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# Approximations in Density Functional Based Excited State Calculations

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## Prelude

What is science?

If this question was posed to random people in the street, then based on our collective high school experience, the most popular answer would probably be that science is the overarching category in which we collect fields such as physics, chemistry and biology. This is not entirely wrong. However, scientists tend to use the word "science" for a different, and arguably much more important concept: the scientific method; the systematic process through which humans organize their knowledge of the world into testable statements.

But how does the scientific method work? How do we actually discover new laws of nature? Richard Feynman explained the essence of the scientific method in such an ingenious way, that one can hardly resist quoting him:

In general, we look for a new law by the following process: First we guess it; then we compute the consequences of the guess to see what would be implied if this law that we guessed is right; then we compare the result of the computation to nature, with experiment or experience, compare it directly with observation, to see if it works. If it disagrees with experiment, it is wrong. In that simple statement is the key to science.

- Richard Feynman in The Character of Physical Law. at Cornell University (1964)

Taken out of context the above quote somewhat seems to downplay the role of the experimentalist, which was surely not Feynman's intention. It is true that it is the experimentalist's job to design and conduct experiments, the outcome of which can be compared to computations based on the proposed law. Quite often, however, experiments are also done before a law has been guessed and the results can give valuable hints to theoreticians for guessing the law. Not to forget that unexpected experimental results are really what makes guessing a new law necessary in the first place!

The first theoretician was arguably Isaac Newton, who in 1687 with the publication of his *Philosophiæ Naturalis Principia Mathematica* introduced (or, as Feynman would say: guessed) the laws of classical mechanics that are still used today. Furthermore, Newton proposed the law of gravitation and showed that the motion of the planets, which was before only understood kinematically, actually followed from the application of his laws to the solar system. In this sense, Newton united planetary with terrestrial motion, and the field of astronomy with the emerging field of physics. In many ways Newton's *Principia* marks the first time that all elements of the modern scientific method came together, making it one of the most influential publications in the history of humanity.

Once the scientific method had been established, it was unstoppable: Not only did mankind unravel the mysteries of nature at a pace never before thought possible, but the newfound way of reasoning also influenced the development of its societies in what is today referred to as the Age of Enlightenment. By the end of the 19th century, classical mechanics introduced by Newton had been crowned by the elegant formulations of Joseph-Louis Lagrange and William Rowan Hamilton. The macroscopic theory of thermodynamics, also motivated by its application in engineering the machines driving the industrial revolution, had been connected to the theory of mechanics in what is now known as statistical mechanics. Electricity, magnetism and light had been recognized to be different aspects of the same phenomenon, i.e. the electromagnetic field. In summary: At the end of 19th century most phenomena seemed to be covered by the existing theories, which we today refer to as classical physics. The mindset of this time is perhaps best illustrated by a quote from Philipp von Jolly, at the time professor of physics at the University of Munich, who in 1874 tried (and luckily failed) to discourage the young Max Planck from enrolling in physics by telling him ...

 $\dots$  dass in dieser Wissenschaft schon fast alles erforscht sei, und es gelte nur noch einige unbedeutende Lücken zu schließen.

... that in this field almost everything is already known, and all that remains to be done is to close a few insignificant gaps.

— Max Planck in Wege zur Physikalischen Erkenntnis. Reden und Vorträge, Band 1. Leipzig 1943

In retrospect it is of course easy to see how terribly wrong Von Jolly was with this statement, but that is not the point here. If anything, his statement goes to show that he, and probably many physicists at the time, did not think that a physical theory for the structure and properties of matter was possible or even necessary. But this was about to change.

Around the turn of the century, experimentalists probed deeper into the nature of matter and its interaction with light, and began to make more and more observations that were inconsistent with the established theories of classical physics. It ultimately became clear that classical mechanics was inadequate for the description of microscopic systems such as atoms, and in the 1920s the theory of quantum mechanics was developed by Werner Heisenberg, Erwin Schrödinger, Wolfgang Pauli, Paul Dirac and others. While quantum mechanics in some ways reduces to classical mechanics in the limit of macroscopic objects, it is conceptually very different: Microscopic particles no longer follow trajectories but are instead described by a function, the so-called wave function, that is related to the probability of observing the particle at a particular time at a particular point in space. Furthermore, the outcome of certain experiments can only be predicted probabilistically, which is in stark contrast to Newton's perfectly deterministic world. This new theory with its psychologically uncomfortable implications was at first met with a healthy skepticism within the scientific community, perhaps best exemplified by Albert Einstein's famous statement that "god does not play dice". However, the undeniable truth that the new theory made correct predictions where previous models failed, made its adoption a simple necessity. Of great practical and technological importance is that quantum mechanics for the first time provides a theoretical basis for the description of matter; its properties and how it interacts in chemical reactions. In this sense quantum mechanics united the fields of physics and chemistry, and showed that the two fields only differ in their approach to the subject, but not in the subject itself.

Of course, the development of modern physics did not stop with quantum mechanics in the 1930s: A quantum mechanical description of the electromagnetic field was unified with quantum mechanics in a theory known as quantum electrodynamics, the first quantum field theory. Later the so called strong and weak interactions merged with quantum electrodynamics into what is now know as the Standard Model of particle physics. The Standard Model explains much, but we also know that it is at least incomplete, and certainly not yet the theory of everything that could possibly conclude the field of physics. Nobody knows whether this elusive theory of everything actually exists, or will ever be found. We seem to be on the right track though, and the curiosity of man will hopefully make sure that we keep searching.

However, on a more practical note, it appears that the most appropriate level of theory for the microscopic description of ordinary matter in our everyday lives is still quantum mechanics as it was developed in the 1920s. A description at a higher level of theory would simply be theoretical overkill: Treating a molecule with a quantum field theory is just as unnecessary as treating a space shuttle quantum mechanically. The quantum mechanical treatment of molecules is already difficult enough as it is. A treatment at a higher level of theory, e.g. with quantum electrodynamics, seems quite impossible.

Applying the laws of quantum mechanics to systems like molecules and solids is actually so difficult that it has evolved into a distinct branch of science, that depending on the point of view is called either quantum chemistry and condensed matter theory. But even after more than 50 years of work in these fields, there are still many situations in which we cannot make predictions of useful accuracy, and overall we have to admit that we are still amateurs when it comes to applying the laws of quantum mechanics to larger systems. In the grand scheme of things, one might say that we are today in the interesting situation that we seem to know the laws, but their mathematical form is so complicated that we struggle to make useful predictions based on them.

The most complicated step in the process of making predictions based on the laws of quantum mechanics is solving the Schrödinger equation, either in its stationary or its time-dependent form. The Schrödinger equation is a complex partial differential equation for the wave function; a function that depends on the positions of all involved particles. This means that the equation gets harder to solve as the studied system gets larger and the number of particles increases. In practice we can only solve the Schrödinger equation analytically for a number of toy systems like non-interacting particles in a rectangular box, the harmonic oscillator, or a single hydrogen atom. For larger systems like molecules or solids we are forced to introduce approximations that make the problem easier to solve (e.g. treating the nuclei classically or neglecting the repulsion between the electrons), and even then one can usually not find analytic solutions but has to resort to numerical methods. Naturally, the larger the system of interest, the more severe approximations need to be made to keep the calculation computationally feasible. Over time this has led to the development of a hierarchy of methods; ranging from highly accurate wave function based approaches only applicable to systems with a few electrons, through density functional theory and semi-empirical methods, to methods that actually forgo the solution of Schrödinger's equation altogether and implement Newton's classical mechanics with forces fitted to quantum mechanical results. Density functional theory is currently very popular for systems in the range of hundreds to thousands of atoms, while the aforementioned

force field based methods cover the range beyond that, up to roughly a hundred million atoms. For the end user, who just wants to know what the (known!) laws of quantum mechanics predict, this diverse zoo of computational methods is certainly inconvenient. Unfortunately, at the moment it looks like there is no way around it, and the discovery of the one, truly perfect and universally applicable method — however desirable — would surely be a huge surprise for everyone.

This thesis will make things worse and add to the zoo of computational methods.

Many molecular properties can already be predicted if one can calculate the molecule's ground state, that is the solution of the Schrödinger equation that has the lowest energy. Methods to determine the ground state of a system are relatively well developed, and density functional theory (DFT) is arguably the most popular method at the moment. However, many other molecular properties, e.g. most optical properties, require knowledge of not only the ground state, but also of the excited states. This is a much more difficult problem, since one would in principle need to find not only one, but all solutions of the Schrödinger equation. Computational methods for this are much younger and less developed than those that focus on the ground state alone. The most widely used method for the calculation of excited states is probably time-dependent density functional theory (TD-DFT), which is closely related to DFT and inherits its favorable balance between good accuracy and reasonable computational cost. Nevertheless, TD-DFT calculations are computationally quite challenging and can only be conducted for relatively small systems up to roughly a few hundred atoms. One step further towards more approximate and less accurate methods for the calculation of excited states is time-dependent density functional based tight binding (TD-DFTB). This method has been around for more than 15 years, but since it builds on the framework of density functional based tight binding (DFTB), which requires an extensive and difficult parametrization, it has not yet reached the popularity of the more easily applicable TD-DFT.

This thesis is about method development and, generally speaking, the effect of various approximations within the framework of TD-DFT. Some of it is based directly on the already more approximate TD-DFTB, making even more approximations in order to be able to treat even larger systems. It also evaluates the performance of TD-DFTB in applications in which it has not been used before. And finally, it introduces a new method for the calculation of electronically excited states that combines the best features of TD-DFT and TD-DFTB. The thesis is structured as follows:

Chapter 1 contains a pedagogical summary of the computational methods which are the basis of this thesis: Density functional theory (DFT), its time-dependent generalization (TD-DFT), and the more approximate density functional based tight binding (DFTB).

In Chapter 2, based on *J. Chem. Theory Comput.* **2015**, *11*, 157–167, we introduce a new approximation that is specifically designed to reduce the computational cost of calculating electronic absorption spectra with TD-DFT(B). We also discuss how the equations of TD-DFTB can be implemented efficiently in a computer program suitable for execution on modern, distributed memory machines.

In Chapter 3, based on *J. Chem. Phys.* **2016**, *145*, 184102, we evaluate the performance of TD-DFTB for the calculation of the vibrational fine-structure of electronic absorption and emission bands. Vibronic effects are due to their prohibitive computational cost often neglected, but their approximate treatment at the TD-DFTB

level has never been investigated. We hope to determine for which systems TD-DFTB predicts sufficiently accurate fine-structures, making the inclusion of vibronic effects possible in a wider array of applications.

In Chapter 4, based on *J. Chem. Phys.* **2016**, *144*, 184103, we combine TD-DFT and the more approximate TD-DFTB into a new method termed TD-DFT+TB, which is based on a DFT ground state calculation and only makes tight binding approximations in the calculation of the excited states. By picking and combining the best features of both methods we hope to obtain a method that is more accurate and more widely applicable than TD-DFTB, but still retains much of its computational efficiency.

The chapters 2, 3 and 4 are based on previously published, separate articles [1–3]. Chapters 3 and 4 reproduce the original articles almost verbatim, the only changes being some added references to recent publications, and some streamlining of the notation throughout the entire thesis. Chapter 2 differs slightly from the original article: After publication of the article we found that there was a technical mistake in the implementation of the TD-DFTB equations, which led to wrong results in case of the ubiquitin example. The article was later corrected in an erratum [4], but this thesis of course presents and discusses the correct results from the outset.

## 1 Summary of the theory

This chapter provides a quick and quite pedagogical introduction to the principal methods that are used, but never really explained, later on in this thesis: Density functional theory, time-dependent density functional theory, and density functional based tight-binding.

## 1.1 Density functional theory

Density functional theory, or short DFT, is an attempt at solving the stationary Schrödinger equation

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$
 . (1.1)

In chemistry and condensed matter physics the systems of interest are usually composed of electrons and nuclei. Quite often, however, the nuclei are treated classically within the Born-Oppenheimer approximation, so that the state  $|\Psi\rangle$  can be written as a wavefunction depending only<sup>1</sup> on the  $N_e$  electron coordinates.

$$\Psi(\vec{r}_1, \dots, \vec{r}_{N_e}) = \langle \vec{r}_1, \dots, \vec{r}_{N_e} | \Psi \rangle \tag{1.2}$$

The Hamiltonian operator  $\hat{H}$  of the interacting electrons can then in position representation and using atomic units be written as

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_{\text{ext}} = \underbrace{-\frac{1}{2} \sum_{n=1}^{N_e} \nabla_n^2}_{\hat{T}} + \underbrace{\frac{1}{2} \sum_{n \neq m}^{N_e} \frac{1}{|\vec{r}_n - \vec{r}_m|}}_{\hat{W}} + \underbrace{\sum_{n=1}^{N_e} v_{\text{ext}}(\vec{r}_n)}_{\hat{V}_{\text{ext}}}, \quad (1.3)$$

where the external potential is usually the combined Coulomb potential of all  $N_{\text{atoms}}$  nuclei located at  $\vec{R}_{\mathcal{A}}$  with their respective atomic number  $Z_{\mathcal{A}}$ , where calligraphic capital indices like  $\mathcal{A}$  label the individual atoms.

$$v_{\rm ext}(\vec{r}) = -\sum_{\mathcal{A}=1}^{N_{\rm atoms}} \frac{Z_{\mathcal{A}}}{|\vec{R}_{\mathcal{A}} - \vec{r}|}$$
(1.4)

Furthermore, due to the Pauli principle, we have the additional constraint that the wavefunction needs to be antisymmetric under exchange of any two electrons.

$$\Psi(\vec{r}_1,\ldots,\vec{r}_n,\ldots,\vec{r}_m\ldots,\vec{r}_{N_e}) = -\Psi(\vec{r}_1,\ldots,\vec{r}_m,\ldots,\vec{r}_n\ldots,\vec{r}_{N_e})$$
(1.5)

<sup>&</sup>lt;sup>1</sup>We neglect the electron spin for now, as it poses no fundamental problem in the derivation of DFT, while making the notation more verbose. We will reintroduce the electron spin later, when we actually use it in the derivation of Casida's equation.

This is the problem we need to solve. Clearly, as a  $3 \times N_e$  dimensional partial differential equation, this is mathematically a very hard problem. If, however, we were able to solve it, we could then use the wavefunction to calculate any physical property O of the system as the expectation value of the corresponding hermitian operator  $\hat{O}$ .

$$O = \langle \Psi | \hat{O} | \Psi \rangle = \int \mathrm{d}^3 r_1 \dots \int \mathrm{d}^3 r_{N_e} \, \Psi^*(\vec{r}_1, \dots, \vec{r}_{N_e}) \, \hat{O} \, \Psi(\vec{r}_1, \dots, \vec{r}_{N_e}) \tag{1.6}$$

This is where density functional theory comes in and provides a shortcut to the solution of our problem: It allows us to calculate expectation values without knowledge of the many-body wavefunction.

As the basis of DFT, the Hohenberg-Kohn theorem [5] establishes a one to one correspondence between the ground state electron density

$$\rho_0(\vec{r}) = \left\langle \Psi_0 \right| \underbrace{\sum_{n=1}^{N_e} \delta(\vec{r}_n - \vec{r})}_{\hat{\rho}(\vec{r})} \left| \Psi_0 \right\rangle = N_e \int \mathrm{d}^3 r_2 \dots \int \mathrm{d}^3 r_{N_e} \left| \Psi_0(\vec{r}, \vec{r}_2, \dots, \vec{r}_{N_e}) \right|^2 \quad (1.7)$$

and the external potential  $v_{\text{ext}}(\vec{r})$ . As the external potential fully determines the system's Hamiltonian via equation (1.3), it by extension also determines the system's ground state  $|\Psi_0\rangle$ .

$$\rho_0(\vec{r}) \longleftrightarrow v_{\text{ext}}(\vec{r}) \longleftrightarrow |\Psi_0\rangle$$
(1.8)

This is often referred to as the first Hohenberg-Kohn theorem. It is interesting to note that the proof of this theorem does not depend on the specific form of  $\hat{W}$ . Ergo, the theorem holds for any interaction  $\hat{W}$ , including the case  $\hat{W} = 0$  of non-interacting particles. Once the state of the system is known, one can of course use it to calculate any expectation value. The implications of this are huge: The expectation value of *any* observable is a functional of *only* the electron density.

$$O[\rho_0] = \left\langle \Psi_0[\rho_0] \left| \hat{O} \right| \Psi_0[\rho_0] \right\rangle$$
(1.9)

This could simplify the situation considerably, as  $\rho_0(\vec{r})$  is a real function in  $\mathbb{R}^3$ , while the many-body ground state wavefunction is a complex function in  $\mathbb{R}^{3N_e}$ , where  $N_e$  is the number of electrons. Furthermore, Hohenberg and Kohn showed that for a given external potential the ground state electron density  $\rho_0(\vec{r})$  is the one that minimizes the energy, that is the expectation value of the Hamiltonian, under the constraint of a fixed total number of electrons  $N_e$ .

$$E[\rho_0] \le E[\rho] \quad \text{for} \quad \int \mathrm{d}^3 r \; \rho(\vec{r}) = N_e$$
 (1.10)

This is usually referred to as the second Hohenberg-Kohn theorem.

If the functional  $E[\rho]$ , which connects the system's electron density with its energy, was known, instead of solving the stationary Schrödinger equation, one could determine the ground state energy  $E_0$  and density  $\rho_0$  simply by minimizing  $E[\rho]$  with respect to  $\rho$ . Unfortunately, this functional is not known. However, we can at least split off the contribution of the external potential, which we can easily write in terms of the density.

$$E[\rho] = \left\langle \Psi_0[\rho] \left| \hat{T} + \hat{W} + \hat{V}_{\text{ext}} \right| \Psi_0[\rho] \right\rangle = \underbrace{\left\langle \Psi_0[\rho] \left| \hat{T} + \hat{W} \right| \Psi_0[\rho] \right\rangle}_{F[\rho]} + \int \mathrm{d}^3 r \, \rho(\vec{r}) \, v_{\text{ext}}(\vec{r})$$
(1.11)

The complicated first term is often referred to as the universal functional  $F[\rho]$ , as it does not depend on the external potential, which is determined by the system under study. Its part  $T[\rho] = \langle \Psi_0[\rho] | \hat{T} | \Psi_0[\rho] \rangle$  is the kinetic energy functional, which is unfortunately unknown. The other part  $\langle \Psi_0[\rho] | \hat{W} | \Psi_0[\rho] \rangle$  is also unknown, but the specific problem with the kinetic energy functional is, that following the virial theorem, the kinetic energy of the system is of the same order of magnitude as its total energy. Therefore, even small inaccuracies in the kinetic energy functional have an overall large effect. Nevertheless, approximations for the universal functional exist, and methods that attempt to minimize equation (1.11) directly are commonly referred to as orbital-free density functional theory. See reference [6] for a recent review of the topic. However, despite being computationally very attractive, orbital free DFT does not yet reach the accuracy of the Kohn-Sham DFT scheme we are about to introduce and has hence not yet seen widespread adoption.

In order to deal with the kinetic energy more accurately, Kohn and Sham proposed the introduction of an auxiliary system of non-interacting particles moving in an effective potential  $v_{\text{eff}}(\vec{r})$  that reproduces the density of the interacting system [7]. For a non-interacting system the ground state is just a single Slater determinant of the orbitals  $\phi_i(\vec{r})$  which solve the effective one-particle Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\vec{r})\right)\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}) , \qquad (1.12)$$

and from which the density can easily be calculated as

$$\rho(\vec{r}) = \sum_{i=1}^{N_e} |\phi_i(\vec{r})|^2 . \qquad (1.13)$$

Furthermore, the kinetic energy of the non-interacting system, while in principle still being a functional of the density, can be calculated from the orbitals directly.

$$T_s[\rho] = -\frac{1}{2} \sum_{i=1}^{N_e} \int d^3 r \, \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r})$$
(1.14)

We can also use the Hohenberg-Kohn theorem, which holds for non-interacting particles, to easily write down the total energy functional of a non-interacting system

$$E_{s}[\rho] = T_{s}[\rho] + \int d^{3}r \,\rho(\vec{r}) \,v_{\text{eff}}(\vec{r})$$
(1.15)

The important question now is: How do we choose the external potential so that the non-interacting system reproduces the density of the interacting system we are actually interested in? Looking at the term for the universal functional  $F[\rho]$  in equation (1.11), we can at least try to calculate some contributions approximately: The kinetic energy functional  $T[\rho]$  is hopefully not too different from the functional  $T_s[\rho]$  of the non-interacting system, and we can surely get a significant part of the interaction if we just consider the Coulomb repulsion within the charge cloud in form of the Hartree term. Everything else we formally put into a quantity called the exchange-correlation functional  $E_{\rm xc}[\rho]$ .

$$F[\rho] = T_s[\rho] + \frac{1}{2} \iint d^3 r \, d^3 r' \, \frac{\rho(\vec{r}) \, \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\rm xc}[\rho] \tag{1.16}$$

It is important to realize that the above equation *defines* the exchange-correlation functional: The exchange-correlation functional is whatever it takes to make the above equation true. While it is unknown, it is hopefully rather small, so that errors in our approximation will not be as crippling as for inaccurate kinetic energy functionals. Substituting the above into equation (1.11) and then taking the functional derivative with respect to  $\rho(\vec{r})$  yields

$$\frac{\delta E[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_{\text{ext}}(\vec{r}) + \underbrace{\int \mathrm{d}^3 r \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|}}_{v_{\mathrm{H}}[\rho](\vec{r})} + \underbrace{\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\vec{r})}}_{v_{\mathrm{xc}}[\rho](\vec{r})} . \tag{1.17}$$

Analogously, we can calculate the functional derivative of equation 1.15.

$$\frac{\delta E_s[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_{\text{eff}}(\vec{r})$$
(1.18)

Due to the second Hohenberg-Kohn theorem we know that the functional derivative is zero at the ground state density  $\rho_0(\vec{r})$  for the interacting system, and since we want the interacting and non-interacting system to have the same density, we require it also to be zero for the non-interacting system.

$$0 = \frac{\delta E[\rho]}{\delta \rho(\vec{r})}\Big|_{\rho_0} = \frac{\delta E_s[\rho]}{\delta \rho(\vec{r})}\Big|_{\rho_0}$$
(1.19)

By comparing the two equations we see that the non-interacting system will reproduce the interacting system's density if the effective potential is chosen as a functional of the density given by

$$v_{\rm eff}[\rho](\vec{r}) = v_{\rm ext}(\vec{r}) + \int d^3r \, \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\rm xc}[\rho]}{\delta \rho(\vec{r})} = v_{\rm ext}(\vec{r}) + v_{\rm H}[\rho](\vec{r}) + v_{\rm xc}[\rho](\vec{r}) \,. \tag{1.20}$$

This presents a practical problem for the solution of the Kohn-Sham equations (1.12): The orbitals are calculated using the effective potential, a functional of the density, which in turn is calculated from the orbitals. Ergo, one has to find a self-consistent solution for the equations, which in practice is done iteratively.

So far we have only used the exchange-correlation functional  $E_{\rm xc}[\rho]$  as a black box into which we put everything we were unable to calculate. If the correct exchangecorrelation functional was known, density functional theory would be exact by definition. Unfortunately it is unknown and we need to make approximations in order to calculate anything in practice. Looking back at equation (1.16) it is easy to see that for a system with only one electron, the exact exchange-correlation functional just has to cancel out the Hartree term: After all a single electron should not experience a Coulomb interaction with itself (the m = n term was excluded in equation (1.3)) and the universal functional  $F[\rho]$ should be the kinetic energy only. While there have been attempts at designing exchange-correlation functionals that exclude the so-called self interaction [8, 9] in multi-electron systems, these methods have so far not become standard, and most approximate exchange-correlation functionals in use today suffer from a spurious self-interaction.

The oldest and simplest approximation for the exchange-correlation functional is known as the local density approximation (LDA). It can be written as

$$E_{\rm xc}^{\rm LDA}[\rho] = \int d^3 r \, \varepsilon_{\rm xc} \left(\rho(\vec{r})\right) \rho(\vec{r}) \,, \qquad (1.21)$$

where  $\varepsilon_{\rm xc}(\rho)$  is the per-particle exchange-correlation energy density of a homogeneous electron gas of density  $\rho$ , which can be calculated using quantum Monte Carlo methods [10, 11]. While LDA usually gives reasonable results, better approximations for the exchange-correlation functional can be constructed if one not only takes the value of the density into account, but also its gradient:

$$E_{\rm xc}^{\rm GGA}[\rho] = \int d^3 r \, \varepsilon_{\rm xc} \left(\rho(\vec{r}), \nabla \rho(\vec{r})\right) \rho(\vec{r}) \tag{1.22}$$

These functionals are known as generalized gradient approximation (GGA), and we will mostly use functionals of this form in the remainder of this thesis. More sophisticated functionals can be constructed if one, in addition to its gradient, also includes the Laplacian of the density (or of the kinetic energy density), which results in the so-called meta-GGA functionals. A review of the classes of exchange-correlation functionals and the methods used to construct them can be found in reference [12]. A special class of functionals are the so called hybrid functionals, where the Hartree-Fock exchange is partially used as the exchange portion of the exchange-correlation functional. The Hartree-Fock exchange energy can be written as

$$E_{\rm x}^{\rm HF}[\{\phi\}] = -\frac{1}{2} \sum_{i,j=1}^{N_e} \iint {\rm d}^3 r \, {\rm d}^3 r' \, \frac{\phi_i^*(\vec{r})\phi_j^*(\vec{r}')\phi_i(\vec{r}')\phi_j(\vec{r}')}{|\vec{r}-\vec{r}'|} , \qquad (1.23)$$

but in contrast to the LDA and GGA functionals, it is no longer a functional of the electron density, but of the set of Kohn-Sham orbitals  $\{\phi\}$ . This is not a practical problem, as the Kohn-Sham orbitals are available anyway. In practice, the form of the exact exchange energy is more problematic: Unlike LDA/GGA functionals it can not be written as the integral over a local quantity. Functionals involving an exact exchange contribution are therefore also called non-local. An in depth discussion of these points can be found in reference [13]. Despite these practical issues, hybrid functionals have become very popular as they improve the accuracy of some molecular properties. Of particular importance for this thesis is that they especially improve the description of some classes of excited states. This point is discussed in more detail later.

We have introduced the Kohn-Sham system as an auxiliary system of non-interacting electrons that by construction reproduces the density of the real system. As a noninteracting system, its wavefunction is given by the Slater determinant of the Kohn-Sham orbitals that solve the single particle stationary Schrödinger equation 1.12. At this point it is natural to ask if the orbitals  $\phi_i$  and the orbital energies  $\epsilon_i$  have any physical meaning. Despite the usefulness of an orbital picture in the rationalization of chemical phenomena, scientists have at first been very cautious with interpreting the Kohn-Sham orbitals. It was only after years of practical experience with Kohn-Sham DFT that the use of the Kohn-Sham orbitals in qualitative reasoning became somewhat accepted [14, 15]. The entire discussion was probably complicated by the fact that one has to distinguish between orbitals and orbital energies obtained with the approximate exchange-correlation functionals discussed above, and those that would be obtained with the exact exchange-correlation functional. For the latter is has been shown that  $-\epsilon_{\text{HOMO}}$  is equal to the first (vertical) ionization energy [16]. It was later shown that the orbital energies of the other valence levels are (for the exact exchange-correlation functional) also good approximations of the experimental ionization potentials |17-20|. Furthermore it has to be said, that the orbitals themselves are not physical observables, and any unitary transformation among the occupied orbitals does not change the Slater determinant or any expectation value calculated with it. In this sense, the question which orbitals are "correct", is somewhat ill-defined. Nevertheless, nowadays the single particle viewpoint based on the Kohn-Sham orbitals is often invoked to aid in the interpretation of DFT results, and in recent years much of the confusion around the meaning of the Kohn-Sham orbitals and the associated eigenvalues has been resolved. We are going to discuss this point in more detail in chapter 4, but one property of the Kohn-Sham orbital energies is of such relevance to the remainder of this thesis, that we already want to state it here: Baerends and Gritsenko have recently shown that the orbital energy differences  $(\epsilon_a - \epsilon_i)$  between the occupied orbitals and the bound virtual orbitals (i.e. those with  $\epsilon_a < 0$ ) are an excellent approximation of the system's excitation energies [21, 22]. This holds for the exact exchange-correlation functional, but more importantly, for transitions into virtual orbitals without Rydberg character it also holds for approximate functionals from the LDA/GGA category. In section 1.2.4 we will indeed see that the orbital energy difference  $(\epsilon_a - \epsilon_i)$  is the leading term in the expression for the excitation energies of the electronic system.

## 1.2 Time-dependent density functional theory

### 1.2.1 Runge-Gross theorem and time-dependent Kohn-Sham equations

Just like DFT is an attempt at solving the stationary Schrödinger equation, timedependent density functional theory (TD-DFT) attempts to solve the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \hat{H}(t)\left|\Psi(t)\right\rangle \ . \tag{1.24}$$

For the electronic systems studied in quantum chemistry and material science the Hamiltonian  $\hat{H}(t)$  is generally given by

$$\hat{H}(t) = \hat{T} + \hat{W} + \hat{V}_{\text{ext}}(t)$$
 (1.25)

$$= -\frac{1}{2} \sum_{n=1}^{N_e} \nabla_n^2 + \frac{1}{2} \sum_{n \neq m}^{N_e} \frac{1}{|\vec{r}_n - \vec{r}_m|} + \sum_{n=1}^{N_e} v_{\text{ext}}(\vec{r}_n, t) , \qquad (1.26)$$

where the external potential  $v_{\text{ext}}(\vec{r}, t)$  is usually the Coulomb potential of the (possibly moving) nuclei plus potentially an external electric field, e.g. the oscillating field of an electromagnetic wave.

This thesis mostly deals with the absorption of light by molecules. Since we later want to treat the electric field of the incoming wave as a perturbation, we assume fixed nuclei, so that the external potential (in dipole approximation) can be written as

$$v_{\text{ext}}(\vec{r},t) = -\sum_{\mathcal{A}=1}^{N_{\text{atoms}}} \frac{Z_{\mathcal{A}}}{|\vec{R}_{\mathcal{A}} - \vec{r}|} + f(t)\sin(\omega t)\vec{E}\cdot\vec{r}.$$
 (1.27)

Here  $\vec{E}$  determines the direction and strength of the electric field and f(t) modulates the intensity of the field in time, e.g. as a laser pulse or switching it on at some point in time. The magnetic component of the electromagnetic wave is neglected, as its effect is small compared to the electric field. Note that the entire time-dependence is in the second term, so we can write the external potential as

$$v_{\text{ext}}(\vec{r},t) = v_{\text{ext}}(\vec{r}) + \delta v_{\text{ext}}(\vec{r},t) , \qquad (1.28)$$

which for sufficiently small  $\delta v_{\text{ext}}$  is exactly the form we need for time-dependent perturbation theory.

