Subproject C3.11

Theoretical Spectroscopy of Molecular Nanostructures

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Introduction and Summary

The aim of the subproject C3.11 is to develop, test and apply novel approaches that allow to calculate spectroscopic properties and the dynamical response of molecular systems (including reservoirs) with an accuracy beyond the present standard methods based on ground-state density functional theories (DFT). Such theoretical investigations are of importance for several reasons:

(i) Most experiments probe the response of molecular systems to an external stimulus. The molecule's spectral properties determine these responses and therefore a detailed understanding of the prior helps the interpretation of the latter.

(ii) The excitation spectrum encodes crucial information about the microscopic state of a molecule and its interaction with the environment. To disentangle environmental impact from genuine molecular affairs usually requires a thorough theoretical analysis.

(iii) Current computational approaches (DFT, coupled cluster methods, configuration interaction approaches, etc.) are either not accurate enough or not applicable to intermediate size molecules [1].

Method development: In the first year of project C3.11 the focus was on deriving the key formulas and the implementation of the *GW*-method [2] into the Karlsruhe quantum chemistry package TURBOMOLE. [3] The method has proven to be efficient and precise when calculating elementary excitations (band gaps) in solids; [1] first applications to molecular systems strongly suggest that it will also be useful for applications in quantum chemistry. [4-7] Our implementation into the TURBOMOLE package is designed to make use of previous achievements of this code in terms of computational efficiency and therefore holds a promise that we can reach system sizes which could not be treated before using the *GW*-approach.

Two sidelines of method development are also pursued. First, we develop in C3.11 the GGA+*U*-method for quantum chemistry applications on magnetic systems. This method can be understood as a strongly simplified variant of *GW*. It is the analogue of the LDA+*U* approach, which is well known in solid state applications. [7] This technology is useful because it allows to test the stability of magnetic ground states obtained in a calculations based on the spin density functional theory (SDFT) in a computationally relatively cheap manner. SDFT calculations often suffer from inaccuracies implied by the generalized gradient approximation (GGA) and can in fact fail to predict magnetically nontrivial ground states. GGA+*U* provides a test suit in which one can investigate, whether a given SDFT ground state is a least close to a magnetic instability or not. Our second sideline of method development relates to ab-intio calculations of the electrical response of molecular metamaterials. The basic idea is to feed (improved) response calculations of individual molecules into computations of optical properties of molecular dielectrics composed of such molecules.

Applications: After a year of active research in C3.11, the methodological developments are in their prototypical test phase. For more complicated applications to experimentally relevant systems we have been relying on previously existing computational machinery. The three main areas of active research are:

Hydrogen storage materials: Since very recently the *GW*-method is available in standard condensed matter codes, e.g., VASP, [8] applications to the formation of hydrides and consecutive comparison with experiments allows to test the method already now. Adopting this strategy, in [C3.11:1] the *GW*-approach was employed to calculate optical properties of hydrides that are relevant for hydrogen storage. In this spirit in [C3.11:2] calculated spectra were used to identify, and exclude, the formation of specific materials

Molecular Spintronics: In an earlier work funded by C4.7 (subproject not continued), which was published only very recently, we explain an experiment performed at IBM Zurich that exhibited a well controlled switching behaviour of the so called "Tour"-molecule. [C3.11:3] Our proposed mechanism responsible for switching is related to a mechanical bistability of the molecules originating from a rotational degree of freedom. The interest in molecular switching also underlies our collaboration with Karin Fink, Mario Ruben and the group at TU Delft (H. van der Zant) where we investigate in theory and experiment the possibility to drive a spin transition in the metal-organic complex $Fe(II)(bpp)_2$ by charging. [C3.11:4] In the closely related subproject C4.11 it was investigated how the molecule's geometry and magnetism manifest themselves in its electronic properties, and consecutively also in transport experiments [C4.11:4,C4.11:5, C4.11:6, C4.11:7]. These studies also benefited from partial support from C3.11.

