

Fortsetzungsantrag für das Großprojekt nip00005 am HLRN

Adsorption of organic molecules on wide band gap insulators

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1 Statusbericht

During the last three quarters of the project nip00021, we have successfully carried out the first-principles calculations dedicated to the understanding of the adsorption of some organic molecules on wide band gap insulators. Follows the summery of the results that we have achieved so far.

1. *Adsorption on alkali halides* - The atomistic picture of the adsorption of various hydroxybenzoic acids on NaCl and KCl surfaces have been determined in terms of the state-of-art first-principles calculations. Not only on the ideal (001) surface, we also studied the adsorption on polar and non-polar step edges of the NaCl and KCl surfaces. We see that the electrostatic interaction between the surface cation and molecular oxygen is mainly responsible for the adsorption of hydroxybenzoic, while the covalent characteristics can also be observed although it does not contribute to the binding energy. The interaction strength is significantly modified only at defects with large dipole moments (e.g., pairs of polar steps) resulting in split-off edge states below the valence band. Resonant coupling to these states leads to an almost rigid down-shift of all molecular orbitals that efficiently reduces the effective band gap at the surface (see Fig. 1). This illustrates that the band gap of the adsorbate system can be tailored by both the adsorbed species and the polarity of the steps where the molecular is adsorbed at.
2. *Adsorption on kieserite* - While the adsorption on the non-polar surface of alkali halides is generally weak and it does not affect the electronic properties of the adsorbate, we see that this is not generally true from the adsorption of gluconic acid on a ternary compound, i.e. $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. The molecular frontier orbitals undergo significant changes when a gluconic acid is adsorbed on the (100) surface, arising from the complex interaction between the molecule and the insulating surface. A detailed analysis reveals that the order of the highest occupied molecular orbital (HOMO) and HOMO-1 is reversed after the molecule is attached to the surface (see the second configuration in Fig. 2). The strong variations in the frontier orbitals upon molecular

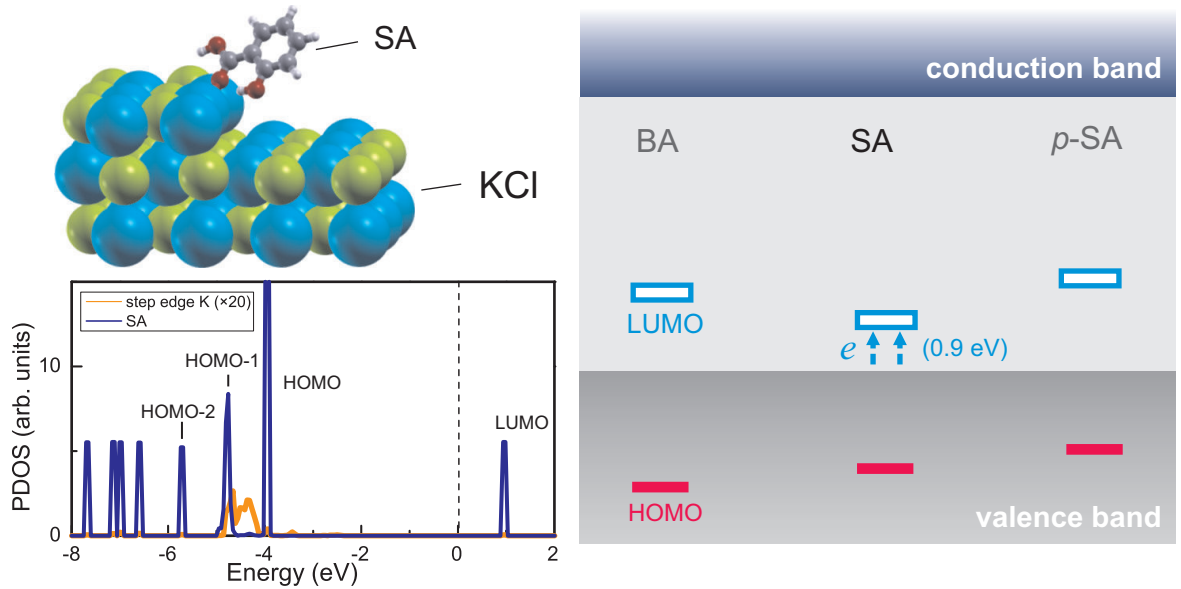


Abbildung 1: The adsorption of salicylic acid on the polar step of KCl surface, along with the Kohn-Sham band gap and density of states.