While the original Hohenberg-Kohn theorem [5] is not applicable to time-dependent external potentials, it has later been generalized to time-dependent problems by Runge and Gross. The Runge-Gross theorem [23] establishes a one to one correspondence between the time-dependent external potential  $v_{\text{ext}}(\vec{r},t)$  and the time-dependent electron density  $\rho(\vec{r},t)$  of a system evolving from a given initial state  $|\Psi(t_0)\rangle$ . In practice the dependence on the initial state is less of a problem as it seems: If the external potential is initially time-independent, the initial state  $|\Psi(t_0)\rangle$  is determined by the density alone by virtue of the Hohenberg-Kohn theorem. This covers many experimental situations, e.g. a molecule in a laser pulse, and is also applicable to the linear response treatment in the next section, in which we are going to switch on the time-dependent perturbation adiabatically. So for this thesis we can basically ignore the initial state dependence and state the Runge-Gross theorem simply as

$$\rho(\vec{r},t) \longleftrightarrow v_{\text{ext}}(\vec{r},t) \longleftrightarrow |\Psi(t)\rangle \quad \text{for} \quad \left. \frac{\partial v_{\text{ext}}(\vec{r},t)}{\partial t} \right|_{t \le t_0} = 0.$$
(1.29)

Of course, if the state is a functional of the electronic density  $\rho(\vec{r},t)$ , so is the expectation value of any observable

$$O[\rho](t) = \left\langle \Psi[\rho](t) \middle| \hat{O} \middle| \Psi[\rho](t) \right\rangle .$$
(1.30)

But how do we do anything with this in practice? For ground state density functional theory, we used the second Hohenberg-Kohn theorem in the derivation of the Kohn-Sham equations. For time-dependent density functional theory we have no such variational principle for the energy, but we can formulate a stationarity condition for the action functional

$$A[\rho] = \int_{t_0}^t \mathrm{d}t' \, \left\langle \Psi[\rho](t') \, \middle| \, \mathrm{i}\frac{\partial}{\partial t'} + \hat{H}(t') \, \middle| \, \Psi[\rho](t') \right\rangle \,. \tag{1.31}$$

For the correct time-dependent density  $\rho(\vec{r},t)$  the action becomes stationary.

$$0 = \frac{\delta A[\rho]}{\delta \rho(\vec{r}, t)} \tag{1.32}$$

Using this, we can now more or less do the same steps as in the derivation of the Kohn-Sham equations in the last subsection. In equation (1.31) we can, in analogy to equation (1.11), split off the contribution of the external potential, which we can easily write down explicitly.

$$A[\rho] = \underbrace{\int_{t_0}^t \mathrm{d}t' \left\langle \Psi[\rho](t') \left| i\frac{\partial}{\partial t'} + \hat{T} + \hat{W} \right| \Psi[\rho](t') \right\rangle}_{B[\rho]} + \int_{t_0}^t \mathrm{d}t' \int \mathrm{d}^3 r \, \rho(\vec{r}, t') \, v_{\mathrm{ext}}(\vec{r}, t') \; .$$

$$(1.33)$$

For the universal action functional  $B[\rho]$  we then explicitly write out the kinetic energy of the non-interacting system as well as the Hartree term for the time-dependent densities. Everything we are missing is formally put into the exchange-correlation action functional  $A_{\rm xc}[\rho]$ .

$$B[\rho] = -\frac{1}{2} \sum_{i=1}^{N_e} \int_{t_0}^t dt' \int d^3 r \, \phi_i^*(\vec{r}, t') \nabla^2 \phi_i(\vec{r}, t')$$

$$+ \frac{1}{2} \int_{t_0}^t dt' \iint d^3 r \, d^3 r' \, \frac{\rho(\vec{r}, t') \, \rho(\vec{r}', t')}{|\vec{r} - \vec{r}'|} + A_{\rm xc}[\rho]$$
(1.34)

Following the exact same argument as for the ground state, we can show that a system of independent particles moving in the now time-dependent effective potential

$$v_{\rm eff}[\rho](\vec{r},t) = v_{\rm ext}(\vec{r},t) + \underbrace{\int d^3 r' \frac{\rho(\vec{r}',t)}{|\vec{r}-\vec{r}'|}}_{v_{\rm H}[\rho](\vec{r},t)} + \underbrace{\frac{\delta A_{\rm xc}[\rho]}{\delta\rho(\vec{r},t)}}_{v_{\rm xc}[\rho](\vec{r},t)}$$
(1.35)

yields the same density  $\rho(\vec{r}, t)$  as the interacting system. The time-dependent equivalent of the Kohn-Sham equations (1.12) can then be written as

$$i\frac{\partial\phi_i(\vec{r},t)}{\partial t} = \left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho](\vec{r},t)\right]\phi_i(\vec{r},t) . \qquad (1.36)$$

Notice in equation (1.35) that the Hartree potential  $v_{\rm H}[\rho](\vec{r},t)$  is local in time, i.e. it depends only on the density at time t and not on the history of the electron density.

This is unfortunately not true for the last term: The exchange-correlation action functional  $A_{\rm xc}[\rho]$  contains an integral over time and therefore in general depends on the entire history of the electronic density. This is of course extremely inconvenient. However, in the limit of slowly varying densities, the exchange-correlation action functional  $A_{\rm xc}[\rho]$  must reduce to the time-independent case discussed in the previous section, and we can write it in terms of the exchange-correlation functional  $E_{\rm xc}[\rho]$ .

$$\lim_{\substack{\partial \rho \\ \partial t} \to 0} A_{\rm xc}[\rho] = \int_{t_0}^t dt' \, E_{\rm xc}[\rho_{t'}] \tag{1.37}$$

Here we have written  $\rho(\vec{r}, t)$  evaluated at time t' as  $\rho_{t'}$ . At this point one commonly assumes that densities are sufficiently slowly varying for this to be a reasonable approximation. This is known as the adiabatic approximation, as it becomes exact in the limit of adiabatically varying densities. It simplifies the functional derivative of  $A_{\rm xc}[\rho]$  in equation (1.35) to

$$v_{\rm xc}[\rho](\vec{r},t) = \frac{\delta A_{\rm xc}[\rho]}{\delta \rho(\vec{r},t)} \approx \frac{\delta E_{\rm xc}[\rho_t]}{\delta \rho_t(\vec{r})} = v_{\rm xc}[\rho_t](\vec{r}) , \qquad (1.38)$$

making the effective potential  $v_{\text{eff}}[\rho](\vec{r},t)$  local in time: We can calculate it knowing only the density at time t, but without knowledge of the time-evolution of the density. It might seem like a ludicrous idea to simulate time-dependent systems using an approximation that becomes exact in the limit of time-independent densities. However, practice shows [24] that this approximation introduces much smaller errors than other approximations that are usually made, e.g. for the exchange-correlation functional  $E_{\rm xc}[\rho]$ . And after all, the adiabatic approximation is certainly no more drastic than the local density approximation for the exchange-correlation functional, which becomes exact for a spatially uniform electron density; something that is evidently not the case for real systems like solids, let alone molecules where the density is zero in the entire universe except for the vicinity of the nuclei.

There is actually a small error in the commonly presented derivation of the timedependent Kohn-Sham equations, which we followed in this section. The problem commonly known as the causality paradox of TD-DFT is this: If the potential

$$v[\rho](\vec{r},t) = \frac{\delta A[\rho]}{\delta \rho(\vec{r},t)}$$
(1.39)

could be written as a functional derivative of the action functional  $A[\rho]$ , then taking the second functional derivative would give

$$\frac{\delta v[\rho](\vec{r},t)}{\delta \rho(\vec{r}',t')} = \frac{\delta^2 A[\rho]}{\delta \rho(\vec{r},t) \delta \rho(\vec{r}',t')} .$$
(1.40)

But this equation has a causality problem: The right hand side is symmetric under exchange of primed and unprimed variables by virtue of the Schwarz' lemma for functionals [25], but the left hand side should not be. The potential at time t should not be influenced by a change in density at time t' > t! Vignale recently showed how the paradox can be resolved in a fairly straightforward manner [26]: The original error is that equation (1.32) is only valid for variations in  $|\Psi[\rho](t')\rangle$  that vanish on the boundaries  $t_0$  and t of the time interval under consideration. This is not the case here, as a change in the density at time t' < t changes the state at time t. If the upper boundary is correctly taken into account one obtains a second term on the right hand side of equation (1.40), which can not be written as a functional derivative of  $A[\rho]$ . This term restores the causality of the right hand side. However, since the boundary condition was also ignored in the calculation of the functional derivatives, the error that was made in the beginning of the canonical derivation canceled out later on, giving correct results in the end. A more in depth discussion of this point can be found in reference [26].

#### 1.2.2 Definition of the density response functions

We now assume that the external potential  $v_{\text{ext}}$  can be written as the sum of a timeindependent potential (e.g. the Coulomb potential of the nuclei) and a time-dependent perturbation.

$$v_{\text{ext}}(\vec{r},t) = v_{\text{ext}}^0(\vec{r}) + \delta v_{\text{ext}}(\vec{r},t)$$
(1.41)

The time-dependent electron density is then written similarly as the sum of the density of the unperturbed system and the density change due to the perturbation.

$$\rho(\vec{r},t) = \rho^0(\vec{r}) + \delta\rho(\vec{r},t) \tag{1.42}$$

In linear response theory we define the response function  $\chi(\vec{r}, \vec{r}', t - t')$  that relates a small change in the external potential  $\delta v_{\text{ext}}$  at  $(\vec{r}', t')$  to a change in the electron density  $\delta \rho$  at  $(\vec{r}, t)$ .

$$\delta\rho(\vec{r},t) = \int \mathrm{d}t' \int \mathrm{d}^3r' \,\chi(\vec{r},\vec{r}',t-t') \,\delta v_{\mathrm{ext}}(\vec{r}',t') \tag{1.43}$$

$$\chi(\vec{r}, \vec{r}', t - t') = \frac{\delta\rho(\vec{r}, t)}{\delta v_{\text{ext}}(\vec{r}', t')}$$
(1.44)

Note that due to the (assumed) uniformity of all physical laws across time, the response function can only depend on the time difference t - t' and not on the times t and t' separately. The response function  $\chi$  of the real system is unfortunately unknown, but we can use the fact that the density  $\rho$ , and therefore also the density change  $\delta\rho$ , are by construction equal in the real and the Kohn-Sham system. Ergo, we can analogously express the density change through the Kohn-Sham system of non-interacting electrons.

$$\delta\rho(\vec{r},t) = \int \mathrm{d}t' \int \mathrm{d}^3r' \,\chi_{\mathrm{KS}}(\vec{r},\vec{r}',t-t') \,\delta v_{\mathrm{eff}}(\vec{r}',t') \tag{1.45}$$

$$\chi_{\rm KS}(\vec{r},\vec{r}',t-t') = \frac{\delta\rho(\vec{r},t)}{\delta v_{\rm eff}(\vec{r}',t')}$$
(1.46)

Substituting the individual terms of the Kohn-Sham effective potential leads to

$$\delta\rho(\vec{r},t) = \int dt' \int d^3r' \,\chi_{\rm KS}(\vec{r},\vec{r}',t-t') \,\left[\delta v_{\rm ext}(\vec{r}',t') + \delta v_{\rm H}(\vec{r}',t') + \delta v_{\rm xc}(\vec{r}',t')\right] \,. \tag{1.47}$$

Using the chain rule for the functional derivative, it is easy to express the changes in the Hartree potential and the exchange-correlation potential through the density change  $\delta \rho$  itself.

$$\delta v_{\rm H}(\vec{r},t) = \int {\rm d}^3 r' \; \frac{\delta v_{\rm H}(\vec{r},t)}{\delta \rho(\vec{r}',t)} \; \delta \rho(\vec{r}',t) = \int {\rm d}^3 r' \; \frac{1}{|\vec{r}-\vec{r}'|} \; \delta \rho(\vec{r}',t) \tag{1.48}$$

$$\delta v_{\rm xc}(\vec{r},t) = \int \mathrm{d}^3 r' \int \mathrm{d}t' \; \frac{\delta v_{\rm xc}[\rho](\vec{r},t)}{\delta \rho(\vec{r}',t')} \; \delta \rho(\vec{r}',t') \approx \int \mathrm{d}^3 r' \; \underbrace{\frac{\delta^2 E_{\rm xc}[\rho^0]}{\delta \rho^0(\vec{r}) \; \delta \rho^0(\vec{r}')}}_{f_{\rm xc}(\vec{r},\vec{r}')} \; \delta \rho(\vec{r}',t)$$
(1.49)

Here we have used the adiabatic approximation to simplify the second equation for the change in the exchange-correlation potential. The density  $\rho_t$  from equation (1.38) was replaced to first order with the unperturbed density  $\rho^0$ , which makes the so called exchange-correlation kernel  $f_{\rm xc}(\vec{r},\vec{r}')$  conveniently time-independent. Substituting all this into equation (1.45) leads to

$$\delta\rho(\vec{r},t) = \int dt' \int d^3r' \,\chi_{\rm KS}(\vec{r},\vec{r}',t-t') \bigg[ \,\delta v_{\rm ext}(\vec{r}',t') + \int d^3r'' \left( \frac{1}{|\vec{r}'-\vec{r}''|} + f_{\rm xc}(\vec{r}',\vec{r}'') \right) \delta\rho(\vec{r}'',t') \bigg] \,,$$
(1.50)

and using the convolution theorem

$$h(t) = \int dt' g(t - t') f(t') \quad \Longleftrightarrow \quad h(\omega) = g(\omega) f(\omega)$$
(1.51)

we can conveniently write the density response in the frequency domain.

$$\delta\rho(\vec{r},\omega) = \int d^3r' \,\chi_{\rm KS}(\vec{r},\vec{r}',\omega) \bigg[ \,\delta v_{\rm ext}(\vec{r}',\omega) + \left( 1.52 \right) \\ \int d^3r'' \left( \frac{1}{|\vec{r}'-\vec{r}''|} + f_{\rm xc}(\vec{r}',\vec{r}'') \right) \delta\rho(\vec{r}'',\omega) \bigg]$$

#### 1.2.3 Response functions calculated from perturbation theory

We now use first order time-dependent perturbation theory to derive an expression for the response functions. The perturbation in the Hamiltonian of the real system is given by

$$\delta \hat{H}(t) = e^{\eta t} \sum_{n=1}^{N_e} \delta v_{\text{ext}}(\vec{r}_n, t) . \qquad (1.53)$$

Here the exponential factor with  $0 < \eta \ll 1$  is used to ensure an adiabatic, slow switching from the unperturbed Hamiltonian at  $t = -\infty$ . Using the density operator  $\hat{\rho}(\vec{r}) = \sum_{i=1}^{N_e} \delta(\vec{r}_i - \vec{r})$  and the Fourier transform<sup>2</sup> of the external potential we can

$$f(\omega) = \int dt e^{+i\omega t} f(t)$$
 and  $f(t) = \frac{1}{2\pi} \int d\omega e^{-i\omega t} f(\omega)$  (1.54)

 $<sup>^{2}</sup>$  We use the following definitions for the Fourier transform:

also write this as

$$\delta \hat{H}(t) = \int d^3r \int \frac{d\omega}{2\pi} e^{-i\tilde{\omega}t} \,\delta v_{\text{ext}}(\vec{r},\omega) \,\hat{\rho}(\vec{r}) \,, \qquad (1.55)$$

where  $\tilde{\omega} = \omega + i\eta$ . The complete Hamiltonian of the real system is given by

$$\hat{H}(t) = \hat{H}^0 + \delta \hat{H}(t) ,$$
 (1.56)

so that the time-dependent Schrödinger equation becomes

$$i\frac{\partial|\Psi(t)\rangle}{\partial t} = \left(\hat{H}^0 + \delta\hat{H}(t)\right)|\Psi(t)\rangle . \qquad (1.57)$$

Within time-dependent perturbation theory, the solution can be written as

$$|\Psi(t)\rangle = \sum_{I} a_{I}(t) e^{-iE_{I}t} |\Psi_{I}^{0}\rangle , \qquad (1.58)$$

where the states solve  $\hat{H}^0 |\Psi_I^0\rangle = E_I |\Psi_I^0\rangle$ . The time-dependent expansion coefficients  $a_I(t)$  are given by

$$a_{I}(t) = a_{I}(-\infty) - i \sum_{J} \int_{-\infty}^{t} dt' \langle \Psi_{I}^{0} | \delta \hat{H}(t') | \Psi_{J}^{0} \rangle \ a_{J}(t') e^{-i(E_{J} - E_{I})t'} .$$
(1.59)

While this expression for the coefficients  $a_I(t)$  is in principle exact, its form, where the coefficients themselves appear below the integral, is far too complex to be useful. However, we can plug the equation for  $a_I(t)$  into itself and then for a first order approximation only keep the first term  $a_J(-\infty)$ .

$$a_I(t) \approx a_I(-\infty) - i \sum_J \int_{-\infty}^t dt' \langle \Psi_I^0 | \delta \hat{H}(t') | \Psi_J^0 \rangle \ a_J(-\infty) \ e^{-i(E_J - E_I)t'}$$
(1.60)

We now use the fact that we know that the system is in the ground state  $|\Psi_0^0\rangle$  of the unperturbed Hamiltonian at  $t = -\infty$ , so we know that the coefficients  $a_I(-\infty) = \delta_{I0}$ .

$$a_{I}(t) = \delta_{I0} - i \sum_{J} \int_{-\infty}^{t} dt' \langle \Psi_{I}^{0} | \delta \hat{H}(t') | \Psi_{J}^{0} \rangle \ \delta_{J0} \ e^{-i(E_{J} - E_{I})t'}$$
(1.61)

$$= \delta_{I0} - i \int_{-\infty}^{t} dt' \langle \Psi_{I}^{0} | \delta \hat{H}(t') | \Psi_{0}^{0} \rangle e^{i \Delta_{I} t'}$$
(1.62)

Here we have introduced  $\Delta_I = E_I - E_0$  as the symbol for the excitation energy. Keeping only the first non-zero term in this expression, we arrive at the following equations for the first order coefficients.

$$a_0(t) \approx 1 \tag{1.63}$$

$$a_I(t) = -i \int_{-\infty}^t dt' \langle \Psi_I^0 | \delta \hat{H}(t') | \Psi_0^0 \rangle e^{i\Delta_I t'} \quad \text{for} \quad I \neq 0$$
 (1.64)

Substituting the expression for  $\delta \hat{H}(t)$  from equation (1.55) gives

$$a_{I}(t) = -i \int_{-\infty}^{t} dt' \int d^{3}r \int \frac{d\omega}{2\pi} \,\delta v_{\text{ext}}(\vec{r},\omega) \,\langle \Psi_{I}^{0} | \hat{\rho}(\vec{r}) | \Psi_{0}^{0} \rangle \,\,\mathrm{e}^{\mathrm{i}(\varDelta_{I}-\tilde{\omega})t'} \tag{1.65}$$

$$= -i \int d^3r \int \frac{d\omega}{2\pi} \,\delta v_{\text{ext}}(\vec{r},\omega) \,\langle \Psi_I^0 | \hat{\rho}(\vec{r}) | \Psi_0^0 \rangle \, \left[ \frac{\mathrm{e}^{\mathrm{i}(\Delta_I - \tilde{\omega})t'}}{\mathrm{i}(\Delta_I - \tilde{\omega})} \right]_{-\infty}^t \tag{1.66}$$

$$= -\int d^3r \int \frac{d\omega}{2\pi} \,\delta v_{\text{ext}}(\vec{r},\omega) \,\langle \Psi_I^0 | \hat{\rho}(\vec{r}) | \Psi_0^0 \rangle \,\frac{\mathrm{e}^{\mathrm{i}(\Delta_I - \tilde{\omega})t}}{\Delta_I - \tilde{\omega}} \qquad \text{for} \quad I \neq 0 \,. \tag{1.67}$$

Note that the evaluation of the square brackets at  $-\infty$  yields zero due to the imaginary part  $\eta$  of  $\tilde{\omega}$  that switches on the perturbation adiabatically. Before putting everything together, it is convenient to split off the initial state  $|\Psi_0^0\rangle$  with expansion coefficient  $a_0(t) = 1$  in equation (1.58).

$$|\Psi(t)\rangle = \mathrm{e}^{-\mathrm{i}E_0 t} |\Psi_0^0\rangle + \sum_{I \neq 0} a_I(t) \,\mathrm{e}^{-\mathrm{i}E_I t} |\Psi_I^0\rangle \tag{1.68}$$

Using this wave-function it is easy to express the change in electronic density.

$$\begin{split} \delta\rho(\vec{r},t) &= \langle \Psi(t)|\hat{\rho}(\vec{r})|\Psi(t)\rangle - \langle \Psi_{0}^{0}|\hat{\rho}(\vec{r})|\Psi_{0}^{0}\rangle \tag{1.69} \\ &= \left( \mathrm{e}^{\mathrm{i}E_{0}t} \langle \Psi_{0}^{0}| + \sum_{I\neq0} a_{I}^{*}(t) \,\mathrm{e}^{\mathrm{i}E_{I}t} \,\langle \Psi_{I}^{0}| \right) \hat{\rho}(\vec{r}) \left( \mathrm{e}^{-\mathrm{i}E_{0}t} \,|\Psi_{0}^{0}\rangle + \sum_{I\neq0} a_{I}(t) \,\mathrm{e}^{-\mathrm{i}E_{I}t} \,|\Psi_{I}^{0}\rangle \right) \\ &- \langle \Psi_{0}^{0}|\hat{\rho}(\vec{r})|\Psi_{0}^{0}\rangle \tag{1.70} \end{split}$$

$$= \sum_{I \neq 0} \left[ a_I(t) \,\mathrm{e}^{-\mathrm{i}\Delta_I t} \,\langle \Psi_0^0 | \hat{\rho}(\vec{r}) | \Psi_I^0 \rangle + a_I^*(t) \,\mathrm{e}^{\mathrm{i}\Delta_I t} \,\langle \Psi_I^0 | \hat{\rho}(\vec{r}) | \Psi_0^0 \rangle \right] \tag{1.71}$$

Here, following our approximation to first order, we have neglected the terms that feature a product  $a_I(t)a_J(t)$  with both I and  $J \neq 0$ . Now we substitute the expression (1.67) for the expansion coefficients.

$$\delta\rho(\vec{r},t) = \int \mathrm{d}^{3}r' \int \frac{\mathrm{d}\omega}{2\pi} \sum_{I\neq0} \left[ \delta v_{\mathrm{ext}}(\vec{r}',\omega) \left\langle \Psi_{I}^{0} | \hat{\rho}(\vec{r}') | \Psi_{0}^{0} \right\rangle \frac{\mathrm{e}^{-\mathrm{i}\tilde{\omega}t}}{\tilde{\omega} - \Delta_{I}} \left\langle \Psi_{0}^{0} | \hat{\rho}(\vec{r}) | \Psi_{I}^{0} \right\rangle \right. \\ \left. \delta v_{\mathrm{ext}}^{*}(\vec{r}',\omega) \left\langle \Psi_{0}^{0} | \hat{\rho}(\vec{r}') | \Psi_{I}^{0} \right\rangle \frac{\mathrm{e}^{+\mathrm{i}\tilde{\omega}^{*}t}}{\tilde{\omega}^{*} - \Delta_{I}} \left\langle \Psi_{I}^{0} | \hat{\rho}(\vec{r}) | \Psi_{0}^{0} \right\rangle \right]$$
(1.72)

In the second term we now substitute the integration variable  $\omega$  with  $-\omega$ . With this substitution  $\tilde{\omega}^* = \omega - i\eta$  becomes  $-\omega - i\eta = -\tilde{\omega}$  and the exponential can be pulled out of the parentheses. Furthermore the Fourier transform of a real function is symmetric under complex conjugation, i.e.  $\delta v_{\text{ext}}(\vec{r}', -\omega) = \delta v_{\text{ext}}^*(\vec{r}', \omega)$  and can hence also be moved in front of the square brackets. We are left with

$$\delta\rho(\vec{r},t) = \int \mathrm{d}^{3}r' \int \frac{\mathrm{d}\omega}{2\pi} \,\delta v_{\mathrm{ext}}(\vec{r}',\omega) \,\mathrm{e}^{-\mathrm{i}\tilde{\omega}t} \sum_{I\neq0} \left[ \frac{\langle \Psi_{I}^{0}|\hat{\rho}(\vec{r}')|\Psi_{0}^{0}\rangle \,\langle \Psi_{0}^{0}|\hat{\rho}(\vec{r})|\Psi_{I}^{0}\rangle}{\tilde{\omega} - \Delta_{I}} - \frac{\langle \Psi_{0}^{0}|\hat{\rho}(\vec{r}')|\Psi_{I}^{0}\rangle \,\langle \Psi_{I}^{0}|\hat{\rho}(\vec{r})|\Psi_{0}^{0}\rangle}{\tilde{\omega} + \Delta_{I}} \right].$$
(1.73)

From this it is easy to see that the density response in the frequency domain is given by

$$\delta\rho(\vec{r},\omega) = \int \mathrm{d}^{3}r' \,\delta v_{\mathrm{ext}}(\vec{r}',\omega) \sum_{I\neq0} \left[ \frac{\langle \Psi_{I}^{0} | \hat{\rho}(\vec{r}') | \Psi_{0}^{0} \rangle \, \langle \Psi_{0}^{0} | \hat{\rho}(\vec{r}) | \Psi_{I}^{0} \rangle}{\tilde{\omega} - \Delta_{I}} - \frac{\langle \Psi_{0}^{0} | \hat{\rho}(\vec{r}') | \Psi_{I}^{0} \rangle \, \langle \Psi_{I}^{0} | \hat{\rho}(\vec{r}) | \Psi_{0}^{0} \rangle}{\tilde{\omega} + \Delta_{I}} \right].$$

$$(1.74)$$

Note that the change in electronic density  $\delta\rho(\vec{r})$  induced by a change in the external potential  $\delta v_{\text{ext}}(\vec{r}')$  at  $\vec{r}'$  is exactly the response function  $\chi(\vec{r}, \vec{r}', \omega)$  we were looking for.

$$\chi(\vec{r},\vec{r}',\omega) = \sum_{I\neq0} \left[ \frac{\langle \Psi_I^0 | \hat{\rho}(\vec{r}') | \Psi_0^0 \rangle \langle \Psi_0^0 | \hat{\rho}(\vec{r}) | \Psi_I^0 \rangle}{\tilde{\omega} - \Delta_I} - \frac{\langle \Psi_0^0 | \hat{\rho}(\vec{r}') | \Psi_I^0 \rangle \langle \Psi_I^0 | \hat{\rho}(\vec{r}) | \Psi_0^0 \rangle}{\tilde{\omega} + \Delta_I} \right]$$
(1.75)

This is clearly a very hard quantity to calculate, as we know neither the ground and excited state wavefunctions of the interacting system, nor the excitation energies  $\Delta_I$ . However, if the effective potential  $\delta v_{\text{eff}}$  takes the place of the external potential  $\delta v_{\text{ext}}$ , the entire derivation of the response function is equally valid for the non-interacting Kohn-Sham system. For the non-interacting system we know that the ground state wavefunction  $|\Psi_0^0\rangle$  is the Slater determinant of the occupied Kohn-Sham orbitals  $\phi_i(\vec{r})$ . Furthermore, we can generate excited states by moving electrons from occupied orbitals into unoccupied orbitals. Due to the one-body nature of the density operator  $\hat{\rho}(\vec{r}) =$  $\sum_{i=1}^{N_e} \delta(\vec{r_i} - \vec{r})$ , the terms  $\langle \Psi_I^0 | \hat{\rho}(\vec{r}) | \Psi_0^0 \rangle$  in the denominator are non-zero only for those excitations where just a single electron is transferred from an occupied orbital  $\phi_i$ into a virtual orbital  $\phi_a$ . We refer to this as the single orbital transition  $i \to a$  and generally use indices i, j for occupied and a, b for unoccupied orbitals. For these excitations the excitation energy is easily calculable from the orbital energy difference as  $\Delta_I = \epsilon_a - \epsilon_i$ . The term  $\langle \Psi_I^0 | \hat{\rho}(\vec{r}) | \Psi_0^0 \rangle$  in the denominator becomes  $\phi_a^*(\vec{r}) \phi_i(\vec{r})$ because the Slater determinants of ground and excited state only differ in a single orbital, and the response function of the Kohn-Sham system can then be written as

$$\chi_{\rm KS}(\vec{r},\vec{r}',\omega) = \sum_{i}^{\rm occ.} \sum_{a}^{\rm virt.} \left[ \frac{\phi_a^*(\vec{r}')\phi_i(\vec{r}')\phi_i^*(\vec{r})\phi_a(\vec{r})}{\tilde{\omega} - (\epsilon_a - \epsilon_i)} - \frac{\phi_i^*(\vec{r}')\phi_a(\vec{r}')\phi_a^*(\vec{r})\phi_i(\vec{r})}{\tilde{\omega} + (\epsilon_a - \epsilon_i)} \right].$$
(1.76)

It is important to realize that the due to the missing (explicit) interaction between the Kohn-Sham electrons the density response function of the Kohn-Sham system is naturally limited to single orbital transitions. Unlike wavefunction based methods for the calculation of excited states, where such a restriction might be introduced a-posteriori, linear response TD-DFT can not be systematically improved through the inclusion of doubly or triply excited determinants. In practice this manifests itself in a rather poor performance of linear response TD-DFT for excited states that have double excitation character. The rigorous solution of this problem is to go beyond the adiabatic approximation by using a frequency dependent exchange-correlation kernel  $f_{\rm xc}(\vec{r}, \vec{r}', \omega)$ , see for example references [27, 28].

#### 1.2.4 Derivation of Casida's equation

We are now almost ready to put all the ingredients together, which after vigorous stirring in this section will in the end yield Casida's equation; the workhorse of this entire thesis. The original derivation of the equation can be found in reference [29], but it is reproduced here in a slightly different notation that is more consistent with the rest of the thesis.

So far, in an attempt to keep notation simple, we have completely neglected the electron spin. At this point we actually have to introduce it, since we later want to separate the excitations into those that produce singlet and triplet excited states. Luckily, this is quite easy. Equation (1.52) for the density response generalizes to the following expression for the spin density response, with the additional spin indices  $\sigma$ ,  $\tau$  and  $\iota$ .

$$\delta\rho_{\sigma}(\vec{r},\omega) = \sum_{\tau} \int d^{3}r' \,\chi_{\sigma\tau}^{\rm KS}(\vec{r},\vec{r}',\omega) \bigg[ \delta v_{\rm ext}(\vec{r}',\omega) + \sum_{\iota} \int d^{3}r'' \left(\frac{1}{|\vec{r}'-\vec{r}''|} + f_{\tau\iota}^{\rm xc}(\vec{r}',\vec{r}'')\right) \delta\rho_{\iota}(\vec{r}'',\omega) \bigg]$$
(1.77)

Here the exchange correlation kernel  $f_{\tau\iota}^{\rm xc}(\vec{r},\vec{r}')$  gets additional spin indices, as there is of course no exchange for electrons of opposite spin. We assume the external potential  $\delta v_{\rm ext}(\vec{r}',\omega)$  to be spin independent. The spin dependent generalization of the Kohn-Sham response function  $\chi_{\rm KS}(\vec{r},\vec{r}',\omega)$  from equation (1.76) is given by

$$\chi_{\sigma\tau}^{\rm KS}(\vec{r},\vec{r}',\omega) = \delta_{\sigma\tau} \sum_{i}^{\rm occ.} \sum_{a}^{\rm virt.} \left[ \frac{\phi_{a\sigma}^*(\vec{r}')\phi_{i\sigma}(\vec{r}')\phi_{i\sigma}(\vec{r})\phi_{a\sigma}(\vec{r})}{\tilde{\omega} - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} - \frac{\phi_{i\sigma}^*(\vec{r}')\phi_{a\sigma}(\vec{r}')\phi_{a\sigma}(\vec{r})\phi_{i\sigma}(\vec{r})}{\tilde{\omega} + (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right].$$
(1.78)

These two equations were really the primary result of all the derivations in the last two sections, and having stated them for the general case with spin, we can move on from here.