Meta-Materials: [PhD work of S. Bernadotte]. A method has been formulated how to translate the dynamical response of a single split ring resonator into the index of refraction of the corresponding metamaterial. For this a general relation between the index of refraction, $n(\omega)$, and the constitutive material tensors, magnetic permeability, $\mu(\omega)$, dielectric response, $\varepsilon(\omega)$, and the bianisotropies, $\zeta(\omega)$ *and* $\xi(\omega)$, had to be derived. [C3.11:4] To prepare a relevant application, the collective response (plasmons) of a large molecular split ring resonator has been calculated from ab-initio (time dependent DFT). It compares favorably well with our analytical results. The calculation of the material response, $n(\omega)$, is under way.

Finally, the publication list also contains a work where the effect of adatoms on the melting transition of small Aluminum clusters is investigated. [C3.11:6] This work was started within C4.7 already and could be finalized while Dr. Bagrets was supported from C3.11.

1. Method Development

1.1 Main development direction: GW-formalism for molecules, clusters, surfaces.
At the heart of the GW-method is solving efficiently the equation

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}} + V_{\text{H}} \right\} \psi_n^{\text{qp}} + \Sigma(\epsilon_n^{\text{qp}}) \cdot \psi_n^{\text{qp}} = \epsilon_n^{\text{qp}} \psi_n^{\text{qp}}$$

It looks formally similar to the Kohn-Sham equation underlying most formulations of DFT, but it has the crucial difference that instead of the exchange-correlation potential a non-local, energy dependent self-energy, Σ, appears. Σ can be constructed from a systematic diagrammatic expansion so as to obtain significantly improved excitation spectra compared to standard DFT treatments [6,7,8].
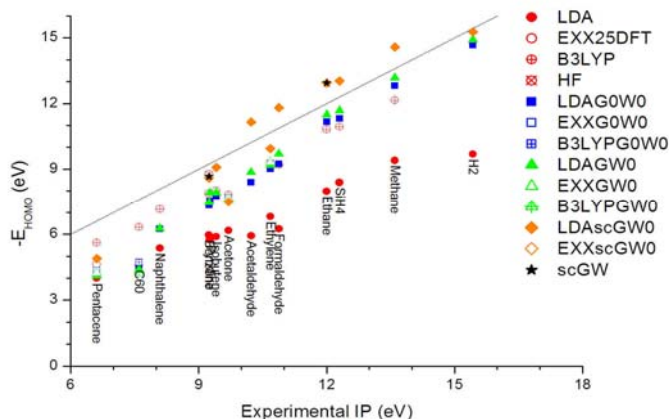

Figure 1: Comparison of experimental ionization potentials against estimates obtained for different approximate exchange correlation potentials. Best results are obtained with the GW-method in its various incarnations. (M. J. van Setten, VASP)

Present implementations of *GW* for solids (like VASP [8]), can also be used for relatively small molecules but are not optimized for the treatment of larger molecular systems. Other groups have also started to develop *GW* for molecular systems, fhi-aims [9]; these are however also in the developmental phase. Our procedure differs from the ones in two crucial aspects:

(i) We represent the polarization operator and Green's function that enter the construction of Σ in terms of Lehman representations, so we can do all the energy integrals analytically.

(ii) We employ the quantum chemistry package TURBOMOLE [3] which already provides a numerically extremely efficient implementation of 3-center integrals. These integrals appear as the crucial time consuming step in every *GW*-treatment. Therefore, prospects are that the size of molecules that can be treated by our *GW*-implementation are competitive.

Status: The set of constituting relations for our implementation of *GW* for molecules have been derived and coded within the first 9 months of the project time in an intensive collaboration with Florian Weigend. At the moment the code is being tested (water and benzene systems). Preliminary benchmarking for the water molecule suggests that the computational speed of our procedure (without optimization) could be orders of magnitude better than the reference VASP calculations (minutes vs. days for H_2O on the G_0W_0-level).

1.2 Sideline: GGA+*U*. As a computationally cheap approximation as compared to *GW* we are also implementing the GGA+*U* approach [7]. It can be considered as a "poor man's" variant of *GW*, which treats the screened interaction *W* as an effective parameter rather than carefully calculating it. The main advantage of the message is that it allows to test how sensitive magnetically non-trivial solutions of spin DFT are, when a local on site interaction, *U*, is being switched on. Only solutions that are "flowing" slowly with *U* have physical significance.