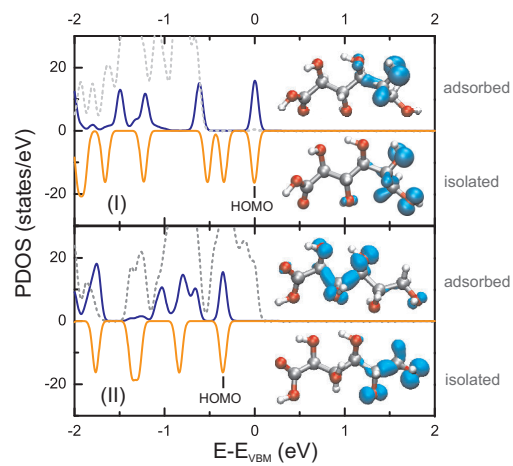


Abbildung 2: Density of states projected on the gluconic acid (adsorbed and isolated) (solid line) and surface (gray dashed line). The electron density of HOMO for the adsorbed and isolated molecules are also illustrated.

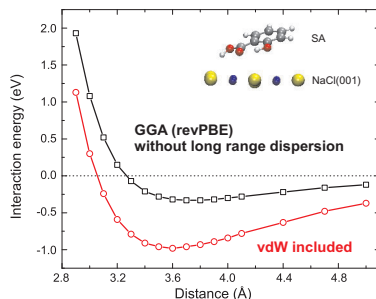


Abbildung 3: The energy potential curves for the adsorption of salicylic acid on NaCl(001) surface by DFT-GGA and vdW-DF.

adsorption stem from the rehybridizations of the water molecule at the kieserite surface.

3. *The role of van der Waals force* - In systems, such as organic molecule on wide gap insulator surface, the long-ranged van der Waals interaction plays an important role in the stabilizing of the molecular adsorption. However, the van der Waals force originates from the long-ranged electronic correlations, and it is not accounted by the popular density functionals, e.g. local density approximation (LDA) and generalized-gradient approximation (GGA). This questions the reliability of density functional theory (DFT) when it comes to describe the adsorption of the above-mentioned systems. Therefore, we evaluated the contribution of the van der Waals interaction by two approaches implemented in DFT (vdW-DF and DFT-D method). We find that van der Waals contributes about half of the total adsorption energy in most cases, an indication that it indeed plays an important role in the stabilization of the adsorbate. This can be seen in Fig. 3. On the other hand, the adsorption geometry does not demonstrate drastic changes if the long-range dispersion force is switched on.
4. *The influence of dynamic polarization* - Recently it has been found by photoemission and electron transport measurements that dynamic polarization effect has a strong influence on the energy level position of the molecular frontier orbital. The polarization in the surface, which is induced by the added electron (hole) in the affinity (ionization) lev-

el, acts back to the molecule and gives rise to a renormalization of the molecular levels. Such non-local correlation is beyond the scope of Kohn-Sham DFT and is thus not properly represented by Kohn-Sham eigenvalues. With the *GW* approximation, we are able to trace the influence of the polarization in the surface and predict a substantial gap reduction of the molecule when it is adsorbed on a wide gap insulating surface. For example, the energy gap of the gluconic acid is reduced by 0.58 eV upon adsorption on $\text{MgSO}_4\cdot\text{H}_2\text{O}(100)$ surface by the *GW* approximation of the self-energy, while the energy gap shows an increase instead within the framework of DFT. These results demonstrate that the dynamic polarization has a sizeable effect in reducing the energy gap of the adsorbate even on an insulating surface with a relatively small dielectric constant. Calculations beyond DFT are therefore indispensable for an accurate description of molecular adsorption on wide gap insulators.

5. *Color centers in NaCl by hybrid functionals* - The adsorption on defective surface, for example, on NaCl surfaces with anion vacancies (color centers) differs drastically from the adsorption on perfect surfaces, and it intimately depends on the properties of the vacancies. We revisited the color centers in NaCl using hybrid density functionals. The reduced self-interaction error alleviated by the exact exchange in hybrid functionals allows for a more accurate description of the atomic relaxations in the vicinity of the vacancy compared to the DFT results. Yet, hybrid functionals are unable to achieve quantitative agreement with experimental optical absorption peaks. We show that this is closely related to the overestimations of the band edges when the fundamental gap is reproduced by an empirical amount of exact exchange. Meanwhile, when the electronic correlation comes into play during the removal (addition) of a second electron from (to) the localized defect level, the ionization (affinity) energy predicted within the framework of DFT is far from satisfactory.

These studies have led to three publications and one manuscript submitted. Please refer to the Anlagen section.

2 Projektzielsetzung

In the preceding section, we have shown that the adsorption of organic molecule on insulating surfaces is a subject that deserves more effort due to both the technological interest and the complications in the computational method. When compared to experiment, the Kohn-Sham band gap is never a good indication because of the intrinsic deficiencies of DFT (such as functional derivative discontinuity and self-interaction error)[1]. DFT is basically a ground-state theory, and it has its own difficulty when trying to interpret the experimental excitation spectrum (e.g. photoemission and electron loss spectroscopy). Accurate predictions of the electronic excitations require more elaborate methods (e.g. *GW* approximations and Bethe-Salpeter equations), and these are the purposes for the extension of the project.