Based on equation (1.71) we can, in the same spirit, also write the spin density response of the Kohn-Sham system as

$$\delta\rho_{\sigma}(\vec{r},\omega) = \sum_{i}^{\text{occ. virt.}} \left[ P_{ia\sigma}(\omega)\phi_{a\sigma}^{*}(\vec{r})\phi_{i\sigma}(\vec{r}) + P_{ai\sigma}(\omega)\phi_{i\sigma}^{*}(\vec{r})\phi_{a\sigma}(\vec{r}) \right], \qquad (1.79)$$

where we take the density matrix elements  $P_{ia\sigma}(\omega)$  and  $P_{ai\sigma}(\omega)$  as free coefficients for the moment, which we will calculate later. We now substitute (1.79) and (1.78) into (1.77). The result can be written as two equations; one giving the occupied to virtual matrix elements of  $v_{\text{ext}}(\vec{r}', \omega)$  and correspondingly one for the virtual to occupied matrix elements. We are going to omit the details of this step here, as the equations are rather long and unwieldy. In the end we obtain

$$\sum_{jb\tau} \left[ \delta_{\sigma\tau} \delta_{ij} \delta_{ab} \left( \epsilon_{a\sigma} - \epsilon_{i\sigma} + \tilde{\omega} \right) + K_{ia\sigma,jb\tau} \right] P_{jb\tau} + \sum_{jb\tau} K_{ia\sigma,bj\tau} P_{bj\tau} = -\delta V_{ia\sigma}^{\text{ext}} \quad (1.80)$$

$$\sum_{jb\tau} \left[ \delta_{\sigma\tau} \delta_{ij} \delta_{ab} \left( \epsilon_{a\sigma} - \epsilon_{i\sigma} - \tilde{\omega} \right) + K_{ai\sigma,bj\tau} \right] P_{bj\tau} + \sum_{jb\tau} K_{ai\sigma,jb\tau} P_{jb\tau} = -\delta V_{ai\sigma}^{\text{ext}} \quad (1.81)$$

where we have omitted any dependence on  $\omega$  to simplify the notation, and have introduced the following shorthands:

$$\delta V_{ia\sigma}^{\text{ext}} = \int d^3 \vec{r} \, \phi_{i\sigma}^*(\vec{r}) \, \delta v_{\text{ext}}(\vec{r},\omega) \, \phi_{a\sigma}(\vec{r}) \tag{1.82}$$

$$K_{ia\sigma,jb\tau} = K_{ia\sigma,jb\tau}^{\rm H} + K_{ia\sigma,jb\tau}^{\rm xc}$$
(1.83)

$$K_{ia\sigma,jb\tau}^{\rm H} = \int d^3\vec{r} \int d^3\vec{r}' \,\phi_{i\sigma}^*(\vec{r})\phi_{a\sigma}(\vec{r}) \,\frac{1}{|\vec{r} - \vec{r}'|} \,\phi_{b\tau}^*(\vec{r}')\phi_{j\tau}(\vec{r}') \tag{1.84}$$

$$K_{ia\sigma,jb\tau}^{\rm xc} = \int \mathrm{d}^3 \vec{r} \int \mathrm{d}^3 \vec{r}' \,\phi_{i\sigma}^*(\vec{r})\phi_{a\sigma}(\vec{r}) \,f_{\sigma\tau}^{\rm xc}(\vec{r},\vec{r}') \,\phi_{b\tau}^*(\vec{r}')\phi_{j\tau}(\vec{r}') \tag{1.85}$$

In the literature it is common to denote the density matrix elements  $P_{ia\sigma} = X_{ia\sigma}$  and  $P_{ai\sigma} = Y_{ia\sigma}$ , which we are going to follow here. It is furthermore easy to see that  $K_{ia\sigma,jb\tau} = K^*_{ai\sigma,bj\tau}$  and  $\delta V^{\text{ext}}_{ai\sigma} = \delta V^{\text{ext}*}_{ia\sigma}$ . If we now also define

$$A_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} \left( \epsilon_{a\sigma} - \epsilon_{i\sigma} \right) + K_{ia\sigma,jb\tau} \tag{1.86}$$

$$B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau} , \qquad (1.87)$$

and use all this in equation (1.80) and (1.81) we have renamed all matrix elements involving virtual to occupied orbital transitions, i.e. we only have ia/jb index pairs left, but no ai/bj pairs.

$$\sum_{ib\tau} A_{ia\sigma,jb\tau} X_{jb\tau} + \sum_{jb\tau} B_{ia\sigma,jb\tau} Y_{jb\tau} + \tilde{\omega} X_{ia\tau} = -\delta V_{ia\sigma}^{\text{ext}}$$
(1.88)

$$\sum_{jb\tau} A^*_{ia\sigma,jb\tau} Y_{jb\tau} + \sum_{jb\tau} B^*_{ia\sigma,jb\tau} X_{jb\tau} - \tilde{\omega} Y_{ia\tau} = -\delta V^{\text{ext}*}_{ia\sigma}$$
(1.89)

In this sense we can interpret A, B as matrices and  $\vec{X}, \vec{Y}, \delta \vec{V}_{\text{ext}}$  as vectors in the  $2 \times n_{\text{occ}} \times n_{\text{virt}}$  dimensional space of single spin orbital transitions. For the remainder of the derivation it is common and convenient to put the two equations into matrix form.

$$\begin{bmatrix} \begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{bmatrix} - \tilde{\omega} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \vec{X} \\ \vec{Y} \end{bmatrix} = - \begin{pmatrix} \delta \vec{V}_{\text{ext}} \\ \delta \vec{V}_{\text{ext}}^* \end{bmatrix}$$
(1.90)

Looking back at equation (1.75), we see that the response function  $\chi(\vec{r}, \vec{r}', \omega)$  has poles at the excitation energies  $\Delta_I$ , i.e. in the limit  $\eta \to 0^+$  a change  $\delta v_{\text{ext}}(\vec{r}', \omega)$  in the external potential leads to an infinitely large density response  $\delta \rho(\vec{r}, \omega)$ . In the equation above, this would mean that the matrix in the square brackets has a zero eigenvalue for  $\omega = \Delta_I$  and we can write

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{pmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} = \Delta_I \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} .$$
(1.91)

Assuming real molecular orbitals and therefore  $A_{ia\sigma,jb\tau} = A^*_{ia\sigma,jb\tau}$  and  $B_{ia\sigma,jb\tau} = B^*_{ia\sigma,jb\tau}$ , we switch the basis from  $\vec{X}, \vec{Y}$  to  $\vec{X} \pm \vec{Y}$ , which simplifies the equation.

$$\begin{pmatrix} \boldsymbol{A} + \boldsymbol{B} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{A} - \boldsymbol{B} \end{pmatrix} \begin{pmatrix} \vec{X}_I + \vec{Y}_I \\ \vec{X}_I - \vec{Y}_I \end{pmatrix} = \Delta_I \begin{pmatrix} \boldsymbol{0} & -1 \\ -1 & \boldsymbol{0} \end{pmatrix} \begin{pmatrix} \vec{X}_I + \vec{Y}_I \\ \vec{X}_I - \vec{Y}_I \end{pmatrix}$$
(1.92)

Solving the linear system for  $\vec{X} + \vec{Y}$  yields

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\vec{X}_I + \vec{Y}_I) = \Delta_I^2(\vec{X}_I + \vec{Y}_I) .$$
(1.93)

As a side note, it is worth mentioning that this equation also holds in time-dependent Hartree-Fock or when exact exchange is incorporated into the DFT exchange-correlation functional. Unfortunately the matrix  $(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})$  is not symmetric, which is rather inconvenient in practice. Assuming a local functional as we have done throughout this derivation, we can, however, easily fix this: Looking back at equation 1.83 for the coupling matrix elements, it is easy to see that  $K_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}$  (which would not be true with exact exchange) and hence

$$A_{ia\sigma,jb\tau} - B_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} \left( \epsilon_{a\sigma} - \epsilon_{i\sigma} \right) . \tag{1.94}$$

So A-B is a diagonal, positive definite matrix with just the orbital energy differences on the diagonal. Multiplying equation (1.93) from the left with  $(A-B)^{\frac{1}{2}}$  and inserting the identity we obtain

$$\underbrace{(\boldsymbol{A}-\boldsymbol{B})^{\frac{1}{2}}(\boldsymbol{A}+\boldsymbol{B})(\boldsymbol{A}-\boldsymbol{B})^{\frac{1}{2}}}_{\Omega}\underbrace{(\boldsymbol{A}-\boldsymbol{B})^{-\frac{1}{2}}(\vec{X}_{I}+\vec{Y}_{I})}_{\vec{F}_{I}} = \Delta_{I}^{2}\underbrace{(\boldsymbol{A}-\boldsymbol{B})^{-\frac{1}{2}}(\vec{X}_{I}+\vec{Y}_{I})}_{\vec{F}_{I}},$$
(1.95)

which is finally what is usually referred to as Casida's equation:

$$\boldsymbol{\Omega}\vec{F}_I = \Delta_I^2 \vec{F}_I \tag{1.96}$$

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} \Delta_{ia\sigma}^2 + 2\sqrt{\Delta_{ia\sigma}} K_{ia\sigma,jb\tau} \sqrt{\Delta_{jb\sigma}}$$
(1.97)

Here we have abbreviated the orbital energy difference  $\Delta_{ia\sigma} = \epsilon_{a\sigma} - \epsilon_{i\sigma}$ . In summary, we have used linear response up to first order with time-dependent density functional theory to obtain a symmetric eigenvalue problem in the space of single spin orbital transitions, where the eigenvalue is the square of the excitation energy  $\Delta_I$ . Information about the nature of the excited state can be extracted from the eigenvector  $\vec{F_I}$ , but we are going to defer the discussion of this point for a moment to look at the special case of a spin-restricted ground state.

For the common case of a spin-restricted ground state calculation, we can make one more simplification of Casida's equation. Going backwards through our derivation we see that the eigenvector components

$$F_{ia\sigma} = \frac{P_{ia\sigma} + P_{ai\sigma}}{\sqrt{\Delta_{ia\sigma}}} \tag{1.98}$$

are directly related to the density matrix elements  $P_{ia\sigma}$  and  $P_{ai\sigma}$ , and through equation 1.79 with the induced density  $\delta \rho_{\sigma}(\vec{r})$ . Given that  $\rho_{\uparrow}(\vec{r}) = \rho_{\downarrow}(\vec{r})$  holds for a spin-restricted ground state calculation, the goal is now to separate the excitations into those which have a spin independent density response  $(\delta \rho_{\uparrow}(\vec{r}) = \delta \rho_{\downarrow}(\vec{r})$ , singlet excitations) and those that do not (triplet excitations). We can separate singlet and triplet excitations by adding/subtracting the equations for  $F_{ia\uparrow}$  and  $F_{ia\downarrow}$ . For singlet excitations we add them and obtain

$$\sum_{bj\tau} \left( \Omega_{ia\uparrow,jb\tau} + \Omega_{ia\downarrow,jb\tau} \right) F_{jb\tau,I} = \Delta_{S,I}^2 (F_{ia\uparrow,I} + F_{ia\downarrow,I}) .$$
(1.99)

Note that  $\boldsymbol{\Omega}$  satisfies  $\Omega_{ia\sigma,jb\tau} = \Omega_{ia\bar{\sigma},jb\bar{\tau}}$ . This is because for a spin restricted calculation orbitals and orbital energies are spin independent, and the exchange correlation kernel  $f^{\rm xc}$  generally satisfies  $f^{\rm xc}_{\sigma\tau} = f^{\rm xc}_{\bar{\sigma}\bar{\tau}}$ , meaning that  $f^{\rm xc}$  only depends on whether  $\sigma$  and  $\tau$  are parallel or antiparallel. Then the prefactor of  $F_{jb\uparrow}$  and  $F_{jb\downarrow}$  in the sum is just the sum of parallel and antiparallel  $\boldsymbol{\Omega}$  elements for both  $F_{jb\uparrow}$  and  $F_{jb\downarrow}$  and w can write

$$\sum_{bj} \underbrace{(\Omega_{ia\uparrow,jb\uparrow} + \Omega_{ia\downarrow,jb\uparrow})}_{\Omega^{\rm S}_{ia,jb}} \underbrace{\frac{1}{\sqrt{2}} (F_{jb\uparrow,I} + F_{jb\downarrow,I})}_{F^{\rm S}_{jb,I}} = \Delta^2_{S,I} \underbrace{\frac{1}{\sqrt{2}} (F_{ia\uparrow,I} + F_{ia\downarrow,I})}_{F^{\rm S}_{ia,I}}, \quad (1.100)$$

which is Casida's equation for singlet excitations. For triplet excitations we analogously subtract the equations for  $F_{ia\uparrow}$  and  $F_{ia\downarrow}$  and obtain

$$\sum_{bj\tau} \left( \Omega_{ia\uparrow,jb\tau} - \Omega_{ia\downarrow,jb\tau} \right) F_{jb\tau,I} = \Delta_{T,I}^2 (F_{ia\uparrow,I} - F_{ia\downarrow,I})$$
(1.101)

Here the prefactor of  $F_{jb\uparrow}$  and  $F_{jb\downarrow}$  in the sum has a different sign (parallel-antiparallel vs. antiparallel-parallel) and we can write

$$\sum_{bj} \underbrace{\left(\Omega_{ia\uparrow,jb\uparrow} - \Omega_{ia\downarrow,jb\uparrow}\right)}_{\Omega_{ia,jb}^{T}} \underbrace{\frac{1}{\sqrt{2}} (F_{jb\uparrow,I} - F_{jb\downarrow,I})}_{F_{jb,I}^{T}} = \Delta_{T,I}^{2} \underbrace{\frac{1}{\sqrt{2}} (F_{ia\uparrow,I} - F_{ia\downarrow,I})}_{F_{ia,I}^{T}} \quad (1.102)$$

In summary, for spin-restricted calculations, we were able to derive two separate eigenvalue problems for singlet and and triplet excitations respectively.

$$\boldsymbol{\Omega}_{S/T} \vec{F}_I^{S/T} = \Delta_{S/T,I}^2 \vec{F}_I^{S/T}$$
(1.103)

$$\Omega_{ia,jb}^{\rm S} = \delta_{ij} \delta_{ab} \left(\epsilon_a - \epsilon_i\right)^2 + 2\sqrt{\epsilon_a - \epsilon_i} \left(2K_{ia,jb}^{\rm H} + K_{ia\uparrow,jb\uparrow}^{\rm xc} + K_{ia\uparrow,jb\downarrow}^{\rm xc}\right) \sqrt{\epsilon_b - \epsilon_j}$$
(1.104)

$$\Omega_{ia,jb}^{\mathrm{T}} = \delta_{ij}\delta_{ab} \left(\epsilon_a - \epsilon_i\right)^2 + 2\sqrt{\epsilon_a - \epsilon_i} \left(K_{ia\uparrow,jb\uparrow}^{\mathrm{xc}} - K_{ia\uparrow,jb\downarrow}^{\mathrm{xc}}\right) \sqrt{\epsilon_b - \epsilon_j}$$
(1.105)

Note that in contrast to equation (1.103) these two eigenvalue problems are in the  $n_{\rm occ} \times n_{\rm virt}$  dimensional space of single orbital transitions, which is only half the size of the space of single spin orbital transitions. Nevertheless, solving these equations is still a computationally formidable task and due to the huge number of single orbital transitions the eigenvalue problem is usually only solvable with iterative eigensolvers. We will discuss the practical details of how to actually solve Casida's equation, as well as methods to reduce the size of the single orbital transition space, in chapter 2.

Once Casida's equation has been solved we can use the elements of the eigenvector  $\vec{F}$  to construct an approximate excited state wavefunction as a linear combination of singly excited Slater determinants.

$$|\Psi_I\rangle = \sum_{ia\sigma} \sqrt{\frac{2\Delta_{ia\sigma}}{\Delta_I}} F_{ia\sigma,I} \,\hat{c}^{\dagger}_{a\sigma} \hat{c}_{i\sigma} \,|\Psi_0\rangle \tag{1.106}$$

Here  $|\Psi_0\rangle$  is the Slater determinant of the occupied Kohn-Sham orbitals and  $\hat{c}^{\dagger}$  and  $\hat{c}$  are the creation and annihilation operators in the molecular spin orbital basis. It is

important to realize that this is not the true excited state; not even in a perfect world where the exact exchange-correlation functional is known. The real excited state would also have contributions from determinants with more than one excited electron, which are not included here. Nevertheless, Casida's assignment ansatz is what people use in practice when they need an approximate excited state wavefunction from a TD-DFT calculation.

Casida also showed that for singlet excitations the oscillator strength  $f_I$ , which determines the probability of an excitation happening through the absorption of light, is given by

$$f_{I} = \frac{2}{3} \Delta_{I} \left| \underbrace{\sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_{I}}} F_{ia,I}^{S} \overleftarrow{\phi_{i}|\vec{r}|\phi_{a}\rangle}}_{\vec{d}_{I}} \right|^{2}.$$
(1.107)

Here  $\vec{d}_{ia}$  is the transition dipole moment of the single orbital transition  $i \to a$ . Their linear combination determines the transition dipole moment  $\vec{d}_I$  of the excitation, from which the oscillator strength is then calculated in the canonical way. It is interesting to note, that even though this equation looks suspiciously like it was based on Casida's approximate assignment ansatz, it is in fact an exact identity. The proof of this statement can be found in reference [29].

## 1.3 Density functional based tight-binding

While density functional theory is already considered computationally fairly efficient and is nowadays used for applications involving hundreds of atoms, there will always be systems too large to be treated with any given method. It is therefore important to have a hierarchy of methods of varying computational complexity and accuracy. Starting from DFT and moving in the direction of less accurate but computationally simpler methods, one immediately comes across density functional based tight-binding, short DFTB. This method is closely related to Kohn-Sham DFT and builds on top of it in many ways, but making certain approximations that in practice make it two to three orders of magnitude faster. The topic of this thesis is the development and evaluation of these DFTB-like approximations in the context of excited state calculations, so it is only natural to quickly review the DFTB method [30–32] here.

The derivation in this section mostly follows the excellent review by Oliveira et al. [33]. A detailed derivation can also be found in the original article on SCC-DFTB by Elstner et al. [31].

We start from the total energy in the Kohn-Sham DFT method.

$$E[\rho] = \sum_{i=1}^{N_e} \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \frac{1}{2} \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \left| \phi_i \right\rangle + E_{\text{xc}}[\rho]$$
(1.108)

It may seem a bit strange that we have written the energy in the external potential and the Hartree term in this form. After all, they are both multiplicative operators and we could have written them out with another integral over just the electronic density, instead of using the Kohn-Sham orbitals explicitly. It will later become clear why we choose to write them in this way for now.

We now decompose the total density  $\rho$  into a reference density  $\rho_0$ , which in practice is the superposition of atomic densities, and a hopefully small density difference  $\delta\rho$ modeling the charge transfer in the system.

$$\rho(\vec{r}) = \rho_0(\vec{r}) + \delta\rho(\vec{r}) \tag{1.109}$$

Let us see what happens if we substitute this into the total energy above. We can separate the Hartree term into three parts, only the first of which contains the full density  $\rho$ , which we again write implicitly using the orbitals.

$$\sum_{i=1}^{N_e} \left\langle \phi_i \left| \frac{1}{2} \int \mathrm{d}^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \right| \phi_i \right\rangle \tag{1.110}$$

$$= \frac{1}{2} \int d^3r \int d^3r' \frac{\left[\rho_0(\vec{r}) + \delta\rho(\vec{r})\right] \left[\rho_0(\vec{r}') + \delta\rho(\vec{r}')\right]}{|\vec{r} - \vec{r}'|}$$
(1.111)

$$= \int d^3r \int d^3r' \frac{\rho_0(\vec{r}')\rho(\vec{r}) - \frac{1}{2}\rho_0(\vec{r}')\rho_0(\vec{r}) + \frac{1}{2}\delta\rho(\vec{r})\delta\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$
(1.112)

$$= \sum_{i=1}^{N_e} \left\langle \phi_i \left| \int d^3 r' \frac{\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} \right| \phi_i \right\rangle - \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho_0(\vec{r})\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{1}{2} \int d^3 r \int d^3 r' \frac{\delta \rho(\vec{r})\delta \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \right|$$
(1.113)

Here we have used the fact that both  $\vec{r}$  and  $\vec{r'}$  are integration variables and can hence be swapped in step (1.112). Note that the last two terms depend only on the reference density  $\rho_0$  and the density difference  $\delta\rho$  respectively. The exchange-correlation part is a bit more tricky and we start by writing down the simple identity

$$E_{\rm xc}[\rho_0 + \delta\rho] = \int d^3r \, v_{\rm xc}[\rho_0](\vec{r}) \, \rho(\vec{r}) - \int d^3r \, v_{\rm xc}[\rho_0](\vec{r}) \left(\rho_0(\vec{r}) + \delta\rho(\vec{r})\right) + E_{\rm xc}[\rho_0 + \delta\rho] \,.$$
(1.114)

Now we expand the exchange-correlation functional up to second order in a Taylorseries around  $\rho_0$ .

$$E_{\rm xc}[\rho_0 + \delta\rho] = E_{\rm xc}[\rho_0] + \int d^3r \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\vec{r})} \Big|_{\rho_0} \delta\rho(\vec{r})$$

$$+ \frac{1}{2} \int d^3r \int d^3r' \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \Big|_{\rho_0} \delta\rho(\vec{r})\delta\rho(\vec{r}') + \mathcal{O}\left(\delta\rho^3\right)$$
(1.115)

Plugging this back into (1.114) and using the definition of the exchange-correlation potential we obtain

$$E_{\rm xc}[\rho_0 + \delta\rho] \approx \sum_{i=1}^{N_e} \langle \phi_i | v_{\rm xc}[\rho_0](\vec{r}) | \phi_i \rangle - \int d^3r \, v_{\rm xc}[\rho_0](\vec{r}) \, \rho_0(\vec{r}) + E_{\rm xc}[\rho_0] + \frac{1}{2} \int d^3r \int d^3r' \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \Big|_{\rho_0} \delta\rho(\vec{r})\delta\rho(\vec{r}') \,.$$
(1.116)

Here we have again written the density  $\rho$  in the first term of (1.114) implicitly using the orbitals. Plugging equations (1.113) and (1.116) back into (1.108) yields

$$E[\rho] = \sum_{i=1}^{N_e} \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \int d^3 r' \frac{\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{\text{xc}}[\rho_0](\vec{r}) \left| \phi_i \right\rangle \right. \\ \left. - \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho_0(\vec{r})\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} - \int d^3 r \, v_{\text{xc}}[\rho_0](\vec{r}) \, \rho_0(\vec{r}) + E_{\text{xc}}[\rho_0] \right.$$
(1.117)  
$$\left. + \frac{1}{2} \int d^3 r \int d^3 r' \, \delta\rho(\vec{r})\delta\rho(\vec{r}') \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \right|_{\rho_0} \right) \\ = E_{\text{orb}}[\rho_0] + E_{\text{rep}}[\rho_0] + E_{\text{SCC}}[\rho_0, \delta\rho] .$$
(1.118)

Let us analyze the equation above in some more detail. The first line is usually called the electronic energy (or orbital contribution) and is just the expectation value of the Hamiltonian

$$\hat{H}_{0} = -\frac{1}{2}\nabla^{2} + \underbrace{v_{\text{ext}}(\vec{r}) + \int \mathrm{d}^{3}r' \frac{\rho_{0}(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{\text{xc}}[\rho_{0}](\vec{r})}_{v_{\text{eff}}[\rho_{0}](\vec{r})}, \qquad (1.119)$$

which only depends on the reference density  $\rho_0$ , and is hence usually called the chargeindependent Hamiltonian. Comparison with equation 1.20 actually reveals that the potential in the Hamiltonian is just the Kohn-Sham effective potential for the reference density  $\rho_0$ . The second line of equation (1.117), called the repulsive energy, collects various terms, all of which also only depend on the reference density  $\rho_0$ . The last term named the self consistent charge (SCC) energy is the only one involving the density difference  $\delta\rho$  and has two components: The Hartree-like Coulomb interaction within the difference density and a term involving the second derivative of the exchangecorrelation energy. Equation (1.117) itself is not yet practically useful, but it is a great basis for approximations.

We now choose the superposition of the atomic densities  $\rho_{\mathcal{A}}^0$  as our reference density  $\rho_0$ , and then approximate the density difference as a sum of spherically symmetric functions  $\xi_{\mathcal{A}}(\vec{r})$  centered on the individual nuclei.

$$\rho_0(\vec{r}) = \sum_{\mathcal{A}}^{N_{\text{atom}}} \rho_{\mathcal{A}}^0(\vec{r}) \quad \text{and} \quad \delta\rho(\vec{r}) \approx \sum_{\mathcal{A}}^{N_{\text{atom}}} \Delta q_{\mathcal{A}} \xi_{\mathcal{A}}(\vec{r}) \quad (1.120)$$

Here the functions  $\xi_A(\vec{r})$  are normalized, so that the total charge of atom  $\mathcal{A}$  is given by  $\Delta q_{\mathcal{A}}$ . Furthermore we expand the molecular orbitals  $\phi_i(\vec{r})$  in a typically minimal basis of atomic valence orbitals  $\chi_{\mu}$ .

$$\phi_i(\vec{r}) = \sum_{\mathcal{A}}^{N_{\text{atom}}} \sum_{\mu \in \mathcal{A}} c_{\mu i} \chi_\mu(\vec{r}) . \qquad (1.121)$$

Once we have a basis like this we can calculate the charge  $\Delta q_A$  of atom A from Mulliken population analysis [34], which due to the minimal basis should be reasonably accurate

and artifact free.

$$\Delta q_{\mathcal{A}} = q_{\mathcal{A}} - q_{\mathcal{A}}^{\text{free atom}} \qquad \text{with} \qquad q_{\mathcal{A}} = \frac{1}{2} \sum_{i}^{N_{\text{occ}}} \sum_{\mu \in \mathcal{A}} \sum_{\nu}^{N_{\text{bas}}} \left( c_{\mu i} S_{\mu \nu} c_{\nu i} + c_{\nu i} S_{\nu \mu} c_{\mu i} \right)$$
(1.122)

We now make the most important approximation in the DFTB method: In the basis introduced above, we calculate the matrix elements of  $\hat{H}^0$  as

$$H^{0}_{\mu\nu} = \left\langle \chi_{\mu} \left| \hat{H}^{0} \right| \chi_{\nu} \right\rangle = \begin{cases} \varepsilon^{\text{free atom}}_{\mu} & \text{for } \mu = \nu \\ \left\langle \chi_{\mu} \left| -\frac{1}{2} \nabla^{2} + v^{\mathcal{AB}}_{\text{eff}} [\rho^{0}_{\mathcal{A}} + \rho^{0}_{\mathcal{B}}](\vec{r}) \right| \chi_{\nu} \right\rangle \\ & \text{for } \mu \in \mathcal{A}, \ \nu \in \mathcal{B}, \ \mathcal{A} \neq \mathcal{B} \\ 0 & \text{otherwise} \end{cases}$$
(1.123)

where  $\varepsilon_{\mu}^{\rm free \ atom}$  is the energy of the corresponding atomic orbital. The effective potential

$$v_{\text{eff}}^{\mathcal{AB}}[\rho_{\mathcal{A}}^{0} + \rho_{\mathcal{B}}^{0}](\vec{r}) = -\frac{Z_{\mathcal{A}}}{|\vec{r} - \vec{R}_{\mathcal{A}}|} - \frac{Z_{\mathcal{B}}}{|\vec{r} - \vec{R}_{\mathcal{B}}|} + \int d^{3}r' \frac{\rho_{\mathcal{A}}^{0}(\vec{r}') + \rho_{\mathcal{B}}^{0}(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{\text{xc}}[\rho_{\mathcal{A}}^{0} + \rho_{\mathcal{B}}^{0}](\vec{r})$$
(1.124)

is just the normal Kohn-Sham effective potential but only including contributions from the atoms A and B. Essentially, for the calculation of the matrix elements, we neglect everything but the two atoms A and B on which the basis functions  $\chi_{\mu}$  and  $\chi_{\nu}$ are centered. The advantage of this is, that the system is essentially decomposed into a set of dimers for which all matrix elements can be precalculated and stored on disk using the Slater-Koster technique [35]. The overlap matrix is precalculated and stored in the same way. Details on this process can be found in the literature [32, 36].

Consistent with the approximations we have made for the matrix elements, we substitute equations (1.120) also into the expression for the SCC energy. We obtain

$$E_{\rm SCC} = \frac{1}{2} \sum_{\mathcal{AB}}^{N_{\rm atom}} \Delta q_{\mathcal{A}} \gamma_{\mathcal{AB}} \Delta q_{\mathcal{B}}$$
(1.125)

with

$$\gamma_{\mathcal{AB}} = \int \mathrm{d}^3 \vec{r} \int \mathrm{d}^3 \vec{r}' \,\xi_{\mathcal{A}}(\vec{r}) \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \bigg|_{\rho^0_{\mathcal{A}} + \rho^0_{\mathcal{B}}} \right) \xi_{\mathcal{B}}(\vec{r}') \,. \tag{1.126}$$

The equation for  $\gamma_{\mathcal{AB}}$  is still a bit too complicated to be used in practice. It is normally approximated based on its limits for large and small internuclear distances  $R_{\mathcal{AB}}$ : The second derivative of the exchange-correlation functional is short ranged, meaning that it approaches zero quickly as  $|\vec{r} - \vec{r'}|$  increases, so that we can write

$$\lim_{R_{\mathcal{AB}}\to\infty}\gamma_{\mathcal{AB}} = \frac{1}{R_{\mathcal{AB}}}.$$
(1.127)

The other limiting case occurs for the on-site element  $\gamma_{\mathcal{A}\mathcal{A}}$ , where both functions  $\xi_{\mathcal{A}/\mathcal{B}}(\vec{r})$  are actually centered on the same atom. In this case we are really just adding fractional

charge to an atom. The energy change associated with this is (for a single atom) related to the atom's Hubbard parameter  $U_{\mathcal{A}}$  or equivalently its chemical hardness  $\eta_{\mathcal{A}}$ , which in DFT is calculated as the second derivative of the atoms total energy with respect to the number of electrons [37].

$$U_{\mathcal{A}} = 2\eta_{\mathcal{A}} = \frac{\partial^2 E_{\text{atom}}}{\partial N_e^2} \ . \tag{1.128}$$

Looking at the SCC energy of a single atom, we can therefore conclude that the on-site element  $\gamma_{\mathcal{A}\mathcal{A}}$  is simply the Hubbard parameter  $U_{\mathcal{A}}$ .

$$\frac{1}{2}\Delta q_{\mathcal{A}}^2 \gamma_{\mathcal{A}\mathcal{A}} = \frac{1}{2}\Delta q_{\mathcal{A}}^2 U_{\mathcal{A}} \implies \gamma_{\mathcal{A}\mathcal{A}} = U_{\mathcal{A}}$$
(1.129)

The Hubbard parameters of all elements are easily calculable from DFT and can also be found tabulated in the literature [38]. A more rigorous discussion of this point can be found in reference [32], which also gives a physically motivated and yet practical interpolation formula

$$\gamma_{\mathcal{A}\mathcal{B}} \approx \gamma_{\mathcal{A}\mathcal{B}}(R_{\mathcal{A}\mathcal{B}}, U_{\mathcal{A}}, U_{\mathcal{B}}) , \qquad (1.130)$$

that depends only on the Hubbard parameters of the involved atoms and the internuclear distance, and connects to two limits discussed above.

The last remaining part of the total energy is the repulsive potential. While recently there have been attempts at calculating the repulsive potential directly from the second line second line of equation 1.117 (see reference [39]), it is more commonly approximated as a pairwise potential  $U_{AB}^{\text{rep}}(R_{AB})$  that is fitted to be the difference between the DFT energy and the sum of the DFTB orbital and SCC energy. This is calculated and tabulated for all the dimers and internuclear distances, so that for these systems DFTB would reproduce the DFT energies exactly.

In summary, with all the approximations we have made, the total energy within the SCC-DFTB method is given by

$$E_{\rm DFTB} = \sum_{i}^{N_e} \langle \phi_i | \hat{H}_0 | \phi_i \rangle + \frac{1}{2} \sum_{\mathcal{AB}}^{N_{\rm atom}} \Delta q_{\mathcal{A}} \gamma_{\mathcal{AB}}(R_{\mathcal{AB}}, U_{\mathcal{A}}, U_{\mathcal{B}}) \Delta q_{\mathcal{B}} + \frac{1}{2} \sum_{\mathcal{AB}}^{N_{\rm atom}} U_{\mathcal{AB}}^{\rm rep}(R_{\mathcal{AB}}) .$$
(1.131)

Applying the variational principle to the energy one obtains the Kohn-Sham equations of DFTB, written in the basis defined above as

$$\sum_{\nu} H_{\mu\nu} c_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i} . \qquad (1.132)$$

Here the full Hamiltonian

$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu} \sum_{\mathcal{C}} \left( \gamma_{\mathcal{AC}} + \gamma_{\mathcal{BC}} \right) \Delta q_{\mathcal{C}} \quad \text{with} \quad \mu \in \mathcal{A}, \nu \in \mathcal{B} .$$
(1.133)

depends on the charges, which through equation 1.122 themselves depend on the orbitals we are trying to obtain. So just like the Kohn-Sham equations of DFT, these equations are in practice solved iteratively until self-consistency is reached.