Status: The method has been formulated for molecules, coded for the TURBMOLE environment and tested by A. Bagrets. First applications relevant to recently performed experiments in the group of Wulf Wulhekel exist, see below.

1.3 **Side line: molecular split ring resonators for applications in meta-materials.**

The general relation between index of refraction, $n(\omega)$, and the constitutive material tensors, magnetic permeability, $\mu(\omega)$, dielectric response, $\varepsilon(\omega)$, and the bianisotropies, $\zeta(\omega)$ *and* $\xi(\omega)$,was derived in [C3.11:5] As a first application the conditions for the appearance of birefringence have been investigated more carefully. It was found somewhat unexpectedly that anisotropic media with pronounced bianisotropy exist which do not exhibit birefringence. [C3.11:5] The finding is somewhat surprising, because each of the two constituents when appearing just by themselves are always accompanied by birefringence. It is only when they appear simultaneously at a certain range of relative strength that their individual effects can annihilate one another.

Status: Method development is completed. An application is under way, see below, thesis is being written**.**

2. Applications: *GW* method for optical properties of thin films

In [C3.11:3] the optical spectra of the hydrides in the prototypical sodiumhydride hydrogen storage system: NaH, $NaAlH_4$, and Na_3AlH_6 have been calculated from first principles at various levels of theory.

Hydrides can be used to store energy produced from renewable sources at volumetric densities much larger than current battery technologies. They are in this approach used to store hydrogen, which is converted into electricity by a fuel cell. The beauty of this approach is twofold. On the one hand hydrides can have volumetric densities of hydrogen almost three times larger than that of liquid hydrogen. On the other hand the rest heat of the fuel cell can be used to drive the hydrogen desorption reaction, making an energy efficient storage system. When using complex hydrides of light elements densities of up to 20 wt.% of hydrogen can be reached. To make the system efficient, the thermodynamics and kinetics of the hydrogen absorption and desorption reaction need to be tuned accurately. To study such properties for entire ranges of compositions in only a single experiments, recently an *optical* technique called hydrogenography was developed. Here the optical response of a thin film with composition gradients is measured as a function of temperature and hydrogen pressure. To evaluate the data from this technique it is extremely helpful to be able to calculate, form first principles, the optical response of any possible compound in this composition gradient with an accuracy of ~0.2 eV on the energy scale. With this accuracy, hypothetical compounds can be identified, or excluded, from the experimental optical data. An accuracy like this is of course way beyond the predictive accuracy of DFT but is within reach of the *GW*-approach.
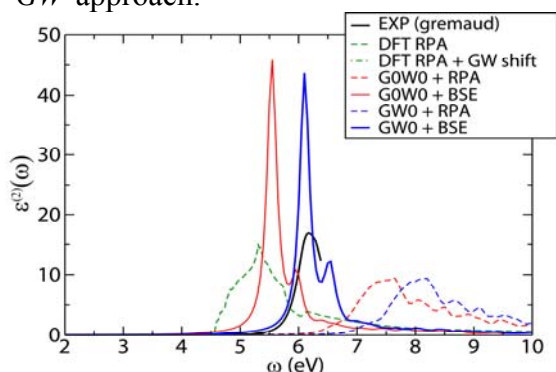

Figure 2: Comparison of the line shape of the dielectric function as obtained on different levels of the GW-approximation with the experimental result. The data illustrates the dramatic failure of a plain DFT-based appraoch,but also the necessity to include the interaction between the electron and the hole, which is at the heart of the BSE-extension of GW.

In this context we studied the effects of systematic improvements of the theoretical description. To benchmark the calculations the optical response of a thin film of NaH in the 0.6 to 6.5 eV range was measured for comparison. The simplest calculated dielectric functions are based upon independent electrons and holes, whose spectrum is obtained at the G_0W_0 level. Successive improvements consist of including partial self-consistency (so-called GW_0) and, accounting for excitonic effects, using the Bethe-Salpeter equation (BSE). Each improvement gives a sizeable blue- or red-shift of the dielectric functions, but always conserves the trend in the optical gap among different materials. Although these shifts partially cancel at the highest (GW_0-BSE) level of approximation, the *shape* of the dielectric functions is strongly modified by excitonic effects. Calculations at the GW_0-BSE level give a good agreement with the dielectric function of NaH extracted from the measurements. It demonstrates that the approach can be used for a quantitative interpretation of spectra in novel hydrogen storage materials.