The treatment of the adsorbate system in the many-body perturbation theory (MBPT) will heavily rely on the code YAMBO[2], which is interfaced with ABINIT[3] and QUANTUM-ESPRESSO[4]. YAMBO is mostly written in Fortran 95, and is very well parallelized with respect to a large number of nodes. Tests on HLRN ICE-II lmem queue confirms that YAMBO is able to solve the state-of-art Bethe-Salpeter equations (BSE) for the adsorbate system with about 100 atoms.

Quarter 1: Electronic excitation for various hydroxybenzoic acids on NaCl and KCl (NPL: 10000)

We shall begin with the study of electronic excitation of benzoic acid on NaCl(001), which serves a fundamental model towards a more realistic system. It has been demonstrated that independent particle approximation (IPA) based on the Kohn-Sham eigenvalues cannot reproduce a realistic absorption spectra referenced to experiment.[5] Meanwhile, the spectrum yielded by IPA-*GW* still fails to agree quantitatively with experiment due to the absence of the exciton. Therefore, one needs to resort to the two-particle BSE to take into account the electron-hole interaction. In this stage, we aim to calculate the absorption and electron loss spectroscopy for a benzoic acid adsorbed on NaCl(001) in terms of a combined *GW* and BSE procedure on top of LDA eigenfunctions.

We now estimate the required NPL in the first quarter. The DFT part is negligible compared to the MBPT calculation, and therefore we skip the estimation of the DFT calculation. For a model system with 4 atomic layers for the NaCl(001) surface and a benzoic acid, there are a total of 47 atoms and 174 electrons if pseudopotentials are used. The evaluation of the self-energy in GW approximation requires a large number of empty states to sum. In our convergence test, 1000 bands have been found to be necessary for a converged quasi-particle (QP) gap. Taken into account the local field effect, one also needs a reasonable response matrix. In short, for a converged GW calculation, the model system costs roughly 9 hours using 384 (64 nodes * 6 cores/node) cores on the lmem queue¹. The number of cores per node is severely limited due to the extraordinary demanding of the memory during the calculation of the dielectric matrix and self-energy. This corresponds to 288 NPL for a single converged GW calculation.

The BSE solver is generally more memory-demanding than GW calculation. Based on the GW QP energies, we tested the performance of the BSE in YAMBO on the ICE-II. We note that the memory requirement of the BSE is proportional to $N_c \times N_v \times N_k$, where N_c is the number of the conduction band, N_v the number of the occupied band, and N_k the number of k-points. We find that about 7.4 GB memory is required per core for a total of 120 electronic bands. The BSE calculation takes about 2 hours using 128 (32 nodes * 4 cores/nodes) cores on lmem, which is equivalent to 128 NPL. Consider the anisotropy of the two-dimensional model system, one should also calculate the optics properties in other two directions of light polarization. Altogether with the GW calculation, we thus estimate that about 672 NPL (= 288 + 128 * 3 NPL) is required for one single calculation of the absorption of the two-dimensional adsorbate system.

An important part of the calculation, which has been neglected so far, is the convergence test. One needs to carefully check the convergence of

¹The YAMBO executable is compiled against Intel Compiler 11.0.083, mvapich2/1.4.1 and netcdf 3.6.2.

the slab size, k-point, number of bands, Coulomb cut-off, size of the response function and etc. This adds some extra NPL requirement, which is estimated to be as expensive as one full calculation of $GW+BSE$. We therefore come to conclude that we will need about 1350 NPL for each adsorbate and surface. Since we have three adsorbates (benzoic acid, salicylic acid and *para*-salicylic acid) and two types of surface (NaCl and KCl), a NPL of 8100 NPL ($= 1350 \times 6$ NPL) is a minimum requirement. Taking account into the additional DFT calculations (optimizations and non-self-consistent-field calculations), we therefore request 10000 NPL for the first quarter.

Quarter 2: Excitation of salicylic acid at the steps of NaCl and KCl (NPL:8000)

Since the surface is never free of defect, it is natural to extend the study to the defect site of the surface. The calculation at the DFT level already suggests some drastic changes when the organic molecule is adsorbed at the polar steps. However, this poses a great challenge for the MBPT calculation because of the large size of the system. We estimate the number of atoms for a stepped surface would need at least 80 atoms. Due to the fact that calculation of dielectric matrix scales as N^3 in the plane-wave basis, we thus expect that the minimum of the NPL for one full $GW+BSE$ calculation is about 2688 ($= 672 \times 4$ NPL). We therefore propose a usage of 8000 NPL as there are two types of surface, and if the convergence test and DFT calculations are also included.