The method outlined above is known as self-consistent charge (SCC-)DFTB or DFTB2, as we included terms up to second order in  $\delta\rho$  in equation 1.117. If one

neglects all quadratic terms, one obtains the DFTB1 method, which in the absence of the SCC term does not have a self-consistency cycle and is therefore computationally much more efficient, though less accurate. On the other hand, the expansion can also be done up to third order, resulting in the DFTB3 method [40], a more accurate and computationally only slightly more expensive method. This thesis mostly deals with SCC-DFTB though, as the linear response formalism based on time-dependent DFTB developed by Niehaus et al. [41] builds on top of SCC-DFTB. So for this thesis, the topic of which are DFTB-like approximations in linear-response time-dependent density functional theory, SCC-DFTB is the natural choice.

## 2 Intensity selection

## 2.1 Introduction

Density functional theory (DFT) based on the Hohenberg-Kohn theorem [5] and implemented in terms of the Kohn-Sham equations [7] is one of the most popular methods in both solid-state physics and quantum chemistry. The reason for this popularity is that DFT is computationally relatively affordable and its accuracy for many systems not far behind more accurate but also much more expensive wavefunction based methods. For systems which are too large to be treated with DFT one can introduce further approximations on top of the DFT framework, most notably density functional based tight binding (DFTB) [30, 31]. In DFTB, tight-binding approximations are made to the DFT total energy expression, most importantly an optimized minimum valence orbital basis that reduces the linear algebra operations, and a two center-approximation that allows to precalculate and store all integrals using the Slater-Koster technique [35]. The self-consistent charge (SCC) technique [32] accounts for density fluctuations and improves results on polar bonds. Detailed information on the DFTB parameterization for all elements have been published recently [36].

As the underlying Hohenberg-Kohn theorem is only a statement about the ground state, standard DFT can not be applied to the broad class of problems involving excited states, most notably the study of optical properties of an electronic system. The extension of DFT to excited states has been accomplished in the form of time-dependent density functional theory (TD-DFT) based on the Runge-Gross theorem [23], which is a time-dependent analogon to the Hohenberg-Kohn theorem. In quantum chemistry TD-DFT is in practice often used in the form of Casida's formalism [29], where the electron density's linear response to a perturbation in the external potential is used to construct an eigenvalue equation in the space of single orbital transitions from which the excitation energies and excited states can be extracted. TD-DFT calculations of excited states are much more expensive than their ground state counterpart, and therefore limited in the size of the systems that can be treated. At the expense of accuracy the computational cost of TD-DFT calculations can be reduced by making further approximations, most notably the Tamm-Dancoff approximation [42] (TDA) and related techniques [43–45]. It is interesting to note that TDA results can even be better than unapproximated TD-DFT results [46] even though TDA violates the Thomas-Reiche-Kuhn f-sum rule [47–49]. Another way to reduce the computational effort is to translate Casida's formalism to the DFTB framework. This was done by Niehaus et al. and is known as time-dependent density functional based tight binding (TD-DFTB) [41]. Note that there is an alternative formulation of TD-DFTB which has recently been developed by Trani et al. [50].

At the heart of both TD-DFT and TD-DFTB is the solution of Casida's eigenvalue equation in the space of single orbital transitions. As the number of transitions grows quadratically with the size of the system, the resulting matrix can only be diagonalized using iterative eigensolvers, and even then the huge size of the matrix quickly becomes the limiting factor. This is especially true for TD-DFTB where the calculation of the matrix elements is rather cheap, so that bigger systems with relatively larger matrices can be investigated.

In this chapter we discuss practical methods to deal with the increasing dimension of the eigenvalue problem encountered in TD-DFTB calculations for large molecules. The remainder of the chapter is organized as follows. In section 2.2 we recapitulate the basic equations of ground state SCC-DFTB and review how adapting Casida's TD-DFT approach to the DFTB framework results in the TD-DFTB method. In section 2.3 we analyze the bottlenecks of the method and show how the TD-DFTB equations can be implemented efficiently. For the specific application of calculating electronic absorption spectra we present ways to reduce the size of the eigenvalue problem through a physically motivated truncation of the single orbital transition space. In section 2.4 we use this truncation to calculate the absorption spectra of a number of example molecules ranging from small model systems to entire proteins in order to validate the precision of the results as well as the computational performance of the method. Section 2.5 summarizes our results.

### 2.2 Review of the methods

#### 2.2.1 DFTB

Let us quickly recapitulate the most important equations of SCC-DFTB [32]. More comprehensive reviews can be found in reference [33] and [51]. The total energy within the SCC-DFTB method is given by

N

$$E_{\rm SCC-DFTB} = E_{\rm orb} + E_{\rm SCC} + E_{\rm rep}$$
(2.1)

$$E_{\rm orb} = \sum_{i}^{N_{\rm occ}} \langle \phi_i | \hat{H}^0 | \phi_i \rangle \tag{2.2}$$

$$E_{\rm SCC} = \frac{1}{2} \sum_{\mathcal{AB}}^{N_{\rm atom}} \Delta q_{\mathcal{A}} \gamma_{\mathcal{AB}} \Delta q_{\mathcal{B}}$$
(2.3)

$$E_{\rm rep} = \frac{1}{2} \sum_{\mathcal{AB}}^{N_{\rm atom}} U_{\mathcal{AB}} , \qquad (2.4)$$

where the individual terms are called the orbital contribution  $E_{\rm orb}$ , the self-consistent charge correction  $E_{\rm SCC}$ , and the repulsive energy  $E_{\rm rep}$ .

DFTB uses a (typically minimal) basis of atomic valence orbitals  $\chi_{\mu}(\vec{r})$  to expand the molecular orbitals  $\phi_i(\vec{r})$  as

$$\phi_i(\vec{r}) = \sum_{\mathcal{A}}^{N_{\text{atom}}} \sum_{\mu \in \mathcal{A}} c_{\mu i} \chi_\mu(\vec{r}) . \qquad (2.5)$$
In this basis the matrix elements of  $\hat{H}^0$  are calculated as

$$\langle \chi_{\mu} | \hat{H}^{0} | \chi_{\nu} \rangle = \begin{cases} \varepsilon_{\mu}^{\text{free atom}} & \text{for } \mu = \nu \\ \left\langle \chi_{\mu} \left| \hat{T} + \hat{V}_{\mathcal{A}\mathcal{B}}^{0} \right| \chi_{\nu} \right\rangle \\ \text{for } \mu \in \mathcal{A}, \ \nu \in \mathcal{B}, \ \mathcal{A} \neq \mathcal{B} \\ 0 \quad \text{otherwise} \end{cases}$$
(2.6)

where  $\varepsilon_{\mu}^{\text{free atom}}$  is the energy of the corresponding atomic orbital of the free atom and  $\hat{V}_{\mathcal{AB}}^{0}$  is a strictly pairwise effective potential, usually implemented in terms of the Kohn-Sham potential and the atomic electron densities  $\rho_{\mathcal{A}}^{0}$  and  $\rho_{\mathcal{B}}^{0}$ . Note that the matrix elements of  $\hat{H}^{0}$  only depend on the elements of atom  $\mathcal{A}$  and  $\mathcal{B}$  and the distance  $R_{\mathcal{AB}} = \left| \vec{R}_{\mathcal{A}} - \vec{R}_{\mathcal{B}} \right|$  between the two nuclei. It is therefore possible to precalculate them by running DFT calculations for all individual atoms as well as all possible dimers at a sufficient number of internuclear distances  $R_{\mathcal{AB}}$ . Details on this parametrization can be found in the literature [32, 36].

The self-consistent charge contribution  $E_{SCC}$  accounts for the fact that the actual ground state density

$$\rho^{\rm GS}(\vec{r}) = \rho^0(\vec{r}) + \delta\rho(\vec{r}) \quad \text{with} \quad \rho^0(\vec{r}) = \sum_{\mathcal{A}} \rho^0_{\mathcal{A}}(\vec{r}) \tag{2.7}$$

differs from the sum of the atomic densities by a density fluctuation  $\delta \rho(\vec{r})$ . Within SCC-DFTB this density fluctuation is then decomposed into atomic contributions  $\delta \rho_{\mathcal{A}}(\vec{r})$  which are subjected to a multipole expansion and a monopolar approximation.

$$\delta\rho(\vec{r}) = \sum_{\mathcal{A}} \delta\rho_{\mathcal{A}}(\vec{r}) \approx \sum_{\mathcal{A}} \Delta q_{\mathcal{A}} \xi_{\mathcal{A}}(\vec{r})$$
(2.8)

Here  $\xi_{\mathcal{A}}(\vec{r})$  is a spherically symmetric function centered on atom  $\mathcal{A}$  and the transferred charges  $\Delta q_{\mathcal{A}}$  are calculated from the expansion coefficients and the overlap matrix  $S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$  through Mulliken population analysis.

$$\Delta q_{\mathcal{A}} = q_{\mathcal{A}} - q_{\mathcal{A}}^{\text{free atom}} \quad \text{with}$$

$$q_{\mathcal{A}} = \frac{1}{2} \sum_{i}^{N_{\text{occ}}} \sum_{\mu \in \mathcal{A}} \sum_{\nu} \left( c_{\mu i} S_{\mu \nu} c_{\nu i} + c_{\nu i} S_{\nu \mu} c_{\mu i} \right)$$
(2.9)

The elements of the matrix  $\gamma$  in equation (2.1) can now be calculated with any exchange-correlation functional  $E_{\rm xc}[\rho]$  through

$$\gamma_{\mathcal{AB}} = \int \mathrm{d}^3 \vec{r} \int \mathrm{d}^3 \vec{r}' \,\xi_{\mathcal{A}}(\vec{r}) \,f_{\mathrm{Hxc}}[\rho^0](\vec{r},\vec{r}') \,\xi_{\mathcal{B}}(\vec{r}') \tag{2.10}$$

with

$$f_{\rm Hxc}[\rho^0](\vec{r},\vec{r}') = \frac{1}{|\vec{r}-\vec{r}'|} + \frac{\delta^2 E_{\rm xc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\Big|_{\rho^0} \,.$$
(2.11)

Note that  $\gamma_{\mathcal{AB}}$  only depends on the type of atom  $\mathcal{A}$  and  $\mathcal{B}$  as well as the distance  $R_{\mathcal{AB}}$ between their nuclei. Due to the locality of the exchange-correlation functional, the SCC contribution reduces in the limit of large  $R_{\mathcal{AB}}$  to just the Coulomb interaction between two point charges at  $\vec{R}_{\mathcal{A}}$  and  $\vec{R}_{\mathcal{B}}$ . The on-site term  $\gamma_{\mathcal{AA}}$  can be approximated by the atom's Hubbard parameter

$$U_{\mathcal{A}} \approx 2\eta_{\mathcal{A}} \approx I_{\mathcal{A}} - A_{\mathcal{A}} , \qquad (2.12)$$

where  $I_{\mathcal{A}}$  is the atomic ionization potential,  $A_{\mathcal{A}}$  the electron affinity, and  $\eta_{\mathcal{A}}$  the chemical hardness which can be calculated by DFT as the second derivative of the energy with respect to the occupation number of the highest occupied atomic orbital. An interpolation formula is then used to calculate  $\gamma_{\mathcal{AB}}$  for intermediate distances  $R_{\mathcal{AB}}$  [32].

While the repulsive term  $E_{\rm rep}$  can also be parametrized from DFT calculations [32], it is for fixed nuclear positions only a global shift in energy that does not influence the absorption spectrum and is hence irrelevant in the context of this chapter.

Finally the molecular orbitals  $\phi_i(\vec{r})$  from equation (2.5) can be obtained by solving the Kohn-Sham equation of SCC-DFTB.

$$\sum_{\nu} H_{\mu\nu} c_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i}$$
(2.13)

$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu} \sum_{\mathcal{C}} \left( \gamma_{\mathcal{AC}} + \gamma_{\mathcal{BC}} \right) \Delta q_{\mathcal{C}} \quad \text{with} \quad \mu \in \mathcal{A}, \nu \in \mathcal{B}$$
(2.14)

Note that this has to be done self-consistently as the  $\Delta q_{\mathcal{C}}$  depend on the expansion coefficients via equation (2.9).

#### 2.2.2 TD-DFT(B)

One of the most popular ways to apply time-dependent density functional theory (TD-DFT) in the field of quantum chemistry is without doubt Casida's formalism [29]. Starting from the electron density's linear response to a small perturbation in the external potential, Casida casts the problem of calculating excitation energies and excited states into an eigenvalue equation in the  $N_{\text{trans}} = N_{\text{occ}}N_{\text{virt}}$  dimensional space of single orbital transitions  $\hat{c}_a^{\dagger}c_i |\Psi_0\rangle$ , where  $|\Psi_0\rangle$  is the Slater determinant of the occupied Kohn-Sham orbitals. The eigenvalue problem can be written as

$$\boldsymbol{\Omega}\vec{F}_I = \Delta_I^2 \vec{F}_I \,, \qquad (2.15)$$

where  $\Delta_I$  is the excitation energy. The elements of the matrix  $\boldsymbol{\Omega}$  are given by

$$\Omega_{ia,jb} = \delta_{ij}\delta_{ab}\Delta_{ia}^2 + 4\sqrt{\Delta_{ia}\Delta_{jb}}K_{ia,jb} , \qquad (2.16)$$

where we have abbreviated  $\Delta_{ia} = \varepsilon_a - \varepsilon_i$ . We adopt the usual convention of using the indices i, j for occupied and a, b for virtual orbitals. The form of the so-called coupling matrix K depends on the multiplicity of the excited state. Neglecting spin-orbit coupling, only the singlet excitations are relevant for the calculation of the absorption spectrum. We therefore restrict our discussion to the singlet case, for which the

coupling matrix is given by

$$K_{ia,jb} = \int d^3 \vec{r} \int d^3 \vec{r}' \phi_i(\vec{r}) \phi_a(\vec{r}) f_{\text{Hxc}}[\rho^{\text{GS}}](\vec{r},\vec{r}') \phi_j(\vec{r}') \phi_b(\vec{r}') . \qquad (2.17)$$

Once the eigenvalue equation (2.15) has been solved, information about the excited state can be extracted from the eigenvectors  $\vec{F_I}$ . Following Casida, we use the components of the eigenvector  $\vec{F_I}$  to expand the excited state  $|\Psi_I\rangle$  in single orbital excitations relative to the Kohn-Sham Slater determinant  $|\Psi_0\rangle$ .

$$|\Psi_I\rangle = \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_I}} F_{ia,I} \, \hat{c}_a^{\dagger} \hat{c}_i \, |\Psi_0\rangle \tag{2.18}$$

While the resulting  $|\Psi_I\rangle$  should only be viewed as approximation to the true excited state, the transition dipole moment  $\vec{d}_I$  of the excitation can be calculated as a linear combination of the transition dipole moments  $\vec{d}_{ia}$  of these single orbital transitions.

$$\vec{d}_I = \langle \Psi_0 | \vec{r} | \Psi_I \rangle = \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_I}} F_{ia,I} \, \vec{d}_{ia} \tag{2.19}$$

with 
$$\vec{d}_{ia} = \langle \phi_i | \vec{r} | \phi_a \rangle$$
 (2.20)

The oscillator strength  $f_I$  of the excitation and thereby the absorption spectrum is then easily obtained from

$$f_I = \frac{2}{3} \Delta_I \left| \vec{d_I} \right|^2 \,. \tag{2.21}$$

While a direct solution of equation (2.15) is in principle possible, the need to store the  $N_{\text{trans}}^2$  elements of  $\boldsymbol{\Omega}$  in practice limits the size of the treatable systems. In the common case that only  $N_{\text{excit}} \ll N_{\text{trans}}$  lowest excitations are needed, this problem can be overcome by the use of iterative eigensolvers, which only need to perform matrix-vector multiplications with  $\boldsymbol{\Omega}$ , which can be done without ever storing  $\boldsymbol{\Omega}$ explicitly. Not storing the elements of  $\boldsymbol{\Omega}$  implies that they have to be recalculated on-the-fly for every iteration of the eigensolver. The diagonal part of  $\boldsymbol{\Omega}$  is trivial, but the coupling matrix elements involve costly two-center integrals, and even though very efficient methods to calculate these are available [52], their evaluation still is the major bottleneck in Casida's formulation of TD-DFT.

Time-dependent density functional based tight-binding is a method put forward by Niehaus et al. [41, 53–55] that builds on SCC-DFTB to approximate the coupling matrix  $\mathbf{K}$  to the point where the costly integrals can be parameterized in advance. Let us quickly recapitulate the most important steps of the derivation. First the transition density  $p_{ia}(\vec{r}) = \phi_i(\vec{r})\phi_a(\vec{r})$  is decomposed into atomic contributions which are then subject to a multipole expansion and approximated by their monopolar term.

$$p_{ia}(\vec{r}) = \sum_{\mathcal{A}} p_{ia,\mathcal{A}}(\vec{r}) \approx \sum_{\mathcal{A}} q_{ia,\mathcal{A}} \xi_{\mathcal{A}}(\vec{r})$$
(2.22)

Here the  $\xi_{\mathcal{A}}(\vec{r})$  are the same atom centered functions that are used in the SCC extension of ground state DFTB, and the atomic transition charges  $q_{ia,\mathcal{A}}$  are calculated from

the coefficient and overlap matrices through

$$q_{ia,\mathcal{A}} = \frac{1}{2} \sum_{\mu \in \mathcal{A}} \sum_{\nu} \left( c_{\mu i} S_{\mu \nu} c_{\nu a} + c_{\nu i} S_{\nu \mu} c_{\mu a} \right).$$
(2.23)

Note that the definition of the atomic transition charges also makes it straightforward to calculate the transition dipole moments of the single orbital transitions:

$$\vec{d}_{ia} = \sum_{\mathcal{A}} q_{ia,\mathcal{A}} \vec{R}_{\mathcal{A}}$$
(2.24)

Inserting equation (2.22) into the expression for the coupling matrix elements yields

$$K_{ia,jb} = \sum_{\mathcal{AB}} q_{ia,\mathcal{A}} \tilde{\gamma}_{\mathcal{AB}} q_{jb,\mathcal{B}} , \qquad (2.25)$$

where the atomic coupling matrix  $\tilde{\gamma}$  is given by

$$\tilde{\gamma}_{\mathcal{AB}} = \int \mathrm{d}^3 \vec{r} \int \mathrm{d}^3 \vec{r}' \,\xi_{\mathcal{A}}(\vec{r}) \,f_{\mathrm{Hxc}}[\rho^{\mathrm{GS}}](\vec{r},\vec{r}') \,\xi_{\mathcal{B}}(\vec{r}').$$
(2.26)

Comparison with equation (2.10) reveals that  $\gamma$  and  $\tilde{\gamma}$  only differ in the density at which the derivative of the exchange-correlation energy functional  $E_{\rm xc}[\rho]$  is evaluated. At this point Niehaus et al. argue that the second derivative of the exchange-correlation energy is short ranged and therefore only contributes to the on-site elements  $\tilde{\gamma}_{\mathcal{A}\mathcal{A}}$ , which are then in analogy to ground state SCC-DFTB approximated by the Hubbard parameters. [32] Domínguez et al. furthermore show that neglecting the dependence of the Hubbard parameters on the atomic charges is consistent within a linear response treatment based on ground state SCC-DFTB [54]. Using the Hubbard parameters of the neutral atoms reduces the atomic coupling matrix  $\tilde{\gamma}$  to the  $\gamma$  matrix from ground state SCC-DFTB, which then leads to a simple equation for the matrix  $\Omega$ .

$$\Omega_{ia,jb} = \delta_{ij} \delta_{ab} \Delta_{ia}^2 + 4\sqrt{\Delta_{ia} \Delta_{jb}} \sum_{\mathcal{AB}} q_{ia,\mathcal{A}} \gamma_{\mathcal{AB}} q_{jb,\mathcal{B}}$$
(2.27)

Note that the orbital energy differences  $\Delta_{ia}$  as well as the coefficient matrix C and the overlap matrix S can easily be extracted from any DFTB ground state calculation, and that no TD-DFTB specific parameters are needed since the  $\gamma$  matrix already had to be parameterized within the SCC-DFTB method. TD-DFTB can therefore immediately be applied to any system for which ground state SCC-DFTB parameters are available. It would be beyond the scope of this chapter to validate the TD-DFTB method itself. Such studies have of course been performed [41, 50, 53, 54] and while the approximations made in TD-DFTB seem drastic at first sight, the overall accuracy of the method has been found to be promising and TD-DFTB has since seen a wide variety of applications [56–65].

In summary, TD-DFTB is a computationally rather simple approximation to TD-DFT where the computational bottleneck is the size of the response matrix  $\boldsymbol{\Omega}$  and the calculation of its eigenvectors. In the next section we will present computational methods to solve the TD-DFTB equations efficiently.

## 2.3 Computational methods

As both the number of occupied  $N_{\rm occ}$  and the number of virtual orbitals  $N_{\rm virt}$ grow linearly with the number of atoms  $N_{\rm atom}$ , the total number of single orbital transitions  $N_{\text{trans}} = N_{\text{occ}} N_{\text{virt}}$  increases quadratically with the system size. This in practice limits the size of the systems treatable with TD-DFT(B), which uses the single orbital transitions as the basis of the space in which Casida's eigenvalue equation (2.15)has to be solved. An exact diagonalization of the full matrix  $\boldsymbol{\Omega}$  is only possible for the smallest systems, as the memory required to store  $\boldsymbol{\Omega}$  scales as  $\mathcal{O}(N_{\text{trans}}^2)$ , which equates to a prohibitive  $\mathcal{O}(N_{\text{atom}}^4)$  scaling. A lot of applications only need a small part of the spectrum at its low energy end, so it is possible to use iterative eigensolvers that avoid storage of the full matrix  $\boldsymbol{\Omega}$  in favor of a series of matrix-vector multiplications. Especially popular in the context of TD-DFT(B) is a class of methods based on an idea by Davidson [66], in which the eigenvalue problem is solved approximately in a small subspace, which is then iteratively extended and refined to include the desired eigenvectors within a certain accuracy. There is a multitude of different Davidson based diagonalization algorithms and reviewing them would be beyond the scope of this chapter. As the eigensolver for TD-DFTB calculations we use a variant of the GD+k method developed by Stathopoulos and Saad [67] and implemented in the PRIMME library [68]. While the eigensolver internally needs to store the subspace basis, this required memory scales as  $\mathcal{O}(N_{\text{trans}})$  and is often negligible in comparison to the  $(N_{\text{trans}} \times N_{\text{excit}})$  matrix of the desired eigenvectors.

# 2.3.1 Efficient implementation of the matrix-vector multiplication

Eigensolvers based on the Davidson method [66] solve the eigenvalue problem approximately in a small subspace which is then iteratively expanded by adding new basis vectors until it contains the desired eigenvectors. They only use the matrix they diagonalize in terms of a matrix-vector multiplication with the newly added basis vectors. In practice this is actually a matrix-matrix multiplication as it is common to add  $N_{\text{block}} \geq 1$  basis vector per iteration. This is known as the block Davidson method which was proposed by Liu [69] as a method to increase computational efficiency and to improve convergence for degenerate eigenvalues. In case of the block Davidson method the only part of the algorithm that is referencing the original matrix  $\Omega$  can be written as

$$\boldsymbol{R} = \boldsymbol{\Omega} \boldsymbol{T} , \qquad (2.28)$$

where T is an  $(N_{\text{trans}} \times N_{\text{block}})$  matrix whose columns are the newly added basis vectors. We want to discuss the implementation of this matrix-vector multiplication in some more detail now, as it is crucial to the performance of the entire TD-DFTB method.

As storage of the full matrix  $\boldsymbol{\Omega}$  is certainly impossible – hence the iterative solution in the first place – we need to recalculate its elements during every matrix-vector multiplication. We can, however, precalculate a set of smaller auxiliary objects from which  $\boldsymbol{\Omega}$  can be obtained more quickly.

Inserting equation (2.27) into (2.28) it is easy to see that one can precalculate a scaled version of the atomic transition charges  $q_{ij,\mathcal{A}}$  in order to turn the multiplication

Operation	Computational complexity of operations per method:				
Operation	direct diag.	Davidson (precalc)	Davidson (on-the-fly)		
direct diag. of full $\boldsymbol{\varOmega}$	$N_{ m trans}^3$	-	-		
subspace basis orthon.	_	$N_{\mathrm{trans}}$	$N_{\rm excit}^2$		
matvec. multiplication	_	$N_{\rm trans}N_{\rm atom}N_{\rm excit}$	$N_{\rm trans}N_{\rm atom}N_{\rm excit}$		
		with a small prefactor	with a large prefactor		

Table 2.1: Computational complexity of operations within the TD-DFTB method.

with the large coupling matrix K into a series of matrix-matrix multiplications involving only smaller matrices.

$$R_{ia,I} = \Delta_{ia}^2 T_{ia,I} + 4 \sum_{\mathcal{A}} \underbrace{\sqrt{\Delta_{ia}} q_{ia,\mathcal{A}}}_{h_{ia,\mathcal{A}}} \sum_{\mathcal{B}} \gamma_{\mathcal{A}\mathcal{B}} \sum_{jb} \underbrace{\sqrt{\Delta_{jb}} q_{jb,\mathcal{B}}}_{h_{jb,\mathcal{B}}} T_{jb,I}$$
(2.29)

$$\boldsymbol{R} = \operatorname{diag}\left(\Delta_{ia}^{2}\right)\boldsymbol{T} + 4\boldsymbol{h}\boldsymbol{\gamma}\boldsymbol{h}^{T}\boldsymbol{T}$$
(2.30)

Here h is of size  $(N_{\text{trans}} \times N_{\text{atom}})$  whereas  $\gamma$  is  $(N_{\text{atom}} \times N_{\text{atom}})$ . In order to ensure the overall cubic scaling of the matrix-matrix products we need to evaluate the subexpressions via temporary objects.

$$X_{\mathcal{B}I} = \sum_{jb} h_{jb,\mathcal{B}} T_{jb,I} \tag{2.31}$$

$$Y_{\mathcal{A}I} = \sum_{\mathcal{B}} \gamma_{\mathcal{A}\mathcal{B}} X_{\mathcal{B}I} \tag{2.32}$$

$$R_{ia,I} = \Delta_{ia}^2 T_{ia,I} + 4 \sum_{\mathcal{A}} h_{ia,\mathcal{A}} Y_{\mathcal{A}I}$$
(2.33)

Here the first and third step scale as  $\mathcal{O}(N_{\text{trans}}N_{\text{atom}}N_{\text{block}})$ , whereas  $\mathcal{O}(N_{\text{atom}}^2N_{\text{block}})$ operations are needed for the intermediate step, which is negligible since  $N_{\text{atom}} \ll N_{\text{trans}}$ . Note that this is only the scaling of a single matrix-vector product, which is different from the total time spent in matrix-vector products: Considering the entire calculation instead of the single product, the total number of trial vectors required for convergence is roughly linear in the number of requested excitations  $N_{\text{excit}}$ , no matter how the trial vectors are blocked during the multiplications. Ergo, it is more insightful to consider the scaling of the total time spent performing matrix-vector products, which is  $\mathcal{O}(N_{\text{trans}}N_{\text{atom}}N_{\text{excit}})$ . The scaling behavior of the different operations involved in TD-DFTB is summarized in table 2.1.

Equation 2.30 provides an extremely fast way to perform the matrix-vector product as only basic linear algebra operations are used which can be offloaded to highly optimized libraries. If for large systems the matrix h of the scaled atomic transition charges becomes too large to be stored though, it is necessary to recalculate its elements during the matrix-vector multiplications. Looking again at equation (2.23) it is easy to see that the sum over  $\nu$  is just a regular matrix-matrix multiplication

Object	Scaling of storage requirements per method:					
Object	direct diag.	Davidson (precalc)	Davidson (on-the-fly)			
full matrix $\boldsymbol{\varOmega}$	$N_{ m trans}^2$	_	-			
eigenvectors $\vec{F}_I$	$N_{ m trans}^2$	$N_{ m trans}N_{ m excit}$				
subspace basis vectors	—	$N_{\rm trans}$ with a large prefactor				
parameter matrix $\boldsymbol{\gamma}$	—	$N_{ m atom}^2$				
atomic transition charges $\boldsymbol{h}$	—	$N_{ m trans}N_{ m atom}$	-			
coefficient matrix $\boldsymbol{c}$	—	_	$N_{ m atom}^2$			
product matrix $\boldsymbol{\Theta} = \boldsymbol{S} \boldsymbol{c}$	_	_	$N_{\rm atom}^2$			

Table 2.2: Memory requirements of the TD-DFTB method. Note that this table only contains the largest objects needed during the diagonalization itself.

between the overlap matrix S and the coefficient matrix c.

$$h_{ia,\mathcal{A}} = \frac{1}{2} \sqrt{\Delta_{ia}} \sum_{\mu \in \mathcal{A}} \sum_{\nu} \left( c_{\mu i} S_{\mu \nu} c_{\nu a} + c_{\nu i} S_{\nu \mu} c_{\mu a} \right)$$
$$= \frac{1}{2} \sqrt{\Delta_{ia}} \sum_{\mu \in \mathcal{A}} \left( c_{\mu i} \Theta_{\mu a} + c_{\mu a} \Theta_{\mu i} \right)$$
(2.34)

The product matrix  $\boldsymbol{\Theta} = \boldsymbol{Sc}$  can be calculated in advance and stored instead of  $\boldsymbol{S}$  without additional memory in a full matrix storage implementation. The calculation of the scaled atomic transition charge  $h_{ij,\mathcal{A}}$  then only contains a sum over the basis functions centered on atom  $\mathcal{A}$ , which is usually a small number due to the minimal basis set and the large frozen core typically used in DFTB calculations. Note that precalculating  $\boldsymbol{\Theta}$  makes it possible to calculate the elements of  $\boldsymbol{h}$  in a system-independent constant time, so that evaluating them on-the-fly does not change the scaling of the matrix-vector multiplication but only increases the prefactor.

In case of precalculated atomic transition charges one can rely on standard libraries to perform the parallelization of the matrix-vector product. This is no longer true for on-the-fly calculated transition charges, where one has to parallelize equation (2.31)and (2.33) manually. Both equations can easily be parallelized, but one has to pay attention to distribute the work such that each scaled atomic transition charge  $h_{ij,\mathcal{A}}$ is in total only calculated once per step: The element  $X_{\mathcal{B}I}$  in equation (2.31) depends both on the atom  $\mathcal{B}$  as well as the trial vector index I, but the element  $h_{ib,\mathcal{B}}$  only depends on the atom  $\mathcal{B}$ . Therefore, the parallelization is chosen to be done over the atoms  $\mathcal{B}$  since parallelizing over the index I would require every processor to calculate  $h_{ib,\mathcal{B}}$ . The matrix-matrix product in equation (2.33) is chosen to be parallelized via the transition index *ia* for the exact same reason. In summary, recalculating the atomic transition charges on-the-fly during the matrix-vector multiplications removes the need to store the matrix h of size  $(N_{\text{trans}} \times N_{\text{atom}})$ . The storage required for the coefficient matrix c and product matrix  $\Theta$  can usually be neglected compared to the  $(N_{\rm trans} \times N_{\rm excit})$  matrix of the desired eigenvectors. The memory requirements for all the different methods are summarized in table 2.2.

At this point it is necessary to mention that while its performance is certainly important, the matrix-vector multiplication is not always the bottleneck of the Davidson eigensolver. The reason for this is that in order to find the Nth eigenvector it is necessary to orthonormalize it against the N-1 already known eigenvectors. This has an  $\mathcal{O}(N_{\text{trans}}N_{\text{excit}}^2)$  scaling which for large  $N_{\text{excit}}$  dominates over the  $\mathcal{O}(N_{\text{trans}}N_{\text{atom}}N_{\text{excit}})$  scaling of the matrix-vector multiplication.

#### 2.3.2 Basis size reduction by transition selection

While iterative eigensolvers make TD-DFTB calculations of larger molecules possible in the first place, the huge dimension  $N_{\text{trans}}$  of the single orbital transition space still limits the size of the treatable systems. It is therefore worthwhile to investigate the possibility of working in a subspace of single orbital transitions in which the (approximately) same result can be obtained using fewer transitions.