As explained above, such quantitative interpretations are crucial in evaluating data obtained from optical, high throughput scanning techniques like hydrogenography, as has been successfully demonstrated in [C3.11:2] in the case of the Ca-B-H hydrogen storage system. Here, for example, the formation of CaH_2 could be confirmed and that of $Ca(OH)_2$ excluded using the calculated spectra.

In our calculations we have used directionally averaged dielectric functions to be able to compare to the experimental, mostly nano-crystalline samples. We were able to show that as long the diameter of the crystallites does not become smaller than about 10 nm this approximation is valid, i.e. the finite size effects renormalizing the electronic levels can be neglected.

3. Magnetic correlation effects in transport through single molecules

3.1 Kondo effect in spin transition compounds: It is known since long that spin transition compounds can exhibit a strong magnetoresponse upon changing external parameters like temperature, pressure or irradiation. In [C3.11:1] we present a comprehensive experimental and theoretical study exploring the possibility to drive such a transition in a *single* molecule by *charging* it. Indeed, an elaborate set of calculations based on DFT and wavefunction based methods (CASSCF and MCCEPA) strongly suggests, that the Fe-core in the $[Fe(bpp)_2]^{2+}$-complex undergoes a transition from $S_{Fe}=0$ to $S_{Fe}=2$ when adding two electrons. This magneto-electrical effect goes along with a change in the magnetic excitation structure of the total molecule. After the transition the ground state has $S=1$, so it ends up in the spin triplet sector. Spin orbit interaction induces a splitting of the triplet into a ground state doublet and a singlet; the excitation energy is calculated to be in the range of 1meV by Karin Fink.
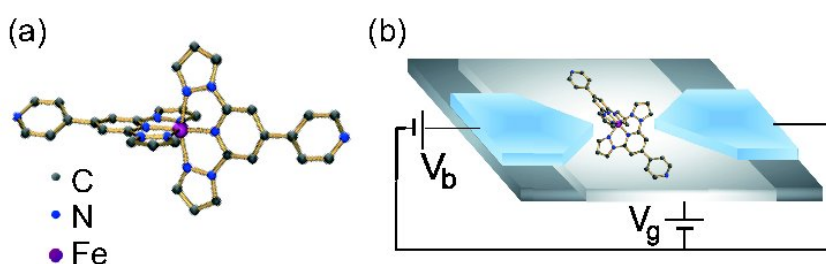

Figure 3: (a) Spin transition complex [Fe(bpp)₂] with an extra anchor group as used in the Delft experiment.
(b) Sketch of the electro-migrated break junction setup used for contacting the molecule.

The molecule has been synthesized by Mario Ruben and transport measurements have been performed in the group of Herre van der Zant at TU Delft, see Fig. 3. One expects, that the spin-transition from $S=0$ to $S=1$ manifests itself experimentally as an additional transport resonance at voltages of the order of the doublet-singlet splitting.
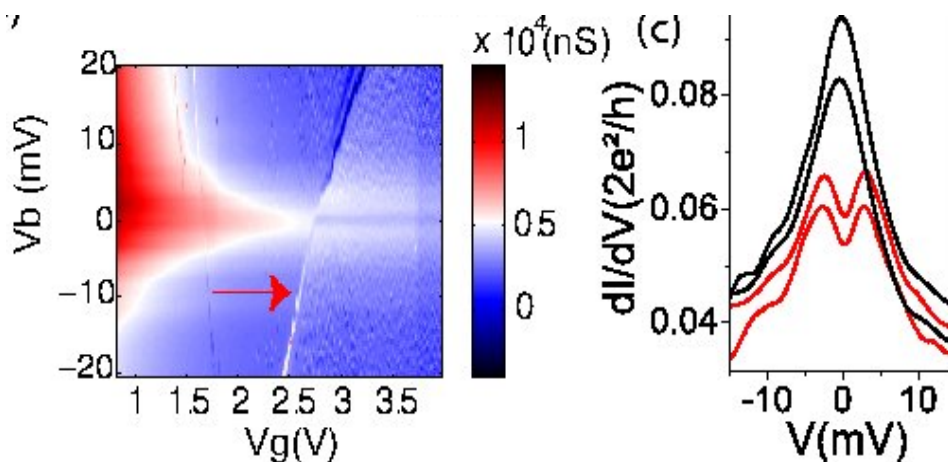

