^\circ$. Other angles can be realized by chemical design introducing additional bridges, e.g., alkane chains. [C3.11:3]

At first sight the result seems to be expected, since the angular dependency seems to merely reflect the change in overlap-matrix elements between the two phenyl systems. Not so obvious, however, is that in the course of tilting the spectral properties (HOMO/LUMO-energies with respect to the chemical potential of the electrodes) do not shift corrupting the simple \cos^2 -law. Careful ab-initio studies show, that indeed such an energy shift occurs, but it is being compensated by a change in the line-shape largely restoring the \cos^2 -law. While results of these calculations have been summarized already in [C3.11:3] a detailed outline was only given in [C3.11:4].

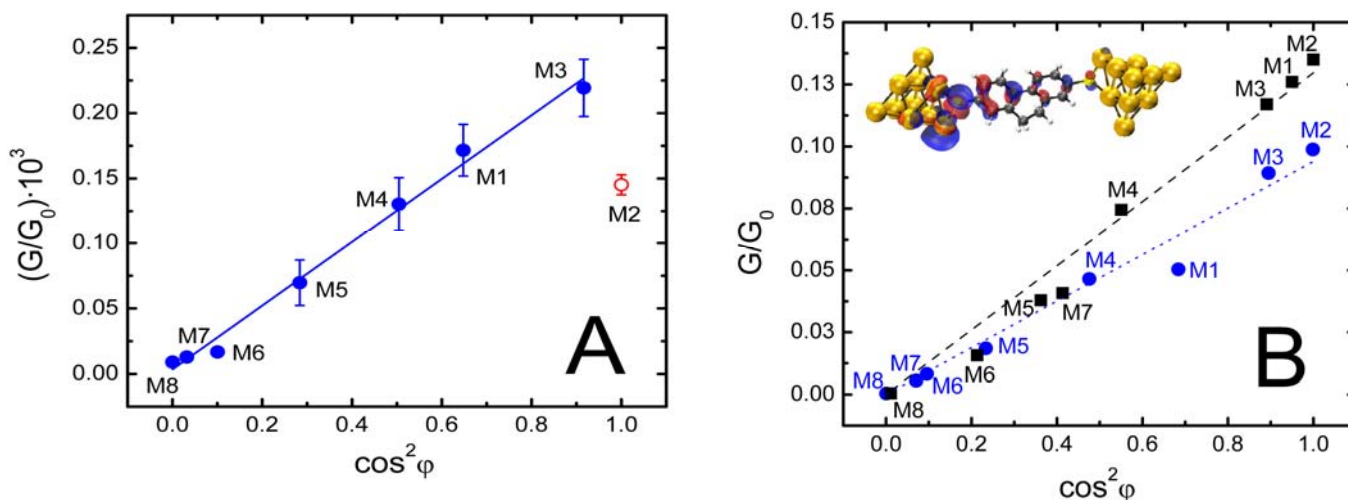


Figure 6: Conductance of a family of biphenyls parameterized by the tilting angle φ . 6A: Measurement performed with a STM-based breakjunction technique at room temperature using Au-electrodes (Wandlowsky group). 6B: Calculations with two different models for the Au-electrodes.

A discussion of the theoretical data should not miss the following point. The information of the experimental data is contained in the (average) slope together with the fluctuations of the data points around it. The slope is not properly reproduced by the DFT-based transport analysis for reasons related to functional artifact that have been discussed in the literature. [11] In addition, trends of the fluctuations of the individual data points about the average trend are also not reproduced, see, e.g., data points M1, M3, M2. It is not clear at the moment, why this is the case. Reasons could be related again to functional issues. But also experimental difficulties related to the self organized character of contact formation could enter, here.

3.2 Giant magnetoresistance effect in H₂Pc on Co(111)

In 2007 the Nobel prize in physics was awarded to P. Gruenberg and A. Fert for their discovery of the giant magnetoresistance effect (GMR) in magnetically structured layers. The recognition was partially related to the fact that GMR soon after its discovery in 1988 became central to the mini-mization of semiconductor based data storage and reading devices.

Recently, Stefan Schmaus and Wulf Wulfhchel were able to measure the GMR effect for single molecules at low temperatures, typically $\sim 4\text{K}$, see subproject C4.10. To this end they use a scanning-tunneling microscope (STM) with a magnetic tip operating on a Cu(111) surface covered with magnetically active Co-islands, see Fig. 7 (left).