The most obvious way to reduce the basis size is a truncation in energy: As the iterative solution of the eigenvalue problem only targets a few of the lowest eigenvectors of a typically diagonally dominant matrix, the eigenvector can be expected to have little overlap with basis vectors for which the diagonal element is large. In physical terms this just means that the transitions from the lowest most tightly bound molecular orbitals to the highest virtuals will usually not contribute to the lowest excitations, which mostly consist of transitions close to the HOMO-LUMO gap.

Our target application of TD-DFTB are UV/Vis absorption spectra, for which the solution of Casida's eigenvalue equation (2.15) produces the excitation energies  $\Delta_I$ , while the corresponding oscillator strengths  $f_I$  can be calculated through equation (2.19). Together these can immediately be used to plot a stick-like spectrum, that using Dirac's  $\delta$ -distribution could be written as

$$A_{\rm stick}(E) = \sum_{I} f_{I} \,\delta(E - \Delta_{I}) \,. \tag{2.35}$$

As these spectra are both hard to interpret and unrealistic, it is common practice to artificially introduce line broadening through a convolution with a peaked function  $\Gamma(E)$ .

$$A_{\text{broad.}}(E) = \int dE' \ \Gamma(E' - E) A_{\text{stick}}(E')$$
  
=  $\sum_{I} f_{I} \ \Gamma(E - \Delta_{I})$  (2.36)

Both Gaussian and Lorentzian functions are common choices for  $\Gamma(E)$ . As the absorption peaks are scaled with the oscillator strength  $f_I$  of the excitation, the absorption spectrum is mostly determined by the excitations which have a large oscillator strength. Looking at equation (2.19) for the transition dipole moment of the excitations, it is easy to see that single orbital transitions with a small transition dipole moment  $\vec{d}_{ia}$  contribute little to the transition dipole moment of the excitation  $\vec{d}_I$ , and hence its oscillator strength  $f_I$ . Consequently it appears to be a reasonable approximation to remove those single orbital transitions from the basis for which the oscillator strength  $f_{ia}$  is small. Note that this is an approximation, as even leaving out a single orbital transition with  $f_{ia} = 0$  might still influence the oscillator strength  $f_I$  through an overall change in the corresponding eigenvector  $\vec{F}_I$ . The benefit of removing single orbital transitions with small oscillator strengths  $f_{ia}$  goes beyond the obvious reduction in computational effort associated with the smaller dimension of the eigenvalue problem: As one is essentially working in the oscillator strength carrying subspace, many of the excitations with small oscillator strength  $f_I$  are also removed from the final spectrum, making it possible to calculate the absorption spectrum in a fixed energy window with fewer excitations. It is in fact an all too common problem that a large number of excitations has to be calculated in order to cover the energy window of interest, while only a few of them actually determine the shape of the absorption spectrum due to their large oscillator strength  $f_I$ .

For a direct diagonalization of the  $\Omega$  matrix it is obvious that the relative reduction in basis size translates quadratically into memory savings and cubically into reduced processor time, compare table 2.1 and 2.2. For the iterative solvers the situation is more complicated due to the fact that the number of excitations that have to be calculated within a fixed energy interval is also reduced: Depending on whether the matrix-vector multiplication or the orthonormalization of the subspace basis is the bottleneck, the relative reduction in basis size will translate either quadratically or cubically into reduced processor time.

The idea to reduce the number of considered single orbital transitions is not entirely new: A truncation of the single orbital transition space based on orbital localization has successfully been used by Besley for the special cases of molecules in solution and on surfaces [70]. The more generally applicable truncation in energy or oscillator strength has recently been also proposed and tested in the PhD thesis of Domínguez [71], but no in-depth evaluation of the method was performed. In the next section we will assess the validity of the approximations introduced by truncating the basis in energy or oscillator strength, and we will show that these techniques can at negligible loss in accuracy lead to orders of magnitude reductions in computer time and required memory.

## 2.4 Examples

The accuracy loss due to the additional approximation introduced by the truncation of the single orbital transition basis certainly needs to be investigated in order to judge whether these approximations can be used in practice. Furthermore we need to determine to which extent the loss in accuracy is justified by the computational benefits of truncation. Detailed timings of the various example calculations can be found in table 2.3 on page 53. Note that we can use arbitrary units as we are only comparing theoretical data in these examples, for comparison with experimental data one may insert the appropriate prefactors for the desired unit system.

## **2.4.1** Fullerene $C_{60}$

The fullerene  $C_{60}$  was used by Niehaus et al. in the original TD-DFTB article [41] as a benchmark to judge the quality of the approximations introduced by TD-DFTB in general. The authors found that the inclusion of coupling between the single orbital transitions is crucial in the description of the optical properties of  $C_{60}$  and that TD-DFTB qualitatively reproduces the main features of the experimental spectrum [72].

We have performed a series of calculations with differently truncated single orbital transition spaces. With 4 valence electrons per atom, the  $C_{60}$  molecule has 120 occupied and 120 virtual orbitals (assuming a minimal basis), which results in a total



Figure 2.1: TD-DFTB calculated absorption spectra of  $C_{60}$  fullerene with different intensity selection thresholds. The percentage in the parentheses is the size of the remaining basis and the required computational time relative to the full calculation.

of 14400 single orbital transitions. For this rather small number of transitions it is still possible to perform an exact diagonalization of the  $\Omega$  matrix. We used the carbon parameters included in the mio-1-1 parameter set. [32]

Figure 2.1 shows absorption spectra calculated using a basis from which single orbital transitions with an oscillator strength  $f_{ia}$  smaller than a user defined threshold  $f_{ia}^{\min}$  have been removed. As expected the quality of the approximation decreases as the threshold  $f_{ia}^{\min}$  is increased and more and more of the single orbital transitions are removed. Note that there is a slight blueshift of the main peaks for larger  $f_{ia}^{\min}$ . Looking at the bottom plot in figure 2.1 one can see that a large part of the basis does not seem to contribute to the absorption spectrum at all, as a threshold of  $f_{ia}^{\min} = 0.001$  already removes three quarters of all single orbital transitions while leaving the obtained absorption spectrum practically unchanged. The reason for this is that for the highly symmetric fullerene C<sub>60</sub> there are a lot of single orbital transitions where the transition dipole moment  $\vec{d}_{ia}$  and hence the oscillator strength  $f_{ia}$  is zero purely due to symmetry. This is a great advantage for the use of intensity selection and leads to a wall time reduction by two orders of magnitude at a negligible loss in accuracy for a selection threshold of  $f_{ia}^{\min} = 0.005$ . We will later look at less symmetric examples though, where this does not play a role.

Figure 2.2 shows absorption spectra calculated using a basis from which single orbital transitions with a large orbital energy difference  $\Delta_{ia}$  have been removed. It is evident that truncation of the basis in energy has a relatively large effect on the absorption spectrum, at least compared to the intensity selection. While the number of peaks is preserved upon energy truncation, they are subject to a sizeable blueshift and their relative oscillator strength is not well preserved. Overall this results in a too strong absorption band around 6eV that does not exist in this form in calculations using the full basis. A possible reason for the mediocre performance of the energy truncation could be the fact that the orbital energy difference directly enters into equation (2.19) for the transition dipole moment  $d_I$  of the linear response excitations, giving high energy transitions a disproportionately large effect on the low energy end of the absorption spectrum, even though the associated eigenvector elements  $F_{ia,I}$ might be rather small. A major disadvantage of the truncation in energy compared to the intensity selection is that it does not reduce the number of excitations per energy interval, so that for the iterative solver the relative reduction in basis size translates only linearly into memory savings and reduced processor time. Our overall experience is that the truncation in energy introduces non-negligible errors while offering only moderate computational advantages. While it is easily possible to combine truncation in energy with truncation in oscillator strength, we have found that even this is consistently outperformed by pure intensity selection on which we will therefore focus in the remainder of this chapter.

## **2.4.2** $Ir(ppy)_3$

The compound Tris(2-phenylpyridine)iridium, abbreviated as  $Ir(ppy)_3$ , has recently been discussed in the context of highly efficient organic light emitting diodes [73]. There are two geometrical isomers, facial (*fac*-Ir(ppy)<sub>3</sub>) and meridional (*mer*-Ir(ppy)<sub>3</sub>), where the former is lower in energy. We will therefore only discuss the *fac*-Ir(ppy)<sub>3</sub> isomer. While the triplet excitations of Ir(ppy)<sub>3</sub> are technically more interesting due to their



Figure 2.2: TD-DFTB calculated absorption spectra of  $C_{60}$  fullerene with different energy truncation thresholds. The percentage in the parentheses is the size of the remaining basis and the required computational time relative to the full calculation.

role in the process called triplet-harvesting [74], theoretical as well as experimentally obtained absorption spectra can also be found in the literature [75, 76]. These show two absorption bands around 3.5eV and 5eV. The former band has been found to originate from metal to ligand charge transfer, while the latter more intense band around 5eV has been attributed to  $\pi - \pi^*$  excitations in the ligand.

We performed TD-DFTB calculations on fac-Ir(ppy)<sub>3</sub> using the parameters developed by Wahiduzzaman et al., which include parameters for the central Iridium atom. Ir(ppy)<sub>3</sub> has a total of 7830 single orbital transitions so that the  $\boldsymbol{\Omega}$  matrix can easily be diagonalized exactly.

Figure 2.3 shows the TD-DFTB calculated absorption spectrum obtained with intensity selection at different oscillator strength thresholds. TD-DFTB reproduces the general shape of the TD-DFT calculated absorption spectra published by Asada et al., though the more intense band at higher energies is blueshifted by about 0.5eV. As was the case for the fullerene example, the absorption spectrum is practically unchanged when imposing an intensity selection threshold of  $f_{ia}^{\min} = 0.001$ . In contrast to the fullerene example though, the resulting reduction of the basis size is far less drastic: A threshold of  $f_{ia}^{\min} = 0.001$  removes 75% of the fullerene single orbital transitions, but only 28% of the transitions in  $Ir(ppy)_3$ . This is due to the fact that the less symmetric fac-Ir(ppy)<sub>3</sub> does not have any single orbital transitions whose transition dipole moment vanishes purely due to symmetry. Increasing the selection threshold decreases the quality of the approximation as seen in figure 2.3, but it is not until  $f_{ia}^{\min} = 0.03$  (which results in a 76% reduction) that the spectrum starts to become qualitatively different. Overall, carefully used intensity selection in case of fac-Ir(ppy)<sub>3</sub> provides sizable computational advantages with wall time reductions up to one order of magnitude and little loss of accuracy.

## 2.4.3 Ubiquitin

Ubiquitin [77] is an extremely common small protein that has various regulatory functions in almost all eukaryotic cells. [78–80] It has recently been used as an example system for UV/VIS spectroscopy of entire proteins in gas phase [81] so that both experimentally observed as well as theoretically calculated absorption spectra are available. [82] The low energy part of the ubiquitin absorption spectrum is dominated by absorption in the single tyrosine amino acid, so that Bellina et al. were able to calculate ubiquitin's absorption spectrum using a QM/MM approach [82], where the tyrosine chromophore is embedded into a classical environment (modeled with the Amber force field [83]), while the chromophore itself is treated quantum mechanically with TD-DFT (B3LYP/aug-cc-pvdz).

We performed TD-DFTB calculations using the mio-1-1 parameter set [32] based on the PBE functional [84]. For such a large system the iterative solution of the eigenvalue problem is essential, but with 1231 atoms and in total 2 284 880 single orbital transitions the 22 gigabyte matrix of atomic transition charges can still be precalculated and stored in memory, so that the matrix-vector multiplication can be implemented as equation 2.30. If one attempts to calculate the absorption spectrum up to 200nm without using intensity selection, one quickly finds that there are almost 16 000 single orbital transitions within this window, so that an equally large number of excitations would have to be calculated to get the interesting part of



Figure 2.3: TD-DFTB calculated absorption spectra of fac-Ir(ppy)<sub>3</sub> with different intensity selection thresholds. The percentage in the parentheses is the size of the remaining basis and the required computational time relative to the full calculation.



Figure 2.4: Number of single orbital transitions per energy interval for ubiquitin for different intensity selection thresholds. Note the large number of low intensity transitions below 4eV that is removed by even a small threshold.

the absorption spectrum. With 18 megabyte of memory per eigenvector, this would require almost 290 gigabyte to store the solution, which is rather excessive. Analysis of the single orbital transitions reveals though, that many of them have a very small oscillator strength. This is visualized in figure 2.4 where the number of single orbital transitions per energy interval is plotted for different oscillator strength thresholds. It is evident that almost all single orbital transitions below 4eV have an oscillator strength  $f_{ia} < 0.001$  and would be removed if intensity selection was applied. Setting a threshold of  $f_{ia}^{\min} = 0.002$  in total removes 94% of the single orbital transitions, and looking only at the relevant part of the spectrum up to 200nm it reduces the number of transitions to about 500, which is a reduction by more than one order of magnitude. This not only makes the solution much faster, but also only requires memory for 500 eigenvectors of 1.1 megabyte each, which is less than 600 megabyte in total and certainly manageable even for personal computers.

The absorption spectrum of ubiquitin calculated using TD-DFTB with different intensity selection thresholds is shown in figure 2.5. Looking at the effect of intensity selection, it is especially remarkable that imposing an oscillator strength threshold of  $f_{ia}^{\min} = 0.0005$  hardly changes the resulting absorption spectrum at all, even though it reduces the number of excitations in the shown energy window by more than one order of magnitude, see table 2.3. Increasing the threshold to  $f_{ia}^{\min} = 0.002$ 



Figure 2.5: TD-DFTB calculated absorption spectra of ubiquitin with different intensity selection thresholds. The percentage in the parentheses is the size of the remaining basis and the required computational (wall) time relative to the full calculation. Detailed timings can be found in table 2.3.

System	$N_{\rm atom}$	$f_{ia}^{\min}$	$N_{\rm trans}$	$N_{\rm excit}$	#CPU	$t_{\rm wall}$	$t_{\rm CPU}$
C <sub>60</sub>	60	—	14400		4	434s	1736s
C <sub>60</sub>	60	0.001	361	0	4	12s	49s
C <sub>60</sub>	60	0.005	258	1	4	5.5s	22s
$C_{60}$	60	0.01	2113		4	3.5s	14s
$C_{60}$	60	0.05	1032		4	0.8s	3.2s
$Ir(ppy)_3$	61	_	7830		4	88s	352s
$Ir(ppy)_3$	61	0.001	5656		4	37s	148s
$Ir(ppy)_3$	61	0.01	3326		4	10s	40s
$Ir(ppy)_3$	61	0.02	2426		4	4.9s	20s
$Ir(ppy)_3$	61	0.03	1896		4	2.8s	11s
Ubiquitin	1231	_	2 284 880	15820	128	12.7h	68d
Ubiquitin	1231	0.0005	598085	939	32	811s	7.2h
Ubiquitin	1231	0.002	141 999	513	16	159s	2544s
Ubiquitin	1231	0.005	42055	292	16	42s	672s
Ubiquitin	1231	0.02	6 5 4 1	127	16	31s	496s

Table 2.3: Measured runtimes of the example TD-DFTB calculations using intensity selection. The calculations for  $C_{60}$  and  $Ir(ppy)_3$  were performed on a workstation with an Intel Core i7-4770 processor and 16GB memory. The ubiquitin calculations were performed on 1 to 8 cluster nodes with two octa-core Intel Xeon E5-2650 v2 processors each and 64GB of memory per node.

removes 94% of the basis while still producing an almost perfect absorption spectrum at a drastically reduced computational cost: While the calculation using the full basis took more than 12 hours and had to be run on 8 cluster nodes due to its substantial memory requirements, the intensity-selected calculation with a  $f_{ia}^{\min} = 0.002$  threshold finished in less than 3 minutes on only a single cluster node. Further increasing the threshold to  $f_{ia}^{\min} = 0.005$  the intensity selection's influence on the spectrum becomes more noticeable: We observe a loss of overall intensity in the 255nm region due to the disappearance of many weak excitations in this region.

The reason why there are so many excitations with practically zero oscillator strength at low energies is that these are mostly charge-transfer excitations, where an electron is transferred from one part of the molecule (the donor) to another part (the acceptor), possibly over a relatively long distance. It is widely known that Kohn-Sham DFT based calculations can drastically underestimate the excitation energies of such charge-transfer excitations, due to the fact that the LUMO energy of the acceptor does not correspond to its electron affinity, as would be correct in case of a chargetransfer excitation where the acceptor essentially gains an additional electron [85]. It is interesting to note though that charge-transfer excited states typically have a small overlap with the ground state and thereby according to equation (2.19) also a rather small transition dipole moment [86]. While intensity selection by no means solves the underlying problem of too small charge-transfer excitation energies in Kohn-Sham DFT, it at least helps to alleviate the worst of the associated computational problems for the specific application of calculating electronic absorption spectra, making these



Figure 2.6: Comparison of the absorption spectra of tyrosine and ubiquitin. The embedding of the tyrosine into the protein environment produces a slight redshift of the absorption band at 264nm.

calculations possible in the first place.

However, while the overall shape of the spectrum agrees very well with the spectra measured and calculated by Bellina et al. in reference [82], our TD-DFTB calculated spectrum is likely wrong.

This is most obvious if one compares our ubiquitin results to the spectrum of a single tyrosine amino acid. Originally this was done to estimate the extent of the spectral shift resulting from the embedding of the tyrosine chromophore into the protein environment. Figure 2.6 shows the TD-DFTB calculated absorption spectra of ubiquitin and the isolated tyrosine in comparison. Instead of the expected slight shift of the peaks from the tyrosine absorption spectrum we see that the absolute absorptivity is overall much larger and many more individual excitations (sticks at the bottom of figure 2.6) contribute to the absorption in this frequency range. This is inconsistent with the idea of tyrosine being the chromophore, and visualization of the involved orbitals indeed shows contributions from other parts of the protein. Unfortunately, the spectrum in reference [82] is shown with arbitrary units on the y-axis, making it impossible to compare absolute absorptivity.

However, even though we can not compare our absorption spectrum directly to experimental data, we think that TD-DFTB results are unlikely to be accurate for ubiquitin. It is quite well established that from all the standard amino acids only tryptophan, tyrosine, and cysteine contribute significantly to the absorption around 280nm [87]. As ubiquitin contains neither tryptophan nor cysteine and only one tyrosine unit, its absorptivity is expected to be close to that of a single tyrosine, which is not what our calculation predicts. What appears to be happening is, that excitations with charge-transfer character are predicted with too low energies and overlay the part of the spectrum that should be dominated by tyrosine. This is supported by our observation that single orbitals transitions involved in many of the excitations in this range tend to connect orbitals with small but still non-zero overlap. While the excitations with charge-transfer character tend to have small oscillator strengths individually, their large number still results in a significant overall absorption.

The problem of energetically too low charge-transfer excitations is usually circumvented with range-separated hybrid functionals [88, 89], also called long-range corrected functionals. This has only very recently been developed for the DFTB framework [55, 90] and is not yet implemented in the DFTB implementation in the ADF modelling suite. The ubiquitin calculations would make an interesting test case for these new methods and should be rerun once these latest developments have been implemented.

### 2.4.4 Parallel scaling

In order to evaluate the performance of our parallel implementation, we have conducted a scaling test for the example calculation of the ubiquitin absorption spectrum with an intensity selection threshold of  $f_{ia}^{\min} = 0.0002$ . The scaling test was performed on 1 to 8 cluster nodes with two octa-core Intel Xeon E5-2650 v2 processors each and 64GB of memory per node. The particular threshold of  $f_{ia}^{\min} = 0.0002$  was chosen as it results in a calculation that (using precalculated atomic transition charges) barely fits into the memory of a single node. In this way we conducted the scaling test on the largest system we were able to solve in serial, allowing us to plot the scaling behavior for the entire range from 1 to 128 cores. The result of the scaling test for both precalculated and on-the-fly atomic transition charges is shown in figure 2.7.

For precalculated transition charges we observe a good scaling both within a single node and across nodes. Within a single node (small panel in figure 2.7) it is interesting to note that we observe a super linear speedup when going from 1 to 2 or 4 cores, while for more than 8 cores the additional speedup is rather small. We attribute this to the cores' competition for shared resources like cache and memory bandwidth, which become available as more subunits of the machine (e.g. both sockets) are used, but are ultimately exhausted when too many processor cores compete for them. The visible oscillations in figure 2.7 are due to the use of ScaLAPACK[91] to implement equation (2.30), which favors even and especially power of two processor grid sizes.

For on-the-fly calculated atomic transition charges the overall performance is worse, but the parallel scaling both within a node and across nodes is better. Within a single node this is due to the absence of the large matrix of atomic transition charges, which reduces reading from main memory and thereby frees shared resources. The better scaling across nodes is simply due to the fact that a relatively large amount of time is spent in the trivially parallel task of recalculating atomic transition charges, for which no communication is required.

# 2.5 Conclusion

In summary, we have shown that the computational cost of absorption spectra calculations using time-dependent density functional tight binding (TD-DFTB) can be significantly reduced by not considering single orbital transitions with small oscillator strengths. We have found that small selection thresholds do not noticeably affect the accuracy of the result, while already providing a sizable reduction in computational



Figure 2.7: Parallel scaling of our TD-DFTB implementation for the test case of ubiquitin with an intensity selection threshold of  $f_{ia}^{\min} = 0.005$ . The calculations were performed on 1 to 8 cluster nodes with two octa-core Intel Xeon E5-2650 v2 processors each and 64GB of memory per node.

cost. The savings are especially great if the low energy part of the absorption spectrum contains a large number of spurious zero-intensity charge-transfer excitations, which are removed by the intensity selection. Note however, that excitations with charge-transfer character and small but non-zero oscillator strengths might still "contaminate" the interesting part of the absorption spectrum, as was observed in section 2.4 for the example of ubiquitin. Recently the problem with energetically too low charge transfer excitations in TD-DFTB has been addressed by porting long-range corrected exchange-correlation functionals to the DFTB framework [55, 90], but lacking an implementation in ADF we were not yet able to test this together with intensity selection.

However, the issue of charge-transfer excitations is unrelated to the idea of intensity selection and we believe that its ease of use together with its computational benefits lower the barrier of performing optical properties calculations of large molecules, and can serve to make such calculations possible in a wider array of applications. Intensity-selection has been implemented in the ADF molecular modeling suite [92] for the TD-DFTB and TD-DFT+TB (see chapter 4) methods.

# 3 Vibrationally resolved spectroscopy with TD-DFTB

# 3.1 Introduction

Linear response time-dependent density functional theory (TD-DFT) based on Casida's equations [29] is probably the most widely used method for the simulation of processes involving excited states, such as photon absorption and emission. In UV/Vis spectroscopy the absorption or emission of a photon changes the electronic as well as the vibrational state of the molecule. Thus, an accurate prediction of UV/Vis spectra needs to take the simultaneous excitation of electrons and nuclear vibrations into account.

When using TD-DFT for the calculation of absorption spectra, these vibrational contributions, which are typically much smaller than the electronic ones, often cannot be included due to the computational cost and complexity of calculating the normal modes of vibration in the electronically excited state. The resulting absorption band is then approximated as a single line at the vertical excitation energy, which is artificially broadened through convolution with a Gaussian or Lorentzian function. This approximation is particularly severe if the absorption spectrum is dominated by a single electronic transition, because then the structure of the spectrum is entirely determined by the vibrational fine structure. Furthermore, the vertical excitation energy is strictly speaking not a physical observable and its use as the center of an absorption band relies heavily on error compensation. In case of emission spectroscopy the emission of a photon occurs mostly from the lowest excited state of a given multiplicity [93] (Kasha's rule), so that the shape of the emission spectrum is in fact mostly determined by vibronic effects.

Based on the framework of density functional based tight-binding (DFTB) [30–32], a computationally very efficient alternative to TD-DFT has been developed in the form of time-dependent DFTB [41, 53–55]. Here, the calculation of excited states is based on a DFTB ground state calculation and additional approximations are made to Casida's TD-DFT equations in order to avoid numerical integration at runtime. The resulting method is orders of magnitude faster than TD-DFT and has successfully been used in a wide variety of applications [56–65]. A recent review of TD-DFTB can be found in Ref. [53].

While the applicability of TD-DFT to the calculation of vibrationally resolved UV/Vis spectra has been confirmed in benchmark calculations [94–99], no such studies have been performed for TD-DFTB. As such it is not clear at the moment whether the additional approximations made in TD-DFTB have a negative influence on the quality of calculated vibronic effects. TD-DFTB has, however, been found to yield satisfactory accuracy for both excited state geometries and excited state normal modes of small molecules [100], which, together with its computational efficiency, makes

its application to vibrationally resolved spectroscopy promising. In this chapter we investigate the applicability of TD-DFTB to the calculation of vibrationally resolved UV/Vis spectra.

This chapter is structured as follows: In Section 3.2 we recapitulate the theory of vibrationally resolved UV/Vis spectroscopy from a TD-DFTB perspective. We furthermore present a method to follow a particular excitation through conical intersections during an exited state geometry optimization. In Section 3.3 we evaluate the performance of TD-DFTB for the calculation of vibronic effects for strongly dipole allowed excitations in various aromatic and polar molecules. We compare the obtained results to both TD-DFT calculations and experimentally obtained data. Section 3.4 summarizes our findings and concludes the chapter.

## 3.2 Theory

### 3.2.1 Excited states from TD-DFTB

In the field of quantum chemistry the most commonly used density functional based approach to excited state calculations is Casida's linear response formalism [29]. Here the problem of calculating excitation energies and excited states is cast into an eigenvalue equation in the space of single orbital transitions  $\hat{c}_a^{\dagger} \hat{c}_i |\psi_0\rangle$ , where  $|\psi_0\rangle$  is the Slater determinant of the occupied Kohn-Sham orbitals. For local exchange-correlation functionals the eigenvalue problem can be written as

$$\mathbf{\Omega}\vec{F} = \Delta^2 \vec{F} , \qquad (3.1)$$

where  $\Delta$  is the vertical excitation energy. For closed-shell systems the elements of the matrix  $\boldsymbol{\Omega}$  are given by

$$\Omega_{ia,jb} = \delta_{ij}\delta_{ab}\Delta_{ia}^2 + 4\sqrt{\Delta_{ia}\Delta_{jb}}K_{ia,jb} .$$
(3.2)

We follow the usual convention of using the indexes i, j for occupied and a, b for virtual orbitals and have abbreviated the difference in the Kohn-Sham orbital energies  $\varepsilon_a - \varepsilon_i = \Delta_{ia}$ . The so-called coupling matrix K differs between TD-DFT and TD-DFTB and also depends on the spin state of the calculated excited state. The TD-DFTB coupling matrix is obtained from the TD-DFT coupling matrix through an approximate decomposition of the transition density into monopolar contributions and is given by [41]

$$K_{ia,jb} = \sum_{\mathcal{AB}} q_{ia,\mathcal{A}} \kappa_{\mathcal{AB}} q_{jb,\mathcal{B}} , \qquad (3.3)$$

where the so called atomic transition charges

$$q_{ia,\mathcal{A}} = \frac{1}{2} \sum_{\mu \in \mathcal{A}} \sum_{\nu} \left( c_{\mu i} S_{\mu \nu} c_{\nu a} + c_{\nu i} S_{\nu \mu} c_{\mu a} \right)$$
(3.4)

are calculated through Mulliken population analysis [34] from the overlap and coefficient matrices S and C. We use capital calligraphic indexes  $\mathcal{A}, \mathcal{B}$  for atoms and Greek

indexes  $\mu, \nu$  for the atomic basis functions. The atomic coupling matrix  $\kappa$  depends on the multiplicity of the calculated excitation and is given by

$$\kappa^{\rm S}_{\mathcal{A}\mathcal{B}} = \gamma_{\mathcal{A}\mathcal{B}}$$
 for singlets (3.5)

or 
$$\kappa_{\mathcal{AB}}^{\mathrm{T}} = \delta_{\mathcal{AB}} M_{\mathcal{A}}$$
 for triplets, (3.6)

where  $\gamma_{\mathcal{AB}}$  is the normal  $\gamma$ -functional used in the SCC (self-consistent charge) extension of DFTB [32] and  $M_{\mathcal{A}}$  is the magnetic Hubbard parameter which is also used in spin-polarized ground state calculations [101].

Detailed information about the excited state  $|\Psi\rangle$  can be extracted from the eigenvectors  $\vec{F}$  in equation (3.1): The electronic transition dipole moment is in TD-DFTB easily calculated as

$$\langle \psi | \hat{\vec{\mu}}_e | \psi_0 \rangle = \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta}} F_{ia} \sum_{\mathcal{A}} q_{ia,\mathcal{A}} \vec{R}_{\mathcal{A}} , \qquad (3.7)$$

where  $\hat{\vec{\mu}}_e = -e \sum_i \hat{\vec{r}}_i$  is the electronic dipole moment operator. Using Casida's assignment ansatz we can construct an approximate excited state wavefunction  $|\psi\rangle$  from a combination of single orbital excitations of the Kohn-Sham Slater determinant  $|\psi_0\rangle$ .

$$|\psi\rangle = \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta}} F_{ia} \, \hat{c}_a^{\dagger} \hat{c}_i \, |\psi_0\rangle \tag{3.8}$$

Following the auxiliary functional approach [102] developed by Furche and Ahlrichs, analytical gradients for the excitation energies have been derived by Heringer et al. [100]. With the following definitions for several auxiliary objects

$$U_{ia} = \sqrt{\frac{\Delta_{ia}}{\Delta}} F_{ia} \tag{3.9}$$

$$\Delta q_{\mathcal{A}}^{\mathrm{ex}} = \sum_{\mu \in \mathcal{A}} \sum_{\nu} P_{\mu\nu} S_{\mu\nu}$$
(3.10)

$$U_{\mathcal{A}} = \sum_{ia} U_{ia} q_{ia,\mathcal{A}} \tag{3.11}$$

$$\Theta_{\mathcal{A}} = \sum_{\mathcal{B}} \gamma_{\mathcal{A}\mathcal{B}} \ \Delta q_{\mathcal{B}} \tag{3.12}$$

$$\Theta_{\mathcal{A}}^{\mathrm{ex}} = \sum_{\mathcal{B}} \gamma_{\mathcal{A}\mathcal{B}} \ \Delta q_{\mathcal{B}}^{\mathrm{ex}} \tag{3.13}$$

$$\Xi_{\mathcal{A}} = \sum_{\mathcal{B}} \kappa_{\mathcal{A}\mathcal{B}} U_{\mathcal{B}} , \qquad (3.14)$$

the gradient of the excitation energy  $\Delta$  can be written as

$$\frac{\mathrm{d}\Delta}{\mathrm{d}\vec{R}_{\mathcal{A}}} = 2 \sum_{\mathcal{B} \neq \mathcal{A}} \sum_{\substack{\mu \in \mathcal{A} \\ \nu \in \mathcal{B}}} \frac{\mathrm{d}H^0_{\mu\nu}}{\mathrm{d}\vec{R}_{\mathcal{A}}} P_{\mu\nu}$$
(3.15)

$$+\sum_{\substack{\mathcal{B}\neq\mathcal{A}}}\sum_{\substack{\mu\in\mathcal{A}\\\nu\in\mathcal{B}}}\frac{\mathrm{d}S_{\mu\nu}}{\mathrm{d}\vec{R}_{\mathcal{A}}}\left(\Theta_{\mathcal{A}}+\Theta_{\mathcal{B}}\right)P_{\mu\nu}$$

$$+ \sum_{\mathcal{B}\neq\mathcal{A}} \frac{\mathrm{d}\gamma_{\mathcal{A}\mathcal{B}}}{\mathrm{d}\vec{R}_{\mathcal{A}}} \left( \Delta q_{\mathcal{A}} \Delta q_{\mathcal{B}}^{\mathrm{ex}} + \Delta q_{\mathcal{A}}^{\mathrm{ex}} \Delta q_{\mathcal{B}} \right) \\ + \sum_{\mathcal{B}\neq\mathcal{A}} \sum_{\substack{\mu\in\mathcal{A}\\\nu\in\mathcal{B}}} \frac{\mathrm{d}S_{\mu\nu}}{\mathrm{d}\vec{R}_{\mathcal{A}}} \left( \Theta_{\mathcal{A}}^{\mathrm{ex}} + \Theta_{\mathcal{B}}^{\mathrm{ex}} \right) D_{\mu\nu} \\ - \sum_{\mathcal{B}\neq\mathcal{A}} \sum_{\substack{\mu\in\mathcal{A}\\\nu\in\mathcal{B}}} \frac{\mathrm{d}S_{\mu\nu}}{\mathrm{d}\vec{R}_{\mathcal{A}}} W_{\mu\nu} \\ + 4 \sum_{\mathcal{B}\neq\mathcal{A}} \frac{\mathrm{d}\kappa_{\mathcal{A}\mathcal{B}}}{\mathrm{d}\vec{R}_{\mathcal{A}}} U_{\mathcal{A}} U_{\mathcal{B}} \\ + 2 \sum_{\mathcal{B}\neq\mathcal{A}} \sum_{\substack{\mu\in\mathcal{A}\\\nu\in\mathcal{B}}} \frac{\mathrm{d}S_{\mu\nu}}{\mathrm{d}\vec{R}_{\mathcal{A}}} \left( \Xi_{\mathcal{A}} + \Xi_{\mathcal{B}} \right) U_{\mu\nu} ,$$

where  $\Delta q_A$  are the Mulliken charges and D is the ground state's density matrix. The exact definition of the one-particle difference density matrix P and the Lagrange multipliers  $W_{\mu\nu}$  can be found in Appendix B of Ref. [100].