Figure 4: Variation of transport current (dI/dV) with gate and bias voltage. Left: Stability diagram exhibiting a charging event that shifts the local gate potential felt by the molecule. Charging drives the transition from a single Kondo-resonance (left side of the indicated line) to a the split Kondo resonance (right side). Right: dI/dV traces when tuning the gate voltage across the line. Measurement temperature is 1.4K.

Deep inside the Coulomb blockade regime experiments indicate a very striking feature. Namely, a charge redistribution at or very close to the molecule is associated with a splitting of the Kondo-resonance. A single resonance Fig. 4 left, in the low gate voltage, Vg, regime, is necessarily indicating the $S=0$ low spin structure of the ground state. A set of additional calculations on the

magnetic structure of this $S=0$ state strongly suggests that it is not compatible with a splitting of the Kondo-resonance at the observed energy scale observed in Fig. 4, right at larger gate voltages. In contrast, this splitting is very well compatible with the theoretically expected values for the high spin, $S=1$, ground state. Together with plausible assumptions about the geometry of the molecular junction, these observations suggest that indeed the charge driven spin transition of a single molecule has been observed in [C3.11:1]. Ongoing work is directed towards gathering further evidence for this claim based on additional calculations employing the numerical renormalization group within a collaboration with Theo Costi, FZ Juelich.

3.2 Magnetotransport in CoPc: Transport through a Cobalt-Phtalocyanine (CoPc) molecule immobilized on a Co-surface has been investigated in the group of Wulf Wulfhekel [10]. Our DFT-calculations suggest the binding geometry depicted below, Fig. 5. The motivation to perform **GGA+U** calculations for this problem came from the somewhat unexpected prediction from spin DFT calculations that ,even though a Cobalt surface atom has a mean magnetic moment of $S=1.8$ μ_B, the magnetic moment of the Co-atom within the Pc remains quenched, $S=0$, at GGA level.
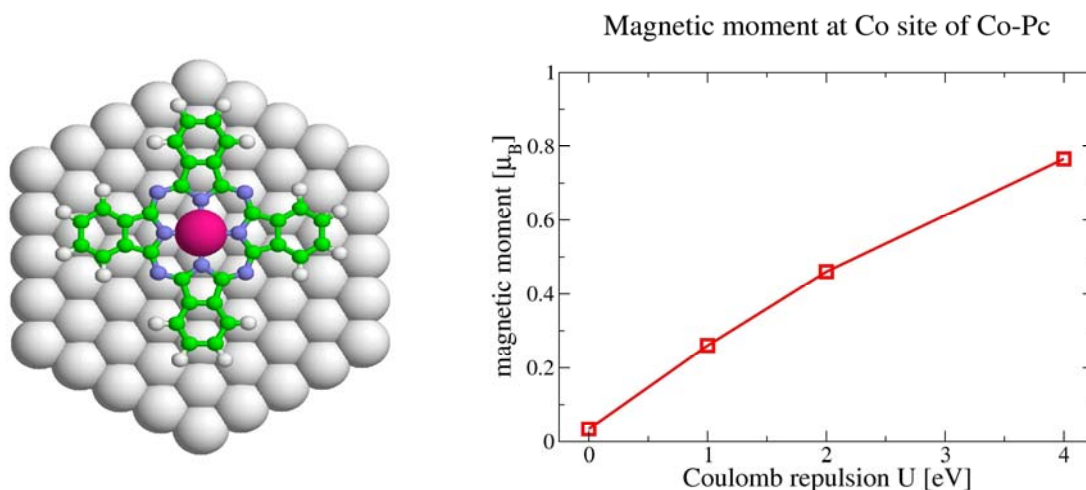

Fig. 5 Calculations based on spin DFT for a Cobalt-Phtalocyanine molecule on a Co(100) surface. Left: Optimal geometry. Right: Increase of the magnetic moment of the central Co-atom as calculated in the presence of an on-site interaction U.