Quarter 3: Optics of alkali halides and the color centers (NPL:8000)

When we have all the information on the excitation of the adsorbate system on NaCl and KCl, we need to turn to the optical properties of the surface alone. It is informative to understand the difference between the bulk and the surface in the electronic excitation (e.g. exciton binding energy). On the other hand, we have shown that DFT has difficulty in reproducing the optical properties of color centers in NaCl even with hybrid functionals. The $GW+BSE$ should be in principle gives a much better description of the excitations of the color centers. In this stage,

we aim to investigate the optical properties of NaCl and KCl with and without color centers in terms of MBPT. For perfect NaCl and KCl, a primitive cell containing two atoms is sufficient so that the calculation cost is negligible. For the color centers, one usually employs a unit cell of 64 atoms and removes one anion from the unit cell. We therefore estimate the calculation cost should be around 1000 NPL for one single calculation. Since we now have three different charge states of the anion vacancy in two types of host (NaCl and KCl), 8000 NPL should be appropriate.

Quarter 4: Excitation of the hydrobenzoic acids (NPL:5000)

In the final stage, we now investigate the electronic excitations in various hydrobenzoic acids and this finalizes the full circle of the picture. In addition to the $GW+BSE$, we also plan to employ the time-dependent DFT (TDDFT) to the hydrobenzoic acid. The TDDFT is an alternative to the BSE. For finite systems like molecules, a simple adiabatic LDA kernel could usually yield a very good excitation spectrum with respect to the BSE[6]. According to the dry run on a benzoic acid, the NPL cost for the converged GW QP energy is about 128 NPL on a lmem queue (= 128 cores \times 2 hrs). The subsequent BSE calculation including the interband transitions among 120 bands costs 8 NPL (= 32 cores \times 0.5 hrs). The TDDFT calculation is much cheaper than the BSE diagonalization solver and the NPL cost could be safely ignored. We note that the hydrobenzoic acid usually has a dimer form, whose excitation spectra could be different from the monomer. Due to the N^3 scaling, the computation cost for the dimer could be as 8 times higher as the that for the monomer. The NPL cost goes beyond 3000 NPL since we have three types of hydrobenzoic acids. If the convergence test is included, a total NPL of 5000 is reasonable for the fourth quarter.

3 Quartalsübersicht

| Quartal | Kurzbeschreibung | NPL |
|---------|--|-------|
| 04/2010 | Electronic excitation for hydroxybenzoic acids on alkali halides | 10000 |
| 01/2011 | Excitation of salicylic acid adsorbed at the steps | 8000 |
| 02/2011 | Optics of alkali halides and the color centers | 8000 |
| 03/2011 | Excitation of the hydrobenzoic acids | 5000 |
| gesamt | | 31000 |

4 Anlagen

1. W. Chen, C. Tegenkamp, H. Pfnür, and T. Bredow, *The interplay of van der Waals and weak chemical forces in the adsorption of salicylic acid on NaCl(001)*, Phys. Chem. Chem. Phys., 11, 9337 (2009)
2. W. Chen, C. Tegenkamp, H. Pfnür, and T. Bredow, *Insight from first-principles calculations into the interactions between hydroxybenzoic acids and alkali chloride surfaces*, J. Phys. Chem. C, 114, 460 (2010)
3. W. Chen, C. Tegenkamp, H. Pfnür, and T. Bredow, *Anomalous molecular orbital variation upon adsorption on a wide band gap insulator*, J. Chem. Phys., 132, 214706 (2010)
4. W. Chen, C. Tegenkamp, H. Pfnür, and T. Bredow, *Color centers in NaCl by hybrid functionals*, submitted to Phys. Rev. B (2010)

Literatur

- [1] Stephan Kümmel and Leor Kronik. Orbital-dependent density functionals: Theory and applications. *Rev. Mod. Phys.*, 80(1):3–60, 2008.
- [2] Andrea Marini, Conor Hogan, Myrta Grüning, and Daniele Varsano. yambo: An ab initio tool for excited state calculations. *Comp. Phys. Comm.*, 180(8):1392–1403, 2009.
- [3] Xavier Gonze and et al. A brief introduction to the abinit software package. *Zeit. Kristallogr.*, 220:558, 2005.

- [4] Paolo Giannozzi and et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matt.*, 21(39):395502, 2009.
- [5] Giovanni Onida, Lucia Reining, and Angel Rubio. Electronic excitations: density-functional versus many-body green's-function approaches. *Rev. Mod. Phys.*, 74(2):601–659, 2002.
- [6] Maurizia Palumbo, Conor Hogan, Francesco Sottile, Paolo Bagalá, and Angel Rubio. Ab initio electronic and optical spectra of free-base porphyrins: The role of electronic correlation. *The Journal of Chemical Physics*, 131(8):084102, 2009.