Analytical second derivatives have not been derived for the TD-DFTB excitation energies. We therefore calculate the Hessian by numerical differentiation of the analytical gradient using a three point approximation with nuclear displacements of  $10^{-4}$  Bohr along the Cartesian axes. While this increases the computational complexity of vibrational frequency calculations by a factor of  $6N_{\rm atom}$ , it also allows derivatives of other properties to be calculated simultaneously at no additional cost. A useful application of this would be the calculation of the electronic transition dipole moment's gradient; a property needed for the incorporation of Herzberg-Teller effects, which are important in the correct description of weakly dipole allowed and dipole forbidden transitions.

#### 3.2.2 Vibrationally resolved spectroscopy

Calculating absorption spectra solely from the vertical excitation energies  $\Delta$  and the corresponding electronic transition dipole moments  $\langle \psi | \hat{\mu}_e | \psi_0 \rangle$  is computationally very attractive, since the entire calculation can be performed at a fixed nuclear geometry. This, however, completely neglects the excitation of nuclear vibrations that happens simultaneously to the electronic transition. These nuclear effects determine the shape of an absorption band belonging to a specific electronic transition and are therefore important if an accurate absorption spectrum is required or if the spectrum is dominated by only a single band.

A more realistic description of the absorption is obtained if both electronic and nuclear effects are considered for the calculation of the transition dipole moment. Using the Born-Oppenheimer approximation [103]

$$\Psi(\vec{r},\vec{R}) = \psi(\vec{r},\vec{R})v(\vec{R}) \tag{3.16}$$

to express the total wavefunction  $\Psi(\vec{r}, \vec{R})$  as a product of electronic  $\psi(\vec{r}, \vec{R})$  and nuclear

wavefunction  $v(\vec{R})$ , the transition dipole moment can be written as

$$\left\langle \Psi' \left| \hat{\vec{\mu}}_e + \hat{\vec{\mu}}_N \right| \Psi \right\rangle = \left\langle \psi' v' | \hat{\vec{\mu}}_e | \psi v \right\rangle + \underbrace{\left\langle \psi' v' | \hat{\vec{\mu}}_N | \psi v \right\rangle}_{=0} . \tag{3.17}$$

Here  $\hat{\vec{\mu}}_N = e \sum_{\mathcal{A}} \vec{R}_{\mathcal{A}}$  is the nuclear dipole moment operator. Primed symbols denoted excited state wavefunctions and unprimed symbols the ground state wavefunctions. The second term vanishes due to the orthogonality of the electronic wavefunctions  $\psi(\vec{r}, \vec{R})$  and  $\psi'(\vec{r}, \vec{R})$  for any nuclear geometry  $\vec{R}$ . The first term involving the electronic dipole moment is then approximated by assuming that the electronic transition dipole moment is constant in the region of configuration space where the nuclear wavefunction  $v(\vec{R})$  is non-zero, which gives the Franck-Condon approximation [104–106] for the transition dipole moment.

$$\left\langle \Psi' \left| \, \hat{\vec{\mu}}_e + \hat{\vec{\mu}}_N \, \middle| \, \Psi \right\rangle \approx \left\langle v' | v \right\rangle \left\langle \psi' | \, \hat{\vec{\mu}}_e | \psi \right\rangle \tag{3.18}$$

The square of the overlap  $\langle v'|v\rangle$  between the initial and final nuclear wavefunction is called the Franck-Condon factor. For strongly dipole allowed transitions this approximation is generally sufficient. Dipole forbidden transitions are, however, poorly described by equation (3.18), as it predicts a zero transition dipole moment. The description of these transitions can be improved if the gradient of the electronic transition dipole moment is explicitly taken into account. These so called Herzberg-Teller effects [107] are beyond the scope of this chapter though, and we will restrict our investigation to dipole allowed transitions.

In order to calculate the overlap  $\langle v'|v\rangle$ , some functional form for the nuclear wavefunction is required. Within the Born-Oppenheimer approximation the nuclei move in the potential given by the electronic energy of the ground state and excited state, respectively. Using a harmonic approximation of the Born-Oppenheimer potential around the equilibrium geometry of the respective state, the nuclear wavefunction can be approximated as a multidimensional harmonic oscillator, for which the wavefunction is well known.

$$v(\vec{n},\vec{q}) = \prod_{i} \left(\frac{\omega_{i}}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^{n_{i}}n_{i}!}} e^{-\frac{1}{2}\omega_{i}q_{i}^{2}} \mathcal{H}_{n_{i}}(\sqrt{\omega_{i}}q_{i})$$
(3.19)

Here  $n_i$  is the number of energy quanta  $\omega_i$  in the *i*-th normal mode of vibration, and  $q_i$  is the normal mode coordinate.  $\mathcal{H}_{n_i}$  is the  $n_i$ -th Hermite polynomial. Before the overlap  $\langle v'|v\rangle$  can be calculated, one has to account for the fact that both the normal modes as well as the equilibrium geometries of ground and excited state are different. Duschinsky showed [108] that the normal mode coordinates of the initial and final state can be related through a linear transformation  $\vec{q}' = J\vec{q} + \vec{k}$ , which allows the overlap integral to be written as

$$\langle v'|v\rangle = (\det \boldsymbol{J})^{-\frac{1}{2}} \int v'(\vec{n}', \boldsymbol{J}\vec{q} + \vec{k}) v(\vec{n}, \vec{q}) \,\mathrm{d}\vec{q} \,.$$
(3.20)

Details on the calculation of these integrals can be found in Ref. [109] and [110].

With the harmonic approximation for the potential experienced by the nuclei, they behave as a multidimensional harmonic oscillator for which the energy can easily be written as

$$E^{\text{nuc}}(\vec{n}) = \sum_{i} \omega_i \left( n_i + \frac{1}{2} \right) . \tag{3.21}$$

Note that even without excitation of nuclear vibrations the nuclei in their ground state still have a vibrational zero point energy given by

$$E^{\text{ZPE}} = E^{\text{nuc}}(\vec{0}) = \frac{1}{2} \sum_{i} \omega_i .$$
 (3.22)

As the thermal energy is usually small compared to the energy necessary for vibrational excitations, it is reasonable to assume that both the electrons and the nuclei are in their respective ground state when the photon is absorbed. The total energy of the system is therefore given by the DFT(B) energy functional  $E_{\text{DFT}(B)}$  plus the nuclear vibrational zero point energy  $E^{\text{ZPE}}$ , both of which are calculated at the equilibrium geometry  $\vec{R}_{\text{CS}}$  of the ground state, that is where  $E_{\text{DFT}(B)}$  is minimal.

$$E_{\rm GS} = E_{\rm DFT(B)}(\vec{R}_{\rm GS}) + E_{\rm GS}^{\rm ZPE}$$
(3.23)

After the absorption the total energy of the excited state is the sum of DFT(B) ground state energy  $E_{\text{DFT}(B)}$ , vertical excitation energy  $\Delta$  and the nuclear vibrational energy according to equation (3.21), where everything is evaluated at the excited state equilibrium geometry  $\vec{R}_{\text{EX}}$ , that is where  $E_{\text{DFT}(B)} + \Delta$  is minimal.

$$E_{\rm EX}(\vec{n}') = E_{\rm DFT(B)}(\vec{R}_{\rm EX}) + \Delta(\vec{R}_{\rm EX}) + E_{\rm EX}^{\rm nuc}(\vec{n}')$$
(3.24)

The difference  $E_{\text{EX}}(\vec{n}\,') - E_{\text{GS}}$  between ground and excited state energies together with the intensities calculated as the square of the overlap  $\langle v'|v \rangle$  from equation 3.20 determine the shape of an absorption band belonging to a specific electronic transition. The smallest possible excitation energy called  $E_{0-0}$  is obtained if the nuclei remain in the ground state during the photon absorption and is given by

$$E_{0-0} = E_{\rm EX}(\vec{0}) - E_{\rm GS} . \tag{3.25}$$

An illustration of the various energies can be found in figure 3.1.

It is interesting to note that despite its widespread use for the calculation of absorption spectra the vertical excitation energy  $\Delta$  is not experimentally observable. Its popularity stems from the fact that it is easily calculable and often a reasonable approximation for the position of an absorption band: The vertical excitation energy  $\Delta$  is always larger than  $E_{0-0}$ , which on the other hand is a lower bound to the photon energy at which the absorption can happen. Depending on the details of ground and excited state potential energy surface it might well happen that these effects compensate and the vertical excitation energy  $\Delta$  is actually not too far from the band maximum. We will later plot the vertical excitation energy into the vibrationally resolved spectra to investigate to what extent it can be used as an approximation to the absorption band's maximum.

So far we have only described absorption spectroscopy. For emission spectroscopy the only necessary modification is that the system is assumed to be in the vibrational



Figure 3.1: Illustration of the quantities involved in vibrationally resolved spectroscopy calculations.

ground state of the electronically excited state prior to the emission of the photon. All vibrational states of the electronic ground state are then valid final states. This includes the vibrational ground state, so that absorption and emission spectrum overlap at the line corresponding to the 0-0 transition.

The method outlined in this section is commonly referred to as adiabatic Hessian Franck-Condon (AH|FC) since it performs an optimization of the excited state, calculates its Hessian and subsequently uses the Franck-Condon approximation for the calculation of the dipole moments. Various other methods for the calculation of vibronic fine structures are available, a comparison of which on the basis of DFT can be found in a recent article by Muniz-Miranda et al. [99]. These methods generally skip one or more steps in the calculation to increase computational efficiency. The vertical gradient Franck-Condon (VG|FC) method [111] (also called linear coupling model) for example requires neither an optimization of the excited state nor a calculation of the excited state Hessian, thereby avoiding the most costly steps in the AH|FC procedure. All of these methods can in principle also be used within the DFTB framework. However, the purpose of this chapter is to investigate the effect of the DFTB approximations on the calculation of vibrational fine structures. We believe that this is best done using the AH|FC method, as it offers the most complete test of the DFTB framework, i.e. excited state geometries and vibrational frequencies as

well as  $E_{0-0}$  energies, all of which would not be tested in e.g. the VG|FC method. We do not expect the DFTB approximations to alter the conclusions of Muniz-Miranda et al. [99], and have hence restricted our investigations to the AH|FC method.

# 3.2.3 Following a particular excitation during geometry optimization

In order to reliably calculate the equilibrium structure of a specific electronically excited state, we need to make sure that at every step of the geometry optimization the excitation energy gradient is calculated for the correct excited state. If the excited states are well separated in energy, this is trivial as one can just use the gradient of the I-th lowest excited state, where I is the number of the excited state of interest at the initial geometry. This, however, does not work if potential energy surfaces (PES) cross and can not only lead to finding equilibrium geometries of excited states other than the originally selected, but can also lead to completely unphysical results. Such a case is illustrated in figure 3.2. Here the excited state of interest A has been identified as the  $S_2$  state at the ground state's equilibrium geometry  $R_{\rm GS}$ , so that the optimization would start at the blue dot on the dotted PES. Optimization on the PES of state A would go through the conical intersection with the other PES and end at the equilibrium geometry  $\vec{R}_{\text{EX}}^A$  of state A. However, if one simply optimizes the second lowest excited state one runs into a problem at the conical intersection: The  $S_2$  surface on which the optimization would take place is the PES of state A left of the conical intersection and the PES of state B right of the intersection. The "minimum" of this surface is at the intersection, but the gradient is not defined there and in practice common optimizers just oscillate around the conical intersection geometry. In order to solve this problem generally and to reliably reach the equilibrium geometry of the originally selected excitation we need a way to follow a particular excited state through a conical intersection.

Let  $\vec{F}_I^k$  be the eigenvector of the *I*-th excitation at the *k*-th step of the geometry optimization. Assuming that the *I*-th excitation is the one for which the geometry is to be optimized, we would use this eigenvector to calculate the gradient which determines the nuclear geometry for the next step. Having solved equation (3.1) at step k + 1 of the optimization it would then be natural to look at the eigenvectors  $\vec{F}_J^{k+1}$  in order to check which of the new eigenvectors is most similar to  $\vec{F}_I^k$ . We use the following measure  $\theta_{IJ}$  for quantifying the similarity between eigenvectors in subsequent steps of the geometry optimization:

$$\theta_{IJ} = \theta(\vec{F}_I^k, \vec{F}_J^{k+1}) = \left| \sum_{\mu\nu} F_{\mu\nu,I}^k F_{\mu\nu,J}^{k+1} \right|$$
(3.26)

Here

$$F^{k}_{\mu\nu,I} = \sum_{ia} c^{k}_{\mu i} F^{k}_{ia,I} c^{k}_{\nu a}$$
(3.27)

are the elements of Casida's eigenvectors in atomic orbital basis. The similarity measure  $\theta_{IJ}$  is calculated for all J and the gradient of the most similar excitation is used to proceed with the next step of the geometry optimization. Switching to atomic orbital basis is necessary as the molecular orbitals can vary drastically from step to



Figure 3.2: An example system where optimization on the  $S_2$  potential energy surface does not converge to a minimum. Note that the ground state's potential energy surface is not shown.

step (i.e. their sign is undefined and their energetic ordering can change), which makes direct comparison of eigenvector elements  $F_{ia}$  difficult.

A more rigorous way to compare two excited states would be to use Casida's assignment ansatz from equation (3.8) to calculate the overlap  $\langle \psi_I^k | \psi_J^{k+1} \rangle$ . This would also take the change in the positions of the atomic basis functions into account, which is neglected in equation (3.26). We have, however, found that this is a small effect for the nuclear displacements typically seen from one step in a geometry optimization to the next, and that the similarity measure  $\theta_{IJ}$  very reliably selects the correct excitation, while having the advantage that it is much easier to calculate than the more rigorous overlap  $\langle \psi_I^k | \psi_J^{k+1} \rangle$  between wavefunctions.

It is important to note that the procedure introduced in this section is only a technical tool that avoids certain problems during geometry optimizations of excited states. By staying on the original PES the result is also easier to interpret for the user. However, great care must be taken in situations where potential energy surfaces cross, as it can in reality happen that the system switches to another PES at the conical intersection. If this is the case, the user should manually restart the optimization from the intersection geometry on the other PES.

### 3.2.4 Technical details

The first step in the calculation is to perform a geometry optimization of the ground state using DFT(B). This determines the ground state's equilibrium geometry  $\vec{R}_{GS}$  at which the vertical excitations are calculated with TD-DFT(B) and the excitation of interest identified. The ground state geometry  $\vec{R}_{GS}$  is then slightly distorted by adding small random vectors to all nuclear positions. This distorted geometry is then used as the initial geometry for a geometry optimization of the desired excited state, which yields the excited state's equilibrium geometry  $\vec{R}_{EX}$ . The random displacement is necessary in order to allow the excited state to break possible symmetries of the ground state, as it might otherwise well happen that the geometry optimization starts on a saddle point or local maximum, making it difficult to define an initial direction for the optimization by following the gradient. Excitation following as introduced in subsection 3.2.3 is used during the geometry optimization of the excited state. Normal

modes of the ground and excited state are calculated at the respective equilibrium geometries and used to calculate the Franck-Condon factors and the vibrationally resolved spectrum. The nuclear system is assumed to be in the vibrational ground state prior to the absorption of the photon. The theoretical spectra are convoluted with Gaussian or Lorentzian functions of suitable widths in order to match the resolution of the respective experimental spectra. Intensities in the theoretical spectra naturally integrate to one over the entire spectral width. Experimental spectra were normalized in the same way, if possible. In cases where this was impossible due to a cut off 0-0 peak or a limited spectral range, the experimental spectrum was scaled to match the intensity of a prominent line to the DFT result. In order to facilitate a comparison of spectral shapes even when absolute excitation energies differ, all spectra have had their  $E_{0-0}$  energy shifted to zero.

All simulations were performed with the 2016 version of the ADF modeling suite. DFT calculations were performed with a TZP basis set and the PBE functional [84]. For the DFTB calculations we used the DFTB3 Hamiltonian [40] and the 3ob:freq parameter set [112]. Conceptually, using the DFTB3 Hamiltonian in the ground state calculation is slightly inconsistent, as TD-DFTB is based on the linear response of SCC-DFTB, not DFTB3. While TD-DFTB has been adapted to the DFTB3 framework [113], the difference in the results is negligible in practice and we used TD-DFTB in its original formulation [41].

# 3.3 Results

In order to evaluate the loss in accuracy introduced through the DFTB approximations, we have calculated vibrationally resolved spectra with both DFT and DFTB. In addition to the comparison between the two theoretical methods, we also compare both of them to experimentally obtained spectra. This allows us to determine whether a deviation is indeed caused by the DFTB approximations or already present at the DFT/GGA level.

A summary of all energies and oscillator strengths can be found in table 3.1. For planar molecules with  $D_{2h}$  symmetry, the *xy*-plane was chosen to be the plane of the molecule, with the *x*-axis along the longer axis of the molecule.

## 3.3.1 Anthracene

Our first example is the  $S_0 \rightarrow S_1$  excitation in anthracene, a typical example of a dipole-allowed  $\pi \rightarrow \pi^*$  transition in a polycyclic aromatic hydrocarbon (PAH). Anthracene is a precursor to anthraquinone from which many technically important dyes such as alizarin are derived. Furthermore, the optical properties of anthracene have recently also been discussed in the context of absorption lines of interstellar molecular clouds of which anthracene is one of the most complex constituents [122].

As expected from experiment [114] we observe a dipole-allowed  $S_0 \rightarrow S_1$  transition ( $L_a$  state in Platt nomenclature[123]) with  $B_{2u}$  symmetry and an oscillator strength f = 0.048 calculated with DFTB, and 0.037 with DFT. The calculated vertical excitation energies are  $\Delta(\vec{R}_{\rm GS}) = 2.988$  with DFTB, and 2.91eV with DFT. Optimization of the excited state leads to an equilibration of the bond lengths in the outer rings and a slight expansion of the outer bonds of the central ring for both

Molecule	Excited State	DFT/PBE			DFTB			Exp.
		$\Delta(\vec{R}_{ m GS})$	$E_{0-0}$	f	$\Delta(ec{R}_{ m GS})$	E <sub>0-0</sub>	f	E <sub>0-0</sub>
Anthracene	$1^1 B_{2u}, L_a$	2.91	2.67	0.037	2.98	2.65	0.048	3.43
Pentacene	$1^1 B_{2u}, L_a$	1.60	1.48	0.059	1.80	1.61	0.033	$2.12^{\dagger}$
Pyrene	$1^1 B_{3u}, L_a$	3.38	3.17	0.211	3.25	2.97	0.201	3.84
Pentarylene	$1^1 B_{3u}, L_a$	1.36	1.31	1.48	1.49	1.38	1.58	$1.66^{\dagger}$
Octatetraene	$1^1B_u$	3.78	3.53	1.40	3.83	3.44	1.14	4.40
trans-Stilbene	$1^1B_u$	3.60	3.32	0.85	3.74	3.34	0.83	$3.80^{\dagger}$
Anisole	$1^1 A'$	4.72	4.38	0.030	4.69	4.22	0.036	4.51
C480	$1^1A$	3.06	2.73	0.23	3.19	2.77	0.22	$\approx 3.22^{\dagger}$
Bithiophene	$1^1B_u$	3.68	3.38	0.40	3.67	3.30	0.40	3.86
Triazoline	$1^{1}B_{2}$	1.67	1.60	0.0006	1.83	1.60	0	$2.15^{\dagger}$

<sup>†</sup>Measured in solution or matrix conditions. A solvent-induced shift of about 0.1–0.2 eV should be considered when comparing with theoretical results.

Table 3.1: Summary of vertical excitation energies,  $E_{0-0}$  energies and oscillator strengths for all example transitions from section 3.3. All energies are given in eV. Experimental  $E_{0-0}$  energies from Ref. [99, 114–121].

DFTB and DFT, with a overall slightly stronger deformation for DFTB. The DFT(B) ground state geometry and its deformation upon excitation is shown in figure 3.3. The deformation qualitatively agrees with the results obtained by Dierksen and Grimme using a hybrid functional [94]. Comparison of the total energy of excited and ground state yields an  $E_{0-0}$  energy of 2.65eV for DFTB, and 2.67eV for DFT, both of which considerably underestimate the experimentally obtained  $E_{0-0}$  of 3.43eV by almost 0.8eV [114]. It is known that density functional theory systematically underestimates energies of  $L_a$  states in acenes [124, 125], though this deficiency is corrected with range-separated hybrid functionals [126].

The vibrational fine structure of the  $S_0 \rightarrow S_1$  absorption band is shown in figure 3.4. The general shape and the peak positions of both the DFT and DFTB calculated spectra agree very well with the experimental reference, though the experimental spectrum is overall a little more intense at higher energies. This was also observed by Dierksen and Grimme who hypothesized that this is due to a skewed baseline in the experimental spectrum [94]. While they have later found that the effect reduces with a larger ratio of Hartree-Fock exchange (see also section 3.3.4), it never quite disappears as it does for other PAHs [95].

Overall it can be said that the vibrational fine structure of the  $S_0 \rightarrow S_1$  transition in anthracene is remarkably accurate compared the absolute energies, which are almost 0.8eV too low. This indicates that the excited state potential energy surface is mostly shifted to smaller energies, but not distorted in the process. The similarity between the DFT and DFTB calculated spectra suggests that the additional approximations of DFTB have little influence on the quality of the obtained spectrum.

### 3.3.2 Pentacene

The next example is the  $S_0 \rightarrow S_1$  transition in pentacene. The  $S_1$  state is of  $B_{2u}$  symmetry and labeled as  $L_a$  in Platt's nomenclature [123]. The transition is dipoleallowed with an oscillator strength f = 0.033 calculated from DFTB and 0.059 from



Figure 3.3: Deformation in the  $S_1$  state of anthracene calculated with DFTB (left) and DFT (right). Distances are given in Ångström.



Figure 3.4: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of anthracene. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [114].



Figure 3.5: Deformation in the  $S_1$  state of pentacene as calculated with DFTB. Due to the symmetry of the deformation, only half of the molecule is shown. Distances are given in Ångström.

DFT. We have calculated a vertical excitation energy of  $\Delta(\vec{R}_{\rm GS}) = 1.80 \text{eV}$  with DFTB and 1.60 eV with DFT. Optimization of the excited state yields an  $E_{0-0}$  energy of 1.61 eV for DFTB and 1.48 eV for DFT, which is again too low when compared to the experimental  $E_{0-0}$  energy of 2.12 eV [115]. The ground state bond distances and the deformation in the S<sub>1</sub> state is shown in figure 3.5. As was the case for anthracene, the internal bonds are hardly affected in the excited state while bond distances on the outside tend to become more uniform, with larger deformations in the outer rings of the molecule.

The vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum is shown in figure 3.6. The experimental spectrum was measured in a *n*-hexadecane Shpol'skii matrix at a temperature of 5K and therefore has a much better spectral resolution than the vapor absorption spectrum we used for comparison in case of anthracene. Both theoretical and experimental spectra show a strong absorption at the  $E_{0-0}$  energy, indicating that there is a large probability for the nuclei to remain in their vibrational ground state during photon absorption. Peak positions of the experimental spectrum are generally reproduced within 50cm<sup>-1</sup> by both DFTB and DFT. Intensities are also generally well reproduced, with the exception of a line at 750cm<sup>-1</sup> which is almost missing with DFTB and a line at 1320cm<sup>-1</sup> that is too intense. However, considering that embedding into different matrices yield slightly different experimental spectra [115], while our calculation corresponds to absorption in the gas phase, both DFT and DFTB are in excellent agreement with the experimental data.

It is interesting to note that the vertical excitation energy (arrows in figure 3.6) is a rather poor approximation to the absorption maxima for both DFT and DFTB: For DFTB it is clearly at too high energies and completely neglects the rather intense 0-0 transition. For DFT it is closer to the "mean absorption energy" but paradoxically ends up at an energy where pentacene does not absorb at all.

#### 3.3.3 Pyrene

Another interesting test system is pyrene, which is not only a precursor to dyes such as pyranine, but as the smallest peri-fused PAH also structurally rather different from the previous acene examples. Experimentally the absorption spectrum of pyrene



Figure 3.6: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of pentacene. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [115].

shows a weak band associated with excitation into the  $L_b$  state with an  $E_{0-0}$  energy of 3.36eV [127] and an intense band of absorption into the  $L_a$  state with  $E_{0-0} =$ 3.84eV [114]. Both DFT and DFTB erroneously predict the  $L_a$  state to be the S<sub>1</sub> state with vertical excitation energies of  $\Delta(\vec{R}_{\rm GS}) = 3.25$ eV with DFTB and 3.38eV with DFT. The excitation into the  $L_a$  state ( $B_{3u}$  symmetry) is dipole allowed with an oscillator strengths of f = 0.201 for DFTB and 0.211 for DFT. The deformation of the molecule upon excitation is shown in figure 3.7 and is dominated by an equilibration of bond lengths along the perimeter of the molecule. Comparing the total energies of ground and excited state we have found  $E_{0-0}$  energies of 2.97eV for DFTB and 3.17eV with DFT, both of which are too low compared to experiment.

The vibrational fine structure of the absorption into the  $L_a$  state (S<sub>1</sub> theoretically, S<sub>2</sub> experimentally) is shown in figure 3.8. The agreement between the theoretical spectra and experiment is almost perfect. This indicates that with DFT and DFTB the excited state potential energy surfaces are not distorted but merely shifted in energy, which is interesting considering that the shift is quite severe and even reverses the energetic ordering of  $L_a$  and  $L_b$  state with respect to experiment.

#### 3.3.4 Pentarylene

The examples so far were rather small molecules where even for DFT the calculation of the vibrational structure of the absorption band belonging to a single electronic excitation is computationally not a problem. For larger molecules or if multiple electronic states have to be considered, performance will be come an issue though. In



Figure 3.7: Deformation in the  $S_1$  state of pyrene as calculated with DFTB. Distances are given in Ångström.



Figure 3.8: Vibrational fine structure of the absorption into the  $L_a$  state of pyrene. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [114].



Figure 3.9: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of pentarylene. The arrows mark the vertical excitation energies. DFT/BH-LYP results from Ref. [95]. Experimental spectrum from Ref. [116].

order to investigate these computational aspects, we have calculated the vibrational fine structure of the  $S_0 \rightarrow S_1$  transition in pentarylene. With 74 atoms, pentarylene is much larger than the previous example molecules.

The S<sub>1</sub> state in pentarylene has  $B_{3u}$  symmetry and the transition from the ground state is strongly dipole allowed with oscillator strengths of f = 1.58 with DFTB and 1.48 with DFT. The calculated  $E_{0-0}$  energies (1.38eV for DFTB, 1.31eV for DFT) again underestimate the experimental value of 1.66eV [116]. The vibrational structure of the absorption band is shown in figure 3.9. The agreement of the calculated spectra with experiment is rather bad: Both DFT/PBE and DFTB show a dominating 0-0 transitions, while the experimental spectrum is fairly wide and features at least 4 distinct maxima of decreasing intensity [116]. This difference indicates that the geometry deformation between ground and excited state is underestimated with both DFT/PBE and DFTB, making the overlap between the nuclear ground state wavefunctions too large and the 0-0 transition too likely. This was also observed by Dierksen and Grimme, who have found that a large ratio of exact exchange (50% with the BH-LYP functional) is needed in order to reproduce the experimental spectrum [95]. However, even though DFT/PBE and DFTB both disagree with experiment, they agree very well with each other, indicating that the deficiency is already present at the level of DFT with GGA functionals and was not introduced with the additional approximations in DFTB.

Looking at the computational performance, it is clear that the calculation of vibrational frequencies in the excited state is the bottleneck for these calculations. With the numerical differentiation of the analytical gradient,  $6N_{\text{atom}}$  single point TD-DFT(B) calculations are necessary to determine the Hessian. Running on an Intel
Core i7-4770 CPU the entire calculation took 49 hours for DFT, out of which 43 hours were spent on the excited state Hessian. With DFTB it is also the evaluation of the Hessian that takes the most time, but the entire calculation finishes within 7 minutes, which is a speedup by a factor of 420 when compared to DFT.

#### 3.3.5 Octatetraene

In addition to the aromatic compounds covered in the previous sections, polyenes are another class of systems known for their optical properties: On the one hand they exhibit intensely absorbing  $\pi \to \pi^*$  transitions, the energy of which can be tuned through the number of conjugated double bonds, making them excellent dyes. On the other hand they can also undergo *cis-trans* isomerization upon absorption of a photon; a process critical in the biochemical conversion of radiative into chemical energy.

Our specific example is the excitation into  $1^1B_u$  state in all-trans octatetraene. This transition is strongly dipole allowed with an oscillator strength of f = 1.14 with DFTB, and 1.40 with DFT. For both DFTB and DFT this is the S<sub>1</sub> state with vertical excitation energies of  $\Delta(\vec{R}_{\rm GS}) = 3.83 \text{eV}$  for DFTB and 3.78eV for DFT. However, experimentally a weak dipole-forbidden absorption into the  $2^1A_g$  state is observed at  $E_{0-0} = 3.60 \text{eV}$  [128], while absorption into the  $1^1B_u$  state only starts at  $E_{0-0} = 4.40 \text{eV}$  [117]. Optimization of the  $1^1B_u$  excited state leads to an equilibration of bond lengths, in which double bonds stretch and single bonds contract. This is shown in figure 3.10. The calculated  $E_{0-0}$  energies are 3.44eV with DFTB and 3.53eV with DFT, both of which are almost 1eV too low compared to experiment.

The vibrationally resolved absorption into the  $1^1B_u$  state is shown in figure 3.11. While both DFTB and DFT predict the experimentally seen, very intense 0-0 transition, the rest of the spectrum is rather poorly described. The most pronounced peaks in the experimental spectrum are found at 1235 cm<sup>-1</sup> and 1645 cm<sup>-1</sup>. Additional absorption peaks are seen at  $2880 \text{cm}^{-1} = (1235 + 1645) \text{cm}^{-1}$  and  $3290 \text{cm}^{-1} = 2 \times 1645 \text{cm}^{-1}$ , corresponding to combined and double excited modes respectively [117]. Compared to the experimental spectrum, both calculated spectra show the prominent peaks at slightly lower energies: With DFTB the corresponding modes are found at  $1125 \text{cm}^{-1}$ and  $1570 \text{cm}^{-1}$ , with the combined and double nuclear excitations visible at  $2695 \text{cm}^{-1}$ and  $3140 \text{ cm}^{-1}$ . Additionally there are rather intense peaks at  $331 \text{ cm}^{-1}$  and  $1460 \text{ cm}^{-1}$ . which were not observed in the experimental spectrum. However, the spectra obtained with DFTB and DFT are almost identical, indicating that these deficiencies are already present at the DFT/GGA level and have not been introduced through the additional approximations in DFTB. As was the case for the PAHs, Dierksen and Grimme have found that the DFT results can be improved by inclusion of exact exchange in the exchange-correlation functional, though for octate traene they have found that an



Figure 3.10: Deformation in the  $1^1B_u$  state of octatetraene as calculated with DFTB. Distances are given in Ångström.



