Summary

Having arrived at the end of the thesis, it is time to take a step back and appreciate the bigger picture. What has been achieved? And maybe more importantly: What has not been achieved?

In Chapter 1 we have briefly reviewed density functional theory (DFT), its time-dependent formulation (TD-DFT), as well as the more approximate density functional based tight-binding (DFTB). Special attention was paid to a clear and detailed derivation of Casida’s linear response formulation of TD-DFT [29], which forms the basis of the remainder of this thesis. This hopefully gives readers who are not already intimately familiar with the theory a chance to understand the chapters that follow.

In Chapter 2 we have reviewed the theory of TD-DFTB as introduced by Niehaus et al. [41], and have discussed how the TD-DFTB equations can be implemented efficiently in a computer program. Chapter 2 also introduced intensity selection: a transition dipole moment based pre-screening of the single orbitals transitions intended to reduce the computational cost of calculating electronic absorption spectra. By simply neglecting all single orbital transitions with an oscillator strength smaller than a user defined threshold $f^\text{min}_{\text{ia}}$, we were able to speed up the calculation of absorption spectra by an order of magnitude at virtually no loss of accuracy. The speed up is not only a result of the reduced size of the single orbital transition basis, but also of the fact that fewer excitations need to be calculated to cover the relevant energy window of the spectrum. We have found that an oscillator strength threshold of $f^\text{min}_{\text{ia}} = 0.001$ generally does not change the resulting absorption spectra significantly. Instead, this constant threshold results in a system dependent reduction in computational cost, with some systems profiting more than other. This makes the approximation very easy to use, and one might (only for the purpose of calculating absorption spectra) almost apply intensity selection by default. The greatest computational savings are observed for large systems, where the low energy end of the absorption spectrum is contaminated with many spurious, but completely dark charge-transfer excitations. However, as the ubiquitin example shows, excitations with partial charge-transfer character and low intensity might still contaminate the spectrum, leading to qualitatively wrong results for these systems. This is a general problem of TD-DFTB and TD-DFT calculations with GGA functionals, and independent of the additional intensity selection. There is nothing that prevents one from using intensity selection in a calculation based on a long-range corrected functional that does not suffer from this problem, and it would indeed be very promising to test intensity selection together with the recently published long-range corrected TD-DFTB [55, 132].

In Chapter 3 we have evaluated the performance of (TD-)DFTB for the calculation of the vibrational fine-structure of electronic absorption and emission bands. Previous results by Heringer et al. indicated that excited state geometries and frequencies are well predicted by TD-DFTB [100], but the vibrational fine-structure should be a more sensitive test. It is also an important practical application of (TD-)DFTB as
the (usually numerical) calculation of the excited state Hessian can be prohibitively expensive at the (TD-)DFT level. We have found that (TD-)DFTB is an excellent and computationally very efficient approximation to GGA/(TD-)DFT for the calculation of vibrational fine-structures. In comparison to experiment, vibrational fine-structures are actually predicted much more accurately than absolute excitation energies, indicating that the potential energy surfaces are merely shifted but not significantly distorted. In cases where TD-DFTB and GGA/TD-DFT do not predict the correct fine-structure, Dierksen and Grimme showed that TD-DFT with hybrid functionals usually makes correct predictions [94], though the optimal amount of Hartree-Fock exchange appears to be system dependent [95]. It would be very promising to test the new long-range corrected (TD-)DFTB [55, 132] for the calculation of vibrational fine-structures, though an efficient implementation would require analytical excited state gradients, which are not yet available for this method.

In Chapter 4 we have introduced TD-DFT+TB, a new method for the calculation of excited states. TD-DFT+TB basically takes molecular orbitals from a DFT ground state calculation and then uses a slightly modified TD-DFTB coupling matrix for the calculation of the excited states via Casida’s equation. The motivation behind this is that orbitals from DFT should be more accurate than those from DFTB and can be calculated for systems where DFTB parameters are not available, making the method more widely applicable than TD-DFTB. Our tests show that TD-DFT+TB offers close to GGA/TD-DFT accuracy at a computational cost closer to that of TD-DFTB. TD-DFTB+TB appears to be especially useful for the calculation of absorption spectra, who are often dominated by $\pi \rightarrow \pi^*$ transitions, which are well described by the TD-DFTB and TD-DFT+TB coupling matrices. We believe that the combination of TD-DFT+TB and intensity selection is an extremely potent method for the calculation of absorption spectra for systems that are well described by local exchange-correlation functionals. It is nice to note that approximate methods based on hybrid functional TD-DFT have recently been developed in the group of Stefan Grimme [43–45], so that end users now have approximate methods based on all varieties of TD-DFT at their disposal.

If any overall conclusion can be drawn from this thesis, it is certainly that the approximations studied in this thesis offer significant computational benefits at only a minor loss in accuracy. The deviations introduced by switching on intensity selection or the various tight-binding approximations are certainly small compared to the differences that can already be observed between TD-DFT calculations with different exchange-correlation functionals. In this sense, the very last level of approximation that was investigated in this thesis is not the one that limits the overall accuracy.

Working on the very approximate end of the method spectrum can at times be a bit disheartening, as one will naturally make wrong predictions on a fairly regular basis. It is, however, important to keep in mind that these methods are really only intended for situations where more accurate methods are not applicable anymore. In these cases, making approximate predictions is still more useful than not predicting anything at all.