Our GGA+U calculations indicate that even at relatively large on-site interaction of $U = 4eV$ the Co in the Pc does not develop a magnetic moment stronger than $S\sim0.7\mu_B$, see Fig. 5, right. This suggests that the original picture based on spin DFT is not seriously invalidated by self interaction effects. It then follows that the d-levels of the CoPc do not participate strongly in the transport current. Most likely the STM-current is carried by a ligand based LUMO orbital.

Status: The result will be combined with an additional study of MnPc before publication together with the experimental results.

4. Molecular split ring resonators

The excitations dominating in the optical response of a split ring resonator are collective oscillations of the charge carriers, i.e. plasmons. Their dispersion (energy over wavenumber) can be estimated with time dependent DFT. Remarkably, we were able to show how this dispersion relation can be much more easily determined in a quantitative way also from an analytical model calculation in the case of simple geometries such as indicated in the Fig. 6, left. The only phenomenological parameter is the Fermi-velocity, which can be fixed by performing a DFT *ground state* calculation, Fig. 6, centre.
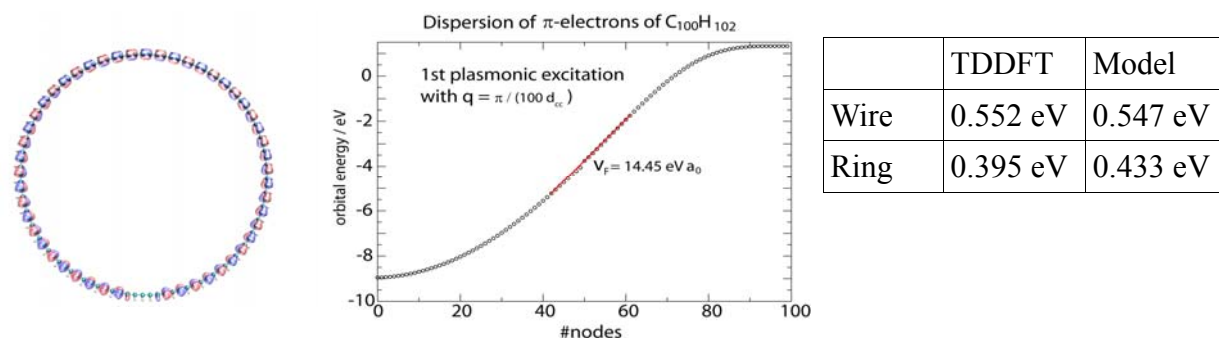

	TDDFT	Model
Wire	0.552 eV	0.547 eV
Ring	0.395 eV	0.433 eV

Fig. 6: Plasmon dispersion for a molecular split ring resonator. Left: HOMO orbital of $C_{100}H_{102}$. Centre: energy dispersion for the molecule as obtained from a DFT groundstate calculation. Right: Comparison of TDDFT and analytical model for the lowest plasmon frequency. The deviation for the ring geometry reflects the differences in the details of the slit modelling. The calculation of the effective index of refraction is work in progress.

This result owes its significance to the fact that it is precisely the plasmon response that enters the constituting tensors of the metamaterial. Therefore one expects that the material response has a straightforward parameterization in terms of the geometry and electronic structure of the consituting molecule. In order to facilitate this, a method should be devised how to translate the dynamical response of a single split ring resonator into the index of refraction of the corresponding metamaterial. To this end a general relation between the index of refraction, $n(\omega)$, and the constitutive material tensors, magnetic permeability, $\mu(\omega)$, dielectric response, $\varepsilon(\omega)$, and the bianisotropies, $\zeta(\omega)$ *and* $\xi(\omega)$, was derived in [C3.11:4].

Status: Publication of applications of the method to the split ring depicted in Fig. 6, left is in preparation.

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