Figure 3.11: Vibrational fine structure of the absorption into the  $1^1B_u$  state of octatetraene. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [117]

especially large amount of exact exchange (>50%) is required for a better agreement with the experimental data.

#### 3.3.6 Stilbene

The optical properties of stilbene are used in various technical applications such as dye lasers, optical brighteners and as a scintillator material. In addition to its technical importance it is also an interesting test system due to the fact that it contains both a conjugated double bond and aromatic rings.

We have studied the  $S_0 \rightarrow S_1$  excitation in *trans*-stilbene. The  $S_1$  state has  $B_u$  symmetry and the absorption is a strongly dipole allowed  $\pi \rightarrow \pi^*$  transition with an oscillator strengths of f = 0.83 for DFTB and 0.85 for DFT. The calculated vertical excitation energies of  $\Delta(\vec{R}_{GS}) = 3.74$ eV from DFTB and 3.60eV agree surprisingly well with the experimental  $E_{0-0}$  energy of 3.80eV [118], though the experimental value was measured in a methyl pentane solution, so a solvent induced shift should be kept in mind. Optimization of the excited state shows the strongest change in geometry at the central double bond and smaller displacements further away, see figure 3.12. The calculated  $E_{0-0}$  energies of 3.34eV with DFTB and 3.32eV with DFT are too small compared to the experimental value of 3.80eV, though the relative error is small compared to some other examples.

The vibrational fine structure of the  $S_0 \rightarrow S_1$  transition in *trans*-stillene is shown in figure 3.13. While peak positions are relatively well described, both DFT and DFTB overestimate the intensity of the 0-0 transition, indicating that the geometric displacement between ground and excited state is underestimated. The same problem



Figure 3.12: Deformation in the  $S_1$  state of *trans*-stilbene as calculated with DFTB. Distances are given in Ångström.



Figure 3.13: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of *trans*-stilbene. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [118].



Figure 3.14: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of anisole. Vertical excitation energies are outside of the plotted spectral range. The experimental spectrum from Ref. [119] has been scaled to match the intensity of the feature at 750cm<sup>-1</sup> with the one calculated from DFT.

was also observed for the pentarylene example, where it was found that a larger amount of exact exchange improves the results [95]. This is also the case for the  $S_0 \rightarrow S_1$  transition in *trans*-stilbene, where Dierksen and Grimme have found that 30–40% of exact exchange give the best agreement with experiment.

#### 3.3.7 Anisole

Moving away from pure hydrocarbons, we have calculated the excitation into the  $1^{1}A'$  state of anisole. The  $1^{1}A'$  state is the  $S_{1}$  at the ground state's equilibrium geometry and its excitation is dipole allowed with an oscillator strength of 0.03 and 0.036 for DFT and DFTB, respectively. With  $E_{0-0}$  energies of 4.22eV with DFTB and 4.38eV with DFT, both methods slightly underestimate the experimental 0-0 energy of 4.51eV. Compared to the ground state geometry, all bonds in the benzene ring expand upon excitation. It is interesting to note that this expansion is larger for DFTB, with a maximum bond elongation of 7pm compared to 4pm with DFT. Furthermore the C-N bond within the methoxy group elongates slightly upon excitation in DFT, while it shrinks by 2pm for DFTB.

The vibrational fine structure of the transition is shown in figure 3.14. With the exception of two peaks at  $100 \text{cm}^{-1}$  and  $860 \text{cm}^{-1}$ , DFT at the GGA level reproduces the experimental spectrum [119] very well. (A spectrum calculated with the B3LYP hybrid functional can be found in Ref. [96] and is almost identical to the GGA calculation.) DFTB qualitatively reproduces the experimental spectrum but compared

to DFT shows larger deviations in peak positions. Peak intensities also seem to be worse with DFTB at first sight. However, one should keep in mind that the experimental data has been scaled to match the intensity of the feature at  $750 \text{cm}^{-1}$  to the DFT spectrum. Nevertheless, considering the entire spectral range (including the region >  $1800 \text{cm}^{-1}$  not shown in figure 3.14), DFTB predicts larger intensities further away from the 0-0 origin. This is consistent with the larger geometric deformation seen in the excited state with DFTB, which due to the displaced minima requires more vibrational quanta in the excited state to reach overlap with the original nuclear wavefunction.

#### 3.3.8 Coumarin dye C480

As an example of a heterocyclic compound we have chosen the coumarin dye C480 (structure inlayed in figure 3.16). As a typical dye molecule, coumarin C480 has a strongly dipole allowed  $S_0 \rightarrow S_1$  transition with  $\pi \rightarrow \pi^*$  character (HOMO  $\rightarrow$  LUMO). We have calculated 0-0 energies of 2.73eV and 2.77eV with DFT and DFTB, respectively. As for all other compounds, both methods underestimate the experimental 0-0 energy of  $\approx 3.22eV$  determined from the inset of the first band in the absorption spectrum measured in methylcyclohexane [99]. The deformation upon excitation is shown in figure 3.15 and is mostly restricted to the core coumarin and the C-N bond linking the nitrogen atom to the coumarin unit. Especially noteworthy is the very strong elongation (+12pm for DFTB; +10pm for DFT) of the C-O bond between the heterocyclic oxygen and the carbonyl carbon. The deformation upon excitation is very similar for DFT and DFTB, although, as was already observed in previous examples, DFTB predicts overall slightly larger deformations.

The vibrational fine structure of the  $S_0 \rightarrow S_1$  transition in C480 is shown in figure 3.16. The DFT calculated spectrum agrees very well with the experimental absorption spectrum measured in methylcyclohexane [99], though contrary to experiment, DFT predicts the first absorption maximum to be slightly more intense than the second. For DFTB the relative intensities of the two maxima agree with experiment, but the absorption band is overall slightly wider, which we attribute to the larger geometric deformations seen in DFTB.

The coumarin C480 dye has recently also been used by Muniz-Miranda et al. in a benchmark study [99] investigating the performance of different (global and rangeseparated hybrid) exchange-correlation functionals on the vibronic structure and absolute band positions. The authors found that the  $\omega$ B97X functional [129] predicts the best spectral shapes but that no single functional simultaneously provides accurate band positions and shapes. In fact  $\omega$ B97X overestimates the  $E_{0-0}$  energy by about as much as we have found PBE to underestimate it. GGA functionals were unfortunately not included in the comparison in Ref. [99], but considering our results, the system seems to be sufficiently well described at the GGA level and by extension with DFTB.

#### 3.3.9 Bithiophene

As another example for a heterocyclic compound we have calculated the  $S_1 \rightarrow S_0$  fluorescence spectrum of planar *trans*-2,2'-bithiophene. The fluorescence of bithiophene has recently also been used in a benchmark study [98] by Stendardo et al. investigating



Figure 3.15: Deformation in the  $S_1$  state of the coumarin dye C480 as calculated with DFTB (top) and DFT (bottom). Distances are given in picometers.



Figure 3.16: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of the coumarin dye C480. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [99].

the effect of different exchange-correlation functionals on the vibrational fine structure of the emission line. The **3ob:freq** parameter set used so far does not include parameters for sulfur. However, different versions of the **3ob** set are cross compatible among each other, so that sulfur parameters from a newer version (with sulfur repulsive potentials not specifically optimized for frequency calculations) were used. For planar bithiophene the S<sub>1</sub> has  $1^{1}B_{u}$  symmetry and we have calculated 0-0 energies of 3.38eV and 3.30eV with DFT and DFTB, respectively. As with all examples so far, this underestimates the experimental  $E_{0-0}$  of 3.86eV.

The fluorescence spectrum of bithiophene is shown in figure 3.17. Both DFT and DFTB show very good agreement in peak positions compared to experiment [130]. The biggest difference between the DFT and DFTB calculated spectra is the relative intensity of the two intense features at  $700 \text{cm}^{-1}$  and  $1450 \text{cm}^{-1}$ . Here DFT predicts a higher intensity of the  $700 \text{cm}^{-1}$  peak, while DFTB predicts the opposite. Stendardo et al. have pointed out that the relative intensity of the two features is extremely sensitive to the choice of the functional, and furthermore depends strongly on the experimental conditions, with the  $1450 \text{cm}^{-1}$  peak being much more intense in a hexane matrix [130] than in a jet-cooled beam [120]. It appears that both DFT and DFTB underestimate to overall intensity in the spectral region  $< -1500 \text{cm}^{-1}$ . However, the experimental spectrum has been scaled to match the intensity of the feature at  $390 \text{cm}^{-1}$  with the one calculated from DFT, so absolute intensities should not be overinterpreted.



Figure 3.17:  $S_1 \rightarrow S_0$  fluorescence spectrum of bithiophene. The experimental spectrum from Ref. [130] has been scaled to match the intensity of the feature at 390cm<sup>-1</sup> with the one calculated from DFT.

#### 3.3.10 Triazoline

The last example we want to look at is the  $S_0 \rightarrow S_1$  excitation in 4-H-1,2,4-triazoline-3,5-diones. As opposed to the other examples, which were  $\pi \rightarrow \pi^*$  transitions, the  $S_0 \rightarrow S_1$  transition in triazoline has  $n \rightarrow \pi^*$  character. This is an interesting test case as TD-DFTB is known to fail for  $\sigma \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions in that it predicts zero oscillator strengths and vanishing singlet-triplet gaps [54]. We therefore expect to see significant differences in the spectra calculated with (TD-)DFTB and (TD-)DFT at the GGA level, which is in contrast to the close correspondence we have observed for the other systems. Note that TD-DFTB's failure for these transitions has recently been corrected by Domínguez et al. through inclusion of one-center integrals of the exchange type [54]. However, this so-called on-site correction to TD-DFTB is fairly involved and analytical excited state gradients are not yet available. We will hence restrict our discussion to TD-DFTB in its original formulation [41].

The  $S_0 \rightarrow S_1$  excitation in triazoline is very weakly dipole-allowed with an oscillator strength of f = 0.0006 for DFT, while DFTB mispredicts the oscillator strength to be exactly zero due to the above mentioned problem. Optimization of the excited state with DFTB leads to a stretching of the N-N double bond and a shrinking of the adjacent C-N bond. This is shown in figure 3.18. The calculated  $E_{0-0}$  energies are 1.60eV with DFTB and 1.42eV with DFT, both of which are considerably too low compared to the experimental value of 2.15eV [121].

The vibrational structure of the absorption band is shown in figure 3.19. DFTB indeed predicts a qualitatively wrong spectrum in which the 0-0 transition has the highest intensity, while both DFT and the experimental spectrum have their absorption



Figure 3.18: Deformation in the  $S_1$  state of triazoline as calculated with DFTB. Distances are given in Ångström.



Figure 3.19: Vibrationally resolved  $S_0 \rightarrow S_1$  absorption spectrum of triazoline. The arrows mark the vertical excitation energies. Experimental spectrum from Ref. [121].

maximum around 1000 cm<sup>-1</sup>. The spectrum obtained with DFT is overall too wide when compared to experiment, but according to Dierksen and Grimme this problem can be resolved by using hybrid exchange-correlation functionals [95].

## 3.4 Conclusion

We have shown that DFTB is an excellent and computationally very efficient approximation to DFT at the GGA level for the calculation of the vibronic fine structure of UV/Vis absorption bands. Using the recent **3ob:freq** parameter set [112, 131] very good agreement with DFT calculated spectra was achieved at a fraction of the computational cost.

We have found that experimentally measured vibrational fine structures are often reproduced by GGA DFT and DFTB, even when absolute excitation energies are in significant error compared to experiment. This shows that the shape of the excited state potential energy surface is well reproduced in both GGA DFT and DFTB, even though the surface may be shifted in energy.

In cases such as pentarylene and stilbene, where the experimentally seen vibronic structure is not well reproduced by DFT at the GGA level and DFTB, better agreement with experiment can usually be obtained using hybrid exchange-correlation functionals [95]. While this is relatively straightforward and well established in DFT, work on including exact exchange in the DFTB framework has only recently begun [90, 132, 133] and analytical TD-DFTB gradients are not yet available for these extensions.

The only example where we found a large discrepancy between DFT and DFTB was the  $S_0 \rightarrow S_1$  excitation in triazoline. This is caused by the known failure of TD-DFTB for  $n \rightarrow \pi^*$  transitions which was recently removed by Domínguez et al. with the so-called on-site correction [54]. However, since analytical gradients are not yet available for on-site corrected DFTB, it can presently not be used efficiently for the calculation of vibronic fine structures.

In summary, we believe that the good performance of (TD-)DFTB for the calculation of vibronic effects in UV/Vis spectra makes the inclusion of these effects possible for applications where they would previously have been neglected due to their computational cost. Care should be taken when the method is applied to excitations with  $\sigma \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  character or excitations that are not well described by (TD-)DFT at the GGA level. However, both these restrictions are likely to be lifted with recent DFTB extensions, i.e. on-site correction [54] and inclusion of exact exchange [90, 132, 133], which due to the lack of analytical (excited state) gradients, can not yet be used for the calculation of vibronic fine structure.

# 4 A combined DFT and TD-DFTB method

## 4.1 Introduction

Owing its success to the good compromise between accuracy and computational cost, density functional theory (DFT) based on the theorems [5] by Hohenberg and Kohn and employing the Kohn-Sham ansatz [7] for the kinetic energy has become the most widely used method in both quantum chemistry and solid state theory over the last few decades. Rooted in the Kohn-Sham DFT framework, density functional based tight binding (DFTB) [30, 31] has been developed as a computationally very efficient approximation to DFT for systems too large to be treated with its parent method. DFTB's efficiency stems from the use of an optimized minimum valence orbital basis that reduces the linear algebra operations, and a two center-approximation for the Kohn-Sham potential that allows precalculation and storage of integrals using the Slater-Koster technique [35]. The self-consistent charge extension (SCC-DFTB, recently also called DFTB2) [32] accounts for density fluctuations and improves results for systems with polar bonds. A further extension known as DFTB3 [40] has been developed to improve the description of hydrogen-bonded complexes and proton affinities. While DFTB is much more efficient than DFT it requires careful parametrization for all involved elements in order to yield accurate results. The limited availability of these parameters has historically slowed down the adoption of DFTB, but general purpose parameter sets covering large parts of the periodic table have recently become available [36, 39, 112, 131, 134, 135].

As the Hohenberg-Kohn theorems only concern the ground state of a system, density functional theory is not applicable to the broad class of problems involving electronically excited states. The foundation for the excited state extension known as time-dependent density functional theory (TD-DFT) was later laid by Runge and Gross, who generalized Hohenberg and Kohn's theorems to time-dependent external potentials [23]. Based on their work, Casida calculated the linear response of the electron density to a perturbation in the external potential and from this derived an eigenvalue equation in the space of single orbital transitions from which the excited states of the electronic system can be obtained [29]. In the field of quantum chemistry, Casida's TD-DFT approach is today probably the most widely used method for the calculation of excited state properties. A recent review of TD-DFT can be found in reference 46.

An excited state calculation using TD-DFT is computationally quite demanding, much more so than the underlying DFT calculation of the ground state. For many systems it is therefore feasible to calculate the ground state, while a calculation of excited states is computationally out of reach. Various ways to reduce the computational complexity of TD-DFT have been put forward; based for example on partitioning into subsystems [136, 137], neglect of terms [42, 43, 45], truncation of the single orbital transition space [1, 43] and approximation of integrals [41, 43–45, 50, 54]. Among the methods that approximate integrals is time-dependent density functional theory based tight binding (TD-DFTB) [41, 50, 54] developed by Niehaus et al., which builds on a DFTB ground state calculation and translates Casida's linear response approach to the framework of DFTB. It has been found to yield very good results for  $\pi \to \pi^*$  transitions [41], making it especially suitable for the calculation of UV/Vis absorption spectra [1]. Being computationally much cheaper than a full TD-DFT calculation and applicable to very large systems, TD-DFTB has been used in a variety of applications [56–65] in which TD-DFT would not have been feasible. A review of TD-DFTB can be found in reference 53.

TD-DFTB inherits certain limitations from the DFTB ground state calculation it is based on: The electronic structure from DFTB, which is the basis of the excited state calculation, is of limited accuracy compared to a DFT calculation with a reasonable choice of exchange-correlation functional and orbital basis. Furthermore, whereas TD-DFT can be used for any system, historically the applicability of TD-DFTB was restricted to systems involving only elements for which DFTB parameters are available. With the development of the QUASINANO parameters, which are available throughout the periodic table, by Wahiduzzaman et al. [36] this drawback was removed for the electronic part (and thus for TD-DFTB), even though TD-DFTB still requires a careful performance validation for the target system class.

These limitations are insofar particularly unfortunate as it is neither the calculation of the ground state's electronic structure that is the computational bottleneck, nor requires the application of tight-binding approximations to the TD-DFT concept within Casida's formulation any parameterization effort. In this chapter we introduce TD-DFT+TB, a new method for calculating electronically excited states that combines a DFT ground state with a linear response treatment that employs approximations similar to the ones used in TD-DFTB. We show that the cost of this calculation is approximately the same as of a ground state DFT calculation, and the accuracy of the excited state properties is much better than TD-DFTB.

The approach proposed in this chapter is inspired by and closely related to the sTDA [43, 45] and sTD-DFT [44] methods developed by Grimme et al., which also use a DFT ground state calculation and make TD-DFTB like approximations in Casida's formalism. The main difference compared to our approach is, that these methods are based on DFT with a hybrid exchange-correlation functional [138]. Hybrid functionals are usually employed to correct the underestimated charge-transfer excitation energies in TD-DFT with local functionals. However, we argue that for the calculation of optical absorption spectra, underestimated charge-transfer excitation energies only constitute a technical problem that can be solved conceptually easier and computationally more efficient by employing a physically motivated truncation of the single orbital transition space [1]. Furthermore, it was recently shown [21, 22] by Baerends et al. that excitations loose their single orbital transition character with the admixture of Hartree-Fock exact exchange, which complicates the interpretation of the results. We therefore believe that the calculation of excited states of large systems should also be approached from a pure density functional standpoint. Both sTDA and sTD-DFT have been developed for hybrid functionals and contain free parameters that have been fitted to yield good results between 20% and 60% exact exchange. As such, they are not intended for and can not directly be used with local functionals. We believe that TD-DFT+TB as proposed in this chapter complements sTDA and sTD-DFT by making approximate TD-DFT methods also available for local exchange-correlation functionals.

The remainder of this chapter is organized as follows. In section 4.2 we recapitulate the most important equations from DFT and DFTB as well as their linear response extensions in order to set the stage for section 4.3, in which we motivate and introduce TD-DFT+TB. We will also discuss its relation to other approximate TD-DFT methods, such as TD-DFTB, sTDA and sTD-DFT. In section 4.4 we evaluate the accuracy and performance of the new method by calculating vertical excitation energies for a benchmark set of molecules as well as the UV/Vis absorption spectra of selected compounds. Section 4.5 summarizes our results and concludes the chapter.

## 4.2 Review of methods

In order to establish the notation for the remainder of this chapter, this section contains a short summary of DFT and DFTB as well as their linear response extensions.

#### 4.2.1 Molecular orbitals from DFT(B)

Electronic structure calculations of molecular systems typically use atom centered basis functions  $\chi_{\mu}(\vec{r})$ , so that the molecular orbitals  $\phi_i(\vec{r})$  can be written as

$$\phi_i(\vec{r}) = \sum_{\mathcal{A}}^{N_{\text{atom}}} \sum_{\mu \in \mathcal{A}} c_{\mu i} \chi_\mu(\vec{r}) .$$
(4.1)

The basis functions  $\chi_{\mu}(\vec{r})$  are composed of primitives that may be Gaussian, Slater, numerical or any other functions that are centered at the atomic positions. For DFT the size of the basis is variable and can within the limits of computational affordability be chosen according to the desired accuracy, while DFTB on the other hand typically uses an optimized minimum valence orbital basis that is fixed during the DFTB parameter creation, and can not be changed at run-time.

The expansion coefficients  $c_{\mu i}$  of the molecular orbitals are obtained by solving the secular equations

$$\sum_{\nu} H_{\mu\nu} c_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i} .$$
(4.2)

Here,

$$S_{\mu\nu} = \int \mathrm{d}\vec{r} \,\chi_{\mu}(\vec{r})\chi_{\nu}(\vec{r}) \tag{4.3}$$

is the overlap between basis functions. In DFT, the Hamiltonian matrix elements  $H_{\mu\nu}$  are calculated as

$$H_{\mu\nu} = \int d\vec{r} \,\chi_{\mu}(\vec{r}) \left( -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\vec{r}) \right) \chi_{\nu}(\vec{r}) \,, \tag{4.4}$$

where

$$v_{\rm eff}(\vec{r}) = v_{\rm ext}(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\vec{r})}$$
(4.5)

is the Kohn-Sham effective potential [7], consisting of the external potential, an electrostatic term and the so-called exchange-correlation potential. Note that the effective potential  $v_{\text{eff}}(\vec{r})$  depends on the molecular orbitals themselves through their electronic density  $\rho(\vec{r})$ , so that equation (4.2) has to be solved self-consistently.

DFTB avoids the evaluation of integrals at run-time by replacing the actual density  $\rho$  by a trial density  $\rho_0$ . This trial density is a superposition of atomic contributions which are optimized within the parameterization process. Within the DFTB-inherent two-center approximation the effective potential is constructed by superposing two spherical atomic effective potentials [30, 31, 36] or trial densities [32, 40], which allows the Hamiltonian and overlap matrix elements to be precalculated and stored using the Slater-Koster technique [35]. This shifts the computational bottleneck from the calculation of matrix elements to linear algebra operations which are dominated by the diagonalization. Together with the small matrix sizes due to the minimal valence basis set, DFTB is computationally extremely efficient.

#### 4.2.2 Excited states and absorption spectra from TD-DFT

Once the electronic structure of the ground state has been determined, excited states can be calculated using Casida's linear response approach [29], which casts the problem of calculating excitation energies and excited states into an eigenvalue equation in the  $N_{\rm trans} = N_{\rm occ} N_{\rm virt}$  dimensional space of single orbital transitions. The eigenvalue problem can be written as

$$\sum_{jk} \Omega_{ia,jb} F_{jb,I} = \Delta_I^2 F_{ia,I} , \qquad (4.6)$$

where  $\Delta_I$  is the vertical excitation energy of the *I*-th excited state. We adopt the usual convention of using the indexes i, j for occupied and a, b for virtual orbitals. The elements  $F_{ia,I}$  correspond to the contribution of the transition from the occupied orbital  $\phi_i$  to the virtual orbital  $\phi_a$  and can be used to construct an approximate excited state wavefunction  $|\psi\rangle$  from the Slater determinant  $|\psi_0\rangle$  of the occupied Kohn-Sham orbitals [29].

$$|\psi_I\rangle = \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_I}} F_{ia,I} \, \hat{c}_a^{\dagger} \hat{c}_i \, |\psi_0\rangle \tag{4.7}$$

Here we use  $\Delta_{ia} = \varepsilon_a - \varepsilon_i$  for the difference in orbital energy between the involved Kohn-Sham orbitals. The elements of the matrix  $\boldsymbol{\Omega}$  are given by

$$\Omega_{ia,jb} = \delta_{ij}\delta_{ab}\Delta_{ia}^2 + 4\sqrt{\Delta_{ia}\Delta_{jb}}K_{ia,jb} , \qquad (4.8)$$

and looking back at equation (4.6), it is easy to see that it is the so-called coupling matrix K that shifts the excitation energies  $\Delta_I$  away from the orbital energy differences  $\Delta_{ia}$ . The coupling matrix depends on the multiplicity of the calculated excitations. For the sake of clarity we will restrict our discussion to singlet excitations for the moment. Triplet excitations pose no additional problems and their calculation will be discussed later. For singlet excitations in TD-DFT the elements of the coupling matrix are given by

$$K_{ia,jb}^{\rm S} = \int d^3 \vec{r} \int d^3 \vec{r}' \phi_i(\vec{r}) \phi_a(\vec{r}) \times f_{\rm Hxc}[\rho^{\rm GS}](\vec{r},\vec{r}') \phi_j(\vec{r}') \phi_b(\vec{r}') , \qquad (4.9)$$

where the kernel

$$f_{\rm Hxc}[\rho^{\rm GS}](\vec{r},\vec{r}') = \frac{1}{|\vec{r}-\vec{r}'|} + \frac{\delta^2 E_{\rm xc}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\Big|_{\rho^{\rm GS}}$$
(4.10)

incorporates both a Coulomb term and the second derivative of the DFT exchangecorrelation functional  $E_{\rm xc}[\rho]$ .

For the prediction of photon absorption spectra it is necessary to calculate both the excitation energies  $\Delta_I$  as well as the corresponding transition dipole moments  $\vec{d_I}$ . Excitation energies are immediately obtained as the eigenvalues of Casida's equation (4.6), and using the eigenvector elements  $F_{ia,I}$  the transition dipole moments  $\vec{d_I}$ can be calculated as a linear combination of the transition dipole moments  $\vec{d_{ia}}$  of the single orbital transitions.

$$\vec{d}_I = \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_I}} F_{ia,I} \, \vec{d}_{ia} \tag{4.11}$$

Here the transition dipole moments  $\vec{d}_{ia}$  of the single orbital transitions are calculated as

$$\vec{d}_{ia} = \int d^3 \vec{r} \, \phi_i(\vec{r}) \phi_a(\vec{r}) \, \vec{r} \,. \tag{4.12}$$

In order to make a connection to experimentally measured quantities, the theoretically calculated oscillator strengths  $f_I$  and excitation energies  $E_I$  can be related [139] to the molar absorptivity

$$\epsilon(E) = \frac{\pi}{2\ln(10)} \frac{N_A e^2 \hbar}{m_e c \varepsilon_0} \sum_I f_I \Gamma(E - E_I) . \qquad (4.13)$$

Here  $\Gamma(E)$  is a normalized, typically peaked function that models the experimental line broadening. Both Gaussian and Lorentzian functions are common choices for  $\Gamma(E)$ .

It would be beyond the scope of this chapter to go into further details on the properties and problems of TD-DFT. A recent review of the strengths and weaknesses of TD-DFT in general can be found in reference 46. There is also an excellent book on TD-DFT, see reference 140. The method put forward in this chapter presents an approximation to TD-DFT and we therefore consider TD-DFT with a GGA exchange-correlation functional as the reference method.

#### 4.2.3 TD-DFTB as an approximation to TD-DFT

The calculation of the TD-DFT coupling matrix elements involves expensive twocenter integrals and even though highly optimized implementations are available [52], evaluating the integrals is still the computational bottleneck of the method. In order to make density functional based excited state calculations applicable to larger systems, Niehaus et al. have put forward TD-DFTB [41, 54], which builds on top of a DFTB ground state calculation and uses DFTB-like approximations for the coupling matrix elements: The transition density  $\phi_i(\vec{r})\phi_a(\vec{r})$  in equation (4.9) is subjected to a multipole expansion truncated at first order (monopole approximation)

$$\phi_i(\vec{r})\phi_a(\vec{r}) \approx \sum_{\mathcal{A}} q_{ia,\mathcal{A}} \,\xi_{\mathcal{A}}(\vec{r}) \,, \qquad (4.14)$$

where  $\xi_{\mathcal{A}}(\vec{r})$  is a spherically symmetric function centered on atom  $\mathcal{A}$ . This allows the singlet-singlet coupling matrix elements in TD-DFTB to be written as

$$K_{ia,jb}^{\rm S} = \sum_{\mathcal{AB}} q_{ia,\mathcal{A}} \, \gamma_{\mathcal{AB}} \, q_{jb,\mathcal{B}} \, . \tag{4.15}$$

The so-called atomic transition charges  $q_{ia,\mathcal{A}}$  are calculated from the molecular orbital coefficient and overlap matrix C and S using Mulliken population analysis [34].

$$q_{ia,\mathcal{A}} = \frac{1}{2} \sum_{\mu \in \mathcal{A}} \sum_{\nu} \left( c_{\mu i} S_{\mu \nu} c_{\nu a} + c_{\nu i} S_{\nu \mu} c_{\mu a} \right)$$
(4.16)

While  $\gamma_{\mathcal{AB}}$  should in principle be calculated as a two-center integral over the product of the atom centered functions  $\xi_{\mathcal{A}/\mathcal{B}}$  and the kernel  $f_{\text{Hxc}}$  from equation (4.10), it is in practice approximated as a function

$$\gamma_{\mathcal{A}\mathcal{B}} = \gamma_{\mathcal{A}\mathcal{B}} \left( \eta_{\mathcal{A}}, \eta_{\mathcal{B}}, \left| \vec{R}_{\mathcal{A}} - \vec{R}_{\mathcal{B}} \right| \right)$$
(4.17)

of the internuclear distance and the chemical hardness  $\eta_{\mathcal{A}}$  and  $\eta_{\mathcal{B}}$  of atom  $\mathcal{A}$  and  $\mathcal{B}$  respectively, converging to the Coulomb interaction between two point charges for long distances [32, 41]. The required atomic chemical hardness is not a free, tunable parameter, but rather an inherent property of the atoms themselves. There is, however, some freedom in the choice of the method used to obtain these values, e.g. from atomic DFT calculations by application of Janak's theorem [32, 141, 142], or using a phenomenological model [38].

So far our discussion has been restricted to singlet-singlet excitations. For the calculation of singlet-triplet excitations the only change required is in the coupling matrix elements, which for singlet-triplet excitations in TD-DFTB are given by

$$K_{ia,jb}^{\mathrm{T}} = \sum_{\mathcal{A}} q_{ia,\mathcal{A}} W_{\mathcal{A}} q_{jb,\mathcal{A}} .$$
(4.18)

Here the so called magnetic Hubbard parameters  $W_{\mathcal{A}}$  are defined as

$$W_{\mathcal{A}} = \frac{1}{2} \left( \frac{\partial \varepsilon_{\uparrow}^{\text{HOMO}}}{\partial n_{\uparrow}^{\text{HOMO}}} - \frac{\partial \varepsilon_{\uparrow}^{\text{HOMO}}}{\partial n_{\downarrow}^{\text{HOMO}}} \right) .$$
(4.19)

and can be calculated from atomic DFT calculations just like the chemical hardnesses.

In addition to the approximation of the coupling matrix, TD-DFTB also approximates the transition dipole moments  $\vec{d}_{ia}$  of the single orbital transitions. With the monopole approximation of the transition density from equation (4.14) the transition dipole moments of the single orbital transitions are easily written as [41]

$$\vec{d}_{ia} = \sum_{\mathcal{A}} q_{ia,\mathcal{A}} \vec{R}_{\mathcal{A}} .$$
(4.20)

One rather obvious limitation of the monopole approximation in equation (4.14) is that basis functions  $\chi_{\mu}$  and  $\chi_{\nu}$  residing on the same atom  $\mathcal{A}$  do not contribute to the atomic transition charge  $q_{ia,\mathcal{A}}$ . This leads to vanishing (or underestimated) transition charges for excitations involving localized molecular orbitals  $\phi_i$  and  $\phi_a$ , such as  $\sigma \to \pi^*$ and  $n \to \pi^*$  promotions. Due to the vanishing coupling matrix elements  $K_{ia,jb}$ these excitations are then predicted to be pure single orbital transitions  $\phi_i \to \phi_a$ with an excitation energy  $\Delta_I = \Delta_{ia}$  exactly. Furthermore, their transition dipole moment  $\vec{d}_I = \vec{d}_{ia}$  is predicted to be zero. This failure has recently been corrected by Domínguez et al. through inclusion of one-center integrals of the exchange type [54]. However, this so-called on-site correction to TD-DFTB is fairly involved and we will restrict our discussion to TD-DFTB in its original formulation [41].

In summary, TD-DFTB is an approximation to TD-DFT that uses molecular orbitals obtained from a DFTB ground state calculation and approximates the coupling matrix and single orbital transition dipole moments in order to avoid integral evaluation at run-time. For a recent review of TD-DFTB we would like to refer the reader to reference 53.

### 4.3 TD-DFT+TB

#### 4.3.1 Motivation and introduction

In subsection 4.2.3 we have outlined how the TD-DFTB coupling matrix can be derived from its TD-DFT counterpart by making a monopole approximation for the transition density. While this is how TD-DFTB was originally introduced [41], it is interesting to note that the same equations can also be obtained as the linear response of the SCC-DFTB Hamiltonian [54], just like TD-DFT was obtained from the linear response of DFT [29]. In this sense all of the approximations that go into TD-DFTB have been done at the ground state level, and the subsequent excited state calculation is merely done consistently with the already present approximations.

