Chapter 6

Conclusions

6.1 Summary

In Sec. 3 we have reviewed the repeated-slab approach for G_0W_0 calculations, identified certain difficulties associated with it and presented appropriate solutions:

- For a numerically stable scheme, the anisotropy in the dielectric screening must be taken into account for the treatment of the $1/k^2$ singularity of the screened interaction (Sec. 3.2.2). A robust scheme for the GW space-time method has been developed.

- An efficient image-charge method has been developed for the calculation of the screened interaction in two-dimensional model systems (homogeneous in two spatial directions with an arbitrary dielectric profile in the third, cf. Sec. B.1). These models proved to be instrumental for the understanding of the screening effects in two-dimensional systems.

- The convergence behaviour of the quasiparticle energies with respect to the **k**-point sampling parallel to the surface is slow (Sec. 3.3.2). This can be attributed to the transition between the local and the average dielectric screening in non-homogeneous systems. For the repeated-slab approach, small vacuum/slab ratios are numerically advantageous. A functional form has been derived from a dielectric model that allows to extrapolate the convergence curves to the limit of infinite **k**-point sampling, thereby reducing the computational cost for accurate G_0W_0 calculations considerably.

- The polarisation of the neighbouring slabs in the repeated-slab approach introduces a slow convergence with respect to the slab separation (vacuum thickness). Dielectric models quantitatively describe this

effect and are used to correct for the finite vacuum thickness *a posteriori* (Sec. 3.3.3). Further modifications to the G_0W_0 scheme are then not necessary.

In Sec. 4, we have analysed ground-state effects for thin oxide films in the context of heterogeneous model catalysts.

- The thin silica film on Mo(112) exhibits the same bonding connectivity as the reconstructed α-quartz surface and other silica thin films or surfaces (Sec. 4.3.1). It can thus be seen as a surface form of silica.

- For oxide films of one or two monolayers thickness, the substrate exerts a significant influence on the atomic structure. The resulting structures can be understood in terms of the same principles that govern the ionic bonding in bulk materials. For this, substrate constraints such as the substrate-defined lattice constants for commensurate films as well as the linkage to the substrate surface must be taken into account.

- The electronic structure of supported thin films is modified by the substrate. This is mainly due to the substrate-induced structural variations, whereas the direct influence e.g. via hybridisation is small (Sec. 4.3.2).

- The thickness of the oxide films significantly influences the atomic and electronic structure of ultrathin films (Sec. 4.4). Once bulk-like layers are present in the centre of the film, the properties quickly converge with increasing thickness.

- Band gaps and band widths have been found to be insensitive to the substrate or the thickness for the investigated cases. For the valence bands this is attributed to the localised nature of these states, whereas the conduction band minimum is pinned by the hybridisation with a surface resonance.

Returning to the fundamental hypothesis of the surface science approach "do ultrathin oxide films resemble oxide surfaces" we can now say: Monolayer films can be regarded as special forms of the oxide materials which in general are not representative for the bulk materials and their surfaces.

Self-energy effects for ultrathin NaCl films have been analysed in Sec. 5 in the context of photoelectron spectroscopy.

- The dominant changes beyond the scissor-like shifts observed in the bulk material can be attributed to dielectric response effects. However, simple models overestimate the magnitude of the effects compared to the full G_0W_0 calculations.

- In free-standing films, the surface polarisation leads to an increase of the quasiparticle gap. This introduces a thickness-dependence of the quasiparticle gap not observed at the level of DFT-LDA (Sec. 5.1).

- In supported films, the image potential is asymmetric (Sec. 5.2.3). The image potentials induced by the change in the dielectric constant at the surface and the interface oppose each other. This weakens the thickness-dependence of the peak positions compared to the free-standing films.

- For delocalised states such as the Cl $3p$ states, the varying self-energy corrections lead to a broadening of the peaks compared to the DFT-LDA DOS. Localised states undergo position-dependent shifts that reflect the local image potential.

- The G_0W_0 calculations agree with available experimental data for the position of the NaCl bands with respect to the Ge valence band maximum.

- As a first prototypical molecule adsorbed on Ge-supported NaCl films, carbon monoxide was studied. The CO levels undergo shifts that depend on the NaCl film thickness. This prediction agrees with the trend observed in STS experiments for pentacene adsorbates for NaCl films on copper.

- The dielectric model has been used to estimate the magnitude of image-charge effects for metal-supported oxide films. We find that they are significant and can shift localised states by more than $1\,\mathrm{eV}$. For silica/Mo(112), the differences in the O $1s$ binding energies observed in XPS are dominated by these final-state effects. Likewise, we expect the energetics of defects and charged adsorbates to be strongly modified by the metal substrate.

Moreover, an atomistic model of the NaCl/Ge(001) interface structure was obtained from DFT-LDA calculations (Sec. 5.2.2).