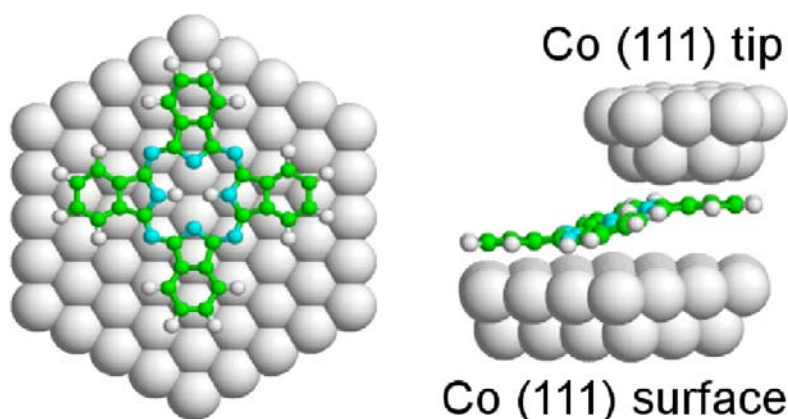
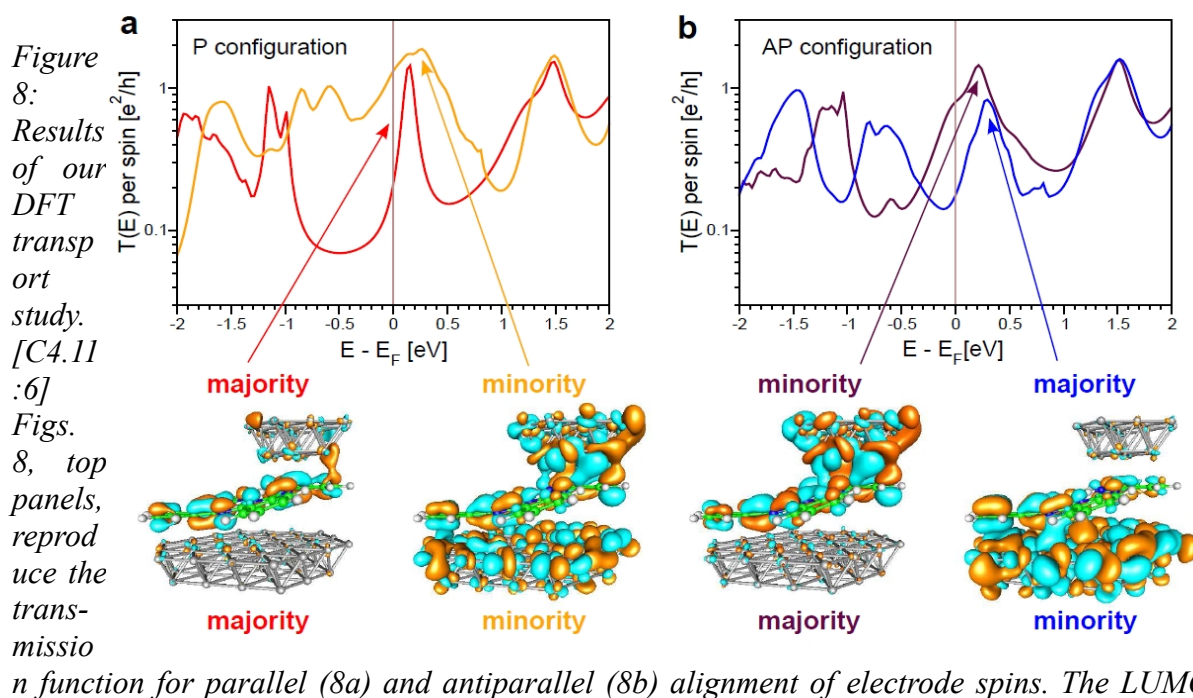


Figure 7: H₂Pc molecule on a Co(111) island. Left: On top view of the geometry obtained after structure optimization in a DFT treatment based on the TURBOMOLE package. Right: Geometry after closing as assumed in the transport calculation. The deformation of the molecule follows the shape of its lowest energy vibration.

Intriguing results have been obtained for H₂Pc, an organic molecule that has been studied before as a test system for molecular memory elements. [12] Namely, it is found that the GMR defined as the ratio of conductivities with parallel and antiparallel alignment of the electrode spins, $GMR = (G_{\uparrow\uparrow} - G_{\uparrow\downarrow}) / G_{\uparrow\downarrow}$, can reach values of 60% even though H₂Pc does not contain magnetic atoms. [C4.11:6] In order to explain this unexpected result extensive DFT based transport calculations have been performed.



transport resonance, that dominates the IV-characteristics at low bias voltages, is clearly visible near 0.3eV. The broadening of the resonance is spin dependent. The orbital plots illustrate how the down shift in energy of the Co-based d-band for the majority carriers makes it more difficult for the corresponding molecule based LUMO orbital to hybridize with the electrodes.

These calculations show that the origin of the effect is related to two observations: (i) due to the presence of Nitrogen, which attracts electrons from the Co-surface, transport is via the molecular LUMO orbital. (ii) The magnetization of Co-electrodes necessarily implies a relative energy shift in the surface density of states of minority and majority charge carriers. The Co-based *d*-band of the majority charge carriers is situated far below the Fermi energy. By contrast, the *d*-band of the minority carriers is only partly occupied, so it is located at the Fermi energy. As a consequence of (ii), only very few states are available for the LUMO based orbital with majority-spin occupation to hybridize with the leads, while many states are available for the LUMO with minority occupation. Therefore, the hybridization of the minority orbitals is much stronger and so is the corresponding broadening of the LUMO transport resonance. [C4.11:6] The DFT study allows to extract the GMR and we find a quantitative agreement with the experiment.

When assuming that the transport resonance is of the Breit-Wigner shape and that the peak positions of minority and majority resonances are close, a simple formula can be derived which expresses the GMR by the ratio of the density of states, ρ , of minority and majority carriers at the Fermi level: $GMR = (1 - \rho^{-1})(\rho - 1)/2$. [C4.11:6]. The formula indicates why there can be a quantitative agreement between experiment and theory despite the usual discrepancy for absolute values of the conductances. [11] Ultimately, the GMR is a ratio of two conductances and the formula shows that this ratio is largely dominated by the ratio of the density of states, ρ . Hybridization matrix elements between electrode and molecule and also the position of the LUMO with respect to the Fermi energy drop out in the specific observable GMR.

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