This brings up an interesting question: Would more accurate results be obtained if the approximation was delayed until the linear response treatment? Or in other words, would it be better to do an approximate linear response of the DFT Hamiltonian than to look at the exact linear response of the SCC-DFTB Hamiltonian? In this chapter we want to propose to do TD-DFTB-like approximations in a linear response excited state calculation based on a DFT ground state. We will henceforth refer to this approach as TD-DFT+TB. The relationship between the different methods is illustrated in figure 4.1.

The basic idea of TD-DFT+TB is to use the molecular orbitals obtained from a DFT ground state calculation as input to an excited state calculation with the TD-DFTB coupling matrix from equation 4.15. Technically, this is very easy to do: Looking back at subsection 4.2.3 it is evident that the only information needed about the ground state is the overlap matrix S, the coefficient matrix C as well as the orbital energies  $\varepsilon_i$  and occupations. Additionally, the information about which atom  $\mathcal{A}$  the basis function  $\chi_{\mu}$  is centered on is also needed for the population analysis. However, all of this information could also be provided by a DFT instead of a DFTB ground state calculation.

One important thing to note is that the basis sets used in DFT are typically larger than the minimal basis set used in DFTB. In fact, the pre-optimized DFTB ground state densities are typically of higher quality compared to those obtained using a minimum basis set DFT approach. Therefore, it is important to employ a DFT basis



Figure 4.1: Relationships among the different computational methods.

that gives a sufficiently accurate ground state, even though this leads to more virtual orbitals and hence a larger coupling matrix in TD-DFT+TB compared to TD-DFTB.

A problem associated with the larger basis set in DFT is that the Mulliken population analysis [34] used in TD-DFTB for the calculation of the atomic transition charges  $q_{ia,\mathcal{A}}$ is known to become unstable for large basis sets, especially if diffuse basis functions are included. While Mulliken analysis is working sufficiently well for the minimal atomic orbital basis set used in TD-DFTB, we have found that for a basis of TZP quality Mulliken transition charges only poorly represent the transition density. This was also observed by Grimme, who instead proposed [43] to use Löwdin population analysis [143] for which the atomic transition charges are calculated as

$$q_{ia,\mathcal{A}} = \sum_{\mu \in \mathcal{A}} c'_{\mu i} c'_{\mu a} \quad \text{with} \quad \mathbf{C}' = \mathbf{S}^{\frac{1}{2}} \mathbf{C} \;. \tag{4.21}$$

We have indeed found Löwdin transition charges to be much more reliable than the ones obtained from Mulliken population analysis, and therefore use Löwdin analysis as the default method of calculating transition charges in TD-DFT+TB. Benchmark results for both Mulliken and Löwdin transition charges can be found in section 4.4.1.

In TD-DFTB the atomic transition charges  $q_{ia,\mathcal{A}}$  are used in both the approximation of the  $(N_{\text{occ}} \times N_{\text{virt}})^2$  coupling matrix elements as well as the approximation of the  $(N_{\text{occ}} \times N_{\text{virt}})$  single orbital transition dipole moments  $\vec{d}_{ia}$ . While the former is what makes TD-DFTB so efficient, the latter has mostly technical reasons: The Slater-Koster files used in DFTB contain the matrix elements, but not the basis functions themselves, making it impossible to evaluate integrals over molecular orbitals at run time. This is a rather unpleasant deficiency introduced by the traditional DFTB Slater-Koster implementation. However, it is not a deficiency of the method itself, and with knowledge of the atomic orbitals obtained during the parameterization process and in combination with a suitable integral engine any expectation value can be calculated correctly using DFTB. This has been demonstrated for other properties, e.g. for NMR chemical shifts [144], and will be applied to the transition dipole matrix elements here. For TD-DFT+TB, we have two possibilities to compute the transition dipole moments:

- 1. The simplest, and most approximate, way is to use the point charge approximation as done in TD-DFTB. This approximation would be most attractive if TD-DFT+TB would be used by employing two independent codes (one for DFT and one for TD-DFTB). However, in our present case there is negligible computational performance gain, so we do not follow this line.
- 2. We calculate the transition dipole moments directly from the DFT molecular orbitals. Thus, we calculate the unapproximated single orbital transition dipole moments  $\vec{d}_{ia}$  from equation (4.12). In different words: We avoid here those TD-DFTB approximations that have been due to restrictions imposed by the Slater-Koster-type implementation and which are not resulting in significant performance gain.

One particularly attractive feature of TD-DFT+TB is that it does not rely at all on the DFTB parametrization. The only parameters used for the construction of the TD-DFTB coupling matrix are the chemical hardness  $\eta_{\mathcal{A}}$  (for singlet excitations) and the magnetic Hubbard  $W_{\mathcal{A}}$  parameter (for triplet excitations). These are just physical properties of the atoms that can be calculated and tabulated for the entire periodic table. We use the chemical hardness as tabulated by Ghosh and Islam [38] and have calculated the values for the magnetic Hubbard parameter  $W_{\mathcal{A}}$  using the same details as specified earlier [36]. The numerical values of  $W_{\mathcal{A}}$  are given in table 4.1. All other parameters entering DFTB which are needed for describing the ground state, i.e. the form of the basis functions, the effective potential, and the repulsive potential needed for calculating the total energy and its gradients are not needed to build the TD-DFTB coupling matrix. TD-DFT+TB is therefore directly applicable to systems containing any combination of elements without the need of further parameterization.

In summary, TD-DFT+TB can be interpreted either as applying DFTB approximations to the Casida equations, or, equivalently, as TD-DFTB based on molecular orbitals from DFT. Technical choices are the calculation of charges and transition dipole moments. We propose to employ Löwdin instead of Mulliken atomic transition charges, and DFT transition dipole moments, but other options are definitely possible. A summarizing comparison of TD-DFT, TD-DFTB and TD-DFT+TB is given in table 4.2.

#### 4.3.2 Relation to other methods

TD-DFT+TB as introduced in the last subsection is quite closely related to the sTDA [43, 45] and sTD-DFT [44] methods developed by Grimme and coworkers: These methods also use molecular orbitals from a DFT calculation and use the same atomic monopole approximation for the transition density (which was originally introduced with TD-DFTB) in order to avoid the calculation of integrals. The major difference is that TD-DFT+TB is a pure density functional approach, while sTDA and sTD-DFT use hybrid exchange-correlation functionals [138] in both the calculation of the ground state and the excited states.

The primary reason why hybrid functionals with a fraction of exact Hartree-Fock exchange are often used in TD-DFT is that local functionals are known to drastically

Element	Z	$W_{\mathcal{A}}$ [Ha]
Н	1	-0.0717
He	2	-0.0865
Li	3	-0.0198
Be	4	-0.0230
В	5	-0.0196
С	6	-0.0226
Ν	7	-0.0254
0	8	-0.0278
F	9	-0.0298
Ne	10	-0.0317
Na	11	-0.0152
Mg	12	-0.0166
Al	13	-0.0140
Si	14	-0.0144
Р	15	-0.0149
S	16	-0.0155
Cl	17	-0.0161
Ar	18	-0.0166
Κ	19	-0.0107
Ca	20	-0.0120
$\operatorname{Sc}$	21	-0.0124
Ti	22	-0.0138
V	23	-0.0141
$\operatorname{Cr}$	24	-0.0138
Mn	25	-0.0150
Fe	26	-0.0154
Co	27	-0.0158
Ni	28	-0.0168
Cu	29	-0.0171
Zn	30	-0.0169
Ga	31	-0.0134
Ge	32	-0.0136
As	33	-0.0136
Se	34	-0.0137
$\operatorname{Br}$	35	-0.0138
$\mathbf{Kr}$	36	-0.0138
Rb	37	-0.0096
$\operatorname{Sr}$	38	-0.0107
Y	39	-0.0097
Zr	40	-0.0107
Nb	41	-0.0113
Mo	42	-0.0125
Tc	43	-0.0127
Ru	44	-0.0132
Rh	45	-0.0134

Table $4.1$ :	Values for	the mag	gnetic	Hubbard	parameters	$W_{\mathcal{A}}$ .

Element	Z	$W_{\mathcal{A}}$ [Ha]
Pd	46	-0.0136
Ag	47	-0.0137
Cd	48	-0.0138
In	49	-0.0115
Sn	50	-0.0117
Sb	51	-0.0116
Te	52	-0.0115
Ι	53	-0.0114
Xe	54	-0.0114
Cs	55	-0.0083
Ba	56	-0.0094
La	57	-0.0089
Ce	58	-0.0090
Pr	59	-0.0111
Nd	60	-0.0116
Pm	61	-0.0120
Sm	62	-0.0124
Eu	63	-0.0127
Gd	64	-0.0091
Tb	65	-0.0132
Dv	66	-0.0134
Ho	67	-0.0137
Er	68	-0.0139
Tm	69	-0.0141
Yb	70	-0.0142
Lu	71	-0.0090
Hf	72	-0.0098
Ta	73	-0.0104
W	74	-0.0107
Re	75	-0.0109
Os	76	-0.0111
Ir	77	-0.0112
Pt	78	-0.0113
Au	79	-0.0108
Hg	80	-0.0114
 	81	-0.0107
Pb	82	-0.0110
Bi	83	-0.0109
 Po	84	-0.0108
At	85	-0.0107
	86	-0.0106
Fr	87	-0.0082
Ba	88	-0.0092
Ac	80	-0.0080
	00	
T 11	90	-0.0004

	TD-DFT	TD-DFT+TB	TD-DFTB	
Molecular orbitals	from DFT		from DFTB	
Coupling matrix $\boldsymbol{K}$	Eq. (4.9) Eq. (4		1.15)	
Atomic transition charges $q_{ia,\mathcal{A}}$	not used	Eq. (4.21)	Eq. (4.16)	
Single orbital transition dipole moments $\vec{d}_{ia}$	Eq. (4.12)		Eq. (4.20)	
Chemical hardness $\eta_{\mathcal{A}} \&$ Magnetic hubbard $W_{\mathcal{A}}$	not used precalculate for spherica		ed by DFT al atoms <sup>1</sup>	

Table 4.2: Comparison of the methods.

underestimate the excitation energies of charge-transfer excitations. It was shown [21, 22, 85] that this failure can be traced back to the different meaning of virtual orbital energies in Kohn-Sham DFT and Hartree-Fock: In DFT the virtual orbitals represent excited electrons interacting with N-1 other electrons, while in Hartree-Fock the virtual orbitals experience interaction with N electrons, so that they represent added rather than excited electrons. In other words, the Kohn-Sham HOMO-LUMO gap corresponds to the optical gap, while the Hartree-Fock HOMO-LUMO gap corresponds the fundamental gap, which is the difference between ionization energy and electron affinity. It is easy to see why this leads to underestimated charge-transfer excitation energies in DFT: If occupied and virtual orbital involved in a transition are localized on different fragments of the system, the transfered electron is essentially added to the acceptor fragment and its energy is determined by the acceptor's fundamental gap, not by its optical gap. The fundamental gap is always larger than the optical gap, the difference being the interaction between the excited electron and the hole in its (now unoccupied) original orbital [21, 145]. In summary, local excitations are well described in Kohn-Sham DFT with local functionals, while charge-transfer excitations profit from admixture of exact exchange. The so-called range-separated hybrid functionals [88, 89, 146], where the amount of exact exchange increases with electron-electron distance, reflect this.

It is interesting to note though, that charge-transfer excitations typically have very small oscillator strengths. Looking at equation (4.12) it is easy to see that the transition dipole moment is zero if the involved orbitals  $\phi_i(\vec{r})$  and  $\phi_a(\vec{r})$  have no significant overlap, as is the case for charge-transfer excitations. So even though charge-transfer excitation energies are severely underestimated in DFT with local functionals, the obtained absorption spectra are usually not affected. There is, however, a technical problem associated with the underestimated charge transfer excitation energies for the specific application of calculating optical absorption spectra: Since, the matrix  $\Omega$  that has to be diagonalized in Casida's equation (4.6) is extremely large, it is typically diagonalized using iterative eigensolvers that only calculate the few lowest eigenvectors. If large numbers of spurious charge-transfer excitations are now predicted at much too low energies, many more excitations have to be calculated in order to cover the relevant energy range. This drastically slows down the calculation even though the spurious charge-transfer excitations do not noticeably affect the obtained absorption spectra. Grimme cites this issue as the main reason for the use of hybrid functionals in sTDA and sTD-DFT. However, as we have recently shown the problem can also be solved by intensity selection [1], that is by simply neglecting single orbital transitions with small transition dipole moments. This does not correct the energy of charge-transfer excitations but instead removes them from the spectrum altogether, leading to both a smaller number of excitations that have to be calculated as well as an overall smaller matrix  $\boldsymbol{\Omega}$  due to the reduced number of single orbital transitions. While hybrid functionals are likely unavoidable if one needs accurate charge-transfer excitation energies, we believe that for the specific application of calculating absorption spectra, intensity selection is a much simpler and computationally more efficient alternative to hybrid functionals.

Furthermore, we would like to point out that while the use of hybrid functionals cures the charge-transfer problem, it introduces other problems that are not present in pure density functional approaches: As pointed out by Baerends et al. virtual orbitals from Kohn-Sham DFT with local functionals represent excited electrons interacting with N-1 other electrons. The coupling matrix in equation (4.8) is usually small compared to the orbital energy differences  $\Delta_{ia}$  on the diagonal, making orbital energy differences  $\Delta_{ia}$  an excellent approximation to excitation energies  $\Delta_I$  [147]. Furthermore the excitations are often dominated by just one single orbital transition  $\phi_i \rightarrow \phi_a$ , which drastically simplifies their interpretation [21, 22]. Hartree-Fock virtual orbitals on the other hand represent added electrons, so that their orbital energy differences  $\Delta_{ia}$ have little relation to excitation energies  $\Delta_I$  and are in fact much larger. It is actually not uncommon for the Hartree-Fock LUMO to be unbound with an orbital energy of  $\varepsilon_a > 0$ . Furthermore, as the Hartree-Fock virtual orbitals interact with N other electrons instead of N-1, they are much more diffuse than in DFT. The Hartree-Fock virtuals are less suitable for the description of excited electrons and in general more of them are needed for the description of an excitation, meaning that excitations often lose the single orbital transition character they have in DFT, making their interpretation much more difficult [21, 22]. These problems are less severe if the employed exchange-correlation functional only has a small fraction of exact exchange. It is, however, important to be aware of the fact that certain undesirable properties of time-dependent Hartree-Fock are reintroduced into TD-DFT if hybrid functionals are used.

In summary, we believe that there are good reasons to also approach excited state calculations for large systems from a pure density functional standpoint.

### 4.4 Method evaluation

#### 4.4.1 Vertical excitation energies

In order to assess the accuracy of TD-DFT+TB we have calculated the lowest few excitation energies for the 28 molecules containing 1st and 2nd period elements in the benchmark set developed by Schreiber et al. [148]. For a direct comparison we have done the same calculations with TD-DFTB using the mio-1-1 set of parameters [32, 40, 149, 150]. We use TD-DFT results as the reference against which TD-DFTB and TD-DFT+TB are compared. Both TD-DFT and TD-DFT+TB results were obtained using the PBE exchange-correlation functional [84] and a TZP basis set.

Note that some excitations in the benchmark set by by Schreiber et al. [148]

Multiplicity	TD-DFTB	TD-DFT+TB
singlet-singlet	$0.30 \mathrm{eV}$	$0.15\mathrm{eV}$
singlet-triplet	$0.49\mathrm{eV}$	0.22 eV

Table 4.3: Root-mean-square deviation in vertical excitation energies of TD-DFTB and TD-DFT+TB for Schreiber et al.'s test set. TD-DFT is used as the reference method.

have significant double excitation character and are hence difficult to describe with conventional TD-DFT. See reference 151 and 152 for a detailed discussion and possible solutions to this problem. However, for the purpose of comparing TD-DFT+TB and TD-DFTB to TD-DFT this does not play a role, as all methods are equally affected by this issue.

The calculated vertical excitation energies and the root-mean-square deviation (RMSD) compared to TD-DFT are shown for the individual molecules in figure 4.2 and figure 4.3 for singlet-singlet and singlet-triplet excitations, respectively. The calculated RMSD of all excitations in all molecules are shown in table 4.3. Following Casida et al.'s recommendation [153] we only considered excitations that have an excitation energy  $\Delta_I < -\varepsilon^{\text{HOMO}}$  and no large contributions from transitions into unbound virtual orbitals with  $\varepsilon_a > 0$ . In cases where the number of excitations satisfying these criteria differs between the methods, we compare the lowest common number of excitations satisfies both of Casida et al.'s criteria, so that these two molecules had to be excluded from the calculation of the overall RMSD for singlet-singlet excitations.

Compared to normal TD-DFTB, TD-DFT+TB is closer to TD-DFT for both singlet-singlet and singlet-triplet excitations. For singlet-singlet excitations switching from TD-DFTB to TD-DFT+TB reduces the RMSD by a factor of two from 0.301eV to 0.153eV. It is known that TD-DFTB is more accurate for singlet-singlet excitations than for singlet-triplet excitations [41] for which we calculated an RMSD of 0.489eV. We observe the same behavior for TD-DFT+TB, although with an RMSD of 0.215eV the difference in accuracy between singlet-singlet and singlet-triplet excitations is slightly smaller.

Note that for the calculation of the RMSD we have simply compared the excitation energies from the different methods according to their order in energy. We have not attempted to compensate for the fact that two excited states might switch in energy ordering when going from TD-DFT to one of the approximate methods. While this does not affect the comparison between TD-DFTB and TD-DFT+TB, the absolute errors in table 4.3 will be slightly underestimated and one should be careful when comparing them to the literature.

As mentioned in section 4.3 we have also run TD-DFT+TB calculations for Schreiber et al.'s test set using Mulliken instead of Löwdin population analysis for the calculation of the atomic transition charges. We found an RMSD of 0.449eV in vertical singletsinglet excitation energies, which is three times larger than the 0.153eV obtained with Löwdin charges, indicating that Mulliken transition charges do not accurately model the transition density for the relatively large TZP basis set used. For singlet-triplet



Figure 4.2: Vertical singlet-singlet excitation energies (left ordinate) for the molecules from Schreiber et al.'s test set [148]. The bars at the bottom represent the RMSD in vertical excitation energies compared to TD-DFT (to scale with the right ordinate).



Figure 4.3: Vertical singlet-triplet excitation energies (left ordinate) for the molecules from Schreiber et al.'s test set [148]. The bars at the bottom represent the RMSD in vertical excitation energies compared to TD-DFT (to scale with the right ordinate).

Method		Excitation		
& Property		${}^{1}\Pi_{u} (\sigma_{u} \to \pi_{g})$	${}^{1}\Sigma_{u}^{+} (\pi_{u} \to \pi_{g})$	
Г	$\Delta_I$	13.47	14.94	
TD-DF	$f_I$	0.32	0.34	
	$\Delta_{ia}$	11.53	9.55	
	$\Delta_I - \Delta_{ia}$	1.94	4.94	
-DFT+TB	$\Delta_I$	11.53	12.99	
	$f_I$	0.64	0.98	
	$\Delta_{ia}$	11.53	9.55	
1 D	$\Delta_I - \Delta_{ia}$	0.00	3.44	
B	$\Delta_I$	12.73	13.90	
DFT	$f_I$	0.00	0.88	
	$\Delta_{ia}$	12.73	10.19	
IT	$\Delta_I - \Delta_{ia}$	0.00	3.71	

Table 4.4: Dipole allowed transitions in N<sub>2</sub>. All energies in eV.  $\Delta_{ia}$  is the orbital energy difference for the dominant single orbital transition.

excitations we have furthermore found that unphysical transition charges sometimes lead to negative eigenvalues in equation (4.6) and hence imaginary excitation energies.

#### 4.4.2 Oscillator strengths and absorption spectra

In the last subsection we looked exclusively at vertical excitation energies. However, for the application of calculating UV/Vis absorption spectra both excitation energies and oscillator strengths have to be calculated.

#### $\mathbf{N}_2$

One difference between TD-DFTB and TD-DFT+TB is that the latter does not use the atomic transition charges for the calculation of the single orbital transition dipole moments. To illustrate the effect of this we have calculated the lowest excitations in  $N_2$  with a nuclear distance of 1.106Å. The results are shown in table 4.4.

According to TD-DFT there are two dipole allowed transitions: A  ${}^{1}\Pi_{u}$  state consisting mainly of a  $\sigma_{u} \rightarrow \pi_{g}$  transition, and a  ${}^{1}\Sigma_{u}^{+}$  state dominated by a  $\pi_{u} \rightarrow \pi_{g}$  transition. Note that even though both of them have excitation energies  $\Delta_{I} > -\varepsilon^{\text{HOMO}}$  we have found them to be well described and largely basis set independent due to the fact that they do not have contributions from transitions into unbound virtual orbitals. The  ${}^{1}\Sigma_{u}^{+}$  state is reasonably well described by both TD-DFTB and TD-DFT+TB, who both predict it to be dipole-allowed. Both methods underestimate the vertical excitation energy  $\Delta_{I}$  of the  ${}^{1}\Sigma_{u}^{+}$  state, with the TD-DFTB energy being closer to the TD-DFT reference. However, this is mostly due to the larger orbital energy difference  $\Delta_{ia}$  in DFTB compared to DFT, since the coupling matrix induced shift  $\Delta_{I} - \Delta_{ia}$  is similar for both TD-DFTB and TD-DFT+TB. The  $\sigma_{u} \rightarrow \pi_{g}$  transition into the  ${}^{1}\Pi_{u}$  state is less well described with the approximate methods. TD-DFT predicts a coupling matrix induced shift  $\Delta_{I} - \Delta_{ia}$  of almost 2eV while both approximate

methods produce exactly a single orbital transition with  $\Delta_I = \Delta_{ia}$ . This is due to the atomic transition charges' inability to model local transitions as mentioned in subsection 4.2.3. Since TD-DFTB also uses the transition charges for the transition dipole moments, it incorrectly predicts the transition into the  ${}^1\Pi_u$  state state to be dipole-forbidden. This is not the case in TD-DFT+TB, so that the method can at least be used to identify dipole-allowed  $\sigma \to \pi^*$  and  $n \to \pi^*$  transitions, even though their excitation energies will be less accurate than those of  $\pi \to \pi^*$  transitions.

However, for the large systems such approximate method are typically used for,  $\pi \to \pi^*$  transitions usually have the largest oscillator strengths, so that TD-DFTB and TD-DFT+TB's problems with localized transitions often do not noticeably affect the calculated absorption spectra.

#### Fullerene $C_{60}$

As an example for the calculation of absorption spectra, we have calculated the UV/Vis spectrum of the  $C_{60}$  fullerene. This was one of the example systems in the original TD-DFTB article and also makes a good technical benchmark as almost a thousand excitations have to be calculated to cover the relevant energy range. For TD-DFT and TD-DFT+TB we used a TZP basis and the PBE exchange-correlation functional [84]. TD-DFTB calculations were performed with both the 3ob-3-1 parameter set [112, 131, 134, 135] and the QUASINANO2013 set by Wahiduzzaman et al. [36]. For calculations with the 3ob-3-1 parameter set the ground state calculation was performed at the DFTB3 [40] level of theory. Conceptually this is slightly inconsistent, as the calculation of the excited states is based on the linear response of a Hamiltonian different from the one used for the calculation of the ground state. However, since the DFTB3 orbitals are generally of better quality than DFTB2 orbitals, this gives rather good results in practice.

The calculated spectra are shown in figure 4.4. TD-DFT+TB reproduces the TD-DFT reference spectrum almost perfectly. TD-DFTB with the 3ob-3-1 parameter performs very well below 5.5eV but underestimates the intensity of an excitation seen at 5.9eV in the TD-DFT spectrum. All three spectra qualitatively reproduce the series of absorption bands of increasing intensity seen in the experimental spectrum [154]. However, the theoretical spectra are redshifted compared to experiment. Absolute intensities should not be compared to experiment, as the experimentally measured cross sections have an uncertainty of 100% due to the sensitive vapor pressure-temperature relation of fullerenes [155].

The TD-DFTB spectrum calculated with the QUASINAN02013.1 parameters shows a substantial blue-shift compared to the other methods and the experimental reference. However, the shape of the spectrum with its three bands of increasing oscillator strength is reasonably well described. The origin of the blue-shift can be traced back to differences in the Kohn-Sham orbital energies: DFT and DFTB with the 3ob-3-1 parameters show a HOMO-LUMO gap of about 1.6eV, while DFTB with the QUASINAN02013.1 parameters produces a gap of 2.3eV. Keeping in mind that the HOMO-LUMO gap in DFT represents the optical gap [21, 22, 147], it is easy to understand why the QUASINAN02013.1 parameters predict overall larger excitation energies. The reason for the larger orbital energy differences with the QUASINAN02013.1 parameters is that they were optimized to reproduce band structures in solids [36], for



Figure 4.4: Absorption spectrum of the C<sub>60</sub> fullerene. Experimental gas phase absorption spectrum from reference 154. Note that the authors quote a 100% uncertainty in the absolute absorption cross sections due to the vapor pressure-temperature relation. Theoretical spectra have been broadened with a  $\sigma = 0.25$ eV Gaussian.

	TD-DFT	TD-DFT+TB	TD-DFTB
ground state	$4 \min 38 s$	$4 \min 33 s$	< 1s
excited states	19h 37min	$11 \min 35 s$	$1 \min 26 s$

Table 4.5: Timings for the calculation of the 988 lowest singlet-singlet excitations in the  $C_{60}$  fullerene. The obtained spectra are shown in figure 4.4. All calculations were performed on an Intel Core i7-4770 processor.

which relatively tight confinement potentials are required in the atomic calculations. However, the additional potential leads to increased orbital energy differences through quantum confinement and produces systematically overestimated excitation energies and blue-shifted absorption spectra. This illustrates how strongly TD-DFTB results can depend on details of the DFTB parametrization; a problem that does not exist in TD-DFT+TB.

Timings for the calculation of the  $C_{60}$  absorption spectra are shown in table 4.5. The benchmark TD-DFT calculation take almost 20 hours on a recent workstation computer, only 5 minutes of which are spent calculating the ground state. With TD-DFT+TB the total wall-time decreases to about 16 minutes, which is a speedup by a factor of 73 compared to TD-DFT. With a total wall-time of less than 90 seconds TD-DFTB is still much faster that TD-DFT+TB. The DFTB ground state calculation takes less than a second and is therefore completely negligible compared to the 5 minutes for the DFT ground state in TD-DFT+TB. Furthermore, due to the minimal basis set the space of single orbital transitions is much smaller in TD-DFTB,



Figure 4.5: Absorption spectrum of chlorophyll A. Experimental spectrum measured in diethyl ether prepared by Scott Prahl based on reference 156 and 157. Theoretical spectra have been broadened with a  $\sigma = 0.06$ eV Gaussian.

leading to a smaller matrix to be diagonalized: For DFT with a TZP basis set there are  $120 \times 900 = 108000$  single orbital transitions, whereas DFTB only has  $120 \times 120 = 14400$  transitions.

#### Chlorophyll A

We have also calculated the UV/Vis absorption spectrum of chlorophyll A. Due to the magnesium ion at the center of the chlorin ring, DFTB parameters that allow calculations of chlorophyll have only recently become available [36, 134]. The calculated spectra are shown in figure 4.5. The agreement between TD-DFT and TD-DFT+TB is again almost perfect throughout the entire energy range and both methods show the well-known  $Q_y$  and Soret absorption bands around 1.95eV and 2.8eV, respectively. The spectrum obtained with TD-DFTB and the 3ob-3-1 parameters is very close to TD-DFT below 3.2eV, but differs somewhat beyond that. All three methods reproduce the essential features of the experimental absorption spectrum [156, 157], although the energy gap between  $Q_y$  and Soret band is slightly underestimated. Note, however, that the experimental spectrum was recorded in solution, while our calculation corresponds to absorption in the gas phase. In the region above 3eV the theoretical spectra show more structure than the relatively flat experimental spectrum, which we attribute to the neglect of vibrational broadening in the theoretical spectra. With the QUASINANO2013 parameters we again observe a blue-shift of the entire spectrum, so that  $Q_y$  and Soret band are predicted at 2.5eV and 3.6eV respectively.



Figure 4.6: Absorption spectrum of Ir(ppy)<sub>3</sub>. Experimental spectrum measured in dichloromethane from reference 158. Note that the experimental reference does not give absolute absorptivities. The experimental spectrum was therefore scaled to reproduce the TD-DFT value at the peak just above 4eV. Theoretical spectra have been broadened with a  $\sigma = 0.2$ eV Gaussian.

#### $Ir(ppy)_3$

Our last example calculation is the UV/Vis absorption spectrum of fac-Ir(ppy)<sub>3</sub> (an abbreviation for fac-Tris(2-phenylpyridine)iridium), a compound that is of interest in the context of highly efficient organic light emitting diodes [73]. The calculated absorption spectra are shown in figure 4.6. Below 4.4eV TD-DFT+TB agrees well with the TD-DFT reference spectrum. Beyond that energy range the oscillator strengths from TD-DFT+TB seem to be overestimated, so that the predicted absorption is overall too strong. Both methods reproduce the principal features of the experimentally measured spectrum [158], though the absorption spectra are slightly redshifted compared to experiment. Note that the experimental spectrum was measured in solution, while our calculations correspond to gas phase absorption. Absolute experimental absorption coefficients were not given in reference 158 and can hence not be compared to theory. Due to the iridium atom at the center of the complex, DFTB calculations of Ir(ppy)<sub>3</sub> can at the moment only be performed with the QUASINANO2013 set of parameters. For both the fullerene and the chlorophyll we had observed a blue-shift in the spectra calculated with these parameters, which is again the case for Ir(ppy)<sub>3</sub>.

## 4.5 Conclusion

In summary we have presented a new method for calculating electronic excitations that combines molecular orbitals from a DFT ground state calculation with TD-DFTB like approximations for the coupling matrix from Casida's linear response formalism. We have shown that the new method named TD-DFT+TB improves vertical excitations energies compared to TD-DFTB and yields electronic absorption spectra that almost perfectly agree with computationally much more costly TD-DFT calculations. In contrast to TD-DFTB, TD-DFT+TB does not rely on DFTB parametrization and is therefore applicable to molecular systems containing any combination of elements.

The new method is very easy to implement into existing DFT codes that already have support for TD-DFT, since it is essentially only a simplification of the coupling matrix. Alternatively it could also very easily be supported by a standalone DFTB implementation with TD-DFTB support: Instead of calculating the molecular orbitals using DFTB, one could read orbitals calculated by an external DFT code from disk and use them as input for the TD-DFTB calculation. While both approaches are viable, we believe that direct integration into a DFT code is the more user-friendly alternative. We have integrated TD-DFT+TB in this way into the 2016 release of the ADF modeling suite [92].

Our method is implemented and can be used for a wide range of systems where TD-DFT is computationally unfeasible. However, there is still room for improvements, and we are currently working on several enhancements and further validations. For heavier elements we are currently investigating whether orbital-dependent hardness parameters give superior performance compared to the presently used atomic ones. We are further assessing the performance of the approach by comparing smaller (DZP) and larger (TZ2P) basis sets.

Looking at the bigger picture, there are by now several related methods for the calculation of exited state properties of large systems, namely TD-DFTB, TD-DFT+TB, sTDA and sTD-DFT. It would be desirable to benchmark all these different methods against experimental data in order to be able to give clear recommendations to end users, regarding applicability and accuracy of the various methods. Based on the discussion in section 4.3.2, we for example expect intensity selected TD-DFT+TB to be very suitable for the calculation and analysis of absorption spectra, while sTD-DFT should yield generally more accurate excitation energies. We believe that a consistently done benchmark study including all the different methods could serve to give end users the right tools for the right applications and would in general make such methods more approachable for non-expert users.

## 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 timedependent 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  $f_{ia}^{\min}$ , 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  $f_{ia}^{\min} = 0.001$ 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  $\pi \to \pi^*$  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.

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