- The adhesion of NaCl films is effectuated by the electrostatic attraction of the ions in the film and the charge modulation in the buckled dimers of the Ge(001) surface. The adhesion mechanism shows a surprising similarity to that found for NaCl/Cu(311).

- The NaCl film induces a strong preference for a p(2×1) ordering of the Ge dimers. Other patterns that are observed for the clean Ge surface such as c(4×2) are energetically unfavourable.

- Flat NaCl films on Ge(001) are only metastable; thermodynamically, three-dimensional islands are favoured.

- In STM experiments with atomic resolution, the Cl atoms at the surface appear as bright spots. The theoretical simulated apparent layer heights agree reasonably with experiment.

The G_0W_0 calculations for repeated-slab systems required several technical improvements of the `gwst` code used (see App. E):

- A new, highly efficient algorithm for computing the contribution of the non-local pseudopotential to the matrix elements of the position operator has been developed.

- A more efficient implementation for the computation of the Green's function has been designed and implemented, which is about six times faster than the original one.

- A block algorithm for the inversion of Hermitean matrices in packed storage form has been devised and implemented. The resulting algorithm is about two times faster than the standard iterative LAPACK algorithm.

- A new storage scheme for the two-point functions reduces the disk space requirements by 30–40%.

6.2 Outlook

The G_0W_0 scheme for slab systems presented in this thesis, combining accurate numerical calculations with extrapolation and corrections procedures, provides an efficient approach for computing the quasiparticle band structure of slab systems. Using the current implementation of the GW space-time method, slab calculations can now be performed routinely. The current developments for metallic systems [32] are conceptually independent of our improvements and will soon extend the applicability also to the metal-supported insulator films. This opens new possibilities for analysing the photoemission spectra of these experimentally well-characterised systems and may help to clarify the role of dielectric response effects for delocalised states.

A further perspective for improving the efficiency of the G_0W_0 calculations is to incorporate the dielectric slab models directly into the treatment of the screened interaction. As stated in Sec. 3.2.2, any model function that

is known in real and reciprocal space may be used for treating the long-range part. Appropriate dielectric profiles could be derived consistently from the inverse dielectric matrix employing e.g. Rohlfing's averaging procedure [61]. The reciprocal-space representation can be obtained from the two-dimensional Ewald summation and a numerical FFT for the z-directions.

Our substrate-influence and thickness-dependence study indicates that monolayer films are special forms of the oxide materials. In order to improve the comparability to the bulk materials, the thickness of the films must be increased. However, this may not be sufficient alone. A second key issue is to produce interfaces compatible with the bulk structures. We emphasise that the growth of flat crystalline films does in general not indicate a good match between the substrate and the bulk oxide; on the contrary a preference for a specific thickness points towards unique structures differing from the bulk. We therefore suggest that the currently employed substrates are not the ideal starting point in the quest for thicker well-defined films. Repp *et al.* suggested that the electrostatic adhesion mechanism for insulator films on corrugated vicinal metal surfaces observed for the NaCl film on Cu(311) may offer a general strategy for the growth of flat crystalline films [6]. This may provide an alternative to the currently prevailing chemical-bond interfaces for silica and alumina.

Before we finish we will comment on the perspectives of the NaCl film on Ge(001). Since this is a computationally feasible system for theoretical investigations, an experimental verification of the predictions in Sec. 5.2.3 would be highly welcome. According to our calculations, the dielectric response effects should introduce noticeable changes in the band structure for the delocalised thin film states. In particular, angle-resolved UPS measurements for films of a few monolayer thickness could provide the data for a direct comparison between experiment and our G_0W_0 results to establish how accurately dielectric response effects are described in the theory. Likewise, new STM experiments could help to clarify the current discrepancy between theory (2×1, as in LEED) and experiment (1×1). Furthermore, the planned extension of the GW space-time method to metallic system will soon allow to study also the copper-supported NaCl films for which a wealth of data is already available.

The study of molecules on surfaces, ranging from biomolecules over molecular switches to small metal clusters, is an active area of research. In particular the use of ultrathin insulating spacer layers allows to reduce the direct coupling of the molecular levels to the metal states of the substrate. The coupling to the insulating spacer layer is much weaker, in particular for molecular levels in the band gap of the insulator film. We expect STS or PES to provide new insights into the electronic structure of the molecules

and its coupling to the substrate in the future. While standard DFT describes the ground-state properties such as the adsorption geometries and energies reasonably well, it fails for the excited states. The G_0W_0 calculations offer an accurate and appropriate framework to describe these new experiments theoretically and to analyse the decisive physical effects in detail. While simple image-charge models are sufficient to qualitatively explain the relevant effects for these systems, the G_0W_0 are required for a quantitative comparison. We have demonstrated that such calculations for composite molecule/insulator/semiconductor systems are feasible with present-day computer codes and resources. This opens the way for a fruitful collaboration of experiment and theory in the future that has been so successful in other areas in the past.